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Studies on Total Syntheses of Antitumor Styryllactones: Stereoselective Total Syntheses of (+)-Goniofufurone, (+)-Goniobutenolide A, and (-)-Goniobutenolide B

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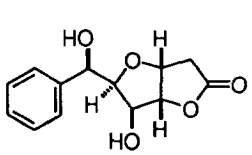
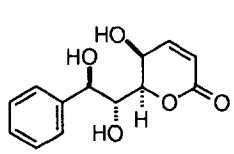
Abstract: A highly stereoselective aldol reaction of the aldehyde **11**, derived from (+)-tricarbonyl(η^6-2-trimethylsilylbenzaldehyde)chromium(0) complex (**4**), with 2-trimethysilyloxyfuran afforded the γ-lactone derivative **13**. The γ-lactone **13** was subsequently converted into three antitumor styryllactones, (+)-goniofufurone, (+)-goniobutenolide A, and (-)-goniobutenolide B.

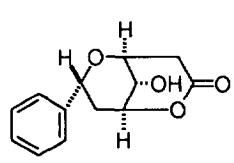
Several styryllactones with unique structural features[1] have recently been isolated along with other bioactive compounds from the stem bark of *Goniothalamus giganteus* Hook. f., Thomas (Annonaceae) grown in Thailand. These styryllactones have been shown to possess significant cytotoxic activities[1] toward human tumor cells. Some of representative styryllactones are exhibited in Figure 1. They can be formally classified into two



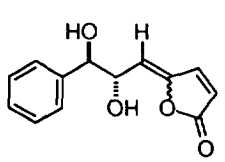
1 : (+)-Goniofufurone



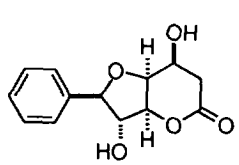
(+)-Goniotriol



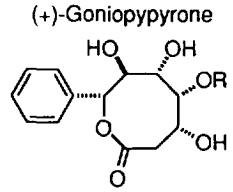
(+)-Goniopypyrone



2 : (+)-Goniobutenolide A (*Z*-isomer)
3 : (-)-Goniobutenolide B (*E*-isomer)



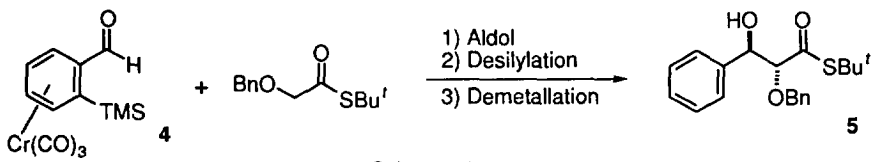
(-)-Goniofupyrone



R = Me : (+)-Gonioheptolide A
R = Et : (+)-Gonioheptolide B

Figure 1

groups by their structural features. The first group consists of styryllactones with the γ-lactone framework like goniofufurone (**1**) and goniobutenolide A and B (**2** and **3**). The second one is represented by goniotriol, goniofupyrone, and goniopypyrone having the δ-lactone skeleton. Furthermore isolation of two eight-membered lactones, gonioheptolide A and B,[2] has also been reported. Since the first publication on isolation[1] of such styryllactones, many efforts[3] have so far been made on total syntheses of them because of their antitumor activities as well as their novel structures.

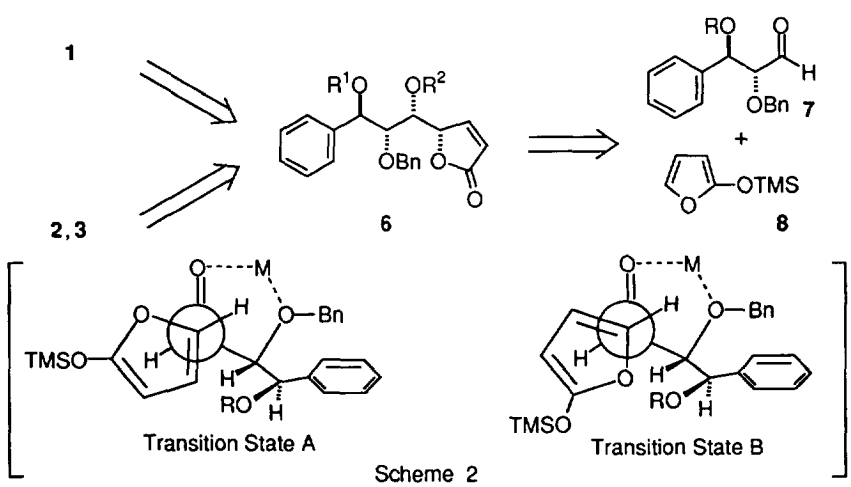


Scheme 1

In the course of our program directed toward the development of highly stereoselective carbon-carbon bond formation reactions mediated by tricarbonyl(η^6-arene)chromium(0) complexes and their application to total syntheses of bioactive compounds, we have completed (i) stereoselective preparation of the C-13 side chains of taxol and taxotère[4] and (ii) highly stereoselective synthesis of the common amino residue of nikkomycin B and Bx[5] based on a highly *anti*-selective aldol reaction of the optically active chromium(0)-complexed benzaldehyde derivative **4**. By taking advantage of the chiral *anti*-aldol product **5**, prepared from the reaction of **4** with *S-tert*-butyl benzyloxyethanethioate in a highly stereoselective manner, we now focus our endeavor on development of highly stereoselective protocol for the synthesis of all kind of antitumor styryllactones. In this paper we describe efficient and stereoselective total syntheses of the γ-lactone derivatives, (+)-goniofufurone (**1**),[6] (+)-goniobutenolide A (**2**), and (-)-goniobutenolide B (**3**) through the common synthetic intermediate.

Synthesis of (+)-Goniofufurone

Retrosynthetic analysis of the γ-lactones, goniofufurone (**1**)[3a-k] and goniobutenolide A and B (**2** and **3**)[3k-n] indicates that the γ-lactone **6** with suitable stereochemistry would become the key intermediate and be direct-



Scheme 2

ly transformed into **1**, **2**, and **3**. We envisioned, therefore, that stereoselective construction of the key intermediate **6** from the aldehyde **7** must be the most crucial point in this research. The γ-lactone **6** having the desirable stereochemistry will be selectively formed if the aldol reaction between the aldehyde **7** and 2-trimethylsilyloxyfuran (**8**)[7] as a C_4-unit proceeds through the transition state like A.

Thus, as our point of departure, the aldol condition under the chelation-controlled circumstances leading to diastereoselective formation of **6** was searched by employing racemic compounds. The methyl ester **9**,[4] prepared from the thioester **5**, was protected with *tert*-butyldimethylsilyl (TBS) group to give the TBS-protected ester **10** in 77% yield. Reduction of **10** with diisobutylaluminum hydride (DIBAL-H) in benzene was followed by the Swern oxidation to provide the labile aldehyde **11**. Because of its instability **11** was immediately exposed to the aldol condition at -78°C in methylene chloride where **8** was used as a carbon nucleophile in the presence of $SnCl_4$ affording the expected **12** together with its 4-epimer **13** in a ratio of *ca.* 1 to 1. It became apparent, however, that a main product is the γ-lactone derivative **14** resulting from carbon-carbon bond formation at C-3 position of **8**, followed by double bond isomerization. Changing Lewis acid to $TiCl_4$, $ZrCl_4$, and $Ti(OPr^i)_2Cl_2$ brought about an interesting observation as indicated in Table 1. In all cases examined except for $SnCl_4$, the unexpected γ-lactone **13** with the stereochemistry of *anti* (between C_4-H and $C_{1'}$-H) and *syn* (between $C_{1'}$-H and $C_{2'}$-H) was found to be preferentially constructed. In particular, use of $Ti(OPr^i)_2Cl_2$ as a Lewis acid led to the exclusive formation of **13**.

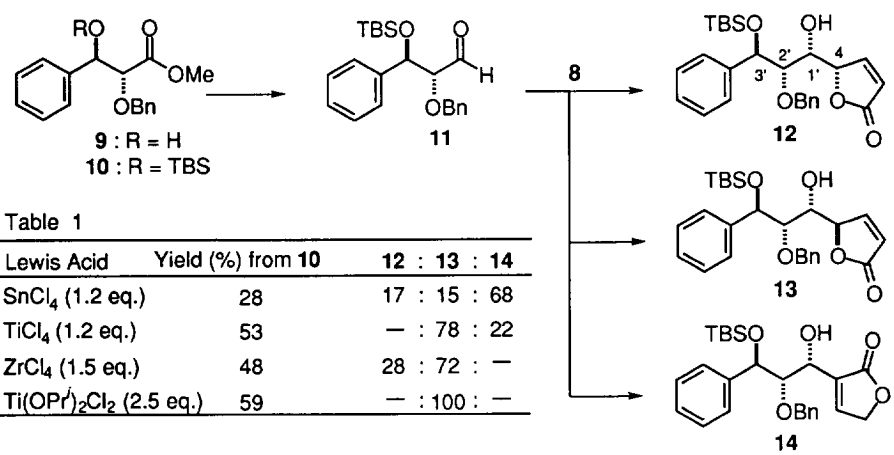


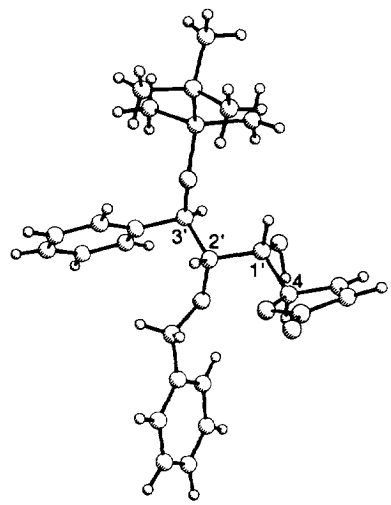
Table 1

Lewis Acid	Yield (%) from **10**	**12** : **13** : **14**
$SnCl_4$ (1.2 eq.)	28	17 : 15 : 68
$TiCl_4$ (1.2 eq.)	53	— : 78 : 22
$ZrCl_4$ (1.5 eq.)	48	28 : 72 : —
$Ti(OPr^i)_2Cl_2$ (2.5 eq.)	59	— : 100 : —

Preferential formation of **13** over **12** might be tentatively rationalized in terms of the transition state B instead of previously assumed transition state A . When **8** approaches to the aldehyde **11** being coordinated with a Lewis acid, the transition states A and B leading to **12** and **13**, respectively could be assumed. In both transition states A and B, sterically less hindered hydrogen atom on the furan ring of **8** should be placed on the most sterically demanding position. There would be a dipole-dipole interaction between the oxygen atom of the furan ring and that of the aldehyde counterpart in the transition state A. Such an unfavorable interaction, however, might not be predicted in the transition sate B. Therefore, **13** would become a major or exclusive product. Stereochemical assignment of **12** and **13** was made by careful consideration of coupling constant as well as comparison of them with the related compounds in the literature.[3a,k,l] ^1H NMR spectrum of **12** disclosed that coupling constant between C_4-H and $C_{1'}$-H has 4.3 Hz, while that of $C_{1'}$-H with $C_{2'}$-H is 2.0 Hz,

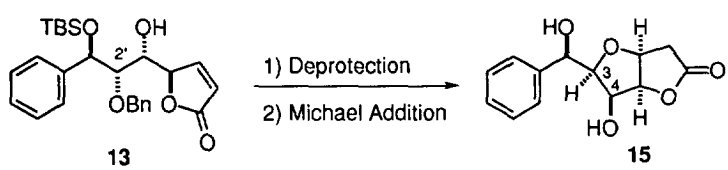
suggesting these consecutive stereogenic centers should be *syn* and *syn*. On the other hand, the preferentially formed **13** has 9.3 and 1.1 Hz for coupling constants between C_4-H and $C_{1'}$-H, and $C_{1'}$-H and $C_{2'}$-H, respectively. These values correspond to the stereochemistry of *anti* (C_4-$C_{1'}$) and *syn* ($C_{1'}$-$C_{2'}$). In addition, relative stereochemistry of these two compounds was unambiguously established by X-ray crystallographic analysis[8] of **13** as depicted in Figure 2. Thus relative stereochemistry of **13** should be assigned as 1'R*, 2'R*, 3'S*, 4S*, therefore, **12** has 1'R*, 2'R*, 3'S*, 4R* configuration.

Although **12** was not obtained in a selective fashion, we reached the idea that **13**, the 4-epimer of **12**, would be useful for our purpose if isomerization at C-4 stereogenic center is easily realized. Molecular model examination of **13** provided a very promising expectation. Direct Michael addition of $C_{2'}$-hydroxy group to the β-carbon of γ-lactone moiety of **13** (after deprotection) would give rise to the formation of a dioxabicyclo[3.3.0]octanone derivative **15** with the stereochemistry depicted in Scheme 3. It would be expected to be severe nonbonding interaction of C_3-benzylic appendage with C_4-hydroxy functionality since they are forced to be located in the concavity. The instability anticipated in the structure of **15** would force retro Michael reaction and result in isomerization to a suitable isomer **12** being able to cyclize to a dioxabicyclo[3.3.0]octanone with a desired stereochemistry. Based on the above consideration, we expected easy isomerization of **13** (in a deprotected form) to **12** (in a deprotected form), followed by cyclization to give goniofufurone under a suitable condition.



Crystal Structure of (±)-13

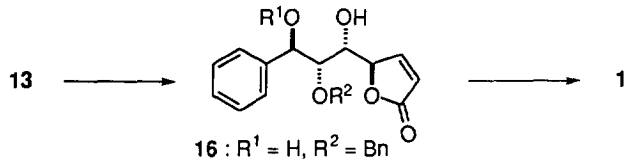
Figure 2



13 **15**

Scheme 3

TBS group of **13** was first removed with sodium iodide and BF_3•OEt_2[9] to afford **16** in 92% yield. Removal of benzyl group of **16** was troublesome under some standard conditions to give an intractable mixture. After screening several conditions, 1M-$SnCl_4$ was found to be the most effective one in the case of **16** producing the triol **17** in 99% yield. Isomerization and cyclization of the triol **17** was examined in the presence of DBU in THF.[3a,k] However, no reaction took place and the starting **17** was completely recovered. During conversion of **13** into **16** the partial isomerization at C-4 position of **16** had been detected when treated with tetra-*n*-butylammonium fluoride (TBAF) in THF. This observation suggested that the fluoride anion might be useful for conversion of **17** into goniofufurone. Treatment of **17** with TBAF in THF at room temperature fortunately effected successive isomerization and cyclization to provide (±)-goniofufurone (**1**) in 87% yield. Thus we have developed an efficient and highly stereoselective way for a total synthesis of (±)-goniofufurone (**1**) by using racemic compounds.

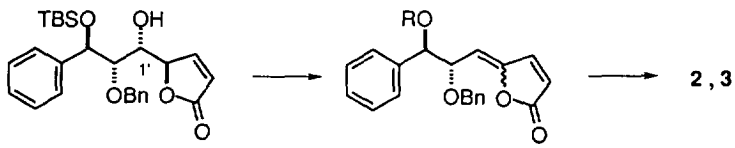


Scheme 4

Next phase of our program is faced to accomplishment of a total synthesis of natural (+)-goniofufurone (**1**) from optically active starting material according to the procedure described in a series of racemates. Reduction of optically active **10** (*anti* : *syn* = 95 : 5),[4] derived from optically active **9** (*anti* : *syn* = 95 : 5), with DIBAL-H and subsequent the Swern oxidation afforded the optically active **11** (*anti* : *syn* = 95 : 5). The aldehyde **11** was immediately exposed to **8** under the aldol condition with $Ti(OPr^i)_2Cl_2$ to furnish, after chromatographic purification, (-)-**13** in enantiomerically as well as diastereomerically pure form in 54% overall yield from **10**. An alternative and more convenient method for getting (-)-**13** was explored. Upon treatment with TBSOTf, optically active **5** (*anti* : *syn* = 95 : 5) yielded the TBS-protected **5** in 86% yield, which was reduced with DIBAL-H to afford the aldehyde **11**. The aldehyde **11** was then treated under the same aldol condition described above affording (-)-**13** in 59% overall yield from the TBS-protected **5**. Successive desilylation (94%) and debenzylation (96%) of (-)-**13** produced the triol (+)-**17** *via* (+)-**16**. Isomerization and spontaneous ring closure occurred on treatment with TBAF to give (+)-**1** in 86% yield. Synthetic (+)-goniofufurone was identified with natural one[10] by comparison of ^1H and ^{13}C NMR spectra.

Synthesis of (+)-Goniobutenolide A and (-)-Goniobutenolide B

Shing *et al.*[3k,l] have recently reported on conversion of **12** (in a deprotected form) into (+)-goniobutenolide A and B (**2** and **3**) *via* the corresponding acetate or trifluoroacetate derivatives, respectively. However, only moderate selectivity (**2** : **3** = 2 : 1 or **2** : **3** = 1 : 3, respectively) could be realized. Two other groups[3m,n] have also succeeded in preparation of goniobutenolide A and B in a nonselective fashion. With the useful intermediate **13** in hand, we next investigated selective as well as voluntary synthesis of goniobutenolide A and B from the common intermediate **13** *via* successive activation of $C_{1'}$-hydroxy group and elimination reaction.



Scheme 5

The $C_{1'}$-hydroxy group of the compound **13** was first of all transformed into the activated forms (mesylate, acetate, and trifluoroacetate), which were subsequently exposed to elimination conditions. After screening various elimination conditions by combination of base and solvent along with reaction temperature,

we finally found two promising and convenient conditions. Mesylation of (-)-**13**, followed by treatment with diisopropylamine in methylene chloride at room temperature for 40 min afforded a mixture of (*Z*)- and (*E*)-**18** in a ratio of 94 to 6 in 93% yield. Desilylation of the crude **18** effected under the standard condition (TBAF-HF) to give pure (*Z*)-**19** in 73% overall yield from **13**, which was converted into (+)-goniobutenolide A (**2**) by debenzylation with titanium tetrachloride in 95% yield. On the other hand, the mesylate derivative of (-)-**13** was exposed to an aqueous potassium carbonate solution in THF at room temperature for 4 h to leave a mixture of (*Z*)- and (*E*)-**18** (15 : 85) in 75% yield. According to the procedure that described for two step conversion of (*Z*)-**18** to (+)-**2**, (-)-goniobutenolide B (**3**, 98%) was obtained from (*E*)-**18** in a pure form through (*E*)-**19** (62% from **13**).

Thus, we could develop an efficient way for getting (+)-goniobutenolide A and B voluntarily from the same intermediate. It should be mentioned that both (*Z*)- and (*E*)-**18** are stable enough under the elimination conditions employed. Indeed no isomerization could be observed and the starting (*Z*)- and (*E*)-**18** were recovered intact when exposed independently to two elimination reactions (diisopropylamine / CH_2Cl_2 and aq. K_2CO_3 / THF) described above. However, it is still uncertain about the reason of selective formation of (+)-goniobutenolide A and (-)-goniobutenolide B by simply changing the reaction condition. Molecular model examination did not give us any clue for understanding the elimination mechanism (E_2, E_{1cB}, or E_1 elimination process). In any event we could succeed in highly stereoselective total synthesis of three antitumor styryllactones, (+)-goniofufurone, (+)-goniobutenolide A, and (-)-goniobutenolide B possessing γ-lactone skeleton as a common structural feature from the common synthetic intermediate **13**.

Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Infrared spectra were measured with a JASCO-102 and Shimadzu IR-460 spectrometers in $CHCl_3$ unless otherwise stated, mass spectra with a Hitachi M-80 mass spectrometer, optical rotations with JASCO DIP-181 digital and Horiba SEPA-300 high sensitive polarimeters, ^1H NMR spectra with JEOL JNM-EX270, and JNM-GSX500 spectrometers in $CDCl_3$ using tetramethylsilane as an internal standard unless otherwise stated, and ^{13}C NMR spectra with a JEOL JNM-EX270 and JNM-GSX500 spectrometers in $CDCl_3$ with $CDCl_3$ (77.00 ppm) as an internal reference unless otherwise stated. CH_2Cl_2 was freshly distilled from P_2O_5, and THF from sodium diphenylketyl prior to use. Aldol reactions were performed in oven-dried glassware under an inert atmosphere of nitrogen. Silica gel (silica gel 60, 230-400 mesh, Nacalai Tesque) was used for chromatography unless otherwise stated. Alumina (Aluminiumoxid 90, Aktivitätsstufe II-III, 70-230 mesh, Merck) was used for chromatography in a few cases. Organic extracts were dried over anhydrous Na_2SO_4.

Methyl (2*R,3*R**)-2-Benzyloxy-3-*tert*-butyldimethylsilyloxy-3-phenylpropanoate [(±)-10].** TBSOTf (0.98 ml, 4.28 mmol) was added to a mixture of (±)-**9** (613 mg, 2.14 mmol, *anti* : *syn* = 95 : 5) and DMAP (329 mg, 3.21 mmol) in dry CH_2Cl_2 (7 ml) at 0°C. The reaction mixture was stirred at rt for 30 min and quenched with MeOH (1 ml). The reaction mixture was taken into CH_2Cl_2 (20 ml) and washed with water, dried, and concentrated to dryness. Chromatography of the residue with hexane - acetone = 20 : 1 gave (±)-**10**

(663 mg, 77%, *anti : syn* = 95 : 5) as a colorless oil; MS *m/z* 400 (M^+, 0.05), 343 (24), 299 (26), 251 (42), 222 (100), 193 (38), 165 (32), 146 (46), 92 (38), 73 (83); IR 1730 (CO) cm^{-1}; ^1H NMR δ 7.36–7.29 (5H, m, Ar-H), 7.25–7.18 (3H, m, Ar-H), 6.99–6.96 (2H, m, Ar-H), 5.00 (0.05H, d, *J* =5.3 Hz, C_3-H), 4.85 (0.95H, d, *J* =7.9 Hz, C_3-H), 4.65 (0.05H, d, *J* =11.9 Hz, Bn-H), 4.44 (0.95H, d, *J* =12.2 Hz, Bn-H), 4.40 (0.05H, d, *J* =11.9 Hz, Bn-H), 4.22 (0.95H, d, *J* =12.2 Hz, Bn-H), 3.95 (0.05H, d, *J* =5.3 Hz, C_2-H), 3.92 (0.95H, d, *J* =7.9 Hz, C_2-H), 3.74 (2.85H, s, OCH_3), 3.55 (0.15H, s, OCH_3), 0.85 (0.45H, s, *t*-Bu), 0.81 (8.55H, s, *t*-Bu), 0.01 (0.15H, s, CH_3), -0.02 (2.85H, s, CH_3), -0.12 (0.15H, s, CH_3), -0.24 (2.85H, s, CH_3); ^{13}C NMR δ (for *anti*-product) 171.72, 141.47, 136.93, 128.14, 127.94, 127.84, 127.75, 127.62, 127.33, 83.69, 75.40, 72.69, 51.79, 25.54, 17.94, -4.69, -5.44. *Anal.* Calcd for $C_{23}H_{32}O_4Si$: C, 68.96; H, 8.05. Found: C, 68.88; H, 8.08.

General Procedure for the Aldol Reaction of Aldehyde (±)-11 with 2-Trimethylsilyloxyfuran (8). To a solution of TBS-protected ester (±)-**10** (1 eq.) in dry benzene (1.5 – 2 ml) was added dropwise a solution of DIBAL-H in toluene (1M solution; 2 eq.) at 0°C. The reaction mixture was stirred for 30 min, quenched with sat. sodium potassium tartrate aq., and diluted with ethyl acetate (30 ml). The organic solution was washed with water, dried, and concentrated to give the crude alcohol which was used for the following reaction. To a solution of oxalyl chloride (1.8 – 2.3 eq.) in CH_2Cl_2 (1 – 2 ml) was added dropwise a solution of DMSO (2.0 – 2.8 eq.) in CH_2Cl_2 (0.7 – 1.5 ml) at -78°C. The reaction mixture was stirred for 10 min, to which a solution of the crude alcohol (1 eq.) in CH_2Cl_2 (1 – 2 ml) was added dropwise. Stirring was continued for 15 min. Triethylamine (4 eq.) was added and the reaction mixture was stirred for 10 min and then allowed to warm to rt. The reaction mixture was diluted with diethyl ether (30 ml), washed with water and brine, dried and concentrated to dryness. The residue was passed through a alumina pad (hexane - acetone = 10 : 1), evaporated to give the aldehyde (±)-**11**. To a solution of aldehyde (±)-**11** (1 eq.) in CH_2Cl_2 (0.7 – 1.5 ml) was added dropwise Lewis acid (1.0M CH_2Cl_2 solution; 1.2 - 2.5 eq.) ($ZrCl_4$ was directly added to the reaction mixture because of its insolubility to CH_2Cl_2) at -78°C. The reaction mixture was stirred for 15 min, and then a solution of 2-trimethylsilyloxyfuran (**8**) [3 eq., in CH_2Cl_2 (0.7 ml – 1.5 ml)] was added dropwise to the reaction mixture. The reaction mixture was stirred for an additional hour at -78°C, and quenched with water. The reaction mixture was taken into CH_2Cl_2 and washed with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane - ethyl acetate = 10 : 3 gave two fractions (F_1 consists of (±)-**12** and (±)-**13** and F_2 involves (±)-**14**). Additional chromatography of F_1 with benzene - ethyl acetate = 30 : 1 afforded pure (±)-**12**, (±)-**13**, and (±)-**14**. The yields and ratio of each compound are listed in Table 1.

$SnCl_4$-mediated Reaction: (±)-**12** (2.4 mg, 5%), (±)-**13** (2.2 mg, 4%), and (±)-**14** (10.0 mg, 19%) were obtained from (±)-**10** (45.5 mg, 0.11 mmol), **8** (44 mg, 0.28 mmol), and a solution of $SnCl_4$ in CH_2Cl_2 (1.0M solution; 0.11 ml, 0.11 mmol). **$TiCl_4$-mediated Reaction:** (±)-**13** (21.9 mg, 41%) and (±)-**14** (6.2 mg, 12%) were obtained from (±)-**10** (46.9 mg, 0.12 mmol), **8** (39.0 mg, 0.25 mmol), and a solution of $TiCl_4$ in CH_2Cl_2 (1.0M solution; 0.10 ml, 0.10 mmol). **$ZrCl_4$-mediated Reaction:** (±)-**12** (5.0 mg, 13%) and (±)-**13** (13.2 mg, 35%) were obtained from (±)-**10** (32.9 mg, 0.08 mmol), **8** (29.0 mg, 0.19 mmol), and $ZrCl_4$ (20.9 mg, 0.09 mmol). **$Ti(OPr^i)_2Cl_2$-mediated Reaction**: (±)-**13** (90.3 mg, 59%) was obtained from (±)-**10** (136 mg, 0.34 mmol), **8** (97.3 mg, 0.62 mmol), and a solution of $Ti(OPr^i)_2Cl_2$ in CH_2Cl_2 (1.0M solution; 0.50 ml, 0.50 mmol).

(1'*R,2'*R**,3'*S**,4*R**)-4-(2'-Benzyloxy-3'-*tert*-butyldimethylsilyloxy-1'-hydroxy-3'-phenylpropyl)-2-buten-4-olide [(±)-12]**: colorless needles. mp 89–91°C (hexane - MeOH); MS *m/z* 454 (M^+, 0.04), 397 (3), 289 (19), 264 (37), 222 (100), 207 (81), 198 (57), 165 (12), 91 (100), 73 (54); IR 1755 (CO) cm^{-1}; ^1H NMR δ ($CDCl_3$ + D_2O) 7.41–7.32 (6H, m, Ar-H), 7.29 (1H, dd, *J* =1.5, 5.9 Hz, C_3-H), 7.28–7.27 (2H, m, Ar-H), 7.09-7.07 (2H, m, Ar-H), 6.06 (1H, d, *J* =2.0, 5.9 Hz, C_2-H), 5.08 (1H, ddd, *J* =1.5, 2.0, 4.3 Hz, C_4-H), 4.87 (1H, d, *J* =7.3 Hz, $C_{3'}$-H), 4.16 (1H, d, *J* =2.0, 4.3 Hz, $C_{1'}$-H), 4.06 (1H, d, *J* =10.7 Hz, Bn-H), 3.94 (1H, d, *J* =10.7 Hz, Bn-H), 3.47 (1H, dd, *J* =2.0, 7.3 Hz, $C_{2'}$-H), 0.87 (9H, s, *t*-Bu), 0.07 (3H, s, CH_3), -0.21 (3H, s, CH_3); ^{13}C NMR δ 172.96, 154.41, 141.44, 136.96, 128.41, 128.37, 128.14, 128.07, 127.30, 121.47, 84.21, 80.94, 75.06, 73.05, 70.35, 25.73, 18.03, -4.51, -5.21. *Anal.* Calcd for $C_{26}H_{34}O_5Si$: C, 68.69; H, 7.54. Found: C, 68.56; H, 7.50.

(1'*R,2'*R**,3'*S**,4*S**)-4-(2'-Benzyloxy-3'-*tert*-butyldimethylsilyloxy-1'-hydroxy-3'-phenylpropyl)-2-buten-4-olide [(±)-13]**: colorless orthorhombic crystals. mp 120-121°C (hexane - MeOH); MS *m/z* 455 (M^++1, 1), 397 (14), 296 (22), 264 (100), 223 (100), 198 (100), 149 (55), 117 (64), 91 (100), 73 (100); IR 1755 (CO) cm^{-1}; ^1H NMR δ 7.74 (1H, dd, *J* =1.5, 5.9 Hz, C_3-H), 7.41–7.28 (8H, m, Ar-H), 7.22–7.21 (2H, m, Ar-H), 6.10 (1H, dd, *J* =1.0, 5.9 Hz, C_2-H), 4.99 (1H, ddd, *J* =1.0, 1.5, 9.3 Hz, C_4-H), 4.93 (1H, d, *J* =5.9 Hz, $C_{3'}$-H), 4.42 (1H, d, *J* =10.8 Hz, Bn-H), 4.24 (1H, d, *J* =10.8 Hz, Bn-H), 3.73 (1H, dd, *J* =1.1, 5.9 Hz, $C_{2'}$-H), 3.65 (1H, dd, *J* =1.1, 9.3 Hz, $C_{1'}$-H), 0.87 (9H, s, *t*-Bu), 0.05 (3H, s, CH_3), -0.16 (3H, s, CH_3); ^{13}C NMR δ 172.90, 156.80, 140.93, 137.25, 128.43, 128.36, 128.09, 128.00, 126.79, 121.37, 82.01, 81.46, 75.15, 73.96, 72.29, 25.68, 18.03, -4.69, -5.25. *Anal.* Calcd for $C_{26}H_{34}O_5Si$: C, 68.69; H, 7.54. Found: C, 68.67; H, 7.59.

(1'*R,2'*S**,3'*R**)-2-(2'-Benzyloxy-3'-*tert*-butyldimethylsilyloxy-1'-hydroxy-3'-phenylpropyl)-2-buten-4-olide [(±)-14]**: a colorless oil; MS *m/z* 397 (M^+- *t*-Bu, 1), 341 (15), 285 (13), 257 (48), 222 (100), 187 (71), 115 (12), 73 (50); IR 1750 (CO) cm^{-1}; ^1H NMR δ 7.43–7.41 (2H, m, Ar-H), 7.37–7.34 (3H, m, Ar-H), 7.31–7.29 (1H, m, C_3-H), 7.28–7.24 (3H, m, Ar-H), 7.03–7.01 (2H, m, Ar-H), 4.92 (1H, d, *J* =6.4 Hz, $C_{3'}$-H), 4.82–4.77 (1H, m, $C_{1'}$-H), 4.71 (1H, br-d, *J* =18.1 Hz, C_4-H), 4.58 (1H, br-d, *J* =18.1 Hz, C_4-H), 4.07 (1H, d, *J* =11.2 Hz, Bn-H), 3.95 (1H, d, *J* =11.2 Hz, Bn-H), 3.91 (1H, dd, *J* =1.5, 6.4 Hz, $C_{2'}$-H), 3.47 (1H, d, *J* =6.9 Hz, OH), 0.91 (9H, s, *t*-Bu), 0.09 (3H, s, CH_3), -0.15 (3H, s, CH_3); ^{13}C NMR δ 171.99, 147.04, 141.53, 137.43, 135.09, 128.37, 128.25, 127.89, 127.82, 127.03, 82.07, 74.88, 73.89, 70.37, 66.96, 25.74, 18.06, -4.65, -5.21. *Anal.* Calcd for $C_{26}H_{34}O_5Si$: C, 68.69; H, 7.54. Found: C, 68.49; H, 7.58.

(1'*R,2'*S**,3'*S**,4*S**)-4-(2'-Benzyloxy-1',3'-dihydroxy-3'-phenylpropyl)-2-buten-4-olide [(±)-16].** A solution of BF_3•OEt_2 in CH_3CN (1.0M solution; 0.23 ml, 0.23 mmol) was added dropwise to a solution of (±)-**13** (70.3 mg, 0.15 mmol) and NaI (50.8 mg, 0.34 mmol) in dry CH_3CN (4 ml) at 0°C. The reaction mixture was stirred for 30 min and poured into cold water (10 ml). After a few drops of 15% $Na_2S_2O_3$ aq. being added (for decolorization), the reaction mixture was diluted with CH_2Cl_2 (20 ml), washed with water and brine, dried and concentrated to dryness. Chromatography of the residue with CH_2Cl_2 - MeOH = 40 : 1 afforded (±)-**16** (48.3 mg, 92%) as colorless crystals. mp 120.5–121.5°C (diisopropyl ether - acetone); MS *m/z*

340 (M^+, 4), 249 (54), 216 (34), 190 (10), 143 (39), 127 (17), 107 (98), 91 (100), 73 (12); IR 3400 (OH), 1755 (CO) cm^{-1}; ^1H NMR δ ($CDCl_3$+ D_2O) 7.70 (1H, dd, *J* =1.5, 5.9 Hz, C_3-H), 7.39–7.35 (5H, m, Ar-H), 7.34–7.29 (3H, m, Ar-H), 7.26–7.23 (2H, m, Ar-H), 6.10 (1H, dd, *J* =2.0, 5.9 Hz, C_2-H), 5.08–5.00 (2H, m, C_4-H and $C_{3'}$-H), 4.52 (1H, d, *J* =10.7 Hz, Bn-H), 4.34 (1H, d, *J* =10.7 Hz, Bn-H), 3.86 (1H, dd, *J* =1.4, 5.8 Hz, $C_{2'}$-H) and 3.67 (1H, dd, *J* =1.4, 8.8 Hz, $C_{1'}$-H); ^{13}C NMR δ 172.83, 156.42, 140.11, 137.05, 128.66, 128.54, 128.32, 128.23, 128.18, 126.24, 121.49, 82.01, 80.85, 73.84, 73.48, 72.15; *Anal.* Calcd for $C_{20}H_{20}O_5$: C, 70.58; H, 5.92. Found: C, 70.65; H, 5.96. High resolution mass calcd for $C_{20}H_{20}O_5$ 340.1310, found 340.1320.

(1'*R,2'*S**,3'*S**,4*S**)-4-(1',2',3'-Trihydroxy-3'-phenylpropyl)-2-buten-4-olide [(±)-17].** To a solution of (±)-**16** (55.2 mg, 0.16 mmol) in dry CH_2Cl_2 (2 ml) was added dropwise a solution of $SnCl_4$ in CH_2Cl_2 (1.0M solution; 0.32 ml, 0.32 mmol) at rt. After being stirred for 30 min, the reaction mixture was quenched by successive addition of MeOH (0.5 ml), sat. $NaHCO_3$ aq. (5 drops) and water (3 drops). The reaction mixture was then dried and concentrated to leave the crude triol. Chromatography of the residue with CH_2Cl_2 - MeOH = 30 : 1 provided (±)-**17** (40.0 mg, 99%) as colorless crystals. mp 125.5–127.5 °C (hexane - ethyl acetate); MS *m/z* 251 (M^++1, 1), 233 (5), 190 (11) 126 (28), 107 (100), 84 (30), 79 (32); IR (KBr) 3320 (OH), 1735 (CO) cm^{-1}; ^1H NMR δ [$(CD_3)_2CO$ + D_2O] 7.88 (1H, dd, *J* =1.5, 5.9 Hz, C_3-H), 7.46–7.44 (2H, m, Ar-H), 7.34–7.31 (2H, m, Ar-H), 7.27–7.23 (1H, m, Ar-H), 6.15 (1H, dd, *J* =2.0, 5.9 Hz, C_2-H), 5.18 (1H, ddd, *J* =1.5, 2.0, 6.8 Hz, C_4-H), 4.77 (1H, d, *J* =7.8 Hz, $C_{3'}$-H), 4.00 (1H, dd, *J* =1.0, 6.8 Hz, $C_{1'}$-H) and 3.82 (1H, dd, *J* =1.0, 7.8 Hz, $C_{2'}$-H); ^{13}C NMR δ [$(CD_3)_2CO$, internal reference; 30.3 ppm] 173.69, 158.13, 144.55, 129.24, 128.50, 128.36, 122,36, 84.76, 75.58, 72.73. *Anal.* Calcd for $C_{13}H_{14}O_5$: C, 62,39; H, 5.64. Found: C, 62.25; H, 5.64.

(1*R,1'*R**,3*R**,4*S**,5*R**)-4-Hydroxy-3-(1'-hydroxy-1'-phenylmethyl)-2,6-dioxabicyclo[3.3.0]octan-7-one [(±)-goniofufurone [(±)-1]].** To a solution of triol (±)-**17** (28.9 mg, 0.12 mmol) was added dropwise TBAF (1.0M THF solution; 0.2 ml, 0.2 mmol) at rt. After being stirred for 30 min, the reaction mixture was quenched with sat. NH_4Cl aq. (3 drops) and EtOH (0.5 ml). The reaction mixture was then dried and concentrated to provide the crude material. Chromatography of the residue with CH_2Cl_2 - MeOH - hexane = 30 : 1 : 1 afforded (±)-**1** (25.1 mg, 87%) as colorless plates. mp 142.5–144°C (hexane - acetone); MS *m/z* 250 (M^+, 0.4), 232 (9), 126 (80), 107 (100), 82 (59), 79 (38); IR (KBr) 3400 (OH), 1755 (CO) cm^{-1} ; ^1H NMR δ 7.44–7.33 (5H, m, Ar-H), 5.18 (1H, dd, *J* =2.9, 4.9 Hz, $C_{1'}$-H), 5.10 (1H, dd, *J* =3.9, 5.9 Hz, C_1-H), 4.86 (1H, dd, *J* =1.5, 3.9 Hz, C_5-H), 4.40 (1H, dt, *J* =1.5, 2.9 Hz, C_4-H), 4.22 (1H, d, *J* =2.9 Hz, C_4-OH), 4.09 (1H, dd, *J* =2.9, 4.9 Hz, C_3-H), 2.96 (1H, d, *J* =2.9 Hz, $C_{1'}$-OH), 2.74 (1H, dd, *J* =5.9, 18.6 Hz, C_8-H), 2.67 (1H, d, *J* =18.6 Hz, C_8-H); ^{13}C NMR δ [$(CD_3)_2CO$] 176.57, 144.06, 129.27, 128.61, 128.16, 89.04, 85.48, 78.53, 75.28, 72.73, 36.97. *Anal.* Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.12; H, 5.94.

Methyl (2*R*,3*R*)-2-Benzyloxy-3-*tert*-butyldimethylsilyloxy-3-phenylpropanoate (10). According to the procedure that described for conversion of (±)-**9** into (±)-**10**, optically active **10** (187 mg, 71%, *anti* : *syn* = 95 : 5) was obtained from optically active **9** (187 mg, 0.65 mmol, *anti* : *syn* = 95 : 5), TBSOTf (0.37

ml, 1.31 mmol), and DMAP (120 mg, 0.98 mmol). Optically active **10**: a colorless oil; *Anal.* Calcd for $C_{23}H_{32}O_4Si$: C, 68.96; H, 8.05. Found: C, 69.11; H, 7.99.

(-)-(1'*S*,2'*S*,3'*R*,4*R*)-4-(2'-Benzyloxy-3'-*tert*-butyldimethylsilyloxy-1'-hydroxy-3'-phenylpropyl)-2-buten-4-olide [(-)-13]. According to the procedure that described for conversion of (±)-**11** into (±)-**13**, (-)-**13** (116 mg, 54%) was obtained from optically active **10** (190 mg, 0.47 mmol), **8** (150 mg, 0.96 mmol). (-)-**13**: a colorless oil; $[\alpha]_D^{17}$ -3.9° (*c* 0.32, $CHCl_3$); *Anal.* Calcd for $C_{26}H_{34}O_5Si$: C, 68.69; H, 7.54. Found: C, 68.75; H, 7.58.

Conversion of Optically Active 5 into (-)-13. According to the procedure that described for conversion of (±)-**9** into (±)-**10**, optically active **5** (120 mg, 0.35 mmol, *anti : syn* = 95 : 5) was treated with TBSOTf (0.2 ml, 0.87 mmol) and DMAP (85.0 mg, 0.70 mmol) to give the *O*-TBS derivative (138 mg, 86%, *anti : syn* = 95 : 5): a colorless oil; MS *m/z* 443 (M^+-CH_3, 0.2), 401 (30), 352 (51), 285 (21), 239 (86), 222 (100), 193 (100), 91 (100), 57 (54); IR 1665 (CO); ^{1}H NMR δ 7.32–7.20 (8H, m, Ar-H), 7.05-7.03 (2H, m, Ar-H), 4.96 (0.05H, d, *J* =4.9 Hz, C_3-H), 4.91 (0.95H, d, *J* =6.4 Hz, C_3-H), 4.60 (0.95H, d, *J* =12.2 Hz, Bn-H), 4.59 (0.05H, d, *J* =11.7 Hz, Bn-H), 4.36 (0.95H, d, *J* =12.2 Hz, Bn-H), 4.28 (0.05H, d, *J* =11.7 Hz, Bn-H), 3.86 (0.95H, d, *J* =6.4 Hz, C_2-H), 3.80 (0.05H, d, *J* =4.9 Hz, C_2-H), 1.47 (0.45H, s, *t*-Bu), 1.46 (8.55H, s, *t*-Bu), 0.85 (0.45H, s, *t*-Bu), 0.84 (8.55H, s, *t*-Bu), 0.01 (2.85H, s, CH_3), 0.00 (0.15H, s, CH_3), -0.17 (0.15H, s, CH_3), -0.23 (2.85H, s, CH_3); ^{13}C NMR δ (for *anti* - product) 200.74, 141.03, 137.20, 128.12, 127.78, 127.74, 127.65, 127.56, 127.52, 88.97, 75.91, 73.10, 47.45, 27.79, 25.76, 18.07, -4.65, -5.15. *Anal.* Calcd for $C_{26}H_{38}O_3SSi$: C, 68.08; H, 8.35. Found: C, 68.19; H, 8.34. To a solution of the crude *O*-TBS derivative (138 mg, 0.30 mmol) in dry toluene (2 ml) was added dropwise a solution of DIBAL-H in toluene (1.0 M solution; 0.66 ml, 0.66 mmol) at 0°C. The reaction mixture was stirred for 30 min, quenched with sat. sodium potassium tartrate aq., passed through celite, and diluted with diethyl ether (20 ml). The organic layer was washed with water, dried, and concentrated to dryness. The residue was passed through an alumina pad (hexane - acetone = 10 : 1) to give the optically active aldehyde **11** (87.6 mg, 0.24 mmol) which was immediately exposed to **8** (110 mg, 0.71 mmol) to provide (-)-**13** (81.3 mg, 59%).

(+)-(1'*S*,2'*R*,3'*R*,4*R*)-4-(2'-Benzyloxy-1',3'-dihydroxy-3'-phenylpropyl)-2-buten-4-olide [(+)-16]. According to the procedure that described for conversion of (±)-**13** into (±)-**16**, (+)-**16** (70.8 mg, 94%) was obtained from (-)-**13** (101 mg, 0.22 mmol), NaI (73 mg, 0.49 mmol) and a solution of BF_3•OEt_2 in CH_3CN (1.0M solution; 0.33 ml, 0.33 mmol). (+)-**16**: colorless needles. mp 103-104°C (diisopropyl ether - acetone); $[\alpha]_D^{22}$ +25.5° (*c* 0.35, $CHCl_3$). *Anal.* Calcd for $C_{20}H_{20}O_5$: C, 70.58; H, 5.92. Found: C, 70.54; H, 5.92. High resolution mass calcd for $C_{20}H_{20}O_5$ 340.1310, found 340.1326.

(+)-(1'*S*,2'*R*,3'*R*,4*R*)-4-(1',2',3'-Trihydroxy-3'-phenylpropyl)-2-buten-4-olide [(+)-17]. According to the procedure that described for conversion of (±)-**16** into (±)-**17**, (+)-**17** (17.0 mg, 96%) was obtained from (+)-**16** (24.0 mg, 0.07 mmol) and a solution of $SnCl_4$ in dry CH_2Cl_2 (1.0M solution; 0.14 ml, 0.14 mmol). (+)-**17**: colorless needles. mp 141–143°C (hexane - ethyl acetate); $[\alpha]_D^{24}$ +99.8° (*c* 0.30, EtOH). *Anal.* Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.24; H, 5.64.

(+)-Goniofufurone [(+)-1]. According to the procedure that described for conversion of (±)-**17** into (±)-goniofufurone [(±)-**1**], (+)-goniofufurone (10.0 mg, 86%) was obtained from (+)-triol **17** (11.6 mg, 0.04 mmol) and TBAF (1.0M THF solution; 0.07 ml, 0.07 mmol). (+)-goniofufurone: colorless crystals. mp 150–152°C (hexane - ethyl acetate) (lit.[1c] mp 152–154 °C); $[\alpha]_D^{23}$ +8.9° (*c* 0.5, EtOH) [lit.[1c] $[\alpha]_D^{22}$ +9.0° (*c* 0.5, EtOH)]. *Anal.* Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.29; H, 5.69.

(*Z*)-(2'*S*,3'*R*)-4-(2'-Benzyloxy-3'-*tert*-butyldimethylsilyloxy-3'-phenylpropylidene)-2-buten-4-olide [(*Z*)-18]. To a solution of (-)-**13** (45.3 mg, 0.10 mmol) in CH_2Cl_2 (1.5 ml) was added triethylamine (0.04 ml) and methanesulfonyl chloride (0.02 ml) at -60°C, and the mixture was stirred for 30 min at the same temperature. The reaction mixture was quenched by addition of sat. NH_4Cl aq. and extracted with CH_2Cl_2. The organic layer was washed with brine, dried, and concentrated to dryness. Diisopropylamine (81.3 mg, 0.80 mmol) was added to a solution of the crude mesylate in CH_2Cl_2 (3.0 ml) and the mixture was stirred for 40 min at rt. The reaction mixture was quenched by sat. NH_4Cl aq. and extracted with CH_2Cl_2. The organic layer was washed with brine, dried and concentrated to dryness. Chromatography of the residue with hexane - ethyl acetate = 20 : 1 gave a mixture of (*Z*)- and (*E*)-**18** (40.3 mg, 93%, *Z* : *E* = 94 : 6). (*Z*)-**18**: IR 1785, 1755(CO) cm^{-1}; ^1H NMR δ 7.33-7.22 (8H, m, Ar-H), 7.35 (1H, d, *J* =5.4 Hz, C_3-H), 7.12-7.11 (2H, m, Ar-H), 6.19 (1H, d, *J* =5.4 Hz, C_2-H), 5.37 (1H, d, *J* =9.8 Hz, $C_{1'}$-H), 4.80 (1H, d, *J* =5.4 Hz, $C_{3'}$-H), 4.56 (1H, dd, *J* =9.8, 5.4 Hz, $C_{2'}$-H), 4.47 (1H, d, *J* =10.7 Hz, Bn-H), 4.33 (1H, d, *J* =10.7 Hz, Bn-H), 0.83 (9H, s, *t*-Bu), 0.02 (3H, s, CH_3), -0.15 (3H, s, CH_3) ; ^{13}C NMR δ 169.45, 151.61, 143.23, 141.40, 137.97, 128.14, 127.85, 127.60, 127.51, 126.86, 120.52, 113.75, 78.65, 76.80, 71.72, 25.64, 18.10, -4.76, -4.92.

(+)-(*Z*)-(2'*S*,3'*R*)-4-(2'-Benzyloxy-3'-hydroxy-3'-phenylpropylidene)-2-buten-4-olide [(+)-(*Z*)-19]. A solution of TBAF - HF in THF (1.0M solution; 2.0 ml, 2.0 mmol) was added dropwise to a solution of a mixture of optically active (*Z*)- and (*E*)-**18** (28.4 mg, 0.07 mmol, *Z* : *E* = 94 : 6) in THF (1.0 ml) at rt. After stirring for 19h, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane - ethyl acetate = 10 : 1 afforded (+)-(*Z*)-**19** (16.7 mg, 73% overall yield from **13**) as colorless crystals. mp 103-105°C (hexane - ethyl acetate); $[\alpha]_D^{25}$ +35.3° (*c* 0.46, $CHCl_3$); CIMS *m/z*: 323 (M^++1, 25), 305 (45), 259 (7), 217 (100), 199 (22), 107 (76), 91(43); IR 1780, 1755(CO) cm^{-1}; ^1H NMR δ 7.35-7.22 (11H, m, Ar-H and C_3-H), 6.16 (1H, d, *J* =5.4 Hz, C_2-H), 5.35 (1H, d, *J* =9.3 Hz, $C_{1'}$-H), 5.02 (1H, d, *J* =3.9 Hz, $C_{3'}$-H), 4.76 (1H, dd, *J* =9.3, 3.9 Hz, $C_{2'}$-H), 4.60 (1H, d, *J* =11.2 Hz, Bn-H), 4.50 (1H, d, *J* =11.2 Hz, Bn-H), 2.70 (1H, brs, OH) ; ^{13}C NMR δ 169.13, 151.93, 143.18, 138.99, 137.59, 128.45, 128.18, 127.92, 127.87, 127.82, 126.33, 120.83, 111.23, 77.16, 75.20, 71.65. *Anal.* Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found C, 74.57, H, 5.51.

(+)-(*Z*)-(2'*S*,3'*R*)-4-(2',3'-Dihydroxy-3'-phenylpropylidene)-2-buten-4-olide [(+)-goniobutenolide A (2)]. To a solution of (+)-**19** (11.6 mg, 0.04 mmol) in dry CH_2Cl_2 (1.0 ml) was added dropwise a solution of $TiCl_4$ in CH_2Cl_2 solution (1.0M solution; 0.1 ml, 0.1 mmol) at rt. After being stirred for 30 min, the reaction mixture was quenched by sat. $NaHCO_3$ aq. and extracted with CH_2Cl_2. The organic layer was washed with brine, dried and concentrated to dryness. Chromatography of the residue with hexane - ethyl acetate = 2 : 1 gave (+)-**2** (goniobutenolide A) (7.9 mg, 95%) as a yellow oil; $[\alpha]_D^{25}$ +183° (*c* 0.17, $CHCl_3$)

[lit.[3k,l] $[\alpha]_D^{27}$ +187° (*c* 0.4, $CHCl_3$)]; CIMS *m/z* 233 (M^++1, 43), 231 (30), 215 (100), 199 (20), 149 (5), 127 (87), 107 (60); IR 3400 (OH), 1780, 1755 (CO) cm^{-1}; ^1H NMR δ 7.38-7.27 (6H, m, Ar-H and C_3-H), 6.17 (1H, d, *J* =5.9 Hz, C_2-H), 5.30 (1H, d, *J* =8.3 Hz, $C_{1'}$-H), 5.01 (1H, dd, *J* =8.3, 4.4 Hz, C_2-H), 4.95 (1H, d, *J* =4.4 Hz, $C_{3'}$-H), 2.61 (2H, brs, OH) ; ^{13}C NMR δ 169.25, 150.46, 143.63, 139.05, 128.32, 128.03, 126.42, 120.43, 112.97, 75.96, 70.62.

(*E*)-(2'*S*,3'*R*)-4-(2'-Benzyloxy-3'-*tert*-butyldimethylsilyloxy-3'-phenylpropylidene)-2-buten-4-olide [(*E*)-18]. Mesylation of (-)-**13** (38.8 mg, 0.09 mmol) under the similar condition described for the preparation of (*Z*)-**18** provided the crude mesylate. To a solution of the crude mesylate in THF (3.0 ml) was added 10% K_2CO_3 aq. (1.5 ml) and the mixture was stirred at rt for 2 h. The reaction mixture was diluted with sat. NH_4Cl aq. and extracted with ethyl acetate. The organic layer was washed with brine, dried and concentrated to dryness. Chromatography of the residue with hexane - ethyl acetate = 20 : 1 gave (*Z*)- and (*E*)-**18** (27.8 mg, 75%, *Z* : *E* = 15 : 85). (*E*)-**18**: IR 1790, 1760(CO) cm^{-1}; ^1H NMR δ 7.31-7.24 (8H, m, Ar-H), 7.22 (1H, dd, *J* =5.4, 1.0 Hz, C_3-H), 7.04-7.01 (2H, m, Ar-H), 6.11 (1H, dd, *J* =5.4, 2.0 Hz, C_2-H), 5.79 (1H, ddd, *J* =8.8, 2.0, 1.0 Hz, $C_{1'}$-H), 4.78 (1H, d, *J* =5.9 Hz, $C_{3'}$-H), 4.50 (1H, d, *J* =11.8 Hz, Bn-H), 4.27 (1H, d, *J* =11.8 Hz, Bn-H), 4.06 (1H, dd, *J* =8.8, 5.9 Hz, $C_{2'}$-H), 0.82 (9H, s, *t*-Bu), 0.00 (3H, s, CH_3), -0.14 (3H, s, CH_3) ; ^{13}C NMR δ 169.33, 152.13, 141.49, 140.47, 137.36, 128.34, 128.00, 127.71, 127.66, 127.60, 126.88, 120.85, 113.26, 79.59, 77.20, 71.02, 25.66, 18.08, -4.81, -4.92.

(-)-(*E*)-(2'*S*,3'*R*)-4-(2'-Benzyloxy-3'-hydroxy-3'-phenylpropylidene)-2-buten-4-olide [(-)-(*E*)-19]. According to the procedure that described for conversion of (*Z*)-**18** into (*Z*)-**19**, a mixture of optically active (*Z*)- and (*E*)-**18** (13.5 mg, 0.03 mmol, *Z* : *E* = 15 : 85) was treated with TBAF-HF to afford (-)-(*E*)-**19** (8.3 mg, 62% overall yield from **13**) as colorless crystals. mp 85-87°C (hexane - ethyl acetate); $[\alpha]_D^{25}$ -1.0° (*c* 0.27, $CHCl_3$); CIMS *m/z* 323 (M^++1, 25), 305 (29), 259 (11), 249 (5), 217 (100), 199 (13), 125 (10), 107 (34), 91 (34); IR 1790, 1760 (CO) cm^{-1}; ^1H NMR δ 7.36-7.20 (10H, m, Ar-H), 7.11 (1H, dd, *J* =5.4, 1.0 Hz, C_3-H), 6.09 (1H, dd, *J* =5.4, 2.0 Hz, C_2-H), 5.75 (1H, ddd, *J* =9.3, 2.0, 1.0 Hz, $C_{1'}$-H), 5.00 (1H, dd, *J* =4.4, 2.9 Hz, $C_{3'}$-H), 4.65 (1H, d, *J* =11.7 Hz, Bn-H), 4.42 (1H, d, *J* =11.7 Hz, Bn-H), 4.25 (1H, dd, *J* =9.3, 4.4 Hz, $C_{2'}$-H), 2.59 (1H, d, *J* =2.9 Hz, OH); ^{13}C NMR δ 169.06, 152.51, 139.75, 139.19, 137.00, 128.57, 128.30, 128.07, 127.96, 127.82, 126.49, 121.33, 110.94, 78.26, 75.83, 70.94. *Anal.* Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found C, 74.30, H, 5.63.

(-)-(*E*)-(2'*S*,3'*R*)-4-(2',3'-Dihydroxy-3'-phenylpropylidene)-2-buten-4-olide [(-)-goniobutenolide B (3)]. According to the procedure that described for conversion of (+)-(*Z*)-**19** into (+)-**2**, (-)-(*E*)-**19** (5.5 mg, 0.01 mmol) was treated with $TiCl_4$ to afford (-)-**3** (goniobutenolide B) (3.9 mg, 98%) as colorless crystals. mp 146-148°C (hexane - ethyl acetate) (lit.[3k,l] 148-149°C); $[\alpha]_D^{19}$ -109° (*c* 0.06, $CHCl_3$) [lit.[3k,l] $[\alpha]_D^{27}$ -112° (*c* 0.2, $CHCl_3$)]; CIMS *m/z* 233 (M^++1, 93), 231 (21), 215 (84), 127 (100), 107 (55), 105 (9); IR 3450 (OH), 1790, 1755 (CO) cm^{-1}; ^1H NMR δ 7.50 (1H, d, *J* =5.4 Hz, C_3-H), 7.38-7.29 (5H, m, Ar-H), 6.12 (1H, dd, *J* =5.4, 2.0 Hz, C_2-H), 5.79 (1H, dd, *J* =7.3, 2.0 Hz, $C_{1'}$-H), 4.88 (1H, d, *J* =4.4 Hz, $C_{3'}$-H), 4.64 (1H, dd, *J* =7.3, 4.4 Hz, $C_{2'}$-H), 2.59 (1H, brs, OH), 2.52 (1H, brs, OH) ; ^{13}C NMR δ 169.27, 151.73, 140.68, 138.96, 128.62, 126.54, 121.11, 112.36, 77.20, 72.15; *Anal.* Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found C, 66.85, H, 5.35.

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8. Crystal data: $C_{26}H_{34}O_5Si$, M= 454.64, orthorhombic, *a*= 20.9 (2) Å, *b*= 37.82 (9) Å, *c*= 6.63 (9) Å, V= 5242 $Å^3$, Z= 8, Dc= 1.152 g/cm^3, space group Pbca (#61), μ (MoKα) = 1.15 cm^{-1}. A colorless needle, *ca.* 0.2 x 0.2 x 0.5 mm, was mounted on a glass fiber. All measurements were made on a Rigaku AFC5S diffractometer. The cell dimensions and intensities were refined by the least-squares method, using 25 reflections on the diffractometer with Mo-Kα radiation with ω-scan mode for 2θ less than 45°. The structure was solved by direct method (MITHRIL method). The final cycle of full-matrix least-squares refinement was based on 3182 observed reflections. The final *R* value was 0.054.
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