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Synthesis of γ-Alkylidenebutenolides by Formal [3+2] Cyclizations of 1,5- and 2,4-Bis(trimethylsilyloxy)-1,3,5-hexatrienes with Oxalyl Chloride

Ilia Freifeld,[a] Gopal Bose,[a] Tobias Eckardt,[b] and Peter Langer*[c,d]

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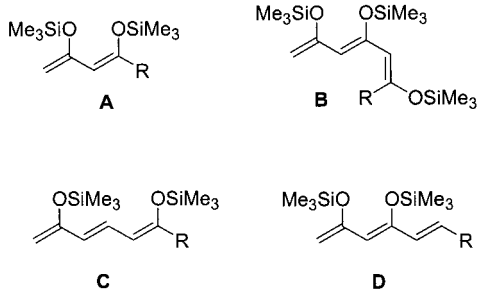
Lewis acid-catalyzed cyclizations of 1,5-bis(trimethylsilyloxy)-1,3,5-hexatrienes and 1,3,5-tris(trimethylsilyloxy)-1,3,5-hexatrienes with oxalyl chloride resulted in the formation of polyunsaturated γ-alkylidenebutenolides, while the cyclization of a 2,4-bis(trimethylsilyloxy)-1,3,5-hexatriene with oxalyl chloride afforded a γ-(2-oxobut-3-en-1-ylidene)butenolide, permitting a formal synthesis of the natural product lucidone.

Introduction

1,3-Bis-silyl enol ethers represent important synthetic building blocks that have been used in a variety of synthetic transformations, including one-pot cyclizations,[1] while reactions between the 1,3,5-tris-silyl enol ether **B** (R = OMe) and acid chlorides have been reported to result in [5+1] cyclizations.[2] Some years ago, we reported the first synthesis of the 1,5-bis(trimethylsilyloxy)-1,3,5-hexatrienes **C**, which can be regarded as vinylogous bis-silyl enol ethers,[3] while recently we have reported a formal synthesis of the acylcyclopentenediones linderone and lucidone based on cyclization reactions of the 2,4-bis(trimethylsilyloxy)-1,3,5-hexatrienes **D**.[4] Here we wish to report full details of the synthesis of silyl enol ethers **B**, **C**, and **D** and their cyclizations with oxalyl chloride.



[a] Institut für Biochemie, Universität Greifswald, Soldmannstr. 16, 17487 Greifswald, Germany
[b] Institut für Organische Chemie, Georg-August-Universität Göttingen, Tammannstr. 2, 37077 Göttingen, Germany
[c] Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, 18059 Rostock, Germany
Fax: +381-4986412
E-mail: peter.langer@uni-rostock.de
[d] Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany
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1,5-Bis(trimethylsilyloxy)-1,3,5-hexatrienes

1,5-Bis(trimethylsilyloxy)-1,3,5-hexatrienes were prepared as follows. The acetals **1a**–**e** were prepared from the corresponding β-keto esters (Scheme 1, Table 1); reduction of the ester groups afforded the alcohols **2a**–**e**, which were oxidized to the aldehydes **3a**–**e** by use of the Swern reaction. Subsequent Wittig treatment of **3a**–**e** with the corresponding phosphoranes afforded **4a**–**e**. Cleavage of the acetal groups then gave the 1,5-keto esters **5a**–**e**,[5] which were transformed into **6a**–**e** by treatment with Me_3SiCl/NEt_3. Deprotonation of **6a**–**e** with LDA/HMPA at –78 °C and subsequent addition of Me_3SiCl afforded the 1,5-bis(trimethylsilyloxy)-1,3,5-hexatrienes **7a**–**e**. The use of HMPA (1.0 equiv.) proved to be essential. The synthesis of **7a**–**c** and **7e** required the use of a spiroketal protective group. In the case of **7d**, all attempts to cleave the spiroketal resulted in decomposition of the molecule, a problem eventually solved through the preparation of a dimethyl acetal.

Treatment of the 1,5-bis(trimethylsilyloxy)-1,3,5-hexatrienes **7a**–**d** with oxalyl chloride in the presence of 0.5 equiv. of Me_3SiOTf afforded the γ-(4-oxobut-2-en-1-ylidene)butenolides **8a**–**d** (Scheme 1, Table 1). Like the cyclization of 1,3-bis-silyl enol ethers **A** with oxalyl chloride, the cyclization proceeds through the terminal carbon atom and the neighboring oxygen atom of the silyl enol ether. In the cases of butenolides **8a**, **8b**, and **8d** the products containing (*Z*)-configured exocyclic double bonds were formed selectively, due to the steric influence of the substituent R^1. The configurations of the products were determined by spectroscopic methods.[3,6]

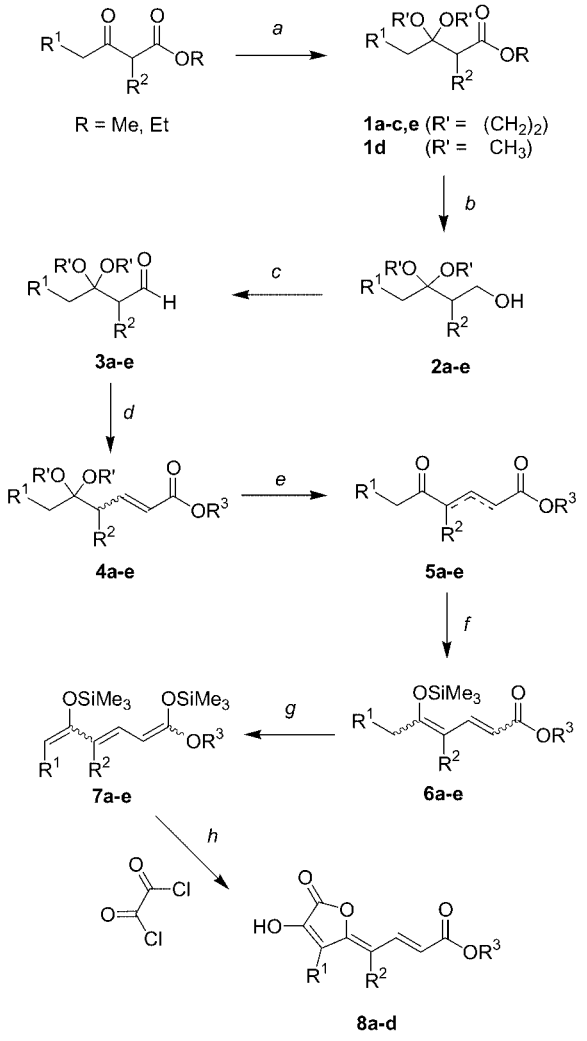
1-Methoxy-1,3,5-tris(trimethylsilyloxy)-1,3,5-hexatriene

The Me_3SiOTf-catalyzed cyclization of the 1,3,5-tris(trimethylsilyloxy)-1,3,5-hexatriene **9** with oxalyl chloride was

Table 1. Synthesis of γ-[3-(alkoxycarbonyl)prop-3-enylidene]butenolides **8a**–**d**.

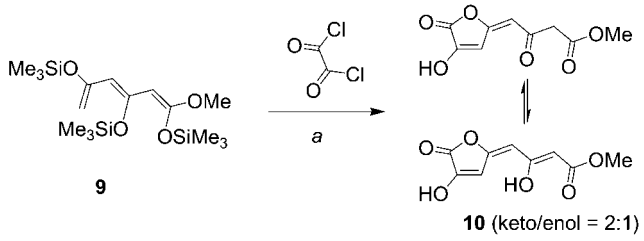
1–7	R^1	R^2	R^3	% (**1**)[a]	% (**2**)[a]	% (**3**)[a]	% (**4**)[a]	% (**5**)[a]	% (**6**)[a]	% (**7**)[a]	% (**8**)[a]	(*Z*)/(*E*)[b]
a	Me	H	Me	77	32	93	60	81	98	91	55	> 98:2
b	Et	H	Et	82	84	92	42	84	77	95	41	> 98:2
c	H	H	Me			74	62	59	70	98	50	2:1
d	OMe	H	Et	62	60	78	72	95	81	70	32	10:1
e	–$(CH_2)_3$–		Et		73	85	68	81	80	95	0	–

[a] Isolated yield. [b] By ^{1}H NMR of the products.

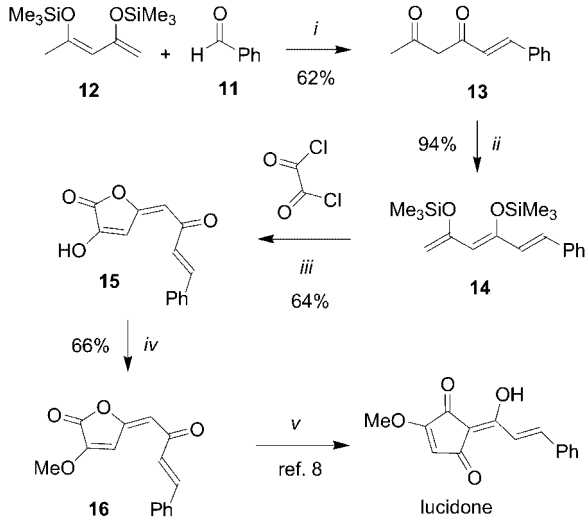


Scheme 1. Synthesis of 1,5-bis(trimethylsilyloxy)-1,3,5-hexatrienes **7a**–**e** and butenolides **8a**–**d**. *a*) **1a**–**c**,**e**: $(CH_2OH)_2$, *p*TosOH, toluene, Dean–Stark trap, reflux, 12 h, 77–80%; **1d**: $(MeO)_3CH$, Amberlist IR-120$^+$, 20 °C, 62%. *b*) $(i\text{Bu})_2\text{AlH}$, CH_2Cl_2, –78→20 °C, 2 h, 20°, 1 h, 60–92%. *c*) Oxalyl chloride, DMSO, NEt_3, –78→20 °C, 78–95%. *d*) $Ph_3P{=}CHCO_2R^3$, THF, 20 °C, 1 h, 42–72%. *e*) **5a**–**c**,**e**: *p*TsOH, acetone, reflux, 12 h, 65–84%; **5d**: TFA, CH_2Cl_2, 95%. *f*) Me_3SiCl, NEt_3, C_6H_6, 20 °C, 24 h, 77–98%. *g*) 1) 1.5 equiv. LDA, HMPA, THF, –78 °C, 1 h, 2) Me_3SiCl, –78→20 °C, 4 h, 70–93%. *h*) Oxalyl chloride, 0.5 equiv. Me_3SiOTf, CH_2Cl_2, –78→20 °C.

studied next, and afforded the γ-(2,4-dioxobut-1-ylidene)-butenolide **10** as a 2:1 mixture of keto and enol tautomers (in [D_6]acetone) (Scheme 2). The product was again formed by cyclization via the terminal carbon and the neighboring oxygen atom of the silyl enol ether. Butenolides **10** and **8c** contain no substituent at carbon atom C-4 of the butenolide and, notably, butenolide **10** (in contrast to **8c**) was formed with excellent (*E*) diastereoselectivity. Likewise, the cyclization of 1,3-bis-silyl enol ethers **A** with oxalyl chloride has been reported to give γ-(2-oxoeth-1-ylidene)butenolides with very (*E*) diastereoselectivity. The selective formation of **10** can be explained by the presence of the additional carbonyl group located at the exocyclic double bond, which is essential for observation of good (*E*)/(*Z*) diastereoselectivity.



Scheme 2. Synthesis of γ-(2,4-dioxobut-1-ylidene)butenolide **10**. *a*) Oxalyl chloride, Me_3SiOTf (0.3 equiv.), CH_2Cl_2, –78→20 °C, 12 h, 55%.



Scheme 3. Formal synthesis of lucidone: *i*) $TiCl_4$ (1.0 equiv.), CH_2Cl_2, –78→20 °C. *ii*) Me_3SiOTf (2.0 equiv.), NEt_3, Et_2O, 0→20 °C. *iii*) Oxalyl chloride, Me_3SiOTf (0.5 equiv.), CH_2Cl_2, –78→20 °C. *iv*) Me_2SO_4, K_2CO_3, acetone, 20 °C. *v*) NaOMe, MeOH (ref.[8]).

2,4-Bis(trimethylsilyloxy)-1,3,5-hexatrienes

The 2,4-bis(trimethylsilyloxy)-1,3,5-hexatriene **14** was prepared by silylation of the 1,3-diketone **13**, available by condensation of the 1,3-bis-silyl enol ether **12** with benzaldehyde (Scheme 3). The Me_3SiOTf-catalyzed cyclization of **14** with oxalyl chloride afforded the (*E*)-configured γ-(2-oxobut-3-en-1-ylidene)butenolide **15**, the (*E*) configuration of the exocyclic double bond of **15** being established by comparison of the spectroscopic data with those reported in the literature.[7] Methylation of **15** (Me_2SO_4/K_2CO_3, acetone) afforded **16**, which had previously been transformed into the natural acylcyclopentenedione lucidone by treatment with NaOMe/MeOH.[8]

The synthetic precursor **16** of lucidone was prepared from **13** via **14** in four steps and in 25% overall yield, which compares well with known syntheses.[7,8]

Conclusion

In summary, we report the synthesis of 1,5-bis(trimethylsilyloxy)-1,3,5-hexatrienes, 1,3,5-tris(trimethylsilyloxy)-1,3,5-hexatrienes, and 2,4-bis(trimethylsilyloxy)-1,3,5-hexatrienes and their cyclization with oxalyl chloride.

Experimental Section

General Comments: All solvents were dried by standard methods and all reactions were carried out under inert atmosphere. For ^1H and ^{13}C NMR spectra, the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (70 eV), chemical ionization (CI, H_2O), or electrospray ionization (ESI). For preparative scale chromatography, silica gel (60–200 mesh) was used. Melting points are uncorrected.

Methyl 2-(2-Ethyl-1,3-dioxolan-2-yl)acetate (1a):[9] A toluene solution (100 mL) of methyl 3-oxopentanoate (15.0 g, 0.115 mol), ethane-1,2-diol (14.3 g, 0.230 mol), and *p*-toluenesulfonic acid monohydrate (0.3 g) was stirred for 14 h under a Dean–Stark trap. $NaHCO_3$ (5%, 50 mL) was added to the cooled solution, the aqueous and the organic layer were separated, and the latter layer was dried (Na_2SO_4). The solution was filtered, the solvent was removed from the filtrate in vacuo, and the residue was distilled in vacuo (bp. 110 °C/20 Torr) to give **1a** as a colorless liquid (15.5 g, 77%). The spectroscopic data are identical with those reported.[9] ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.95 (t, J = 7 Hz, 3 H, CH_3), 1.83 (q, J = 7 Hz, 2 H, CH_3CH_2), 2.66 (s, 2 H, CH_2), 3.69 (s, 3 H, OCH_3), 3.98 [m, 4 H, $O(CH_2)_2O$] ppm.

2-(2-Ethyl-1,3-dioxolan-2-yl)ethanal (3a):[10] DiBAlH (21 mL, 1 M solution in toluene) was slowly added at –78 °C to a dichloromethane solution (40 mL) of **1a** (5.0 g, 0.029 mol) and the mixture was stirred for 1 h. Water (50 mL) was slowly added, the mixture was allowed to warm to 20 °C, and an aqueous solution of HCl (4 M, 40 mL) was slowly added. The organic and the aqueous layer were separated, the latter was extracted with dichloromethane (2 × 30 mL), the combined organic layers were dried (Na_2SO_4) and filtered, and the filtrate was concentrated in vacuo to give a 1:1 mixture of **3a** (1.38 g, 32%) and **2a**. **2a**:[9] ^1H NMR ($CDCl_3$, 200 MHz): δ = 0.95 (t, J = 7 Hz, 3 H, CH_3), 1.67 (q, J = 7 Hz, 2 H, CH_3CH_2), 1.93 (t, J = 4 Hz, 2 H, CH_2CH_2OH), 3.75 (t, J = 4 Hz, 2 H, CH_2CH_2OH), 3.98 [m, 4 H, $O(CH_2)_2O$] ppm.

Transformation of 2a into 3a: A dichloromethane solution (15 mL) of oxalyl chloride (1.186 g, 0.0094 mol) was added at –78 °C to a dichloromethane solution (3 mL) of DMSO (1.60 g, 0.02 mol). After this system had been stirred for 10 min, a dichloromethane solution (5 mL) of **2a** (1.25 g, 8.55 mmol) was added. After this system had in turn been stirred for 15 min, triethylamine (4.3 g, 43 mmol) was slowly added and the solution was allowed to warm to 20 °C over 30 min. Water (20 mL) was added, the solution was stirred for 20 min, the organic and the aqueous layer were separated, and the latter was extracted with dichloromethane (50 mL). The combined organic layers were then washed with an aqueous solution of HCl (10%, 30 mL), with H_2O (30 mL), with a dilute aqueous solution of Na_2CO_3 (30 mL), and with H_2O (30 mL), the solution was dried (Na_2SO_4) and filtered, and the filtrate was concentrated in vacuo to give **3a** as a yellow liquid (1.15 g, 93%). The spectroscopic data are identical with those reported.[10] **3a**: ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.97 (t, J = 7 Hz, 3 H, CH_3), 1.71 (q, J = 7 Hz, 2 H, CH_3CH_2), 2.68 (m, 2 H, CH_2), 3.98 [m, 4 H, $O(CH_2)_2O$], 9.72 (t, 1 H, OCH) ppm.

Methyl 4-(2-Ethyl-1,3-dioxolan-2-yl)-2-butenoate (4a): $Ph_3P{=}CHCO_2Me$ (3.85 g, 11.5 mmol) was added to a THF solution (10 mL) of **3a** (1.66 g, 11.5 mmol) and the solution was stirred for 2 h at 20 °C. The solvent was removed in vacuo and the residue was purified by chromatography (silica gel, ether/petroleum ether 1:3) to give **4a** as a yellow liquid (1.39 g, 60%). ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.92 (t, J = 7 Hz, 3 H, CH_3), 1.66 (q, J = 7 Hz, 2 H, CH_2CH_3), 2.53 (d, J = 8 Hz, 2 H, CH_2), 3.62 (s, 3 H, OCH_3), 3.96 [s, 4 H, $O(CH_2)_2O$], 5.88 (d, J = 15 Hz, 1 H, C*H*COOMe), 6.93 (dt, J = 15 Hz, J = 8 Hz, 1 H, C*H*CHCOOMe) ppm.

Methyl (*E*)-5-Oxohept-2-enoate and Methyl (*E*)-5-Oxohept-3-enoate (5a): An acetone solution (35 mL) of **4a** (1.5 g, 7.5 mmol) and *p*TsOH·H_2O (120 mg) was stirred under reflux for 12 h. $NaHCO_3$ (9 g) was added to the solution at 20 °C and the suspension was vigorously stirred for 20 min. The suspension was filtered and the filtrate was concentrated in vacuo to give **5a** as a yellow liquid (0.95 g, 81%, 1:1 mixture of positional isomers). ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.06, 1.09 (2 × t, J = 7 Hz, 1 × 1.5 H, CH_3), 2.49, 2.59 (2 × q, J = 7 Hz, 2 × 1 H, CH_2), 3.24, 3.33 (2 × d, J = 7 Hz, 2 × 1 H, H-4), 3.72 (s, 3 H, OCH_3), 5.87, 6.17 (2 × d, J = 16 Hz, 2 × 0.5 H, H-2), 6.86, 7.03 (2 × dt, J = 16 Hz, J = 7 Hz, 2 × 0.5 H, H-3) ppm.

Methyl 5-(Trimethylsilyloxy)hepta-2,4-dienoate (6a): Triethylamine (0.68 g, 6.7 mmol) and Me_3SiCl (0.73 g, 6.7 mmol) were added to a benzene solution (25 mL) of **5a** (0.70 g, 4.49 mmol) and the reaction mixture was stirred for 2 d at 20 °C under inert atmosphere (N_2). The solution was filtered and the filtrate was concentrated in vacuo to give **6a** as a brownish oil (0.97 mg, 98%). ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.27 [s, 9 H, $Si(CH_3)_3$], 1.09 (m, 3 H, CH_3), 2.17 (q, J = 7 Hz, 2 H, CH_2), 3.73 (s, 3 H, OCH_3), 5.24 (d, J = 12 Hz, 1 H, C*H*COOMe), 5.68 (d, J = 15 Hz, 1 H, TMSOCC*H*), 7.59 (dd, J = 15 Hz, J = 12 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 0.6 [$(CH_3)_3$], 11.2 (CH_3), 30.0 (CH_2), 51.1 (OCH_3), 106.7 (C-2), 114.9 (C-4), 140.4 (C-3), 163.1, 168.2 (C) ppm.

1-Methoxy-1,5-bis(trimethylsilyloxy)hepta-1,3,5-triene (7a): *n*BuLi (0.63 mL, 15% solution in *n*-hexane) and HMPA (0.17 g, 0.95 mmol) were added at 0 °C to a THF solution (5 mL) of diisopropylamine (0.098 g, 0.97 mmol) and the solution was stirred for 15 min. Compound **6a** (150 mg, 0.66 mmol) was added to the solution at –78 °C and the system was stirred at –78 °C for 1.5 h. Chlorotrimethylsilane (0.127 g, 1.17 mmol) was added and the solution was allowed to warm to 20 °C over 3 h, the solvent was removed in vacuo, and *n*-pentane was added to the residue. The suspension

was filtered under inert atmosphere (N_2) and the solvent was removed from the filtrate in vacuo to give **7a** as a brownish oil (0.18 g, 91%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.19 [m, 18 H, 2 × Si(CH_3)$_3$], 1.64 (d, J = 6 Hz, 3 H, CH_3), 3.14 (m, 1 H, C*H*CH_3), 3.68 (s, 3 H, OCH_3), 4.85 (m, 1 H, C*H*COMe), 5.97 [m, 1 H, C(OTMS)C*H*], 6.32 (d, J = 12 Hz, 1 H, CH) ppm.

(5*Z*)-3-Hydroxy-5-[(2*E*)-3-methoxycarbonyl-prop-2-enylidene]-4-methyl-2(5*H*)-furanone (8a): Oxalyl chloride (0.08 g, 0.62 mmol) and TMSOTf (0.07 g, 0.31 mmol) were added at –78 °C to a dichloromethane solution (10 mL) of **7a** (0.15 g, 0.50 mmol) and the mixture was allowed to warm to 20 °C over 12 h. The solution was extracted with brine (20 mL) and aqueous HCl (10%, 20 mL), the aqueous layer was extracted with dichloromethane (2 × 20 mL), the combined organic layers were dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, ether/petroleum ether 1:2→2:1) to give **8a** as a yellow solid (58 mg, 55%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.03 (s, 3 H, CH_3), 3.78 (s, 3 H, OCH_3), 5.81 (d, J = 12 Hz, 1 H, 1′-H), 6.00 (d, J = 14 Hz, 1 H, 3′-H), 7.76 (dd, J = 14 Hz, J = 12 Hz, 1 H, 2′-H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 7.2 (CH_3), 52.8 (OCH_3), 105.5 (C-1′), 120.9 (C), 122.2 (C-3′), 136.2 (C-2′), 141.9, 152.6, 164.4, 166.9 (C) ppm. MS (EI, 70 eV): m/z (%) = 210 [M]$^+$ (66), 179 (43), 95 (100), 83 (43), 57 (40). The exact molecular mass for $C_{11}H_{12}O_5$ m/z = 210.0528 ± 2 ppm (M^+) was confirmed by HRMS (70 eV, EI).

(5*E*)-5-[1-(Methoxycarbonyl)-2-oxopropylidene]-3-hydroxy-2-furanone (10): TMSOTf (0.5 mmol, 0.09 mL) was added at –78 °C to a CH_2Cl_2 solution (20 mL) of oxalyl chloride (1.5 mmol, 0.13 mL) and **9** (1.5 mmol, 0.65 g). The solution was allowed to warm to 20 °C over 6 h. After the system had been stirred for 3 h at 20 °C, a saturated aqueous solution of NaCl (100 mL) was added, the organic and the aqueous layer were separated, the latter was extracted with diethyl ether (4 × 100 mL), the combined organic layers were dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel) to give **10** (174 mg, 55%) as a yellow solid. ^{1}H NMR ([D_6]acetone, 250 MHz, keto/enol 1:3): δ = 3.62 (s, 2 H, keto, CH_2, 3′-H), 3.64 (s, 3 H, enol, OCH_3), 3.72 (3 H, keto, OCH_3), 5.33 (s, 1 H, enol, CH, 3′-H), 5.85 (s, 1 H, keto, CH, 1′-H), 6.14 (s, 1 H, enol, 3′-H), 7.02 and 7.04 (2 × s, 1 H, keto, 1 H, enol, 4-H), 12.21 (br., 1 H, OH) ppm. ^{13}C NMR ([D_6]acetone, 50 MHz): δ_C = 50.8 (CH_2), 51.8, 52.2 (OCH_3), 94.2, 103.7, 104.4, 108.9, 110.2 (CH, C-4, C-1′, C-3′, keto, enol), 149.1, 152.3, 154.9, 160.4, 161.4, 164.3, 168.3, 169.7, 173.9 (C), 192.5 (C-2′, keto). MS (70 eV, EI): m/z (%) = 212 [M]$^+$ (48), 194 (8), 181 (8), 156 (26), 139 (100). The exact molecular mass for $C_9H_8O_6$ m/z = 212.0321 ± 2 ppm (M^+) was confirmed by HRMS (70 eV, EI).

6-Phenylhex-5-ene-2,4-dione (13): Benzaldehyde (3.1 g, 29.3 mmol) was added at –78 °C to a stirred solution of 2,4-bis(trimethysilyloxy)penta-1,3-diene (7.0 g, 28.7 mmol) in CH_2Cl_2 (300 mL), which was followed by dropwise addition of $TiCl_4$ (3.1 mL, 28.2 mmol; dissolved in 10 mL of CH_2Cl_2). The temperature was allowed to rise to 20 °C over 6 h, the solution was stirred for an additional 6 h at 20 °C, and an aqueous solution of HCl (10%, 100 mL) was added. The organic and the aqueous layer were separated, the latter was extracted with CH_2Cl_2 (2 × 100 mL), the combined organic layers were dried (Na_2SO_4) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (EtOAc/hexane 1:9) to give **13** (3.3 g, 62%) as yellow crystals, mp. 84–85 °C; R_f = 0.62 (EtOAc/hexane 1:9). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 15.34 (br s, 1 H, OH), 7.59 (d, J = 16.0 Hz, 1 H, =CH), 7.55–7.49 (m, 2 H, ArH), 7.41–7.34 (m, 3 H, ArH), 6.46 (d, J = 16.0 Hz, 1 H, =CH), 5.65 (s, 1 H, =CH), 2.16 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.8, 176.9 (C), 139.7 (CH), 135.0 (C), 129.8, 128.3 (2 C), 127.8 (2 C), 122.7, 101.1 (CH), 27.0 (CH_3) ppm. MS (EI, 70 eV): m/z (%) = 188.1 (100), 173.0 (31), 144.8 (83), 131.1 (47), 102.8 (50), 85.1 (62), 43.1 (64); elemental analysis: calcd. (%) for $C_{12}H_{12}O_2$: C 76.57, H 6.42; found: C 76.75, H 6.62.

6-Phenyl-2,4-bis(trimethysilyloxy)hexa-1,3,5-triene (14): Triethylamine (1.21 mL, 8.75 mL) was added to a diethyl ether solution (10 mL) of **13** (0.750 g, 4.0 mmol) and the solution was stirred for 30 min at 0 °C. TMSOTf (1.52 mL, 8.35 mL) was added and the solution was stirred for 12 h at 20 °C. To the solution was added an aqueous solution of HCl (10%, 100 mL). The ether layer was separated from the liquid salt layer by syringe under inert atmosphere, ether (10 mL) was added to the liquid salt layer, and the mixture was stirred. The ether layer was again separated from the liquid salt layer by syringe under inert atmosphere, this procedure was repeated, and the combined organic layers were concentrated in vacuo to give **14** (1.250 g, 94%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 7.63, 6.70 (d, J = 15.6 Hz, 1 H, =CH) [(*E*)/(*Z*) isomer], 7.41–7.17 (m, 10 H, ArH) [(*E*)/(*Z*) isomer], 6.80, 6.50 (d, J = 15.6 Hz, 1 H, =CH) [(*E*)/(*Z*) isomer], 5.36, 5.19 (s, 1 H, =CH) [(*E*)/(*Z*) isomer], 4.78, 4.25 (s, 1 H, =CH_2) [(*E*)/(*Z*) isomer], 4.43, 4.23 (s, 1 H, =CH_2) [(*E*)/(*Z*) isomer] ppm. ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ = 154.5, 152.8 [(*E*)/(*Z*) isomer], 150.6, 150.0 [(*E*)/(*Z*) isomer], 137.3, 136.7 [(*E*)/(*Z*) isomer] (C), 130.1, 129.7 [(*E*)/(*Z*) isomer], 128.6, 128.6 (2 C) [(*E*)/(*Z*) isomer], 127.7, 126.6 [(*E*)/(*Z*) isomer], 127.6, 127.5 [(*E*)/(*Z*) isomer], 126.9, 123.5 (2 C) [(*E*)/(*Z*) isomer], 113.6, 112.1 (CH) [(*E*)/(*Z*) isomer], 97.0, 96.0 (CH_2) [(*E*)/(*Z*) isomer], 1.3, 0.3 (3C) [(*E*)/(*Z*) isomer], 0.9, 0.2 (3C, CH_3) [(*E*)/(*Z*) isomer] ppm.

3-Hydroxy-5-(2-oxo-4-phenylbut-3-enylidene)-5*H*-furan-2-one (15): The reaction was carried out according to the procedure given for the synthesis of **10**. Starting with **14** (0.332 g, 1.00 mmol), oxalyl chloride (0.090 mL, 1.03 mmol), and Me_3SiOTf (0.11 mL, 0.50 mmol; in 1 mL CH_2Cl_2), **15** was isolated (0.155 g, 64%) as a yellow solid; m.p. 128–129 °C; R_f = 0.47 (hexane/ethyl acetate 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.67 (m, 3 H, ArH, =CH), 7.46–7.42 (m, 3 H, ArH), 7.12–7.03 (m, 2 H, =CH), 6.59 (s, 1 H, =CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.3, 163.7, 159.3, 151.4 (C), 152.3 (CH), 134.4 (C), 130.5, 128.9 (2 C), 128.5 (2 C), 128.2, 107.7, 103.6 (CH) ppm. IR (KBr): $\tilde{\nu}$ = 3002 (br), 1800 (s), 1628 (s), 1612 (s), 1552 (s), 1398 (m), 1267 (s), 1213 (m), 1045 (s), 979 (m), 767 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 242 [M]$^+$ (1), 226 (2), 214 (3), 131 (1), 103 (1), 77 (1), 44 (7), 28 (100); elemental analysis: calcd. (%) for $C_{14}H_{10}O_4$: C 69.41, H 4.16; found: C 69.17, H 4.49.

3-Hydroxy-5-(2-oxo-4-phenylbut-3-enylidene)-5*H*-furan-2-one (16): K_2CO_3 (0.051 g, 0.37 mmol) was added at 20 °C to an acetone solution of **15** (0.060 g, 0.025 mmol). After the mixture had been stirred for 30 min, Me_2SO_4 (0.042 g, 0.33 mmol) was added dropwise and the solution was stirred for 12 h. The reaction mixture was filtered, the residue was washed with acetone (2 × 15 mL), and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc 4:1) to give **16** (0.042 g, 66%) as a yellow solid. R_f = 0.17 (hexane/ethyl acetate 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (d, J = 16.2 Hz, 1 H, =CH), 7.60–7.55 (m, 2 H, ArH), 7.43–7.39 (m, 4 H, ArH, =CH), 6.87 (d, J = 16.2 Hz, 1 H, =CH), 6.41 (s, 1 H, =CH), 3.99 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.6, 162.4, 158.6, 153.1 (C), 143.5 (CH), 134.3 (C), 130.9, 129.0 (2 C), 128.5 (2 C), 127.7, 108.1, 105.2 (CH), 59.4 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 1792 (s),

1652 (w), 1617 (s), 1449 (w), 1334 (w), 1223 (m), 1067 (s), 986 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 256 $[M]^+$ (31), 228 (5), 213 (13), 185 (15), 152 (13), 131 (13), 103 (25), 77 (22), 70 (38), 28 (100).

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