New Strategies for the Efficient Synthesis of Medium-Sized Bicyclic γ-Alkylidenebutenolides Based on Regioselective Cyclizations of 1,3-Bis(trimethylsilyloxy)-1,3-butadienes with Oxalyl Chloride

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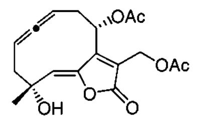
Keywords: Cyclizations / Homogeneous catalysis / Medium-sized rings / Ring-closing metathesis / Silyl enol ethers

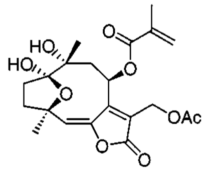
Medium-sized bicyclic γ-alkylidenebutenolides were efficiently prepared by Me_3SiOTf-catalyzed cyclization of cyclic bis(silyl enol ethers) with oxalyl chloride. In addition, a new strategy for the synthesis of medium-sized bicyclic hybrids of butenolides and medium-sized cyclic ethers – based on sequential [3+2] cyclization of 1,3-bis(trimethylsilyloxy)-1,3-butadienes, Mitsunobu reaction, and ring-closing metathesis – is reported.

Introduction

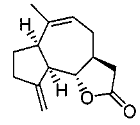
Bicyclic γ-alkylidenebutenolides are present in a variety of biologically relevant natural products. These include structures containing medium-sized rings, which are often difficult to prepare. A number of antibiotics belong to the highly oxygenated sesquiterpene classes of the hirsutinolides and glaucolides.[1] Other natural products, such as calaxin, tagitinin A, zexbrevin and ciliarin, are included in the group of the tagitinins.[2] The germacranolides, lactone analogues of the sesquiterpene germacrone, exhibit cytotoxic activity.[3] In the context of our interest in the development of cyclization reactions of dianions and dianion equivalents with 1,2-dielectrophiles,[4,5] we have recently reported a new synthesis of γ-alkylidenebutenolides by means of the first reported cyclizations of 1,3-dicarbonyl dianions with oxalic acid dielectrophiles.[4a,4b] Here we wish to report full details of our studies related to the synthesis of C-1′/C-4-annulated 5,*n*-bicyclic γ-alkylidenebutenolides ($n = 5-12$), which represent analogues of pharmacologically relevant sesquiterpene natural products.[6] In addition, we report on a new and efficient approach to C-3/C-4-annulated 5,*n*-bicyclic butenolides ($n = 7, 8$), which can be regarded as hybrids of γ-alkylidenebutenolides[7,8] and medium-sized cyclic ethers,[9] both of which are biologically relevant substructures. These compounds were efficiently prepared by sequential Me_3SiOTf-catalyzed cyclization of functionalized 1,3-bis(trimethylsilyloxy)-1,3-butadienes with oxalyl chloride, Mitsunobu reaction, and ring-closing metathesis (RCM).[10] The hybrid concept for the construction of biologically active compounds has been devised recently, since new natural products and analogues often constitute promising lead structures, but their isolation is generally very difficult and time-consuming.[11] The hybrid concept is also found in nature in the biosynthesis of vitamin E, which is formed from a terpene and shikimic acid.[12] The hybrid vincristine is made up of an aspidosperma and an iboga alkaloid component.[13]



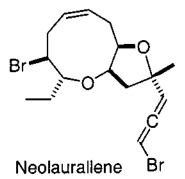
Lupeol Acetate



Piptocarphin A



Guaianolide



Neolaurallene

Results and Discussion

Synthesis of C-1′/C-4-Bicyclic γ-Alkylidenebutenolides

Application of our recently reported dianion methodology[4a] for the synthesis of γ-alkylidenebutenolides to cyclic 1,3-dicarbonyl compounds was unsuccessful; treatment of the dianion of ethyl 2-oxocyclohexanecarboxylate with *N*,*N*′-dimethoxy-*N*,*N*′-dimethylethanediamide, the Weinreb amide of oxalic acid, resulted in formation of a complex mixture. We therefore considered the use of electroneutral dianion equivalents (masked dianions).[14]

The 12-membered cyclic 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3a**, a masked dianion of **1a**, was prepared in two

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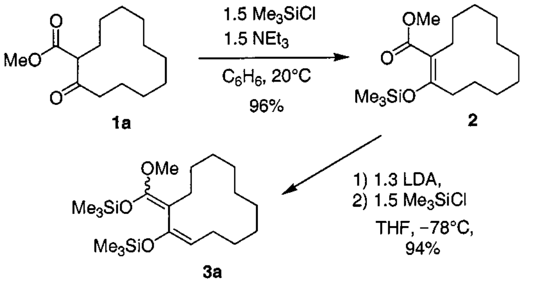
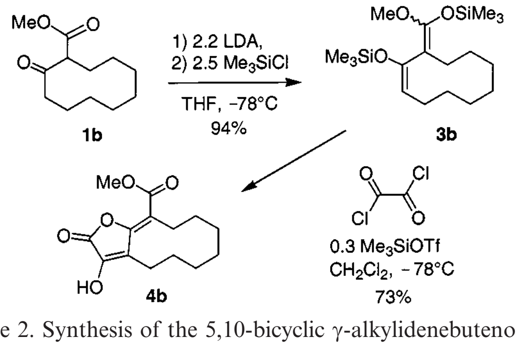
steps as described for the synthesis of related open-chain dienes.[14b,14c] Silylation of methyl 2-oxocyclododecanecarboxylate (**1a**) afforded the silyl enol ether **2** (96% yield), which was transformed into **3a** in high yield by treatment with LDA at −78 °C and subsequent addition of Me_3SiCl (Scheme 1).[15] Surprisingly, this methodology was not successful for substrates of smaller ring size. However, the 10-, 8-, 7-, 6-, and 5-membered cyclic 1,3-bis(trimethylsilyloxy)-1,3-butadienes **3b−n** could be prepared in high yields by treatment of the dianions of the corresponding 1,3-dicarbonyl compounds **1b−n** with 2 equiv. of Me_3SiCl (Scheme 2).[15] Interestingly, treatment of Me_3SiCl with the dianions of open-chain β-oxo esters has been reported to result in silylation of the terminal carbon atom of the dianion rather than in formation of 1,3-bis(trimethylsilyloxy)-1,3-butadienes.[14b]



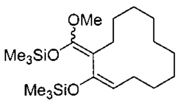
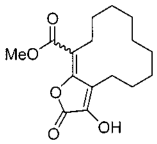
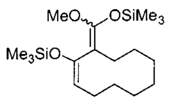
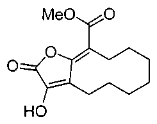
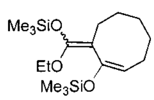
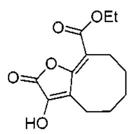
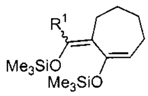
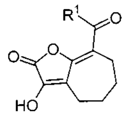
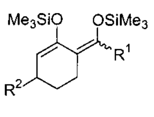
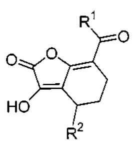
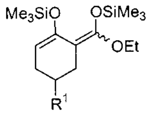
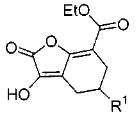
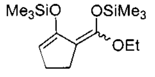
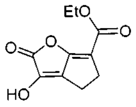
Scheme 1. Synthesis of the 12-membered cyclic 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3a** according to Molander et al.[15]



Scheme 2. Synthesis of the 5,10-bicyclic γ-alkylidenebutenolide **4b**

The Me_3SiOTf-catalyzed cyclization of oxalyl chloride with bis(silyl enol ether) **3b**, prepared from methyl 2-oxocyclodecanecarboxylate in 94% yield, afforded the (*Z*)-configured 5,10-bicyclic γ-alkylidenebutenolide **4b** in 73% yield and with very good regioselectivity (Scheme 2). The reaction proceeded by attack of the terminal carbon atom of the diene onto the dielectrophile and subsequent cyclization through the oxygen atom of the diene. In order to study the preparative scope of this reaction, the ring size and the substituents on the 1,3-bis(trimethylsilyloxy)-1,3-butadienes were varied systematically (Table 1). Cyclization of oxalyl chloride with bis(silyl enol ether) **3a** gave the 5,12-bicyclic butenolide **4a** as a mixture of geometric isomers [(*E*)/(*Z*) = 4:1].

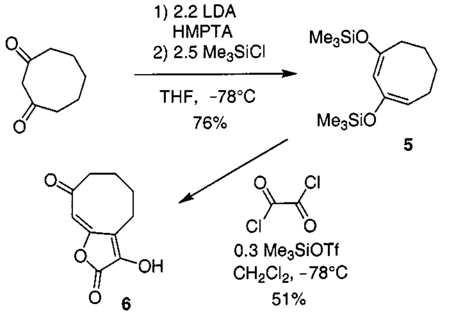
Table 1. Synthesis of bicyclic γ-alkylidenebutenolides **4a−n**

	3	4	R^1	R^2	%[a]
a			–	–	70
b			–	–	73
c			–	–	74
d			OEt	–	84
e			*t*Bu	–	75
f			OEt	H	76
g			O*i*Pr	H	74
h			$O(CH_2)_2OMe$	H	75
i			Ph	H	68
j			OEt	Me	65
k			OMe	Et	68
l			Ph	–	66
m			*t*Bu	–	52
n			–	–	55

[a] Isolated yield. Only one isomer was formed for **4b−n**. Butenolide **4a** was obtained as a mixture of isomers [(*E*)/(*Z*) = 4:1].

Cyclization of oxalyl chloride with bis(silyl enol ether) **3c** regioselectively afforded the 5,8-bicyclic butenolide **4c**. From dienes **3d** and **3e**, the 5,7-bicyclic butenolides **4d** and **4e** were obtained in good yields and with very good regioselectivities, while cyclization of the 6-membered cyclic dienes **3f−m** afforded the corresponding 5,6-bicyclic products **4f−m** in good yields. The presence of an additional substituent in the cases of dienes **3j** and **3k** did not result in any significant decrease in the yield. From 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3n**, the 5,5-bicyclic γ-alkylidenebutenolide **4n** was obtained.

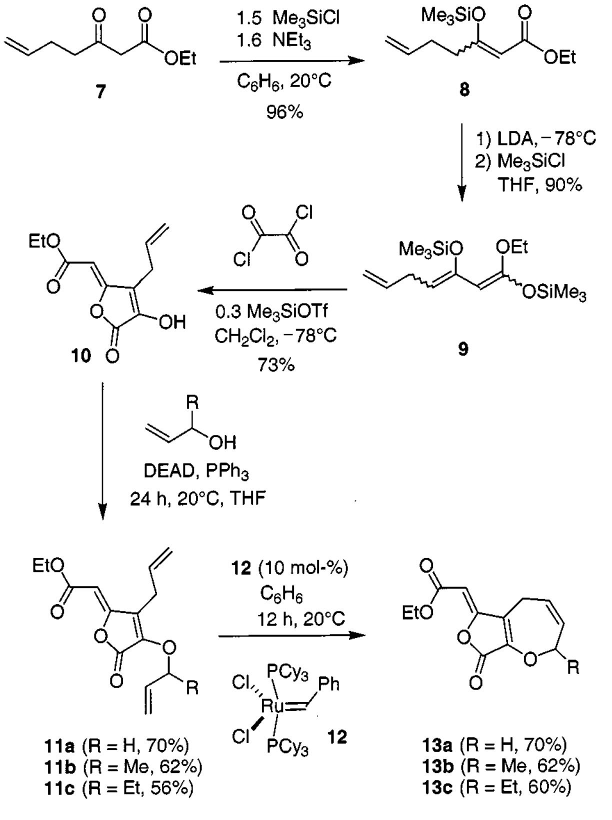
The applicability of our methodology to the synthesis of medium-sized bicyclic butenolides with different substitution patterns was studied next. 1,3-Bis(trimethylsilyloxy)-1,3-butadiene **5** was prepared from cyclooctane-1,3-dione in one step. The Me_3SiOTf-catalyzed cyclization of **5** with oxalyl chloride afforded the 5,8-bicyclic butenolide **6** in acceptable yield and with very good regioselectivity (Scheme 3).



Scheme 3. Synthesis of 5,8-bicyclic γ-alkylidenebutenolide **6**

Synthesis of C-3/C-4-Bicyclic Hybrids of γ-Alkylidenebutenolides and Medium-Sized Cyclic Ethers

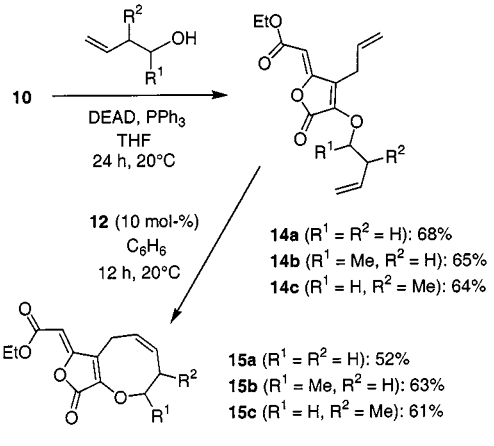
Ethyl 3-oxohept-6-enoate (**7**) was prepared in 82% yield by treatment of the dianion of ethyl acetoacetate with allyl bromide. Direct cyclization of the dianion of **7** with *N*,*N'*-dimethoxy-*N*,*N'*-dimethylethanediamide was unsuccessful. To overcome this problem, the corresponding masked dianion **9**[14c] was prepared in high yield by silylation of the carbanion of silyl enol ether **8**, which was readily available from **7** in 96% yield (Scheme 4). To our satisfaction, the Me$_3$SiOTf-catalyzed cyclization of diene **9** with oxalyl chloride afforded the desired γ-alkylidenebutenolide **10** in 73% yield with very good regio- and (*Z*)-diastereoselectivities.



Scheme 4. Synthesis of 5,7-bicyclic γ-alkylidenebutenolides **13a−c**

Chemoselective alkylation of the α-hydroxy group of butenolide **10** initially proved difficult; treatment of **10** with allyl bromide in the presence of K$_2$CO$_3$ afforded the desired butenolide **11a**, but only in 22% yield. The low yield can be explained by base-induced ring-opening. Moreover, treatment of **10** with 2-bromo-3-butene resulted in formation of an inseparable mixture of products, presumably due to decomposition and competing S$_N$/S$_N$' reactions. The problem was eventually solved by use of the Mitsunobu reaction. Treatment of **10** with allylic alcohol, 2-hydroxy-3-butene, and 3-hydroxy-1-pentene in the presence of PPh$_3$/DEAD afforded the corresponding butenolides **11a−c** in good yields. These transformations represent the first examples (to the best of our knowledge) of chemoselective *O*-alkylation reactions of γ-alkylidene-α-hydroxybutenolides.[16] To our satisfaction, ring-closing metathesis (RCM)[17] of **11a−c** using Grubbs' catalyst **12** proceeded uneventfully and afforded the 5,7-bicyclic γ-alkylidenebutenolides **13a−c** (Scheme 4).

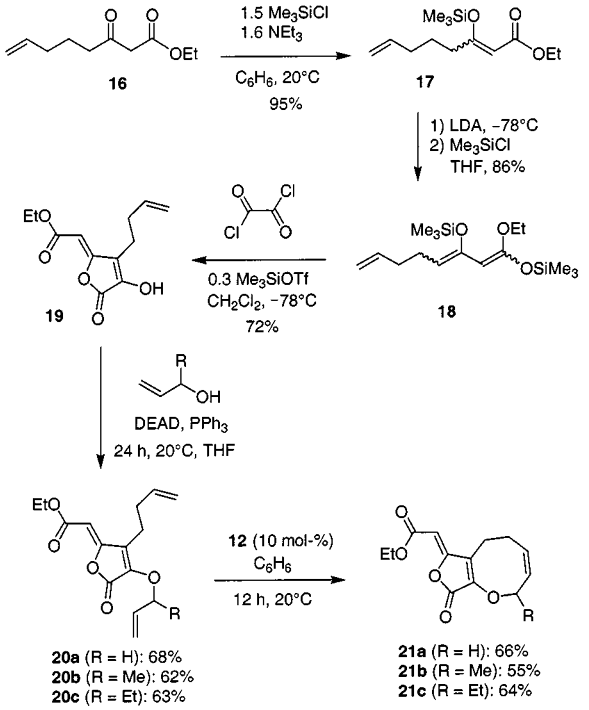
The application of the RCM reaction to the formation of medium-sized rings is currently the object of some attention, although only relatively few examples have been reported so far.[18] In this context, the synthesis of butenolide ring ether hybrids containing eight-membered rings was of special interest. Mitsunobu reaction of **10** with 1-hydroxy-3-butene, 2-hydroxy-4-pentene, and 1-hydroxy-2-methyl-3-butene gave butenolides **14a−c** in good yields. RCM treatment of **14a−c** afforded the 5,8-bicyclic butenolides **15a−c** in acceptable yields (Scheme 5).



Scheme 5. Synthesis of 5,8-bicyclic γ-alkylidenebutenolides **15a−c**

To control the position of the endocyclic double bond and to construct isomers of 5,8-bicyclic butenolides **15**, the masked dianion **18** was prepared as follows. Treatment of dilithiated ethyl acetoacetate with 1-bromo-3-butene afforded ethyl 3-oxooct-7-enoate (**16**). Silylation of **16** gave silyl enol ether **17** (95%), which was transformed into the 1,3-bis(trimethylsilyloxy)-1,3-butadiene **18** in 86% yield (Scheme 6). The Me$_3$SiOTf-catalyzed cyclization of **18** with oxalyl chloride afforded the γ-alkylidenebutenolide **19** in 72% yield and with very good regio- and (*Z*)-selectivities. Mitsunobu reaction of **19** with allylic alcohol, 2-hydroxy-3-butene, and 3-hydroxy-1-pentene gave the cyclization precursors **20a−c**, respectively. To our satisfaction, RCM of

20a−c proceeded uneventfully and afforded the medium-sized 5,8-bicyclic butenolides **21a−c**. Butenolides **21a** and **21b** are isomers of butenolides **15a** and **15b**, respectively.



Scheme 6. Synthesis of 5,8-bicyclic γ-alkylidenebutenolides **21a−c**

Single-crystal X-ray structure determination showed that **21a** had crystallized in the monoclinic space group $P2_1/c$, with one molecule in the asymmetric unit. The γ-alkylidene-butenolide part of the molecule [including the ethoxy group and the C(8)−C(3)−C(4)−O(3)−C(12) part of the cyclooctane-1,5-diene ring] forms one plane with a mean deviation of 0.07 Å. Another plane, with a dihedral angle of 110.4(4)° to the first one, is formed by the atoms C(8) to C(12) (mean deviation 0.02 Å). The exocyclic double bond possesses the (*Z*) configuration. Figure 1 gives a picture of the structure, with selected bond lengths and angles.

In summary, we have developed an efficient synthesis of bicyclic γ-alkylidenebutenolides containing 5- to 12-membered ring moieties. The products were prepared in good yields from readily available starting materials. In addition, an efficient synthesis of γ-alkylidenebutenolide/medium-sized cyclic ether hybrids has been developed, relying on the chemo-, regio-, and (*Z*)-diastereoselective Me$_3$SiOTf-catalyzed cyclization of allyl- and homoallyl-substituted 1,3-bis(trimethylsilyloxy)-1,3-butadienes with oxalyl chloride. Application of Mitsunobu reaction conditions allowed chemoselective *O*-alkylation of γ-alkylidenebutenolides to be accomplished for the first time. Cyclization was achieved by RCM, clearly demonstrating the applicability of this methodology to the construction of medium-sized cyclic ethers. The bicyclic butenolides reported here represent analogues of biologically relevant sesquiterpene natural products.

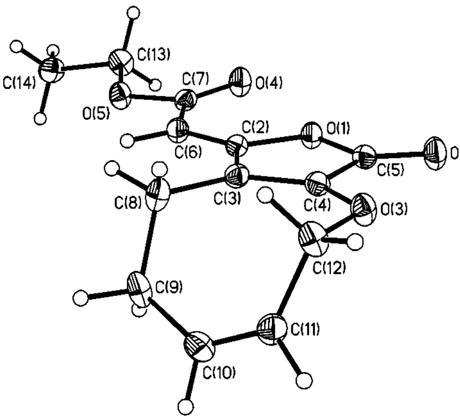


Figure 1. ORTEP plot of **21a**; the thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms; selected bond lengths [Å] and angles [°]: O(3)−C(4) 1.3365(14), O(3)−C(12) 1.4656(14), C(12)−C(11) 1.4997(17), O(2)−C(5) 1.1993(15), C(11)−C(10) 1.3327(18), O(1)−C(5) 1.3773(14), O(1)−C(2) 1.3890(13), C(10)−C(9) 1.5004(18), O(4)−C(7) 1.2071(14), C(9)−C(8) 1.5327(17), O(5)−C(7) 1.3516(14), C(8)−C(3) 1.5053(16), C(3)−C(4) 1.3533(16), C(3)−C(2) 1.4631(15), C(4)−C(5) 1.4791(16), C(2)−C(6) 1.3421(16), C(6)−C(7) 1.4777(16); C(4)−O(3)−C(12) 116.10(9); O(3)−C(12)−C(11) 112.11(10), C(10)−C(11)−C(12) 128.58(11), C(5)−O(1)−C(2) 107.53(9), C(10)−C(9)−C(8) 118.16(10), C(3)−C(8)−C(9) 113.03(10), C(4)−C(3)−C(2) 105.56(10), O(3)−C(4)−C(3) 135.24(11), O(2)−C(5)−O(1) 122.03(11), O(4)−C(7)−C(6) 126.85(11)

Experimental Section

General: All solvents were dried by standard methods and all reactions were carried out under an inert gas. − For the ^{1}H and ^{13}C NMR spectra (^{1}H NMR: 250 and 300 MHz; ^{13}C NMR: 62.5 and 75 MHz) the deuterated solvents indicated were used. − Mass-spectrometric data (MS) were obtained using the electron ionization (70 eV) or the chemical ionization techniques (CI, H$_2$O). − For preparative-scale chromatography, silica gel (60−200 mesh) was used. − Melting points are uncorrected. − Elemental analyses were performed at the microanalytical laboratory of the University of Göttingen.

Methyl 2-Trimethylsilyloxycyclododec-1-ene-1-carboxylate (2): NEt$_3$ (2.22 g, 22 mmol) and TMSCl (2.40 g, 22 mmol) were added at 20 °C to a THF solution (20 mL) of methyl 2-oxocyclododecanecarboxylate (3.15 g, 13.11 mmol). After the suspension had been stirred for 24 h, the solvent was removed in vacuo. Petroleum ether was added to the residue, the suspension was filtered under nitrogen and the filtrate solvent was removed in vacuo. The residue was distilled using a Kugelrohr apparatus (oven temp. 110 °C; 0.1 Torr) to give **2** as a colourless oil (3.68 g, 90%).[15] − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.18, (s, 9 H, Me$_3$Si), 1.05−1.50 (m, 14 H, CH$_2$), 1.55−1.65 (m, 2 H, CH$_2$), 1.80, 2.22, 2.46, 3.52 (4 × m, 4 × 1 H, CH$_2$), 3.72 (s, 3 H, OCH$_3$). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 0.68, 24.10, 24.75, 24.83, 24.85, 25.13, 25.40, 25.52, 25.72, 25.80, 33.50, 50.62, 115.12, 165.52, 169.98. − MS (EI, 70 eV): *m*/*z* (%) = 312 (62) [M$^+$], 297 (100), 73 (80); the exact molecular mass *m*/*z* = 312.2121 ± 2 mD [M$^+$] for C$_{17}$H$_{32}$O$_3$Si was confirmed by HRMS (EI, 70 eV).

3-[Methoxy(trimethylsilyloxy)methylidene]-2-trimethylsilyloxycyclododec-1-ene (3a): A THF solution (1.5 mL) of silyl enol ether **2** (1.18 g, 3.8 mmol) was added at −78 °C to a THF solution of

LDA [prepared by addition of *n*BuLi (4.4 mmol, 2.35 M solution in *n*-hexane) to a THF solution (7 mL) of diisopropylamine (4.4 mmol) at 0 °C]. After this had stirred for 1.5 h at −78 °C, TMSCl (0.52 g, 4.8 mmol) was added. The temperature of the solution was allowed to rise to 0 °C over 1 h and the solution was stirred for 4 h. The solvent was removed in vacuo and pentane was added to the residue. The precipitated lithium chloride was removed by filtration under nitrogen and the filtrate solvent was removed in vacuo to give **3a** as a light yellow oil [1.38 g, 95%, (*E*)/(*Z*) = 4:1].[15] − ^{1}H NMR (CDCl$_3$, 250 MHz, major isomer): δ = 0.14, 0.18 (2 × s, 2 × 9 H, Me$_3$Si), 1.20−1.40 (m, 14 H, CH$_2$), 2.00−2.10 (m, 4 H, CH$_2$), 3.48 (s, 3 H, OCH$_3$), 4.54 (t, *J* = 7.0 Hz, 1 H, CH). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 0.26, 0.35, 24.33, 24.75, 25.79, 26.15, 26.25, 26.15, 26.25, 26.60, 26.84, 56.40, 101.26, 113.78, 146.07, 151.15. − MS (EI, 70 eV): *m*/*z* (%) = 384 (56) [M$^+$], 369 (40), 353 (92), 73 (100); the exact molecular mass *m*/*z* = 384.2616 ± 2 mD [M$^+$] for C$_{20}$H$_{40}$O$_3$Si$_2$ was confirmed by HRMS (EI, 70 eV).

General Procedure for the Preparation of Bis(silyl enol ethers) 3b−n: Ethyl 2-oxocycloheptanecarboxylate (**1d**) (2.69 g, 14.6 mmol) was added dropwise at 0 °C to a THF solution (30 mL) of LDA [prepared by addition of *n*BuLi (23.8 mL, 36.5 mmol, solution in *n*-hexane) to a THF solution of diisopropylamine (4.2 mL, 32.0 mmol)]. After stirring of the yellow solution for 1.5 h at 0 °C (for **3b**: stirring for 2 h at −78 °C), chlorotrimethylsilane (5.5 mL, 43.8 mmol, 3 equiv.) was added in one portion (for **3b**: 5 equiv.). After this had stirred for 3 h at 0 °C, the solvent was removed in vacuo (for **3b**: warming to 0 °C within 1 h and stirring for 3 h). Petroleum ether was added to the residue and the suspension obtained was filtered under nitrogen. The filtrate solvent was removed in vacuo to give essentially pure 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3d** in 95% crude yield. The bis(silyl enol ether)s **3** were used without further purification and were stored at −30 °C under nitrogen.

3-[Methoxy(trimethylsilyloxy)methylidene]-2-trimethylsilyloxycyclodec-1-ene (3b): Starting from methyl 2-oxocyclodecanecarboxylate (1.00 g, 4.71 mmol), **3b** was isolated as a slightly yellow oil (1.58 g, 94%).[15] − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.10, 0.18 (2 × s, 2 × 9 H, Me$_3$Si), 1.20−1.45 (m, 10 H, CH$_2$), 2.00, 2.10 (2 × m, 2 × 2 H, CH$_2$), 3.48 (s, 3 H, OCH$_3$), 4.74 (t, *J* = 8.0 Hz, 1 H, CH). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 0.32, 0.50, 24.48, 24.55, 24.60, 25.34, 25.64, 26.94, 28.20, 56.24, 101.64, 115.02, 145.48, 149.96. − MS (EI, 70 eV): *m*/*z* (%) = 356 (92) [M$^+$], 341 (62), 73 (100); the exact molecular mass *m*/*z* = 356.2203±2 mD [M$^+$] for C$_{18}$H$_{36}$O$_3$Si$_2$ was confirmed by HRMS (EI, 70 eV).

3-[Ethoxy(trimethylsilyloxy)methylidene]-2-trimethylsilyloxycyclooct-1-ene (3c): Starting from ethyl 2-oxocyclooctanecarboxylate (1.98 g, 10.00 mmol), **3c** was isolated as a slightly yellow oil (3.25 g, 95%).[15] − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.17, 0.20 (2 × s, 2 × 9 H, Me$_3$Si), 1.25 (t, *J* = 7.0 Hz, 3 H, CH$_3$), 1.45−1.55 (m, 6 H, CH$_2$), 1.95, 2.18 (2 × m, 2 × 2 H, CH$_2$), 3.82 (q, *J* = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.75 (t, *J* = 7.0 Hz, 1 H, CH). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 0.92, 1.32, 15.74, 26.42, 27.34, 28.30, 30.02, 30.22, 64.82, 99.36, 107.68, 149.88, 150.66. − MS (EI, 70 eV): *m*/*z* (%) = 342 (80) [M$^+$], 317 (32), 73 (100); the exact molecular mass *m*/*z* = 342.2047 ± 2 mD [M$^+$] for C$_{17}$H$_{34}$O$_3$Si$_2$ was confirmed by HRMS (EI, 70 eV).

3-[Ethoxy(trimethylsilyloxy)methylidene]-2-trimethylsilyloxycyclohept-1-ene (3d): Starting from ethyl 2-oxocycloheptanecarboxylate (2.69 g, 14.60 mmol), **3d** was isolated as a slightly yellow oil (4.55 g, 95%).[15] − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.10, 0.21 (2 × s, 2 × 9 H, Me$_3$Si), 1.22 (t, *J* = 7.0 Hz, 3 H, CH$_3$), 1.45−1.65 (2 × m, 2 × 2 H, CH$_2$), 1.95, 2.18 (2 × m, 2 × 2 H, CH$_2$), 3.82 (q, *J* = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.94 (t, *J* = 6.5 Hz, 1 H, CH). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 0.30, 0.34, 15.04, 25.64, 26.84, 27.57, 30.38, 63.52, 98.75, 109.35, 150.66, 152.22. − MS (EI, 70 eV): *m*/*z* (%) = 328 (62) [M$^+$], 199 (25), 73 (100); the exact molecular mass *m*/*z* = 328.1890 ± 2 mD [M$^+$] for C$_{16}$H$_{32}$O$_3$Si$_2$ was confirmed by HRMS (EI, 70 eV).

3-[*tert*-Butyl(trimethylsilyloxy)methylidene]-2-trimethylsilyloxycyclohept-1-ene (3e): Starting from 2-pivaloylcycloheptanone (1.76 g, 9.00 mmol), **3e** was isolated as a slightly yellow oil (2.94 g, 96%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.10, 0.19 (2 × s, 2 × 9 H, Me$_3$Si), 1.18 (s, 9 H, CH$_3$), 1.35−1.75 (m, 6 H, CH$_2$), 1.98 (m, 2 H, CH$_2$), 4.90 (t, *J* = 6.5 Hz, 1 H, CH). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 0.56, 1.26, 25.78, 26.90, 29.17, 30.32, 31.70, 37.26, 109.25, 117.10, 154.81, 155.69. − MS (EI, 70 eV): *m*/*z* (%) = 340 (56) [M$^+$], 283 (36), 215 (57), 73 (100); the exact molecular mass *m*/*z* = 340.2254 ± 2 mD [M$^+$] for C$_{18}$H$_{36}$O$_2$Si$_2$ was confirmed by HRMS (EI, 70 eV).

3-[Ethoxy(trimethylsilyloxy)methylidene]-2-trimethylsilyloxycyclohex-1-ene (3f): Starting from ethyl 2-oxocyclohexanecarboxylate (1.02 g, 6.00 mmol), **3f** was isolated as a slightly yellow oil (1.73 g, 92%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.14, 0.21 (2 × s, 2 × 9 H, Me$_3$Si), 1.22 (t, *J* = 8.0 Hz, 3 H, CH$_3$), 1.58 (m, 2 H, CH$_2$), 2.06, 2.31 (2 × m, 2 × 2 H, CH$_2$), 3.79 (q, *J* = 8.0 Hz, 2 H, OCH$_2$), 4.78 (t, *J* = 6.0 Hz, 1 H, CH). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 0.61, 0.66, 14.80, 23.38, 24.88, 25.62, 63.84, 97.19, 107.25, 147.46, 147.92. − MS (EI, 70 eV): *m*/*z* (%) = 314 (60) [M$^+$], 73 (100); the exact molecular mass *m*/*z* = 314.1734 ± 2 mD [M$^+$] for C$_{15}$H$_{30}$O$_3$Si$_2$ was confirmed by HRMS (EI, 70 eV).

3-[Isopropoxy(trimethylsilyloxy)methylidene]-2-trimethylsilyloxycyclohex-1-ene (3g): Starting from isopropyl 2-oxocyclohexanecarboxylate (1.012 g, 5.50 mmol), **3g** was isolated as a slightly yellow oil (1.73 g, 96%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.18, 0.21 (2 × s, 2 × 9 H, Me$_3$Si), 1.20 (d, *J* = 8.0 Hz, 6 H, CH$_3$), 1.60 (m, 2 H, CH$_2$), 2.11, 2.32 (2 × m, 2 × 2 H, CH$_2$), 4.30 (sept, *J* = 8.0 Hz, 1 H, OCH), 4.80 (t, *J* = 6.0 Hz, 1 H, CH). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 0.22, 0.23, 21.87, 23.44, 24.98, 25.98, 69.30, 98.48, 107.55, 146.61, 147.62. − MS (EI, 70 eV): *m*/*z* (%) = 328 (52) [M$^+$], 73 (100); the exact molecular mass *m*/*z* = 328.1890 ± 2 mD [M$^+$] for C$_{16}$H$_{32}$O$_3$Si$_2$ was confirmed by HRMS (EI, 70 eV).

3-[(2-Methoxyethoxy)(trimethylsilyloxy)methylidene]-2-trimethylsilyloxycyclohex-1-ene (3h): Starting from 2-methoxyethyl 2-oxocyclohexanecarboxylate (1.20 g, 6.00 mmol), **3h** was isolated as a slightly yellow oil (1.96 g, 95%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.11, 0.20 (2 × s, 2 × 9 H, Me$_3$Si), 1.58 (m, 2 H, CH$_2$), 2.08, 2.32 (2 × m, 2 × 2 H, CH$_2$), 3.36 (s, 3 H, OCH$_3$), 3.55, 3.89 (2 × m, 2 × 2 H, OCH$_2$), 4.80 (t, *J* = 6.0 Hz, 1 H, CH). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 0.11, 0.17, 23.27, 24.82, 25.37, 58.81, 67.08, 71.06, 97.45, 107.54, 147.25, 147.60. − MS (EI, 70 eV): *m*/*z* (%) = 344 (62) [M$^+$], 73 (100); the exact molecular mass *m*/*z* = 344.1839 ± 2 mD [M$^+$] for C$_{16}$H$_{32}$O$_4$Si$_2$ was confirmed by HRMS (EI, 70 eV).

3-[Phenyl(trimethylsilyloxy)methylidene]-2-trimethylsilyloxycyclohex-1-ene (3i): Starting from 2-benzoylcyclohexanone (1.21 g, 6.00 mmol), **3i** was isolated as a slightly yellow oil (1.97 g, 95%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.12, 0.20 (2 × s, 2 × 9 H, Me$_3$Si), 1.40−1.70 (2 × m, 2 H, CH$_2$), 1.90−2.20 (m, 4 H, CH$_2$), 4.90 (t, *J* = 6.0 Hz, 1 H, CH), 7.10−7.50 (m, 5 H, Ph). − MS (EI, 70 eV): *m*/*z* (%) = 346 (22) [M$^+$], 73 (100); the exact molecular mass m/z = 346.1784 ± 2 mD [M^+] for $C_{19}H_{30}O_2Si_2$ was confirmed by HRMS (EI, 70 eV).

3-[Ethoxy(trimethylsilyloxy)methylidene]-6-methyl-2-trimethylsilyloxycyclohex-1-ene (3j): Starting from ethyl 5-methyl-2-oxocyclohexanecarboxylate (938 mg, 5.09 mmol), **3j** was isolated as a slightly yellow oil (1.652 g, 99%). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.17, 0.21 (2 × s, 2 × 9 H, Me_3Si), 0.96 (d, *J* = 8.0 Hz, 3 H, $CHC\mathit{H}_3$), 1.23 (t, *J* = 8.0 Hz, 3 H, $CH_2C\mathit{H}_3$), 1.15, 2.70, 2.12, 2.32, 2.50 (5 × m, 5 × 1 H, CH, CH_2), 4.81 (q, *J* = 8.0 Hz, 2 H, OCH_2), 4.68 (d, *J* = 5.0 Hz, 1 H, =CH). − ^{13}C NMR [$CDCl_3$, 62.5 MHz, (*E*)/(*Z*) mixture]: δ = 0.11, 0.20, 1.83, 2.86, 14.40, 14.78, 19.19, 21.11, 22.24, 24.29, 24.71, 30.36, 31.94, 40.45, 47.35, 59.43, 63.83, 97.05, 108.95, 114.11, 146.87, 148.03, 158.54, 167.50.

6-Ethyl-3-[methoxy(trimethylsilyloxy)methylidene]-2-trimethylsilyloxycyclohex-1-ene (3k): Starting from methyl 6-ethyl-2-oxocyclohexanecarboxylate (693 mg, 3.76 mmol), **3k** was isolated as a slightly yellow oil (751 mg, 61%). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.12, 0.22 (2 × s, 2 × 9 H, Me_3Si), 0.88 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.10−1.40 (m, 4 H, CH_2), 1.75, 2.10, 2.45 (3 × m, 3 × 1 H, CH, CH_2), 3.50 (s, 3 H, OCH_3), 4.75 (d, *J* = 5.0 Hz, 1 H, =CH).

3-[Ethoxy(trimethylsilyloxy)methylidene]-5-phenyl-2-trimethylsilyloxycyclohex-1-ene (3l): Starting from ethyl 2-oxo-4-phenylcyclohexanecarboxylate (2.804 g, 11.38 mmol), **3l** was isolated as a slightly yellow oil (3.905 g, 88%). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.25, 0.35 (2 × s, 2 × 9 H, Me_3Si), 1.28 (t, *J* = 7.0 Hz, 3 H, CH_3), 2.45, 2.95 (m, 5 H, CH, CH_2), 3.90 (q, *J* = 7.0 Hz, 2 H, OCH_2), 4.98 (t, *J* = 5.0 Hz, 1 H, =CH).

5-*tert*-Butyl-3-[ethoxy(trimethylsilyloxy)methylidene]-2-trimethylsilyloxycyclohex-1-ene (3m): Starting from ethyl 4-*tert*-butyl-2-oxocyclohexanecarboxylate (2.299 g, 10.16 mmol), **3m** was isolated as a slightly yellow oil (2.820 g, 75%). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.10−0.30 (4 × s, 18 H, Me_3Si), 0.80−0.95 (s × s, 9 H, *t*Bu), 1.25 (m, 3 H, CH_3), 1.60−2.75 (m, 5 H, CH, CH_2), 3.80 (q, *J* = 7.0 Hz, 2 H, OCH_2), 4.80 (m, 1 H, CH).

3-[Ethoxy(trimethylsilyloxy)methylidene]-2-trimethylsilyloxycyclopent-1-ene (3n): Starting from ethyl 2-oxocyclopentanecarboxylate (1.02 g, 6.53 mmol), **3n** was isolated as an inseparable 2:1 mixture with the corresponding monosilyl enol ether. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.21, 0.23 (2 × s, 2 × 9 H, Me_3Si), 1.21 (t, *J* = 8.0 Hz, 3 H, CH_3), 1.20−1.30 (m, 2 H, CH_2), 2.24 (m, 2 H, CH_2), 3.80 (q, *J* = 8.0 Hz, 2 H, $OC\mathit{H}_2CH_3$), 4.71 (t, *J* = 5.0 Hz, 1 H, CH). − MS (EI, 70 eV): m/z (%) = 300 (12) [M^+], 73 (100).

General Procedure for the Synthesis of γ-Alkylidenebutenolides 4a−n: A CH_2Cl_2 solution (7 mL) of Me_3SiOTf (0.18 mL, 0.3 equiv.) was added at −78 °C to a CH_2Cl_2 solution (60 mL) of oxalyl chloride (3.94 mmol, 0.34 mL) and 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3d** (3.28 mmol, 1.08 g). The temperature of the reaction mixture was allowed to rise to 20 °C over 12 h. After the mixture had stirred for 2 h at 20 °C, a saturated solution of NaCl was added, the organic layer was separated and the aqueous layer was repeatedly extracted with ether. The combined organic extracts were dried ($MgSO_4$) and filtered, and the filtrate solvent was removed in vacuo. The residue was purified by column chromatography (silica gel; ether/petroleum ether, 1:10 → 1:1) to give **4d** (781 mg, 84%) as a colourless solid, m.p. 78 °C.

γ-Alkylidenebutenolide 4a: Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3a** (1.152 g, 3.00 mmol), **4a** was isolated as a colourless solid [615 mg, 70%, (*E*)/(*Z*) = 4:1], m.p. 82 °C. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.20−1.60 (m, 14 H, CH_2), 2.32−2.55 (m, 4 H, CH_2), 3.78 (s, 3 H, OCH_3), 8.00 (br, 1 H, OH). − ^{13}C NMR ($CDCl_3$, 62.5 MHz): (*Z*) isomer: δ = 20.30, 20.42, 23.22, 23.27, 24.61, 24.89, 25.39, 25.54, 25.65 (CH_2), 52.33 (OCH_3), 117.69, 126.33, 142.75, 146.60, 164.64, 167.61 (C); (*E*) isomer: δ = 20.40, 22.63, 23.01, 23.22, 23.97, 24.45, 25.07, 25.23, 26.67, 29.28 (CH_2), 52.00 (OCH_3), 118.06, 126.83, 145.48, 154.16, 164.16, 168.30 (C). − IR (KBr): ṽ = 3384 (br), 2926 (s), 2854 (s), 1747 (s), 1714 (s), 1668 (m), 1468 (m), 1445 (m), 1402 (m), 1274 (m), 1157 (m) cm^{-1}. − MS (EI, 70 eV): m/z (%) = 294 (40) [M^+], 263 (58), 249 (39), 234 (79). − $C_{16}H_{22}O_5$ (294.3): C 65.29, H 7.53; found C 64.87, H 7.32.

γ-Alkylidenebutenolide 4b: Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3b** (1.032 g, 2.90 mmol), **4b** was isolated as a colourless solid (564 mg, 73%). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.50 (m, 6 H, CH_2), 1.68 (m, 4 H, CH_2), 2.72 (m, 4 H, CH_2), 3.79 (s, 3 H, OCH_3), 7.90 (br, 1 H, OH). − ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 20.75, 21.59, 22.95, 24.62, 25.45, 26.41, 27.05 (CH_2), 52.39 (OCH_3), 117.70, 127.38, 143.39, 148.75, 164.81, 167.49 (C). − IR (neat): ṽ = 3319 (br), 2933 (s), 2870 (m), 1776 (s), 1713 (s), 1650 (s), 1619 (s), 1438 (s), 1306 (m), 1245 (s), 1220 (s), 1071 (m) cm^{-1}. − MS (EI, 70 eV): m/z (%) = 266 (60) [M^+]; the exact molecular mass m/z = 266.1154 ± 2 mD [M^+] for $C_{14}H_{18}O_5$ was confirmed by HRMS (EI, 70 eV).

γ-Alkylidenebutenolide 4c: Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3c** (1.094 g, 3.20 mmol), **4c** was isolated as a colourless solid (596 mg, 74%), m.p. 92 °C. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.27 (t, *J* = 7.0 Hz, 3 H, $CH_2C\mathit{H}_3$), 1.48 (m, 2 H, CH_2), 1.72 (m, 4 H, CH_2), 2.75, 2.80 (2 × t, *J* = 6.0 Hz, 2 × 2 H, CH_2), 4.24 (q, *J* = 7.0 Hz, 2 H, OCH_2), 8.00 (br, 1 H, OH). − ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 14.02 (CH_3), 21.35, 22.38, 25.33, 25.34, 26.41 (CH_2), 61.36 (OCH_2), 111.73, 125.80, 142.75, 153.06, 165.26, 166.83 (C). − IR (KBr): ṽ = 3320 (s), 3060 (m), 2991 (s), 2939 (s), 2922 (s), 2913 (s), 2856 (s), 1748 (s), 1710 (s), 1664 (s), 1613 (s), 1488 (m), 1450 (s), 1402 (s), 1359 (s), 1279 (s), 1258 (s), 1207 (s), 1177 (s), 1159 (s), 1138 (s) 1080 (s) cm^{-1}. − MS (EI, 70 eV): m/z (%) = 252 (32) [M^+], − $C_{13}H_{16}O_5$ (252.3): C 61.89, H 6.39; found C 62.15, H 6.34.

γ-Alkylidenebutenolide 4d: Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3d** (1.08 g, 3.29 mmol), **4d** was isolated as a colourless solid (656 mg, 84%), m.p. 78 °C. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.28 (t, *J* = 6.0 Hz, 3 H, CH_3), 1.65−1.90 (m, 4 H, CH_2), 2.64 (m, 4 H, CH_2), 4.25 (q, *J* = 6.0 Hz, 2 H, $OC\mathit{H}_2CH_3$), 8.00 (br, 1 H, OH). − ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 13.91 (CH_3), 23.88, 24.01, 26.59, 28.53 (CH_2), 61.55 ($O\mathit{C}H_2CH_3$), 117.21, 126.85, 141.60, 148.68, 164.82, 167.18 (C). − IR (KBr): ṽ = 3300 (s), 3058 (w), 2992 (m), 2961 (m), 2939 (m), 2904 (m), 1741 (s), 1713 (s), 1656 (s), 1611 (s), 1456 (m), 1410 (s), 1350 (s), 1242 (s), 1198 (s), 1153 (s), 1139 (s), 1047 (s) cm^{-1}. − MS (EI, 70 eV): m/z (%) = 238 (100) [M^+]. − $C_{12}H_{14}O_5$ (238.2): C 60.50, H 5.92; found C 60.34, H 5.58.

γ-Alkylidenebutenolide 4e: Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3e** (1.088 g, 3.20 mmol), **4e** was isolated as a colourless solid (600 mg, 75%), m.p. 84 °C. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.15 (s, 9 H, CH_3), 1.65−1.90 (m, 4 H, CH_2), 2.42, 2.59 (2 × t, *J* = 5.0 Hz, 2 × 2 H, CH_2), 7.90 (br, 1 H, OH). − ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 24.64, 24.75 (CH_2), 27.07 (CH_3), 27.15, 30.91 (CH_2), 44.18 [$\mathit{C}(CH_3)_3$], 126.38, 127.24, 140.14, 141.54, 164.85, 213.56 (C). − IR (KBr): ṽ = 3299 (s), 2976 (m), 2944 (m), 2932 (m), 1755 (s), 1690 (s), 1652 (m), 1477 (m), 1433 (m), 1412 (s), 1240 (m), 1159 (s), 1040 (m) cm^{-1}. − MS (EI, 70 eV): m/z (%) = 250 (58) [M^+]. − $C_{14}H_{18}O_4$ (250.3): C 67.18, H 7.25; found C 67.07, H 6.80.

γ-Alkylidenebutenolide 4f:[4b] Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3f** (566 mg, 1.80 mmol), **4f** was isolated as a slightly yellow oil (305 mg, 76%). − ^{1}H NMR ([D$_6$]acetone, 250 MHz): δ = 1.28 (t, J = 6.0 Hz, 3 H, CH$_3$), 1.80 (quint, J = 5.0 Hz, 2 H, CH$_2$), 2.52 (t, J = 5.0 Hz, 2 H, CH$_2$), 2.58 (t, J = 5.0 Hz, 2 H, CH$_2$), 4.18 (q, J = 6.0 Hz, 2 H, OCH$_2$). − ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 14.57 (CH$_3$), 21.16, 22.53, 25.14 (CH$_2$), 60.99 (OCH$_2$), 107.91, 123.13, 139.97, 152.72 (C), 165.08, 165.37 (CO). − IR (KBr): $\tilde{\nu}$ = 3282 (br), 2989 (m), 2952 (m), 2900 (w), 1785 (s), 1672 (s), 1644 (s), 1473 (m), 1398 (s), 1382 (s), 1357 (m), 1323 (s), 1286 (s), 1193 (s), 1161 (s), 1136 (s), 1045 (s) cm^{-1}. − MS (EI, 70 eV): m/z (%) = 224 (35) [M^{+}], 178 (100), 150 (61). − C$_{11}$H$_{12}$O$_5$ (224.2): C 58.93, H 5.39; found C 59.08, H 5.30.

γ-Alkylidenebutenolide 4g: Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3g** (590 mg, 1.80 mmol), **4g** was isolated as a slightly yellow oil (318 mg, 74%). − ^{1}H NMR ([D$_6$]acetone, 250 MHz): δ = 1.24 (d, J = 6.0 Hz, 6 H, CH$_3$), 1.76 (quint, J = 6.0 Hz, 2 H, CH$_2$), 2.46 (t, J = 6.0 Hz, 2 H, CH$_2$), 2.54 (t, J = 6.0 Hz, 2 H, CH$_2$), 4.99 (sept, J = 6.0 Hz, 1 H, OCH). − ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 20.99 (CH$_2$), 21.98 (CH$_3$), 22.34, 24.98 (CH$_2$), 68.46 [O*C*H(CH$_3$)$_2$], 108.23, 123.09, 139.64, 152.43, 164.47, 165.20 (C). − IR (KBr): $\tilde{\nu}$ = 3238 (br), 2981 (w), 2954 (w), 1789 (s), 1670 (s), 1645 (m), 1378 (m), 1333 (m), 1288 (s), 1137 (m), 1051 (m) cm^{-1}. − MS (EI, 70 eV): m/z (%) = 238 (42) [M^{+}]. − C$_{12}$H$_{14}$O$_5$ (238.2): C 60.50, H 5.92; found C 61.06, H 6.10.

γ-Alkylidenebutenolide 4h: Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3h** (1.032 g, 3.00 mmol), **4h** was isolated as a slightly yellow oil (572 mg, 75%). − ^{1}H NMR ([D$_4$]MeOH, 250 MHz): δ = 1.78 (quint, J = 7.0 Hz, 2 H, CH$_2$), 2.50 (2 × t, J = 7.0 Hz, 4 H, CH$_2$), 3.38 (s, 3 H, CH$_3$), 3.62, 4.27 (2 × t, J = 5.0 Hz, 2 × 2 H, OCH$_2$). − ^{13}C NMR ([D$_4$]MeOH, 62.5 MHz): δ = 21.39, 22.88, 25.35 (CH$_2$), 59.22 (OCH$_3$), 64.90, 71.46 (OCH$_2$), 107.57, 122.98, 140.90, 154.25, 166.14, 166.27 (C). − IR (KBr): $\tilde{\nu}$ = 3379 (br), 2988 (m), 2955 (m), 2885 (m), 1787 (s), 1698 (s), 1662 (s), 1644 (s), 1440 (m), 1375 (s), 1358 (s), 1265 (s), 1244 (s), 1086 (s) cm^{-1}. − MS (EI, 70 eV): m/z (%) = 254 (40) [M^{+}]. − C$_{12}$H$_{14}$O$_6$ (254.2): C 56.69, H 5.55; found C 56.94, H 5.36.

γ-Alkylidenebutenolide 4i:[4b] Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3i** (622 mg, 1.80 mmol), **4i** was isolated as a slightly yellow oil (312 mg, 68%). − ^{1}H NMR ([D$_6$]acetone, 250 MHz): δ = 1.90 (quint, J = 5.0 Hz, 2 H, CH$_2$), 2.66 (2 × t, J = 5.0 Hz, 4 H, CH$_2$), 5.80 (br, 1 H, OH), 7.40−7.85 (m, 5 H, Ph). − ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 19.23 (CH$_3$), 20.74, 21.33, 22.77 (CH$_2$), 115.34, 122.51 (C), 128.93, 129.93, 133.43 (CH, Ph), 139.54, 149.96 (C), 164.79, 194.14 (CO). − MS (EI, 70 eV): m/z (%) = 256 (100) [M^{+}], 227 (46), 105 (58), 77 (56).

γ-Alkylidenebutenolide 4j: Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3j** (1.652 mg, 5.03 mmol), **4j** was isolated as a slightly yellow oil (778 mg, 65%). − ^{1}H NMR ([D$_6$]acetone, 250 MHz): δ = 1.25 (d, J = 6.0 Hz, 3 H, CHCH$_3$), 1.26 (t, J = 6.0 Hz, 3 H, CH$_2$CH$_3$), 1.55, 1.85 (2 × m, 2 × 1 H, CH$_2$), 2.35−2.70 (m, 2 H, CH$_2$), 2.88 (quint, J = 5.0 Hz, 1 H, CH), 4.19 (q, J = 6.0 Hz, 2 H, OCH$_2$), 9.55 (br, 1 H, OH). − ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 13.72, 16.82 (CH$_3$), 22.48 (CH$_2$), 27.27 (CH), 29.76 (CH$_2$), 60.20 (OCH$_2$), 107.09, 126.03, 139.21, 151.57, 164.12, 164.69 (C). − IR (KBr): $\tilde{\nu}$ = 3270 (br), 2989 (m), 2967 (m), 2941 (m), 1786 (s), 1669 (s), 1643 (s), 1399 (s), 1380 (s), 13610 (s), 1272 (s), 1142 (m), 1115 (m), 1072 (s) cm^{-1}. − MS (EI, 70 eV): m/z (%) = 238 (42) [M^{+}], 192 (100), 164 (50). − C$_{12}$H$_{14}$O$_5$ (238.2): C 60.50, H 5.92; found C 60.70, H 5.66.

γ-Alkylidenebutenolide 4k: Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3k** (751 mg, 2.28 mmol), **4k** was isolated as a colourless solid (368 mg, 68%). − ^{1}H NMR ([D$_6$]acetone, 250 MHz): δ = 0.96 (t, J = 6.0 Hz, 3 H, CH$_3$), 1.45−1.90 (m, 4 H, CH$_2$), 2.46 (m, 2 H, CH$_2$), 2.75 (quint, J = 5.0 Hz, 1 H, CH), 3.75 (s, 3 H, OCH$_3$), 9.65 (br, 1 H, OH). − ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 11.67 (CH$_3$), 22.61, 25.16, 26.85 (CH$_2$), 34.13 (CH), 51.88 (OCH$_3$), 107.34, 126.03, 140.22, 152.52, 165.32, 165.40. − IR (KBr): $\tilde{\nu}$ = 3216 (br), 3012 (m), 2963 (m), 2879 (w), 1782 (s), 1667 (s), 1647 (s), 1395 (m), 1290 (m), 1265 (m), 1136 (m), 1072 (m) cm^{-1}. − MS (EI, 70 eV): m/z (%) = 238 (73) [M^{+}], 206 (100), 178 (65). − C$_{12}$H$_{14}$O$_5$ (238.2): C 60.50, H 5.92; found C 60.77, H 5.82.

γ-Alkylidenebutenolide 4l: Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3l** (2.804 g, 11.38 mmol), **4l** was isolated as a colourless solid (2.254 g, 66%). − ^{1}H NMR ([D$_6$]acetone, 250 MHz): δ = 1.25 (t, J = 7.0 Hz, 2 H, CH$_2$), 2.50−2.75 (m, 2 H, CH$_2$), 2.80−3.20 (m, 3 H, CH, CH$_2$), 4.19 (q, J = 7.0 Hz, 2 H, OCH$_2$), 7.15−7.45 (m, 5 H, Ph). − ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 14.52 (CH$_3$), 28.06, 32.91 (CH$_2$), 40.69 (CH), 61.10 (OCH$_2$), 107.27, 123.12 (C), 127.57, 127.73, 129.38 (CH, Ph), 140.16, 144.75, 152.58, 164.78, 165.50 (C). − IR (KBr): $\tilde{\nu}$ = 3310 (br), 3063 (w), 3028 (w), 2992 (w), 2929 (w), 1790 (s), 1675 (s), 1643 (m), 1400 (s), 1374 (m), 1288 (m), 1265 (s), 1245 (m), 1161 (m), 1136 (m), 1032 (m) cm^{-1}. − MS (EI, 70 eV): m/z (%) = 300 (41) [M^{+}], 272 (14), 254 (38), 226 (100); the exact molecular mass m/z = 300.0997 ± 2 mD [M^{+}] for C$_{12}$H$_{14}$O$_5$ was confirmed by HRMS (EI, 70 eV).

γ-Alkylidenebutenolide 4m: Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3m** (1.012 g, 2.70 mmol), **4m** was isolated as a slightly yellow oil (393 mg, 52%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.90 (m, 2 H, CH$_2$), 0.97 (s, 9 H, *t*Bu), 1.35 (t, J = 7.0 Hz, 3 H, CH$_2$C*H*$_3$), 2.00−2.25 (m, 2 H, CH$_2$), 2.75−2.95 (dt, 2 H, CH$_2$), 4.30 (q, J = 7.0 Hz, 2 H, OCH$_2$). − ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 14.26, 21.89, 27.35, 32.43, 44.40, 61.22, 109.46, 124.27, 138.10, 151.19, 165.05, 166.20, 168.10. − IR (neat): $\tilde{\nu}$ = 3214 (br), 3063 (m), 2962 (s), 2870 (m), 1793 (s), 1735 (m), 1673 (s), 1653 (m), 1398 (m), 1366 (m), 1282 (m), 1260 (m), 1044 (m) cm^{-1}. − MS (EI, 70 eV): m/z (%) = 280 (22) [M^{+}], 252 (12), 224 (22), 177 (51). − A small amount of an unknown impurity could not be separated from the product.

γ-Alkylidenebutenolide 4n: Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **3n** (540 mg, 1.80 mmol), **4n** was isolated as a colourless solid (208 mg, 55%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 1.35 (t, J = 6.0 Hz, 3 H, CH$_3$), 2.78, 3.02 (2 × m, 2 × 2 H, CH$_2$), 4.28 (q, J = 6.0 Hz, 2 H, OCH$_2$), 5.30 (br, 1 H, OH). − ^{13}C NMR ([D$_6$]acetone, 62.5 MHz): δ = 13.75 (CH$_3$), 20.35, 31.79 (CH$_2$), 60.00 (O*C*H$_2$CH$_3$), 108.19, 132.80, 135.91, 156.49, 162.39, 168.34 (C). − IR (KBr): $\tilde{\nu}$ = 3296 (s), 2989 (m), 2966 (m), 2940 (m), 1799 (s), 1759 (m), 1676 (s), 1647 (s), 1463 (m), 1422 (s), 1402 (s), 1386 (s), 1367 (s), 1357 (s), 1305 (s), 1286 (s), 1255 (s), 1238 (s), 1127 (s) 1029 (s) cm^{-1}. − MS (EI, 70 eV): m/z (%) = 210 (68) [M^{+}], 180 (31), 165 (100); the exact molecular mass m/z = 210.0528 ± 2 mD [M^{+}] was confirmed by HRMS (EI, 70 eV). − C$_{10}$H$_{10}$O$_5$ (210.2): C 57.14, H 4.80; found C 57.97, H 5.15.

Synthesis of 1,3-Bis(trimethylsilyloxy)-1,3-cyclooctadiene (5): Diene **5** was prepared according to the procedure for the synthesis of dienes **3b−n**, in the presence of HMPTA (2 equiv.). Starting from cyclooctane-1,3-dione (840 mg, 6.00 mmol), **5** was isolated as a yellowish oil (1.30 g, 76%). The crude product was used for the cyclization with oxalyl chloride. − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.12, 0.22 (2 × s, 2 × 9 H, Me$_3$Si), 1.40−1.70 (m, 4 H, CH$_2$), 1.98, 2.24 (2 × m, 2 × 2 H, CH$_2$), 4.90 (t, J = 11.0 Hz, 1 H, CH), 4.98 (s, 1 H, CH). − MS (EI, 70 eV): m/z (%) = 284 (12) [M^{+}], 73 (100); the exact molecular mass m/z = 284.1628 ± 2 mD [M^{+}] for C$_{14}$H$_{28}$O$_2$Si$_2$ was confirmed by HRMS (EI, 70 eV).

Synthesis of γ-Alkylidenebutenolide 6: Butenolide **6** was prepared according to the procedure for the synthesis of butenolides **4a−n**. Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **5** (425 mg, 1.49 mmol), **6** was isolated as a slightly yellow oil (148 mg, 51%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 1.72, 1.95 (2 × m, 2 × 2 H, CH$_2$), 2.57 (m, 4 H, CH$_2$), 5.79 (s, 1 H, CH), 7.40 (br, 1 H, OH). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 19.68, 21.81, 25.67, 41.75 (CH$_2$), 108.02 (CH), 122.78, 144.44, 157.08, 164.48 (C), 204.71 (CO). − MS (EI, 70 eV): *m/z* (%) = 194 (28) [M$^+$]. − A small amount of an unknown impurity could not be separated.

Ethyl 3-Trimethylsilyloxyhepta-2,6-dienoate (8): Triethylamine (8.88 mL, 64 mmol) and Me$_3$SiCl (8.1 mL, 64 mmol) were added to a benzene solution (100 mL) of ethyl 3-oxohept-6-enoate (8.28 g, 49 mmol). After stirring for 24 h at 20 °C, the mixture was filtered and the filtrate was concentrated in vacuo. The residue was distilled (75−80 °C, 0.005 mbar) to give **8** as a colourless oil (11.50 g, 96%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.27 (s, 9 H, Me$_3$Si), 1.26 (t, *J* = 6.0 Hz, 3 H, CH$_3$), 2.25 (dt, 2 H, CH$_2$), 2.81 (t, *J* = 6.0 Hz, 2 H, CH$_2$), 4.11 (q, *J* = 6.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.85−5.10 (m, 2 H, CH$_2$CH=C*H*$_2$), 5.06 (s, 1 H, CC*H*CO), 5.83 (tt, 1 H, CH$_2$C*H*=CH$_2$).

1-Ethoxy-1,3-bis(trimethylsilyloxy)-hepta-1,3,6-triene (9): Compound **8** (5.34 g, 22 mmol) was added at −78 °C to a THF solution (50 mL) of LDA [prepared by addition of *n*BuLi (15.7 mL, 39 mmol) to a THF solution of diisopropylamine (5.2 mL, 39 mmol)]. After this had stirred for 60 min, Me$_3$SiCl (6.2 mL, 48 mmol) was added. The solution was stirred for a further 60 min, allowed to warm to 20 °C over 2 h and stirred for 60 min at 20 °C. The solvent was removed in vacuo and petroleum ether was added. The mixture was filtered and the filtrate was concentrated in vacuo. The residue was distilled (60−63 °C, 0.05 mbar) to give **9** as a colourless oil (6.21 g, 90%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.17, 0.25 (2 × s, 2 × 9 H, Me$_3$Si), 1.28 (t, *J* = 6.0 Hz, 3 H, CH$_3$), 2.81 (dd, 2 H, 5-H), 3.81 (q, *J* = 6.0 Hz, 2 H, OC*H*$_2$CH$_3$), 3.87 (s, 1 H, 2-H), 4.85−5.15 (m, 3 H, 4-H, CH$_2$CH=C*H*$_2$), 5.81 (tt, 1 H, CH$_2$C*H*=CH$_2$).

Ethyl 3-Trimethylsilyloxyocta-2,7-dienoate (17): Silyl enol ether **17** was prepared according to the procedure for the synthesis of **8**, without distillation. Starting from ethyl 3-oxooct-7-enoate (3.06 g, 16.6 mmol), **17** was isolated as a slightly yellow oil (4.06 g, 95%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.27 (s, 9 H, Me$_3$Si), 1.26 (t, *J* = 7.0 Hz, 3 H, CH$_3$), 1.60 (pent, 2 H, 5-H), 2.07 (m, 2 H, 4-H), 2.71 (t, *J* = 6.0 Hz, 6-H), 4.10 (q, *J* = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.90−5.02 (m, 2 H, CH$_2$CH=C*H*$_2$), 5.06 (s, 1 H, CC*H*CO), 5.80 (m, 1 H, CH$_2$C*H*=CH$_2$).

1-Ethoxy-1,3-bis(trimethylsilyloxy)octa-1,3,7-triene (18): Bis(silyl enol ether) **18** was prepared according to the procedure for the synthesis of **9**, without distillation. Starting from **17** (9.00 g, 35.1 mmol), **18** was isolated as a slightly yellow oil (9.90 g, 86%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.10−0.30 (4 × s, 18 H, Me$_3$Si), 1.10−2.20 (m, 4 H, CH$_2$), 3.70−3.90 (m, 3 H, OC*H*$_2$CH$_3$, 2-H), 4.80−5.10 (m, 3 H, 4-H, CH$_2$CH=C*H*$_2$), 5.80 (m, 1 H, CH$_2$C*H*=CH$_2$).

Synthesis of γ-Alkylidenebutenolide 10: Butenolide **10** was prepared according to the procedure for the synthesis of butenolides **4a−n**. Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **9** (566 mg, 1.80 mmol), **10** was isolated as a colourless solid (295 mg, 73%), m.p. 88 °C. − ^{1}H NMR ([D$_6$]acetone, 250 MHz): δ = 1.31 (t, *J* = 5.0 Hz, 3 H, CH$_3$), 3.31 (d, *J* = 5.0 Hz, 2 H, CC*H*$_2$CH), 4.21 (q, *J* = 5.0 Hz, 2 H, OC*H*$_2$CH$_3$), 5.21 (m, 2 H, CH$_2$CH=C*H*$_2$), 5.48 (s, 1 H, CC*H*CO), 5.94 (m, 1 H, CH$_2$C*H*=CH$_2$). − ^{13}C NMR ([D$_6$]acetone, 62.5 MHz): δ = 14.52 (CH$_3$), 26.61 (*C*H$_2$CHCH$_2$), 60.64 (O*C*H$_2$CH$_3$), 96.42 (C*C*HCO), 117.16 (CH$_2$CH=*C*H$_2$), 122.60 (C), 133.99 (CH, *C*H=CH$_2$), 144.97, 157.61 (C), 163.57, 164.62 (C=O). − MS (EI, 70 eV): *m/z* (%) = 224 (11) [M$^+$], 178 (34), 168 (26), 150 (84), 122 (27), 109 (100); the exact molecular mass *m/z* = 224.0684 ± 2 mD [M$^+$] for $C_{11}H_{12}O_5$ was confirmed by HRMS (EI, 70 eV). − $C_{11}H_{12}O_5$ (224.2): C 58.93, H 5.39; found C 58.78, H 5.66.

Synthesis of γ-Alkylidenebutenolide 19: Butenolide **19** was prepared according to the procedure for the synthesis of butenolides **4a−n**. Starting from 1,3-bis(trimethylsilyloxy)-1,3-butadiene **18** (590 mg, 1.80 mmol), **19** was isolated as a colourless oil (308 mg, 72%). − ^{1}H NMR ([D$_6$]acetone, 250 MHz): δ = 1.23 (t, *J* = 7.0 Hz, 3 H, CH$_3$), 2.33 (m, 2 H, C*H*$_2$CH=CH$_2$), 2.54 (m, 2 H, CCH$_2$), 4.14 (q, *J* = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.92−5.10 (m, 2 H, CH$_2$CH=C*H*$_2$), 5.45 (s, 1 H, =C*H*CO$_2$Et), 5.80−6.00 (m, 1 H, CH$_2$C*H*=CH$_2$), 10.10 (br, 1 H, OH). − ^{13}C NMR ([D$_6$]acetone, 62.5 MHz): δ = 14.48 (CH$_3$), 22.17, 32.59 (*C*H$_2$CH$_2$), 60.61 (O*C*H$_2$CH$_3$), 96.03 (C*C*HCO), 115.96 (CH$_2$CH=*C*H$_2$), 124.58 (C), 137.84 (CH, *C*H=CH$_2$), 144.60, 157.80 (C), 163.59, 164.63 (C=O). − MS (EI, 70 eV): *m/z* (%) = 238 (22) [M$^+$]; the exact molecular mass *m/z* = 238.0841 ± 2 mD [M$^+$] for $C_{12}H_{14}O_5$ was confirmed by HRMS (EI, 70 eV). − $C_{12}H_{14}O_5$ (238.2): C 60.50, H 5.92; found C 60.24, H 6.10.

General Procedure for Mitsunobu Treatment of γ-Alkylidenebutenolides: A THF solution (2 mL) of DEAD (0.205 mL, 1.32 mmol) was added to a degassed THF solution (6 mL) of **10** (240 mg, 1.1 mmol), 3-hydroxy-1-pentene (114 mg, 1.32 mmol) and PPh$_3$ (347 mg, 1.32 mmol). The solution was stirred at 20 °C for 14 h. The solvent was removed in vacuo and the residue was purified by chromatography (silica gel; ether/petroleum ether, 1:3) to give **11c** as a slightly yellow oil (180 mg, 56%).

γ-Alkylidenebutenolide 11a: Starting from **10** (450 mg, 2.0 mmol), **11a** was isolated as a slightly yellow oil (370 mg, 70%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 1.28 (t, *J* = 7.0 Hz, 3 H OCH$_2$C*H*$_3$), 3.16 (m, 2 H, C*H*$_2$CH=CH$_2$), 4.21 (q, *J* = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.94−5.41 (m, 7 H, C*H*C=O, OC*H*$_2$CH=CH$_2$, CH=C*H*$_2$), 5.73−6.01 (m, 2 H, CH$_2$C*H*=CH$_2$). − MS (70 eV, EI): *m/z* (%) = 264 (24) [M$^+$]; the exact molecular mass *m/z* = 264.0998 ± 2 mD [M$^+$] for $C_{14}H_{16}O_5$ was confirmed by HRMS (EI, 70 eV).

γ-Alkylidenebutenolide 11b: Starting from **10** (448 mg, 2.0 mmol), **11b** was isolated as a slightly yellow oil (345 mg, 62%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 1.25 (t, *J* = 7.0 Hz, 3 H, CH$_2$C*H*$_3$), 1.35 (d, *J* = 6.0 Hz, 3 H, CH$_3$), 3.08 (m, 2 H, C*H*$_2$CH=CH$_2$), 4.18 (q, *J* = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 5.05−5.25 (m, 5 H, C*H*CH$_3$, 2 × CH=C*H*$_2$), 5.30 (s, 1 H, C*H*C=O), 5.65−5.90 (m, 2 H, C*H*=CH$_2$). − MS (70 eV, EI): *m/z* (%) = 278 (18) [M$^+$]; the exact molecular mass *m/z* = 278.1154 ± 2 mD [M$^+$] for $C_{15}H_{18}O_5$ was confirmed by HRMS (EI, 70 eV).

γ-Alkylidenebutenolide 11c: Starting from **10** (240 mg, 1.1 mmol), **11c** was isolated as a slightly yellow oil (180 mg, 56%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.95, 1.28 (2 × t, *J* = 7.0 Hz, 2 × 3 H, 2 × CH$_3$), 1.75 (m, 2 H, CHC*H*$_2$), 3.10 (m, 2 H, C*H*$_2$CH=CH), 4.22 (q, *J* = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 5.00−5.40 (m, 6 H, C*H*CH$_2$CH$_3$, C*H*C=O, 2 × CH=C*H*$_2$), 5.60−5.90 (m, 2 H, C*H*=CH$_2$). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 9.15, 14.16, 26.50, 28.03, 60.69, 82.99, 96.86, 117.56, 119.05, 129.61, 132.18, 136.27, 144.60, 155.46, 162.49, 163.37. − MS (70 eV, EI): *m/z* (%) = 292 (20) [M$^+$]; the exact molecular mass *m/z* = 292.1311 ± 2 mD [M$^+$] for $C_{16}H_{20}O_5$ was confirmed by HRMS (EI, 70 eV).

γ-Alkylidenebutenolide 14a: Starting from **10** (300 mg, 1.26 mmol), **14a** was isolated as a slightly yellow oil (238 mg, 68%). − ^{1}H NMR

($CDCl_3$, 250 MHz): δ = 1.24 (t, *J* = 6.0 Hz, 3 H, CH_3), 2.23, 2.41 (2 × m, 2 × 2 H, CH_2), 4.18 (q, *J* = 6.0 Hz, 2 H, OCH_2CH_3), 4.92 (d, *J* = 6.0 Hz, 2 H, $OCH_2CH{=}CH_2$), 4.90−5.05, 5.20−5.40 (2 × m, 2 × 2 H, $CH_2CH{=}CH_2$), 5.35 (s, 1 H, $=CHCO_2Et$), 5.65−6.00 (2 × m, 2 × 1 H, $CH_2CH{=}CH_2$). − ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 13.93 (CH_3), 21.91, 31.94, 60.69, 71.35 (CH_2), 96.46 ($=CHCO_2Et$), 116.17, 119.44 ($CH_2CH{=}CH_2$), 130.62 (C), 132.22, 136.12 ($CH{=}CH_2$), 144.23, 155.63, 162.31, 163.30 (C). − MS (70 eV, EI): *m*/*z* (%) = 278 (38) [M^+]; the exact molecular mass *m*/*z* = 278.1154 ± 2 mD [M^+] for $C_{15}H_{18}O_5$ was confirmed by HRMS (EI, 70 eV).

γ-Alkylidenebutenolide 14b: Starting from **10** (300 mg, 1.26 mmol), **14b** was isolated as a slightly yellow oil (240 mg, 65%). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.07 (d, t, 2 × 3 H, CH_2CH_3, $CHCH_3$), 2.25−2.50 (m, 2 H, $CHCH_2CH{=}CH_2$), 3.11 (d, *J* = 6.0 Hz, 2 H, $CH_2CH{=}CH_2$), 4.23 (q, *J* = 6.0 Hz, 2 H, OCH_2CH_3), 5.05−5.20 (m, 4 H, $CH_2CH{=}CH_2$), 5.22 (sext, *J* = 7.0 Hz, 1 H, $OCHCH_3$), 5.34 (s, 1 H, $=CHCO_2Et$), 5.68−5.90 (m, 2 H, $CH_2CH{=}CH_2$). − ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 14.21, 20.38 (CH_3), 26.55, 41.15 (CH_2), 60.73 (OCH_2), 76.88 (CH), 96.85 ($=CHCO_2Et$), 117.58, 118.29 ($CH_2CH{=}CH_2$), 128.77 (C), 132.18, 132.99 ($CH{=}CH_2$), 144.45, 155.51, 162.44, 163.41 (C). − MS (70 eV, EI): *m*/*z* (%) = 292 (8) [M^+]; the exact molecular mass *m*/*z* = 292.1310±2 mD [M^+] for $C_{16}H_{20}O_5$ was confirmed by HRMS (EI, 70 eV).

γ-Alkylidenebutenolide 14c: Starting from **10** (300 mg, 1.26 mmol), **14c** was isolated as a slightly yellow oil (236 mg, 64%). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.07 (d, *J* = 7.0 Hz, 3 H, $CHCH_3$), 1.31 (t, *J* = 6.0 Hz, 3 H, CH_2CH_3), 2.56 (quint, *J* = 7.0 Hz, 1 H, $CHCH_3$), 3.11 (d, *J* = 6.0 Hz, 2 H, $CH_2CH{=}CH_2$), 4.23 (q, *J* = 6.0 Hz, 2 H, OCH_2CH_3), 4.34 (dd, *J* = 7, *J* = 3.0 Hz, 2 H, OCH_2CH), 5.00−5.20 (m, 4 H, $CH_2CH{=}CH_2$), 5.34 (s, 1 H, $=CHCO_2Et$), 5.66−5.90 (m, 2 H, $CH_2CH{=}CH_2$). − ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 14.22, 15.92 (CH_3), 26.62 (CH_2), 38.14 (CH), 60.75, 75.08 (OCH_2), 96.90 ($=CHCO_2Et$), 115.57, 117.64 ($CH_2CH{=}CH_2$), 127.54 (C), 132.18, 139.27 ($CH{=}CH_2$), 144.89, 155.47, 162.32, 163.39 (C). − MS (70 eV, EI): *m*/*z* (%) = 292 (9) [M^+], 247 (8), 225 (18), 196 (18), 69 (100); the exact molecular mass *m*/*z* = 292.1310 ± 2 mD [M^+] for $C_{16}H_{20}O_5$ was confirmed by HRMS (EI, 70 eV).

γ-Alkylidenebutenolide 20a: Starting from **19a** (200 mg, 0.84 mmol), **20a** was isolated as a slightly yellow oil (159 mg, 68%). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.28 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 2.26, 2.42 (2 × m, 2 × 2 H, CH_2CH_2), 4.21 (q, *J* = 7.0 Hz, 2 H, OCH_2CH_3), 4.92 (d, *J* = 8.0 Hz, 2 H, $OCH_2CH{=}CH$), 5.32 (s, 1 H, $CHC{=}O$), 4.95−5.40 (m, 4 H, $CH{=}CH_2$), 5.65−6.00 (2 × m, 2 × 1 H, $CH{=}CH_2$). − ^{13}C NMR (C_6D_6, 62.5 MHz): δ = 14.12 (OCH_2CH_3), 21.91, 31.94 (CH_2CH_2), 60.69, 71.35 (OCH_2), 96.46 ($CHC{=}O$), 116.17, 119.44 ($CH{=}CH_2$), 130.62 (C), 132.22, 136.12 ($CH{=}CH$), 144.24, 155.63, 162.31, 163.30 (C). − MS (70 eV, EI): *m*/*z* (%) = 278 (4) [M^+], 233 (22), 209 (100); the exact molecular mass *m*/*z* = 278.1154 ± 2 mD [M^+] for $C_{15}H_{18}O_5$ was confirmed by HRMS (EI, 70 eV).

γ-Alkylidenebutenolide 20b: Starting from **19b** (200 mg, 0.84 mmol), **20b** was isolated as a slightly yellow oil (152 mg, 62%). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.30 (t, *J* = 7.0 Hz, 3 H, 3 H, CH_2CH_3), 1.39 (d, *J* = 6.0 Hz, 3 H, 3 H, $CHCH_3$), 2.28, 2.42 (2 × m, 2 × 2 H, CH_2CH_2), 4.23 (q, *J* = 7.0 Hz, 2 H, OCH_2CH_3), 4.98−5.30 (m, 4 H, $CH{=}CH_2$), 5.32 (s, 1 H, $=CHCO_2Et$), 5.60−5.75 (quint, *J* = 6.0 Hz, 1 H, $OCHCH_3$), 5.80−5.90 (m, 2 H, $CH{=}CH_2$). − ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 14.22, 21.11 (CH_3), 21.99, 32.02 (CH_2), 60.77 (OCH_2), 77.70 (CH), 96.43 ($=CHCO_2Et$), 116.19, 117.90 ($CH{=}CH_2$), 131.74 (C), 136.29, 137.71 (CH), 144.16, 155.84, 162.58, 163.45 (C). − MS (70 eV, EI): *m*/*z* (%) = 292 (2) [M^+]. − A small amount of an unknown impurity could not be separated.

γ-Alkylidenebutenolide 20c: Starting from **19c** (200 mg, 0.84 mmol), **20c** was isolated as a slightly yellow oil (162 mg, 63%). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.95 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.31 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 1.55−1.90 (m, 2 H, $CHCH_2CH_3$), 2.32, 2.44 (2 × m, 2 × 2 H, CH_2CH_2), 4.23 (q, *J* = 7.0 Hz, 2 H, OCH_2CH_3), 5.00−5.30 (m, 4 H, $CH{=}CH_2$), 5.31 (s, 1 H, $=CHCO_2Et$), 5.43 (q, J = 7.0 Hz, 1 H, $OCHCH_2$), 5.70−5.90 (m, 2 H, $CH{=}CH_2$). − ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 9.24, 14.22, 22.02, 28.10, 32.05, 60.78, 82.77, 96.28, 116.19, 119.19, 131.52, 136.32, 136.35, 144.42, 155.90, 162.58, 163.50. − IR (neat): $\tilde{\nu}$ = 3444 (br), 3061 (w), 2981 (m), 2933 (m), 1735 (s), 1656 (s), 1599 (s), 1589 (s), 1572 (s), 1447 (m), 1384 (s), 1254 (m), 1164 (s), 1022 (m) cm^{-1}. − MS (70 eV, EI): *m*/*z* (%) = 306 (2) [M^+], 239 (40), 69 (100); the exact molecular mass *m*/*z* = 306.1467 ± 2 mD [M^+] for $C_{17}H_{22}O_5$ was confirmed by HRMS (EI, 70 eV). − $C_{17}H_{22}O_5$ (306.4): C 66.65, H 7.24; found C 66.38, H 7.50.

General Procedure for the Synthesis of Bicyclic γ-Alkylidenebutenolides by Ring-Closing Metathesis: Grubbs' catalyst **12** (19 mg, 10 mol %) was added to a degassed benzene solution (8 mL) of butenolide **11c** (66 mg, 0.23 mmol). The solution was stirred for 12 h under argon and for 4 h in air. The solvent was removed in vacuo and the residue was purified by chromatography (silica gel; ether/petroleum ether, 1:1) to give **13c** as a slightly yellow oil (36 mg, 60%).

γ-Alkylidenebutenolide 13a: Starting from **11a** (41 mg, 0.16 mmol), **13a** was isolated as a slightly yellow oil (26 mg, 70%). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.24 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 3.25 (d, *J* = 5.0 Hz, 2 H, $OCH_2CH{=}CHCH_2$), 4.21 (q, *J* = 7.0 Hz, 2 H, OCH_2CH_3), 4.75 (d, *J* = 7.0 Hz, 2 H, $CH{=}CHCH_2O$), 5.29 (s, 1 H, $CHC{=}O$), 5.99−6.21 (m, 2 H, $CH_2CH{=}CHCH_2O$). − ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 13.97 (OCH_2CH_3), 23.12 $CH_2CH{=}CHCH_2O$), 60.85 (OCH_2CH_3), 67.79 ($CH_2CH{=}CHCH_2O$), 95.97 ($CHC{=}O$), 121.22 (C), 126.87, 132.88 ($CH_2CH{=}CHCH_2O$), 147.37, 156.03 (C), 162.69, 163.33 (CO). − MS (70 eV, EI): *m*/*z* (%) = 236 (100) [M^+]; the exact molecular mass *m*/*z* = 236.0685 ± 2 mD [M^+] for $C_{12}H_{12}O_5$ was confirmed by HRMS (EI, 70 eV). − $C_{12}H_{12}O_5$ (236.2): C 61.01, H 5.12; found C 60.72, H 5.27.

γ-Alkylidenebutenolide 13b: Starting from **11b** (216 mg, 0.78 mmol), **13b** was isolated as a slightly yellow oil (120 mg, 62%). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.31 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 1.52 (d, *J* = 7.0 Hz, 3 H, $CHCH_3$), 2.92 (dd, ^2J = 20.0, ^3J = 8.0 Hz, 1 H, $CCH_2CH{=}CH$), 3.47 (dd, *J* = 20.0, *J* = 3.0, 1 H, $CCH_2CH{=}CH$), 4.23 (q, *J* = 7.0 Hz, 2 H, OCH_2CH_3), 5.13 (m, 1 H, $CHCH_3$), 5.26 (s, 1 H, $CHC{=}O$), 5.80−5.87, 6.00−6.06 (2 × m, 2 × 1 H, $CH{=}CH$). − ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 14.21, 20.69 (CH_3), 22.45 (CH_2), 60.70 (OCH_2), 75.33 ($CHCH_3$), 95.63 ($=CHCO$), 120.49 (C), 130.99, 133.05 (CH), 146.58, 156.21, 163.33, 163.34 (C). − MS (70 eV, EI): *m*/*z* (%) = 250 (100) [M^+]; the exact molecular mass *m*/*z* = 250.0841 ± 2 mD [M^+] for $C_{13}H_{14}O_5$ was confirmed by HRMS (EI, 70 eV). − $C_{13}H_{14}O_5$ (250.3): C 62.39, H 5.64; found C 62.10, H 5.42.

γ-Alkylidenebutenolide 13c: Starting from **11c** (66 mg, 0.23 mmol), **13c** was isolated as a slightly yellow oil (36 mg, 60%). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.05, 1.31 (2 × t, *J* = 7.0 Hz, 2 × 3 H, CH_2CH_3), 1.85 (m, 2 H, CH_2), 2.93 (dd, *J* = 17.0, *J* = 7.0, 1 H, $CCH_2CH{=}CH$), 3.45 (dt, *J* = 17.0, *J* = 3.0, 1 H, $CCH_2CH{=}CH$), 4.22 (q, *J* = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.87 (m, 1 H, C*H*CH$_2$CH$_3$), 5.25 (s, 1 H, C*H*C=O), 5.85, 6.10 (2 × m, 2 × 1 H, C*H*=C*H*). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 9.31, 14.21, 22.60, 27.62, 60.78, 80.14, 95.59, 120.57, 131.23, 131.86, 146.74, 156.30, 162.81, 163.44. − MS (70 eV, EI): *m*/*z* (%) = 264 (100) [M$^+$]; the exact molecular mass *m*/*z* = 264.0998 ± 2 mD [M$^+$] for $C_{14}H_{16}O_5$ was confirmed by HRMS (EI, 70 eV). − $C_{14}H_{16}O_5$ (264.3): C 63.63, H 6.10; found C 63.35, H 6.32.

γ-Alkylidenebutenolide 15a: Starting from **14a** (112 mg, 0.40 mmol), **15a** was isolated as a slightly yellow oil (52 mg, 52%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 1.23 (t, *J* = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 2.72, 3.25 (2 × m, *J* = 5.0 Hz, 2 × 2 H, C*H*$_2$CH=CHC*H*$_2$), 4.21 (q, *J* = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 5.38 (t, *J* = 6.0 Hz, 2 H, OCH$_2$), 5.41 (s, 1 H, C*H*C=O), 5.65−5.90 (m, 2 H, CH$_2$C*H*=C*H*CH$_2$O). − ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 14.17 (OCH$_2$*C*H$_3$), 20.86, 32.87 (*C*H$_2$CH=CH*C*H$_2$), 60.73, 68.72 (OCH$_2$), 95.94 (*C*HC=O), 124.20 (C), 123.64, 129.42 (*C*H=*C*H), 145.78, 156.05, 163.31, 163.32 (C). − MS (70 eV, EI): *m*/*z* (%) = 250 (12) [M$^+$]; the exact molecular mass *m*/*z* = 250.0841 ± 2 mD [M$^+$] for $C_{13}H_{14}O_5$ was confirmed by HRMS (EI, 70 eV).

γ-Alkylidenebutenolide 15b: Starting from **14b** (125 mg, 0.53 mmol), **15b** was isolated as a slightly yellow oil (88 mg, 63%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 1.07 (t, *J* = 7.0 Hz, 3 H, CH$_2$C*H*$_3$), 1.41 (d, *J* = 6.0 Hz, 3 H, CHC*H*$_3$), 2.91 (dd, *J* = 17.0, *J* = 7.0, 2 H, CHC*H*$_2$CH=CH), 3.35 (dd, *J* = 17.0, *J* = 7.0, 2 H, C*H*$_2$CH=CH), 4.23 (q, *J* = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.88 (m, 1 H, OC*H*CH$_3$), 5.40 (s, 1 H, =C*H*CO$_2$Et), 5.65−5.90 (m, 2 H, CH=CH). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 14.17 (CH$_3$), 21.78 (CH$_2$), 21.86 (CH$_3$), 38.00 (CH$_2$), 60.79 (OCH$_2$), 77.05 (CH), 96.23 (=*C*HCO$_2$Et), 123.99 (CH), 127.75 (C), 129.23 (CH), 144.82, 156.14, 163.42, 163.52 (C). − IR (neat): ṽ = 3360 (br), 3062 (m), 2960 (s), 2924 (s), 2852 (s), 1780 (s), 1732 (s), 1668 (s), 1651 (s), 1462 (s), 1448 (s), 1372 (s), 1262 (s), 1158 (s), 1095 (s), 1030 (s) cm^{-1}. − MS (70 eV, EI): *m*/*z* (%) = 264 (59) [M$^+$]; the exact molecular mass *m*/*z* = 264.0998 ± 2 mD [M$^+$] for $C_{14}H_{16}O_5$ was confirmed by HRMS (EI, 70 eV). − $C_{14}H_{16}O_5$ (264.3): C 63.63, H 6.10; found C 63.38, H 6.28.

γ-Alkylidenebutenolide 15c: Starting from **14c** (155 mg, 0.66 mmol), **15c** was isolated as a slightly yellow oil (106 mg, 61%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 1.12 (d, *J* = 7.0 Hz, 3 H, CHC*H*$_3$), 1.31 (t, *J* = 7.0 Hz, 3 H, CH$_2$C*H*$_3$), 2.87 (m, 1 H, C*H*CH$_3$), 3.14 (t, *J* = 5.5 Hz, 2 H, C*H*$_2$CH=CH$_2$), 4.24 (q, *J* = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.25−4.52 (m, 2 H, OC*H*$_2$CH), 5.42 (s, 1 H, =C*H*CO$_2$Et), 5.55−5.80 (m, 2 H, CH=CH). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 14.17, 17.38 (CH$_3$), 21.07 (CH$_2$), 37.20 (CH), 60.81, 74.02 (OCH$_2$), 96.17 (=*C*HCO$_2$Et), 122.01 (CH), 125.41 (C), 135.83 (CH), 146.01, 156.00, 163.02, 163.40 (C). − IR (neat): ṽ = 3407 (br), 2978 (m), 2935 (m), 1793 (s), 1721 (m), 1635 (s), 1448 (m), 1372 (m), 1311 (m), 1277 (m), 1123 (s), 1035 (s) cm^{-1}. − MS (70 eV, EI): *m*/*z* (%) = 264 (59) [M$^+$]; the exact molecular mass *m*/*z* = 264.0998 ± 2 mD [M$^+$] for $C_{14}H_{16}O_5$ was confirmed by HRMS (EI, 70 eV). − $C_{14}H_{16}O_5$ (264.3): C 63.63, H 6.10; found C 63.45, H 6.22.

γ-Alkylidenebutenolide 21a: Starting from **20a** (125 mg, 0.50 mmol), **21a** was isolated as a slightly yellow oil (83 mg, 66%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 1.29 (t, *J* = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 2.63, 2.77 (2 × m, 2 × 2 H, C*H*$_2$C*H*$_2$CH=CH), 4.22 (q, *J* = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.86 (d, *J* = 8.0 Hz, 2 H, OC*H*$_2$CH=CH), 5.38 (s, 1 H, C*H*C=O), 5.77−5.85, 6.00−6.10 (2 × m, 2 × 1 H, C*H*=C*H*). − ^{13}C NMR (C$_6$D$_6$, 62.5 MHz): δ = 14.34 (OCH$_2$*C*H$_3$), 21.83, 29.06 (CH=CH*C*H$_2$*C*H$_2$), 60.45, 65.15 (OCH$_2$), 95.19 (*C*HC=O), 122.50 (*C*H=CH), 124.28 (C), 136.67 (*C*H=CH), 144.56, 157.11, 163.30, 163.35 (C). − IR (KBr): ṽ = 3088 (w), 3001 (w), 2991 (w), 2969 (w), 2917 (w), 1794 (s), 1718 (m), 1654 (m), 1629 (s), 1432 (m), 1392 (m), 1331 (m), 1293 (m), 1159 (s), 1129 (m), 1086 (m), 1041 (m) cm^{-1}. − MS (70 eV, EI): *m*/*z* (%) = 250 (44) [M$^+$], 204 (100), 176 (99), 148 (43); the exact molecular mass *m*/*z* = 250.0841 ± 2 mD [M$^+$] for $C_{13}H_{14}O_5$ was confirmed by HRMS (EI, 70 eV). − $C_{13}H_{14}O_5$ (250.3): C 62.39, H 5.64; found C 62.05, H 5.88.

Crystal Structure Analysis of 21a: $C_{13}H_{14}O_5$, M_r = 250.24, crystal size: 0.4 × 0.2 × 0.1 mm, monoclinic, $P2_1/c$, unit cell dimensions: *a* = 7.537(2) Å, *b* = 11.207(2) Å, *c* = 14.357(3) Å, β = 103.97(3)°, *V* = 1176.7(4) Å^3, *Z* = 4, $\rho_{\text{calcd.}}$ = 1.412 Mg/m^3, μ = 0.109 mm^{-1}, *F*(000) = 528; total number of reflections measured 27908, unique 2683 (R_{int} = 0.0440). Data/restraints/parameters 2683/0/164, data collection range 2.3° ≤ θ ≤ 27.4°. Final *R* indices: $R1 = \Sigma|F_o - F_c|/\Sigma|F_o|$ = 0.0380, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma wF_o{}^4]^{1/2}$ = 0.0993 on data with $I > 2\sigma(I)$ and *R*1 = 0.0408, *wR*2 = 0.1014 on all data, goodness of fit $S = [\Sigma w(F_o{}^2 - Fc^2)^2/\Sigma(n - p)]^{1/2})$ = 1.076; largest difference peak/hole 0.306/−0.243 e·Å^{-3}. The crystal was mounted on a glass fibre in a rapidly cooled perfluoropolyether.[19] Diffraction data were collected with a Stoe−Siemens−Huber four-circle diffractometer coupled to a Siemens CCD area detector at 133(2) K, with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), performing - and ω-scans. The structure was solved by direct methods using SHELXS-97[20] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[21] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The final fractional atomic coordinates and other crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158694. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

γ-Alkylidenebutenolide 21b: Starting from **20b** (125 mg, 0.55 mmol), **21b** was isolated as a slightly yellow oil (80 mg, 55%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 1.28 (t, *J* = 7.0 Hz, 3 H, CH$_2$C*H*$_3$), 1.51 (d, *J* = 6.0 Hz, 3 H, CHC*H*$_3$), 2.40−3.10 (3 × m, 4 H, CH$_2$CH$_2$), 4.22 (q, *J* = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 5.38 (s, 1 H, =C*H*CO$_2$Et), 5.40−5.60, 5.90 (m, 3 H, OC*H*CH$_3$, CH=CH). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 14.24, 21.43 (CH$_3$), 22.33, 29.42 (CH$_2$), 60.76 (OCH$_2$), 72.97 (OCH), 95.13 (*C*HCO$_2$Et), 123.87 (C), 129.41, 133.94 (CH), 144.63, 156.84, 163.38, 163.60 (C). − MS (70 eV, EI): *m*/*z* (%) = 264 (68) [M$^+$], 218 (80), 190 (100); the exact molecular mass *m*/*z* = 264.0998 ± 2 mD [M$^+$] for $C_{14}H_{16}O_5$ was confirmed by HRMS (EI, 70 eV). − A small amount of a minor isomer could not be separated.

γ-Alkylidenebutenolide 21c: Starting from **20c** (140 mg, 0.56 mmol), **21c** was isolated as a slightly yellow oil (100 mg, 64%). − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 1.02 (t, *J* = 7.0 Hz, 3 H, CH$_3$), 1.30 (t, *J* = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 1.63−2.00 (m, 2 H, CHC*H*$_2$CH$_3$), 2.40−2.60 (m, 2 H, C*H*$_2$CH=CH), 2.75, 3.05 (2 × m, 2 × 1 H, C*H*$_2$CH=CH), 4.22 (q, *J* = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 5.21 (m, 1 H, OC*H*CH$_2$), 5.36 (s, 1 H, =C*H*CO$_2$Et), 5.45, 5.95 (2 × m, 2 × 1 H, CH=CH). − ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ = 9.65, 14.21 (CH$_3$), 22.38, 28.49, 29.24 (CH$_2$), 60.70 (OCH$_2$), 28.17 (OCH), 95.05 (=*C*HCO$_2$Et), 124.07 (C), 128.30, 134.38 (CH), 144.77, 156.86, 163.34, 163.57 (C). − IR (neat): ṽ = 3415 (w), 3022 (m), 2969 (s), 2933 (s), 2903 (m), 2887 (m), 1796 (s), 1718 (s), 1660 (s), 1632 (s), 1474 (m), 1461 (m), 1431 (m), 1395 (s), 1336 (s), 1296 (s), 1283 (s), 1160 (s), 1044 (s) cm^{-1}. − MS (70 eV, EI): *m*/*z* (%) = 278

(71) [M$^+$], 232 (63), 204 (100); the exact molecular mass $m/z = 278.1154 \pm 2$ mD [M$^+$] for $C_{15}H_{18}O_5$ was confirmed by HRMS (EI, 70 eV).

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[1] [1a] F. Bohlmann, G. Brindöpke, R. C. Rastogi, *Phytochemistry* **1982**, *21*, 695. – [1b] K. H. Lee, T. A. Geissman, *Phytochemistry* **1970**, *9*, 403. – [1c] W. Vichnewski, W. Herz, N. Kumar, *J. Org. Chem.* **1979**, *44*, 2575. – [1d] F. Bohlmann, C. Zdero, R. M. King, H. Robinson, *Phytochemistry* **1982**, *21*, 695. – [1e] A. Bardón, S. Montanaro, C. A. N. Catalán, J. G. Diaz, W. Herz, *Phytochemistry* **1992**, *34*, 253. – [1f] J. Jakupovic, G. Schmeda-Hirschmann, A. Schuster, C. Zdero, F. Bohlmann, R. M. King, H. Robinson, J. Pickardt, *Phytochemistry* **1986**, *25*, 145. – [1g] J. N. Bazon, J. L. C. Lopes, W. Vichnewski, D. A. Dias, K. Nagamiti, W. R. Cunha, W. Herz, *Phytochemistry* **1997**, *44*, 1535.

[2] [2a] P. K. Chowdhury, R. P. Sharma, G. Thyagarajan, W. Herz, S. V. Govindan, *J. Org. Chem.* **1980**, *45*, 4993. – [2b] P. L. Cowall, J. M. Cassady, C.-j. Chang, J. F. Kozlowski, *J. Org. Chem.* **1981**, *46*, 1108.

[3] [3a] F. Bohlmann, G. Brindöpke, R. C. Rastogi, *Phytochemistry* **1982**, *21*, 695. – [3b] K. H. Lee, T. A. Geissman, *Phytochemistry* **1970**, *9*, 403. – [3c] W. Vichnewski, W. Herz, N. Kumar, *J. Org. Chem.* **1979**, *44*, 2575.

[4] For recent cyclization reactions of dianions and dianion equivalents from our laboratory, see: [4a] P. Langer, M. Stoll, *Angew. Chem.* **1999**, *111*, 1919; *Angew. Chem. Int. Ed.* **1999**, *38*, 1803. – [4b] P. Langer, T. Schneider, M. Stoll, *Chem. Eur. J.* **2000**, *6*, 3204. – [4c] P. Langer, E. Holtz, *Angew. Chem.* **2000**, *112*, 3208; *Angew. Chem. Int. Ed.* **2000**, *39*, 3086. – [4d] P. Langer, T. Eckardt, *Angew. Chem.* **2000**, *112*, 4503; *Angew. Chem. Int. Ed.* **2000**, *39*, 4343. – [4e] P. Langer, T. Krummel, *Chem. Commun.* **2000**, 967. – [4f] P. Langer, T. Eckardt, *Synlett* **2000**, 844. – [4g] P. Langer, T. Schneider, *Synlett* **2000**, 497. – [4h] P. Langer, J. Wuckelt, M. Döring, H. Görls, *J. Org. Chem.* **2000**, *65*, 3603. – [4i] P. Langer, I. Karimé, *Synlett* **2000**, 743. – [4j] P. Langer, V. Köhler, *Org. Lett.* **2000**, 1597. – [4k] P. Langer, V. Köhler, *Chem. Commun.* **2000**, 1653. – [4l] P. Langer, B. Kracke, *Tetrahedron Lett.* **2000**, 4545. – [4m] P. Langer, M. Döring, *Chem. Commun.* **1999**, 2439. – [4n] P. Langer, *Chem. Commun.* **1999**, 1217. – [4o] P. Langer, J. Wuckelt, M. Döring, R. Beckert, *Eur. J. Org. Chem.* **1998**, 1467. – [4p] P. Langer, M. Döring, *Synlett* **1998**, 396. – [4q] P. Langer, I. Freifeld, *Synlett* **2001**, 523. – [4r] P. Langer, U. Albrecht, *Synlett* **2001**, 526. – [4s] P. Langer, T. Krummel, *Chem. Eur. J.* **2001**, *7*, 1720. – [4t] P. Langer, J. Wuckelt, M. Döring, P. R. Schreiner, H. Görls, *Eur. J. Org. Chem.* **2001**, 2245.

[5] For multicomponent reactions of dianions from our laboratory, see: [5a] P. Langer, M. Döring, H. Görls, R. Beckert, *Liebigs Ann./Receuil* **1997**, 2553. – [5b] P. Langer, M. Döring, D. Seyferth, *Chem. Commun.* **1998**, 1927. – [5c] J. Wuckelt, M. Döring, R. Beckert, P. Langer, *Synlett* **1999**, 1100. – [5d] P. Langer, J. Wuckelt, M. Döring, *J. Org. Chem.* **2000**, *65*, 729. – [5e] P. Langer, J. Wuckelt, M. Döring, H. Görls, *Eur. J. Org. Chem.* **2001**, 1503. – [5f] P. Langer, M. Döring, D. Seyferth, *Synlett* **1999**, 135. – [5g] P. Langer, M. Döring, H. Görls, *Eur. J. Org. Chem.* **2001**, 1511. – [5h] P. Langer, M. Döring, P. R. Schreiner, H. Görls, *Chem. Eur. J.* **2001**, *7*, 2617.

[6] For a preliminary communication, see: P. Langer, N. N. R. Saleh, *Org. Lett.* **2000**, 3333.

[7] Reviews: [7a] Y. S. Rao, *Chem. Rev.* **1976**, *76*, 625. – [7b] G. Pattenden, *Prog. Chem. Nat. Prod.* **1978**, *35*, 133. – [7c] D. W. Knight, *Contemp. Org. Synth.* **1994**, *1*, 287. – [7d] E.-i. Negishi, M. Kotora, *Tetrahedron* **1997**, *53*, 6707.

[8] For other approaches to γ-alkylidenebutenolides, see for example: [8a] K. Siegel, R. Brückner, *Chem. Eur. J.* **1998**, *4*, 1116. – [8b] F. Goerth, A. Umland, R. Brückner, *Eur. J. Org. Chem.* **1998**, 1055. – [8c] F. v. d. Ohe, R. Brückner, *Tetrahedron Lett.* **1998**, 1909. – [8d] F. C. Görth, R. Brückner, *Synthesis* **1999**, 1520. – [8e] I. Hanisch, R. Brückner, *Synlett* **2000**, 374. – [8f] E.-i. Negishi, M. Kotora, *Tetrahedron* **1997**, *53*, 6707. – [8g] D. W. Knight, G. Pattenden, *J. Chem. Soc., Perkin Trans. 1* **1979**, 62. – [8h] C. F. Ingham, R. A. Massy-Westropp, G. D. Reynolds, W. D. Thorpe, *Aust. J. Chem.* **1975**, *28*, 2499.

[9] Medium-sized cyclic ethers are found in a number of biologically active marine natural products, such as *brevetoxin A* and *B*, *yessotoxin*, *ciguatoxin*, *laurencin*, and *maitotoxin.* See for example: [9a] H.-J. Altenbach, in: *Organic Synthesis Highlights* (Eds.: J. Mulzer, H.-J. Altenbach, M. Braun, K. Krohn, H.-U. Reissig), VCH, Weinheim, **1991**. – [9b] K. C. Nicolaou, C.-K. Hwang, B. E. Marron, S. A. DeFrees, E. A. Couladouros, Y. Abe, P. J. Carroll, J. P. Snyder, *J. Am. Chem. Soc.* **1990**, *112*, 3040 and cited literature. – [9c] L. E. Overman, *Acc. Chem. Res.* **1992**, *25*, 358. – [9d] A. Brandes, H. M. R. Hoffmann, *Tetrahedron* **1995**, *51*, 145. – [9e] E. Alvarez, M. T. Diaz, R. Perez, J. L. Ravelo, A. Regueiro, J. A. Vera, D. Zurita, J. D. Martin, *J. Org. Chem.* **1994**, *59*, 2848. – [9f] R. A. Robinson, J. S. Clark, A. B. Holmes, *J. Am. Chem. Soc.* **1993**, *115*, 10400. – [9g] L. A. Paquette, T. J. Sweeney, *Tetrahedron* **1990**, *46*, 4487.

[10] For a preliminary communication, see: P. Langer, T. Eckardt, M. Stoll, *Org. Lett.* **2000**, 2991.

[11] [11a] S. Hoppen, U. Emde, T. Friedrich, L. Grubert, U. Koert, *Angew. Chem.* **2000**, *112*, 2181; *Angew. Chem. Int. Ed.* **2000**, *39*, 2099. – [11b] L. F. Tietze, G. Schneider, J. Wölfling, T. Nöbel, C. Wulff, I. Schubert, A. Rübeling, *Angew. Chem.* **1998**, *110*, 2644; *Angew. Chem. Int. Ed.* **1998**, *37*, 2469. – [11c] J. Wang, P. J. De Clerq, *Angew. Chem.* **1995**, *107*, 1698; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1749. – [11d] K. M. Depew, M. Zeman, S. H. Boyer, D. J. Denhart, N. Ikemoto, D. M. Crothers, S. Danishefsky, *Angew. Chem.* **1996**, *108*, 2972; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2797.

[12] [12a] T. Netscher, *Chimia* **1996**, *50*, 563. – [12b] F. Furuya, T. Yoshikawa, T. Kimura, H. Kaneko, *Phytochemistry* **1987**, *26*, 2741. – [12c] A. Stocker, H. Fretz, H. Frick, A. Rüttimann, W.-D. Woggon, *Bioorg. Med. Chem.* **1996**, *4*, 1129.

[13] [13a] P. Magnus, J. S. Mendoza, A. Stamford, M. Ladlow, P. Willis, *J. Am. Chem. Soc.* **1992**, *114*, 10232. – [13b] W. G. Bornmann, M. E. Kuehne, *J. Org. Chem.* **1992**, *57*, 1752.

[14] [14a] K. Krohn, H.-H. Ostermeyer, K. Tolkiehn, *Chem. Ber.* **1979**, *112*, 2640. – [14b] T. H. Chan, P. Brownbridge, *J. Am. Chem. Soc.* **1980**, *102*, 3534. – [14c] G. A. Molander, K. O. Cameron, *J. Am. Chem. Soc.* **1993**, *115*, 830.

[15] For precedence in the synthesis of cyclic bis(silyl enol ether)s, see: G. A. Molander, B. Bessières, P. R. Eastwood, B. C. Noll, *J. Org. Chem.* **1999**, *64*, 4124.

[16] For Mitsunobu reactions of tetronic acid, see: J. S. Bajwa, R. C. Anderson, *Tetrahedron Lett.* **1990**, *48*, 6973.

[17] Reviews: [17a] M. Schuster, S. Blechert, *Angew. Chem.* **1997**, *109*, 2124; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2036. – [17b] S. K. Armstrong, *J. Chem. Soc., Perkin Trans. 1* **1998**, 371. – [17c] R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, *54*, 4413.

[18] For the synthesis of medium-sized rings by RCM, see: [18a] M. E. Maier, *Angew. Chem.* **2000**, *112*, 2153; *Angew. Chem. Int. Ed.* **2000**, *39*, 2073. – [18b] M. T. Crimmins, A. L. Choy, *J. Am. Chem. Soc.* **1999**, *121*, 5653. – [18c] S. J. Miller, S.-H. Kim, Z.-R. Chen, R. H. Grubbs, *J. Am. Chem. Soc.* **1995**, *117*, 2108.

[19] J. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615.

[20] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[21] G. M. Sheldrick, *SHELX 97*, Universität Göttingen, **1997**.

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