Stepwise Cross-Couplings of a Dibromo-γ-methylenebutenolide as an Access to *Z*-Configured α-Alkenyl-γ-alkylidenebutenolides. Straightforward Synthesis of the Antibiotic Lissoclinolide

Achim Sorg, Frederik Blank, Reinhard Brückner*

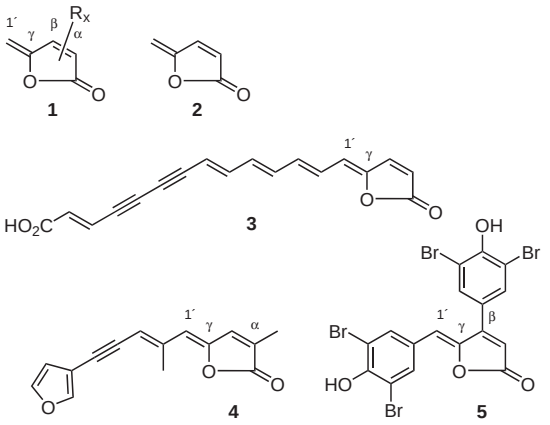
Institut für Organische Chemie und Biochemie, Albert-Ludwigs-Universität Freiburg, Albertstr. 21, 79104 Freiburg, Germany
Fax +49(761)2036100; E-mail: reinhard.brueckner@organik.chemie.uni-freiburg.de

Received 28 March 2005

Abstract: The *Z*-isomer of α-bromo-γ-(bromomethylene)butenolide was prepared from α-angelica lactone or levulinic acid in three and four steps, respectively. Successive Stille-couplings with an unsaturated stannane, with the potential to use a different second unsaturated stannane, involved the γ-substituent first and the α-substituent thereafter. Thereby, α-alkenyl-γ-alkylidenebutenolides and their arene analogs were obtained *Z*-selectively.

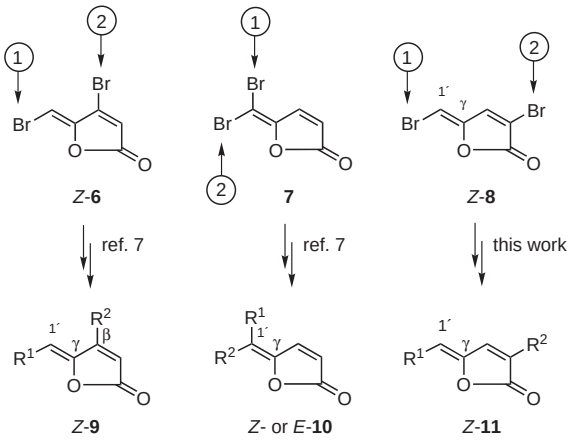
Key words: enol lactone, natural product synthesis, palladium, regioselectivity, stereoselectivity, Stille-coupling

The simplest naturally occurring γ-alkylidenebutenolide **1** is the antibiotic γ-methylenebutenolide or 'protoanemonin' (**2**;[1] Scheme 1). Higher naturally occurring γ-alkylidenebutenolides include xerulinic acid (**3**;[2] 1′-monosubstituted), an inhibitor of the biosynthesis of cholesterol; freelingyne (**4**;[3] 1′,α-disubstituted), a wood oil constituent; and rubrolide A (**5**;[4] 1′,β-disubstituted), an inhibitor of protein phosphatases. In each of these compounds the $C^{1'}$=C^{γ} bond is stereogenic and *Z*-configured. Since, in the absence of a β-substituent, the thermodynamic bias for the *Z*- vs. *E*-configuration at this bond is fairly small, laboratory syntheses of such γ-alkylidenebutenolides **1** require kinetic control to ensure a stereoselective reaction.[5]



Scheme 1

Having been involved in the development of the stereoselective syntheses of γ-alkylidenebutenolides for some time,[5c,6] we recently added stepwise C,C-couplings with dibrominated γ-methylenebutenolides *Z*-**6** or **7** to the methodological arsenal (Scheme 2):[7] under Pd-catalysis the respective bromine atoms are replaced in a strictly regiocontrolled manner (Scheme 2 indicates the order). Thereby, two successive C,C-couplings produce γ-alkylidenebutenolides *Z*-**9** and *Z*- or *E*-**10**, respectively, as single stereoisomers.

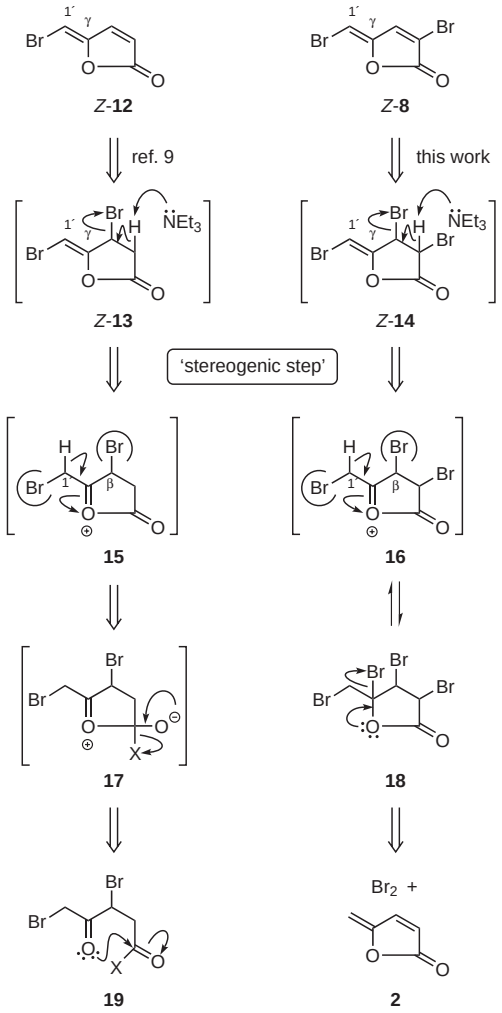


Scheme 2

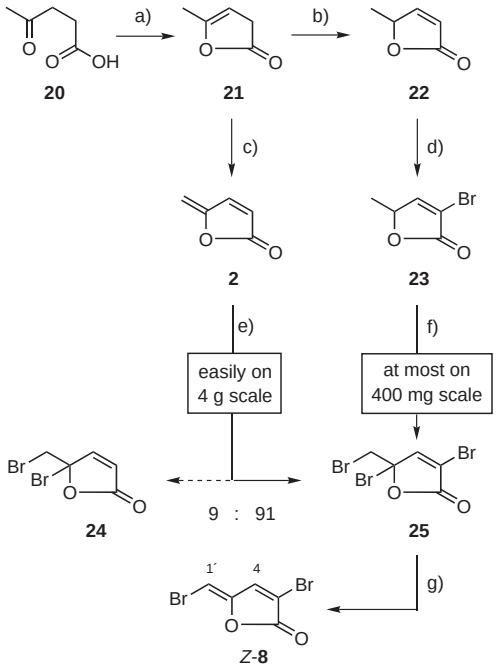
The present communication extends this strategy: we complement dibromomethylenebutenolide *Z*-**8** as a substrate for tandem Stille-couplings,[8] which provides α-alkenyl-γ-alkylidenebutenolides *Z*-**11** in a very straightforward manner (Scheme 2).

Contemplating how to make dibromomethylenebutenolide *Z*-**8** stereoselectively, we took recourse to our rationalization of the *Z*-selectivity of the recent synthesis of the analogous monobromomethylenebutenolide *Z*-**12**[9] (Scheme 3). The step establishing the $C^{1'}$=C^{γ} bond configuration appears to be the deprotonation of carboxonium-ion **15** (in the presence of polyphosphorous acid): while this reaction is underway, the bromine substituents at C^{β} and $C^{1'}$ strive to position themselves a maximum distance apart, which causes the *cis*-orientation of the $C^{1'}$–Br and C^{γ}–O bonds in intermediate *Z*-**13**. The latter and triethylamine give butenolide *Z*-**12** by a β-elimination. Based on

SYNLETT 2005, No. 8, pp 1286–1290
Advanced online publication: 03.05.2005
DOI: 10.1055/s-2005-868506; Art ID: G10905ST



Scheme 3



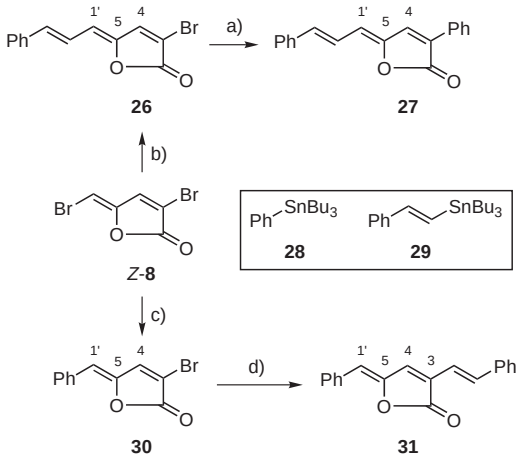
Scheme 4 *Reagents and conditions:* a) H_3PO_4 (cat.), distillation (60%; Ref.[10] 90%); b) Et_3N (0.5 equiv), benzene, Δ, 15 h (43%; Ref.[17] 58%); c) Br_2 (0.98 equiv), CCl_4, 0 °C, 1 h; quinoline (2.1 equiv), benzene, 0 °C → r.t., 5 h [50% (when mixed with residual quinoline) or 37% (pure); Ref.[11] 90%]; d) Br_2 (1.52 equiv), CCl_4, reflux, 3 h; Et_3N (1.52 equiv), 4 h (46%; Ref.[12] 71%); e) Br_2 (2.2 equiv), CCl_4, 0 °C→reflux, 2.5 h; Et_3N (1.0 equiv), 0 °C → r.t. (**25**: 73%, **24**: 7%); f) NBS (2.7 equiv, added in 12 h intervals), AIBN (0.22 equiv), CCl_4, reflux, 39 h (34%; Ref.[12] 63%); g) Hydroquinone (cat.), Et_3N (1.10 equiv), CH_2Cl_2, –78 °C→0 °C, 1 h (78%).

this analysis, it seemed likely that the same order of events would transform carboxonium-ion **16** via intermediate *Z*-**14** into butenolide *Z*-**8**. We conceived that carboxonium-ion precursor **16** would be generated differently than carboxonium-ion **17**; we assumed that **16** would form through heterolysis of the tetrabromolactone **18**, which in turn would result from the addition of excess bromine to protoanemonin (**2**).

Scheme 4 shows how Scheme 3 translated into practice, starting from α-angelica lactone (**21**). This compound can be purchased or prepared by the lactonization of levulinic acid (**20**).[10] Adding bromine to **21** and eliminating HBr according to the literature[11] rendered protoanemonin (**2**) in 37–50% yield. Heating this compound at reflux temperature in CCl_4 in the presence of 2.2 equiv of bromine gave the intermediate **18**, which upon addition of 1 equivalent of triethylamine (→elimination of HBr) yielded the desired tribromobutenolide **25**[12] (73%) and the undesired dibromobutenolide **24**[13] (7%) after separation by flash-chromatography[14] on silica gel. Treatment of tribromobutenolide **25** with another equivalent of triethylamine induced once more the elimination of HBr. The dibromobutenolide *Z*-**8**[15] resulted in 78% yield and isomerically pure; the *Z*-configuration was confirmed by the NOE's upon integration of 4-H (δ = 7.49 ppm) while irradiating 1′-H (δ = 6.19 ppm), and vice versa.[16] Surprisingly, we could not combine the dibromination of protoanemonin (**2**) and the two β-eliminations of HBr in a one-pot procedure leading directly to *Z*-**8**; when such a procedure was carried out the yield of *Z*-**8** was low and it could not be separated from the inevitable contamination by dibromobutenolide **24**.

The original route from α-angelica lactone (**21**) via β-angelica lactone (**22**[17]) and monobromobutenolide **23**[12] to tribromobutenolide **25**[12] was less efficient in our hands (7% overall yield) than the new synthesis via **2** (27–37% overall yield). Moreover, the bromination **23**→**25** was unsuitable for preparing even one-gram-amounts of compound **25** at a time.[18]

Scheme 5 depicts two-stage Stille-couplings[8] between dibromobutenolide *Z*-**8** as a bis(electrophile) and aryl tributylstannane **28**[19] and alkenyl tributylstannane **29**[20] as representative nucleophiles. When these stannanes were allowed to couple in the indicated order, using $Pd(dba)_2$/$AsPh_3$ as the catalyst,[21] monocoupled product **26** was obtained first and bis-coupled product **27** thereafter. The yield of each step was 71%. Inverting the order of couplings, butenolide *Z*-**8** furnished bis-coupled product **31** via the intermediate monocoupled product **30**, the

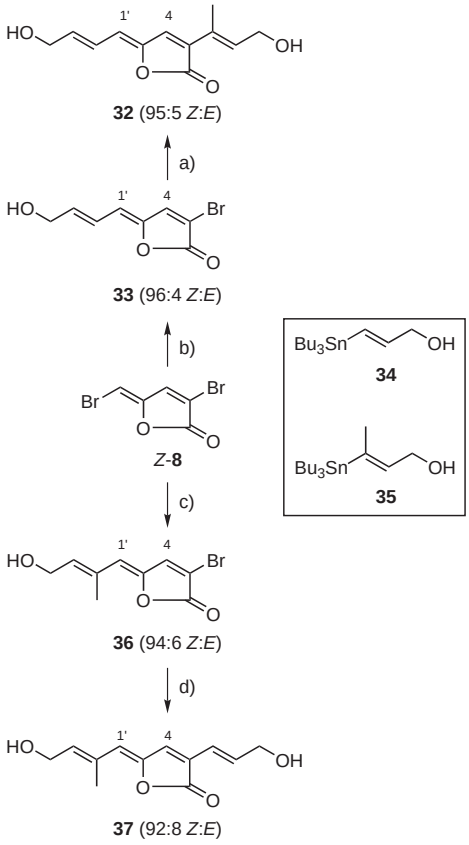


Scheme 5 *Reagents and conditions:* a) **28** (1.11 equiv), $Pd(dba)_2$ (5 mol%), $AsPh_3$ (0.15 equiv), CuI (9 mol%), THF, 50 °C, 4 h (71%); b) **29** (1.1 equiv), $Pd(dba)_2$ (5 mol%), $AsPh_3$ (0.19 equiv), CuI (0.48 equiv), THF, 40 °C, 2 h (71%); c) **28** (1.17 equiv), $Pd(dba)_2$ (4 mol%), $AsPh_3$ (0.11 equiv), CuI (4 mol%), THF, 40–50 °C, 3 h (65%); d) **29** (1.16 equiv), $Pd(dba)_2$ (4 mol%), $AsPh_3$ (0.13 equiv), CuI (7 mol%), THF, 40 °C, 4 h (65%).

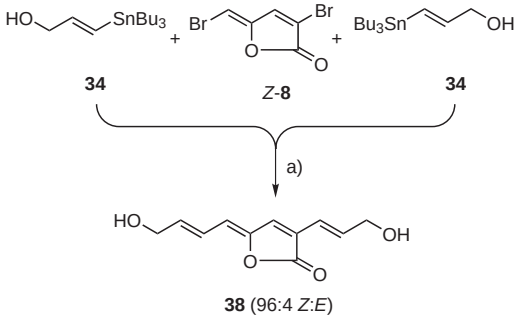
yield being 65% per step. The regioselectivity of both sequences emerged from the ^1H NMR coupling pattern of the β-proton on the styrene moiety. When the styryl group binds to C^3 of the butenolide core as in compound **31**, the β-proton shows one vicinal coupling as opposed to two such couplings when the styryl group is attached to $C^{1'}$ as in compounds **26** and **27**. The *Z*-geometry is attributable to the $C^{1'}$=C^5 bonds of all coupled products of Scheme 5 on the basis of the NOE's visible between their respective 1′-H and 4-H resonances.

Continuing to explore the Stille cross-coupling chemistry of dibromobutenolide *Z*-**8** but accessing α-alkenyl-γ-alkylidenebutenolides with more resemblance to natural products we used alkenyl tributylstannanes **34**[22] and **35**[23] as coupling partners (Scheme 6). Mono-coupling with the primary alkenyl stannane **34** provided the α-bromo-γ-alkylidenebutenolide **33** in 94% yield (96:4 *Z*:*E*-mixture). Mono-coupling of *Z*-**8** with the more hindered secondary alkenyl stannane **35** was slower and less efficient, furnishing the α-bromo-γ-alkylidenebutenolide **36**[24] in 63% yield (94:6 *Z*:*E*-mixture). Stille-couplings of mono-coupled product **33** with stannane **35** and mono-coupled product **36** with stannane **34** led to the isomeric bis-coupled products **32**[25] (54%, 94:6 *Z*:*E*-mixture) and **37**[26] (86%, 92:8 *Z*:*E*-mixture), respectively. The regioselectivity of the couplings in Scheme 6 and the configuration of the emerging $C^{1'}$=C^5 bonds were ascertained as exemplified for the analogous couplings in Scheme 5.

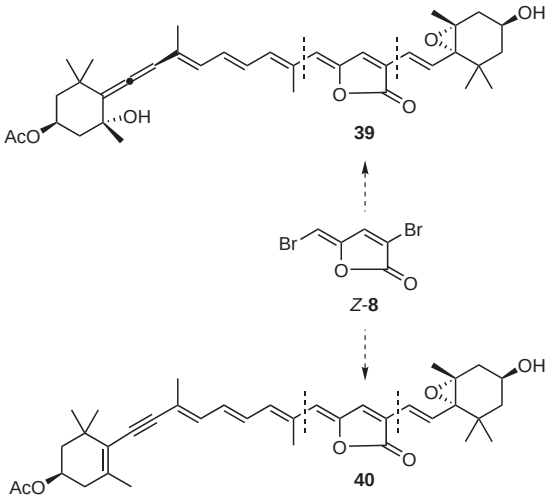
Finally, catalysis by $Pd(dba)_2$ and $AsPh_3$ (in the absence of CuI) allowed a double Stille-reaction of dibromobutenolide *Z*-**8** with alkenylstannane **34** (Scheme 7). After heating in THF solution at 50–60 °C for 90 minutes followed by chromatographic work-up, we isolated a 96:4 *Z*:*E*-mixture of the α-alkenyl-γ-alkylidenebutenolide **38** in 66% yield.[27] **38** is the common[28] structure of the antibiotics lissoclinolide (from *Lissoclinum patella*)[29] and tetrenolin (from *Micropolyspora venezuelensis*).[30] This synthesis of lissoclinolide is the shortest reported to date, comprising just four steps from angelica lactone (**21**) or five steps from levulinic acid (**20**). In addition it is the only one accomplished without using protecting groups. By comparison, Negishi's synthesis of lissoclinolide required nine steps,[31] Rossi's eight steps,[32] and Görth's earlier synthesis from our laboratory six steps.[28]



Scheme 6 *Reagents and conditions:* a) **35** (1.20 equiv), $Pd(dba)_2$ (5 mol%), $AsPh_3$ (0.14 equiv), CuI (9 mol%), THF, 40–50 °C, 4 h (54%); b) **34** (1.10 equiv), $Pd(dba)_2$ (4 mol%), $AsPh_3$ (0.13 equiv), CuI (8 mol%), THF, r.t., 4 h (94%); c) **35** (1.16 equiv), $Pd(dba)_2$ (6 mol%), $AsPh_3$ (0.12 equiv), THF, 50–60 °C, 1.5 h (63%); d) **34** (1.13 equiv), $Pd(dba)_2$ (5 mol%), $AsPh_3$ (0.15 equiv), THF, 40–50 °C, 1 h (86%).



Scheme 7 *Reagents and conditions:* a) **34** (2.20 equiv), $Pd(dba)_2$ (5 mol%), $AsPh_3$ (0.16 equiv), THF, 50–60 °C, 1.5 h (66%).



Scheme 8

In conclusion, we have presented a powerful new strategy for the stereoselective synthesis of *Z*-configured α-alkenyl-γ-alkylidenebutenolides. The transformation ***Z*-8→36→37** (Scheme 6) models specifically how sequential Stille couplings between ***Z*-8** and more complex alkenylstannanes than **34**/**35** should develop into novel and concise approaches to totally synthetic specimens of peridinin (**39**[33]) and pyrrhoxanthin (**40**[34]), key carotenoids for marine photosynthesis (Scheme 8).

Acknowledgment

We are grateful to the Fonds der Chemischen Industrie for general financial support.

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(15) All new compounds except **23** gave satisfactory ^{1}H and ^{13}C NMR spectra and provided either correct combustion analyses or HRMS.
(16) **(*Z*)-3-Bromo-5-(bromomethylene)-2(5*H*)-furanone** (***Z*-8**): Et_3N (0.46 mL, 0.34 g, 3.3 mmol, 1.1 equiv) was added dropwise at –78 °C to a solution of 3,5-dibromo-5-(bromomethyl)-2(5*H*)-furanone (**25**) (1.002 g, 2.993 mmol) and hydroquinone (a few crystals) in CH_2Cl_2 (5 mL). The mixture was allowed to warm to 0 °C where it darkened gradually. After 1 h and without aqueous work-up, purification by flash chromatography on silica gel (cyclohexane–EtOAc, 10:1→5:1) furnished the title compound (0.5826 g, 78%) as a colorless solid (mp 72–73 °C). ^{1}H NMR (300.1 MHz, $CDCl_3$/TMS): δ = 6.19 (s, 1′-H), 7.49 (s, 4-H). ^{13}C NMR (125.7 MHz, $CDCl_3$/$CHCl_3$): δ = 93.17 (C-1′), 114.53 (C-3), 139.36 (C-4), 150.85 (C-5), 163.97 (C-2). Anal. calcd for $C_5H_2Br_2O_2$ (251.8): C 23.65; H 0.79. Found: C 23.67; H 0.51.
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(18) The difficulty of this step also devaluated an improved preparation of bromobutenolide **23** from *trans*-2-pentenoic acid: 1) NBS (1.04 equiv), AIBN (7.6 mol%), CCl_4, reflux, 3 h; Et_3N (1.5 equiv); filtration; Br_2 (1.20 equiv), reflux, 1.5 h; 91%; 2) H_2O, reflux, 5 h; 74%.
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(24) The reaction of ***Z*-8** with **35** under the hitherto used conditions [$Pd(dba)_2$, $AsPh_3$, CuI] was troublesome, leading to inseparable isomeric mixtures of **36** with up to 15% of its 1′-*E*-isomer. Running the same reaction in the absence of CuI increased the *Z*:*E*-ratio to 94:6.

(25) (***Z*)-5-(*trans*-4-Hydroxy-2-butenylidene)-3-[(*Z*)-3-hydroxy-1-methyl-1-propenyl]-2(5*H*)-furanone** (**32**; 95:5 mixture with the *E*-isomer): Yellow solid; mp 154–156 °C. ^{1}H NMR (499.9 MHz, CD_3OD–D_2HCOD): δ = 1.93 (d, $^4J_{1''\text{-Me},2''}$ = 1.1 Hz, 1″-H_3), 4.20 (dd, $J_{4',3'}$ = 5.2 Hz, $^4J_{4',2'}$ = 1.7 Hz, 4′-H_2), 4.30 (d, $J_{3'',2''}$ = 6.5 Hz, 3″-H_2), 6.00 (d, $J_{1',2'}$ = 11.4 Hz, 1′-H), 6.16 (dtd, $J_{3',2'}$ = 15.4 Hz, $J_{3',4'}$ = 5.3 Hz, $^4J_{3',1'}$ = 0.9 Hz, 3′-H), 6.76 (ddt, $J_{2',3'}$ = 15.5 Hz, $J_{2',1'}$ = 11.4 Hz, $^4J_{2',4'}$ = 1.9 Hz, 2′-H), 6.96 (incompletely resolved br tq, $J_{2'',3''}$ = 6.5 Hz, $^4J_{2'',1''\text{-Me}}$ = 1.1 Hz, 2″-H), 7.41 (s, 4-H). ^{13}C NMR (125.7 MHz, CD_3OD–D_2HCOD): δ = 14.71 (1″-CH_3), 59.79 (C-3″), 63.14 (C-4′), 114.39 (C-1′), 123.89 (C-2′), 128.10 (low intensity; C-1″), 134.75 (C-2″), 135.80 (C-4), 140.29 (C-3′), 148.53 (C-5), 169.18 (C-2). HRMS (EI, 70 eV): *m*/*z* calcd for $C_{12}H_{12}O_3$, 204.078645; found, 204.078238 ($M^+ - H_2O$).

(26) (***Z*)-5-(*trans*-4-Hydroxy-2-methyl-2-butenylidene)-3-(*trans*-3-hydroxy-1-propenyl)-2(5*H*)-furanone** (**37**; 92:8 mixture with the *E*-isomer): Yellow solid; mp 111–113 °C. ^{1}H NMR (499.9 MHz, CD_3OD–D_2HCOD): δ = 2.06 (d, $^4J_{\text{Me},1'}$ = 1.1 Hz, 2′-Me), 4.22 (dd, $J_{3'',2''}$ = 5.1 Hz, $^4J_{3'',1''}$ = 1.9 Hz, 3″-H_2), 4.26 (d, $J_{4',3'}$ = 6.5 Hz, 4′-H_2), 5.83 (br s, 1′-H), 5.99 (incompletely resolved tqd, $J_{3',4'}$ = 6.6 Hz, $^4J_{3',2'\text{-Me}}$ = $^4J_{3',1'}$ = 1.1 Hz, 3′-H), 6.45 (dt, $J_{1'',2''}$ = 16.0 Hz, $^4J_{1'',3''}$ = 1.9 Hz, 1″-H), 6.90 (dt, $J_{2'',1''}$ = 16.0 Hz, $J_{2'',3''}$ = 5.0 Hz, 2″-H), 7.38 (s, 4-H). ^{13}C NMR (125.7 MHz, CD_3OD–D_2HCOD): δ = 15.46 (2′-CH_3), 59.56 (C-4′), 63.18 (C-3″), 118.89 (C-1′), 119.13 (C-1″), 138.38 (C-2″), 138.51 (C-4), 139.14 (C-3′), 148.09 (very low intensity, C-5), 170.50 (very low intensity, C-2); the signals of C-3 and C-2′ were not identified unambiguously. Anal. calcd for $C_{12}H_{14}O_4$ (204.1): C 64.85; H 6.35. Found: C 64.55; H 6.32.

(27) (***Z*)-5-(*trans*-4-Hydroxy-2-butenylidene)-3-(*trans*-3-hydroxy-1-propenyl)-2(5*H*)-furanone** (**38**): Stannane **34** (586 mg, 1.69 mmol, 2.20 equiv) was added to a degassed solution of dibromobutenolide *Z*-**8** (192 mg, 0.768 mmol), $Pd(dba)_2$ (20.2 mg, 35.1 μmol, 5 mol%), and $AsPh_3$ (37.2 mg, 0.122 mmol, 0.16 equiv) in THF (2.0 mL). The resulting solution was heated at 50–60 °C for 1.5 h, cooled to room temperature, and concentrated in vacuo. Flash chromatography (cyclohexane–EtOAc, 2:1→1:1; *tert*-butylmethylether–EtOAc, 1:1) provided the title compound (105.0 mg, 66%) as a yellow solid; mp 124–126 °C (Ref.[28] 126–127 °C).

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