Tetrahedron: Asymmetry Vol. 4, No. 7, pp. 1573-1578, 1993
Printed in Great Britain

0957-4166/93 $6.00+.00
Pergamon Press Ltd

Enantioselective Synthesis of (-)-Serricornin, a Sex Pheromone of a Female Cigarette Beetle (*Lasioderma serricorne* F.)

Masaaki Miyashita, Yuuko Toshimitsu, Tomonori Shiratani, and Hiroshi Irie*

Faculty of Pharmaceutical Sciences, Nagasaki University, Bunkyo-machi, Nagasaki 852, Japan

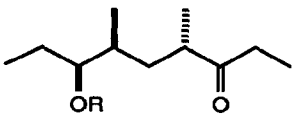
(*Received in Japan* 22 *March* 1993; *accepted* 19 *April* 1993)

Abstract: (-)-Serricornin, a sex pheromone of a cigarette beetle (*Lasioderma serricorne* F.), has been synthesized highly stereoselectively starting from (*Z*)-4-benzyloxy-2-buten-1-ol by employing the Katsuki-Sharpless asymmetric epoxidation and two stereospecific methylation reactions, the regioselective γ-methylation of a γ,δ-epoxy acrylate by trimethylaluminum and α-methylation of a δ-lactone, as key steps.

There have been several reports [1-9] concerning the synthesis of serricornin (**1**), a sex pheromone of a female cigarette beetle (*Lasioderma serricorne* F.).[1] The structure-activity relationship of the pheromone was revealed by the synthesis of its stereoisomers including two enantiomers with only the 4*S*,6*S*,7*S*-isomer exhibiting the pheromone activity.[2-4] We now report here a synthesis of enantiomerically pure serricornin (**1**) starting from (*Z*)-4-benzyloxy-2-buten-1-ol by using the two stereospecific methylation reactions, i.e., the regioselective γ-methylation of a γ,δ-epoxy acrylate by trimethylaluminum[10] and the stereoselective α-methylation of a δ-lactone, as key steps.

The known (2*R*,3*S*)-4-benzyloxy-2,3-epoxybutanol (**2**),[11] readily obtainable from (*Z*)-4-benzyloxy-2-buten-1-ol by the Katsuki-Sharpless asymmetric epoxidation,[12] was chosen as our starting material. Swern oxidation of **2** followed by the Horner-Emmons reaction of the resulting aldehyde with triethyl phosphonoacetate furnished ethyl (4*R*,5*S*)-6-benzyloxy-4,5-epoxy-2-hexenoate (**3**), a γ,δ–epoxy acrylate, in 81% yield. In common with the racemic compound,[10] the methylation reaction on **3** with trimethylaluminum in 1,2-dichloroethane in the presence of a small amount of water at -35°C[10] gave solely the syn alcohol **4** in 95% yield. ^{1}H-NMR spectrum of the product did not indicate the presence of any stereoisomers.[10] Hydrogenation of **4** over platinum oxide in ethanol followed by brief treatment of the reduction product with PPTS in 1,2-dichloroethane at 90 °C resulted in the formation of the lactone **5** in 90% overall yield. Methylation at the α-position of the lactone carbonyl under conventional conditions produced the expected dimethyl lactone **6** (mp 53 °C) in 79% yield as a single crystalline compound.

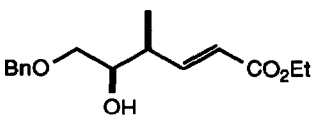
All attempts to transform the benzyloxymethyl group of **6** into an ethyl group were fruitless owing to an inevitable isomerization of the α-methyl group of the lactone under debenzylation conditions. Eventually, this step was circumvented as follows. Thus treatment of **6** with N,O-dimethylhydroxylamine hydrochloride and trimethylaluminum[13] in dichloromethane (CH_2Cl_2) gave the amide **7** in 85% yield. The amide was smoothly converted to the mesylate **8** in 82% overall yield by the following three step reaction sequence: 1) acetylation;



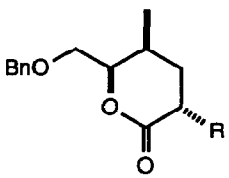
(1) R=H, Serricornin
(11) R=Ac

(2)

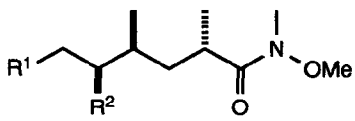
(3)



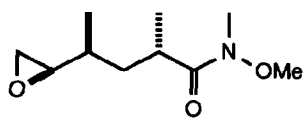
(4)



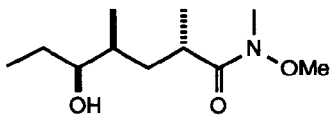
(5) R=H
(6) R=Me



(7)R^1=OBn, R^2=OH
(8) R^1=OMs, R^2=OAc



(9)



(10)

2) catalytic hydrogenation (debenzylation); 3) mesylation. The resulting mesylate **8** was transformed into the oxide **9** by treatment with potassium carbonate in methanol in 74% yield. Ring opening of the epoxide **9** with lithium dimethylcuprate in ether cleanly produced the hydroxyamide **10** in 57% yield.. Finally, conversion of the hydroxyamide **10** to serricornin (**1**) was accomplished by treatment with ethyllithium in ether in 93% yield.

Since all the reported identification of the synthetic compound was carried out on its acetate,[2-8] the synthetic serricornin was converted to the corresponding acetate **11** with acetic anhydride in pyridine. All the spectral data (IR ,^{1}H-NMR, and ^{13}C-NMR) of the acetate including its $[\alpha]_D$ value (-16.6 (*c* 0.1, hexane)) were in agreement with those of the authentic serricornin acetate ($[\alpha]_D$ -17.7, -16.8) [2] Thus the present synthesis provides an alternative synthetic route to the optically pure serricornin (**1**).

Experimental

All operations were carried out under an argon atmosphere with oven-dried glassware. IR spectra were recorded on a Shimadzu IR-408 spectrometer in chloroform unless otherwise stated.. ^{1}H-NMR spectra and ^{13}C-NMR spectrum were recorded on a JEOL FX 90 Q (90 MHz) spectrometer using $CDCl_3$ as solvent and tetramethylsilane as an internal standard. Optical rotations were measured with a JASCO DIP-181 digital polarimeter and high-resolution mass spectra (HR-MS) were recorded on a JEOL JMS-DX 303 instrument. Merck Kieselgel Art. 9385 was used for flash column chromatography, and Merck Kieselgel precoated plates 60 F-254 were used for preparative thin layer chromatography.

Ethyl (4*R*,5*S*)-6-benzyloxy-4,5-epoxy-2-hexenoate (3). To a solution of oxalyl chloride (1.17

mL, 13.36 mmol) in CH_2Cl_2 (120 mL) at -60 °C was added a solution of DMSO (1.89 mL, 26.72 mmol) in CH_2Cl_2 (5 mL). After 10 min, a solution of the epoxide **2** (1.30 g, 6.68 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred at -60 °C for 1 h, then treated with triethylamine (4.65 mL, 33.4 mmol), and allowed to warm up to room temperature. The reaction mixture was successively washed with water and saturated brine, dried, and concentrated to leave an aldehyde which was used for the next reaction without further purification.

To a suspension of sodium hydride (347 mg, 8.68 mmol) in tetrahydrofuran (THF, 120 mL) was added dropwise at 0 °C a solution of triethyl phosphonoacetate (1.91 mL, 9.35 mmol) in THF (8 mL) and the mixture was stirred for 30 min at the same temperature. The resulting solution was cooled to -70°C to which a solution of the foregoing aldehyde (6.68 mmol) in THF (8 mL) was added. After stirring for 30 min at the same temperature, the mixture was diluted with ethyl acetate. The organic solution was washed three times with half-saturated brine, and aqueous washes were extracted with ethyl acetate . Combined organic layers were concentrated to leave an oily residue which was purified by silica gel flash chromatography (hexane-ethyl acetate = 5:1) to give the γ,δ-epoxy acrylate **3** (1.42 g, 81%). $[\alpha]_D^{20}$ -6.1 (*c* 1.12, $CHCl_3$). IR: 3050, 3000, 1711, 1658, 1312, 1095, 979, 845 cm^{-1}. ^{1}H-NMR: 1.29 (t, 3H, *J*=7.2 Hz), 3.35-3.71 (m, 4H), 4.20 (q, 2H, *J*=7.2 Hz), 4.48 (d, 1H, *J*=11.9 Hz), 4.64 (d, 1H, *J*=11.9 Hz), 6.12 (dd, 1H, *J*=15.8, 0.8 Hz), 6.76 (dd, 1H, *J*=15.8, 6.6 Hz), 7.32 (s, 5H). HR-MS calcd for $C_{15}H_{18}O_4$: 262.1205. Found: 262.1198.

Ethyl (4*S*,5*R*)-6-benzyloxy-5-hydroxy-4-methyl-2-hexenoate (4). A mixture of **3** (689 mg, 2.63 mmol), water (379 μL, 21.04 mmol), and 1,2-dichloroethane (45 mL) was cooled to -35°C, to which trimethylaluminum (a 2 M hexane solution, 13.1 mL, 26.2 mmol) was rapidly added and the resulting mixture was stirred at the same temperature for 1 h. Then the mixture was warmed up to 0 °C and the excess reagent was carefully decomposed by dropwise addition of water. After the emulsion formed was dissolved by the aid of 2% HCl, the product was thoroughly extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed with brine, dried, and concentrated. The oily residue was purified by silica gel flash chromatography (hexane-ethyl acetate = 3:1) to give the alcohol **4** (694 mg, 95%). $[\alpha]_D^{18}$ -37.3 (*c* 1.10, $CHCl_3$). IR: 3570, 3025, 2980, 1708, 1651, 1277, 1100, 1032, 988 cm^{-1}. ^{1}H-NMR: 1.13 (d, 3H, *J*=6.8 Hz), 1.28 (t, 3H, *J*=7.0 Hz), 2.30-2.70 (m, 1H), 2.45 (d, 1H, *J*=4.1 Hz, -OH), 3.35 (dd, 1H, *J*=9.4, 7.1 Hz), 3.53 (dd, 1H, *J*=9.4, 3.2 Hz), 3.70 (m, 1H), 4.18 (q, 2H, *J*=7.0 Hz), 4.52 (s, 2H), 5.83 (dd, 1H, *J*=15.8, 1.1 Hz), 6.89 (dd, 1H, *J*=15.8, 8.2 Hz), 7.32 (s, 5H). HR-MS: calcd for $C_{16}H_{22}O_4$: 278.1518. Found: 278.1525.

(4*S*,5*R*)-6-Benzyloxy-4-methyl-δ-valerolactone (5). A solution of the unsaturated ester **4** (627 mg, 2.26 mmol) in ethanol (17 mL) was hydrogenated over PtO_2 (170 mg) for 7 h. After removal of the catalyst by a membrane filter, the filtrate was concentrated to leave an oily residue. A solution of the residue and PPTS (112 mg, 0.44 mmol) in 1,2-dichloroethane (28 mL) was heated at 90 °C for 3 h. After cooling, the reaction mixture was passed through a silica gel column by the aid of ether. The eluate was concentrated and the residue was purified by silica gel flash chromatography (hexane-ethyl acetate = 3:1) to give the δ-lactone **5** (476 mg, 90%). $[\alpha]_D^{16}$ -31.7 (*c* 0.98, $CHCl_3$). IR: 3010, 2880, 1728, 1076, 1006 cm^{-1}. ^{1}H-NMR: 0.96 (d, 3H, *J*=7.0 Hz), 1.52-2.40 (m, 3H), 2.51 (d, 1H, *J*=6.8 Hz), 2.58 (dd, 1H, *J*=6.8, 1.1 Hz), 3.56 (dd, 1H, *J*=6.7, 2.3 Hz), 3.70 (dd, 1H, *J*=6.7, 1.7 Hz), 4.40-4.65 (m, 1H), 4.55 (s, 2H), 7.32 (s, 5H). Anal. calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found:C, 71.73; H, 7.77.

Methylation of the Lactone (5). A solution of the lactone **5** (367 mg, 1.57 mmol) in THF (8 mL) was added dropwise at -78°C to a solution of LDA over 15 min, which was prepared from diisopropylamine (238 mg, 2.35 mmol) and butyllithium (a 1.52 M hexane solution, 1.55 mL, 2.35 mmol) in THF (8 mL) at -78°C. After stirring for 40 min at the same temperature, methyliodide (891 mg, 6.28 mmol) was added and the whole was further stirred for 2 h at -78°C. The reaction was quenched with 2% HCl (8 mL) and the product was extracted with ethyl acetate. The extract was washed twice with half-saturated brine and once with saturated brine. The organic layer was dried and concentrated in vacuo to leave an oily residue which was purified by silica gel column flash chromatography to give the dimethyl lactone **6** (308 mg, 79%) as crystals. Mp 53°C (hexane-acetone). $[\alpha]_D^{24}$ -21.9 (*c* 0.68, $CHCl_3$). IR: 3025, 3000, 2930, 1720, 1095, 1000 cm^{-1}. ^{1}H-NMR: 0.98 (d, 3H, *J*=7.0 Hz), 1.29 (d, 3H, *J*=7.0 Hz), 1.48-2.00 (m, 2H), 2.00-2.36 (m, 1H), 2.40-2.86 (m, 1H), 3.52 (dd, 1H, *J*=10.0, 6.4 Hz), 3.66 (dd, 1H, *J*=10.0, 5.8 Hz), 4.48 (d, 1H, *J*=12.0 Hz), 4.53 (dt, 1H, *J*=6.4, 3.1 Hz), 4.60 (d, 1H, *J*=12.0 Hz), 7.32 (s, 5H). Anal. calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.48, H, 8.11.

(2*S*,4*S*,5*R*)-6-Benzyloxy-2,4-dimethyl-5-hydroxy-N-methoxy-N-methylhexanamide (7). To a solution of N,O-dimethylhydroxylamine hydrochloride (76 mg, 0.77 mmol) in CH_2Cl_2 (5 mL) was added a solution of trimethylaluminum (a 1 M hexane solution, 0.77 mL, 0.77 mmol) under argon and the mixture was stirred for 15 min at room temperature. Then a solution of the foregoing lactone **6** (95 mg, 0.38 mmol) in CH_2Cl_2 (3 mL) was added and the resulting mixture was stirred for 2.5 h at room temperature. The reaction mixture was cooled to 0 °C and the excess aluminum reagent was decomposed by water. After addition of 4% HCl, the product was thoroughly extracted with CH_2Cl_2. The extract was washed with water and saturated brine, dried, and concentrated. The residual oil was purified by silica gel column flash chromatography (hexane-ethyl acetate = 2:3) to give the amide **7** (100 mg, 85%). $[\alpha]_D^{22}$ -9.02 (*c* 0.37, $CHCl_3$). IR: 3575, 3420, 2995, 1642, 1096, 997, 906, 695 cm^{-1}. ^{1}H-NMR: 0.91 (d, 3H, *J*=6.2 Hz), 1.09 (d, 3H, *J*=6.8 Hz), 1.30-1.80 (m, 3H), 2.28 (br s, 1H, -OH), 2.95 (q, 1H, *J*=8.0 Hz), 3.16 (s, 3H), 3.40 (dd, 1H, *J*=10.9, 5.7 Hz), 3.50 (dd, 1H, *J*=10.9, 1.8 Hz), 3.67 (s, 3H), 3.52-3.80 (m, 1H), 4.54 (s, 2H), 7.32 (s, 5H). HR-MS calcd for $C_{17}H_{27}NO_4$: 309.1940. Found: 309.1937.

(2*S*,4*S*,5*R*)-5-Acetoxy-2,4-dimethyl-6-methanesulfonyloxy-N-methoxy-N-methylhexanamide (8). A mixture of **7** (91 mg, 0.29 mmol), pyridine (242 mg, 2.9 mmol), Ac_2O (17 mg, 1.8 mmol), and a catalytic amount of 4-dimethylaminopyridine in CH_2Cl_2 (10 mL) was stirred for 25 h at room temperature. The reaction mixture was diluted with ethyl acetate and successively washed with cold 2% HCl, water, and saturated brine. Removal of the solvent left an oil which was purified by silica gel column flash chromatography (hexane-ethyl acetate = 2:1) to give quantitatively the (2*S*,4*S*,5*R*)-5-acetoxy-6-benzyloxy-2,4-dimethyl-N-methoxy-N-methylhexanamide (102 mg). $[\alpha]_D^{20}$ -0.39 (*c* 0.86, $CHCl_3$). IR: 3025, 3000, 1726, 1642, 1250, 998, 695 cm^{-1}. ^{1}H-NMR: 0.89 (d, 3H, *J*=6.8 Hz), 1.08 (d, 3H, *J*=6.8 Hz), 1.20-1.92 (m, 3H), 2.07 (s, 3H), 3.01 (q, 1H, *J*=6.8 Hz), 3.16 (s, 3H), 3.49 (dd, 1H, *J*=7.2, 0.9 Hz), 3.55 (dd, 1H, *J*=7.2, 2.2 Hz), 3.69 (s, 3H), 4.50 (s, 2H), 5.11 (m, 1H), 7.30 (s, 5H). HR-MS calcd for $C_{19}H_{29}NO_5$: 351.2046. Found: 351.2046.

A solution of the acetate (114 mg, 0.32 mmol) in ethanol (4.5 mL) was hydrogenated over 10% Pd-C (57 mg) for 2.5 h. After removal of the catalyst, the filtrate was concentrated to leave an oily residue which was purified by silica gel flash chromatography (hexane-ethyl acetate = 1:5) to give (2S,4S,5R)-5-acetoxy-6-hydroxy-2,4-dimethyl-N-methoxy-N-methylhexanamide (81 mg, 97%). $[\alpha]_D^{20}$ -6.74 (*c* 0.36, $CHCl_3$). IR: 3440, 3025, 3000, 1724, 1644, 1252, 998 cm^{-1}. ^{1}H-NMR: 0.91 (d, 3H, *J*=6.7 Hz), 1.09 (d, 3H, *J*=6.8 Hz), 1.20-2.05 (m, 4H), 2.10 (s, 3H), 2.99 (q, 1H, *J*=7.1 Hz), 3.18 (s, 3H), 3.68 (d, 2H, *J*=3.3 Hz), 3.71 (s, 3H), 4.76-4.96 (m, 1H). HR-MS calcd for $C_{12}H_{23}NO_5$: 261.1576. Found: 261.1574.

A solution of the foregoing hydroxy acetate (71 mg, 0.27 mmol), pyridine (215 mg, 2.72 mmol), and methanesulfonyl chloride (218 mg, 1.91 mmol) in CH_2Cl_2 (3 mL) was stirred for 2 h at room temperature. The mixture was diluted with ethyl acetate and successively washed with 2% HCl, water, and brine. After evaporation of the solvent, the residue was purified by silica gel flash chromatography (hexane-ethyl acetate = 1:2) to give the mesylate **8** (79 mg, 85%). The mesylate thus obtained was immediately submitted to the next reaction.

(2*S*,4*S*,5*R*)-5,6-Epoxy-2,4-dimethyl-N-methoxy-N-methylhexanamide (9). A mixture of **8** (79 mg, 0.23 mmol) and K_2CO_3 (192 mg, 1.39 mmol) in methanol (10 mL) was stirred for 2 h at room temperature. The mixture was diluted with ethyl acetate and washed with water and saturated brine. After evaporation of the solvent, the residue was purified by silica gel flash chromatography (hexane-ethyl acetate = 3:2) to give the epoxide **9** (34 mg, 74%). $[\alpha]_D^{21}$ +28.7 (*c* 0.12, $CHCl_3$). IR: 3000, 2975, 1645, 998, 900 cm^{-1}. ^{1}H-NMR: 1.01 (d, 3H, *J*=5.8 Hz), 1.11 (d, 3H, *J*=6.8 Hz), 1.20-1.84 (m, 3H), 2.52 (dd, 1H, *J*=4.0, 3.8 Hz), 2.67 (dd, 1H, *J*=4.0, 3.3 Hz), 2.76 (dd, 1H, *J*=3.8, 3.3 Hz), 3.02 (q, 1H, *J*=7.1 Hz), 3.18 (s, 3H), 3.70 (s, 3H). HR-MS calcd for $C_{10}H_{19}NO_3$: 201.1365. Found: 201.1353.

(2*S*,4*S*,5*S*)-2,4-Dimethyl-5-hydroxy-N-methoxy-N-methylhexanamide (10). A solution of **9** (28 mg, 0.14 mmol) in THF (1 mL) was added at 0 °C to a solution of lithium dimethylcuprate freshly prepared from copper (I) iodide (108 mg, 0.56 mmol) and methyllithium (a 1.4 M hexane solution, 0.7 mL, 0.98 mmol) in ether (1 mL) at 0°C and the resulting mixture was stirred for 20 min at the same temperature. After the reaction was quenched by saturated ammonium chloride, the product was thoroughly extracted with ethyl acetate. The extract was washed with water and brine, dried, and concentrated to leave an oil which was subjected to preparative thin layer chromatography (hexane-ethyl acetate =1:2) to give the alcohol **10** (17 mg, 57%). $[\alpha]_D^{15}$ -6.3 (*c* 0.16, $CHCl_3$). IR: 3445, 2975, 1728, 1640, 998 cm^{-1}. ^{1}H-NMR: 0.86 (d, 3H, *J*=6.6 Hz), 0.94 (t, 3H, *J*=6.6 Hz), 1.11 (d, 3H, *J*=6.8 Hz), 1.10-1.80 (m, 6H), 3.00 (q, 1H, *J*=6.8 Hz), 3.18 (s, 3H), 3.42 (dt, 1H, *J*=6.2, 2.4 Hz), 3.70 (s, 3H). HR-MS calcd for $C_{11}H_{23}NO_3$: $(M+H)^+$ 218.1756. Found: 218.1763.

Serricornin Acetate (11) To a solution of the amide **10** (16 mg, 0.07 mmol) in THF (1 mL) was added ethyllithium (a 0.31 M pentane solution, 1.12 mL, 0.35 mmol) at -78°C under argon. After stirring for 20 min at the same temperature, the reaction was quenched by saturated ammonium chloride and the product was extracted with ether. The organic extract was washed with water and brine, and dried. Removal of the solvent gave the crude serricornin (**1**) which was acetylated with acetic anhydride (72 mg, 0.7 mmol) in pyridine (0.7 mL) in a usual manner. The crude oil was purified by silica gel flash chromatography (hexane-ethyl acetate=15:1) to give serricornin acetate **11** (15 mg, 93% for the two steps). $[\alpha]_D^{22}$ -16.6 (*c* 0.10, hexane), lit. -17.7, [2] -16.7.[2]

IR (CCl_4): 2975, 2930, 2875, 1733, 1717, 1460, 1250 cm^{-1}. ^{1}H-NMR: 0.86 (t, 3H, J=7.5 Hz), 0.87 (d, 3H, J=6.1 Hz), 1.03 (d, 3H, J=6.8 Hz), 1.04 (t, 3H, J=7.3 Hz), 1.10-1.84 (m, 5H), 2.06 (s, 3H), 2.47 (q, 2H, J=7.5 Hz), 2.30-2.76 (m, 1H), 4.75 (dt, 1H, J=6.6, 3.5 Hz). ^{13}C-NMR: 7.86, 10.13, 14.44, 16.61, 21.05, 24.16, 33.67, 34.24, 35.89, 43.51, 78.13, 170.93, 214.93. All these spectral data of the synthetic compound are identical with those of natural specimen.[1,2]

Acknowledgment: We are grateful to The Fujisawa Foundation for their financial support.

References

1) T. Chuman, M. Kohno, K. Kato, and M. Noguchi, *Tetrahedron Lett.*, **1979**, 2361.
2) K. Mori, H. Nomi, T. Chuman, M. Kohno, K. Kato, and M. Noguchi, *Tetrahedron*, **38**, 3705 (1982).
3) M. Mori, T. Chuman, K. Kato, and K. Mori, *Tetrahedron Lett.*, **23**, 4593 (1982).
4) K. Mori and H. Watanabe, *Tetrahedron*, **41**, 3423 (1985).
5) Y. Kobayashi, Y. Kitano, Y. Takeda, and F. Sato, *Tetrahedron*, **42**, 2937 (1986).
6) T. Katsuki and M. Yamaguchi, *Tetrahedron Lett.*, **28**, 651 (1987).
7) H. Redrich, K. Samm, J. B. Lenfers, and W. Bruns, *Carbohydrate Research*, **174**, 341 (1988).
8) S. Takano, Y. Sekiguchi, and K. Ogasawara, *Heterocycles*, **29**, 445 (1989).
9) I. Shimizu, K. Hayashi, and M. Oshima, *Tetrahedron Lett.*, **31**, 4757 (1990). I. Shimizu, K. Hayashi, N. Ide, and M. Oshima, *Tetrahedron*, **47**, 2991 (1991).
10) M. Miyashita, M. Hoshino, and A. Yoshikoshi, *J. Org. Chem.*, **23**, 6483 (1991).
11) H. Shibuya, K. Kawashima, N. Narita, M. Ikeda, and I. Kitagawa, *Chem. Pharm. Bull.*, **40**, 1154 (1992).
12) T. Katsuki and K. B. Sharpless, *J. Am. Chem. Soc.*, **102**, 5976 (1980).
13) A. Basha, M. Lipton, and M. Weinreb, *Tetrahedron Lett.*, **1977**, 4171.