From Sugar Lactones to Stereodefined γ-Alkylidenebutenolides − Synthesis of Analogs of the γ-Alkylidenebutenolide Antibiotics Lissoclinolide and Tetrenolin

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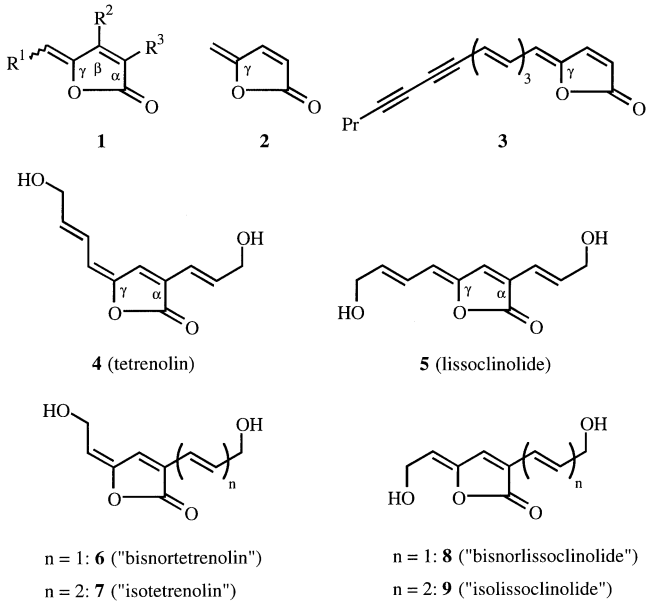
A novel strategy for the stereoselective synthesis of *E*- or *Z*-configured γ-alkylidenebutenolides was applied to the preparation of the model compounds **6/7** (*E*) and **8/9** (*Z*) of the antibiotics tetrenolin (*E*) and lissoclinolide (*Z*), respectively. For introducing the α-substituents of the target molecules the butenolide triflates *ul*- and *lk*-**16** were subjected to Stille couplings with *trans*-Bu_3Sn–CH=CH–CH_2–OH or *trans,trans*-Bu_3Sn–CH=CH–CH=CH–CH_2–OH (room temp., 10 min). Acetonide cleavages and bis(*tert*-butyldimethylsilylations) set the stage for introducing the $C_{exocyclic}$=C_γ bonds through *anti*-selective (*ds* = 96:4–99:1) eliminations of triflic acid (*ul*-**21**→ *E*-**23**, *lk*-**21**→ *Z*-**23**, *ul*-**22**→ *E*-**24**, *lk*-**22**→ *Z*-**24**).

The Beilstein database lists 1600 γ-alkylidene-α,β-unsaturated γ-lactones of substitution pattern **1** ("γ-alkylidenebutenolides"; Scheme 1). Many of them are natural products, some are physiologically active, and several are accessible through laboratory synthesis.[1] The structural complexity of γ-alkylidenebutenolides varies between core structure **2**, which is the antibiotic protoanemonin,[2] and uriolide, which is an algal C_{40} pigment.[3] "Medium-sized" γ-alkylidenebutenolides include the inhibitor of cholesterol biosynthesis dihydroxerulin (**3**[4]) and the antibiotics tetrenolin (**4**[5]) and lissoclinolide (**5**[6]).

Scheme 1



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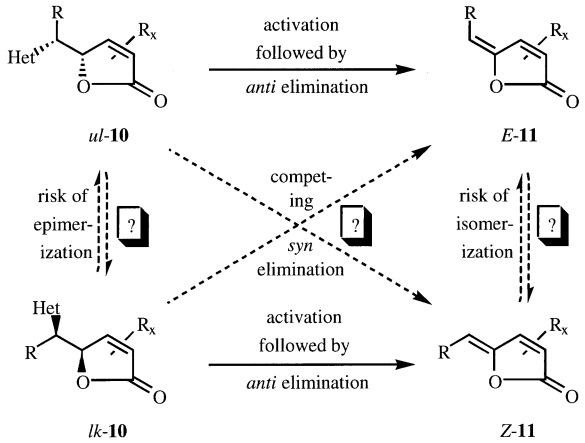
It is unknown whether the configuration of the C=C_γ bond influences the bioactivity of γ-alkylidenebutenolides in general but one knows that it does so in the specific case of the *E*,*Z* isomers tetrenolin (**4**) and lissoclinolide (**5**): Tetrenolin (**4**) acts against Gram positive and lissoclinolide (**5**) against Gram negative bacteria. This observation raised our interest in synthesizing γ-alkylidenebutenolides and assuring stereocontrol concomitantly. The viability of the approach which emerged[7] is illustrated in the following by stereoselective syntheses of the tetrenolin analogs **6** and **7** and of the lissoclinolide analogs **8** and **9**.

Scheme 2. "Het" designates a halogen atom or a heteroatom-bound substituent



Scheme 2 summarizes the key point of our strategy. γ-(α-Hetero-substituted alkyl)butenolides **10** which have well-defined relative configurations *ul* or *lk* − while their absolute configuration is irrelevant − must be obtained first. Then, H−Het is eliminated resulting in the formation of γ-alkylidenebutenolides **11**. Depending on whether the substrate **10** is *ul*- or *lk*-configured and on whether an *anti* or

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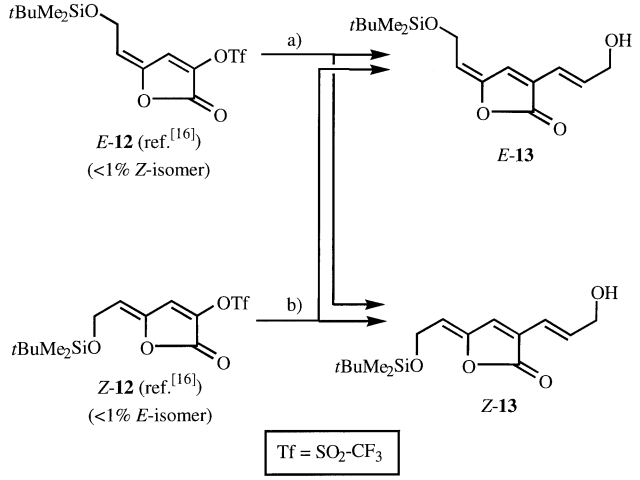
a *syn* elimination of H−Het occurs, the alkylidenebutenolides **11** will be equipped with a *Z*- or an *E*-configured C_γ=C bond. For obtaining thereby γ-alkylidenebutenolides *stereospecifically* three conditions must be fulfilled. (1) The substrates *ul*-**10** and *lk*-**10** must not interconvert under the elimination conditions; (2) the products *Z*-**11** and *E*-**11** must not interconvert under the elimination conditions nor in a subsequent reaction; (3) each H−Het elimination must be entirely *anti*- or entirely *syn*-selective.

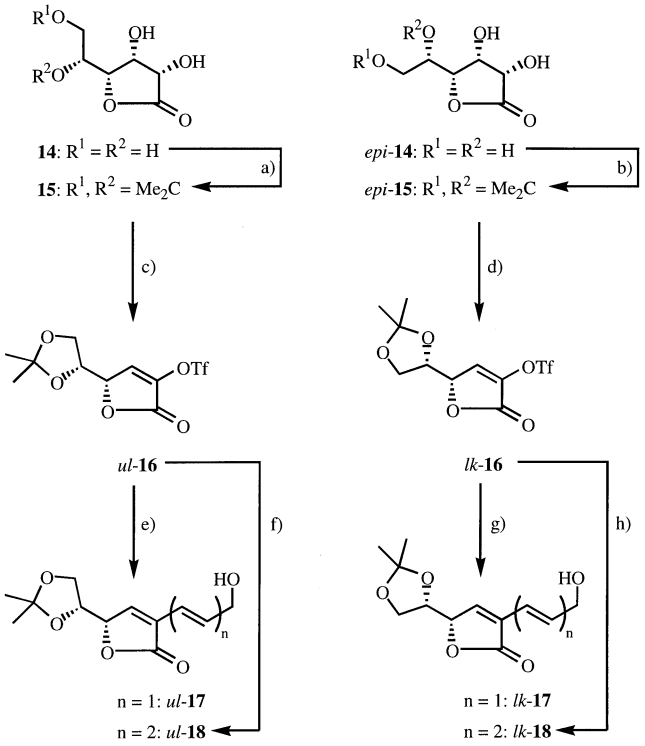
The literature reveals only a few β eliminations from substrates **10** which lead to γ-alkylidenebutenolides **11** at all.[8][9][10][11][12][13][14] Still less abundant are β-eliminations **10**→**11** whose stereochemistry has been studied.[9][10][11][12][13][14] They encompass a single set of stereospecific H−OTs eliminations *ul*-**10**→*E*-**11** and *lk*-**10**→*Z*-**11** giving γ-alkylidenebutenolides **1** (R^1 = R−CH_2, R^2 = R^3 = OMe).[9] Two highly stereoselective β eliminations of H−OSiMe$_2$*tert*Bu converted 27:73 *ul*-**10**/*lk*-**10** mixtures cleanly into *Z*-configured alkylidenebutenolides **1** (R^1 = Ar, R^2 = *i*Pr, R^3 = CH_2−Ph) but, accordingly, lacked stereospecifity.[10] Another β elimination − of H−OPiv from a 18:82 *ul*-**10**/*lk*-**10** mixture − was stereoselective because the formed $C=C_\gamma$ bond was part of a 6-membered ring; naturally, there was no stereospecifity.[11] An H−Br elimination from a butenolide *ul*-**10** led with a 90:10 preference to the *anti* elimination product *Z*-**1** (R^1 = Me, R^2 = R^3 = H).[12] Preparatively worthless 67:33 and 55:45 *Z* selectivities were encountered in β eliminations of H−OAc[13] and H−OBz[14] from *ul*-**10**-type esters. Realizing the strategy of Scheme 2 is obviously a challenge.[15]

Scheme 3. a) *trans*,*trans*-5-(Tributylstannyl)-2,4-pentadien-1-ol (1.3 equiv.), $Pd_2(dba)_3{\cdot}CHCl_3$ (2 mol-%), $AsPh_3$ (16 mol-%), LiCl (3.0 equiv.), THF, room temp., 25 min; 70%, *ds* = 31:69. − b) Same as (a); 82%, *ds* = 77:23



Recently, we turned this strategy into practice by performing >99:1 *anti* selective β eliminations of triflic acid which provided the stereo*pure* γ-alkylidenebutenolides *E*-**12** and *Z*-**12** (Scheme 3).[16] As enol triflate, these compounds were treated with *trans*-Bu_3Sn−CH=CH−CH_2OH[17] in the presence of various Pd(0) catalysts effecting Stille couplings.[18] They furnished the mono-*tert*-butyl dimethylsilyl ethers *E*-**13** (*Z*-**13**) of our target molecules **6** (**8**) in yields up to 70% (82%) starting from *E*-**12** (*Z*-**12**). However, starting from *E*-**12** (98% *E*) the *E*-content in the elimination product **13** shrunk to 31%, starting from *Z*-**12** (99%) the *Z*-content to 77%. This seems to be due to isomerizations of the *starting* butenolides *E*- and *Z*-**12** since exposing them in THF solution to LiCl[18a] alone − an additive compulsory for observing couplings at all − destroyed their stereochemical homogeneity. Perhaps, the respective O=S−O−C−C=O moiety chelates a lithium cation whereupon the C,H acidity increases so that a butenolide/5-alkenyl-2-hydroxyfuran tautomerism is facilitated by which *E*- and *Z*-**12** interconvert. We circumvented such isomerizations almost entirely when we performed the C−OTf → C−CH=CH−CH_2−OH conversions en route to targets **6**/**8** and the analogous C−OTf → C−CH=CH−CH=CH−CH_2−OH conversions en route to targets **7**/**9** first and introduced the configurationally labile $C=C_\gamma$ bonds thereafter (Schemes 4−5).

Scheme 4. a) 2,2-Dimethoxypropane (1.3 equiv.), Amberlyst-15 (2.5 weight-%), DMF, room temp., 24 h; 60°C, 3 h; 74% (ref.[19] 77%). − b) Same as (a); 68% (ref.[19] 60%, ref.[20] 70%). − c) Triflic anhydride (2.4 equiv.), pyridine (4.0 equiv.), CH_2Cl_2, −78°C → −25°C, 3 h; 70% (ref.[21] 74%). − d) Same as (c); 74% (ref.[21] 70%). − e) *trans*-3-(Tributylstannyl)-2-propen-1-ol (1.05 equiv.), $Pd_2(dba)_3{\cdot}CHCl_3$ (2 mol-%), $AsPh_3$ (16 mol-%), LiCl (3.0 equiv.), THF, room temp., 10 min; 68%. − f) *trans*,*trans*-5-(Tributylstannyl)-2,4-pentadien-1-ol (1.1 equiv.), $Pd_2(dba)_3{\cdot}CHCl_3$ (2 mol-%), $AsPh_3$ (16 mol-%), LiCl (3.0 equiv.), THF, room temp., 10 min; 75%. − g) Same as (e); 78%. − h) Same as (f); 57%



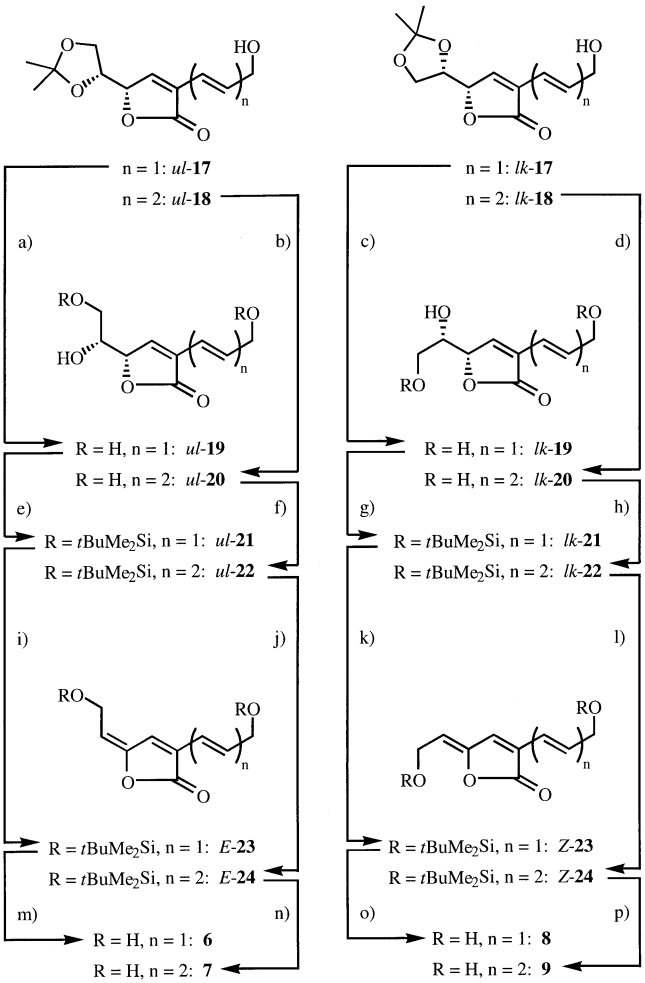
The four syntheses start from D-mannono- (**14**) and L-gulono-1,4-lactone (*epi*-**14**), respectively (Scheme 4). Acetonide formation of the former delivered mono-acetonide **15**,[19] acetonide formation of the latter mono-acetonide *epi*-**15**.[20] Treatment of these compounds with triflic anhy-

dride (2.4 equiv.) and pyridine (4.0 equiv.) in CH_2Cl_2 between −78°C and −25°C gave bistriflates as short-lived intermediates which expelled one triflate group immediately delivering the butenolide triflates *ul*-**16** (70%) and *lk*-**16** (74%), respectively.[21] Introducing the α-substituents of our target molecules **6/8** and **7/9** by Stille couplings[18b] between these triflates and *trans*-$Bu_3Sn-CH=CH-CH_2-OH$[17] or *trans,trans*-$Bu_3Sn-CH=CH-CH=CH-CH_2-OH$,[16] respectively, required searching for the best catalyst/additive combination. Farina's modification[22] of the original procedure[18a] brought success utilizing $Pd_2dba_3{\cdot}CHCl_3$ (2 mol-%) as a Pd(0) source and $AsPh_3$ (16 mol-%) as secondary ligand. In addition, adding 3 equiv. of LiCl to the reaction mixtures[18] was a "must" for observing rapid (10 min at room temperature) and therefore clean couplings. The coupling products between triflates *ul*-**16** or *lk*-**16** and *trans*-$Bu_3Sn-CH=CH-CH_2-OH$ arose in 68% (*ul*-**17**) and 78% yield (*lk*-**17**), respectively, the analogous coupling products with *trans,trans*-$Bu_3Sn-CH=CH-CH=CH-CH_2-OH$ in 75% (*ul*-**18**) and 57% yield (*lk*-**18**), each of them diastereomerically pure.

Next, we removed the acetonide protecting groups from coupling products *ul*-**17**/*lk*-**17** and *ul*-**18**/*lk*-**18** (Scheme 5) by HCl-catalyzed transacetalizations with methanol. The primary OH groups of the so formed triols *ul*-**19** (65%), *lk*-**19** (78%), *ul*-**20** (73%), and *lk*-**20** (51%) had to be reprotected prior to incorporating the secondary OH group into a leaving group. *tert*-Butyldimethylsilyl chloride and imidazole was the reagent combination of choice.[23] It converted triol *ul*-**19** into bis(silyl ether) *ul*-**21**, triol *lk*-**19** into bis(silyl ether) *lk*-**21**, triol *ul*-**20** into bis(silyl ether) *ul*-**22**, and triol *lk*-**20** into bis(silyl ether) *lk*-**22** in 48−73% yield.

Compounds *ul*-**21**, *lk*-**21**, *ul*-**22**, and *lk*-**22** are not only bis(silyl ethers) but also γ-(α-hydroxyalkyl)butenolides. In the latter role they acted now as type-**10** precursors of alkylidenebutenolides (cf. Scheme 2). To this end, they were subjected to the crucial $C=C_\gamma$ bond-forming dehydrations of Scheme 5 by β eliminations of triflic acid. The substrates of these eliminations were the triflates which one obtained in situ through low-temperature reactions between the γ-(α-hydroxyalkyl)butenolides *ul*-**21**, *lk*-**21**, *ul*-**22**, or *lk*-**22**, 1.3 equiv. of triflic anhydride, and 2.0 equiv. of pyridine. If the resulting alkylidenebutenolides **23** or **24** were allowed to reach temperatures ≥ −25°C they decomposed rapidly. Concomitantly, the material which stayed intact lost its stereochemical integrity with respect to the configuration of the $C=C_\gamma$ bond. In the worst cases, ≈ 2:1 *Z*/*E* alkylidenebutenolide mixtures resulted − tentatively interpreted as equilibrium *Z*/*E* mixtures. Separating excess pyridine and the byproduct pyridinium triflate from the desired alkylidenebutenolides *under very mild conditions* became the main concern in working up these reactions. Our best solution was cooling the crude mixture to −78°C and pouring it directly onto a column filled with silica gel for flash chromatography.[24] Prompt elution gave crude products which were rechromatographed by flash chromatography. Only, this time they were left for ca. 0.5 h on the silica before elution starts; our impression is that this delay only completes the elimi-

Scheme 5. a) HCl (12 M), CH_2Cl_2/MeOH (2:1), room temp., 24 h; 65%. − b) Same as (a) but 3 d; 71%. − c) Same as (a) but 4 h; 78%. − d) Same as (a) but 3 d; 73%. − e) *t*$BuMe_2SiCl$ (1.9 equiv.), imidazole (3.9 equiv.), molecular sieves (4 Å), DMF, −78°C → 0°C, 3 h; 70%. − f) Same as (e) but 5 h; 51%. − g) Same as (e) but 24 h; 73%. − h) Same as (e) but 6 h; 48%. − i) Triflic anhydride (1.3 equiv.), pyridine (2.0 equiv.), CH_2Cl_2, −78°C → −25°C, 5 h; 63% of a 96:4 *E*-**23**/*Z*-**23** mixture. − j) Same as (i) but 4 h; 73% of a 97:3 *E*-**24**/*Z*-**24** mixture. − k) Same as (i); 81% of a 99:1 *Z*-**23**/*E*-**23** mixture. − l) Same as (i) but 4 h; 69% of a 97:3 *Z*-**24**/*E*-**24** mixture. − m) HF/Pyridine complex (23−25 equiv.), THF, 0°C, 4 h; 86% of a 94:6 **6/8** mixture. − n) Same as (m) but 5 h; 96% of a 95:5 **7/9** mixture. − o) Same as (m); 96% of a 94:6 **8/6** mixture. − p) Same as (m) but 5 h; 92% of diastereopure **9**



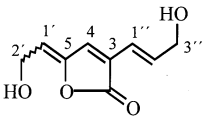
nations. They delivered the bissilylated alkylidenebutenolides *E*-**23** (63%; 96:4 mixture with the *Z* isomer), *Z*-**23** (81%; 99:1 mixture with the *E* isomer), *E*-**24** (73%; 97:3 mixture with the *Z* isomer), and *Z*-**24** (69%; 97:3 mixture with the *E* isomer). The *E*,*Z* assignment of these compounds is based upon the kind of ^{1}H-NMR evidence described for their desilylation products **6**−**9** explicitly (vide infra). Our *E*/*Z* ratios mean that the $C=C_\gamma$ forming elimination reactions exhibit *anti* selectivities of 96:4−99:1.

The sequences of Scheme 5 were terminated by removing the silyl ether protecting groups from the bis(silyl ethers) *E*-**23**, *Z*-**23**, *E*-**24**, and *Z*-**24**. Thereby, the tetrenolin-analogs

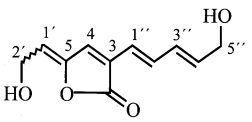
"bisnortetrenolin" (**6**) and "isotetrenolin" (**7**) and the lissoclinolide-analogs "bisnorlissoclinolide" (**8**) and "isolissoclinolide" (**9**) were obtained in 86%, 96%, 96%, and 92% yield, respectively. These compounds were a 94:6 *E*/*Z* (**6**:**8**) mixture, a 95:5 *E*/*Z* (**7**:**9** mixture), a 94:6 *Z*/*E* (**8**:**6**) mixture, and the diastereopure *Z* isomer **9**, respectively, isomer ratios stemming from suitable integrals in the 300 or 500 MHz ^{1}H-NMR spectra of these products.

Whether butenolides **6**−**9** contain *E*- or *Z*-configured C=C$_\gamma$ bonds was inferred from the chemical shifts of their protons 1′-H or 4-H: They are shifted down-field by 0.3−0.4 ppm in *E* vs. *Z* isomers (Table 1).[25] Additional distinctions might be the high-field shifts of C-4 (Δδ = −2.5 to −2.6 ppm) and C-1′ (Δδ = −0.6 ppm) and the low-field shifts of C-5 (Δδ = 2.6 ppm) and C-2′ (Δδ = 0.7 ppm) in *E* vs. *Z* isomers (Table 1). The *trans* configuration of the CH=CH bonds in the α substituents of butenolides **6**−**9** is deduced from the magnitude of the corresponding vicinal H,H coupling constants (15.1−16.1 Hz).

Table 1: Stereochemically relevant 500 MHz (**6**, **8**, **9**) or 300 MHz (**7**) ^{1}H- and 75.5 MHz (**6**, **8**, **9**) or 125.7 MHz (**7**) ^{13}C-NMR data of "bisnortetrenolin" (**6**), "isotetrenolin" (**7**), "bisnorlissoclinolid" (**8**), and "isolissoclinolid" (**9**) (CD_3OD, coupling constants in Hz)



E: **6**; *Z*: **8**



E: **7**; *Z*: **9**

	6	**8**	**7**	**9**
4-H	7.77	7.38	7.75	7.37
1′-H	5.81	5.47	5.80	5.47
$J_{4'',3''}$	−	−	15.7	15.1
$J_{2'',1''}$	16.1	16.1	15.6	15.4
C-4	133.34	136.80	132.51	135.89
C-5	151.40	149.80	151.53	149.90
C-1′	114.49	115.04	114.32	114.89
C-2′	57.86	57.15	57.88	57.18

The syntheses of Schemes 4−5 are straightforward and allow to choose the orientation of γ-substituents in γ-alkylidenebutenolides freely. They contribute to making the elimination strategy of Scheme 2 a general stereoselective synthesis of γ-alkylidenebutenolides. The underlying principles should be applicable to synthesizing tetrenolin (**4**) and lissoclinolide (**5**) as well.

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Experimental Section

All reactions were performed in oven-dried (100°C) glassware under N_2. THF was freshly distilled from K, CH_2Cl_2 from CaH_2. Products were purified by flash chromatography[24] on Merck silica gel 60 (eluents and column diameter given in brackets). Yields refer to analytically pure samples. Isomer ratios were derived from suitable ^{1}H-NMR integrals. − ^{1}H NMR tetramethylsilane (0.00 ppm), $CHCl_3$ (7.26 ppm), CHD_2OD (3.30 ppm) or HOD (4.90 ppm) as internal standard in the indicated solvent, in $CDCl_3$, CD_3OD or $D_3CS(=O)CD_3$, respectively] and ^{13}C NMR tetramethylsilane (0.00 ppm) in the indicated solvent or $CDCl_3$ (77.00) ppm) or CD_3OD (49.00 ppm) as internal standard in the same solvent]: Varian VXR 200, Bruker AMX 300, and Varian VXR 500S; integrals in accord with assignments; coupling constants in Hz. APT ^{13}C-NMR spectra: "+" for CH or CH_3, "−" for CH_2 or C_{quat}. The assignments of ^{1}H- and ^{13}C-NMR resonances refer to the IUPAC nomenclature primed numbers belonging to the side-chain(s in the order of their appearance IUPAC in the name). Combustion analyses: F. Hambloch, Institute of Organic Chemistry, University of Göttingen. − MS: G. Remberg, Institute of Organic Chemistry, University of Göttingen. − IR spectra: Perkin-Elmer 1600 Series FTIR as $CDCl_3$ solution in a NaCl cuvette or in KBr. − Optical rotations: Perkin-Elmer polarimeter 241 at 589 nm; rotational values are the average of 5 measurements of α in a given solution of the respective sample.

5-(E-2-Hydroxyethylidene)-3-(trans-3-hydroxy-1-propenyl)-2(5H)-furanone (**6**) was prepared analogously as described for **8** from alcohol *E*-**23** (96:4 mixture *E*-**23**/*Z*-**23**; 58.0 mg, 0.140 mmol) and a 2:1 (v:v) HF/pyridine mixture (580 µl, 638 mg, 3.24 mmol, 23 equiv.) as a white solid (21.5 mg, 86%, m.p. 101−104°C) which was a 94:6 mixture **6**/**8** (as determined by averaging the integral ratios over the 4-H resonances at δ = 7.77 and δ = 7.38 ppm, over the 1′-H resonances at δ = 5.81 and δ = 5.48 ppm, and over the 2′-H resonances at δ = 4.35 and δ = 4.38 ppm, respectively). − ^{1}H NMR (500 MHz, [D$_4$]methanol): δ = 4.23 (dd, $J_{3'',2''}$ = 4.8, $^4J_{3'',1''}$ = 1.8, 3′′-H$_2$), 4.35 (d, $J_{2'',1'}$ = 7.4, 2′-H$_2$), 5.81 (t, $J_{1',2'}$ = 7.4, 1′-H), 6.49 (hardly resolved dtd, J_{trans} = 16.0, $^4J_{1'',3''}$ = 1.7, $^4J_{1'',4}$ = 0.5, 1′′-H), 6.98 (dt, J_{trans} = 16.1, $J_{2'',3''}$ = 4.8, 2′′-H), 7.77 (d, $^4J_{4,1''}$ = 0.7, 4-H). − A H,H-correlation spectrum (500 MHz, [D$_4$]methanol) shows cross-peaks between the following resonances: 3′′-H$_2$ ⇔ 1′′-H and 2′′-H, 2′-H$_2$ ⇔ 1′-H. − ^{13}C NMR (75.5 MHz, [D$_4$]methanol): δ = "−" 57.86 (C-2′), "−" 63.08 (C-3′′), "+" 114.49 (C-1′), "+" 119.01 (C-1′′), "−" 130.25 (C-3), "+" 133.34 (C-4), "+" 139.76 (C-2′′), "−" 151.40 (C-5), "−" 170.08 (C-2). − A H,C-correlation spectrum (300 MHz/75.5 MHz) shows cross-peaks between the following resonances: C-2′ ⇔ 2′-H$_2$, C-3′ ⇔ 3′′-H$_2$, C-1′ ⇔ 1′-H, C-1′′ ⇔ 1′′-H, C-4 ⇔ 4-H, C-2′′ ⇔ 2′′-H. − IR ($CDCl_3$): ṽ = 3370, 3235, 1755, 1650, 1400, 1330, 1080, 1015, 960, 910 cm^{-1}. − UV (MeOH): λ_{max} (lg ε) = 298 (4.31) nm. − $C_9H_{10}O_4$ (182.2): calcd. C 59.34, H 5.53; found C 59.61, H 5.71. − The exact molecular mass *m*/*z* 182.0579±2 mDa (M^+) was confirmed by HRMS (EI, 70 eV).

5-(E-2-Hydroxyethylidene)-3-(trans,trans-5-hydroxy-1,3-pentadienyl)-2(5H)-furanone (**7**) was prepared analogously as described for **8** from alcohol *E*-**24** (97:3 mixture *E*-**24**/*Z*-**24**; 95.9 mg, 0.222 mmol) and a 2:1 (v:v) HF/pyridine mixture (1.00 ml, 1.10 g, 5.58 mmol, 25 equiv.) as a white solid (44.2 mg, 96%; m.p. 92°C) which was a 95:5 mixture **7**/**9** (as determined by averaging the integral ratios over the 1′-H resonances at δ = 5.80 and δ = 5.47 ppm). − ^{1}H NMR (300 MHz, [D$_4$]methanol): δ = 4.17 (br. d, $J_{5'',4''}$ = 5.3, 5′′-H$_2$), 4.35 (d, $J_{2',1'}$ = 7.1, 2′-H$_2$), 5.80 (t, $J_{1',2'}$ = 7.3, 1′-H), 6.08 (dt, J_{trans} = 15.5, $J_{4'',5''}$ = 5.3, 4′′-H), 6.35−6.46 [m, 1′′-H, 3′′-H; speculatively interpretable as follows: 6.39 (br. d, J_{trans} = 15.4, 1′′-H), superimposes 6.41 (ddm$_c$, J_{trans} = 15.8, $J_{3'',2''}$ = 13.2, 3′′-H)], 7.37 (dd, J_{trans} = 15.7, $J_{2'',3''}$ = 10.8, 2′′-H), 7.75 (s, 4-H). − A H,H-correlation spectrum (500 MHz, [D$_4$]methanol) shows cross-peaks between the following resonances: 5′′-H$_2$ ⇔ 4′′-H, 2′-H$_2$ ⇔ 1′-H. − ^{13}C NMR [gated-decoupled, 125.7 MHz, [D$_4$]methanol; small signals at 57.19 (C2′′), 114.91 (C-1′), 121.20 (C-1′′), 135.96 (C-4), 137.34 (C-2′′), 138.61 (C-4′′) due to the minor diastereomer **9**:]: δ = 57.88 (C-2′), 63.02 (C-5′′), 114.32 (C-1′), 121.35

(C-1′′), 130.65 (C-3), 131.16 and 137.73 (C-2′′, C-3′′), 132.51 (C-4), 138.82 (C-4′′), 151.53 (C-5), "−" 169.91 (C-2). − A H,C-correlation spectrum (300 MHz/75.5 MHz) shows cross-peaks between the following resonances: C-2′ ⇔ 2′-H_2, C-5′ ⇔ 5′′-H_2, C-1′ ⇔ 1′-H, C-1′′ ⇔ 1′′-H, C-2′′/C-3′′ ⇔ 2′′-H/3′′-H, C-4 ⇔ 4-H. − IR ($CDCl_3$): $\tilde{\nu}$ = 3355, 2925, 2865, 1770, 1665, 1650, 1615, 1420, 1175, 1065, 990 cm^{-1}. − UV (MeOH): λ_{max} (lg ε) = 316 (4.76) nm. − $C_9H_{10}O_4$ (208.2): calcd. C 63.45, H 5.81; found C 63.55, H 5.90. − The exact molecular mass *m/z* 208.0735 ± 2 mDa (M^+) was confirmed by HRMS (EI/70 eV).

5-(Z-2-Hydroxyethylidene)-3-(trans-3-hydroxy-1-propenyl)-2(5H)-furanone (**8**): The alcohol *Z*-**23** (96:4 mixture *Z*-**23**/*E*-**23**, 64.2 mg, 0.161 mmol) was dissolved in THF (5 ml) and a 2:1 (v:v) HF/pyridine mixture (640 µl, 704 mg, 3.57 mmol, 22 equiv.) was added at 0°C. A spatula tip of silica gel (Macherey-Nagel MN Kieselgel 60) was added after 4 h and the mixture was stirred for additional 5 min. The silica gel was filtered off and the solvent was removed in vacuo. Flash chromatography (1 cm, *tert*-butyl methyl ether/AcOEt, 1:1) led to a white solid (28.3 mg, 96%, m.p. 107°C) which was a 94:6 mixture **8/6** (as determined by averaging the integral ratios over the 4-H resonances at δ = 7.37 and δ = 7.75 ppm, and over the 1′-H resonances at δ = 5.47 and δ = 5.81 ppm, respectively). − ^{1}H NMR (500 MHz, [D_4]methanol): δ = 4.22 (dd, $J_{3'',2''}$ = 4.7, $^4J_{3''1''}$ = 1.5, 3′′-H_2), 4.38 (d, $J_{2',1'}$ = 7.1, 2′-H_2), 5.47 (t, $J_{1',2'}$ = 7.0, 1′-H), 6.46 (dt, J_{trans} = 16.1, $^4J_{1'',3''}$ = 1.9, 1′′-H), 6.94 (dt, J_{trans} = 16.0, $J_{2'',3''}$ = 4.9, 2′′-H), 7.38 (s, 4-H). − A H,H-correlation spectrum (500 MHz, [D_4]methanol) shows cross-peaks between the following resonances: 3′′-H_2 ⇔ 1′′-H, 3′′-H_2 ⇔ 2′′-H, 3′′-H_2 ⇔ 4-H (less intensive), and 2′-H_2 ⇔ 1′-H. − ^{13}C NMR [75.5 MHz, [D_4]methanol; small signals at "−" 57.85 (C-2′), "+" 114.50 (C-1′), "+" 118.99 (C-1′′), "+" 133.32 (C-4′), "+" 139.73 (C-2′′) due to the minor diastereomer **6**]: δ = "−" 57.15 (C-2′), "−" 63.06 (C-3′′), "+" 115.04 (C-1′), "+" 118.86 (C-1′′), "−" 129.93 (C-3), "+" 136.80 (C-4), "+" 139.29 (C-2′′), "−" 149.80 (C-5), "−" 169.88 (C-2). − A H,C-correlation spectrum (300 MHz/75.5 MHz) shows cross-peaks between the following resonances: C-2′ ⇔ 2′-H_2, C-3′′ ⇔ 3′′-H_2, C-1′ ⇔ 1′-H, C-1′′ ⇔ 1′′-H, C-4 ⇔ 4-H, C-2′′ ⇔ 2′′-H. − IR ($CDCl_3$): $\tilde{\nu}$ = 3140, 1755, 1400, 1085, 1025 cm^{-1}. − UV (MeOH): λ_{max} (lg ε) = 298.0 (4.44) nm. − $C_9H_{10}O_4$ (182.2): calcd. C 59.34, H 5.53; found C 59.44, H 5.68. − The exact molecular mass *m/z* 182.0579 ± 2 mDa (M^+) was confirmed by HRMS (EI/70 eV).

5-(Z-2-Hydroxyethylidene)-3-(trans,trans-5-hydroxy-1,3-pentadienyl)-2(5H)-furanone (**9**) was prepared analogously as described for **8** from alcohol *Z*-**24** (96:4 mixture *Z*-**24**/*E*-**24**; 49.2 mg, 0.111 mmol) and a 2:1 (v:v) HF/pyridine mixture (500 µl, 0.550 mg, 2.79 mmol, 25 equiv.) as a white solid (21.3 mg, 92%, m.p. 110°C). − ^{1}H NMR (500 MHz, [D_4]methanol): δ = 4.17 (dd, $J_{5'',4''}$ = 5.2, $^4J_{5'',3''}$ = 1.4, 5′′-H_2), 4.38 (d, $J_{2',1'}$ = 7.1, 2′-H_2), 5.47 (t, $J_{1',2'}$ = 7.1, 1′-H), 6.07 (dt, J_{trans} = 15.2, $J_{4'',5''}$ = 5.4, 4′′-H), 6.36 (br. d, J_{trans} = 15.1, 1′′-H), superimposes in parts 6.40 (ddm$_c$, J_{trans} = 14.63, $J_{3'',2''}$ = 10.8, 3′′-H), 7.33 (dd, J_{trans} = 15.8, $J_{2'',3''}$ = 11.0, 2′′-H), superimposes in parts 7.37 (s, 4-H). − A H,H-correlation spectrum (500 MHz, [D_4]methanol) shows cross-peaks between the following resonances: 5′′-H_2 ⇔ 4′′-H, 2′-H_2 ⇔ 1′-H, 2′′-H ⇔ 1′′-H/3′′-H, 3′′-H ⇔ 4′′-H and 5′′-H. − ^{13}C NMR (APT spectrum, 75.5 MHz, [D_4]methanol): δ = "−" 57.18 (C-2′), "−" 63.01 (C-5′′), "+" 114.89 (C-1′), "+" 121.16 (C-1′′), "−" 130.32 (C-3), "+" 131.15 (C-3′′), "+" 135.89 (C-4), "+" 137.29 (C-2′′), "+" 138.56 (C-4′′), "−" 149.90 (C-5), "−" 169.67 (C-2). − A H,C-correlation spectrum (300 MHz/75.5 MHz) shows cross-peaks between the following resonances: C-2′ ⇔ 2′-H_2, C-5′′ ⇔ 5′′-H_2, C-1′ ⇔ 1′-H, C-1′′ ⇔ 1′′-H, C-2′′/C-3′′ ⇔ 2′′-H/3′′-H, C-4 ⇔ 4-H. − IR ($CDCl_3$): $\tilde{\nu}$ = 3165, 1770, 1675, 1620, 1560, 1400, 1310, 1275, 1210, 1075, 1055, 1010, 985, 925, 765 cm^{-1}. − UV (MeOH): λ_{max} (lg ε) = 317.0 (4.33) nm. − $C_{11}H_{12}O_4$ (208.2): calcd. C 63.45, H 5.81; found C 63.17, H 6.01. − The exact molecular mass *m/z* 208.0735 ± 2 mD (M^+) was confirmed by HRMS (EI/70 eV).

(−)-(4′R,5S)-[5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-3-(trans-3-hydroxy-1-propenyl)-2(5H)-furanone (*ul*-**17**) was prepared analogously as described for *lk*-**17** from LiCl (1.51 g, 35.7 mmol, 3.0 equiv.), $Pd_2(dba)_3{\cdot}CHCl_3$ (238.5 mg, 0.2306 mmol, 0.02 equiv.), triphenylarsine (564.8 mg, 1.845 mmol, 0.16 equiv.), triflate *ul*-**16** (3.82 g, 11.5 mmol), and (*E*)-3-(tributylstannyl)-2-propen-1-ol (4.33 g, 12.5 mmol, 1.05 equiv.) (1.89 g, 68%) as a white solid (m.p. 41°C) which was diastereomerically pure as evidenced by the absence of the 4-H signal of *lk*-**17** at δ = 7.13. − $[\alpha]_D^{22}$ = −142 (*c* = 1.73 in CH_2Cl_2). − ^{1}H NMR (300 MHz, $CDCl_3$; contains 10 weight-% *tert*-butyl methyl ether): δ = 1.35 and 1.47 [2s, 2′-$(CH_3)_2$], 1.68 (br. s, 3′′-OH), 3.89 (ddd, $J_{4',5}$ = 8.0, $J_{4'5'\text{-H(B)}}$ = 6.1, $J_{4',5'\text{-H(A)}}$ = 3.9, 4′-H), AB signal (δ_A = 4.09, δ_B = 4.15, J_{AB} = 9.2, in addition split by $J_{A,4'}$ = 3.9, $J_{B,4'}$ = 6.1, 5′-H_2), 4.33 (ddd, $J_{3'',2''}$ = 4.7, $^4J_{3'',1''}$ = $J_{3'',OH}$ = 0.9, 3′′-H_2), 4.77 (br. d, $J_{5,4'}$ = 7.9, 5-H), 6.40 (dm$_c$, J_{trans} = 15.8, 1′′-H), 6.99 (dt, J_{trans} = 16.0, $J_{2'',3''}$ = 4.7, 2′′-H), 7.32 (hardly resolved d, $J_{4,5}$ = 1.7, 4-H). − IR ($CDCl_3$): $\tilde{\nu}$ = 3445, 3085, 2985, 2935, 1760, 1685, 1455, 1380, 1345, 1255, 1215, 1150, 1070, 1010, 970, 915, 845, 730 cm^{-1}. − $C_{12}H_{16}O_5$ (240.3): calcd. C 59.99, H 6.71; found C 59.87, H 6.99. The exact molecular mass *m/z* 240.0997 ± 2 mDa (M^+) was confirmed by HRMS (EI, 70 eV).

(−)-(4′S,5S)-[5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-3-(trans-3-hydroxy-1-propenyl)-2(5H)-furanone (*lk*-**17**): LiCl (1.70 g, 39.20 mmol, 3.0 equiv.), $Pd_2(dba)_3{\cdot}CHCl_3$ (270.3 mg, 0.2614 mmol, 0.02 equiv.), and triphenylarsine (640.0 mg, 2.092 mmol, 0.16 equiv.) were dissolved in THF (80 ml) at room temp. The triflate *lk*-**28** (4.33 g, 13.07 mmol) and (*E*)-3-(tributylstannyl)-2-propen-1-ol (4.76 g, 13.72 mmol, 1.05 equiv.) were added and the reaction mixture was stirred for 10 min. The reaction was quenched by adding H_2O (40 ml) and extracted with *tert*-butyl methyl ether (90 ml). The resulting solution was dried (Na_2SO_4/charcoal) and concentrated in vacuo. Flash chromatography (5 cm, petroleum ether → *tert*-butyl methyl ether) led to the title compound (2.44 g; 78%) as a crystalline solid (m.p. 66°C) which was diastereomerically pure as evidenced by the absence of the 4-H signal of *ul*-**17** at δ = 7.32. − $[\alpha]_D^{22}$ = −73.4 (*c* = 1.40 in CH_2Cl_2). − ^{1}H NMR (300 MHz, $CDCl_3$ contains 16 weight-% *tert*-butyl methyl ether): δ = 1.35 and 1.43 [2s, 2′-$(CH_3)_2$], 1.64 (br. s, 3′′-OH), AB signal (δ_A = 3.81, δ_B = 4.08, J_{AB} = 8.8, in addition split by $J_{A,4'}$ = 5.5, $J_{B,4'}$ = 6.8, 5′-H_2), 4.33 (br. d, $J_{3'',2''}$ = 4.5, 3′′-H_2), 4.40 (ddd, $J_{4',5'\text{-H(B)}}$ = 6.5, $J_{4',5'\text{-H(A)}}$ = 5.6, $J_{4',5}$ = 3.8, 4′-H), 5.01 (hardly structured br. m$_c$, 5-H), 6.42 (dm$_c$, J_{trans} = 16.2, 1′′-H), 7.01 (dt, J_{trans} = 16.0, $J_{2'',3''}$ = 4.7, 2′′-H), 7.13 (br. s, 4-H). − IR ($CDCl_3$): $\tilde{\nu}$ = 3420, 2985, 2925, 1755, 1375, 1260, 1215, 1155, 1070, 975 cm^{-1}. − $C_{12}H_{16}O_5$ (240.3): calcd. C 59.99, H 6.71; found C 60.03, H 6.80.

(−)-(4′R,5S)-5-(2,2-Dimethyl-1,3-dioxolane-4-yl)-3-(trans,trans-5-hydroxy-1,3-pentadienyl)-2(5H)-furanone (*ul*-**18**) was prepared analogously as described for *lk*-**17** from LiCl (1.77 g, 40.8 mmol, 3.0 equiv.), $Pd_2(dba)_3{\cdot}CHCl_3$ (281,0 mg, 0.2717 mmol, 0.02 equiv.), triphenylarsine (665.9 mg, 2.176 mmol, 0.16 equiv.), triflate *ul*-**16** (4.50 g, 13.6 mmol), and (2*E*,4*E*)-5-(tributylstannyl)-2,4-pentadien-1-ol (5.56 g, 15.0 mmol, 1.1 equiv.) as an oily compound (2.70 g, 75%) which was diastereomerically pure as evidenced by the absence of the 4-H signal of *lk*-**18** at δ = 5.01. − $[a]_D^{23}$ = −121 (*c* = 0.88 in CH_2Cl_2). − ^{1}H NMR (300 MHz, $CDCl_3$; contains 8 weight-% *tert*-butyl methyl ether): δ = 1.35 and 1.46 [2s, 2′-$(CH_3)_2$],

1.76 (br. s, 5′′-OH), 3.91 (ddd, $J_{4',5}$ = 8.9, $J_{4',5'\text{-H(B)}}$ = 5.1, $J_{4',5'\text{-H(A)}}$ = 4.2, 4′-H), AB signal (δ_A = 4.09, δ_B = 4.15, J_{AB} = 9.2, in addition split by $J_{A,4'}$ = 4.7, $J_{B,4'}$ = 6.0, 5′-H_2), 4.26 (br. d, $J_{5'',4''}$ = 6.3, 5′′-H_2), 4.79 (incompletely resolved dd, $J_{5,4'}$ = 7.6, $J_{5,4}$ = 1.1, 5-H), 6.07 (dt, J_{trans} = 15.0, $J_{4'',5''}$ = 5.2, 4′′-H), 6.25 (d, J_{trans} = 15.5 1′′-H), 6.35 (br. dd whose shoulders indicate an unresolved allylic coupling to 5′′-H, J_{trans} = 15.0, $J_{3'',2''}$ = 11.0, 3′′-H), 7.29 (d, $J_{4,5}$ = 2.2, 4-H), superimposes in part 7.33 (dd, J_{trans} = 15.9, $J_{2'',3''}$ = 10.9, 2′′-H). − IR ($CDCl_3$): $\tilde{\nu}$ = 3420, 2985, 2935, 1760, 1645, 1455, 1375, 1320, 1255, 1220, 1150, 1065, 995, 840 cm^{-1}. − $C_{14}H_{18}O_5$ (266.3): calcd. C 63.15, H 6.81; found C 63.01, H 6.66. The exact molecular mass *m/z* 266.1154 ± 2 mDa (M^+) was confirmed by HRMS (EI/70 eV).

(−)-(4′S,5S)-5-(2,2-Dimethyl-1,3-dioxolane-4-yl)-3-(trans, trans-5-hydroxy-1,3-pentadienyl)-2(5H)-furanone (*lk*-**18**) was prepared analogously as described for the preparation of compound *lk*-**17** from LiCl (1.77 g, 40.8 mmol, 3.0 equiv.), $Pd_2(dba)_3{\cdot}CHCl_3$ (281.2 mg, 0.2719 mmol, 0.02 equiv.), triphenylarsine (665.9 mg, 2.176 mmol, 0.16 equiv.), triflate *lk*-**16** (4.50 g, 13.60 mmol), and (2*E*,4*E*)-5-(tributylstannyl)-2,4-pentadien-1-ol (5.57 g, 14.96 mmol, 1.1 equiv.) as an oily compound (2.06 g, 57%) which was diastereomerically pure as evidenced by the absence of the 5-H signal of *ul*-**18** at δ = 4.79. − $[a]_D^{23}$ = −77.1 (*c* = 1.15 in CH_2Cl_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35 and 1.44 [2s, 2′-$(CH_3)_2$], 1.53 (br. s, 5′′-OH), AB signal (δ_A = 3.83, δ_B = 4.06, J_{AB} = 8.8, in addition split by $J_{A,4'}$ = 5.6, $J_{B,4'}$ = 6.8, 5′-H_2), 4.27 (br. d, $J_{5'',4''}$ = 5.3, 5′′-H_2), 4.39 (ddd, $J_{4',5'\text{-H(B)}}$ = 6.6, $J_{4',5'\text{-H(A)}}$ = 5.7, $J_{4',5}$ = 4.0, 4′-H), 5.01 (m_c, 5-H), 6.08 (dt, J_{trans} = 15.4, $J_{4'',5''}$ = 5.3, 4′′-H), 6.27 (d, J_{trans} = 15.9, 1′′-H), superimposed i. p. 6.34 (ddm_c whose shoulders indicate an unresolved allylic coupling to 5′′-H, J_{trans} = 15.3, $J_{3'',2''}$ = 10.8, 3′′-H)*, 7.11 (d, $J_{4,5}$ = 1.9, 4-H), 7.36 (dd, J_{trans} = 15.7, $J_{2'',3''}$ = 10.8, 2′′-H). − IR ($CDCl_3$): $\tilde{\nu}$ = 3415, 3145, 1750, 1635, 1620, 1400, 1270, 1210, 1065, 995 cm^{-1}. − $C_{14}H_{18}O_5$ (266.3): calcd. C 63.15, H 6.81; found C 63.34, H 6.83. The exact molecular mass *m/z* 266.1154 ±2 mDa (M^+) was confirmed by HRMS (EI/70 eV).

(−)-(1′R,5S)-5-(1,2-Dihydroxyethyl)-3-(trans-3-hydroxy-1-propenyl)-2(5H)-furanone (*ul*-**19**) was prepared analogously as described for *lk*-**19** from acetonide *ul*-**17** (1.86 g, 7.75 mmol) and 30 drops of HCl (12 M) as a solid compound (1.01 g, 65%), m.p. 112°C, which was diastereomerically pure as evidenced by the absence of the 4-H signal of *lk*-**19** at δ = 7.48. − $[\alpha]_D^{24}$ = −103 (*c* = 0.67 in MeOH). − ^{1}H NMR (300 MHz, [D_6]DMSO, [D_5]DMSO as internal standard; slightly contaminated): δ = 3.48 (d, $J_{2',1'}$ = 5.6, 2′-H_2), 3.69 (dddd, $J_{1',OH} = J_{1',5} = J_{1',2\text{-H(1)}} = J_{1',2\text{-H(2)}}$ = 5.5, 1′-H), 4.06 (br. d, $J_{3'',2''}$ = 4.1, 3′′-H_2), superimposed ap. 4.1−4.4 (m, 3 × OH), 5.07 (br. d, $J_{5,1'}$ = 3.4, 5-H), 6.30 (br. d, J_{trans} = 15.8, 1′′-H), 6.76 (dt, J_{trans} = 15.9, $J_{2'',3''}$ = 4.7, 2′′-H), 7.56 (br. s, 4-H). − IR (KBr): $\tilde{\nu}$ = 3140, 1735, 1400, 1225, 1110, 1010, 975, 925, 885, 810, 670 cm^{-1}. − $C_9H_{12}O_5$ (200.2): calcd. C 54.00, H 6.04; found C 53.82, H 6.06.

(−)-(1′S,5S)-5-(1,2-Dihydroxyethyl)-3-(trans-3-hydroxy-1-propenyl)-2(5H)-furanone (*lk*-**19**): The acetonide *lk*-**17** (2.44 g, 10.17 mmol) in CH_2Cl_2 (50 ml) and MeOH (30 ml) was treated with 30 drops of HCl (12 M) and stirred for 4 h at room temp. Evaporation of the solvent and washing of the residue with Et_2O (100 ml) and pentane (100 ml) led to a solid (m.p. 112°C) compound (1.59 g, 78%) which was diastereomerically pure as evidenced by the absence of the 4-H signal of *ul*-**19** at δ = 7.56. − $[a]_D^{21}$ = −19.9 (*c* = 1.33 in MeOH). − ^{1}H NMR (300 MHz, [D_6]DMSO, [D_5]DMSO as internal standard): δ = 3.44 (d, $J_{2',1'}$ = 6.4, 2′-H_2), 3.64 (m_c, 1′-H), 4.07 (br. d, $J_{3'',2''}$ = 4.1, 3′′-H_2), 4.83 (br. s, 2 OH), 4.99 (br. s, OH), 5.10 (br. s, 5-H), 6.29 (incompletely resolved dt, J_{trans} = 15.9, $^4J_{1'',3''}$ = 1.7, 1′′-H), 6.75 (dt, J_{trans} = 15.9, $J_{2'',3''}$ = 4.7, 2′′-H), 7.48 (br. d, $J_{4,5}$ = 1.1, 4-H). − IR (KBr): $\tilde{\nu}$ = 3175, 1740, 1400, 1100, 1070, 1030, 970 cm^{-1}. − $C_9H_{12}O_5$ (200.2): calcd. C 54.00, H 6.04; found C 54.23, H 6.23.

(−)-(1′R,5S)-[5-(1,2-Dihydroxyethyl)]-3-(trans,trans-5-hydroxy-1,3-pentadienyl)-2(5H)-furanone (*ul*-**20**) was prepared from acetonide *ul*-**18** (2.70 g, 10.2 mmol) and 25 drops of HCl (12 M) analogously as described for *lk*-**19** as a solid (m.p. 126°C) compound (1.64 g, 71%) which was diastereomerically pure as evidenced by the absence of the 4-H signal of *lk*-**20** at δ = 7.51. − $[a]_D^{21}$ = −42 (*c* = 0.42 in DMF). − ^{1}H NMR (300 MHz, [D_6]DMSO, [D_5]DMSO as internal standard; slightly contaminated): δ = 3.48 (dd, $J_{2',1'} = J_{2',2'\text{-OH}}$ = 5.5, 2′-H_2), 3.70 (tdd, $J_{1',2'} = J_{1',5} = J_{1',1'\text{-OH}}$ = 5.3, 1′-H), 4.03 (br. dd, $J_{5'',4''}$ Å $J_{5'',5''\text{-OH}}$ = 4.4, 5′′-H_2), 4.79 (t, $J_{OH,2'}$ bzw. $J_{OH,5''}$ = 5.5, 2′-OH, 5′′-OH), 5.17 (d, $J_{OH,1'}$ = 5.7, 1′-OH), 5.10 (hardly resolved dd, $J_{5,1'}$ = 4.2, $J_{5,4}$ = 1.5, 5-H), 5.99 (dt, J_{trans} = 15.2, $J_{4'',5''}$ = 5.0, 4′′-H), 6.27 (d, J_{trans} = 15.1, 1′′-H), superimposes severely 6.31 (incompletely resolved ddm_c whose shoulders indicate an unresolved allylic coupling to 5′′-H, J_{trans} = 15, $J_{3'',2''}$ = 11.5, 3′′-H), 7.18 (dd, J_{trans} = 15.4, $J_{2'',3''}$ = 10.9, 2′′-H), 7.59 (d, $J_{4,5}$ = 1.9, 4-H). − IR (KBr): $\tilde{\nu}$ = 3415, 3145, 1740, 1635, 1615, 1400, 1070, 990 cm^{-1}. − $C_{11}H_{14}O_5$ (226.08): calcd. C 58.40, H 6.24; found C 58.35, H 6.42.

(−)-(1′S,5S)-[5-(1,2-Dihydroxyethyl)]-3-(trans,trans-5-hydroxy-1,3-pentadienyl)-2(5H)-furanone (lk-**20**) was prepared analogously as described for *lk*-**19** from acetonide *lk*-**18** (2.06 g, 7.74 mmol) and 24 drops of HCl (12 M) as a solid (m.p. 126°C) compound (1.277 g, 73%). A contamination by *ul*-**20** cannot be completely excluded in view of an impurity dublet at δ = 7.59 which could be due to 4-H of *ul*-**20**. − $[a]_D^{21}$ = −73 (*c* = 0.48 in DMF). − ^{1}H NMR (300 MHz, [D_6]DMSO, [D_5]DMSO as an internal standard; slightly impure): δ = ca. 3.35 (extremely br. "s", superimposed by the H_2O peak, OH), 3.44 (m_c, $J_{2',1'}$ = 5.7, 2′-H_2), 3.65 (ddd, $J_{1',2'\text{-H(1)}}$ = 6.4, $J_{1',2'\text{-H(2)}}$ = 6.4, $J_{1',5}$ = 3.4, 1′-H), 4.04 (br. d, $J_{5'',4''}$ = 4.6, 5′′-H_2), ca. 4.5−5.2 (br. s, 2 × OH), partly superimposes 5.12 (br. s, 5-H), 5.98 (dt, J_{trans} = 15.3, $J_{4'',5''}$ = 5.0, 4′′-H), 6.27 (d, J_{trans} = 15.9, 1′′-H), superimposes 6.30 (br. dd, whose shoulders indicate an unresolved allylic coupling to 5′′-H, J_{trans} = 15.1, $J_{3'',4''}$ = 10.9, 3′′-H), 7.18 (dd, J_{trans} = 15.9, $J_{2'',3''}$ = 10.6, 2′′-H), 7.51 (d, $J_{4,5}$ = 1.9, 4-H). − IR (KBr): $\tilde{\nu}$ = 3130, 1750, 1655, 1635, 1615, 1400, 1080, 985 cm^{-1}. − $C_{11}H_{14}O_5$ (226.08): calcd. C 58.40, H 6.24; found C 58.59, H 6.52.

(−)-(1′R,5S)-5-[(1-Hydroxy-2-(tert-butyldimethylsiloxy)ethyl)]-3-[trans-(3-(tert-butyldimethylsiloxy)-1-propenyl]-2(5H)furanone (*ul*-**21**) was prepared analogously as described for *lk*-**21** from the triol *ul*-**19** (1.00 g, 5.00 mmol), imidazole (1.29 g, 19.0 mmol, 3.9 equiv.), and a 50%- solution of Me_2*t*BuSiCl in toluene (3.30 ml, 1,43 g, 9.5 mmol, 1.9 equiv.) as a yellow oil (1.50 g, 70%) becoming a waxy solid in the refrigerator (m.p. 51°C). The product was diastereomerically pure as evidenced by the absence of the 4-H signal of *lk*-**21** at δ = 7.18. − $[\alpha]_D^{24}$ = −43.6 (*c* = 1.15 in CH_2Cl_2). − ^{1}H NMR (300 MHz, $CDCl_3$; contains traces of *tert*-butyl methyl ether): δ = 0.09, 0.109 and 0.114 (3 s à 6, 3, and 3 H, respectively, 2 $SiMe_2$), 0.92 and 0.93 (2s, 2 *t*BuSi), 2.66 (d, $J_{OH,1'}$ = 7.6, 1′-OH), 3.53 (dddd, $J_{1',OH} = J_{1',5}$ = 7.7, $J_{1',2'\text{-H(A)}} = J_{1',2'\text{-H(B)}}$ = 3.7, 1′-H), extreme AB signal (δ_A = 3.83, δ_B = 3.87, J_{AB} = 10.5, in addition split by $J_{A,1'} = J_{B,1'}$ = 3.8, 2′-H_2), 4.33 (m_c, 3′′-H_2), 4.88 (br. d, $J_{5,1'}$ = 7.9, 5-H), 6.40 (hardly resolved dt, J_{trans} = 15.8, $J_{1'',3''}$ = 2.1, 1′′-H), 6.93 (dt, J_{trans} = 15.8, $J_{2'',3''}$ = 4.2, 2′′-H), 7.38 (br. s, 4-H). − IR ($CDCl_3$,): $\tilde{\nu}$ = 3450, 2995, 2930, 2885, 2855, 1765, 1470, 1385, 1255, 1130, 1010, 965, 835, 780 cm^{-1}. − $C_{21}H_{40}O_5Si_2$ (428.7): calcd. C 58.83, H 9.40; found C 58.60, H 9.25.

(+)-(1′S,5S)-5-[(1-Hydroxy-2-(tert-butyldimethylsiloxy)ethyl)]-3-[trans-(3-(tert-butyldimethylsiloxy)-1-propenyl]-2(5H)-furanone (*lk*-**21**): One spatula tip of molecular sieves (4 Å) was added to a solution of triol *lk*-**18** (1.49 g, 7.45 mmol) in DMF (50 ml) and the mixture cooled to −78°C. Addition of imidazole (1.93 g, 28.3 mmol, 3.8 equiv.) was followed by the dropwise addition of a 50% solution of $Me_2tBuSiCl$ in toluene (4.96 ml, 2.13 g, 14.1 mmol, 1.9 equiv.). The mixture was allowed to warm to 0°C and stirred for 24 h. The reaction was quenched with H_2O (50 ml) and extracted with *tert*-butyl methyl ether. The resulting solution was dried (Na_2SO_4) and concentrated in vacuo. Flash chromatography (4 cm, *tert*-butyl methyl ether/PE, 1:10) led to a yellow oil (2.32 g, 73%) which was a 98:2 mixture *lk*-**21**/*ul*-**21** (as determined by averaging the integral ratios over the 4-H resonances at 7.18 and 7.38 ppm and over the 5-H resonances at 5.06 and 4.88 ppm, respectively). It became a waxy solid in the refrigerator (m.p. 56°C). − $[\alpha]_D^{24}$ = +7.7 (*c* = 0.96 in THF). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07 and 0.09 (2 s à 3 and 9 H, respectively, 2 $SiMe_2$), 0.90 and 0.93 (2 s, 2 *t*BuSi), 2.39 (d, $J_{OH,1'}$ = 6.0, 1′-OH), extreme AB signal (δ_A = 3.68, δ_B = 3.72, J_{AB} = 10.5, in addition split by $J_{A,1'}$ = 5.5, $J_{B,1'}$ = 6.0, 2′-H_2), 3.86 (dddd, $J_{1',2'\text{-H(A)}} = J_{1',2'\text{-H(B)}} = J_{1',OH} = J_{1',5}$ = 5.2, 1′-H), 4.33 (m_c, 3′′-H_2), 5.06 (br. d, $J_{5,1'}$ = 3.8, 5-H), 6.39 (br. d, whose 4 shoulders indicate it to be a dt, J_{trans} = 15.8, 1′′-H), 6.95 (dt, J_{trans} = 15.8, $J_{2'',3''}$ = 3.8, 2′′-H), 7.18 (br. s, 4-H). − IR ($CDCl_3$): $\tilde{\nu}$ = 3435, 2930, 2860, 1760, 1465, 1255, 1115, 965, 840, 780 cm^{-1}. − $C_{21}H_{40}O_5Si_2$ (428.7): calcd. C 58.83, H 9.40; found C 58.57, H 9.15.

(−)-(1′R,5S)-5-[2-(tert-Butyldimethylsiloxy)-1-hydroxyethyl]-3-[trans,trans-5-(tert-butyldimethylsiloxy)-1,3-pentadienyl]-2(5H)-furanone (*ul*-**22**) was prepared analogously as described for *lk*-**21** from the triol *ul*-**20** (0.3003 g, 1.326 mmol), imidazole (0.3520 g, 5.1725 mmol, 3.9 equiv.), and $Me_2tBuSiCl$ (0.3900 g, 2.586 mmol, 1.95 equiv.) as an oily compound (0.307 g, 51%) which was diastereomerically pure as evidenced by the absence of the 4-H signal of *lk*-**22** at δ = 7.18. − $[\alpha]_D^{24}$ = −51.4 (*c* = 0.58 in CH_2Cl_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.08, 0.107, 0.112 (3 s , 2 $SiMe_2$), 0.916 and 0.919 (2 s, 2 *t*BuSi), 2.66 (d, $J_{OH,1'}$ = 7.5, 1′-OH), 3.52 (dddd, $J_{1',OH} = J_{1',5}$ = 7.6, $J_{1',2'\text{-H(A)}} = J_{1',2'\text{-H(B)}}$ = 3.5, 1′-H), extreme AB signal (δ_A = 3.82, δ_B = 3.88, J_{AB} = 10.2, in addition split by $J_{A,1'}$ = 3.8, $J_{B,1'}$ = 3.6, 2′-H_2), 4.28 (br. d, $J_{5'',4''}$ = 4.1, 5′′-H_2), 4.89 (hardly resolved dd, $J_{5,1'}$ = 7.7, $J_{5,4}$ = 0.9, 5-H), 6.00 (dt, J_{trans} = 15.1, $J_{4'',5'''}$ = 4.7, 4′′-H), 6.23 (d, J_{trans} = 15.8, 1′′-H), 6.33 (ddd$_c$ whose shoulders indicate an unresolved allylic coupling to 5′′-H, J_{trans} = 15.1, $J_{2'',3''}$ = 10.6, 3′′-H), 7.30 (dd, J_{trans} = 15.4, $J_{2'',3''}$ = 10.5, 2′′-H), 7.38 (d, $J_{4,5}$ = 1.9, 4-H). − IR ($CDCl_3$): $\tilde{\nu}$ = 3425, 2955, 2925, 2855, 2360, 1765, 1470, 1255, 1125, 1070, 995, 835 cm^{-1}. − $C_{23}H_{42}O_5Si_2$ (428.7): calcd. C 60.75, H 9.31; found C 60.53, H 9.27.

(−)-(1′S,5S)-5-[2-(tert-Butyldimethylsiloxy)-1-hydroxyethyl]-3-[trans,trans-5-(tert-butyldimethylsiloxy)-1,3-pentadienyl]-2(5H)-furanone (*lk*-**22**) was prepared analogously as described for *lk*-**21** from the triol *lk*-**20** (1.11 g, 4.91 mmol), imidazole (1.27 g, 18.7 mmol, 3.8 equiv.), and a 50% solution of $Me_2tBuSiCl$ in toluene (3.30 ml, 1.41 g, 9.32 mmol, 1.90 equiv.) as an oily compound (1.00 g, 48%) which was diastereomerically pure as evidenced by the absence of the 4-H signal of *ul*-**22** at δ = 7.38. − $[\alpha]_D^{24}$ = −8.19 (*c* = 3.82 in CH_2Cl_2). − ^{1}H NMR (300 MHz, $CDCl_3$; contains an impurity singulet at δ = 0.915 and traces of *tert*-butyl methyl ether): δ = 0.07, 0.08 and 0.10 (3 s à 3, 6, and 3 H, respectively, 2 $SiMe_2$), 0.90 and 0.92 (2 s, 2 *t*BuSi), 2.41 (d, $J_{OH,1'}$ = 6.0, 1′-OH), extreme AB signal (δ_A = 3.68, δ_B = 3.72, J_{AB} = 10.5, in addition split by $J_{A,1'}$ = 5.5, $J_{B,1'}$ = 5.7, 2′-H_2), 3.87 (dddd, $J_{1',OH} = J_{1',5}$ = 7.6 Å $J_{1',2'\text{-H(A)}} = J_{1',2'\text{-H(B)}}$ = 5.3, 1′-H), 4.28 (br. d, $J_{5'',4''}$ = 4.2, 5′′-H_2), 5.09 (br. d, $J_{5,1'}$ = 3.6, 5-H), 6.00 (dt, J_{trans} = 15.1, $J_{4'''5''}$ = 4.7, 4′′-H), 6.22 (d, J_{trans} = 15.5, 1′′-H), 6.32 (br. dd whose shoulders indicate an unresolved allylic coupling to 5′′-H, J_{trans} = 15.1, $J_{3'',2''}$ = 11.0, 3′′-H), 7.18 (d, $J_{4,5}$ = 1.9, 4-H), 7.31 (dd, J_{trans} = 15.9, $J_{2'',3''}$ = 11.1, 2′′-H). − IR ($CDCl_3$): $\tilde{\nu}$ = 3415, 2955, 2930, 2855, 1760, 1470, 1255, 1085, 835, 780 cm^{-1}. − $C_{23}H_{42}O_5Si_2$ (454.8): calcd. C 60.75, H 9.31; found C 60.53, H 9.27.

5-[Z-2-(tert-Butyldimethylsiloxy)ethylidene]-3-[3-trans-(tert-butyldimethylsiloxy)-1-propenyl]-2(5H)-furanone (*Z*-**23**): The alcohol *lk*-**21** (diastereomerically pure; 400 mg, 935 mmol) was dissolved in CH_2Cl_2 (30 ml) at −78°C. Addition of pyridine (151 µl, 148 g, 1.87 mmol, 2.0 equiv.) was followed by slow addition of Tf_2O (199 µl, 338 mg, 1.22 mmol, 1.3 equiv.) and stirring of the reaction mixture for 5 h. TLC indicated that the elimination of the triflate started slowly. The pyridine was removed by passing the unchanged reaction mixture through a silicagel column (4 cm, CH_2Cl_2). The elimination was completed on a second silica gel column (4 cm, *tert*-butyl methyl ether/PE, 1:10) by leaving the crude product on it for 30 min before elution to a yellow oil (310.5 mg, 81%) which was a 99:1 mixture *Z*-**23**/*E*-**23** (as determined by averaging the integral ratios over the 1′-H resonances at 5.33 and 5.75 ppm and over the 2′-H_2 resonances at 4.54 and 4.45, respectively). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.090 and 0.093 (2 s, 2 $SiMe_2$), 0.91 and 0.93 (2 s, 2 *t*BuSi), 4.35 (dd, $J_{3'',2''}$ = 3.8, $^4J_{3'',1''}$ = 2.3, 3′′-H_2), 4.54 (d, $J_{2',1'}$ = 6.4, 2′-H_2), 5.33 (t, $J_{1',2'}$ = 6.8, 1′-H), 6.44 (dt, J_{trans} = 15.8, $^4J_{1'',3''}$ = 2.1, 1′′-H), 6.98 (dt, J_{trans} = 15.8, $J_{2'',3''}$ = 4.1, 2′′-H), slightly superimposed by 7.02 (s, 4-H). − IR ($CDCl_3$): $\tilde{\nu}$ = 2955, 2930, 2855, 1775, 1470, 1380, 1255, 1130, 835, 780 cm^{-1}. − $C_{21}H_{38}O_4Si_2$ (428.7): calcd. C 61.41, H 9.33; found C 61.15, H 9.18. − The exact molecular mass *m/z* 410.2308±2 mDa (M^+) was confirmed by HRMS (EI, 70 eV).

5-[E-2-(tert-Butyldimethylsiloxy)ethylidene]-3-[3-trans-(tert-butyldimethylsiloxy)-1-propenyl]-2(5H)-furanone (*E*-**23**) was prepared analogously as described for *Z*-**23** from alcohol *ul*-**21** (400 mg, 935 mmol), pyridine (150 µl, 148 mg, 1.87 mmol, 2.0 equiv.), and Tf_2O (199 µl, 343 mg, 1.22 mmol, 1.3 equiv.) as an oil (241.5 mg, 63%) which was a 96:4 mixture of *E*-**23**/*Z*-**23** (as determined by averaging the integral ratios over the 1′-H resonances at 5.75 and 5.33 ppm and over the 2′-H_2 resonances at 4.45 and 4.54, respectively). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.09 and 0.11 (2 s, 2 $SiMe_2$), 0.92 and 0.93 (2 s, 2 *t*BuSi), 4.36 (dd, $J_{3'',2''}$ = 3.7, $^4J_{3'',1''}$ = 1.9, 3′′-H_2), 4.45 (d, $J_{2',1'}$ = 6.4, 2′-H_2), 5.75 (t, $J_{1',2'}$ = 6.4, 1′-H), 6.46 (dt, J_{trans} = 15.6, $^4J_{1'',3''}$ = 2.0, 1′′-H), 7.00 (dt, J_{trans} = 15.7, $J_{2'',3''}$ = 4.0, 2′′-H), 7.45 (s, 4-H). − IR ($CDCl_3$): $\tilde{\nu}$ = 2930, 2850, 1770, 1650, 1455, 1250, 1100, 835 cm^{-1}. − $C_{21}H_{38}O_4Si_2$ (428.7): calcd. C 61.41, H 9.33; found C 61.21, H 9.11. − The exact molecular mass *m/z* 410.2308 ±2 (M^+) was confirned by HRMS (EI/70 eV).

5-[Z-2-(tert-Butyldimethylsiloxy)ethylidene]-3-[trans,trans-5-(tert-butyldimethylsiloxy)-1,3-pentadienyl)-2(5H)-furanone (*Z*-**24**) was prepared analogously as described for *Z*-**23** from alcohol *lk*-**22** (300 mg, 0.661 mmol), pyridine (107 µl, 104 mg, 1.32 mmol, 2.0 equiv.), and Tf_2O (141 µl, 242 mg, 0.858 mmol, 1.3 equiv.) as a yellow oil (198.6 mg, 69%), which was a 97:3 mixture *Z*-**24**/*E*-**24** (as determined by averaging the integral ratios over the 4-H resonances at 7.02 and 7.44 ppm, over the 1′-H resonances at 5.34 and 5.74 ppm, and over the 2′-H_2 resonances at 4.54 and 4.45 respectively). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.08 and 0.09 (2 s, 2 $SiMe_2$), 0.91 and 0.93 (2 s, 2 *t*BuSi), 4.29 (br. d, $J_{5'',4''}$ = 4.2, 5′′-H_2), 4.54 (d, $J_{2',1'}$ = 6.8, 2′-H_2), 5.34 (t, $J_{1',2'}$ = 6.6, 1′-H), 6.04 (dt, J_{trans} = 15.2, $J_{4'',5''}$ = 4.6, 4′′-H), 6.28 (d, J_{trans} = 15.8, 1′′-H), superimposes 6.36 (ddm$_c$ whose shoulders indicate an unre-

solved allylic coupling to 5′′-H J_{trans} = 15.1, $J_{3'',2''}$ = 11.0, 3′′-H), 7.02 (s, 4-H), 7.35 (dd, J_{trans} = 15.8, $J_{2'',3''}$ = 10.9, 2′′-H). − IR ($CDCl_3$): $\tilde{\nu}$ = 2955, 2930, 2855, 1775, 1460, 1380, 1255, 1100, 1045, 995, 840 cm^{-1}. − $C_{23}H_{40}O_4Si_2$ (436.7): calcd. C 63.25, H 9.23; found C 63.04, H 9.22. − The exact molecular mass *m/z* 436.2465±2 mDa (M^+) was confirmed by HRMS (EI, 70 eV).

5-[E-2-(tert-Butyldimethylsiloxy)ethylidene]-3-[trans,trans-5-(tert-butyldimethylsiloxy)-1,3-pentadienyl]-2(5H)-furanone (*E*-**24**) was prepared analogously as described for *Z*-**23** from alcohol *lk*-**22** (570.0 mg, 1.255 mmol), pyridine (203 µl, 199 mg, 2.51 mmol, 2.0 equiv.), and Tf_2O (268 µl, 461 mg, 1.63 mmol, 1.3 equiv.) as a yellow oil (402.7 mg, 73%) which was a 97:3 mixture of *E*-**24**/*Z*-**24** (as determined by averaging the integral ratios over the 4-H resonances at 7.02 and 7.44 ppm, over the 1′-H resonances at 5.74, and 5.35 ppm, and over the 2′-H_2 resonances at 4.45 and 4.54, respectively). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.09 and 0.11 (2 s, 2 $SiMe_2$), 0.93 (s, 2 *t*BuSi), 4.29 (br. d, $J_{5'',4''}$ = 4.1, 5′′-H_2), 4.45 (d, $J_{2',1'}$ = 6.8, 2′-H_2), 5.74 (t, $J_{1',2'}$ = 6.6, 1′-H), 6.05 (dt, J_{trans} = 15.0, $J_{4'',5''}$ = 4.7, 4′′-H), 6.29 (d, J_{trans} = 15.5, 1′′-H), superimposes in part 6.36 (ddm_c whose shoulders indicate an unresolved allylic coupling to 5′′-H, J_{trans} = 15.2, $J_{3'',2''}$ = 11.1, 3′′-H), 7.37 (dd, J_{trans} = 15.4, $J_{2'',3''}$ = 10.9, 2′′-H), one branch is superimposed by 7.44 (s, 4-H). − IR ($CDCl_3$): $\tilde{\nu}$ = 2955, 2930, 2885, 2855, 1770, 1610, 1470, 1385, 1255, 1125, 1065, 995, 835, 780 cm^{-1}. − $C_{23}H_{40}O_4Si_2$ (436.7): calcd. C 63.25, H 9.23; found C 63.20, H 9.31. − The exact molecular mass *m/z* 436.2465±2 mDa (M^+) was confirmed by HRMS (EI/70 eV).

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