Stereoselective Syntheses of (+)-Goniotriol, (+)-8-Acetylgoniotriol, (+)-Goniodiol, (+)-9-Deoxygoniopypyrone, (+)-Altholactone, and (−)-Goniofupyrone

Chisato Mukai,* Syuichi Hirai, and Miyoji Hanaoka*

Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan

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The γ-lactone intermediate (−)-**7**, derived from (+)-tricarbonyl(η^6-*o*-(trimethylsilyl)benzaldehyde)chromium(0) complex, was efficiently converted into the corresponding δ-lactone intermediate (−)-**11**. This second intermediate has been shown to be a versatile compound for stereoselective syntheses of natural styryllactones possessing a six-membered lactone moiety, isolated from *Goniothalamus giganteus*, by transforming it into (+)-goniotriol, (+)-8-acetylgoniotriol, (+)-goniodiol, (+)-9-deoxygoniopypyrone, (+)-altholactone, and (−)-goniofupyrone.

Introduction

Recent publications from McLaughlin's group[1] have disclosed isolation and characterization of a number of novel so-called styryllactones from *Goniothalamus giganteus*, which were found to be marginally to significantly cytotoxic against human tumors.[1,2] Because of their antitumor activities, much effort[2−11] has so far been centered on the development of methodology for the synthesis of these styryllactones. These styryllactones can be mainly classified into two groups according to their structural features, especially the size of the lactone ring. The first group consists of styryllactones with a five-membered lactone moiety involving (+)-goniofufurone, (+)-goniobutenolide A, and (−)-goniobutenolide B, and the second group is made up of styryllactones having a six-membered lactone functionality. Some representatives of the latter are shown in Figure 1.

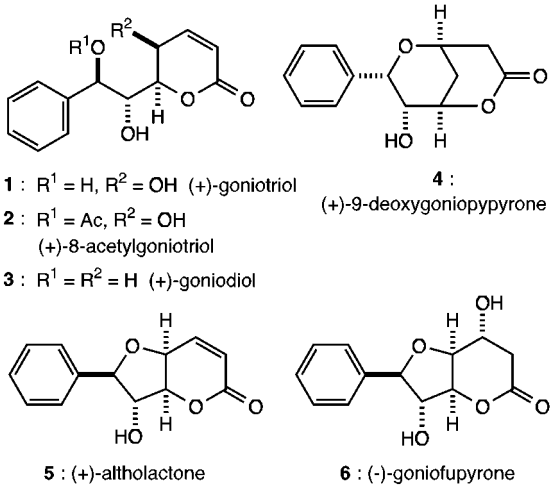

Figure 1.

In the course of our program directed toward stereoselective total syntheses of all types of antitumor styryllactones, we have recently completed the total syntheses of the γ-lactone natural products[12] (+)-goniofufurone, (+)-goniobutenolide A, and (−)-goniobutenolide B from the (+)-tricarbonyl(η^6-*o*-(trimethylsilyl)benzaldehyde)-chromium(0) complex[13] *via* the common key intermediate (−)-**7**. Compound **7** has not only a carbon framework required for all types of styryllactones but also four hydroxy groups with different protecting groups. Therefore, our next endeavor focused on successful modification of the intermediate **7** for synthesis of six-membered lactone natural products **1-6** (Figure 1). This paper describes a highly stereoselective transformation of the intermediate **7** to styryllactones possessing the δ-lactone moiety.

Results and Discussion

The first concern and most significant requirement for our synthetic plan of the δ-lactone natural products **1**−**6**

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

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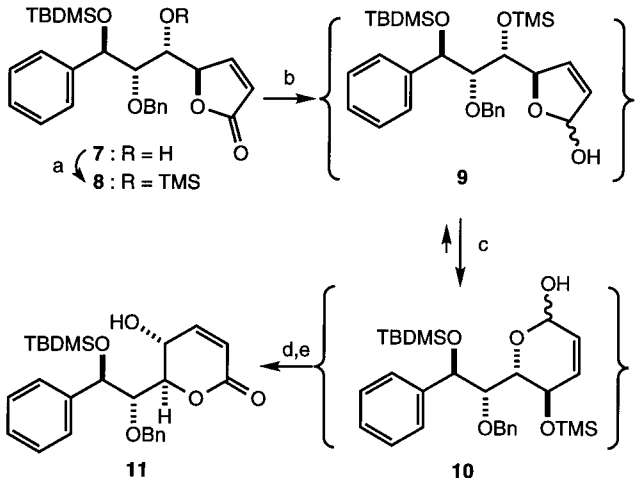
Scheme 1[a]

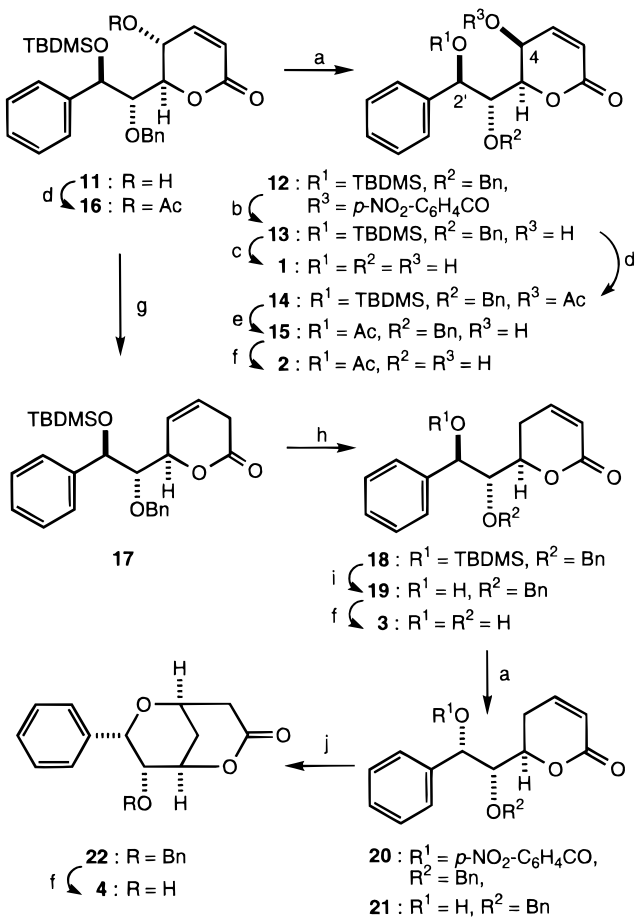


[a]Reaction conditions: (a) TMS-imidazole, CH_2Cl_2, 97%; (b) DIBALH, Et_2O, −78 °C; (c) ^{t}BuOK, THF, −70 °C; (d) PDC, AcONa, CH_2Cl_2; (e) 10% HCl, MeOH, 69% from **8**.

from the intermediate **7** was an efficient transformation of the γ-lactone moiety of the latter to the corresponding δ-lactone derivative. Direct conversion of **7** into **11** under acidic or basic conditions, however, gave decomposed products and/or recovery of a starting material. Kitazume[14] and co-workers have recently reported on a useful method for ring transformation of butenolide derivatives into pentenolide ones through lactol intermediates with migration of the silyl group (Scheme 1). By taking advantage of Kitazume's procedure,[14] we tried to convert **7** into **11**. The secondary hydroxy group of (−)-**7** was first protected with the TMS group to give **8** in 97% yield. Because of its instability, **8** was immediately reduced with DIBALH to afford the five-membered lactol **9**, which on exposure to potassium *tert*-butoxide at −70 °C underwent ring transformation accompanied with silyl group migration producing the desired six-membered lactol **10** predominantly. Oxidation of a mixture of **9** and **10** with PDC was followed by hydrolysis with 10% hydrochloric acid to provide the δ-lactone derivative (−)-**11** in 69% overall yield from **8** together with a small amount of **7** (5%).

Syntheses of (+)-Goniotriol, (+)-8-Acetylgoniotriol, (+)-Goniodiol, and (+)-9-Deoxygoniofupyrone. With the potential δ-lactone intermediate **11** for target natural products in hand, we completed the syntheses of monocyclic natural products **1**, **2**, and **3** as well as dioxabicyclo[3.3.1]nonanone one **4**. Inversion of the allylic hydroxy functionality of **11** was carried out under standard Mitsunobu conditions[15] using *p*-nitrobenzoic acid to furnish the *p*-nitrobenzoate (+)-**12** in 96% yield, which was subsequently hydrolyzed with 1% aqueous potassium carbonate to produce (+)-**13** in 74% yield with inverted stereochemistry at the allylic position (Scheme 2). Successive desilylation and debenzylation was realized by treatment with (i) sodium iodide/BF_3•OEt_2[16] and (ii) $TiCl_4$[17] to afford (+)-goniotriol (**1**) [mp 169−170 °C,

Scheme 2[a]



[a]Reaction conditions: (a) PPh_3, DEAD, *p*-$NO_2C_6H_4CO_2H$, C_6H_6, **11** → **12** (96%), **19** → **20** (49%); (b) 1% aq K_2CO_3, THF, 74%; (c) NaI, BF_3•OEt_2, CM_3CN, 0 °C, (ii) $TiCl_4$, CH_2Cl_2, 65%; (d) Ac_2O, DMAP, CH_2Cl_2, **13** → **14** (96%), **11** → **16** (100%); (e) TBAF−HF, THF, 86%; (f) $TiCl_4$, CH_2Cl_2, **15** → **2** (77%), **22** → **4** (96%); (g) Zn−Hg, satd HCl in Et_2O, −20 °C, 88%; (h) DBU, THF, 90%; (i) NaI, BF_3•OEt_2, CM_3CN, 0 °C, 97%; (j) (i) 1 N LiOH, THF, (ii) TFA, THF, (iii) DBU, THF, 84%.

$[\alpha]^{21}_D$ +118 (*c* 0.1, MeOH)] [lit.[1b] mp 170 °C, $[\alpha]^{25}_D$ +121 (MeOH)] in 65% yield.

On the other hand, **13** was acetylated with acetic anhydride to give the acetate (+)-**14** in 96% yield. It was predicted that the $C_{2'}$-hydroxy functionality or its anion of **14** would intramolecularly attack the acetyl group on the C_4-position resulting in formation of **15**, a precursor of **2** under suitable conditions. Thus **14** was treated with tetra-*n*-butylammonium fluoride (TBAF) in THF (basic condition), however, to give only decomposed products. When the reaction medium was changed from basic to acidic conditions, **14** was again exposed to TBAF in the presence of hydrofluoric acid in THF (ca. pH 5) to provide the acyl group migrated product (+)-**15** in 86% yield. Acetyl group migration was easily confirmed by comparison of the ^{1}H NMR spectra of **14** and **15**, especially chemical shift consideration. C_4-H of **14** appeared at δ 5.27 as a doublet and $C_{2'}$-H resonated at δ 4.96 as a doublet. In the ^{1}H NMR spectrum of **15**, both diagnostic a higher field shift of C_4-H (δ 5.27 to 4.39−4.34) and a lower field shift of $C_{2'}$-H (δ 4.96 to 6.08) were observed. Finally (+)-8-acetylgoniotriol (**2**) [mp 159−161 °C, $[\alpha]^{24}_D$ +37.0 (*c* 0.4, EtOH)][lit.[1c] mp 158−159 °C, $[\alpha]^{22}_D$ +30 (*c* 0.4 EtOH)] was obtained in 77% yield from **15** under debenzylation conditions with $TiCl_4$. Synthetic (+)-goniotriol (**1**) and (+)-8-acetylgoniotriol (**2**) were identical

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with natural compounds by comparison with spectral as well as physical data.

In order to convert the intermediate **11** to (+)-goniodiol (**3**) and (+)-9-deoxygoniopypyrone (**4**), removal of the C_4-hydroxy group was essential. Treatment of **11** with acetic anhydride afforded (−)-**16** quantitatively, which was then exposed to zinc amalgam[18] in Et_2O in the presence of hydrogen chloride at −20 °C to furnish the dehydroxylated product (+)-**17** accompanied with double-bond migration in 88% yield. Isomerization of the β,γ-unsaturated lactone structure of **17** to the corresponding α,β one was easily achieved by DBU treatment at room temperature to leave (+)-**18** in 90% yield, deprotection of which was undertaken according to the procedure described for conversion of **13** into **1** to produce (+)-goniodiol (**3**) [$[\alpha]^{21}_D$ +72.7 (*c* 0.3, $CHCl_3$)] [lit.[1d] $[\alpha]^{22}_D$ +74.4 (*c* 0.3 $CHCl_3$)] in 97% yield *via* **19**.

Synthesis of (+)-9-deoxygoniopypyrone (**4**) required inversion of the alcohol moiety at the benzylic position of **19**. Although Mitsunobu reaction[15] of **19** under several typical conditions was examined, the condition that provided a satisfactory chemical yield is not established yet. The best result so far obtained is production of (−)-**20** in 49% yield when **19** was treated with triphenylphosphine, diethyl azodicarboxylate (DEAD), and *p*-nitrobenzoic acid in benzene at room temperature. Hydrolysis of **20** with 1 N lithium hydroxide in THF at room temperature unexpectedly gave fairly polar compounds which might arise from removal of the *p*-nitrobenzoate moiety and concomitant cleavage of the δ lactone ring. On treatment with trifluoroacetic acid, the plausible dihydroxy acid derivatives underwent ring closure to provide (−)-**22** in 59% yield along with **21** in 31% yield. Compound **21** was shown to be easily converted into **22** in 80% yield when treated with DBU. Thus, **22** was formed in 84% overall yield from **20**. (+)-9-Deoxygoniopypyrone (**4**) [mp 201−204 °C, $[\alpha]^{16}_D$ +12.0 (*c* 0.10, EtOH)] [lit.[1d] mp 203−204 °C, $[\alpha]^{22}_D$ +12 (*c* 0.1 EtOH)] was synthesized in 96% yield from **22** by $TiCl_4$ treatment. Synthetic (+)-goniodiol and (+)-9-deoxygoniopypyrone were identical with natural compounds, respectively, by comparison with spectral and physical data.

Syntheses of (+)-Altholactone and (−)-Goniofupyrone.[19] The allylic alcohol of the key intermediate **11** was tosylated by conventional procedures to give the tosylate (−)-**23** in 96% yield. Desilylation of **23** with TBAF brought about spontaneous ring closure to provide the dioxabicyclo[4.3.0]nonenone derivative (+)-**24** in 89% yield, which was subsequently exposed to $SnCl_4$[17] producing (+)-altholactone (**5**) [mp 108−109 °C, $[\alpha]^{25}_D$ +182 (*c* 0.10, EtOH)][lit.[1a] mp 110 °C, $[\alpha]^{25}_D$ +184.7 (*c* 0.1 EtOH)] in 98% yield.

(−)-Goniofupyrone was isolated from the stem bark of *G. giganteus* grown in Thailand in 1991.[1e] Its structure was deduced as (1*R**,5*R**,6*R**,8*S**, 9*S**)-5,9-dihydroxy-8-phenyl-2,7-dioxabicyclo[4.3.0]nonan-3-one (**31**) on the basis of its spectroscopic analysis involving comparison with ^{1}H NMR data of the related compound, altholactone (**5**). No reports on synthesis and determination of absolute stereochemistry of (−)-goniofupyrone had been made when we started out this program. Therefore, our effort was directed toward transformation of the dioxabicyclo[4.3.0]nonenone derivative (+)-**24** into the proposed structure for goniofupyrone, thereby the absolute stereochemistry would be established unambiguously. Stereochemical outcome for introduction of the hydroxy functionality to the α,β-unsaturated moiety of **24** was first worked out by employing racemic **24**. *cis*-Dihydroxylation of (±)-**24** with osmium tetraoxide[20] afforded the diol (±)-**25** in 79% yield, acetylation of which provided the diacetate (±)-**26** in 94% yield. NOE experiment of (±)-**26** revealed 4.5% enhancement between C_4-H and C_9-H. This observation strongly indicated that dihydroxylation occurred from the α-face (convex face) resulting in formation of **26** exclusively. Furthermore, X-ray crystallographic analysis[21] of (±)-**26** unambiguously confirmed the relative stereochemistry of **26** as depicted in Scheme 3.[25]

By analogy to conversion of racemic **24** into **25** in a model study, we prepared (+)-**25** from (+)-**24** in 75% yield. Selective removal of the C_4-OH group of **25** was undertaken by samarium diiodide[22] in the presence of ethylene glycol to furnish (+)-**27** in 62% yield. It should be mentioned that no reaction took place when methanol was used instead of ethylene glycol and **25** was completely recovered. Debenzylation of **27** with $SnCl_4$ yielded (−)-**6** [$[\alpha]^{18}_D$ −6.9 (*c* 0.15, $CHCl_3$)] [lit.[1e] $[\alpha]^{25}_D$ −5.0 (*c* 0.1 $CHCl_3$)] in 80% yield. Spectral data and the specific rotation of (−)-**6** were unexpectedly in good accordance with those of natural (−)-goniofupyrone. The diacetate (−)-**28**, derived from **6**, again exhibited similar spectral data to those[1e] of the diacetate derivative of natural goniofupyrone. Thus, it was at this stage that we noticed that natural (−)-goniofupyrone should have the relative as well as absolute configuration shown in (−)-**6** rather than **31**.

In order to confirm that unambiguously, we completed a synthesis of **31**. A direct and straightforward method such as Mitsunobu reaction and SN_2 type displacement for inversion of the C_5-hydroxy group of **27** was unsuccessful. These negative results could be tentatively rationalized in terms of (i) the β-hydroxy carbonyl structure of **27** leading to easy β-elimination (ii) and/or steric hindrance associated with approach of the nucleophile from the concave face. Therefore, the lactone moiety of **27**, on treatment with DIBALH, was first converted into the lactol derivative, which was subsequently transformed into the corresponding methyl acetal **29** as a mixture of diastereoisomers (*ca.* 1:1 mixture) in 77% yield. The acetal **29** was oxidized with tetra-*n*-propylammonium perruthenate (TPAP)[23] to give the C_5-carbonyl derivative, reduction of which with lithium

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(21) Crystal data: $C_{24}H_{24}O_8$, M = 440.45, triclinic, a = 10.846(2) Å, b = 11.527(2) Å, c = 10.190(2) Å, α = 114.14(1)°, β = 102.64(2)°, γ = 71.33(2)°, V = 1095.8 (4) Å^3, Z = 2, D_c = 1.335 g/cm^3, space group $P1$ (No. 2), μ(Mo Kα) = 0.94 cm^{-1}. A colorless prisms crystal, *ca.* 0.7 × 0.7 × 0.5 mm, was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R 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 55.1°. The structure was solved by direct method (MITHRIL method). The final cycle of full-matrix least-squares refinement was based on 3018 observed reflections. The final R value was 0.043.

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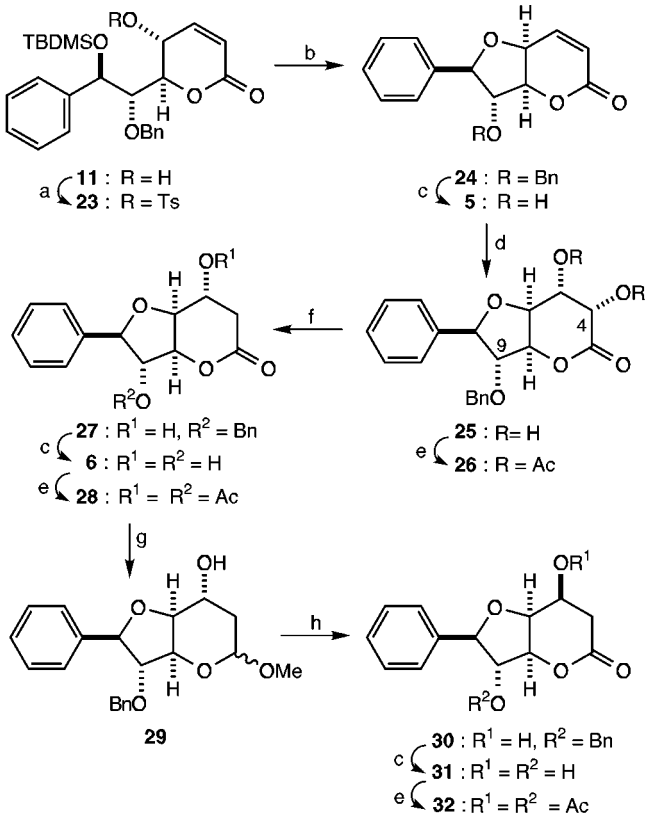
Scheme 3[a]



[a]Reaction conditions: Reaction conditions: (a) TsCl, DMAP, CH_2Cl_2, 96%; (b) TBAF−HF THF, 89%; (c) $SnCl_4$, CH_2Cl_2, 40 °C, **24** → **5** (98%), **27** → **6** (80%), **30** → **31** (74%); (d) cat. OsO_4, NMO, acetone−H_2O, 75%; (e) Ac_2O, DMAP, CH_2Cl_2, **25** → **26** (94%), **6** → **28** (76%), **31** → **32** (89%); (f) SmI_2, ethylene glycol, THF 62%; (g) (i) DIBALH, Et_2O, −78 °C, (iii) *p*-TsOH, MeOH, 77%; (h) (i) TPAP, NMO, MS4Å, CH_3CN, (ii) LAH, THF, −20 °C, (iii) $BF_3{\cdot}OEt_2$, *m*-CPBA, CH_2Cl_2, 40 °C, 61%.

aluminum hydride (LAH) was followed by exposure to *m*-CPBA in the presence of $BF_3{\cdot}OEt_2$[24] regenerating the lactone moiety to leave (−)-**30** in 61% overall yield from **29** along with (−)-**27** (14%). Debenzylation of **30** with $SnCl_4$ afforded (−)-**31** [$[\alpha]^{18}_D$ −59.2 (*c* 0.1, $CHCl_3$)] in 74% yield. Acetylation of **31** under the standard conditions gave (−)-**32**. Comparison of spectral and physical data of **31** and **32** with those of natural goniofupyrone and its diacetate, respectively, disclosed obvious differences not only in chemical shift and coupling constant for some protons but also in specific rotation. Thus, we concluded that (−)-goniofupyrone possesses the (1*S*,5*R*,6*S*,8*R*,9*R*)-5,9-dihydroxy-8-phenyl-2,7-dioxabicyclo[4.3.0]nonan-3-one (**6**) structure as depicted in Scheme 3.

Conclusion

We have succeeded in an efficient transformation of the previously prepared γ-lactone intermediate **7** to the δ-lactone compound **11**. The latter intermediate **11** has been found to be a useful key compound for stereoselective syntheses of (+)-goniotriol, (+)-8-acetylgoniotriol, (+)-goniodiol, (+)-9-deoxygoniopypyrone, (+)-altholactone, and (−)-goniofupyrone. In addition, synthesis of (−)-goniofupyrone elucidated its absolute stereochemistry. In connection with previous efforts on total syntheses of (+)-goniofufurone, (+)-goniobutenolide A, and (−)-goniobutenolide B from our laboratory, we have now accomplished syntheses of all types of alicyclic antitumor styryllactone natural products except for eight-membered ones, goniopheptolides A and B from optical active tricarbonyl(η^6-*o*-(trimethylsilyl)benzaldehyde)chromium(0) complex *via* two significant intermediates in a stereoselective manner.

Experimental Section

Melting points are uncorrected. IR spectra were measured in $CHCl_3$ unless otherwise mentioned. ^1H NMR spectra were taken in $CDCl_3$ unless otherwise indicated. $CHCl_3$ (7.26 ppm) was used as an internal standard for silyl compounds. TMS was employed as an internal standard for other compounds. ^{13}C NMR spectra were recorded in $CDCl_3$ with $CDCl_3$ (77.00 ppm) as an internal standard. CH_2Cl_2 was freshly distilled from phosphorus pentoxide and THF from sodium diphenyl ketyl, prior to use. Silica gel (silica gel 60, 230−400 mesh, Merck) was used for chromatography. Organic extracts were dried over anhydrous Na_2SO_4.

(−)-(1′*S*,2′*R*,4*R*,5*R*)-5-(1′-(Benzyloxy)-2′-((*tert*-butyldimethylsilyl)oxy)-2′-phenylethyl)-4-hydroxy-2-penten-5-olide (11). To a solution of (−)-**7** (395 mg, 0.87 mmol) in CH_2Cl_2 (8.7 mL) was added TMS-imidazole (0.15 mL, 1.04 mmol) at rt. After being stirred for 10 h, the reaction mixture was washed with water and brine, dried, and concentrated to leave the residual oil, which was passed through a short pad of silica gel with hexane−AcOEt (20:1) to give **8** (444 mg, 97%): IR 1755 (CO) cm^{-1}; ^1H NMR δ 7.33−7.25 (m, 8H), 7.16−7.14 (m, 2H), 6.89 (dd, 1H, *J* = 5.9, 1.5 Hz), 6.02 (dd, 1H, *J* = 5.9, 2.0 Hz), 5.19 (ddd, 1H, *J* = 4.9, 2.0, 1.5 Hz), 4.91 (d, 1H, *J* = 4.9 Hz), 4.48 (d, 1H, *J* = 11.2 Hz), 4.29 (t, 1H, *J* = 4.9 Hz), 4.24 (d, 1H, *J* = 11.2 Hz), 3.59 (t, 1H, *J* = 4.9 Hz), 0.91 (s, 9H), 0.09 (s, 3H), 0.07 (s, 9H), −0.13 (s, 3H); ^{13}C NMR δ 172.97, 154.18, 141.89, 137.72, 128.19, 128.10, 127.66, 126.86, 122.53, 85.14, 83.38, 74.83, 74.32, 74.13, 25.84, 18.17, 0.78, −4.58, −4.72. DIBALH (1.0 M hexane solution; 1.0 mL, 1.0 mmol) was added to a solution of **8** (444 mg, 0.85 mmol) in dry Et_2O (8.5 mL) at −78 °C. The reaction mixture was kept at the same temperature for 10 min, then quenched by addition of a saturated Na_2SO_4 solution, passed through a short pad of Celite, dried, and concentrated to dryness. The crude **9** was dissolved in THF (17 mL), to which $KOBu^t$ (258 mg, 2.11 mmol) was added at −60 °C. The reaction mixture was stirred at the same temperature for 5 h, diluted with a saturated NH_4Cl solution, and extracted with AcOEt. The organic layer was dried and evaporated off to give a crude mixture of **9** and **10**, which was dissolved in CH_2Cl_2 (8.5 mL). AcONa (777 mg, 8.5 mmol), 4 Å molecular sieves (1.7 g), and PDC (318 mg, 0.85 mmol) were added to a mixture of **9** and **10** in CH_2Cl_2. The reaction mixture was stirred at rt for 4 h, passed through a short pad of Florisil, and concentrated to dryness. To a solution of the residue in MeOH (7.8 mL) was added a 10% HCl solution (1.0 mL) at rt. After being stirred 30 min, the reaction mixture was neutralized with a saturated $NaHCO_3$ solution and extracted with AcOEt. The organic layer was washed with water and brine, dried, and concentrated to leave the residual oil which was chromatographed with hexane−AcOEt (10 :1) to afford (−)-**11** (266 mg, 69% from **8**) and (−)-**7** (19.6 mg, 5% from **8**). **(−)-11**: colorless crystals; mp 183−184 °C (MeOH); $[\alpha]^{25}_D$ −36.3 (*c* 0.40, $CHCl_3$); IR 3600, 1730 (CO) cm^{-1}; ^1H NMR δ 7.53−7.51 (m, 2H), 7.41−7.31 (m, 6H), 7.12−7.10 (m, 2H), 6.70 (dd, 1H, *J* = 10.3, 2.0 Hz), 5.88 (dd, 1H, *J* = 10.3, 2.0 Hz), 4.97 (d, 1H, *J* = 8.8 Hz), 4.56 (dd, 1H, *J* = 10.3, 1.5 Hz), 4.32 (m, 1H), 4.01 (d, 1H, *J* =11.7 Hz), 3.65 (dd, 1H, *J* = 8.8, 1.5 Hz), 3.36 (d, 1H, *J* = 11.7 Hz), 0.97 (d, 1H, *J* = 3.0 Hz), 0.83 (s, 9H), 0.05 (s, 3H), −0.21 (s, 3H); ^{13}C NMR δ 162.81, 150.43, 142.70, 137.49, 128.92, 128.57, 128.34, 128.25, 128.02, 127.73, 119.60, 80.50, 79.18, 73.35, 72.43, 62.91, 25.71, 17.94, −4.58, −5.16; CIMS *m*/*z* (%) 455 (M^+ + 1, 45), 348 (6),

(24) Greico, P. A.; Oguri, T.; Yokoyama, Y. *Tetrahedron Lett.* **1978**, 419.

(25) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

323 (100), 305 (8), 221 (15), 91 (7). Anal. Calcd for $C_{26}H_{34}O_5Si$: C, 68.69; H, 7.54. Found: C, 68.42; H, 7.48.

(+)-(1′*S*,2′*R*,4*S*,5*S*)-5-(1′-(Benzyloxy)-2′-((*tert*-butyldimethylsilyl)oxy)-2′-phenylethyl)-4-((*p*-nitrobenzoyl)oxy)-2-penten-5-olide (12). DEAD (0.06 mL, 0.37 mmol) was added to a solution of (−)-**11** (55.6 mg, 0.12 mmol), triphenylphosphine (96.4 mg, 0.37 mmol), and *p*-nitrobenzoic acid (61.8 mg, 0.37 mmol) in dry benzene (2.4 mL). After being stirred for 5 h at rt, the reaction mixture was diluted with water and extracted with AcOEt, which was washed with a saturated $NaHCO_3$ solution, water, and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane−AcOEt (20:1) to afford (+)-**12** (70.9 mg, 96%) as a colorless oil; $[\alpha]^{26}_D$ +135 (*c* 0.33, $CHCl_3$); IR 1730 (CO) cm^{-1}; ^1H NMR δ 8.12 (d, 2H, *J* = 8.2 Hz), 7.80 (d, 2H, *J* = 8.2 Hz), 7.32−7.14 (m, 7H), 7.09 (dd, 1H, *J* = 9.8, 5.9 Hz), 7.01 (t, 2H, *J* = 7.3 Hz), 6.88 (t, 1H, *J* = 7.3 Hz), 6.20 (d, 1H, *J* = 9.8 Hz), 5.46 (dd, 1H, *J* = 5.9, 2.9 Hz), 5.04 (d, 1H, *J* = 3.9 Hz), 4.96 (dd, 1H, *J* = 6.4, 2.9 Hz), 4.69 (d, 1H, *J* = 11.2 Hz), 4.47 (d, 1H, *J* = 11.2 Hz), 4.01 (dd, 1H, *J* = 6.4, 3.9 Hz), 0.90 (s, 9H), 0.09 (s, 3H), −0.10 (s, 3H); ^{13}C NMR δ 150.55, 141.01, 140.02, 137.63, 133.68, 130.76, 128.25, 127.96, 127.67, 127.28, 125.88, 125.21, 123.15, 82.27, 78.53, 74.92, 74.02, 64.13, 25.84, 18.17, −4.85, −4.90; CIMS *m*/*z* (%) 604 (M^+ + 1, 11), 472 (19), 439 (74), 437 (36), 331 (12), 329 (23), 323 (11), 307 (100), 237 (15), 221 (34), 215 (21), 168 (10), 147 (11), 138 (53), 133 (31), 107 (74), 91 (22). Anal. Calcd for $C_{33}H_{37}O_8NSi$: C, 65.65; H, 6.18; N, 2.32. Found: C, 65.65; H, 6.50; N, 2.31.

(+)-(1′*S*,2′*R*,4*S*,5*R*)-5-(1′-(Benzyloxy)-2′-((*tert*-butyldimethylsilyl)oxy)-2′-phenylethyl)-4-hydroxy-2-penten-5-olide (13). To a solution of (+)-**12** (6.8 mg, 0.01 mmol) in THF (1.0 mL) was added a 1% K_2CO_3 solution (0.5 mL) at 0 °C. The reaction mixture was stirred at rt for 4 h, diluted with water, and extracted with AcOEt. The organic layer was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane-AcOEt (10:1) to afford (+)-**13** (3.8 mg, 74%). **(+)-13**: colorless crystals; mp 175−176 °C (MeOH); $[\alpha]^{28}_D$ +62.8 (*c* 0.25, $CHCl_3$); IR 3450 (OH), 1730 (CO) cm^{-1}; ^1H NMR δ 7.47−7.33 (m, 5H), 7.25−7.23 (m, 3H), 7.04−7.01 (m, 2H), 6.93 (dd, 1H, *J* = 9.8, 5.9 Hz), 6.10 (d, 1H, *J* = 9.8 Hz), 4.98 (d, 1H, *J* = 7.8 Hz), 4.74 (t, 1H, *J* = 3.4 Hz), 4.38 (m, 1H; D_2O; dd, *J* = 5.9, 3.4 Hz), 4.25 (d, 1H, *J* =10.3 Hz), 3.92 (dd, 1H, *J* = 7.8, 3.4 Hz), 3.74 (d, 1H, *J* = 10.3 Hz), 3.42 (d, 1H, *J* = 4.9 Hz), 0.84 (s, 9H), 0.06 (s, 3H), −0.20 (s, 3H); ^{13}C NMR δ 163.13, 144.28, 141.56, 136.82, 128.43, 128.32, 128.25, 127.98, 127.62, 122.61, 83.83, 78.04, 74.54, 73.59, 62.52, 25.75, 18.03, −4.54, −5.01; CIMS *m*/*z* (%) 455 (M^+ + 1, 15), 323 (100), 221 (12), 215 (6), 91 (7). Anal. Calcd for $C_{26}H_{34}O_5Si$: C, 68.69; H, 7.54. Found: C, 68.62; H, 7.57.

(+)-(1′*R*,2′*R*,4*S*,5*R*)-4-Hydroxy-5-(1′,2′-dihydroxy-2′-phenylethyl)-2-penten-5-olide [Goniotriol (1)]. To a solution of (+)-**13** (48.4 mg, 0.11 mmol) and NaI (49.6 mg, 0.33 mmol) in dry CH_3CN (1.0 mL) was added $BF_3{\cdot}OEt_2$ (1.0 M CH_3CN solution; 0.30 mL, 0.30 mmol) slowly at 0 °C. After 20 min, the reaction mixture was diluted with a saturated $Na_2S_2O_3$ solution and extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried, and concetrated to leave the residual oil, which was taken up in CH_2Cl_2 (5.0 mL). $TiCl_4$ (1.0 M CH_2Cl_2 solution; 1.0 mL, 1.0 mmol) was addded to the above CH_2Cl_2 solution and the reaction mixture was stirred at rt for 30 min, diluted with a saturated $NaHCO_3$ solution, and extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried, and concentrated to give the crude solids which were recrystallized from hexane−AcOEt to afford (+)-**1** (17.2 mg, 65%). **(+)-1** (goniotriol): colorless crystals; mp 169−171 °C (hexane−EtOH); $[\alpha]^{21}_D$ +118 (*c* 0.10, MeOH) [lit.[1b] mp 170 °C, $[\alpha]^{25}_D$ +121 (MeOH)]; IR (KBr) 3400 (OH), 1735 (CO) cm^{-1}; ^1H NMR (CD_3OD) δ 7.47−7.25 (m, 5H), 7.01 (dd, 1H, *J* = 9.8, 5.9 Hz), 6.08 (d, 1H, *J* = 9.8 Hz), 4.73 (d, 1H, *J* = 7.8 Hz), 4.59 (dd, 1H, *J* = 3.9, 2.9 Hz), 4.43 (dd, 1H, *J* = 5.9, 2.9 Hz), 4.17 (dd, 1H, *J* = 7.8, 3.9 Hz); ^{13}C NMR (CD_3OD) δ 166.03, 146.41, 143.37, 129.14, 128.83, 128.73, 122.96, 80.26, 75.63, 73.91, 63.47; CIMS *m*/*z* (%) 251 (M^+ + 1, 12), 233 (47), 215 (12), 137 (36), 119 (13), 107 (62), 97 (100). Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.20; H, 5.91.

(+)-(1′*S*,2′*R*,4*S*,5*S*)-4-Acetoxy-5-(1′-(benzyloxy)-2′-((*tert*-butyldimethylsilyl)oxy)-2′-phenylethyl)-2-penten-5-olide (14). A solution of (+)-**13** (6.3 mg, 0.01 mmol) and 4-*N*,*N*-dimethylaminopyridine (DMAP) (3.5 mg, 0.03 mmol) and Ac_2O (one drop) in CH_2Cl_2 (0.2 mL) was stirred at rt for 10 min, diluted with water, and extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (20:1) gave (+)-**14** (6.6 mg, 96%) as a colorless oil: $[\alpha]^{24}_D$ +139 (*c* 0.10, $CHCl_3$); IR 1735 (CO) cm^{-1}; ^1H NMR δ 7.34−7.22 (m, 10H), 6.92 (dd, 1H, *J* = 9.8, 4.9 Hz), 6.07 (d, 1H, *J* = 9.8 Hz), 5.27 (dd, 1H, *J* = 4.9, 3.4 Hz), 4.96 (d, 1H, *J* = 4.4 Hz), 4.81 (dd, 1H, *J* = 6.4, 3.4 Hz), 4.68 (d, 1H, *J* = 11.2 Hz), 4.35 (d, 1H, *J* = 11.2 Hz), 3.91 (dd, 1H, *J* = 6.4, 4.4 Hz), 1.69 (s, 3H), 0.90 (s, 9H), 0.08 (s, 3H), −0.11 (s, 3H); ^{13}C NMR δ 169.52, 162.46, 141.34, 140.75, 137.93, 128.30, 128.25, 127.98, 127.62, 127.53, 126.49, 124.28, 82.32, 78.29, 74.97, 74.25, 63.16, 25.86, 20.11, 18.19, −4.76, −4.90; FABMS *m*/*z* (%) 497 (M^+ + 1,11), 323 (50), 305 (39), 289 (26), 221 (100), 209 (27), 193 (28), 181 (52), 165 (23), 154 (38), 136 (50), 117 (33), 115 (26), 107 (35), 105 (53), 91 (100), 73 (100). Anal. Calcd for $C_{28}H_{36}O_6Si$: C, 67.71; H, 7.31. Found: C, 67.49; H, 7.33.

(+)-(1′*R*,2′*R*,4*S*,5*R*)-5-(2′-Acetoxy-1′-(benzyloxy)-2′-phenylethyl)-4-hydroxy-2-penten-5-olide (15). To a solution of (+)-**14** (33.3 mg, 0.07 mmol) in THF (1.4 mL) was added a solution of TBAF−hydrofluoric acid (0.7 mL; prepared from 1.0 M TBAF in a THF solution and 47% hydrofluoric acid, *ca*. pH 5 solution) at rt. The reaction mixture was stirred for 3.5 h at the same temperature, diluted with water, and extracted with AcOEt. The organic layer was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (3:1) gave (+)-**15** (22.2 mg, 86%). **(+)-15**: colorless crystals; 125−127 °C (hexane−MeOH); $[\alpha]^{22}_D$ +17.5 (*c* 0.10, $CHCl_3$); IR 3400 (OH), 1730 (CO) cm^{-1}; ^1H NMR δ 7.49−7.22 (m, 10H), 6.90 (dd, 1H, *J* = 9.8, 5.4 Hz), 6.09 (d, 1H, *J* = 9.8 Hz), 6.08 (d, 1H, *J* = 5.4 Hz), 4.61 (d, 1H, *J* = 11.2 Hz), 4.39−4.34 (m, 3H), 4.22 (t, 1H, *J* = 5.4 Hz), 2.95 (brs, 1H), 2.06 (s, 3H); ^{13}C NMR δ 170.12, 162.57, 143.58, 137.32, 136.37, 128.79, 128.55, 128.43, 128.39, 128.14, 127.96, 122.82, 79.64, 79.59, 75.13, 74.18, 61.22, 21.10; CIMS *m*/*z* (%) 383 (M^+ + 1, 22), 323 (100), 307 (16), 233 (12), 215 (31), 107 (31), 91 (19). Anal. Calcd for $C_{22}H_{22}O_6$: C, 69.10; H, 5.80. Found: C, 68.90; H, 5.85.

(+)-(1′*R*,2′*R*,4*S*,5*R*)-5-(2′-Acetoxy-1′-hydroxy-2′-phenylethyl)-4-hydroxy-2-penten-5-olide [8-acetylgoniotriol (2)]: colorless crystals (77%); mp 159−161 °C (hexane−AcOEt); $[\alpha]^{24}_D$ +37.0 (*c* 0.40, EtOH) [lit.[1c] mp 158−159 °C (hexane−AcOEt), $[\alpha]^{22}_D$ +30 (*c* 0.4, EtOH)]; IR (KBr) 3550 (OH), 3400 (OH), 1725 (CO), 1695 (CO) cm^{-1}; ^1H NMR(acetone-d_6) δ 7.50−7.28 (m, 5H), 7.01 (dd, 1H, *J* = 9.8, 5.4 Hz), 6.01 (d, 1H, *J* = 9.8 Hz), 5.86 (d, 1H, *J* = 7.3 Hz), 4.57 (dd, 1H, *J* = 5.4, 3.4 Hz), 4.49 (t, 1H, *J* = 3.4 Hz), 4.46 (dd, 1H, *J* = 7.3, 3.4 Hz), 2.84 (brs, 2H), 2.00 (s, 3H); ^{13}C NM(acetone-d_6) δ 170.06, 163.84, 145.50, 139.64, 129.39, 129.14, 123.38, 78.72, 75.07, 74.03, 63.57, 21.36; EIMS *m*/*z* (%) 292 (M^+, 0.3), 149 (34), 143 (25), 126 (80), 120 (10), 107 (100), 97 (51), 91 (43). Anal. Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.76; H, 5.77.

(−)-(1′*S*,2′*R*,4*R*,5*S*)-4-Acetoxy-5-(1′-benzyloxy-2′-((*tert*-butyldimethylsilyl)oxy)-2′-phenylethyl)-2-penten-5-olide (16): colorless needles (100%); mp 106−108 °C (hexane); $[\alpha]^{21}_D$ −78.1 (*c* 0.50, $CHCl_3$); IR 1735 (CO) cm^{-1}; ^1H NMR δ 7.48−7.46 (m, 2H), 7.38−7.29 (m, 3H), 7.22−7.20 (m, 3H), 6.93−6.90 (m, 2H), 6.69 (dd, 1H, *J* = 9.8, 2.9 Hz), 6.03 (dd, 1H, *J* = 9.8, 1.5 Hz), 5.46 (ddd, 1H, *J* = 7.3, 2.9, 1.5 Hz), 4.97 (dd, 1H, *J* = 7.3, 1.5 Hz), 4.90 (d, 1H, *J* = 9.3 Hz), 3.68 (d, 1H, *J* = 10.8 Hz), 3.56 (d, 1H, *J* = 10.8 Hz), 3.51 (dd, 1H, *J* = 9.3, 1.5 Hz), 2.10 (s, 3H), 0.86 (s, 9H), 0.08 (s, 3H), −0.20 (s, 3H); ^{13}C NMR δ 169.76, 161.87, 142.70, 142.30, 136.86, 128.36, 128.23, 128.07, 127.87, 127.21, 122.59, 82.03, 78.31, 74.16, 72.56, 64.78, 25.73, 20.85, 17.99, −4.51, −5.19; CIMS *m*/*z* (%) 497 (M^+ + 1, 63), 365 (100), 329 (38), 305 (19), 221 (16), 215

(27), 147 (10), 133 (19), 107 (23), 91 (26). Anal. Calcd for $C_{28}H_{36}O_5Si$: C, 67.71; H, 7.31. Found: C, 67.51; H, 7.30.

(+)-(1′*S*,2′*R*,5*R*)-5-(1′-(Benzyloxy)-2′-((*tert*-butyldimethylsilyl)oxy)-2′-phenylethyl)-3-penten-5-olide (17). Zn(Hg) (1.5 g) was added to a solution of (−)-**16** (307 mg, 0.62 mmol) in dry Et_2O (7.5 mL). The reaction mixture was cooled to −20 °C, to which a solution of saturated hydrogen chloride in Et_2O (3.0 mL) was added dropwise. The reaction mixture was stirred at the same temperature for 30 min, washed with a saturated $NaHCO_3$ solution, water, and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (30:1) gave (+)-**17** (238 mg, 88%): colorless crystals; mp 67−69 °C (hexane−AcOEt); $[\alpha]^{20}_D$ +187 (*c* 0.51, $CHCl_3$); IR 1730 (CO) cm^{-1}; ^1H NMR δ 7.44−7.42 (m, 2H), 7.34−7.27 (m, 3H), 7.20−7.18 (m, 3H), 6.88−6.85 (m, 2H), 5.85 (s, 2H), 5.40 (s, 1H), 4.82 (d, 1H, *J* = 9.3 Hz), 3.91 (d, 1H, *J* = 10.3 Hz), 3.54 (d, 1H, *J* = 10.3 Hz), 3.38 (d, 1H, *J* = 9.3 Hz), 2.93−2.90 (m, 2H), 0.87 (s, 9H), 0.10 (s, 3H), −0.18 (s, 3H); ^{13}C NMR δ 169.43, 142.57, 137.48, 128.07, 128.01, 127.84, 127.75, 127.60, 127.55, 124.06, 123.59, 85.28, 77.90, 75.06, 72.76, 30.80, 25.75, 18.01, −4.54, −5.12; CIMS *m*/*z* (%) 439 (M^+ + 1, 86), 381 (15), 307 (100), 221 (53). Anal. Calcd for $C_{26}H_{34}O_4Si$: C, 71.19; H, 7.81. Found: C, 71.17; H, 7.90.

(+)-(1′*S*,2′*R*,5*R*)-5-(1′-(Benzyloxy)-2′-((*tert*-butyldimethylsilyl)oxy)-2′-phenylethyl)-2-penten-5-olide (18). DBU (one drop) was added to a solution of (+)-**17** (120 mg, 0.27 mmol) in THF (2.7 mL). The reaction mixture was allowed to stand at rt for 26 h, diluted with saturated NH_4Cl, and extracted with AcOEt. The organic layer was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue hexane−AcOEt (30:1) gave (+)-**18** (108 mg, 90%) along with **17** (6.6 mg, 5%). **(+)-18**: colorless crystals; mp 133−134 °C (hexane); $[\alpha]^{20}_D$ +70.8 (*c* 0.51, $CHCl_3$); IR 1720 (CO) cm^{-1}; ^1H NMR δ 7.48−7.45 (m, 2H), 7.37−7.18 (m, 6H), 7.02−7.00 (m, 2H), 6.86 (ddd, 1H, *J* = 9.8, 6.4, 2.4 Hz), 5.98 (dd, 1H, *J* = 9.8, 2.4 Hz), 4.99 (d, 1H, *J* = 8.3 Hz), 4.90 (ddd, 1H, *J* = 12.7, 3.4, 2.0 Hz), 3.78 (s, 2H), 3.39 (dd, 1H, *J* = 8.3, 2.0 Hz), 2.57 (ddt, 1H, *J* = 18.6, 12.7, 2.4 Hz), 2.01 (ddd, 1H, *J* = 18.6, 6.4, 3.4 Hz), 0.83 (s, 9H), 0.06 (s, 3H), −0.20 (s, 3H); ^{13}C NMR δ 163.88, 145.59, 142.66, 137.38, 128.32, 128.18, 127.76, 127.64, 121.08, 83.88, 77.20, 76.35, 74.39, 72.69, 26.02, 25.75, 17.99, −4.58, −5.08; CIMS *m*/*z* (%) 439 (M^+ + 1, 100), 381 (8), 332 (8), 307 (64), 221 (6). Anal. Calcd for $C_{26}H_{34}O_4Si$: C, 71.19; H, 7.81. Found: C, 71.32; H, 7.77.

(+)-(1′*R*,2′*R*,5*R*)-5-(1′-(Benzyloxy)-2′-hydroxy-2′-phenylethyl)-2-penten-5-olide (19): colorless crystals (100%); mp 120−122 °C (hexane−AcOEt); $[\alpha]^{20}_D$ +106 (*c* 0.50, $CHCl_3$); IR 3400 (OH), 1720 (CO) cm^{-1}; ^1H NMR δ 7.49−7.47 (m, 2H), 7.40−7.26 (m, 6H), 7.14−7.11 (m, 2H), 6.85 (ddd, 1H, *J* = 9.8, 6.4, 2.4 Hz), 5.98 (dd, 1H, *J* = 9.8, 2.4 Hz), 5.11 (dd, 1H, *J* = 7.8, 3.4 Hz), 4.79 (dt, 1H, *J* = 12.2, 3.4 Hz), 4.17 (d, 1H, *J* = 11.2 Hz), 4.14 (d, 1H, *J* = 11.2 Hz), 3.54 (dd, 1H, *J* = 7.8, 3.4 Hz), 2.66 (br-d, 1H, *J* = 3.4 Hz), 2.63 (ddt, 1H, *J* = 18.1, 12.2, 2.4 Hz), 2.04 (ddd, 1H, *J* = 18.1, 6.4, 3.4 Hz); ^{13}C NMR δ 163.77, 145.57, 141.53, 137.20, 128.54, 128.36, 128.32, 128.10, 127.98, 127.01, 120.92, 82.12, 77.20, 73.89, 72.06, 25.81; CIMS *m*/*z* (%) 325 (M^+ + 1, 100), 307 (14), 218 (8), 107 (7). Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 73.75; H, 6.22.

(+)-(1′*R*,2′*R*,5*R*)-5-(1′,2′-Dihydroxy-2′-phenylethyl)-2-penten-5-olide [goniodiol (3)]: colorless oil (97%); $[\alpha]^{21}_D$ +72.7 (*c* 0.32, $CHCl_3$) [lit.[1d] $[\alpha]^{22}_D$ +74.4 (*c* 0.3, $CHCl_3$)]; IR 3600 (OH), 3420 (OH), 1725 (CO) cm^{-1}; ^1H NMR δ 7.42−7.30 (m, 5H), 6.93 (ddd, 1H, *J* = 9.8, 6.4, 2.0 Hz), 6.01 (ddd, 1H, *J* = 9.8, 2.9, 1.0 Hz), 4.95 (d, 1H, *J* = 7.3 Hz), 4.80 (ddd, 1H, *J* = 12.7, 3.9, 2.0 Hz), 3.73 (dd, 1H, *J* = 7.3, 2.0 Hz), 2.80 (dddd,1H,*J* = 18.6, 12.7, 2.9, 2.0Hz), 2.55 (s, 1H), 2.27 (brs, 1H), 2.19 (dddd,1H,*J* = 18.6, 6.4, 3.9, 1.0 Hz); ^{13}C NMR δ 163.65, 146.11, 140.74, 128.77, 128.32, 120.61, 76.77, 75.02, 73.73, 26.06; FABMS *m*/*z* (%) 235 (M^+ + 1, 19), 217 (14), 154 (100), 136 (81), 120 (13), 107 (33), 105 (11), 97 (14); CIMS *m*/*z* (%) 235 (M^+ + 1, 100), 217 (86), 173 (17), 107 (23); HRFABMS calcd for $C_{13}H_{15}O_4$ (M^+ + 1) 235.0970, found 235.0964.

(−)-(1′*S*,2′*S*,5*R*)-5-(1′-(Benzyloxy)-2′-((*p*-nitrobenzoyl)oxy)-2′-phenylethyl)-2-penten-5-olide (20): colorless crystals (49%); mp 87−89 °C (MeOH−hexane); $[\alpha]^{16}_D$ −2.9 (*c* 0.60, $CHCl_3$); IR 1735 (CO) cm^{-1}; ^1H NMR δ 8.30−8.17 (m, 4H), 7.55−7.52 (m, 2H), 7.41−7.33 (m, 3H), 7.29−7.21 (m, 5H), 6.79 (ddd, 1H, *J* = 9.8, 6.4, 2.4 Hz), 6.52 (d, 1H, *J* = 7.3 Hz), 5.94 (ddd, 1H, *J* = 9.8, 2.4, 1.0 Hz), 4.77 (d, 1H, *J* = 11.2 Hz), 4.74 (d, 1H, *J* = 11.2 Hz), 4.22 (dt, 1H, *J* = 12.2, 3.4 Hz), 3.96 (dd, 1H, *J* = 7.3, 3.4 Hz), 2.68 (ddt, 1H, *J* = 18.1, 12.2, 2.4 Hz), 2.11 (dddd,1H, *J* = 18.1, 6.4, 3.4, 1.0 Hz); ^{13}C NMR δ 163.43, 163.02, 150.60, 144.73, 137.29, 136.64, 130.73, 128.95, 128.46, 128.03, 127.92, 127.31, 123.61, 121.12, 82.07, 78.13, 77.20, 75.49, 25.82; CIMS *m*/*z* (%) 474 (M^+ + 1, 63), 444 (22), 325 (11), 307 (92), 219 (13), 217 (26), 138 (48), 127 (19), 120 (14), 107(100), 91(27). Anal. Calcd for $C_{27}H_{23}O_7N$: C, 68.49; H, 4.90; N, 2.96. Found: C, 68.13; H, 4.83; N, 3.08.

(1′*R*,2′*S*,5*R*)-5-(1′-(Benzyloxy)-2′-hydroxy-2′-phenylethyl)-2-penten-5-olide and (−)-(1*R*,5*R*,7*S*,8*R*)-8-Benzyloxy-7-phenyl-2,6-dioxabicyclo[3.3.1]nonan-3-one (21 and 22). To a solution of (+)-**20** (15.3 mg, 0.03 mmol) in THF (4.5 mL) was added a 1 N LiOH solution (0.5 mL). The reaction mixture was stirred at rt for 1 h and then cooled to 0 °C, to which trifluoroacetic acid (2.5 mL) was added. The mixture was gradually warmed to rt and then allowed to stand overnight. The reaction mixture was diluted with saturated $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (10:1) gave **21** (3.2 mg, 31%) and (−)-**22** (6.2 mg, 59%). DBU (one drop) was added to a solution of **21** (3.2 mg, 0.01 mmol) in THF (0.6 mL). The reaction mixture was stirred at rt for 24 h, diluted with a saturated NH_4Cl solution, and extracted with AcOEt. The organic layer was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (10:1) gave (−)-**22** (2.6 mg, 80%; total amount of **22** is 8.8 mg, 84% overall yield from **20**). **21** was a colorless oil: IR 1735 (CO) cm^{-1}; ^1H NMR δ 7.44−7.21 (m, 10H), 6.87 (ddd, 1H, *J* = 9.8, 6.5, 2.9 Hz), 6.00 (ddd, 1H, *J* = 9.8, 2.9, 1.0 Hz), 5.08 (d, 1H, *J* = 4.4 Hz), 4.67 (d, 1H, *J* = 11.2 Hz), 4.57 (d, 1H, *J* = 11.2 Hz), 4.39 (dt, 1H, *J* = 12.7, 4.4 Hz), 3.70 (t, 1H, *J* = 4.4 Hz), 2.74 (ddt, 1H, *J* = 18.6, 12.7, 2.9 Hz), 2.70 (brs, 1H), 2.27 (dddd, 1H, *J* = 18.6, 6.5, 4.4, 1.0 Hz); ^{13}C NMR δ 163.61, 145.30, 141.13, 137.32. 128.59, 128.48, 128.25, 128.10, 127.94, 126.33, 121.08, 83.43, 77.70, 75.31, 72.85, 25.88; EIMS *m*/*z* (%) 324 (M^+, 1), 233 (43), 218 (67), 174 (22), 127 (64), 109 (13), 107 (69), 105 (16), 97 (14), 91 (100). HREIMS calcd for $C_{20}H_{20}O_4$ 324.1361, found 324.1358. (−)-**22**: colorless crystals; mp 126−127 °C (hexane−AcOEt); $[\alpha]^{17}_D$ −40.8 (*c* 0.15, $CHCl_3$); IR 1735 (CO) cm^{-1}; ^1H NMR δ 7.40−7.30 (m, 5H), 7.26−7.19 (m, 3H), 6.96−6.92 (m, 2H), 4.92 (d, 1H, *J* = 2.0 Hz), 4.75 (tt, 1H, *J* = 3.9, 2.0 Hz), 4.53 (m, 1H), 4.02 (s, 2H), 3.65 (t, 1H, *J* = 2.0 Hz), 2.95 (dd, 1H, *J* = 19.5, 1.5 Hz), 2.84 (dd, 1H, *J* = 19.5, 4.9 Hz), 2.63 (ddt, 1H, *J* = 14.2, 4.4, 2.0 Hz), 1.83 (dd, 1H, *J* = 14.2, 3.9 Hz); ^{13}C NMR δ 169.31, 137.63, 137.11, 128.30, 128.23, 127.87, 127.78, 126.61, 75.04, 73.73, 73.60, 70.42, 65.95, 36.33, 24.57; EIMS *m*/*z* (%) 324 (M^+, 2), 233 (100), 127 (30), 107 (41), 91 (88). Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 74.36; H, 6.26.

(+)-(1*R*,5*R*,7*S*,8*R*)-8-Hydroxy-7-phenyl-2,6-dioxabicyclo[3.3.1]nonan-3-one [9-deoxygoniopypyrone (4)]: colorless crystals(96%); mp 201−204 °C (hexane−AcOEt); $[\alpha]^{16}_D$ +12.0 (*c* 0.10, EtOH) [lit.[1d] mp 203−204 °C (hexane−AcOEt), $[\alpha]^{22}_D$ +12 (*c* 0.1, EtOH)]; IR (KBr) 3450 (OH), 1715 (CO) cm^{-1}; ^1H NMR δ 7.43−7.33 (m, 5H), 4.97 (d, 1H, *J* = 1.0 Hz), 4.89 (tt, 1H, *J* = 3.9, 2.0 Hz), 4.54 (m, 1H), 3.95 (dd, 1H, *J* = 3.9, 1.0 Hz), 2.99 (dt, 1H, *J* = 19.5, 2.0 Hz), 2.88 (dd, 1H, *J* = 19.5, 5.4 Hz), 2.61 (ddt, 1H, *J* = 14.2, 3.9, 2.0 Hz), 1.86 (dd, 1H, *J* = 14.2, 3.9 Hz), 1.60 (s, 1H); ^{13}C NMR δ 169.16, 136.66, 128.91, 128.34, 126.11, 74.65, 70.50, 68.27, 66.09, 36.32, 23.97; EIMS *m*/*z* (%) 234 (M^+, 58), 177 (13), 144 (13), 128 (38), 120 (13), 107 (100), 105 (30), 91 (51). Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.49; H, 6.02.

(−)-(1′*S*,2′*R*,4*R*,5*S*)-5-(1′-(Benzyloxy)-2′-((*tert*-butyldimethylsilyl)oxy)-2′-phenylethyl)-4-(*p*-toluenesulfonyloxy)-2-penten-5-olide (23). To a solution of (−)-**11** (377 mg, 0.83 mmol) in CH_2Cl_2 (8.3 mL) were added DMAP (305 mg, 2.49 mmol) and TsCl (236 mg, 0.83 mmol). The reaction mixture was stirred for 1.5 h, washed with water and brine, dried, and

concentrated to dryness. Chromatography of the residue with hexane−AcOEt (10:1) gave (−)-**23** (485 mg, 96%) as a colorless oil: $[\alpha]^{27}_D$ −58.1 (*c* 0.65, $CHCl_3$); IR 1740 (CO) cm^{-1}; ^1H NMR δ 7.77−7.75 (m, 2H), 7.43−7.22 (m, 10H), 6.95−6.92 (m, 2H), 6.49 (dd, 1H, *J* = 10.3, 3.4 Hz), 6.01 (dd, 1H, *J* = 10.3, 1.5 Hz), 5.22 (m, 1H), 5.01 (d, 1H, *J* = 6.9 Hz), 4.85 (d, 1H, *J* = 8.8 Hz), 3.77 (d, 1H, *J* = 10.7 Hz), 3.50 (d, 1H, *J* = 8.8 Hz), 3.43 (d, 1H, *J* = 10.7 Hz), 2.46 (s, 3H). 0.83 (s, 9H), 0.04 (s, 3H), −0.22 (s, 3H); ^{13}C NMR δ 161.02, 145.71, 142.14, 140.61, 137.23, 133.35, 130.23, 128.28, 128.14, 128.00, 127.85, 127.73, 123.47, 82.14, 78.55, 73.68, 72.58, 70.57, 25.73, 17.97, −4.54, −5.19; CIMS *m*/*z* (%) 609 (M^+ + 1, 0.9), 437 (94), 341 (14), 329 (36), 323 (55), 287 (100), 215 (73), 147 (14), 133 (17), 107 (27), 97 (28), 91 (19). Anal. Calcd for $C_{33}H_{40}O_7SSi$: C, 65.10; H, 6.62. Found: C, 65.40; H, 6.86.

(+)-(1*S*,6*S*,8*R*,9*R*)-9-(Benzyloxy)-8-phenyl-2,7-dioxabicyclo[4.3.0]non-4-en-3-one (24): colorless crystals (89%); 84−86 °C (MeOH); $[\alpha]^{28}_D$ +151.9 (*c* 0.53, $CHCl_3$); IR 1735 (CO) cm^{-1}; ^1H NMR δ 7.34−7.28 (m, 10H), 7.00 (dd, 1H, *J* = 9.8, 5.4 Hz), 6.25 (d, 1H, *J* = 9.8 Hz), 5.01 (dd, 1H, *J* = 4.9, 1.5 Hz), 4.86 (d, 1H, *J* = 5.4 Hz), 4.68 (d, 1H, *J* = 11.7 Hz), 4.61 (d, 1H, *J* = 11.7 Hz), 4.58 (dd, 1H, *J* = 5.4, 4.9 Hz), 4.24 (dd, 1H, *J* = 5.4, 1.5 Hz); ^{13}C NMR δ 160.95, 139.46, 138.22, 136.84, 128.61, 128.50, 128.30, 128.09, 127.78, 126.18, 124.26, 90.76, 85.30, 84.22, 72.76, 68.70; EIMS *m*/*z* (%) 322 (M^+, 8), 231 (14), 216 (8), 107 (45), 105 (8), 91 (100), 79 (16). Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.18; H, 5.65.

(+)-(1*S*,6*S*,8*R*,9*R*)-9-Hydroxy-8-phenyl-2,7-dioxabicyclo[4.3.0]non-4-en-3-one [altholactone (5)]: colorless crystals (98%); mp 108−109 °C (EtOH−benzene); $[\alpha]^{25}_D$ +182.0 (*c* 0.10, EtOH) [lit.[1a] mp 110 °C; $[\alpha]^{25}_D$ +184.7 (EtOH)]; IR 3400 (OH), 1730 (CO) cm^{-1}; ^1H NMR δ 7.36−7.30 (m, 5H), 7.00 (dd, 1H, *J* = 9.9, 5.0 Hz), 6.21 (d, 1H, *J* = 9.9 Hz), 4.92 (dd, 1H, *J* = 5.0, 2.3 Hz), 4.73 (d 1H, *J* = 5.6 Hz), 4.63 (t, 1H, *J* = 5.0 Hz), 4.44 (dd, 1H, *J* = 5.6, 2.3 Hz), 3.37 (s, 1H); ^{13}C NMR δ 161.35, 140.38, 138.10, 128.64, 128.36, 126.11, 123.61, 86.42, 85.99, 83.67, 68.16; EIMS *m*/*z* (%) 232 (M^+, 43), 136 (45), 126 (21), 107 (78), 97 (100), 95 (80), 91 (43), 79 (41), 77 (45). Anal. Calcd for $C_{13}H_{12}O_4Si$: C, 67.23; H, 5.21. Found: C, 66.96; H, 5.40.

(±)-(1*R*,4*R*,5*S*,6*R*,8*S*,9*S*)-9-(Benzyloxy)-4,5-dihydroxy-8-phenyl-2,7-dioxabicyclo[4.3.0]nonan-3-one (25). To a solution of (±)-**24** (21.0 mg, 0.07 mmol) and *N*-methylmorpholine *N*-oxide (NMO) (11.7 mg, 0.10 mmol) in acetone (1.0 mL) and water (0.5 mL) was added a 4% solution of osmium tetraoxide in water (0.1 mL, 0.02 mmol) dropwise. The reaction mixture was stirred at rt for 1.5 h and then a saturated $NaHSO_3$ solution was added. After being stirred for 30 min, the reaction mixture was extracted with AcOEt, which was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (1:1) gave (±)-**25** (18.4 mg, 79%). **(±)-25**: colorless crystals; mp 155−158 °C (hexane−AcOEt); IR 3550 (OH), 1745 (CO) cm^{-1}; ^1H NMR δ 7.37−7.26 (m, 10), 5.19 (dd, 1H, *J* = 4.9, 2.4 Hz), 4.81 (d, 1H, *J* = 6.4 Hz), 4.71 (d, 1H, *J* = 11.7 Hz), 4.58−4.55 (m, 3H), 4.54 (dd, 1H, *J* = 2.9, 2.0 Hz), 4.04 (dd, 1H, *J* = 6.4, 2.4 Hz), 3.41 (s, 1H), 2.85 (s, 1H); ^{13}C NMR δ 172.15, 137.83, 136.62, 128.68, 128.50, 128.43, 128.10, 127.80, 125.80, 90.33, 85.82, 84.24, 76.30, 72.62, 68.50, 68.36; EIMS *m*/*z* (%) 356 (M^+, 7), 265 (79), 107 (81), 91 (100), 79 (20), 77 (10); HREIMS calcd for $C_{20}H_{20}O_6$ 356.1260, found 356.1254. Similar treatment of (+)-**24** (126 mg, 0.39 mmol) afforded (+)-(1*S*,4*S*,5*R*,6*S*,8*R*,9*R*)-9-(benzyloxy)-4,5-dihydroxy-8-phenyl-2,7-dioxabicyclo[4.3.0]nonan-3-one (**25**) (104 mg, 75%). **(+)-25**: colorless crystals; mp 116−117 °C (hexane−AcOEt); $[\alpha]^{23}_D$ +33.4 (*c* 0.19, $CHCl_3$). Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66. Found: C, 67.32; H, 5.67.

(±)-(1*R*,4*R*,5*R*,6*R*,8*S*,9*S*)-4,5-Diacetoxy-9-(benzyloxy)-8-phenyl-2,7-dioxabicyclo[4.3.0]nonan-3-one (26): colorless prisms (94%); 127−128 °C (hexane−AcOEt); IR 1760 (CO) cm^{-1}; ^1H NMR δ 7.39−7.26 (m, 10H), 5.83 (d, 1H, *J* = 2.9 Hz), 5.74 (t, 1H, *J* = 2.9 Hz), 5.11 (dd, 1H, *J* = 5.4, 2.4 Hz), 4.82 (d, 1H, *J* = 6.8 Hz), 4.69 (d, 1H, *J* = 11.7 Hz), 4.56 (d, 1H, *J* = 11.7 Hz), 4.49 (dd, 1H, *J* = 5.4, 2.9 Hz), 4.10 (dd, 1H, *J* = 6.8, 2.4 Hz), 2.19 (s, 3H), 2.16 (s, 3H); ^{13}C NMR δ 169.24, 164.76, 137.25, 128.77, 128.54, 128.16, 127.76, 125.80, 90.24, 85.41, 84.37, 74.59, 72.74, 68.81, 66.25, 20.69, 20.43; EIMS *m*/*z* (%) 440 (M^+, 7), 397 (16), 338 (9), 243 (69), 183 (11), 144 (5), 113 (16), 91 (100), 79 (6), 77 (5). Anal. Calcd for $C_{24}H_{24}O_8$: C, 65.45; H, 5.49. Found: C, 65.25; H, 5.45.

(+)-(1*S*,5*R*,6*S*,8*R*,9*R*)-9-(Benzyloxy)-5-hydroxy-8-phenyl-2,7-dioxabicyclo[4.3.0]nonan-3-one (27). To a solution of (+)-**25** (9.3 mg, 0.03 mmol) in THF (0.5 mL) were successively added SmI_2 (0.1 M THF solution; 0.9 mL, 0.09 mmol) and ethylene glycol (10% THF solution; 0.06 mL, 0.10 mmol) at rt. The reaction mixture was stirred for 10 min, diluted with a saturated $NaHCO_3$ solution, and extracted with AcOEt. The organic layer was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (4:1) gave (+)-**27** (5.5 mg, 62%) as a colorless oil; $[\alpha]^{23}_D$ +39.0 (*c* 0.09, $CHCl_3$); IR 3400 (OH), 1740 (CO) cm^{-1}; ^1H NMR δ 7.36−7.26 (m, 10H), 5.06 (dd, 1H, *J* = 4.4, 2.0 Hz), 4.82 (d, 1H, *J* = 5.9 Hz), 4.68 (d, 1H, *J* = 11.7 Hz), 4.57 (d, 1H, *J* = 11.7 Hz), 4.47 (m, 1H), 4.33 (t, 1H, *J* = 4.4 Hz), 4.10 (dd, 1H, *J* = 5.9, 2.0 Hz), 2.92 (dd, 1H, *J* = 7.1, 3.9 Hz), 2.68 (dd, 1H, *J* = 7.1, 5.4 Hz), 2.34 (brs, 1H); ^{13}C NMR δ 168.57, 138.11, 136.82, 128.66, 128.48, 128.39, 128.07, 127.78, 126.06, 90.39, 84.91, 84.28, 72.63, 65.81, 35.19; EIMS *m*/*z* (%) 340 (M^+, 6), 249 (61), 145 (12), 115 (7), 107 (96), 105 (10), 97 (15), 91 (100), 79 (26), 77 (16). Anal. Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.18; H, 5.95.

(−)-(1*S*,5*R*,6*S*,8*R*,9*R*)-5,9-Dihydroxy-8-phenyl-2,7-dioxabicyclo[4.3.0]nonan-3-one [goniofupyrone (6)]: colorless oil (80%); $[\alpha]^{18}_D$ −6.9 (*c* 0.15, $CHCl_3$) [lit.[1e] $[\alpha]^{25}_D$ −5.0 (*c* 0.10, $CHCl_3$)]; IR 3400 (OH), 1735 (CO) cm^{-1}; ^1H NMR δ 7.37−7.29 (m, 5H), 4.96 (dd, 1H, *J* = 5.4, 2.4 Hz), 4.70 (d, 1H, *J* = 6.4 Hz), 4.44 (dt, 1H, *J* = 5.9, 3.9 Hz), 4.36 (ddd, 1H, *J* = 5.4, 3.9, 1.0 Hz),4.29 (dd, 1H, *J* = 6.4, 2.4 Hz), 3.31 (brs, 1H), 2.91 (dd, 1H, *J* = 16.6, 3.9 Hz), 2.78 (brs, 1H), 2.68 (ddd, 1H, *J* = 16.6, 5.9, 1.0 Hz); ^{13}C NMR δ 169.29, 137.93, 128.72, 128.46, 126.00, 86.76, 85.72, 83.65, 76.37, 65.82, 35.08; EIMS *m*/*z* (%) 250 (M^+, 36), 160 (18), 144 (44), 133 (30), 120 (50), 117 (29), 115 (13), 107 (93), 105 (48), 97 (17), 91 (100), 79 (43), 77 (45), 73 (33), 71 (25). Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.03; H, 5.64.

(−)-(1*R*,5*R*,6*S*,8*R*,9*R*)-5,9-Diacetoxy-8-phenyl-2,7-dioxabicyclo[4.3.0]nonan-3-one (28). Colorless oil (76%); $[\alpha]^{21}_D$ −116.4 (*c* 0.15, $CHCl_3$); IR 1750 (CO) cm^{-1}; ^1H NMR δ 7.38−7.30 (m, 5H), 5.49 (q, 1H, *J* = 3.9 Hz), 5.34 (dd, 1H, *J* = 3.9, 1.0 Hz), 4.96 (dd, 1H, *J* = 3.9, 1.0 Hz), 4.94 (d, 1H, *J* = 3.9, Hz), 4.36 (t, 1H, *J* = 3.9 Hz), 3.03 (dd, 1H, *J* = 17.6, 3.9 Hz), 2.75 (ddd, 1H, *J* = 17.6, 3.9, 1.0 Hz), 2.15 (s, 3H), 2.13 (s, 3H); ^{13}C NMR δ 169.42, 169.27, 166.18, 137.07, 128.75, 128.61, 126.16, 86.00, 83.36, 82.89, 73.80, 66.67, 31.97, 20.85, 20.78; CIMS *m*/*z* (%) 335 (M^+ + 1, 100), 275 (76), 215 (15); FABMS *m*/*z* (%) 335 (M^+ + 1, 18), 215 (21), 181 (10), 154 (23), 149 (16), 144 (10), 136 (29), 115 (14), 107 (19), 105 (20), 97 (11), 95 (16), 91 (100). HRFABMS calcd for $C_{17}H_{19}O_7$ (M^+ + 1) 335.1131, found 335.1138.

(−)-(1*S*,5*S*,6*S*,8*R*,9*R*)-9-(Benzyloxy)-5-hydroxy-8-phenyl-2,7-dioxabicyclo[4.3.0]nonan-3-one (30). DIBALH (1.0 M hexane solution; 0.15 mL, 0.15 mmol) was added to a solution of (+)-**27** (42.6 mg, 0.13 mmol) in dry Et_2O (2.4 mL) at −78 °C. The reaction mixture was kept at the same temperature for 10 min, then quenched by addition of a saturated Na_2SO_4 solution, passed through a short pad of Celite, dried, and concentrated to dryness. The residue was dissolved in MeOH (2.5 mL), to which *p*-TsOH·H_2O (2.0 mg, 0.01 mmol) was added. The reaction mixture was stirred at rt for 15 h, neutralized with a saturated $NaHCO_3$ solution, and extracted with AcOEt. The organic layer was washed with water, dried, and concentrated to dryness. The residue was passed through a short column with hexane-AcOEt (5:1) to afford **29** (32.6 mg, 77%) as a mixture of two diastereoisomers. To a solution of **29** (12.7 mg, 0.04 mmol) in dry CH_3CN (1.0 mL) were successively added 4 Å molecular sieves (250 mg), NMO (8.3 mg, 0.08 mmol), and TPAP (4.0 mg, 0.01 mmol) at rt. The reaction mixture was stirred for 30 min, diluted with AcOEt, and passed through a short pad of Celite. The filtrate was concnetrated to dryness. LAH (3.8 mg, 0.10 mmol) was added to a solution of the residue in THF (1.0 mL) at −20 °C.

After being stirred for 20 min at the same temperature, the reaction mixture was quenched by addition of water, passed through a short pad of Celite, dried, and concentrated to give the residual oil. The residue was taken up in CH_2Cl_2 (1.0 mL), to which *m*-CPBA (19.4 mg, 0.09 mmol) and $BF_3 \cdot OEt_2$ (1.0 M CH_2Cl_2 solution; 0.15 mL, 0.15 mmol) were added successively. The reaction mixture was stirred at rt for 1.5 h, diluted with CH_2Cl_2, and washed with a saturated $Na_2S_2O_3$ solution. The organic layer was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (5:1) gave **27** (1.7 mg, 14%) and (−)-**30** (7.4 mg, 61%). (−)-**30**: colorless needles; mp 133−134 °C (hexane-AcOEt); $[\alpha]^{17}_D$ −8.0 (*c* 0.10, $CHCl_3$); IR 1750 (CO) cm^{-1}; ^1H NMR δ 7.39−7.24 (m, 10H), 4.93 (dd, 1H, J = 5.4, 2.4 Hz), 4.86 (d, 1H, J = 6.8 Hz), 4.68 (d, 1H, J = 11.7 Hz), 4.56 (d, 1H, J = 11.7 Hz), 4.49 (dd, 1H, J = 5.4, 3.9 Hz), 4.37 (m, 1H), 4.16 (dd, 1H, J = 6.8, 2.4 Hz), 2.90 (dd, 1H, J = 16.1, 7.8 Hz), 2.67 (dd, 1H, J = 16.1, 3.9 Hz), 2.62 (d, 1H, J = 5.4 Hz); ^{13}C NMR δ 168.39, 137.70, 136.80, 128.73, 128.63, 128.46, 128.05, 127.75, 126.27, 90.32, 84.24, 74.92, 72.74, 63.69, 34.95; EIMS *m*/*z* (%) 340(M^+, 4), 249 (38), 143 (10), 133 (6), 107 (73), 97 (13), 91 (100), 79 (21), 77 (10). Anal. Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.17; H, 5.95.

(−)-(1*S*,5*S*,6*S*,8*R*,9*R*)-5,9-Dihydroxy-8-phenyl-2,7-dioxabicyclo[4.3.0]nonan-3-one [5-*epi*-goniofupyrone (31)]: colorless crystals (74%); mp 124−125 °C ($CHCl_3$); $[\alpha]^{18}_D$ −59.2 (*c* 0.10, $CHCl_3$); IR 3400 (OH), 1745 (CO) cm^{-1}; ^1H NMR δ 7.40−7.34 (m, 5H), 4.88 (dd, 1H, J = 6.4, 3.9 Hz), 4.76 (d, 1H, J = 7.3 Hz), 4.49 (dd, 1H, J = 6.4, 3.9 Hz), 4.38−4.35 (m, 2H), 2.91 (dd, 1H, J = 16.6, 7.8 Hz), 2.63 (dd, 1H, J = 16.6, 3.4 Hz), 2.58 (brs, 1H); ^{13}C NMR δ, 168.88, 137.43, 128.79, 128.72, 126.25, 85.93, 84.57, 83.31, 74.11, 63.67, 34.83; CIMS *m*/*z* (%) 251 (M^+ + 1, 100), 233 (8), 144 (9); FABMS *m*/*z* (%) 251 (M^+ + 1, 15), 165 (10), 154 (100), 149 (16), 136 (88), 124 (10), 120 (17), 115 (12), 107 (38), 91 (40). HRFABMS calcd for $C_{13}H_{15}O_5$ (M^+ + 1) 251.0920, found 251.0920.

(−)-(1*R*,5*S*,6*S*,8*R*,9*R*)-5,9-Diacetoxy-8-phenyl-2,7-dioxabicyclo[4.3.0]nonan-3-one (32): colorless oil (89%); $[\alpha]^{21}_D$ −74.2 (*c* 0.09, $CHCl_3$); IR 1740 (CO) cm^{-1}; ^1H NMR δ 7.36−7.26 (m, 5H), 5.40 (ddd, 1H, J = 11.2, 5.9, 2.9 Hz), 5.31 (dd, 1H, J = 3.4, 1.0 Hz), 4.94 (d, 1H, J = 3.4 Hz), 4.85 (dd, 1H, J = 2.9, 1.0, Hz), 4.63 (t, 1H, J = 2.9 Hz), 3.03 (dd, 1H, J = 17.1, 11.2 Hz), 2.91 (dd, 1H, J = 17.1, 5.9 Hz), 2.14 (s); ^{13}C NMR δ 170.13, 169.25, 166.45, 137.18, 128.77, 128.61, 126.24, 86.16, 83.13, 82.77, 73.86, 65.46, 31.32, 20.88, 20.78; CIMS *m*/*z* (%) 335 (M^+ + 1, 100), 275 (47), 215 (9), 144 (14); FABMS *m*/*z* (%) 335 (M^+ + 1, 46), 307 (12), 289 (12), 215 (29), 165 (10), 163 (12), 154 (100), 152 (14), 144 (16), 136 (92), 124 (12), 120 (18), 115 (13), 107 (39), 105 (22), 91 (35). HRFABMS calcd for $C_{17}H_{19}O_7$ (M^+ + 1) 335.1131, found 335.1109.

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Supporting Information Available: Procedures for preparation of compounds (+)-**2**, (+)-**3**, (+)-**4**, (+)-**5,** (−)-**6**, (−)-**16**, (+)-**19**, (−)-**20**, (+)-**24**, (±)-**26**, (−)-**28**, (−)-**31**, and (−)-**32**, ^{13}C NMR spectra for compounds (+)-**3**, **21**, (±)-**25**, **28**, (−)-**31**, and (−)-**32**, and ORTEP drawing of (±)-**26** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microform version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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