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Enantioselective Synthesis of (−)-Vertinolide

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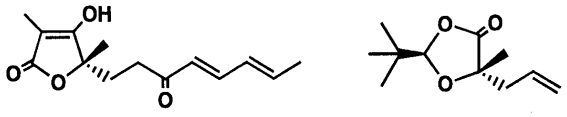
(−)-Vertinolide, a β-tetronic acid derivative isolated from *Verticillium intertextum* as one of the mycotoxins, was synthesized starting from (*R*)-lactic acid as the chiral source by using Seebach's chiral self-reproduction method. The β-tetronic acid moiety was constructed by reductive dehydroxylation of α,β-dihydroxybutanolide with samarium(II) iodide and subsequent oxidation.

Key words (−)-vertinolide; β-tetronic acid; mycotoxin; enantioselective synthesis; samarium(II) iodide

(−)-Vertinolide (**1**) is a β-tetronic acid derivative isolated from a culture of *Verticillium intertextum* as one of the mycotoxins.[1] Its chemical structure was determined by X-ray crystallographic analysis in 1982.[2] Four total syntheses have since confirmed the original assignment and unambiguously established the 5-(*S*)-absolute configuration.[3] The first synthesis of (−)-**1** by Wrobel and Ganem[3a] consisted of the Sharpless asymmetric epoxidation of geraniol while Yamashita and Takaiwa[3b] in the second synthesis obtained the starting chiral lactone by optical resolution of the racemate. Desmaële[3c] used the addition reaction of the enamine prepared from 2-methyl-4,5-dihydro-3-furanone and (*R*)-1-phenylethylamine to methyl acrylate as the key reaction. Finally, Schmidt *et al.*[3d] synthesized the chiral lactone by the addition reaction of the chiral lithium reagent to ethyl levulinate.

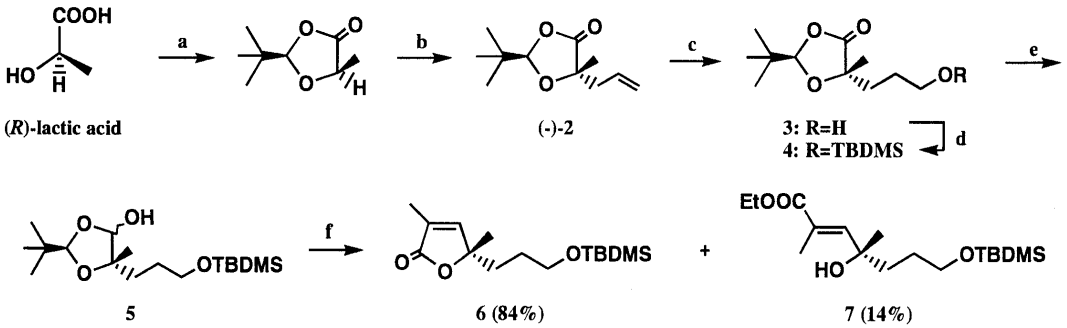
During the course of our chiral synthetic studies on biologically active natural products, which have a chiral quaternary carbon atom substituted by one oxygen, we have reported the synthesis of (−)-malyngolide[4] and (−)-frontalin[5] starting from D-lactose and (+)-ipomeamarone[6] from (*S*)-lactic acid as chiral sources. (−)-Vertinolide (**1**) has a chiral quaternary carbon atom that is substituted by one oxygen atom. Therefore, we investigated the synthesis of (−)-**1** as our next synthetic target.

In our synthetic work on (−)-**1**,[7] the dioxolanone derivative (−)-**2** was chosen as the starting synthon, because (−)-**2** possesses the proper chiral center required for the synthesis of (−)-**1** and the allyl group is convenient for the construction of the side chain present in (−)-**1**. The synthon (−)-**2** had been synthesized by us[6b] in the optically pure form using Seebach's chiral self-reproduction method,[8] involving the stereoselective allylation of (2*R*,5*R*)-(−)-2-*tert*-butyl-5-methyl-1,3-dioxolan-4-one, prepared by the condensation of (*R*)-lactic acid with 2,2-dimethylpropanal. Hydroboration of (−)-**2** with 9-borabicyclo[3.3.1]nonane (9-BBN) and subsequent H_2O_2 oxidation under basic conditions gave the alcohol **3** in 97% yield,[9] of which the hydroxyl group was protected as *tert*-butyldimethylsilyl (TBDMS) ether to afford **4** in 91% yield. For the construction of the β-tetronic acid nucleus, a straightforward reaction was first examined. Thus, we attempted to react lithium 2-lithiopropanoate with **4** at 0 °C or −78 °C, but unreacted **4** was recovered in both cases.[10] As the carbonyl group of **4** was inert to the above nucleophilic reagents, **4** was converted to the hemiacetal **5** with diisobutylaluminum hydride (DIBAL-H) in CH_2Cl_2 in 98% yield.[11] Treatment of **5** with 2-bromopropionic acid in the presence of lithium diisopropylamide (LDA) at −78 °C gave 1-hydroxy-4-pentanone TBDMS ether in 45% yield, but not the desired lactone. The Reformatsky-type reaction of **5** with methyl 2-bromopropionate in the presence of activated zinc and iodine[12] in tetrahydrofuran (THF) at refluxing tempera-



(-)-Vertinolide 1 **(-)-2**

Fig. 1



(*R*)-lactic acid **(-)-2** **5** **6 (84%)** **7 (14%)**

Reagents and conditions: a) *p*-TsOH, c. H_2SO_4, 2,2-dimethylpropanal in refluxing pentane (56%); b) LDA, allyl bromide in THF, -78 °C (62%); c) 1) 9-BBN in THF; 2) 31% H_2O_2, 3M NaOH (97%); d) TBDMSCl, imidazole in CH_2Cl_2 (91%); e) DIBAL-H in CH_2Cl_2, -78 °C (98%); f) triethyl 2-phosphonopropionate, NaH in THF.

Chart 1

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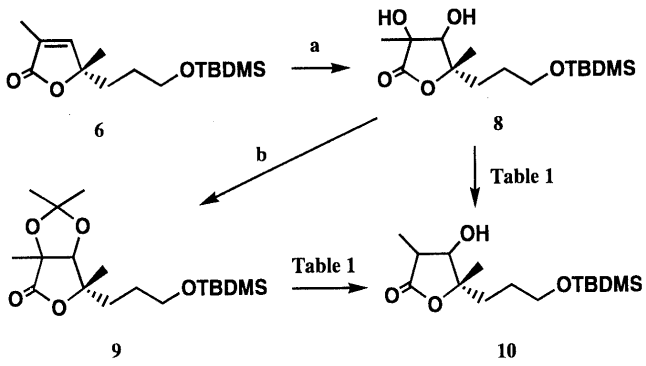
ture resulted in the formation of a complex mixture.

In our (+)-ipomeamarone synthesis,[6] the Wittig–Horner reaction of a hemiacetal similar to **5** gave good results. Therefore, the Wittig–Horner reaction of triethyl 2-phosphonopropionate and **5** in the presence of sodium hydride in THF was performed, and the desired butenolide **6** and the hydroxyester **7** were obtained in 84 and 14% yields, respectively. Therefore, we next tried to convert the butenolide **6** into the β-tetronic acid derivative. Dihydroxylation of **6** with osmium tetroxide (OsO_4) in the presence of 4-methylmorpholine *N*-oxide (NMO) gave the desired lactone **8** in 45% yield.[13] When the dihydroxylation of **6** was performed with ruthenium(III) chloride and sodium metaperiodate in a mixture of H_2O–ethyl acetate–acetonitrile at 0 °C, the yield of **8** was improved to 68%.[14] As the dihydroxylactone **8** was available, the reductive dehydroxylation of the α-position of the carbonyl group of **8** was next examined. Hegedus and Reed[14] reported the reductive dehydroxylation of the protected α-hydroxycarbonyl compounds with samarium(II) iodide (SmI_2).[15] Recently, Hanessian and Girard[16] reported the direct dehydroxylation of α-hydroxycarbonyl compounds with SmI_2 using H_2O as the proton source. Therefore, we tried the reductive dehydroxylation of both **8** and **9**. Compound **9** was prepared by the treatment of **8** with 2,2-dimethoxypropane in the presence of *p*-toluenesulfonic acid (*p*-TsOH) in 85% yield. The results are summarized in Table 1. In the case of **9**, when 5 eq of SmI_2 and ethylene glycol as the proton source were used in the presence of hexamethylphosphoric triamide (HMPA), the desired compound **10** was obtained in 70% yield (run 2).[17] On the other hand, when **8** was treated with 6 eq of SmI_2 prepared *in situ* from Sm turnings and diiodomethane[18] and H_2O as the proton source in the presence of HMPA, the reaction



Reagents and conditions: a) OsO_4, NMO in acetone-H_2O (45%) or $RuCl_3 \cdot n\,H_2O$, $NaIO_4$ in H_2O-AcOEt-MeCN, 0°C (68%).

Chart 2

was completed within 2 h and **10** was isolated in 83% yield (run 5).

The protecting group of **10** was removed with 1% concentrated HCl–EtOH to afford **11** in 92% yield. Oxidation of both the primary and secondary hydroxyl groups with dimethylsulfoxide (DMSO), trifluoroacetic anhydride and triethylamine (Et_3N)[3a] at −78 °C in one step resulted in the formation of a complex mixture and failed to give **12**. Pyridinium chlorochromate (PCC)–AcO-Na or Sarett oxidation gave similar results. Therefore, **10** was oxidized with DMSO, trifluoroacetic anhydride and Et_3N at −78 °C to give the tetronic acid derivative **13**, of which the hydroxyl group was protected as a methoxymethyl (MOM) ether to form **14** in 88% yield from **10**.[3b] When the above oxidation was tried with pyridinium dichromate (PDC) in the presence of molecular sieves (Ms), the alcohol **10** was recovered.

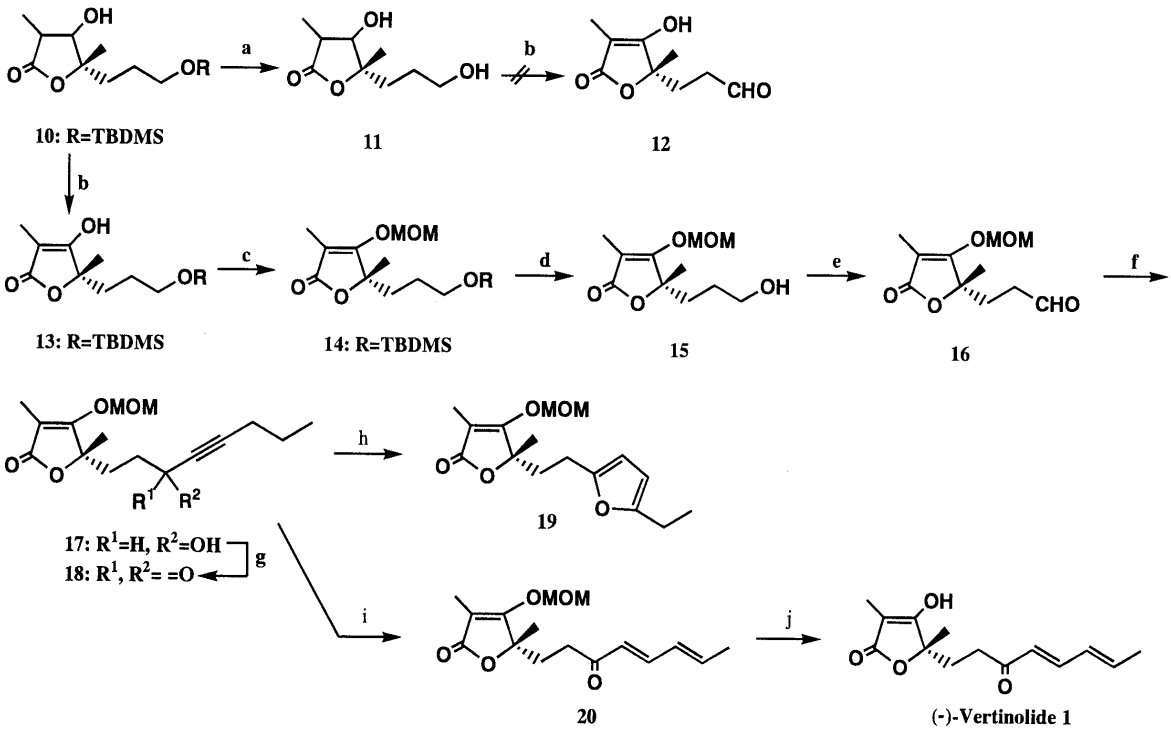
As the tetronic acid moiety was constructed as described above, we next examined the modification of the side chain. The silyl protecting group of **14** was removed by treatment with tetrabutylammonium fluoride (TBAF)[19] to afford the alcohol **15** in 87% yield, which was oxidized to the aldehyde **16** with DMSO–trifluoroacetic anhydride–Et_3N in 67% yield. The yield of **16** was improved to 77% by employing PCC and sodium acetate in the presence of Ms.[6b] The aldehyde **16** was treated with *n*-butyllithium and 1-pentyne in THF at −20 °C to give the alkynol **17** in 87% yield,[3c,20] and this was oxidized with DMSO–trifluoroacetic anhydride–Et_3N in CH_2Cl_2 at −78 °C to give the alkynone **18** in 83% yield.

Trost and Schmidt[21] reported the isomerization reaction of alkynones to dienones using palladium(II) acetate ($Pd(OAc)_2$) and triphenylphosphine (Ph_3P). According to this report, the alkynone **18** was treated with $Pd(OAc)_2$ and Ph_3P in toluene at 100 °C, but the isolated product in the yield of 71% was not the desired known dienone **20**[3b] or the furan derivative **19**.[22] When **18** was heated in toluene at refluxing temperature in the presence of Ph_3P,[23] the desired dienone **20** was cleanly obtained in 88% yield. Finally, the dienone **20** was treated with 5% HCl in methanol at room temperature to give (−)-vertinolide (**1**) in 62% yield; mp 145—149 °C, $[\alpha]_D^{21}$ −24.9° (c=0.52, $CHCl_3$); lit.[1] mp 149.2—152.3 °C, $[\alpha]_D^{20}$ −25.0° (c=0.05, $CHCl_3$). Although (+)-**1** or the racemate of **1** was not in our hands, HPLC analysis of the synthetic (−)-**1** using a chiral column (Daicel Chiralcel OB-H) showed a single peak. The IR, ^{1}H-NMR, and MS spectral data of the synthetic (−)-**1** are identical with reported values.[1,3] Thus, (−)-vertinolide was synthesized starting from the known chiral synthon (−)-**2** with 10% overall

Table 1. Reduction of **8** and **9** with SmI_2

Run	Compound	SmI_2 (eq.)	Additive	Proton source	Temp.	Time (h)	Yield (%)
1	**9**	3[a]	HMPA	Ethylene glycol	r.t.	4	45
2	**9**	5[a]	HMPA	Ethylene glycol	r.t.	3.5	70
3	**8**	4.5[a]	—	H_2O	0 °C	6	52
4	**8**	4[b]	HMPA	*tert*-BuOH	r.t.	16	0
5	**8**	6[c]	HMPA	H_2O	0 °C	2	83

a) 0.1 M THF solution. *b*) Prepared from Sm turnings and 1,2-diiodoethane in THF. *c*) Prepared from Sm turnings and diiodomethane in THF. r.t. = room temperature.



Reagents and conditions: a) 1% c. HCl-EtOH (92%); b) DMSO, $(CF_3CO)_2O$; Et_3N in CH_2Cl_2, -78 °C; c) NaH, MOMCl in THF-HMPA, 0 °C (88% from **10**); d) TBAF in THF in an ice bath (87%); e) PCC, AcONa, MS 3A in CH_2Cl_2 (77%); f) *n*-BuLi, 1-pentyne in THF, -20 °C (87%); g) DMSO, $(CF_3CO)_2O$; Et_3N in CH_2Cl_2, -78 °C (83%); h) Ph_3P, $Pd(OAc)_2$ in toluene, 100 °C (71%); i) Ph_3P in refluxing toluene (88%); j) 5% HCl in MeOH (62%).

Chart 3

yield and high optical purity.

Experimental

Unless otherwise stated, the following procedures were adopted. Melting points were determined using a Yanagimoto micro-melting point apparatus, model MP-S3, and are uncorrected. IR spectra were measured with a Hitachi 260-30 infrared spectrophotometer. ^{1}H-NMR spectra were recorded using a JEOL JNM-GSX270 (270 MHz) spectrometer using tetramethylsilane as the internal standard. High-resolution mass spectra (HRMS) were measured with a JEOL JMS-HX100 instrument at 70 eV. Optical rotations were recorded using a JASCO DIP-370 polarimeter.

(2*R*,5*S*)-(−)-2-*tert*-Butyl-5-methyl-5-(2-propenyl)-1,3-dioxolan-4-one (2) A mixture of (*R*)-lactic acid (29.961 g, 332.6 mmol), 2,2-dimethylpropanal (85.0 ml, 782.6 mmol), *p*-TsOH (785 mg), 8 drops of concentrated H_2SO_4 and *n*-pentane (316 ml) was refluxed for 7 h with azeotropic removal of the water formed. The mixture was washed with water and brine, and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave a residue, which was crystallized from *n*-pentane at −78 °C. Recrystallization at low temperature was repeated twice. The filtrates were combined and concentrated under reduced pressure to give a residue, which was crystallized again at low temperature as already described. The combined product was distilled to give (2*S*,5*R*)-2-*tert*-butyl-5-methyl-1,3-dioxolan-4-one (29.246 g, 56%) as a colorless oil; bp 78— 80 °C (24 Torr). IR (neat) cm^{-1}: 1800. ^{1}H-NMR ($CDCl_3$) δ: 0.98 (9H, s, $C(CH_3)_3$), 1.48 (3H, d, J=6.5 Hz, $CHC\underline{H}_3$), 4.36 (1H, dq, J=6.5, 1.0 Hz, $OC\underline{H}CH_3$), 5.15 (1H, d, J= 1.0 Hz, OCHO). $[\alpha]_D^{22}$ −44.7° (c=1.89, $CHCl_3$). This compound was treated with allyl bromide in the presence of LDA in THF to give (−)-**2** in 62% yield as previously reported.[6b]

(2*R*,5*S*)-2-*tert*-Butyl-5-(3-hydroxypropyl)-5-methyl-1,3-dioxolan-4-one (3) A mixture of (−)-**2** (3.00 g, 15.1 mmol) and 9-BBN (45 ml, 0.5 M THF solution, 22.5 mmol) in dry THF (32 ml) was stirred at room temperature under N_2 for 3 h. Water (1.3 ml) and 3 M NaOH aqueous solution were added. To the obtained mixture, 31% H_2O_2 aqueous solution (2.96 ml, 27.0 mmol) was added at a rate that kept the temperature at 30—50 °C. The entire mixture was stirred at room temperature for 2.5 h. After the addition of ether, the mixture was washed with water then brine, and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave an oil, which was purified by SiO_2 column chromatography ($CHCl_3$: MeOH = 50 : 1) to afford **3** (3.174 g, 97%) as a colorless oil. IR (neat) cm^{-1}: 3400, 1790. ^{1}H-NMR ($CDCl_3$) δ: 0.96 (9H, s, $C(CH_3)_3$), 1.46 (3H, s, CCH_3), 1.48—1.96 (5H, m, $C(C\underline{H}_2)_2CH_2O\underline{H}$), 3.68 (2H, t, J=6 Hz, $CH_2C\underline{H}_2OH$), 5.21 (1H, s, OCHO). HRMS m/z: 159.0658 (Calcd for $C_7H_{11}O_4$ ($M^+ - C_4H_9$): 159.0657).

(2*R*,5*S*)-2-*tert*-Butyl-5-(3-*tert*-butyldimethylsilyloxypropyl)-5-methyl-1,3-dioxolan-4-one (4) *tert*-Butyldimethylsilyl chloride (2.071 g, 13.7 mmol) was added to a solution of **3** (1.699 g, 7.86 mmol) and dry imidazole (1.504 g, 22.1 mmol) in dry CH_2Cl_2 (50 ml) at 2—3 °C, and the mixture was stirred at room temperature for 4 h. After the addition of saturated $NaHCO_3$ solution, the mixture was extracted with CH_2Cl_2. The combined ether extracts were washed with water then brine, and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave an oil, which was purified by SiO_2 column chromatography (benzene : *n*-hexane = 5 : 1) to afford **4** (2.353 g, 91%) as a colorless oil. IR (neat) cm^{-1}: 1800. ^{1}H-NMR ($CDCl_3$) δ: 0.05 (6H, s, $Si(CH_3)_2$), 0.89 (9H, s, $SiC(CH_3)_3$), 0.96 (9H, s, $C(CH_3)_3$), 1.44 (3H, s, CCH_3), 1.50—1.91 (4H, m, $C(C\underline{H}_2)_2CH_2OSi$), 3.63 (2H, t, J=6 Hz, $CH_2C\underline{H}_2OSi$), 5.18 (1H, s, OCHO). HRMS m/z: 273.1521 (Calcd for $C_{13}H_{25}O_4Si$ ($M^+ - C_4H_9$): 273.1522). $[\alpha]_D^{23}$ −24.1° (c=1.206, $CHCl_3$).

(2*R*,5*S*)-2-*tert*-Butyl-5-(3-*tert*-butyldimethylsilyloxypropyl)-5-methyl-1,3-dioxolan-4-ol (5) DIBAL-H (6.2 ml, 1.5 M toluene solution, 9.3 mmol) was added dropwise to a solution of **4** (2.533 g, 7.7 mmol) in dry CH_2Cl_2 (18 ml) at −78 °C under N_2, and the mixture was stirred for 20 min. After the addition of MeOH (10 ml) at −78 °C, the mixture was stirred at room temperature for 30 min. Celite was added to the mixture which was then filtered. The filtrate was concentrated to give an oil, which was purified by SiO_2 column chromatography (acetone : *n*-hexane = 1 : 5) to afford **5** (2.497 g, 98%) as a colorless oil. IR (neat) cm^{-1}: 3400. ^{1}H-NMR ($CDCl_3$) δ: 0.05 and 0.06 (total 6H, each s, $Si(CH_3)_2$), 0.87—0.94 (18H, m, $SiC(CH_3)_3$, $C(CH_3)_3$), 1.22 and 1.25 (total 3H, each s, CCH_3), 1.38—1.82 (4H, m, $C(C\underline{H}_2)_2CH_2OSi$), 2.24 and 2.97 (total 1H, each d, J=9 Hz, OH), 3.59—3.68 (2H, m, $CH_2C\underline{H}_2OSi$), 4.66 and 4.89 (total 1H, each s, OCHO), 5.00 and 5.11 (total 1H, each d, J=9, 5 Hz, $C\underline{H}OH$). HRMS m/z: 275.1694 (Calcd for $C_{13}H_{27}O_4Si$ ($M^+ - C_4H_9$): 275.1678).

(4*S*)-7-(*tert*-Butyldimethylsilyloxy)-2,4-dimethyl-2-hepten-4-olide (6) and (4*S*)-Ethyl 7-(*tert*-Butyldimethylsilyloxy)-4-hydroxy-2,4-dimethyl-2-heptenoate (7) Triethyl 2-phosphonopropionate (4.85 ml, 22.6 mmol) was added to a suspension of NaH (903 mg, 60% in mineral oil, 22.6 mmol) in dry THF (156 ml) under N_2 and the mixture was stirred at room temperature for 1 h. A solution of **5** (3.004 g, 9.0 mmol) in dry THF (16 ml) was added, and the whole was stirred at room temperature for 3 h. After the addition of saturated NH_4Cl solution under ice-cooling, the mixture was extracted with ether and the combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave an oil, which was purified twice by SiO_2 column chromatography (first, $CHCl_3$; second, benzene : AcOEt = 5 : 1) to afford **6** (2.156 g, 84%) and **7** (426 mg, 14%) as colorless oils, respectively. **6**: bp 123—125 °C (1 Torr). IR (neat) cm^{-1}: 1750, 1660. ^{1}H-NMR ($CDCl_3$) δ: 0.03 (6H, s, $Si(CH_3)_2$), 0.88 (9H, s, $C(CH_3)_3$), 1.34—1.88 (4H, m, $C(C\underline{H}_2)_2CH_2OSi$), 1.42 (3H, s, $COOCH_3$), 1.90 (3H, d, J = 1.5 Hz, $=CCH_3$), 3.58 (2H, t, J = 6 Hz, $CH_2C\underline{H}_2OSi$), 6.94 (1H, q, J = 1.5 Hz, C=CH). HRMS m/z: 227.1096 (Calcd for $C_{11}H_{19}O_3Si$ ($M^+ - C_4H_9$): 227.1103). $[\alpha]_D^{20}$ +26.2° (c = 1.096, $CHCl_3$). **7**: IR (neat) cm^{-1}: 3430, 1700, 1640. ^{1}H-NMR ($CDCl_3$) δ: 0.07 (6H, s, $Si(CH_3)_2$), 0.90 (9H, s, $C(CH_3)_3$), 1.29 (3H, t, J = 7 Hz, $C\underline{H}_3CH_2OCO$), 1.37 (3H, s, $C\underline{H}_3COH$), 1.60—1.93 (4H, m, $C(C\underline{H}_2)_2CH_2OSi$), 2.08 (3H, d, J = 1.5 Hz, $=CCH_3$), 3.41 (1H, br s, OH), 3.58—3.74 (2H, m, $CH_2C\underline{H}_2OSi$), 4.19 (2H, q, J = 7 Hz, $CH_3C\underline{H}_2OCO$), 6.76 (1H, q, J = 1.5 Hz, C=CHC). HRMS m/z: 330.2264 (Calcd for $C_{17}H_{34}O_4Si$ (M^+): 330.2226).

(4*S*)-7-(*tert*-Butyldimethylsilyloxy)-2,3-dihydroxy-2,4-dimethylheptan-4-olide (8) Method A: A solution of **6** (100 mg, 0.35 mmol), NMO (88 mg, 0.75 mmol), 2% OsO_4 aqueous solution (0.32 ml, 0.025 mmol) in acetone (1 ml) and water (2 ml) was stirred under N_2 at room temperature for 63 h. After the addition of a solution of $Na_2S_2O_3$ (45 mg) in water (2 ml), the mixture was stirred for 10 min. An aqueous solution of NH_4Cl was added and acetone was removed under reduced pressure. The residue was extracted with AcOEt and the combined extracts were washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave an oil which was purified by SiO_2 PTLC (AcOEt : benzene = 1 : 4) to afford **8** (50 mg, 45%) as a colorless oil.

Method B: A solution of **6** (500 mg, 1.76 mmol) in a mixture of AcOEt (13 ml) and MeCN (13 ml) was added dropwise to a solution of $RuCl_3$ (26 mg, 0.13 mmol) and $NaIO_4$ (564 mg, 2.64 mmol) in H_2O (5 ml) at 0 °C, and the whole was stirred vigorously for 15 min. After the addition of a saturated $Na_2S_2O_3$ aqueous solution, the mixture was extracted with AcOEt and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave an oil which was purified by SiO_2 column chromatography (AcOEt : benzene = 1 : 4) to afford **8** (381 mg, 68%) as a colorless oil. IR (neat) cm^{-1}: 3400, 1760. ^{1}H-NMR ($CDCl_3$) δ: 0.05 and 0.07 (each 3H, s, $Si(CH_3)_2$), 0.89 and 0.90 (total 9H, each s, $C(CH_3)_3$), 1.42, 1.46, 1.53, 1.57 (total 6H, each s, CH_3COCO, CH_3CCOO), 1.60—1.94 (4H, m, $C(C\underline{H}_2)_2CH_2OSi$), 3.00 (1H, d, J = 8.5 Hz, $CHO\underline{H}$), 3.07 (1H, br s, COH), 3.56—3.72 (2H, m, $CH_2C\underline{H}_2OSi$), 3.79 (1H, d, J = 8.5 Hz, $C\underline{H}OH$). HRMS m/z: 261.1189 (Calcd for $C_{11}H_{21}O_5Si$ ($M^+ - C_4H_9$): 261.1159).

Acetalization of 8 A solution of dry *p*-TsOH (20 mg), **8** (1.530 g, 4.8 mmol) and 2,2-dimethoxypropane (15 ml, 122.0 mmol) in dry CH_2Cl_2 (79 ml) was stirred at room temperature for 2 h and refluxed for 2.5 h. After cooling, the mixture was diluted with CH_2Cl_2, then washed with $NaHCO_3$ solution followed by brine. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to give an oil, which was purified by SiO_2 column chromatography (acetone : *n*-hexane = 1 : 7) to afford **9** (1.465 g, 85%) as a colorless oil. IR (neat) cm^{-1}: 1770. ^{1}H-NMR ($CDCl_3$) δ: 0.04 (6H, s, $Si(CH_3)_2$, 0.88 (9H, s, $C(CH_3)_3$), 1.42, 1.44, 1.45 (total 9H, each s, CH_3COCO, $C(CH_3)_2$), 1.66 (3H, s, CH_3CCOO), 1.60—1.80 (4H, m, $C(CH_2)_2CH_2$-OSi), 3.55—3.77 (2H, m, CH_2CH_2OSi), 4.17 (1H, s, CH).

(4*S*)-7-(*tert*-Butyldimethylsilyloxy)-3-hydroxy-2,4-dimethylheptan-4-olide (10) Method A (Table 1, Run 1): A solution of SmI_2 in THF (0.1 M, 62 ml, 6.2 mmol) was added dropwise to a solution of **9** (739 mg, 2.06 mmol), dry ethylene glycol (1.4 ml, 25.10 mmol) and dry HMPA (3.1 ml) in dry THF (21 ml) under N_2 at room temperature, and the mixture was stirred for 4 h. After the addition of saturated $NaHCO_3$ solution, the whole was extracted with ether, and the combined organic layers were washed with a saturated $Na_2S_2O_3$ solution, H_2O, and brine. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to give an oil, which was purified by SiO_2 column chromatography ($CHCl_3$: MeOH = 100 : 1) to afford **10** (280 mg, 45%) as a colorless oil.

Method B (Table 1, Run 2): A solution of SmI_2 in THF (0.1 M, 51 ml, 5.1 mmol) was added dropwise to a solution of **9** (365 mg, 1.02 mmol), dry ethylene glycol (0.68 ml, 12.19 mmol) and dry HMPA (1.6 ml) in dry THF (21 ml) under N_2 at room temperature and the mixture was stirred for 3.5 h. After addition of a saturated $NaHCO_3$ solution, the whole was extracted with ether, and the combined organic layers were washed with a saturated $Na_2S_2O_3$ solution, H_2O, then brine. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to give an oil, which was purified by SiO_2 column chromatography ($CHCl_3$: MeOH = 100 : 1) to afford **10** (216 mg, 70%) as a colorless oil.

Method C (Table 1, Run 3): A solution of SmI_2 in THF (0.1 M, 18.8 ml, 1.88 mmol) was added dropwise to a solution of **8** (200 mg, 0.63 mmol) in H_2O (6 ml) under N_2 at 0 °C, and the mixture was stirred at the same temperature for 3 h. A solution of SmI_2 in THF (0.1 M, 9.4 ml, 0.94 mmol) was added, and the reaction mixture was stirred for 3 h. After the addition of $NaHCO_3$ solution, the whole was extracted with ether and the organic layer was washed with a saturated $Na_2S_2O_3$ solution, then brine. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to give an oil, which was purified by SiO_2 column chromatography ($CHCl_3$: AcOEt = 5 : 1) to afford **10** (98 mg, 52%) as a colorless oil. Compound **8** (70 mg) was recovered.

Method D (Table 1, Run 4): A solution of 1,2-diiodoethane (1.547 g, 5.49 mmol) in dry THF (5 ml) was added to a suspension of Sm (990 mg, 6.58 mg atom) in dry THF (8 ml) under N_2, and the mixture was stirred at room temperature for 1 h. Dry HMPA (1.4 ml) was added and stirring was continued for 5 min, then a solution of **8** (437 mg, 1.37 mmol) in dry THF (3 ml) and *tert*-BuOH (0.52 ml, 5.44 mmol) were added. The reaction mixture was stirred at room temperature for 16 h. A saturated $NaHCO_3$ aqueous solution was added and the whole was extracted with ether. The combined organic layers were washed with a solution of $Na_2S_2O_3$, H_2O, then brine, and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave the starting **8**.

Method E (Table 1, Run 5): Diiodomethane (2.85 ml, 35.38 mmol) was added dropwise to a suspension of Sm (6.025 g, 40.07 mg atom) in dry THF (55 ml) under Ar and the mixture was stirred at room temperature for 1.5 h. Dry HMPA (6.3 ml) was added and the whole was stirred for 15 min. This mixture was added dropwise to a solution of **8** (1.804 g, 5.66 mmol) in a mixture of THF (13 ml) and H_2O (59 ml) at 0 °C and the whole was stirred at 0 °C for 2 h. After addition of a saturated $NaHCO_3$ solution, the mixture was extracted with ether and the combined organic layers were washed with a saturated $Na_2S_2O_3$ solution, H_2O, then brine. The organic layer was dried over anhydrous Na_2SO_4 and removal of the solvent under reduced pressure gave an oil, which was purified by SiO_2 column chromatography ($CHCl_3$: AcOEt = 5 : 1) to afford **10** (1.415 g, 83%) as a colorless oil. IR (neat) cm^{-1}: 3430, 1750. ^{1}H-NMR ($CDCl_3$) δ: 0.06 (6H, s, $Si(CH_3)_2$), 0.89 (9H, $C(CH_3)_3$), 1.31 (3H, d, J = 7 Hz, $C\underline{H}_3CHCO$), 1.35 (3H, s, CH_3C), 1.58—1.86 (4H, m, $C(C\underline{H}_2)_2CH_2OSi$), 2.49 (1H, br d, J = 5 Hz, OH), 2.67 (1H, dq, J = 10, 7 Hz, $CH_3C\underline{H}$), 3.56—3.74 (2H, m, $CH_2C\underline{H}_2OSi$), 3.88 (1H, dd, J = 10, 5 Hz, $C\underline{H}OH$).

(4*S*)-3,7-Dihydroxy-2,4-dimethylheptan-4-olide (11) A solution of **10** (100 mg, 0.33 mmol) in 1% concentrated HCl–EtOH solution (5 ml) was stirred at room temperature for 30 min. After removal of EtOH under reduced pressure, the residue was diluted with H_2O. The mixture was extracted with AcOEt, and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure furnished an oil, which was purified by SiO_2 column chromatography ($CHCl_3$: MeOH = 50 : 3) to afford **11** (57 mg, 92%) as a colorless oil. IR (neat) cm^{-1}: 3300, 1760. ^{1}H-NMR ($CDCl_3$) δ: 1.30 (3H, d, J = 7 Hz, $C\underline{H}_3CH_2$), 1.35 (3H, s, CH_3C), 1.52—2.04 (4H, m, $C(C\underline{H}_2)_2CH_2OH$), 2.45 (1H, br s, $CH_2O\underline{H}$), 2.68 (1H, dq, J = 10, 7 Hz, $CH_3C\underline{H}$), 3.55 (1H, br d, J = 4 Hz, $CHO\underline{H}$), 3.68 (2H, br t, J = 6 Hz, $CH_2C\underline{H}_2OH$), 3.87 (1H, br dd, J = 10, 4 Hz, $C\underline{H}OH$).

(4*S*)-7-(*tert*-Butyldimethylsilyloxy)-3-(methoxymethyloxy)-2,4-dimethyl-2-hepten-4-olide (14) A mixture of dry DMSO (0.067 ml, 0.94 mmol) and trifluoroacetic anhydride (0.075 ml, 0.53 mmol) in dry CH_2Cl_2 (2 ml) was stirred at −78 °C under N_2 for 30 min. A solution of **10** (83 mg, 0.27 mmol) in dry CH_2Cl_2 (2 ml) was added dropwise to it, and the mixture was stirred at the same temperature for 15 min. After the

addition of Et_3N (0.15 ml, 1.08 mmol), the reaction mixture was stirred for 30 min and then diluted with H_2O (4 ml). The whole was warmed to room temperature and extracted with AcOEt. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave crude **13**, which was directly used for the next reaction. Sodium hydride (20 mg, 60% in mineral oil, 0.50 mmol) was added to a solution of **13** (71 mg, 0.24 mmol) in dry THF (3 ml) and dry HMPA (0.3 ml) at 0 °C, and the mixture was stirred for 1 h. After the addition of a solution of chloromethyl methyl ether (43 mg, 0.53 mmol) in dry THF (1 ml), the reaction mixture was stirred at room temperature for 6.5 h. A saturated solution of NH_4Cl was added and the whole was extracted with ether. The combined organic layers were washed with H_2O then brine, and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave an oil, which was purified by SiO_2 PTLC (acetone : *n*-hexane = 1 : 5) to afford **14** (71 mg, 88% from **10**) as a colorless oil. IR (neat) cm^{-1}: 1750, 1660. ^{1}H-NMR ($CDCl_3$) δ: 0.02, 0.03 (each 3H, s, $Si(CH_3)_2$), 0.87 (9H, s, $C(CH_3)_3$), 1.30—1.85 (4H, m, $C(CH_2)_2CH_2OSi$), 1.44 (3H, s, CH_3CO), 1.92 (3H, s, $CH_3C=C$), 3.52 (3H, s, CH_3OCH_2), 3.53—3.65 (2H, m, CH_2CH_2OSi), 5.25, 5.28 (each 1H, d, J = 6 Hz, OCH_2O). HRMS *m/z*: 287.1318 (Calcd for $C_{13}H_{23}O_5Si$ ($M^+ - C_4H_9$): 287.1315). $[\alpha]_D^{15}$ +2.08° (*c* = 1.764, $CHCl_3$).

(4*S*)-7-Hydroxy-3-(methoxymethyloxy)-2,4-dimethyl-2-hepten-4-olide (15) Tetrabutylammonium fluoride (0.25 ml, 1.0 M THF solution, 0.25 mmol) was added to a solution of a **14** (67 mg, 0.19 mmol) in dry THF (3 ml) under ice-cooling and the mixture was stirred at 0 °C for 2.5 h. After the addition of a saturated NH_4Cl solution, the whole was extracted with ether and the combined extracts were washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and removal of the solvent gave an oil, which was purified by SiO_2 PTLC ($CHCl_3$: MeOH = 25 : 1) to afford **15** as a colorless oil. IR (neat) cm^{-1}: 3400, 1720, 1660. ^{1}H-NMR ($CDCl_3$) δ: 1.36—1.42 (1H, m, OH), 1.45 (3H, s, CH_3CO), 1.46—1.91 (4H, m, $C(CH_2)_2CH_2OH$), 1.92 (3H, s, $CH_3C=C$), 3.52 (3H, s, CH_3OCH_2), 3.635 (2H, br t, J = 6 Hz, CH_2CH_2OH), 5.27 (2H, s, OCH_2O). HRMS *m/z*: 230.1138 (Calcd for $C_{11}H_{18}O_5$ (M^+): 230.1155). $[\alpha]_D^{21}$ −5.38° (*c* = 1.59, $CHCl_3$).

(5*S*)-5-Formylethyl-4-(methoxymethyloxy)-3,5-dimethyl-2(5*H*)-furanone (16) Method A: A mixture of dry DMSO (0.035 ml, 0.49 mmol) and trifluoroacetic anhydride (0.039 ml, 0.28 mmol) in dry CH_2Cl_2 (2 ml) was stirred under N_2 at −78 °C for 30 min. A solution of **15** (33 mg, 0.14 mmol) in dry CH_2Cl_2 (2 ml) was added to it and the reaction mixture was stirred at that temperature for 1 h. After addition of Et_3N (0.079 ml, 0.57 mmol), the mixture was stirred at that temperature for 1 h. Water (4 ml) was added and the whole was warmed to room temperature, then extracted with AcOEt. The combined extracts were washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and removal of the solvent under reduced pressure gave an oil, which was purified by SiO_2 PTLC ($CHCl_3$: MeOH = 25 : 1) to give **16** (20 mg, 67%) as a colorless oil.

Method B: A solution of **15** (608 mg, 2.64 mmol) in dry CH_2Cl_2 (12 ml) was added dropwise to a mixture of PCC (2.208 g, 10.24 mmol), anhydrous AcONa (183 mg, 2.23 mmol) and powdered Ms 3A (2.76 g) in dry CH_2Cl_2 (18 ml) at room temperature. The whole was stirred at that temperature for 1 h, then filtered using Celite. The filtrate was concentrated under reduced pressure to give a residue, which was passed through an SiO_2 short column (ether). Pure **16** (461 mg, 77%) was obtained by SiO_2 column chromatography ($CHCl_3$: MeOH = 25 : 1) as a colorless oil. IR (neat) cm^{-1}: 1750, 1720, 1660. ^{1}H-NMR ($CDCl_3$) δ: 1.47 (3H, s, CH_3CO), 1.92 (3H, s, $CH_3C=C$), 1.98—2.22 (2H, m, CCH_2CH_2CHO), 2.28—2.60 (2H, m, CH_2CH_2CHO), 3.52 (3H, s, CH_3OCH_2), 5.27 (2H, s, OCH_2O), 9.75 (1H, br s, CHO). HRMS *m/z*: 228.0971 (Calcd for $C_{11}H_{16}O_5$ (M^+): 228.0998). $[\alpha]_D^{22}$ +18.8° (*c* = 1.53, $CHCl_3$).

(5*S*)-5-(3-Hydroxy-4-octynyl)-4-(methoxymethyloxy)-3,5-dimethyl-2(5*H*)-furanone (17) *n*-BuLi (2.62 ml, 1.6 M *n*-hexane solution, 4.19 mmol) was added to a solution of 1-pentyne (0.44 ml, 4.46 mmol) in dry THF (23 ml) at −78 °C under N_2 and the mixture was stirred at −20 °C for 15 min. A solution of **16** (477 mg, 2.09 mmol) in dry THF (48 ml) was added at −78 °C and the reaction mixture was stirred at −20 °C for 3 h. After the addition of a saturated NH_4Cl solution at −78 °C, the whole was gradually warmed to room temperature and then extracted with CH_2Cl_2. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave an oil, which was purified by SiO_2 column chromatography (acetone : *n*-hexane = 1 : 2) to afford **17** (537 mg, 87%) as a colorless oil. IR (neat) cm^{-1}: 3400, 1740, 1660. ^{1}H-NMR ($CDCl_3$) δ: 0.97 (3H, dt, J = 7.5, 1.5 Hz, CH_2CH_3), 1.46 (3H, s, CH_3CO), 1.46—2.13 (7H, m, $(CH_2)_2CHOH$, $CH_2CH_2CH_3$), 1.92 (3H, s, $CH_3C=C$), 2.13—2.22 (2H, m, $CH_2CH_2CH_3$), 3.53 (3H, s, CH_3OCH_2), 4.30—4.40 (1H, m, CHOH), 5.27 (2H, s, OCH_2O). HRMS *m/z*: 296.1584 (Calcd for $C_{16}H_{24}O_5$ (M^+): 296.1624); 251.1280 (Calcd for $C_{14}H_{19}O_4$ ($M^+ - C_2H_5O$): 251.1283).

(5*S*)-4-(Methoxymethyloxy)-3,5-dimethyl-5-(3-oxo-4-octynyl)-2(5*H*)-furanone (18) A mixture of dry DMSO (0.42 ml, 5.92 mmol) and trifluoroacetic anhydride (0.47 ml, 3.33 mmol) in dry CH_2Cl_2 (13 ml) was stirred under N_2 at −78 °C for 30 min. A solution of **17** (505 mg, 1.7 mmol) in dry CH_2Cl_2 (13 ml) was added and stirring was continued at that temperature for 30 min. After the addition of Et_3N (0.94 ml, 6.74 mmol), the reaction mixture was stirred for 1 h, then diluted with H_2O (26 ml), warmed to room temperature and extracted with AcOEt. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave an oil, which was purified by SiO_2 column chromatography ($CHCl_3$: MeOH = 100 : 1) to afford **18** (414 mg, 83%) as a colorless oil. IR (neat) cm^{-1}: 2200, 1740, 1660. ^{1}H-NMR ($CDCl_3$) δ: 1.01 (3H, t, J = 7.5 Hz, CH_2CH_3), 1.46 (3H, s, CH_3CO), 1.56—1.69 (2H, m, $CH_2CH_2CH_3$), 1.93 (3H, s, $CH_3C=C$), 2.00—2.68 (6H, $C(CH_2)_2CO$, $CCH_2CH_2CH_3$), 3.51 (3H, s, CH_3OCH_2), 5.25, 5.28 (each 1H, d, J = 6 Hz, OCH_2O). HRMS *m/z*: 294.1444 (Calcd for $C_{16}H_{22}O_5$ (M^+): 294.1467). $[\alpha]_D^{24}$ +2.27° (*c* = 1.77, $CHCl_3$).

Treatment of 18 with Ph_3P and $Pd(OAc)_2$ A mixture of **18** (200 mg, 0.68 mmol), Ph_3P (84 mg, 0.32 mmol) and $Pd(OAc)_2$ (10 mg, 0.04 mmol) in dry toluene (11 ml) was stirred under N_2 at room temperature for 15 min and at 100 °C for 3 h. After cooling, the reaction mixture was concentrated under reduced pressure to give an oil, which was purified by SiO_2 column chromatography ($CHCl_3$) to afford **19** (141 mg, 71%) as a colorless oil. IR (neat) cm^{-1}: 1740, 1690, 1660, 1610, 1570. ^{1}H-NMR ($CDCl_3$) δ: 1.19 (3H, t, J = 7.5 Hz, CH_2CH_3), 1.47 (3H, s, CH_3CO), 1.92 (3H, $CH_3C=C$), 1.99—2.18 (2H, m, CCH_2CH_2-furyl), 2.35—2.68 (2H, m, CCH_2CH_2-furyl), 2.575 (2H, q, J = 7.5 Hz, CH_2CH_3), 3.51 (3H, s, CH_3OCH_2), 5.21, 5.23 (each 1H, d, J = 6 Hz, OCH_2O), 5.82 (2H, s, $C=CHCH=C$). HRMS *m/z*: 294.1455 (Calcd for $C_{16}H_{22}O_5$ (M^+): 294.1468).

(5*S*)-4-(Methoxymethyloxy)-3,5-dimethyl-5-(3-oxo-4,6-octadienyl)-2(5*H*)-furanone (20) A mixture of **18** (20 mg, 0.07 mmol) and Ph_3P (2 mg, 0.01 mmol) in dry toluene was refluxed under N_2 for 2.5 h and then stirred at room temperature for 38 h. After the addition of Ph_3P (2 mg, 0.01 mmol), the reaction mixture was refluxed for 6 h and concentrated under reduced pressure to give an oil, which was purified by SiO_2 PTLC (benzene : AcOEt = 6 : 1) to give **20** (14 mg, 88% based on the changed **18**) and **18** (4 mg) as oils. IR (neat) cm^{-1}: 1740, 1690, 1660, 1630, 1590. ^{1}H-NMR ($CDCl_3$) δ: 1.46 (3H, s, CH_3CO), 1.87 (3H, d, J = 5.5 Hz, $CH=CHCH_3$), 1.91 (3H, s, $CH_3C=C$), 2.06—2.12 (2H, m, CCH_2CH_2), 2.32—2.68 (2H, m, CH_2CH_2CO), 3.50 (3H, s, CH_3OCH_2), 5.25 (2H, s, OCH_2O), 6.02 (1H, d, J = 16 Hz, $COCH=CH$), 6.08—6.30 (2H, m, $CH=CHCH_3$), 7.05—7.18 (1H, m, $COCH=CH$). HRMS *m/z*: 294.1451 (Calcd for $C_{16}H_{22}O_5$ (M^+): 194.1467). $[\alpha]_D^{24}$ −7.29° (*c* = 1.04, $CHCl_3$).

(−)-Vertinolide (1) Five percent HCl (29 ml) was added to a solution of **20** (96 mg, 0.33 mmol) in MeOH (19 ml) and the mixture was stirred at room temperature for 10 h, then concentrated under reduced pressure and extracted with $CHCl_3$. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave an oil, which was purified by SiO_2 PTLC ($CHCl_3$: MeOH = 4 : 1) to afford **1** (38 mg, 62% based on the changed **20**) as prisms and **20** (23 mg). HPLC analysis using a chiral column (Daicel Chiralcel OB-H, 0.46 × 25 cm, 2-propanol : *n*-hexane = 1 : 50) showed that the synthesized (−)-**1** was optically pure, mp 145—149 °C (lit.[1] mp 149.2—152.3 °C). IR ($CHCl_3$) cm^{-1}: 3600—2400, 1740, 1720, 1690, 1660, 1630, 1590, 1440, 1400, 1300, 1160, 1100, 1060, 990, 950, 900. ^{1}H-NMR ($CDCl_3$) δ: 1.49 (3H, s, CH_3CO), 1.70 (3H, s, $CH_3C=COH$), 1.89 (3H, d, J = 6 Hz, $CH=CHCH_3$), 2.05—2.26 (2H, m, CCH_2CH_2CO), 2.48, 2.68 (each 1H, ddd, J = 16.5, 8.5, 6 Hz, CH_2CH_2CO), 6.05 (1H, d, J = 15.5 Hz, $COCH=CH$), 6.10—6.38 (2H, m, $CH=CHCH_3$), 7.19 (1H, dd, J = 15.5, 10 Hz, $COCH=CH$). HRMS *m/z*: 250.1221 (Calcd for $C_{14}H_{18}O_4$ (M^+): 250.1205). $[\alpha]_D^{21}$ −24.9° (*c* = 0.17, $CHCl_3$) [lit.[1] $[\alpha]_D^{20}$ −25.0° (*c* = 0.05, $CHCl_3$)].

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