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# Enantio- and Diastereo-Selective Synthesis of (+)-Grandisol

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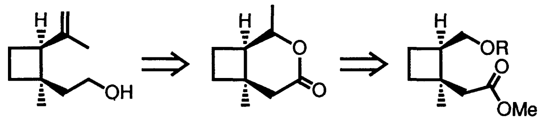
(+)-Grandisol, an insect pheromone having cyclobutane skeleton, is synthesized enantio- and diastereoselectively. The key steps in the synthesis are the asymmetric [2+2] cycloaddition reaction catalyzed by a chiral titanium reagent and the diastereoselective conjugate addition reaction by the combined use of $Me_2CuLi$ and trimethylsilyl trifluoromethanesulfonate.

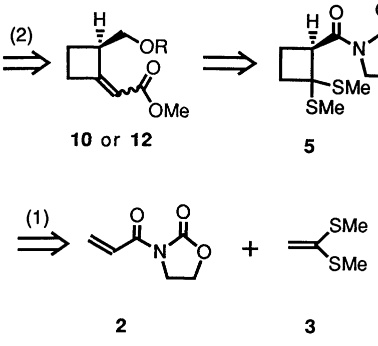
(+)-Grandisol, which was first isolated by Tumlinson et al. in 1967,[1] is one of the components of the male-produced pheromone of the cotton boll weevil (*Anthonomus Grandis*). This compound attracted much attention of many synthetic organic chemists not only due to its biological activity but also to its unique cyclobutane structure, and many synthetic studies have been reported[2,3] including several asymmetric syntheses.[4–6] The crucial step in these asymmetric syntheses is the preparation of optically active cyclobutanes, which includes optical resolutions of cyclobutane derivatives,[4] syntheses from chiral building blocks of natural compounds,[5] and diastereoselective [2+2] photocycloaddition reactions using substrates having chiral auxiliaries.[6]

We have recently reported the asymmetric [2+2] cycloaddition reaction between 3-acryloyl-1,3-oxazolidin-2-one derivatives and ketene dithioacetal promoted by a catalytic amount of the chiral titanium reagent prepared from dichlorodiisopropoxytitanium and a tartrate-derived chiral diol.[7] This reaction gives chiral cyclobutane derivatives in high enantioselectivity and, furthermore, both enantiomers of the chiral cyclobutanes are easily obtained by choosing the appropriate enantiomer of the chiral 1,4-diol. These chiral products are expected to be synthetically useful chiral building blocks. In fact, the total synthesis of carbocyclic oxetanocin analogues was performed starting from the optically active [2+2] adduct.[8] For a further application, the asymmetric synthesis of (+)-grandisol **1** has been attempted and, in this report, the detail of the synthesis is summarized.

In the following retrosynthetic scheme, the key steps are: (1) the construction of the chiral cyclobutane **5** with high enantioselectivity, (2) the diastereoselective introduction of α-methyl group to the methyl cyclobutylideneacetate **10** or **12**.

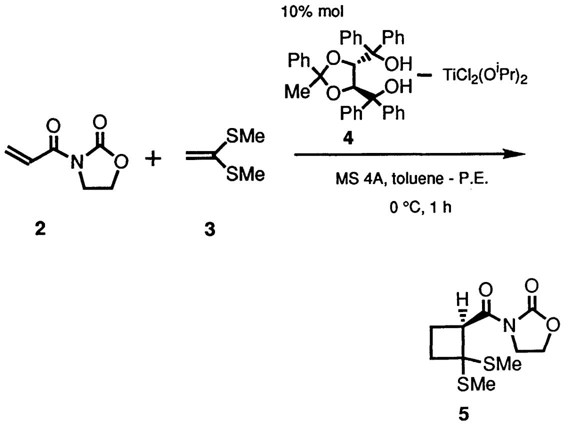


(+)-Grandisol **1**



## Results and Discussion

The asymmetric [2+2] cycloaddition reaction between 3-acryloyl-1,3-oxazolidin-2-one (**2**) and 1,1-bis(methylthio)ethylene (**3**) was examined. The chiral titanium reagent was prepared *in situ* by mixing dichlorodiisopropoxytitanium and (−)-(2*S*,3*S*)-1,1,4,4,-tetraphenyl-2,3-*O*-(1-phenylethylidene)-1,2,3,4-butanetetrol (**4**) derived from (−)-tartaric acid.[9] The reaction of **2** and **3** in the presence of 10% mol of the above chiral titanium catalyst and Molecular Sieves 4A in a toluene–petroleum ether mixture at 0 °C for 1 h afforded the corresponding cyclobutanecarboxylic acid derivative **5** in 80% yield with 88% ee.



80% yield, 88% ee
recryst. from benzene - hexane >98% ee

The optically pure material **5** (>98% ee) was obtained by the recrystallization from benzene–hexane. The optical purity was checked by the 500 MHz $^1$H NMR analysis of the Mosher's (+)-methoxy trifluoromethyl phenyl acetate ((+)-MTPA ester)[10] derived from **7**. The X-ray crystallographic analysis of the single crystal of **5** was shown in the following figure. Although the absolute configuration of **5** could not be determined by this X-ray analysis, it is considered to be *S* based on the previously reported [2+2] cycloaddition reaction of 3-[3-(methoxycarbonyl)acryloyl]-1,3-oxazolidin-2-one and ketene dithioacetal **3**.[7]

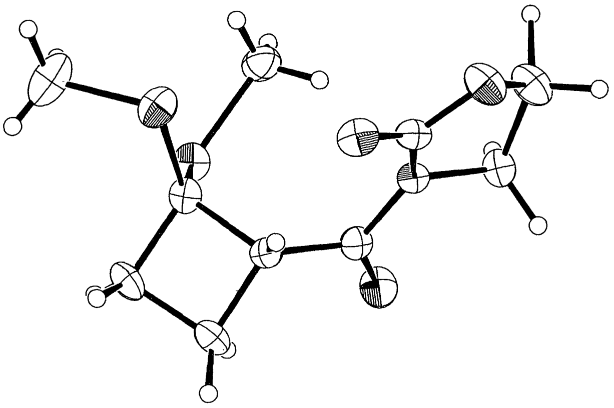


Fig. 1. The ORTEP drawing of **5**.

The transformation of the optically pure cyclobutane **5** to the $\alpha,\beta$-unsaturated ester **10a** was performed as shown in Scheme 1. Treatment of **5** with magnesium methoxide gave the methyl ester **6**. Reduction of **6** with $LiAlH_4$ afforded the alcohol **7**, whose hydroxyl group was protected as *t*-butyldiphenylsilyl (TBDPS) ether **8** in 94% overall yield from **5** in 3 steps. Subsequently, hydrolysis of dithioacetal group of **8** with *N*-chlorosuccinimide and silver nitrate[11] gave the cyclobutanone **9** in 95% yield. The Peterson olefination of **9** [LiN($c$-$C_6H_{11}$)$_2$, $TMSCH_2CO_2Me$ (TMS=trimethylsilyl)][12] gave the (*Z*)-$\alpha,\beta$-unsaturated ester **10a** quantitatively as a single stereoisomer.

Then, the introduction of methyl group to the (*Z*)-ester **10a** was investigated. The (*Z*)-**10a**, a $\beta,\beta$-disubstituted unsaturated ester, was considered to be a poor Michael acceptor toward organocopper(I) reagents.[13] In fact, as shown in Table 1, the reactions of **10a** with lithium dimethylcuprate(I) and methylcopper(I) did not proceed (Entries 1 and 2). The mixed reagents, $MeCu$–$BF_3$·$OEt_2$ or $Me_2CuLi$–$BF_3$·$OEt_2$,[13,14] also did not give the methylated product (Entries 3 and 4). By the use of $Me_2CuLi$–TMSCl,[15,16] however, the addition product **11a** was obtained, but the yield was not sufficiently high (60%) (Entry 5). Since more effective activation reagent was thought to be required, the reaction was examined by using trimethylsilyl trifluoromethanesulfonate (TMSOTf), a much stronger Lewis acid (Entry 6). Treatment of **10a** with $Me_2CuLi$ in the presence of TMSOTf in $Et_2O$ at −78 °C afforded the addition product **11a** almost quantitatively as an inseparable mixture of *cis* and *trans* isomers (*cis*:*trans*=2.5:1). Relative stereochemistry of these two isomers were determined by NOESY spectrum (see Experimental Section).

In order to realize much higher stereoselectivity, the reaction was further examined in detail. And it was found that the stereoselectivity was not influenced on

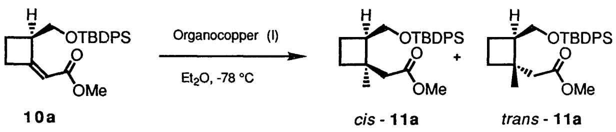
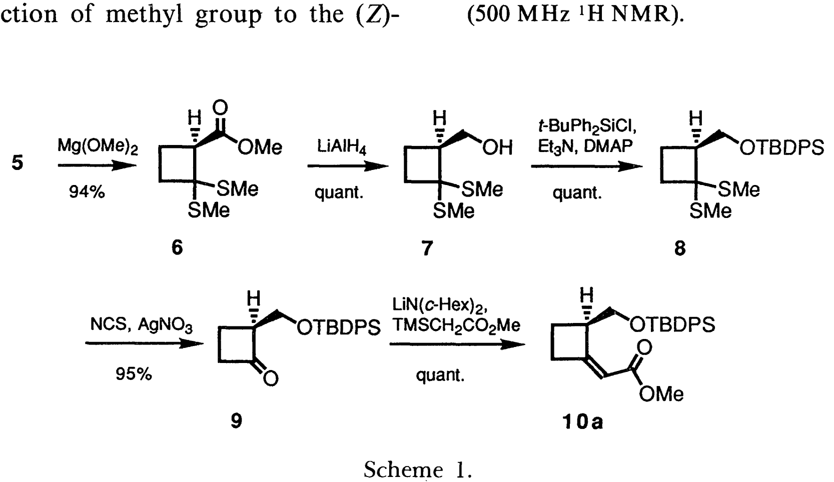


Table 1. The Conjugate Addition Reaction of Organocopper (I) Reagents with **10a**

| Entry | Organocopper (I) | Lewis acid | Yield ($x$/%) | **11a** *cis*:*trans*[a] |
|---|---|---|---|---|
| 1 | MeCu | | 0 | |
| 2 | $Me_2CuLi$ | | 0 | |
| 3 | MeCu | $BF_3$·$OEt_2$ | 0 | |
| 4 | $Me_2CuLi$ | $BF_3$·$OEt_2$ | 0 | |
| 5 | $Me_2CuLi$ | TMSCl | 60 | 2:1 |
| 6 | $Me_2CuLi$ | TMSOTf | quant. | 2.5:1 |

a) The ratio of *cis*:*trans* was determined by the integration ratio of the singlet peak of the quaternary methyl groups (500 MHz $^1$H NMR).



Scheme 1.

the solvent and the reaction temperature. The use of higher order organocuprates(I) was also ineffective. On the other hand, the diastereoselectivity was found to be largely dependent on the protective group of the hydroxyl group and the geometry of the α,β-unsaturated ester moiety.

The (*E*)-α,β-unsaturated esters having various hydroxyl protective groups were prepared from the (*Z*)-ester **10a** as shown in Scheme 2. The desilylation of the (*Z*)-ester **10a** with $Bu_4N^+F^-$ in THF at room temperature was accompanied with the isomerization to the (*E*)-ester **13**, though the complete racemization occurred at the same time with the fluoride anion. The isomerization was, therefore, tried with PhSLi in THF and the (*E*)-ester **12a** was obtained in 73% yield (the (*Z*)-ester **10a** was recovered in 26% yield). Deprotection of **12a** with hydrochloric acid in MeOH and the introduction of various protective groups gave the corresponding (*E*)-esters **12b,c**. By the $^1H$ NMR analysis of the (+)-MTPA ester[10)] of the alcohol **13**, no sign of racemization could be detected. The (*Z*)-esters **10b,c** were prepared by desilylation of **10a** with hydrochloric acid followed by the protection of the resulting alcohol.

The addition reaction to various (*Z*)- and (*E*)-esters **10** and **12** were examined with $Me_2CuLi$ and TMSOTf at −78 °C in $Et_2O$. When the (*Z*)- or (*E*)-esters protected as *t*-butyldiphenylsilyl ether or methyl ether **10a,b** and **12a,b** were employed, the stereoselectivity was not improved (Table 2, Entries 1—4). In the case of the reaction of the (*Z*)-ester having TMS ether **10c**, the selectivity was also low (Entry 5). On the contrary,

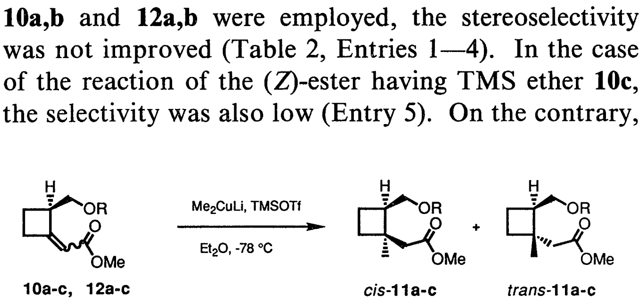
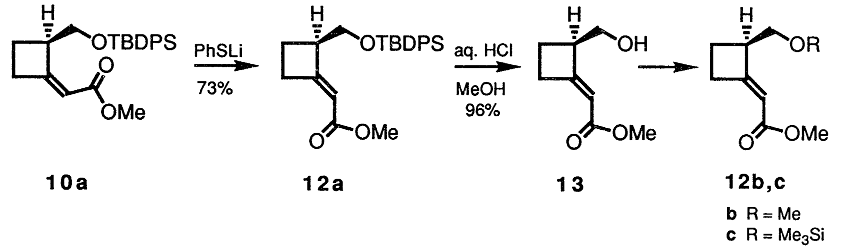


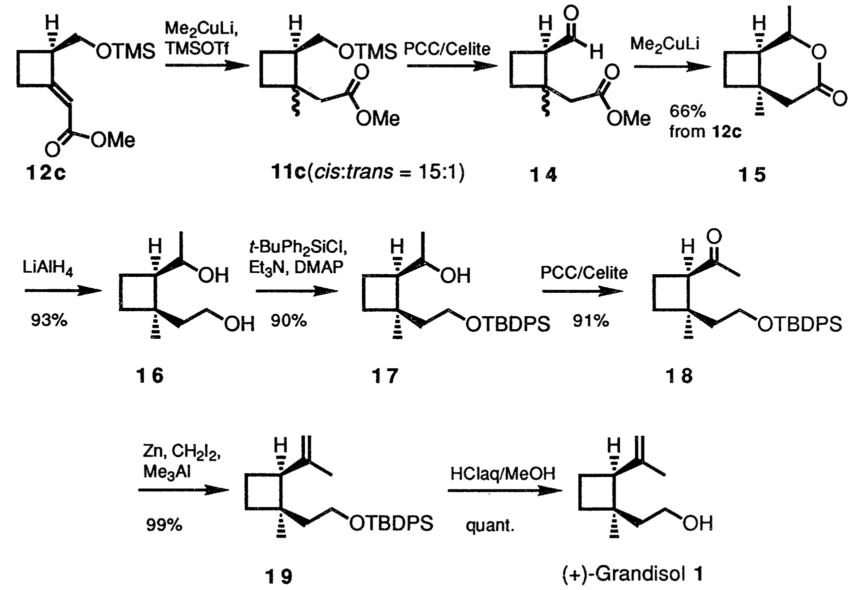
Table 2. The Conjugate Addition Reaction to (*Z*) and (*E*)-Esters **10** and **12**[a)]

| Entry | R | | **11a**—**c** ratio of *cis*:*trans*[b)] |
|---|---|---|---|
| 1 | *t*-$BuPh_2Si$ | **10a** | 2.5:1 |
| 2 | *t*-$BuPh_2Si$ | **12a** | 2.5:1 |
| 3 | Me | **10b** | 1.5:1 |
| 4 | Me | **12b** | 2:1 |
| 5 | $Me_3Si$ | **10c** | 2:1 |
| 6 | $Me_3Si$ | **12c** | 15:1 |

a) The yields of the addition products **11a**—**c** were almost quantitative. b) The ratio of *cis*:*trans* was determined by the integration ratio of the quaternary methyl peaks (500 MHz $^1H$ NMR).



Scheme 2.



Scheme 3.

it was noted that the reaction of the TMS ether of the (*E*)-ester **12c** gave the addition product **11c** in high stereoselectivity (the ratio of *cis*:*trans*=15:1) (Entry 6). These results indicate that the introduction of a small silyl group and the (*E*)-geometry of the double bond are indispensable to achieve high stereoselectivity.

Then the transformation of the stereoselectively prepared **11c** to (+)-grandisol **1** was executed as shown in Scheme 3. Oxidation of the crude Michael product **11c** (*cis*:*trans*=15:1) with pyridinium chlorochromate (PCC)/Celite in $CH_2Cl_2$ followed by the treatment with $Me_2CuLi$ in $Et_2O$ gave the *cis* bicyclic lactone **15** as a single stereoisomer (stereochemistry not determined) in 66% yield from **12c** in 3 steps. Reduction of the lactone **15** with $LiAlH_4$ afforded the diol **16** (93% yield), whose primary hydroxyl group was protected as *t*-butyldiphenylsilyl ether **17** in 90% yield. Oxidation of **17** with PCC/Celite (91% yield) and the treatment of the resulting ketone **18** with Zn, $CH_2I_2$ and $Me_3Al$[17] gave the methylenation product **19** in 99% yield. Finally, deprotection of **19** with hydrochloric acid in MeOH afforded (+)-grandisol **1** quantitatively.

The overall yield of **1** from **2** was ca. 25% in 17 steps. The spectral data were in good agreement with those of the literature.[4b,c,5b] The optical rotation of the synthesized (+)-grandisol was $[\alpha]_D^{27}$ +18.6° ($c$=1.00, hexane). The dextrorotatory of **1** confirmed the absolute stereochemistry of **5** to be *S* as expected.

To avoid the risk of determining the optical purity from the $[\alpha]_D$ value, the present sample **1** was converted to the corresponding Mosher's (+)-MTPA ester.[10] By the 500 MHz $^1$H NMR analysis of this (+)-MTPA ester, the optical purity of our (+)-grandisol was confirmed to be >98% ee.

## Experimental

**General.** NMR spectra were recorded on Hitachi R24B and Bruker AM500 spectrometers using tetramethylsilane as the internal standard. $CDCl_3$ was used as solvent. IR spectra were measured with Horiba FT-300S spectrometer. High-mass spectra were obtained with JEOL JMS-D300 mass spectrometer operating at 70 ev. The optical rotations were measured with JASCO DIP-370 digital polarimeter.

Column chromatography was conducted on silica gel (E. Merck, 7734, 70—230 mesh) and Florisil (Wako, 100—200 mesh) and medium pressure column chromatography was performed with the YFLC-254 system of Yamazen Corp. Preparative thin-layer chromatography (TLC) was carried out on a silica gel (Wakogel B-5F).

Dichloromethane was distilled from $P_2O_5$, then from $CaH_2$, and dried over MS 4A. Toluene and petroleum ether were distilled and dried over MS 4A. Tetrahydrofuran (THF) and diethyl ether ($Et_2O$) were freshly distilled from sodium diphenylketyl. Dichlorodiisopropoxytitanium was prepared from titanium(IV) chloride and titanium(IV) isopropoxide according to the literature method.[18] 1,1-Bis(methylthio)ethylene (**3**)[19] and (2*S*,3*S*)-1,1,4,4-tetraphenyl-2,3-*O*-(1-phenylethylidene)-1,2,3,4-butanetetrol (**4**)[9] were prepared according to the literature procedures. All the operations were performed under an argon atmosphere.

**3-Acryloyl-1,3-oxazolidin-2-one (2).** To a THF suspension (200 ml) of NaH (60% oil dispersion, 12.2 g, 0.30 mol) was added 1,3-oxazolidin-2-one (26.5 g, 0.30 mol) and the mixture was heated to reflux for 1 h and then cooled to 0 °C. A THF solution (100 ml) of acryloyl chloride (25.0 g, 0.28 mol) was added dropwise, and the mixture was stirred for 4 h. The pH 7 phosphate buffer was slowly poured into the mixture and the organic materials were extracted with ethyl acetate. The organic layers were washed with brine and dried over $Na_2SO_4$ with a catalytic amount of hydroquinone to prevent polymerization at 0 °C. Solvent was evaporated in vacuo below 10 °C. When the solvent was removed, the crude product was immediately purified by column chromatography (silica gel, dichloromethane) to give the title compound **2** (12.6 g, 42% yield). The pure material should be kept in a refrigerator. $^1$H NMR (60 MHz) $\delta$=3.83—4.13 (2H, m), 4.28—4.57 (2H, m), 5.82 (1H, dd, $J$=2.0, 10.0 Hz), 6.47 (1H, dd, $J$=2.0, 16.8 Hz), 7.43 (1H, dd, $J$=10.0, 16.8 Hz).

**(*S*)-3-[2,2-Bis(methylthio)-1-cyclobutylcarbonyl]-1,3-oxazolidin-2-one (5).** Toluene (300 ml) was added to dichlorodiisopropoxytitanium (1.40 g, 5.9 mmol), the chiral diol **4** (3.12 g, 5.9 mmol), and Molecular Sieves 4A (powder, 3.0 g) at 0 °C and the mixture was stirred for 30 min. Then **2** (10.0 g, 71 mmol) and petroleum ether (200 ml) were added. And a petroleum ether solution (100 ml) of **3** (10.0 g, 83 mmol) was added to the mixture, which was stirred at 0 °C for 1 h. The reaction was quenched by pH 7 phosphate buffer and inorganic materials were removed by filtration. The organic materials were extracted with ethyl acetate and the extracts were washed with brine and dried over $Na_2SO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexane:ethyl acetate=5:1) to afford the title compound **5** (14.8 g, 80% yield, 88% ee). The optically pure **5** was obtained by two recrystallizations from benzen-hexane (80% recovery). The optically pure **5** was used in the following experiments. Mp 90.5—92.0 °C; IR (KBr) 1780, 1690 cm$^{-1}$; $^1$H NMR (500 MHz) $\delta$=2.00 (3H, s), 2.12 (3H, s), 2.25—2.31 (1H, m), 2.32—2.38 (1H, m), 2.42—2.47 (1H, m), 2.53—2.60 (1H, m), 4.07 (2H, dt, $J$=5.5, 8.1 Hz), 4.41 (2H, t, $J$=8.1 Hz), 4.61—4.65 (1H, m); $^{13}$C NMR (125 MHz) $\delta$=12.36, 12.66, 18.81, 33.61, 42.62, 49.47, 61.55, 61.96, 153.03, 170.51; $[\alpha]_D^{26}$ −59.4° ($c$ 1.17, $CH_2Cl_2$), >98% ee; Anal. Calcd for $C_{10}H_{15}NO_3S_2$: C, 46.00; H, 5.78; N, 5.36; S, 24.53%. Found: C, 45.88; H, 5.69; N, 5.36; S, 24.92%.

Crystallographic data: M. F.=$C_{10}H_{15}NO_3S_2$, M. W.=261.35, orthorhombic, $a$=8.285 (3), $b$=22.304 (7), $c$=6.726 (2) (Å), $V$=1242.8 (7) (Å$^3$), space group $P2_12_12_1$, $Z$=4, $D_c$=1.40 g cm$^{-3}$, $\mu$(Mo$K\alpha$)=4.11 cm$^{-1}$. Data collection: crystal size=0.10×0.25×1.00 mm, $T_c$=25 °C, Mo$K\alpha$ radiation (graphite monochrometer), 1704 reflections ($2\theta$<55.0°). The structure was finally refined anisotropically for S, C, O, and N, and isotropically for H to give an $R$ factor of 0.052 for 1192 independent reflections with $I$>3.0$\sigma$ ($I$).

**Methyl (*S*)-2,2-Bis(methylthio)cyclobutane-1-carboxylate (6).** Dry methanol (40 ml) and a few drops of carbon tetrachloride was added to metal magnesium (1.9 g, 78 mmol) at 0 °C to generate magnesium methoxide. When all the magnesium dissolved, a THF (30 ml) solution of the [2+2] adduct **5** (6.7 g, 26 mmol) was added. The reaction was immediately quenched with saturated aqueous ammonium chloride solution and the methyl ester was extracted with ethyl acetate. The organic layers were washed with brine and dried over $Na_2SO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexane:ethyl acetate=14:1) to afford the methyl ester **6** (5.0 g, 94% yield). IR (KBr) 1736 $cm^{-1}$; $^{1}H$ NMR (500 MHz) $\delta$=2.01 (3H, s), 2.10 (3H, s), 2.21—2.34 (3H, m), 2.51—2.56 (1H, m), 3.38—3.42 (1H, m), 3.73 (3H, s); $^{13}C$ NMR (125 MHz) $\delta$=12.27, 12.69, 16.80, 33.43, 51.53, 51.71, 60.70, 171.12; $[\alpha]_D^{24}-119.3°$ (*c* 1.12, $CH_2Cl_2$); HRMS Found: *m*/*z* 206.0431. Calcd for $C_8H_{14}O_2S_2$: M, 206.0436.

**(*S*)-[2,2-Bis(methylthio)-1-cyclobutyl]methanol (7).** A THF solution (20 ml) of **6** (2.66 g, 12.9 mmol) was added to a THF suspension (30 ml) of lithium aluminum hydride (1.0 g, 26 mmol) at 0 °C and the mixture was stirred for 5 min. Then saturated aqueous sodium sulfate solution was added dropwise until hydrogen evolution ceased. Inorganic materials were removed by filtration and washed with portions of hot isopropyl alcohol. The filtrate was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, hexane:ethyl acetate=9:1) to give the title compound **7** (2.30 g, quant.). IR (KBr) 3394 $cm^{-1}$; $^{1}H$ NMR (500 MHz) $\delta$=1.89—1.94 (1H, m), 2.05 (3H, s), 2.07 (3H, s), 2.20—2.29 (4H, m), 2.65—2.69 (1H, m), 3.73 (1H, dd, *J*=4.8, 11.7 Hz), 3.83 (1H, dd, *J*=7.8, 11.7 Hz); $^{13}C$ NMR (125 MHz) $\delta$=12.39, 12.50, 19.08, 33.59, 49.33, 61.04, 63.46; $[\alpha]_D^{25}-34.1°$ (*c* 1.02, $CH_2Cl_2$); HRMS Found: *m*/*z* 178.0485. Calcd for $C_7H_{14}OS_2$: M, 178.0487.

**Optical Purity of 7.** The optical purity was checked by the $^{1}H$ NMR (500 MHz) analysis of the corresponding (+)-MTPA ester[10] of the alcohol **7**. The two sets of two singlet signals due to the methylthio groups of the racemate appeared at 1.89, 1.92 and 1.92, 1.95 ppm. In the present sample, only one set of two singlet peaks was observed at 1.92, 1.95 ppm and the other set could not be detected. So this sample was determined to be >98% ee.

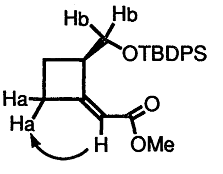
***t*-Butyldiphenylsilyl Ether of 7.** To a dichloromethane ($CH_2Cl_2$) solution (20 ml) of **7** (1.47 g, 8.2 mmol) was added a $CH_2Cl_2$ solution (5 ml) of triethylamine (1.68 g, 16.6 mmol) at 0 °C. Then a $CH_2Cl_2$ solution (5 ml) of *t*-butylchlorodiphenylsilane (2.73 g, 9.9 mmol) and a catalytic amount of 4-dimethylaminopyridine were added. After being stirred overnight, the reaction was quenched by pH 7 phosphate buffer and the organic materials were extracted with $CH_2Cl_2$. The extracts were washed with brine and dried over $Na_2SO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexane:ethyl acetate=14:1) to afford the TBDPS ether **8** (3.49 g, quant). $^{1}H$ NMR (500 MHz) $\delta$=1.04 (9H, s), 1.70—1.77 (1H, m), 2.02 (3H, s), 2.06 (3H, s), 2.07—2.24 (3H, m), 2.77—2.81 (1H, m), 3.58 (1H, dd, *J*=5.8, 10.8 Hz), 3.95 (1H, dd, *J*=8.6, 10.8 Hz), 7.36—7.44 (6H, m), 7.66—7.71 (4H, m); $[\alpha]_D^{25}-15.6°$ (*c* 1.00, $CH_2Cl_2$).

**(*S*)-2-*t*-Butyldiphenylsiloxymethyl-1-cyclobutanone (9).** A solution of **8** (2.20 g, 5.3 mmol) in acetonitrile (20 ml) was added quickly to a well-stirred solution of *N*-chlorosuccinimide (2.11 g, 15.8 mmol) and silver nitrate (3.14 g, 18.5 mmol) in aqueous 90% acetonitrile (20 ml) at 0 °C. The mixture was stirred for 5 min and treated successively at 1-min intervals with saturated aqueous sodium sulfite, saturated aqueous sodium carbonate, and brine (10 ml each). And then inorganic materials were removed by filtration. The organic material was extracted with ethyl acetate and the organic layers were washed with brine and dried over $Na_2SO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexane:ethyl acetate=14:1) to give the title compound **9** (1.69 g, 95% yield). IR (KBr) 1784 $cm^{-1}$; $^{1}H$ NMR (500 MHz) $\delta$=1.04 (9H, s), 2.08—2.23 (2H, m), 3.02 (2H, t, *J*=8.5 Hz), 3.40—3.44 (1H, m), 3.70 (1H, dd, *J*=3.8, 10.6 Hz), 3.98 (1H, dd, *J*=4.1, 10.6 Hz), 7.37—7.44 (6H, m), 7.59—7.69 (4H, m); $^{13}C$ NMR (125 MHz) $\delta$=13.54, 19.28, 26.74, 45.96, 61.23, 62.43, 127.70, 129.71, 133.00, 135.51, 210.85; $[\alpha]_D^{27}-16.0°$ (*c* 1.02, $CH_2Cl_2$).

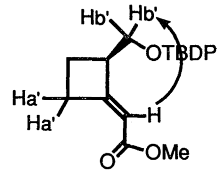
**Methyl [(*R*),(*Z*)-2-(*t*-Butyldiphenylsiloxy)methyl-1-cyclobutylidene]acetate (10a).** A solution of dicyclohexylamine (2.65 g, 14.6 mmol) in THF (20 ml) was treated with BuLi (8.8 ml, 1.66 M (1 M=1 mol $dm^{-3}$) in hexane) at −78 °C. After the mixture was stirred for 30 min at −78 °C, a solution of methyl trimethylsilylacetate (2.14 g, 14.6 mmol) in THF (10 ml) was added dropwise, and the resulting solution was stirred for 30 min at −78 °C. Then to this solution was added dropwise a THF (10 ml) solution of **9** (2.42 g, 7.2 mmol) at −78 °C. The reaction mixture was stirred for 1 h and then treated with pH 7 phosphate buffer. The organic materials were extracted with ethyl acetate and the extracts were washed with brine and dried over $Na_2SO_4$. After the solvent was removed in vacuo, the crude material was purified by column chromatography (silica gel, hexane:ethyl acetate=14:1) to afford the title compound **10a** (2.82 g, quant.). IR (KBr) 1718, 1676 $cm^{-1}$; $^{1}H$ NMR (500 MHz) $\delta$=1.05 (9H, s), 2.19—2.24 (2H, m), 2.62—2.69 (1H, m), 2.88—2.96 (1H, m), 3.54 (3H, s), 3.52—3.58 (1H, m), 3.88 (1H, dd, *J*=3.8, 9.9 Hz), 4.03 (1H, dd, *J*=5.5, 9.9 Hz), 5.64 (1H, dd, *J*=2.2, 4.3 Hz), 7.32—7.40 (6H, m), 7.62—7.68 (4H, m); $^{13}C$ NMR (125 MHz) $\delta$=19.34, 20.70, 26.81, 30.73, 47.78, 50.71, 63.89, 113.55, 127.51, 129.52, 133.70, 135.59, 166.23, 168.09; $[\alpha]_D^{25}-124.4°$ (*c* 0.95, $CH_2Cl_2$).

**Methyl [(*R*),(*E*)-2-(*t*-Butyldiphenylsiloxy)methyl-1-cyclobutylidene]acetate (12a).** To a solution of thiophenol (31.7 mg, 0.29 mmol) in THF (2 ml) was added a hexane solution (0.18 ml) of BuLi (1.57 M in hexane) at 0 °C and the resulting solution was stirred for 10 min. Then a THF (2 ml) solution of **10a** (115.4 mg, 0.29 mmol) was added. After the mixture was stirred overnight, the reaction was quenched by pH 7 phosphate buffer and the organic materials were extracted with ethyl acetate. The organic layers were washed with brine and dried over $Na_2SO_4$. After the solvent was evaporated, the crude product was purified by column chromatography (silica gel, hexane:ethyl acetate=9:1) to afford the (*E*)-form ester **12a** (83.8 mg, 73% yield) and the recovered starting material **10a** (30.2 mg, 26% yield). Then the same operations with the recovered **10a** were carried out once again. The (*E*)-form compound **12a** was totally obtained in 91% yield. IR (KBr) 1718, 1676 $cm^{-1}$; $^{1}H$ NMR (500 MHz) $\delta$=1.06 (9H,s), 1.85—1.91 (1H, m), 2.15 (1H, ddt, *J*=6.1, 9.3, 11.2 Hz), 2.96—3.10 (2H, m), 3.23—3.28 (1H, m), 3.69 (3H, s), 3.73 (2H, d, *J*=6.4 Hz), 5.74 (1H, dd, *J*=2.4, 4.6 Hz), 7.34—7.45 (6H, m), 7.65—7.68 (4H, m); $^{13}C$ NMR (125 MHz) $\delta$=19.22, 20.67, 26.80, 31.05, 46.52, 50.84, 65.28, 112.32, 127.65, 129.65, 133.50, 135.59, 166.94, 168.54; $[\alpha]_D^{27}+1.5°$ (*c* 1.61, $CH_2Cl_2$).

**Assignment of the Stereochemistry of 10a and 12a.** The stereochemistry (*E* or *Z*) of the $\alpha,\beta$-unsaturated ester **10a** and **12a** was determined by NOESY spectra. The NOEs were observed between the olefinic proton and Ha in **10a** and between the olefinic proton and $H_{b'}$ in **12a** as shown in the figure.



**10a** (*Z*)-form



**12a** (*E*)-form

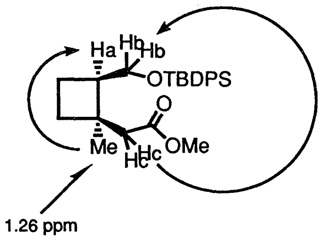
**Methyl [(*R*),(*E*)-2-Hydroxymethyl-1-cyclobutylidene]acetate (13).** To a methanol solution (10 ml) of **12a** (245 mg, 0.62 mmol) was added a few drops of concd hydrochloric acid at room temperature. After being stirred for 3.5 h, the mixture was treated with pH 7 phosphate buffer and the organic materials were extracted with ethyl acetate. The extracts were washed with brine and dried over $Na_2SO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexane: ethyl acetate=9 : 1) to give the alcohol **13** (92.8 mg, 96% yield). IR (KBr) 3450, 1711, 1676 $cm^{-1}$; $^1H$ NMR (500 MHz) $\delta$=1.61—1.64 (1H, bs), 1.89—1.96 (1H, m), 2.22 (1H, ddt, $J$=6.1, 9.2, 11.3 Hz), 3.00—3.14 (2H, m), 3.25—3.31 (1H, m), 3.69 (3H, s), 3.68—3.72 (1H, m), 3.78 (1H, dd, $J$=6.3, 10.9 Hz), 5.74 (1H, dd, $J$=2.5, 4.8 Hz); $[\alpha]_D^{25}$+20.7° ($c$ 1.45, $CH_2Cl_2$); HRMS Found: $m/z$ 156.0763. Calcd for $C_8H_{12}O_3$: M, 156.0786.

**Methyl [(*R*),(*E*)-2-(Trimethylsiloxy)methyl-1-cyclobutylidene]-acetate (12c).** A $CH_2Cl_2$ solution (3 ml) of triethylamine (313 mg, 3.1 mmol) was added to a $CH_2Cl_2$ solution (5 ml) of **13** (152 mg, 0.97 mmol) at 0 °C. Then a $CH_2Cl_2$ solution (2 ml) of chlorotrimethylsilane (218 mg, 2.0 mmol) and a catalytic amount of 4-dimethylaminopyridine were added to the mixture. After being stirred overnight at room temperature, the resulting solution was quenched by pH 7 phosphate buffer and the organic materials were extracted with $CH_2Cl_2$. The organic layers were washed with brine and dried over $Na_2SO_4$. After the solvent was removed, the crude product was purified by column chromatography (florisil, hexane: ethyl acetate=9 : 1) to give the TMS ether **12c** (212 mg, 95% yield). IR (KBr) 1716, 1676 $cm^{-1}$; $^1H$ NMR (500 MHz) $\delta$=0.09 (9H, s), 1.76—1.83 (1H, m), 2.12—2.20 (1H, m), 2.94—3.08 (2H, m), 3.17—3.23 (1H, m), 3.63 (2H, d, $J$=7.0 Hz), 3.66 (3H, s), 5.69—5.71 (1H, m); $[\alpha]_D^{23}$+5.9° ($c$ 1.43, $CH_2Cl_2$).

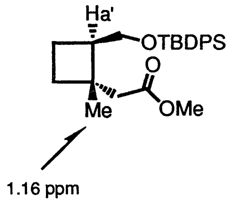
(*Z*)-form **10c**: $^1H$ NMR (500 MHz) $\delta$=0.08 (9H, s), 1.97—2.03 (1H, m), 2.16 (1H, ddd, $J$=8.6, 11.1, 17.3 Hz), 2.58—2.65 (1H, m), 2.77—2.86 (1H, m), 3.38—3.53 (1H, m), 3.65 (3H, s), 3.78 (1H, dd, $J$=8.1, 10.5 Hz), 3.90 (1H, dd, $J$=4.0, 10.5 Hz), 5.60—5.62 (1H, m).

**Methyl [(*R*)-1-Methyl-2-(trimethylsiloxy)methyl-1-cyclobutyl]-acetate (11c).** To an $Et_2O$ suspension (5 ml) of CuI (324 mg, 1.7 mmol) was added dropwise MeLi (3.0 ml, 1.15 M in $Et_2O$) at −23 °C to generate lithium dimethylcuprate(I). The resulting solution was stirred for 30 min and then cooled to −78 °C. An $Et_2O$ solution (3 ml) of **12c** (77.2 mg, 0.34 mmol) and TMSOTf (375 mg, 1.7 mmol) was added dropwise at −78 °C. After being stirred overnight at that temperature, the mixture was treated with saturated aqueous sodium hydrogencarbonate and inorganic materials were filtered off. The organic materials were extracted with ether and the extracts were washed with brine and dried over $Na_2SO_4$. After evaporation of the solvent, the crude product **11c** was directly used for further transformation. IR (KBr) 1739 $cm^{-1}$; $^1H$ NMR (500 MHz) *cis*-**11c** $\delta$=0.07 (9H, s), 1.20 (3H, s), 1.50—1.67 (2H, m), 1.88—2.02 (2H, m), 2.14—2.17 (1H, m), 2.37 (1H, d, $J$=14.5 Hz), 2.53 (1H, d, $J$=14.5 Hz), 3.53 (1H, dd, $J$=6.3, 10.6 Hz), 3.61 (3H, s), 3.59—3.63 (1H, s); *trans*-**11c** $\delta$=1.10 (3H, s), 3.65 (3H, s); $^{13}C$ NMR (125 MHz) $\delta$=−0.52, 18.64, 27.59, 30.57, 38.73, 40.00, 46.29, 51.09, 63.00, 173.27; HRMS Found: $m/z$ 244.1502. Calcd for $C_{12}H_{24}O_3Si$: M, 244.1495.

**Assignment of the Stereochemistry of the Conjugate Addition Product.** The relative stereochemistry of the conjugate addition products was determined by the NOESY spectrum of **11a**. In the major isomer, the NOEs were observed between the quaternary methyl group and $H_a$ proton, $H_b$ and $H_c$ respectively, as shown in the following figure. The stereochemistry of the major isomer was assigned as *cis* and the minor was *trans*. The singlet signal of the methyl group of the *cis* isomer appeared at 1.26 ppm and that of *trans* isomer appeared at 1.16 ppm.



the major isomer (*cis*)



the minor isomer (*trans*)

In the case of the compound **11c**, the stereochemistry was assigned from the chemical shift of the quaternary methyl group. The major isomer of **11c**, whose methyl singlet signal appeared at lower field (1.20 ppm), was determined to be *cis* isomer and the minor isomer (the methyl signal was observed at 1.10 ppm) was assigned as *trans*. These assignments of the stereochemistry were confirmed by the formation of the lactone **15** from the major isomer. The minor isomer (*trans*) could not form a lactone.

**Methyl [(*R*)-1-Methyl-2-formyl-1-cyclobutyl]acetate (14).** To a well-stirred suspension of pyridinium chlorochromate (PCC) (150 mg, 0.7 mmol) and celite (300 mg) in $CH_2Cl_2$ (3 ml) was added a $CH_2Cl_2$ solution (2 ml) of the crude product **11c** at 0 °C. After being stirred for 3 h, the mixture was filtered through silica gel. Then the filtrate was concentrated and the crude product **14** was directly used for further transformation. IR (KBr) 1736, 1714 $cm^{-1}$; $^1H$ NMR (500 MHz) the *cis*-isomer $\delta$=1.31 (3H, s), 1.72—1.78 (1H, m), 1.81—1.96 (2H, m), 2.20—2.27 (1H, m), 2.35 (1H, d, $J$=15.7 Hz), 2.52 (1H, d, $J$=15.7 Hz), 2.95—2.98 (1H, m), 3.57 (3H, s), 9.81 (1H, d, $J$=1.8 Hz); the *trans*-isomer $\delta$=1.12 (3H, s), 1.58—1.64 (1H, m), 1.81—1.96 (2H, m), 2.35—2.39 (1H, m), 2.44 (1H, d, $J$=15.0 Hz), 2.56 (1H, d, $J$=15.0 Hz), 3.11—3.14 (1H, m), 3.62 (3H, s), 9.76 (1H, s).

**(1*R*,6*R*)-2,6-Dimethyl-3-oxabicyclo[4.2.0]octan-4-one (15).** To an $Et_2O$ suspension (5 ml) of CuI (325 mg, 1.7 mmol) was added dropwise MeLi (3.0 ml, 1.15 M in $Et_2O$) at −23 °C to generate lithium dimethylcuprate(I). The resulting solution was stirred for 30 min and then cooled to −78 °C, to which an $Et_2O$ solution (2 ml) of the crude **14** was added dropwise at

−78 °C. After being stirred for 15 min, the mixture was treated with saturated aqueous sodium hydrogencarbonate and inorganic materials were filtered off. The organic materials were extracted with ether and the extracts were washed with brine and dried over Na$_2$SO$_4$. After distillation of the solvent, the crude product was purified by thin-layer chromatography (hexane:ethyl acetate=3:1) to give the *cis* bicyclic lactone **15** (34.4 mg) in 66% overall yield from **12c** in 3 steps. IR (KBr) 1739 cm$^{-1}$; $^1$H NMR (500 MHz) $\delta$=1.19 (3H, s), 1.29 (3H, d, $J$=6.4 Hz), 1.62—1.68 (1H, m), 1.88—1.92 (1H, m), 1.94 (2H, t, $J$=8.5 Hz), 2.21 (1H, ddd, $J$=8.7, 12.6, 17.5 Hz), 2.36 (1H, d, $J$=15.0 Hz), 2.58 (1H, d, $J$=15.0 Hz), 4.34 (1H, dq, $J$=6.4, 8.7 Hz); $^{13}$C NMR (125 MHz) $\delta$=17.93, 19.06, 28.22, 32.21, 35.71, 42.24, 44.34, 78.93, 173.14; $[\alpha]_D^{24}$ −102.9° ($c$ 1.13, CH$_2$Cl$_2$); HRMS Found: $m/z$ 154.0947. Calcd for C$_9$H$_{14}$O$_2$: M, 154.0994.

**2-[(1*R*,2*R*)-1-Methyl-2-(1-hydroxyethyl)-1-cyclobutyl]ethanol (16).** A THF solution (2 ml) of **15** (43.3 mg, 0.28 mmol) was added to a THF suspension (3 ml) of lithium aluminum hydride (37.0 mg, 0.97 mmol) at 0 °C and the mixture was stirred for 5 min. Then saturated sodium sulfate solution was added dropwise until hydrogen evolution ceased. Inorganic materials were removed by filtration and washed with portions of hot isopropyl alcohol. After the filtrate was concentrated in vacuo, the crude product was purified by thin-layer chromatography (hexane:ethyl acetate=2:1) to give the title compound **16** (41.3 mg, 93% yield). IR (KBr) 3323 cm$^{-1}$; $^1$H NMR (500 MHz) $\delta$=0.99 (3H, d, $J$=6.1 Hz), 1.11 (3H, s), 1.37—1.44 (1H, m), 1.49—1.60 (3H, m), 1.79—1.85 (2H, m), 2.02 (1H, ddd, $J$=7.5, 8.7, 14.2 Hz), 3.00—3.10 (2H, bs), 3.60 (1H, ddd, $J$=4.2, 7.4, 10.5 Hz), 3.71 (1H, ddd, $J$=6.5, 8.9, 10.5 Hz), 3.81 (1H, dq, $J$=6.1, 9.7 Hz); $[\alpha]_D^{24}$ +27.3° ($c$ 1.59, CH$_2$Cl$_2$).

***t*-Butyldiphenylsilyl Ether of 16.** To a CH$_2$Cl$_2$–dimethylformamide 1:1 solution (6 ml) of **16** (36.7 mg, 0.23 mmol) was added a CH$_2$Cl$_2$ solution (1.5 ml) of triethylamine (79.5 mg, 0.79 mmol) at 0 °C. Then a CH$_2$Cl$_2$ solution (1.5 ml) of *t*-butylchlorodiphenylsilane (114 mg, 0.42 mmol) and a catalytic amount of 4-dimethylaminopyridine were added. After being stirred overnight, the mixture was treated with pH 7 phosphate buffer and the organic materials were extracted with CH$_2$Cl$_2$. The extracts were washed with brine and dried over Na$_2$SO$_4$. After evaporation of the solvent, the crude product was purified by thin-layer chromatography (hexane: ethyl acetate=5:1) to afford the silyl ether **17** (82.8 mg, 90% yield). IR (KBr) 3392 cm$^{-1}$; $^1$H NMR (500 MHz) $\delta$=1.01 (3H, d, $J$=6.3 Hz), 1.03 (3H, s), 1.05 (9H, s), 1.38—1.48 (2H, m), 1.50—1.60 (2H, m), 1.74—1.82 (2H, m), 1.84 (2H, t, $J$=7.2 Hz), 3.66—3.71 (1H, m), 3.74—3.81 (2H, m), 7.35—7.43 (6H, m), 7.68—7.72 (4H, m); $[\alpha]_D^{25}$ +15.5° ($c$ 0.81, CH$_2$Cl$_2$).

**(1*R*,2*R*)-2-[2-(*t*-Butyldiphenylsiloxy)ethyl]-2-methyl-1-cyclobutyl Methyl Ketone (18).** To a well-stirred suspension of pyridinium chlorochromate (PCC) (42.5 mg, 0.17 mmol) and celite (85 mg) in CH$_2$Cl$_2$ (2 ml) was added a solution of the alcohol **17** (34.2 mg, 0.09 mmol) in CH$_2$Cl$_2$ (2 ml) at 0 °C. After being stirred for 4 h, the mixture was filtered through silica gel. Then the filtrate was concentrated in vacuo and the crude product was purified by thin-layer chromatography (hexane:ethyl acetate=5:1) to afford the title compound **18** (31.1 mg, 91% yield). IR (KBr) 1705 cm$^{-1}$; $^1$H NMR (500 MHz) $\delta$=1.02 (9H, s), 1.23 (3H, s), 1.54—1.61 (1H, m), 1.68—1.74 (2H, m), 1.79 (1H, ddd, $J$=6.0, 8.0, 13.4 Hz), 1.99 (3H, s), 2.23 (1H, ddd, $J$=8.8, 11.2, 18.3 Hz), 2.91 (1H, t, $J$=8.2 Hz), 3.60 (1H, ddd, $J$=6.0, 8.0, 10.4 Hz), 3.66 (1H, ddd, $J$=6.0, 8.0, 10.4 Hz), 7.35—7.43 (6H, m), 7.63—7.65 (4H, m); $^{13}$C NMR (125 MHz) $\delta$=16.19, 19.02, 26.80, 28.00, 29.52, 30.42, 37.31, 42.86, 57.28, 60.44, 127.60, 129.55, 133.71, 135.53, 208.34; $[\alpha]_D^{24}$ −29.5° ($c$ 1.32, CH$_2$Cl$_2$).

***t*-Butyldiphenylsilyl Ether of (+)-Grandisol 19.** The operations were carried out according to the literature procedure.[17] A solution of diiodomethane (220 mg, 0.82 mmol) in THF (3 ml) was added to activated zinc powder (135 mg, 2.1 mmol) and then a hexane solution (1.6 ml) of trimethylaluminum (1.0 M in hexane) was added. The resulting suspension was stirred for 10 min. A THF solution (2 ml) of the ketone **18** (66.2 mg, 0.17 mmol) was added dropwise to the mixture. After being stirred for 1 h, the mixture was cooled to 0 °C and diluted with ether and 1 M hydrochloric acid was added dropwise until all the zinc dissolved. The organic materials were extracted with ether and the extracts were washed with brine and dried over Na$_2$SO$_4$. After evaporation of the solvent, the crude product was purified by thin-layer chromatography (hexane:ethyl acetate=5:1) to give the title compound **19** (65.4 mg, 99% yield). $^1$H NMR (500 MHz) $\delta$=1.05 (9H, s), 1.08 (3H, s), 1.40 (1H, dddd, $J$=1.2, 6.1, 8.9, 13.7 Hz), 1.46—1.59 (2H, m), 1.62 (3H, d, $J$=0.7 Hz), 1.70—1.79 (2H, m), 1.83—1.92 (1H, m), 2.47 (1H, t, $J$=9.1 Hz), 3.66 (1H, ddd, $J$=5.8, 8.9, 10.0 Hz), 3.72 (1H, ddd, $J$=6.0, 8.9, 10.2 Hz), 4.60 (1H, bs), 4.80 (1H, bs), 7.36—7.43 (6H, m), 7.67—7.69 (4H, m); $^{13}$C NMR (125 MHz) $\delta$=19.10, 19.15, 23.17, 26.88, 28.41, 29.22, 36.17, 41.29, 52.69, 61.17, 109.55, 127.56, 129.49, 134.08, 135.61, 145.25; $[\alpha]_D^{23}$ +2.6° ($c$ 1.28, CH$_2$Cl$_2$).

**(+)-Grandisol (1).** To a methanol solution (5 ml) of **19** (64.0 mg, 0.16 mmol) was added as few drops of concd hydrochloric acid at room temperature. After being stirred for 2 h, the mixture was diluted with pH 7 phosphate buffer and the organic materials were extracted with ether. The extracts were washed with brine and dried over Na$_2$SO$_4$. After distillation of the solvent, the crude product was purified by thin-layer chromatography (hexane:ethyl acetate=2:1) to give the (+)-grandisol **1** (25.3 mg, quant.). IR (KBr) 3342, 3080, 2949, 2868, 1645, 1450, 1375, 1240, 1053, 1012, 887 cm$^{-1}$; $^1$H NMR (500 MHz) $\delta$=1.15 (3H, s), 1.42 (1H, dddd, $J$=1.2, 6.2, 9.4, 13.4 Hz), 1.35—1.45 (1H, m), 1.55—1.67 (2H, m), 1.65 (3H, s), 1.70—1.81 (2H, m), 1.91—1.99 (1H, m), 2.52 (1H, bt, $J$=9.0 Hz), 3.63 (1H, ddd, $J$=5.6, 9.4, 10.2 Hz), 3.66 (1H, ddd, $J$=6.2, 9.4, 10.2 Hz), 4.62 (1H, bs), 4.81 (1H, bs); $^{13}$C NMR (125 MHz) $\delta$=19.14, 23.20, 28.34, 29.30, 36.91, 41.28, 52.48, 59.94, 109.73, 145.19; $[\alpha]_D^{27}$ +18.6° ($c$ 1.00, hexane), >98% ee.

**Optical Purity of 1.**[5b)] The optical purity of **1** was determined by the $^1$H NMR (500 MHz) analysis of the (+)-MTPA ester[10)] of **1**. A set of the singlet signals of the methyl group adjacent to the quaternary carbon of the racemate appeared at 1.141 and 1.151 ppm. The corresponding (+)-MTPA ester of the optically active sample **1** showed only one singlet signal of the methyl group at 1.151 ppm. Therefore, the enantiomeric excess of **1** was determined absolutely to be >98% ee.

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