Uncatalyzed, Solvent-Free [2+2] Cycloaddition of Cyclic Ketene Trimethylsilyl Acetals with Electrophilic Acetylenes

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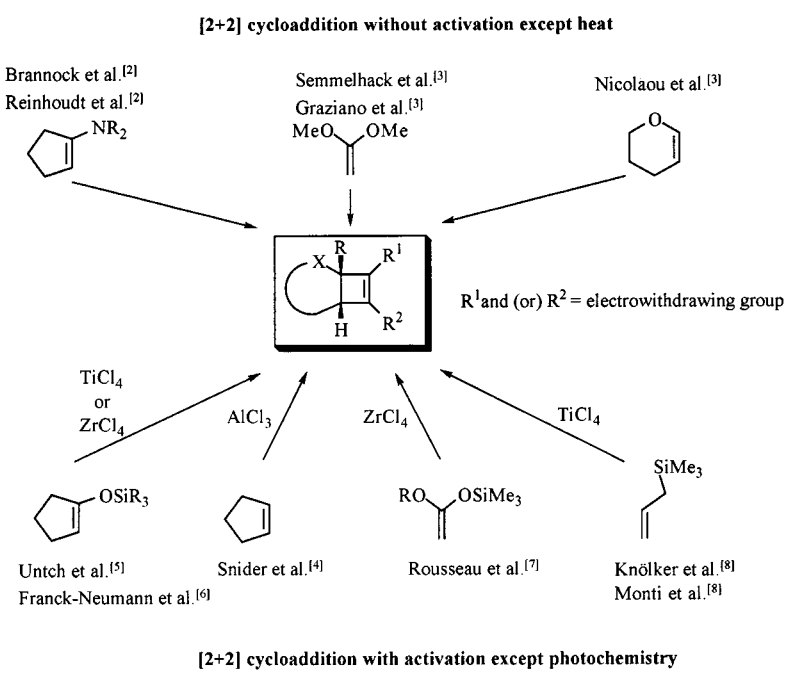
Keywords: β-Oxocyclobutanecarboxylates / Cyclobutenes / Furans / Lactones / Lewis acids

Cyclic ketene trimethylsilyl acetals reacted with electrophilic acetylenes (ethyl propynoate, dimethyl acetylenedicarboxylate and ethynyl methyl ketone) to afford the corresponding [2+2] cycloadducts. The reactions were run at room temperature, without a catalyst and under solvent-free conditions. α-Alkylidenelactones, β-oxocyclobutanecarboxylates and substituted furan derivatives proved to be readily available from the [2+2] cycloadducts by treatment either with TBAF in THF solution or with $BF_3{\cdot}Et_2O$.

Introduction

Four-membered carbocycles not only represent important building blocks for the total synthesis of natural products, but are also present as substructures in numerous natural products.[1] Many of these products are biologically active, so that the development of new reaction pathways giving access to polyfunctionalized four-membered rings is still of interest. Among the possible options for synthesising unsaturated four-membered carbocycles, the [2+2] cycloaddition of alkynes to alkenes remains one of the most powerful methodologies. This type of [2+2] cycloaddition can be conducted either without activation (except heat) or with activation (in general, Lewis acid or photoexcitation). Thus, the addition of enamines to electrophilic acetylenes leads to the corresponding cyclobutenes; this reaction takes place without any activation.[2] This also proves to be true for the [2+2] cycloaddition of 1,1-dimethoxyalkenes and cyclic enol ethers to acetylenecarboxylates.[3] On the other hand, [2+2] cycloadditions of alkenes,[4] silyl enol ethers,[5,6] acyclic ketene trimethylsilyl acetals[7] and allylsilanes[8] with electrophilic acetylenes need to be promoted by Lewis acid to afford the corresponding cyclobutenes (Scheme 1).



Scheme 1. [2+2] Cycloaddition without activation and with activation

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We report here our own results on the reactivity of *cyclic* ketene trimethylsilyl acetals with electrophilic acetylenes.[9] Most investigations to date have dealt with the reactivity of *acyclic* ketene trimethylsilyl acetals with electrophilic part-

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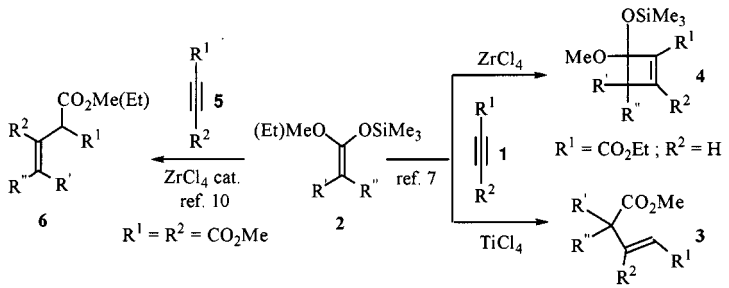
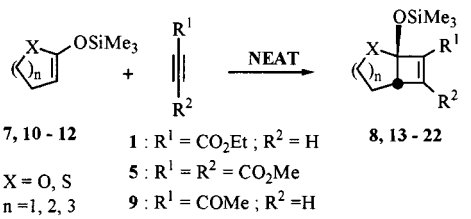


Scheme 2. Addition of *acyclic* ketene trimethylsilyl acetals to electrophilic acetylenes

ners. Thus, Rousseau et al. showed that the reaction of *acyclic* ketene trimethylsilyl acetals **2** with ethyl propynoate (EP, **1**) led to Michael-type addition products **3** or to [2+2] cycloaddition products **4**, depending on the Lewis acid used.[7] However, when dimethyl acetylenedicarboxylate (DMAD, **5**) was used as an electrophilic partner, compound **6**, resulting from the ring-opening of the intermediate [2+2] cycloadduct, could be isolated as the sole product[10] (Scheme 2).



Scheme 4. [2+2] Cycloaddition of *cyclic* ketene trimethylsilyl acetals and electrophilic acetylenes

Results and Discussion

We started our studies by using the conditions we had developed in our previous work concerning the production of electrophilic cyclobutenes by reaction of silyl enol ethers with EP (**1**); i.e. the reaction is performed with one equivalent of $ZrCl_4$.[6] However, when the addition of ketene trimethylsilyl acetal **7** with EP (**1**) was carried out using these conditions, only decomposition occurred. When the same reaction was carried out in the presence of only a catalytic amount of $ZrCl_4$, a formal [2+2] cycloaddition took place, leading to the electrophilic cyclobutene **8**, isolated in 37% yield; the side products were not identified. Other Lewis acids, such as $AlCl_3$, $HfCl_4$, $TiCl_4$ etc., were then used, but no improvement in yield took place. Various reaction conditions were also tried (temperature, concentration etc.) without any success.

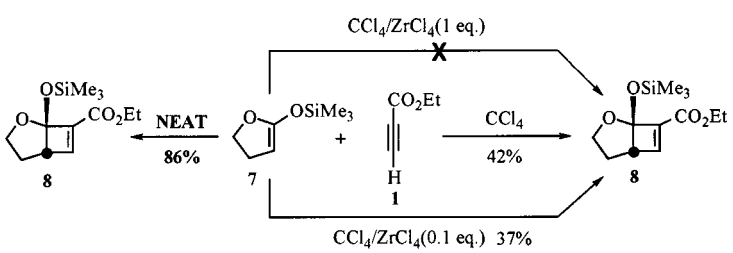
We finally found that the cycloaddition proceeded smoothly when the reaction of **7** with EP (**1**) was carried out at room temperature, without a promoter. Even better results were obtained when the reaction was run under solvent-free conditions (Scheme 3).

These reaction conditions also proved valuable when DMAD (**5**)[11] and ethynyl methyl ketone (**9**) were employed as the acetylene derivatives. Moreover, we observed similar reactivities when the trimethylsilyl enol ethers **10**, **11** and **12** − derived, respectively, from δ-valerolactone, ε-caprolactone and γ-thiobutyrolactone − reacted with EP (**1**), DMAD (**5**) or ethynyl methyl ketone (**9**) under the same conditions, leading to the corresponding cyclobutenes **13**−**22**[12] (Scheme 4, Table 1, Figure 1.

When the ketene trimethylsilyl acetal **23**, derived from γ-valerolactone, was added to EP (**1**) or DMAD (**5**), a stereoselective [2+2] cycloaddition took place, leading to the two diastereomeric cyclobutenes **24a** and **24b** (ratio: 3:1) and **25a** and **25b** (ratio: 3:1). The relative configuration of the latter pair was determined by a NOESY experiment (Scheme 5).

In general, the desired cyclobutenes were isolated in high yields, but these compounds proved to be unstable to chromatography on silica gel. It should also be noted that the use of CCl_4 as solvent dramatically decreased cyclobutene yields, especially when EP (**1**) and ethynyl methyl ketone (**9**) were involved as electrophilic partners. Moreover, we were unable to isolate the cyclobutenes **14**, **17** and **20** when the cycloaddition was carried out in the presence of $ZrCl_4$.

The high reactivity of cyclic ketene trimethyl acetals towards electrophilic acetylenes could be explained by the fact that their nucleophilicities are in the same range as those of enamines, as has been shown by Mayr et al.[13] Indeed, it is well known that the addition of EP (**1**) or DMAD (**5**) to the morpholino enamine **26** − derived from cyclopentanone



Scheme 3. [2+2] Cycloaddition of EP (**1**) with the cyclic ketene trimethylsilyl acetal **7**

Table 1. [2+2] Cycloaddition of *cyclic* ketene trimethylsilyl acetals and electrophilic acetylenes; reaction conditions: a: CCl_4/0.1 equiv. $ZrCl_4$; b: CCl_4; **c: neat**

Ketene silyl acetal (X, *n*)	Electrophilic acetylene	Reaction conditions	Product [yield (crude)]
7 (X = O; *n* = 1)	**1**	a	**8** [13% (37%)]
		b	**8** [10% (42%)]
		c	**8 [48% (86%)]**
	5	a	**13** [90% (98%)]
		b	**13** [94% (98%)]
		c	**13 [98%]**[a]
	9	a	**14** [0%]
		b	**14** [13% (55%)]
		c	**14 [39% (83%)]**
10 (X = O; *n* = 2)	**1**	a	**15** [5% (24%)]
		b	**15** [5% (55%)]
		c	**15 [32% (64%]**
	5	a	**16** [30% (71%)]
		b	**16** [40% (81%)]
		c	**16 [45% (92%)]**
	9	a	**17** [0%]
		b	**17** [20% (46%)]
		c	**17 [54% (89%)]**
11 (X = O; *n* = 3)	**1**	a	**18** [20% (57%)]
		b	**18** [5% (48%)]
		c	**18 [20% (67%)]**
	5	a	**19** [42% (83%)]
		b	**19** [45% (84%)]
		c	**19 [50% (93%)]**
	9	a	**20** [0%]
		b	**20** [40% (57%)]
		c	**20 [49% (75%)]**
12 (X = S; *n* = 1)	**1**	a	[0%]
		b	[0%]
		c	traces
	5	a	**21** [0%]
		b	**21** [0%]
		c	**21 [62% (99%)]**
	9	a	**22** [0%]
		b	**22** [0%]
		c	**22 [38% (86%)]**

[a] Chromatography on silica gel was not necessary in this case.

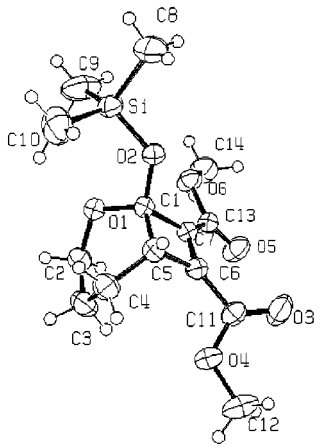
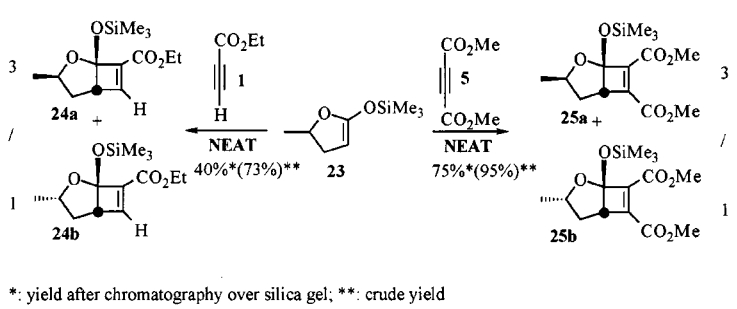


Figure 1. X-ray structure of compound **16**

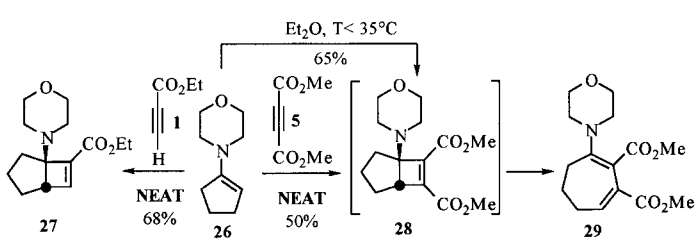
− led to the corresponding [2+2] cycloadducts **27** and **28**, respectively, when the reaction was carried out in ether below 35° C. However, we found that the addition of EP (**1**) to the enamine **26**, *when performed under solvent-free conditions*, led to the corresponding [2+2] cycloadduct **27**, while, when DMAD (**5**) was used as the acetylenic partner, the cycloheptadiene derivative **29**, resulting from the ring expansion of the initially formed [2+2] cycloadduct **28**, was isolated. It should be noted that such a ring-expansion reaction was never observed during the addition of ketene trimethylsilyl acetal **8** to DMAD (**5**). Moreover, when the cycloadduct **13** was heated in toluene at reflux,[14] the starting material was recovered completely (Scheme 6).

With the cyclobutenes **8** and **13**−**25** now readily available, we undertook a study of their reactivities. At first, we focused our attention on two-carbon ring-enlargement reactions of these cyclobutenes, in order to develop a new methodology for preparing lactones of medium ring size[15] (Scheme 7).

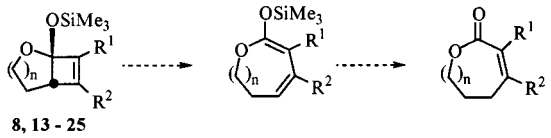


*: yield after chromatography over silica gel; **: crude yield

Scheme 5. Stereoselective [2+2] cycloaddition of **23** with EP (**1**) and DMAD (**5**)

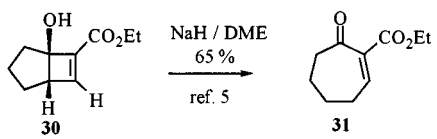


Scheme 6. [2+2] Cycloaddition of enamine **26** with EP (**1**) and DMAD (**5**)



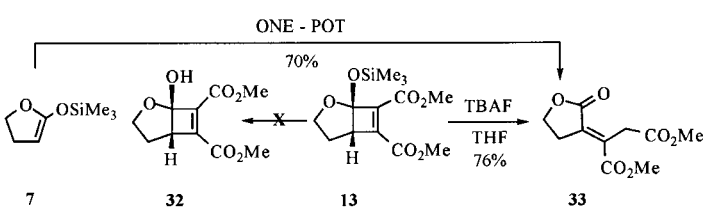
Scheme 7. Possible ring enlargement of cycloadducts **8**, **13**−**25**

For this purpose we investigated various methods, using as a model compound the very readily available cyclobutene **13**. First of all, we attempted to cleave the silyl ether group to obtain the corresponding alcohol. Indeed, it had previous been shown that basic treatment of the isosteric functionalized 1-hydroxybicyclo[3.2.0]cycloheptene **30** afforded the corresponding ring-expansion product **31** (Scheme 8).



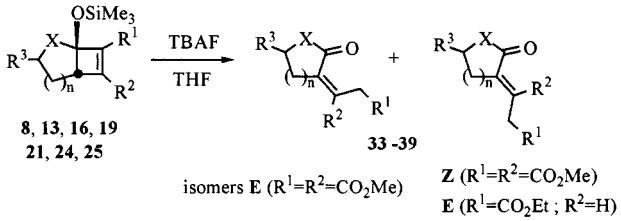
Scheme 8. Ring-enlargement reaction of 1-hydroxybicyclo[3.2.0]heptene **30**

In our case, the deprotection of cyclobutene **13** with TBAF led directly to the functionalized α-alkylidenebutyrolactone **33** (*E* isomer). The corresponding alcohol **32** was never isolated and a reaction of retro-aldol type took place (vide infra) instead of a ring-expansion reaction. It should be noted that this reaction sequence can be performed just as well in a one-pot fashion, starting from the silyl enol ether **7** and giving **33** in 70% yield. Thus, this reaction sequence represents a new, very efficient and easily performed method for the synthesis of substituted α-alkylidenelactones (Scheme 9).



Scheme 9. Deprotection of the silyl ether **13** with TBAF

This also proved true for the cyclobutenes **8**, **21**, **24** and **25**. For compounds **16** and **19** − derived from δ-valerolactone and ε-caprolactone, respectively − the α-alkylidenelactones were also obtained, but as mixtures of *Z* and *E* isomers. When this "deprotection" reaction was applied to the cyclobutenes **14**, **15**, **17**, **18**, **20** and **22**, only decomposition occurred (Scheme 10, Table 2).



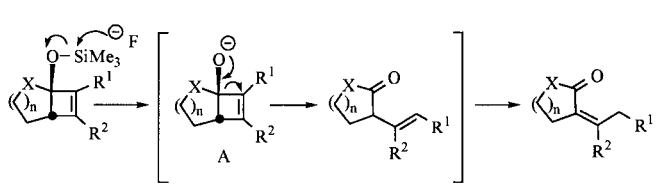
Scheme 10. Deprotection of the silyl ethers **8**, **13**, **16**, **19**, **21**, **24** and **25** with TBAF

Table 2. Deprotection of the silyl ethers **8**, **13**, **16**, **19**, **21**, **24**, **25** with TBAF

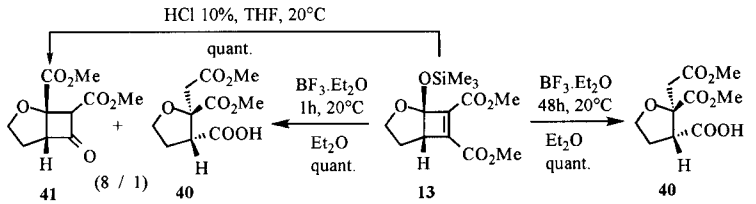
Starting cyclobutene	A	*n*	R^1	R^2	R^3	Product (*E*/*Z* ratio; yield)
13	O	1	CO_2Me	CO_2Me	H	**33** (100:0; 76%)
8	O	1	CO_2Et	H	H	**34** (100:0; 43%)
25	O	1	CO_2Me	CO_2Me	Me	**35** (100:0; 50%)
24	O	1	CO_2Et	H	Me	**36** (100:0; 50%)
16	O	2	CO_2Me	CO_2Me	H	**37** (50:50; 73%)
19	O	3	CO_2Me	CO_2Me	H	**38** (50:50; 77%)
21	S	1	CO_2Me	CO_2Me	H	**39** (100:0; 45%)

These results could be explained as follows: The addition of TBAF to the cyclobutene silyl ether induces the formation of an alkoxide anion **A**, which undergoes a reaction of retro-aldol type, leading mainly to the α-alkylidenelactones **33**−**39** after prototropic isomerizations (Scheme 11).

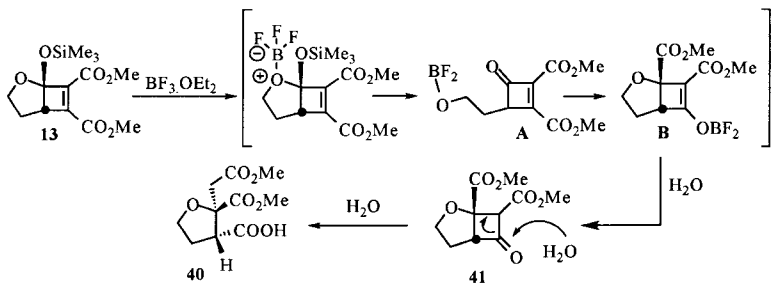
We next investigated whether a ring expansion could be conducted with a Lewis acid like $BF_3{\cdot}Et_2O$. In fact, when the reaction was carried out with an excess of $BF_3{\cdot}Et_2O$ for 48 h at room temperature, the cyclobutene **13** quantitatively afforded the furan derivative **40**. If the same reaction was carried out with 1 equiv. of $BF_3{\cdot}Et_2O$ for 20 h at room temperature, a mixture of the cyclobutane derivative **41** together with the furan derivative **40** was obtained (ratio **40**/**41** = 1:8). Surprisingly, it was possible to isolate the oxocyclobutanecarboxylate **41** quantitatively when the reaction was carried out with dilute HCl for 15 min in THF at room temperature (Scheme 12).



Scheme 11. Proposed mechanism for the formation of the α-alkylidenelactones



Scheme 12. Treatment of compound **13** with $BF_3{\cdot}OEt_2$, leading to compounds **40** and **41**



Scheme 13. Proposed mechanism for the formation of compounds **40** and **41**

The formation of these compounds could be explained as follows: The reaction is thought to proceed by a mechanism involving the coordination of the boron atom to the furan oxygen atom, followed by deprotection and ring-opening. The intermediate **A** would then undergo an intramolecular 1,4-addition, giving rise to the intermediate **B**, which after hydrolysis gives rise to the highly reactive β-oxo ester **41**. The latter then undergoes an acid-promoted ring opening to afford the furan derivative **40**, as has been shown by Conia et al. for similar compounds (Scheme 13).[16]

On the other hand, for ease of identification, compounds **40** and **41** were treated with diazomethane (DAM), leading to the citric ester derivative **42** (which represents an important substructure of trachypsic acid, a natural antibiotic recently isolated by Shiozawa et al.[17]) and to the cyclobutene derivative **43**, respectively. The structural assignment for compound **43** was based on spectral data[18] and was confirmed by an X-ray crystal structure determination (Figure 2), hence confirming the structural assignment for the β-oxocyclobutanecarboxylate **41**. It should also be noted that compound **42** could be obtained by treatment of β-oxo ester **41** with a dilute HCl solution in methanol (Scheme 14).

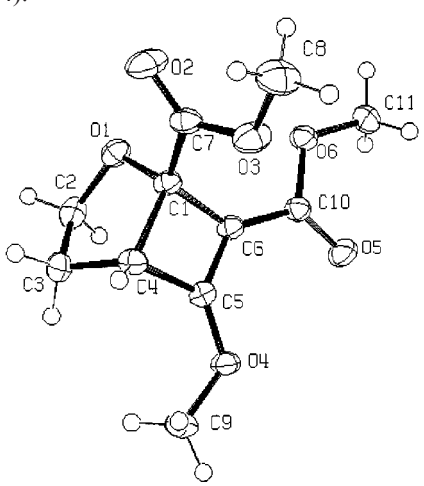
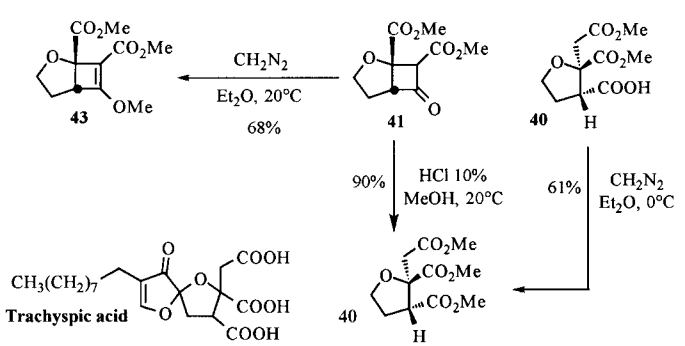


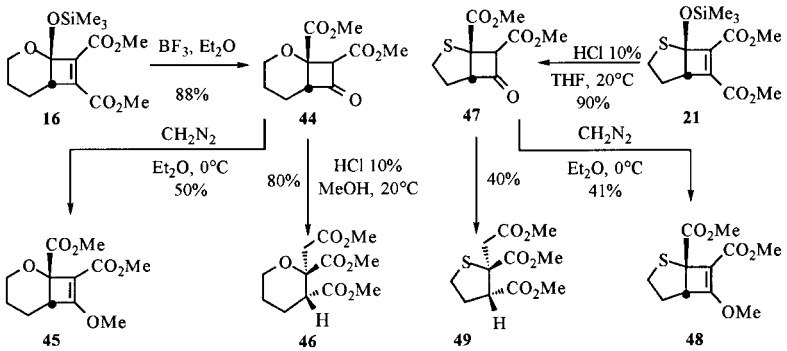
Figure 2. X-ray structure of compound **43**

These reaction conditions also proved valuable for the cyclobutenes **16** and **21**, leading to the furan derivatives **46**



Scheme 14. Confirmation of the formation of compounds **40** and **41**

and **49**,[19] respectively, and to the cyclobutane derivatives **45** and **48** (after treatment with dilute HCl in MeOH or with diazomethane) via the β-oxo esters **44** and **47**. For cyclobutenes derived from EP and ethynyl methyl ketone, only decomposition occurred (Scheme 15, Figure 3).



Scheme 15

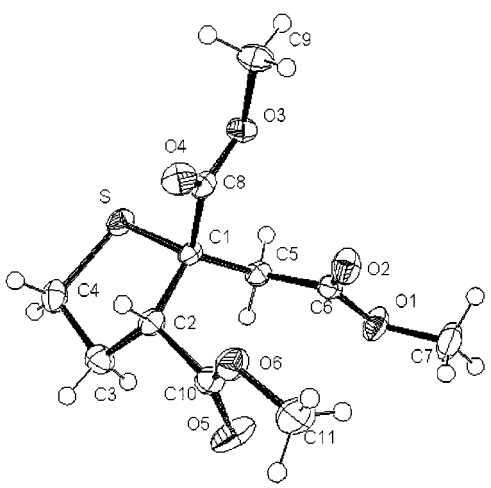


Figure 3. X-ray structure of compound **49**

Conclusion

In conclusion, we have succeeded in developing a new, easily performed reaction sequence involving a non-photochemical and uncatalyzed [2+2] cycloaddition between cyclic ketene trimethylsilyl acetals and electrophilic acetylenes under solvent-free conditions. Moreover, these reactions can be performed in a "one-pot" fashion, starting from the corresponding readily available cyclic ketene trimethylsilyl acetals. Work is in progress to expand the synthetic utility of this method.

Experimental Section

General Remarks: Reactions were carried out under argon, with magnetic stirring and degassed solvents. Ether and THF were distilled from sodium/benzophenone under nitrogen before use. CH_2Cl_2 was dried and distilled from P_2O_5. Thin layer chromatography (TLC) was carried out on silica gel plates (Merck Silicagel 60 F_{254}) and the spots were made visible under UV lamps (254 nm or 360 nm) or by spraying with a solution of vanillin (25 g) in $EtOH/H_2SO_4$ (98:2; 1 L) followed by heating on a hot plate. For column chromatography, Merck Silicagel 60 (40−60 mm) was used. Melting points were measured with a Reichert hot stage. IR spectra were recorded as CCl_4 solutions with a Perkin−Elmer IR 881 spectrophotometer. UV/Vis spectra were recorded in CH_3CN solution with a Perkin−Elmer UV-550 spectrophotometer. ^1H NMR spectra were recorded with a Bruker WP-200, AC-200, 200 MHz and ^{13}C NMR spectra with a Bruker AC-200 50 MHz, using the signal of the residual nondeuteriated solvent as internal reference (δ=7.26 for $CDCl_3$ or 7.16 for C_6D_6 in ^1H NMR spectra). Significant ^1H NMR data are tabulated in order: chemical shift (δ) expressed in ppm relative to residual $CHCl_3$ in $CDCl_3$, multiplicity (s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet), number of protons and coupling constants in Hz. Elemental analyses (C,H ±0.3%) were performed by the Laboratoire de Microanalyses of the Université Louis Pasteur in Strasbourg. − Ethynyl methyl ketone (but-3-yn-2-one, **9**) was obtained by Jones oxidation of the corresponding alcohol, but-3-yn-2-ol, according to ref.[20] − Alkyl trimethylsilyl ketene (thio)acetals **7**, **10**−**12** and **23** were prepared in good yields from the corresponding (thio)lactones as previously described by Rubottom et al.[21]

Preparation of Cycloadducts 8, 13−22, 24, 25

General Procedure I: To the ketene silyl (thio)acetal **7**, **10**−**12** or **23** (1 equiv.) was added at room temperature neat ethyl propynoate (EP, **1**), dimethyl acetylenedicarboxylate (DMAD, **5**) or ethynyl methyl ketone (**9**) (1 equiv.). The mixture was stirred for 5 h at room temperature. The volatile products were removed at room temperature in vacuo (0.1 Torr) for 30 min. Purification of the crude reaction mixture by silica gel column chromatography (ethyl acetate/hexane, 5:95) afforded cycloadducts **8**, **13**−**22**, **24** and **25** [yield (crude)].

Ethyl 1-(Trimethylsilyloxy)-2-oxabicyclo[3.2.0]hept-6-ene-7-carboxylate (8): Ketene silyl acetal **7** (715 mg; 4.5 mmol); EP (**1**) (443 mg; 4.5 mmol). Product formed: **8** [553 mg; 2.2 mmol; yield: 48% (crude yield: 86%)]. Colourless oil. − UV (CH_3CN): λ_{max} = 217 nm (ε = 5166). − IR (CCl_4): $\tilde{\nu}$ = 1721 (C=O), 1619 (C=C) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.33 [s, 9 H, $-Si(CH_3)_3$], 0.95 (t, 3 H, J = 7.1 Hz, $-O-CH_2CH_3$), 0.90−0.96 (m, 1 H, $-CHH-$), 1.24−1.45 (m, 1 H, $-CHH-$), 2.72 [dd, 1 H, J = 7.9, 0.8 Hz, $-CH-CH=C(E)-$], 3.31−3.44 (m, 1 H, $-CHH-O$), 3.80−3.89 (m, 1 H, $-CHH-O$), 3.97 (q, 2 H, J = 7.1 Hz, $-O-CH_2-CH_3$), 6.54 [d, 1 H, J = 0.8 Hz, $-CH=C(E)-$]. − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.3 [$Si(CH_3)_3$], 14.2 (CH_3), 26.0 (CH_2), 53.9 (CH), 60.4 (OCH_2), 67.0 (OCH_2), 108.2 (O−C−OSi), 139.6 (−C=CH−), 146.1 (−CH=C−), 160.8 (C=

O). − $C_{12}H_{20}O_4Si$ (256.4): calcd. C 56.22, H 7.56; found C 56.00, H 8.03.

Dimethyl 1-(Trimethylsilyloxy)-2-oxabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (13): Ketene silyl acetal **7** (461 mg; 2.9 mmol); DMAD (**5**) (414 mg; 2.9 mmol). Product formed: **13** (852 mg; 2.8 mmol; yield: 98%). Colourless oil. − UV (CH_3CN): λ_{max} = 219 nm (ε = 7532). − IR (CCl_4): $\tilde{\nu}$ = 1730 (C=O), 1651 (C=C) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.17 [s, 9 H, −Si(CH_3)$_3$], 1.76−1.93 (m, 2 H, −CH_2−), 3.29 [d, 1 H, *J* = 6.9 Hz, −C*H*−C(E)=C(E)−], 3.67−3.80 (m, 1 H, −C*H*H−O−), 3.80 (s, 3 H, −CO_2CH_3), 3.82 (s, 3 H, −CO_2CH_3), 4.21−4.33 (m, 1 H, −CH*H*−O−). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.1 [Si(*C*H_3)$_3$], 25.5 (*C*H_2), 51.9 (O*C*H_3), 52.2 (O*C*H_3), 54.9 (*C*H), 67.0 (*C*H_2−O), 106.2 (O−*C*−OSi), 141.2 (*C*=C), 141.4 (C=*C*), 160.3 (*C*=O), 162.3 (*C*=O). − $C_{13}H_{20}O_6Si$ (300.4): calcd. C 51.98, H 6.71; found C 51.87, H 6.84.

1-[1-(Trimethylsilyloxy)-2-oxabicyclo[3.2.0]hept-6-en-7-yl]ethanone (14): Ketene silyl acetal **7** (230 mg; 1.5 mmol); ethynyl methyl ketone (**9**) (99 mg; 1.5 mmol). Product formed: **14** [129 mg; 0.6 mmol; yield: 39% (crude yield: 83%)]. Colourless oil. − UV (CH_3CN): λ_{max} = 228 nm (ε = 6715). − IR (CCl_4): $\tilde{\nu}$ = 1605 (C=O), 1689 (C=C) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.20 [s, 9 H, −Si(CH_3)$_3$], 1.63 (ddd, 1 H, *J* = 12.8 Hz, 6.0 Hz, 0.7 Hz, −C*H*H−), 1.83 (ddt, 1 H, *J* = 12.8 Hz, 11.8 Hz, 7.6 Hz, 7.6 Hz, −CH*H*−) 2.30 (s, 3 H, −COCH_3), 3.07 [dd, 1 H, *J* = 7.6 Hz, 1.0 Hz, −C*H*−CH=C(E)−], 3.62 (ddd, 1 H, *J*= 11.8 Hz, 9.5 Hz, 6.0 Hz, −C*H*H−O−), 4.18−4.27 (ddd, 1 H, *J* = 9.5 Hz, 7.6 Hz, 0.7 Hz, −CH*H*−O−), 6.85 [d, 1 H, *J* = 1.0 Hz, −C*H*=C(E)−]. − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.2 [Si(*C*H_3)$_3$], 26.1 (*C*H_2), 28.1 (*C*H), 53.2 (*C*H_3), 66.7 (CH_2), 108.1 (O−*C*−O−Si), 143.2 (−*C*H=C−), 146.1 (−CH=*C*−), 193.6 (*C*=O). − $C_{11}H_{18}O_3Si$ (226.4): calcd. C 58.37, H 8.016; found C 58.00, H 7.88.

Ethyl 1-(Trimethylsilyloxy)-2-oxabicyclo[4.2.0]oct-7-ene-8-carboxylate (15): Ketene silyl acetal **10** (444 mg; 2.6 mmol); EP (**1**) (253 mg; 2.6 mmol). Product formed: **15** [220 mg; 0.8 mmol; yield: 32% (crude yield: 64%)]. Colourless oil. − UV (CH_3CN): λ_{max} = 212 nm (ε = 7040). − IR (CCl_4): $\tilde{\nu}$ = 1723 (C=O), 1616 (C=C) cm^{-1}. − ^1H NMR (200 MHz, C_6D_6): δ = 0.39 [s, 9 H, −Si(CH_3)$_3$], 0.97 (t, 3 H, *J* = 7.0 Hz, −OCH_2CH_3), 1.08−1.34 (m, 3 H), 1.43−1.57 (m, 1 H), 2.72 [ddd, 1 H, *J* = 7.1 Hz, 4.7 Hz, 1.2 Hz, −C*H*−CH=C(E)−], 3.56−3.73 (m, 2 H, −CH_2−O−), 3.99 (q, 2 H, *J* = 7.0 Hz, −O*C*H_2CH$_3$), 6.68 [d, 1 H, *J* = 1.2 Hz, −CH−C*H*=C(E)−]. − ^{13}C NMR (50 MHz, C_6D_6): δ = 1.9 [Si(*C*H_3)$_3$], 14.3 (*C*H_3), 20.5 (*C*H_2), 23.0 (*C*H_2), 50.4 (*C*H), 60.0 (O*C*H_2), 62.0 (O*C*H_2), 98.2 (O−C−OSi), 143.9 (−*C*=CH−), 149.1 (−C=*C*H−), 160.6 (*C*=O). − $C_{13}H_{22}O_4Si$ (270.4): calcd. C 57.75, H 8.20; found C 57.63, H 8.38.

Dimethyl 1-(Trimethylsilyloxy)-2-oxabicyclo[4.2.0]oct-7-ene-7,8-dicarboxylate (16): Ketene silyl acetal **10** (434 mg; 2.5 mmol); DMAD (**5**) (358 mg; 2.5 mmol). Product formed: **16** [352 mg; 1.1 mmol; yield: 45% (crude yield: 92%)]. White crystals. − M.p. 68 °C. − UV (CH_3CN): λ_{max} = 215 nm (ε = 5986). − IR (CCl_4): $\tilde{\nu}$ = 1727 (C=O), 1620 (C=C) cm^{-1}. − ^1H NMR (200 MHz, C_6D_6): δ = 0.31 [s, 9 H, −Si(CH_3)$_3$], 1.03−1.19 (m, 1 H), 1.26−1.53 (m, 1 H), 1.57−1.69 (m, 1 H), 1.72−1.90 (m, 1 H), 3.14−3.20 [dd, 1 H, *J* = 6.9 Hz, 3.7 Hz, −C*H*−C(E)=C(E)−], 3.32 (s, 3 H, −CO_2CH_3), 3.38 (s, 3 H, −CO_2CH_3), 3.51−3.70 (m, 2 H, −CH_2−O−). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.3 [Si(*C*H_3)$_3$], 20.1 (*C*H_2), 21.9 (*C*H_2), 50.6 (*C*H_2O), 51.9 (O*C*H_3), 52.1 (O*C*H_3), 63.2 (*C*H), 95.9 (O−*C*−OSi), 143.7 (*C*=C), 144.9 (C=*C*), 160.6 (*C*=O), 162.4 (*C*=O). − $C_{14}H_{22}O_6Si$ (314.4): calcd. C 53.29, H 6.95; found C 53.49, H 7.05.

1-[1-(Trimethylsilyloxy)-2-oxabicyclo[4.2.0]oct-7-en-8-yl]ethanone (17): Ketene silyl acetal **10** (720 mg; 4.2 mmol); ethynyl methyl ketone (**9**) (284 mg; 4.2 mmol). Product formed: **17** [560 mg; 2.3 mmol; yield: 54% (crude yield: 89%)]. Yellowish oil. − UV (CH_3CN): λ_{max} = 228 nm (ε = 6744). − IR (CCl_4): $\tilde{\nu}$ = 1687 (C=O), 1609 (C=C) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.17 [s, 9 H, −Si(CH_3)$_3$], 1.52−1.76 (m, 3 H), 1.80−2.01 (m, 1 H), 2.23 (s, 3 H, −COCH_3), 2.90 [ddd, 1 H, *J* = 6.0 Hz, 4.7 Hz, 1.3 Hz, −C*H*−CH=C(E)−], 3.71−3.91 (m, 2 H, −CH_2−O), 6.88 [d, 1 H, *J* = 1.3 Hz, −CH−C*H*=C(E)−]. − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.4 [Si(*C*H_3)$_3$], 20.3 (*C*H_2), 22.9 (*C*H_2), 49.8 (O*C*H_2), 62.2 (*C*H_2), 97.3 (O−*C*−OSi), 147.5 (−H*C*=C−), 149.8 (−*C*=CH−), 193.2 (*C*=O). − $C_{12}H_{20}O_3Si$ (240.4): calcd. C 59.96, H 8.39; found C 59.74, H 8.28.

Ethyl 1-(Trimethylsilyloxy)-2-oxabicyclo[5.2.0]non-8-ene-9-carboxylate (18): Ketene silyl acetal **11** (543 mg; 2.9 mmol); EP (**1**) (287 mg; 2.9 mmol). Product formed: **18** [163 mg; 0.6 mmol; yield: 20% (crude yield: 67%)]. Colourless oil. − UV (CH_3CN): λ_{max} = 215 nm (ε = 7304). − IR (CCl_4): $\tilde{\nu}$ = 1723 (C=O), 1623 (C=C) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.17 [s, 9 H, −Si(CH_3)$_3$], 1.31 (t, 3 H, *J* = 7.0 Hz, −$CO_2CH_2CH_3$), 1.34−1.47 (m, 2 H, −CH_2−), 1.69−1.94 (m, 4 H), 2.92 [ddd, 1 H, *J* = 11.0 Hz, 4.4 Hz, 1.0 Hz, −C*H*−CH=C(E)−], 3.64−3.75 (m, 1 H, −C*H*H−O−), 3.94−4.06 (m, 1 H, −CH*H*−O−), 4.20 (q, 2 H, *J* = 7.0 Hz, −$CO_2CH_2CH_3$), 7.08 [d, 1 H, *J* = 1.0 Hz, −CH−C*H*=C(E)−]. − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.3 [Si(*C*H_3)$_3$], 14.3 (*C*H_3), 26.1 (*C*H_2), 30.0 (*C*H_2), 32.2 (*C*H_2), 59.1 (*C*H), 60.4 (O*C*H_2), 102.8 (O−*C*−OSi), 140.2 (*C*=CH), 152.1 (C=*C*H), 161.2 (*C*=O). − $C_{14}H_{24}O_4Si$ (284.4): calcd. C 59.12, H 8.51; found C 58.73, H 8.68.

Dimethyl 1-(Trimethylsilyloxy)-2-oxabicyclo[5.2.0]non-8-ene-8,9-dicarboxylate (19): Ketene silyl acetal **11** (315 mg; 1.7 mmol); DMAD (**5**) (240 mg; 1.7 mmol). Product formed: **19** [250 mg; 0.8 mmol; yield: 45% (crude yield: 93%)]. Colourless oil. − UV (CH_3CN): λ_{max} = 216 nm (ε = 7298). − IR (CCl_4): $\tilde{\nu}$ = 1728 (C=O), 1653 (C=C) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.30 [s, 9 H, −Si(CH_3)$_3$], 1.21−1.46 (m, 4 H), 1.59−1.71 (m, 1 H), 1.84−1.94 (m, 1 H), 3.22−3.35 [m, 1 H, −C*H*−C(E)=C(E)−], 3.35 (s, 3 H, −CO_2CH_3), 3.40 (s, 3 H, −CO_2CH_3), 3.56−3.65 (m, 1 H, −CH*H*−O−), 3.81−3.93 (s, 3 H, −C*H*H−O−). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.2 [Si(*C*H_3)$_3$], 25.7 (*C*H_2), 28.8 (*C*H_2), 31.9 (*C*H_2), 51.8 (O*C*H_3), 52.1 (O*C*H_3), 59.8 (*C*H), 65.0 (O*C*H_2), 101.3 (O−*C*−OSi), 147.2 (*C*=*C*), 160.7 (*C*=O), 162.58 (*C*=O). − $C_{15}H_{24}O_6Si$ (328.4): calcd. C 54.69, H 7.34; found C 54.56, H 7.45.

1-[1-(Trimethysilyloxy)-2-oxabicyclo[5.2.0]non-8-en-9-yl]ethanone (20): Ketene silyl acetal **11** (693 mg; 3.7 mmol); ethynyl methyl ketone (**9**) (253 mg; 3.7 mmol). Product formed: **20** [461 mg; 1.8 mmol; yield: 49% (crude yield: 75%)]. Colourless oil. − UV (CH_3CN): λ_{max} = 228 nm (ε = 6725). − IR (CCl_4): $\tilde{\nu}$ = 1683 (C=O), 1603 (C=C) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$) : δ = 0.16 [s, 9 H, −Si(CH_3)$_3$], 1.41−1.55 (m, 2 H, −CH_2−), 1.66−1.95 [m, 4 H, −(CH_2)$_2$−], 2.23 (s, 3 H, −COCH_3), 2.95 [ddd, 1 H, *J* = 11.0 Hz, 4.5 Hz, 1.2 Hz, −C*H*−CH=C(E)−], 3.63−3.72 (m, 1 H, −C*H*H−O−), 3.93−4.02 (m, 1 H, −CH*H*−O−), 6.98 [d, 1 H, *J* = 1.2 Hz, −CH−C*H*=C(E)−]. − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.2 [Si(*C*H_3)$_3$], 26.1 (*C*H_2), 27.0 (*C*H), 30.0 (*C*H_2), 32.2 (*C*H_2), 58.8 (*C*H_3), 64.5 (*C*H_2−O), 102.5 (O−*C*−OSi), 147.1 (−*C*=CH−), 150.0 (−C=*C*H−), 193.5 (*C*=O). − $C_{13}H_{22}O_3Si$ (254.40): calcd. C 61.38, H 8.72; found C 61.14, H 8.75.

Dimethyl 1-(Trimethylsilyloxy)-2-thiabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (21): Ketene silyl acetal **12** (435 mg; 2.5 mmol);

DMAD (**5**) (355 mg; 2.5 mmol). Product formed: **21** [520 mg; 1.7 mmol; yield: 66% (crude yield: 99%)]. Colourless oil. − UV (CH_3CN): λ_{max} = 246 nm (ε = 430). − IR (CCl_4): $\tilde{\nu}$ = 1737 (C=O), 1646 (C=C) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.20 [s, 9 H, −Si(CH_3)$_3$], 1.86 (dddd, 1 H, *J* = 13.4 Hz, 12.5 Hz, 6.4 Hz, 6.0 Hz, −C*H*H−), 2.18 (dddd, 1 H, *J* = 13.4 Hz, 4.8 Hz, 1.5 Hz, 0.5 Hz, −CH*H*−), 2.58 (td, 1 H, *J* = 12.5 Hz, 12.5 Hz, 4.8 Hz, −C*H*H−S−), 3.05 (ddt, 1 H, *J*= 12.5 Hz, 6.0 Hz, 1.5 Hz, 1.5 Hz, −CH*H*−S−), 3.32 [d, br., 1 H, *J* = 6.4 Hz, −C*H*−C(E)=C(E)−], 3.50 (s, 3 H, CO_2CH_3), 3.82 (s, 3 H, CO_2CH_3). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.6 [Si(*C*H_3)$_3$], 28.8 (*C*H_2), 33.3 (*C*H_2S), 52.0 (O*C*H_3), 52.2 (O*C*H_3), 58.9 (*C*H), 94.1 (O−*C*−OSi), 136.6 (*C*=C), 142.9 (C=*C*), 160.1 (*C*=O) 162.4 (*C*=O). − $C_{13}H_{20}O_5SSi$ (316.4): calcd. C 49.34, H 6.37; found C 49.20, H 6.12.

1-[1-(Trimethylsilyloxy)-2-thiabicyclo[3.2.0]hept-6-en-7-yl]ethanone (22): Ketene silyl acetal **12** (187 mg; 1.1 mmol); ethynyl methyl ketone (**9**) (73 mg; 1.1 mmol). Product formed: **22** [95 mg; 0.4 mmol; yield: 38% (crude yield: 86%)]. Colourless oil. − UV (CH_3CN): λ_{max} = 235 nm (ε = 2460). − IR (CCl_4): $\tilde{\nu}$ = 1716 (C=O), 1689, 1604 (C=C) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.19 [s, 9 H, −Si(CH_3)$_3$], 1.79−1.99 (m, 2 H, −CH_2), 2.28 (s, 3 H, −COCH_3), 2.40−2.55 (m, 1 H, −C*H*H−S−), 2.96−3.06 (ddt, 1 H, *J* = 12.4 Hz, 6.0 Hz, 1.5 Hz, 1.5 Hz, −CH*H*−S−), 3.13 [ddd, 1 H, *J* = 6.4 Hz, 1.5 Hz, 0.5 Hz, −C*H*−CH=C(E)−], 6.61 [d, 1 H, *J* = 0.5 Hz, −CH−C*H*=C(E)−]. − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.7 [Si(*C*H_3)$_3$], 27.7 (*C*H), 29.5 (*C*H_2), 33.3 (*C*H_2), 57.3 (CO*C*H_3), 95.5 (O−*C*−OSi), 138.9 (−*C*H=C−), 147.5 (−CH=*C*−), 193.3 (*C*OCH$_3$). $-C_{11}H_{18}O_2SiS$ (242.41): calcd. C 54.50, H 7.48; found C 54.47, H 7.67.

Ethyl 3-Methyl-1-(trimethylsilyloxy)-2-oxabicyclo[3.2.0]hept-6-ene-7-carboxylate (24): Ketene silyl acetal **23** (168 mg; 1.0 mmol); EP (**1**) (95 mg; 1.0 mmol). Products formed: **24a** (major product) and **24b** (minor product) [108 mg; 0.4 mmol; overall yield: 40% (crude yield: 73%)]. Colourless oil. − **24a:** UV (CH_3CN): λ_{max} = 211 nm (ε = 6982). − IR (CCl_4): $\tilde{\nu}$ = 1721 (C=O), 1618 (C=C) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.21 [s, 9 H, −Si(CH_3)$_3$], 1.29 (t, 3 H, *J* = 7.1 Hz, −$CO_2CH_2CH_3$), 1.36 (d, 3 H, *J* = 6.1 Hz, CH_3), 1.44 (ddd, 1 H, *J* = 12.8 Hz, 10.8 Hz, 7.9 Hz, −C*H*H−), 1.77 (dd, 1 H, *J* = 12.8 Hz, 5.1 Hz, −CH*H*−), 3.11 [dd, 1 H, *J* = 7.9 Hz, 0.9 Hz, −C*H*−CH=C(E)−], 3.88−3.99 [m, 1 H, −C*H*(CH$_3$)−O−], 4.20 (q, 2 H, −$CO_2CH_2CH_3$), 6.94 [d, 1 H, *J* = 0.9 Hz, −CH−C*H*=C(E)−]. − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.5 [Si(*C*H_3)$_3$], 14.3 (*C*H_3), 19.6 (*C*H_3), 34.1 (*C*H_2), 55.2 (*C*H), 60.3 (O*C*H_2), 74.4 (*C*H), 107.9 (−O−*C*−OSi), 139.5 (−CH=*C*−), 146.5 (−*C*H=C−), 162.1 (*C*=O). − $C_{13}H_{22}O_4Si$ (270.4): calcd. C 57.74, H 8.20; found C 57.71, H 8.30. − **24b:** UV (CH_3CN): λ_{max} = 211 nm (ε = 6982). − IR (CCl_4): $\tilde{\nu}$ = 1721 (C=O), 1618 (C=C) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.20 [s, 9 H, −Si(CH_3)$_3$], 1.24 (d, 3 H, *J* = 6.6 Hz, CH_3), 1.26 (t, 3 H, *J* = 7.1 Hz, −$CO_2CH_2CH_3$), 1.47−1.57 (m, 1 H, −C*H*H−), 2.02−2.21 (m, 1 H, −CH*H*−), 3.24 [ddd, 1 H, *J* = 9.1 Hz, 3.2 Hz, 0.9 Hz, −C*H*−CH=C(E)−], 4.20 (q, 2 H, *J* = 7.1 Hz, −$CO_2CH_2CH_3$), 4.74 [m, 1 H, −C*H*(CH$_3$)−O−], 7.04 [d, 1 H, *J* = 0.9 Hz, −CH−C*H*=C(E)−]. − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.5 [Si(*C*H_3)$_3$], 14.2 (*C*H_3), 19.5 (*C*H_3), 33.5 (*C*H_2), 55.2 (*C*H), 60.2 (O*C*H_2), 74.4 (*C*H), 107.9 (O−*C*−O−Si), 139.5 (−HC=*C*−), 146.5 (−H*C*=C−), 162.1 (*C*=O). − $C_{13}H_{22}O_4Si$ (270.4): calcd. C 57.74, H 8.20; found C 57.71, H 8.30.

Dimethyl 3-Methyl-1-(trimethylsilyloxy)-2-oxabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (25): Ketene silyl acetal **23** (318 mg; 1.8 mmol); DMAD (**5**) (262 mg; 1.8 mmol). Products formed: **25a** (major product) and **25b** (minor product) [440 mg; 1.4 mmol; overall yield: 75% (crude yield: 95%)]. Colourless oil. − **25a:** UV (CH_3CN): λ_{max} = 216 nm (ε = 8814). − IR (CCl_4): $\tilde{\nu}$ = 1721 (C=O), 1654 (C=C) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.19 [s, 9 H, −Si(CH_3)$_3$], 1.36 (d, 3 H, *J* = 6.0 Hz, CH_3), 1.47 (ddd, 1 H, *J* = 13.2 Hz, 10.8 Hz, 7.6 Hz, −C*H*H−), 2.01 (dd, 1 H, *J* = 13.2 Hz, 4.9 Hz, −CH*H*−), 3.33 [d, 1 H, *J* = 7.6 Hz, −C*H*−C(E)=C(E)−], 3.80 (s, 3 H, −CO_2CH_3), 3.81 (s, 3 H, −CO_2CH_3), 4.01 [dqd, 1 H, *J* = 10.8 Hz, 6.0 Hz, 4.9 Hz, −C*H*(CH$_3$)−]. − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.4 [Si(*C*H_3)$_3$], 19.5 (*C*H_3), 33.6 (*C*H_2), 51.9 (O*C*H_3), 52.2 (O*C*H_3), 56.2 (*C*H), 74.0 [−*C*H(CH$_3$)−O−], 105.9 (O−*C*−OSi), 141.6 (*C*=C), 141.7 (C=*C*), 160.4 (*C*=O), 162.4 (*C*=O). − $C_{14}H_{22}O_6Si$ (314.4): calcd. C 53.48, H 7.05; found C 43.71, H 7.11. − **25b**. − UV (CH_3CN): λ_{max} = 216 nm (ε = 8814). − IR (CCl_4) : $\tilde{\nu}$ = 1721 (C=O), 1654 (C=C) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.18 [s, 9 H, −Si(CH_3)$_3$], 1.26 (d, 3 H, *J* = 6.8 Hz, CH_3), 1.68 (ddd, 1 H, *J* = 8.9 Hz, 13.3 Hz, 7.6 Hz, −C*H*H−), 2.21 (ddd, 1 H, *J* = 2.9 Hz, 13.3 Hz, 4.9 Hz, −CH*H*−), 3.40 [dd, 1 H, *J* = 2.9 Hz, 8.9 Hz, −C*H*−C(E)=C(E)−], 3.79 (s, 3 H, −CO_2CH_3), 3.83 (s, 3 H, −CO_2CH_3), 4.75 [dqd, 1 H, *J* = 7.6 Hz, 6.8 Hz, 4.9 Hz, −C*H*(CH$_3$)−]. − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.1 [Si(*C*H_3)$_3$], 23.1 (*C*H_3), 32.7 (*C*H_2), 51.9 (O*C*H_3), 52.2 (O*C*H_3), 56.1 (*C*H), 74.7 [−*C*H(CH$_3$)−O], 105.9 (O−*C*−OSi), 141.6 (*C*=C), 141.7 (C=*C*), 160.4 (*C*=O), 162.4 (*C*=O). − $C_{14}H_{22}O_6Si$ (314.4): calcd. C 53.48, H 7.05; found C 43.71, H 7.11.

Preparation of α-Alkylidene(thio)lactones 33 to 39

General Procedure II: To a stirred solution of cyclobutene **8**, **13**−**22**, **24** and **25** (1 equiv.) in dry THF (4 mL) was added dropwise a 1 M solution of TBAF in THF (1 equiv.). The dark solution was stirred at room temperature for one hour, washed with water (10 mL) and extracted with Et_2O (2 × 10 mL) and CH_2Cl_2 (2 × 10 mL). The organic layers were then washed with a saturated solution of NaCl (10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure (15 Torr) on a rotary evaporator. The residue was chromatographed on a silica gel column (15 g SiO_2:ethyl acetate/hexane 10:90 then 20:80) to give α-alkylidene(thio)lactones **33** to **39**.

Dimethyl Dihydro-2-oxo-3(2*H*)-furanylidenebutanedioate (*E* Isomer, 33): TBAF (0.31 mL; 0.31 mmol); cyclobutene **13** (93 mg; 0.31 mmol). Product formed: **33** (54 mg; 0.24 mmol; yield: 76%). Colourless oil. − UV (CH_3CN): λ_{max} = 237 nm (ε = 7511). − IR (CCl_4): $\tilde{\nu}$ = 1746 (C=O), 1730 (C=O), 1436 (C=C) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 3.46 [tt, 2 H, *J* = 7.1 Hz, 1.7 Hz, −CH_2−C=C(E)−], 3.70 (s, 3 H, −CO_2CH_3), 3.82 (s, 3 H, −CO_2CH_3), 4.18 (t, 2 H, *J* = 1.7 Hz, −CH_2−E), 4.40 (t, 2 H, *J* = 7.1 Hz, −CH_2−O−). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 30.1 (*C*H_2), 32.2 (*C*H_2), 52.1 (O*C*H_3), 52.6 (O*C*H_3), 65.3 (O*C*H_2), 133.4 (*C*=C−E), 135.7 (C=*C*−E), 166.6 (*C*=O), 169.8 (*C*=O), 170.7 (*C*=O). − $C_{10}H_{12}O_6$ (228.2): calcd. C 52.63, H 5.30; found C 52.77, H 5.54.

Ethyl Dihydro-2-oxo-3-furanylidene-3-propionate (*E* Isomer, 34): TBAF (0.42 mL; 0.42 mmol); cyclobutene **8** (107 mg; 0.49 mmol). Product formed: **34** (33 mg; 0.18 mmol; yield: 43%). Yellowish oil. − UV (CH_3CN): λ_{max} = 224 nm (ε = 5145). − IR (CCl_4): $\tilde{\nu}$ = 1771 (C=O), 1740 (C=O) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.29 (t, 3 H, *J* = 7.1 Hz, −$CO_2CH_2CH_3$), 2.91 (ttd, 2 H, *J* = 7.4 Hz, 2.9 Hz, 1.7 Hz, −CH_2−CH_2−O−), 3.22 (dt, 2 H, *J* = 7.4 Hz, 1.7 Hz, −C=CH−CH_2−E), 4.17 (q, 2 H, *J* = 7.1 Hz, −$CO_2CH_2CH_3$), 4.41 (t, 2 H, *J* = 7.4 Hz, −CH_2−O−), 6.90 (tt, 1 H, *J* = 7.4 Hz, 2.9 Hz, −C=CH−CH_2−E). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.2 (*C*H_3), 25.3 (*C*H_2), 35.8 (*C*H_2), 61.0 (*C*H_2), 61.4

(O*C*H$_2$), 123.0 (−*C*=CH−), 128.6 (*C*=O), 131.4 (−C=*C*H−), 169.4 (*C*=O). − $C_9H_{12}O_4$ (184.19): calcd. C 58.69, H 6.57; found C 59.86, H 6.84.

Dimethyl 5-Methyl-dihydro-2-oxo-3-furanylidenebutanedioate (*E* Isomer, 35): TBAF (0.60 ml; 0.60 mmol); cyclobutene **25** (188 mg; 0.60 mmol). Product formed: **35** (73 mg; 0.30 mmol; yield: 50%). Yellowish oil. − UV (CH_3CN): λ_{max} = 234 nm (ε = 10533). − IR (CCl_4): $\tilde{\nu}$ = 1746 (C=O), 1730 (C=O), 1651 (C=O), 1435 (C=C) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.23 (d, 3 H, *J* = 9.4 Hz, −C*H*$_3$), 2.95 [ddt, 1 H, *J* = 19.6 Hz, 5.9 Hz, 1.7 Hz, −C*H*H−C(R)=C(E)−], 3.49 [ddt, 1 H, *J* = 19.6 Hz, 7.5 Hz, 1.2 Hz, −CH*H*−C(R)=C(E)−], 3.69 (s, 3 H, −CO$_2$C*H*$_3$), 3.81 (s, 3 H, −CO$_2$C*H*$_3$), 4.15 (s, 2 H, −C=C−C*H*$_2$−E), 4.67 [ddd, 1 H, *J* = 9.4 Hz, 7.5 Hz, 5.9 Hz, −C*H*(CH$_3$)−O−]. − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.1 (*C*H$_3$), 32.3 (*C*H$_2$), 37.9 (*C*H$_2$), 52.2 (O*C*H$_3$), 52.6 (O*C*H$_3$), 74.0 (*C*H), 133.3 (−*C*H=C−), 137.1 (−CH=*C*−) 166.7 (*C*=O), 169.5 (*C*=O), 170.8 (*C*=O). − $C_{11}H_{14}O_6$ (242.2): calcd. C 54.49, H 5.83; found C 54.71, H 5.90.

Ethyl 5-Methyl dihydro-2-oxo-3-furanylidene-3-propionate (*E* Isomer, 36): TBAF (0.21 mL; 0.20 mmol); cyclobutene **24** (57 mg; 0.20 mmol). Product formed: **36** (20 mg; 0.10 mmol; yield: 50%). Yellowish oil. − UV (CH_3CN): λ_{max} = 213 nm (ε = 14985). − IR (CCl_4): $\tilde{\nu}$ = 1770 (C=O), 1742 (C=O), 1651 (C=O) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.28 (t, 3 H, *J* = 7.1 Hz, −CO$_2$CH$_2$C*H*$_3$), 1.41 (d, 3 H, *J* = 6.1 Hz, −C*H*$_3$), 2.37−2.55 [m, 1 H,−C*H*H−C=C(E)−], 2.96−3.12 [m, 1 H, −CH*H*−C=C(E)−], 3.20 [dt, 2 H, *J* = 7.4 Hz, 1.7 Hz, −C(R)=CH−C*H*$_2$−E], 4.19 (q, 2 H, *J* = 7.1 Hz, −CO$_2$C*H*$_2$CH$_3$), 4.70 [m, 1 H, −C*H*(CH$_3$)−O−], 6.87 [tt, 1 H, *J* = 7.4 Hz, 3.2 Hz, −C(R)=C*H*−]. − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.2 (*C*H$_3$), 22.3 (*C*H$_3$), 33.0 (*C*H$_2$), 35.7 (*C*H$_2$), 61.0 (*C*H$_2$), 74.0 (*C*H), 124.3 (−*C*=CH−), 130.0 (C=O), 131.2 (−C=*C*H−), 169.4 (*C*=O). − $C_{10}H_{14}O_4$ (198.2): calcd. C 60.60, H 7.12; found C 60.54, H 7.05.

Dimethyl Dihydro-2-oxo-3-pyranylidenebutanedioate (*Z* Isomer, 37a, and *E* Isomer, 37b): TBAF (0.34 mL; 0.34 mmol); cyclobutene **16** (107 mg; 0.34 mmol). Products formed: **37a** (30 mg; 0.13 mmol; yield: 37%) and **37b** (30 mg; 0.13 mmol; yield: 37%). Colourless oil. − **Compound 37a:** − UV (CH_3CN): λ_{max} = 215 nm (ε = 7219). − IR (CCl_4): $\tilde{\nu}$ = 1737 (C=O), 1435 (C=C) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.00 (tt, 2 H, *J* = 7.1 Hz, 5.4 Hz, −C*H*$_2$−CH$_2$−O−), 2.64 [t, 2 H, *J* = 7.1 Hz, −C*H*$_2$−C=C(E)−], 3.40 [s, 2 H, −C=C(E)−C*H*$_2$−E], 3.72 (s, 3 H, −CO$_2$C*H*$_3$), 3.80 (s, 3 H, −CO$_2$C*H*$_3$), 4.31 (t, 2 H, *J* = 5.4 Hz, −C*H*$_2$−O−). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.5 (*C*H$_2$), 24.6 (*C*H$_2$), 35.9 (*C*H$_2$−E), 52.6 (O*C*H$_3$), 52.8 (O*C*H$_3$), 68.1 (O*C*H$_2$), 130.5 [−*C*=C(E)−], 137.4 [−C=*C*(E)−], 165.2 (*C*=O), 167.3 (*C*=O), 168.9 (*C*=O). − $C_{11}H_{14}O_6$ (242.23): calcd. C54.54, H 5.83; found C 54.51, H 5.81. − **Compound 37b:** − UV (CH_3CN): λ_{max} = 223 nm (ε = 7395). − IR (CCl_4): $\tilde{\nu}$ = 1742 (C=O), 1435 (C=C) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.00 (tt, 2 H, *J* = 7.1 Hz, 5.4 Hz, −C*H*$_2$−CH$_2$−O−), 3.00 [t, 2 H, *J* = 7.1 Hz, −C*H*$_2$−C=C(E)−], 3.69 (s, 3 H, −CO$_2$C*H*$_3$), 3.80 (s, 3 H, −CO$_2$C*H*$_3$), 3.82 [s, 2 H, −C=C(E)−C*H*$_2$−E], 4.29 (t, 2 H, *J* = 5.4 Hz, −C*H*$_2$−O−). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.8 (*C*H$_2$), 26.6 (*C*H$_2$), 35.9 (*C*H$_2$−E), 52.2 (O*C*H$_3$), 52.4 (O*C*H$_3$), 68.0 (O*C*H$_2$), 134.3 [−*C*=C(E)−], 136.8 [−C=*C*(E)−], 166.5 (*C*=O), 167.3 (*C*=O), 170.8 (*C*=O). − $C_{11}H_{14}O_6$ (242.23): calcd. C 54.54, H 5.83; found C 54.61, H 5.79.

Dimethyl Dihydro-2-oxo-3-oxepanylidenebutanedioate (*Z* Isomer, 38a, and *E* Isomer, 38b): TBAF (0.37 mL; 0.37 mmol); cyclobutene **19** (124 mg; 0.37 mmol). Products formed: **38a** (37 mg; 0.14 mmol; yield: 39%) and **38b** (37 mg; 0.14 mmol; yield: 39%). − **Compound 38a:** Colourless oil. − UV (CH_3CN): λ_{max} = 213 nm (ε = 8401). − IR (CCl_4): $\tilde{\nu}$ = 1743 (C=O), 1435 (C=C) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.69−1.90 (m, 4 H, −C*H*$_2$−C*H*$_2$−CH$_2$−O−), 2.37−2.43 [m, 2 H, −C*H*$_2$−C=C(E)−], 3.43 [s, 2 H, −C=C(E)−CH$_2$−E], 3.68 (s, 3 H, −CO$_2$C*H*$_3$), 3.73 (s, 3 H, −CO$_2$C*H*$_3$), 4.26−4.31 (m, 2 H, −CH$_2$−O−). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.7 (*C*H$_2$), 28.2 (*C*H$_2$), 29.2 (*C*H$_2$), 33.0 (*C*H$_2$−E), 52.4 (O*C*H$_3$), 52.6 (O*C*H$_3$), 68.8 (O*C*H$_2$), 125.3 [−*C*=C(E)−], 146.5 [−C=*C*(E)−], 166.1 (*C*=O), 170.6 (*C*=O), 172.5 (*C*=O). − $C_{12}H_{16}O_6$ (256.25): calcd. C 56.25, H 6.29; found C 56.41., H 6.36.− **Compound 38b:** − UV (CH_3CN): λ_{max} = 215 nm (ε = 8783). − IR (CCl_4): $\tilde{\nu}$ = 1743 (C=O), 1435 (C=C) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.78−2.00 (m, 4 H, −C*H*$_2$−C*H*$_2$−CH$_2$−O−), 2.76 [m, 2 H, −C*H*$_2$−C=C(E)−], 3.50 [s, 2 H,−C=C(E)−CH$_2$−E], 3.69 (s, 3 H, −CO$_2$C*H*$_3$), 3.79 (s, 3 H, −CO$_2$C*H*$_3$), 4.33 (m, 2 H,−C*H*$_2$−O−). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.5 (*C*H$_2$), 28.2 (*C*H$_2$), 29.6 (*C*H$_2$), 35.9 (*C*H$_2$−E), 52.2 (O*C*H$_3$), 52.3 (O*C*H$_3$), 69.4 (O*C*H$_2$), 125.9 [−*C*=C(E)−], 147.7 [−C=*C*(E)−], 166.3 (*C*=O), 171.1 (*C*=O), 171.6 (*C*=O). − $C_{12}H_{16}O_6$ (256.25): calcd. C 56.25, H 6.29; found C 56.39, H 6.25.

Dimethyl Dihydro-2-oxo-3-thienylidenebutanedioate (*E* Isomer, 39): TBAF (0.49 mL; 0.49 mmol); cyclobutene **21** (156 mg; 0.49 mmol). Product formed: **39** (54 mg; 0.22 mmol; yield: 45%). Colourless oil. − UV (CH_3CN): λ_{max} = 242 nm (ε = 6114). − IR (CCl_4) : $\tilde{\nu}$ = 1746 (C=O), 1682 (C=O), 1435 (C=C) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.29−3.39 (m, 2 H, −C*H*$_2$−), 3.41−3.53 (m, 2 H, −C*H*$_2$−), 3.69 (s, 3 H, −CO$_2$C*H*$_3$), 3.81 (s, 3 H, −CO$_2$C*H*$_3$), 4.00 (t, 2 H, *J* = 1.2 Hz, −C*H*$_2$−E). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.1 (*C*H$_2$), 32.7 (*C*H$_2$), 52.1 (O*C*H$_3$), 52.6 (O*C*H$_3$), 128.8 (−*C*=C−E), 143.9 (−C=*C*−E), 167.2 (*C*=O), 167.8 (*C*=O), 170.7 (*C*=O). − $C_{10}H_{12}O_5S$ (244.26): calcd. C 49.17, H 4.95; found C 49.53, H 5.15.

Preparation of β-Oxo Esters 41, 44 and 47 and β-Oxo Ester Derivatives 43, 45 and 48

Dimethyl 6-Oxo-2-oxabicyclo[3.2.0]heptane-1,7-dicarboxylate (41): To a stirred solution of cyclobutene **13** (99 mg; 0.33 mmol) in THF (6 mL) was added H_2O (2 mL), followed by HCl 10% (0.2 mL). The solution immediately became rather cloudy and, after 15 min of stirring at room temp, water (6 mL) was added, and the crude reaction mixture was extracted with Et_2O (3 × 8 mL) and washed with a saturated solution of $NaHCO_3$ (8 mL). The organic layers were then dried with $MgSO_4$ and filtered. Concentration under reduced pressure in a rotary evaporator (15 Torr) afforded **41** (67 mg; 0.30 mmol; 90%) as a colourless oil. − IR (CCl_4): $\tilde{\nu}$ = 1780 (C=O), 1732 (C=O) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.03−2.43 (m, 2 H, −C*H*$_2$−CH$_2$−O−), 3.75 (s, 3 H, −CO$_2$C*H*$_3$), 3.89 (s, 3 H, −CO$_2$C*H*$_3$), 4.07−4.38 [m, 3 H, −C*H*$_2$−O− + −C*H*−C(O)−], 4.84 [d, 1 H, *J* = 3.6 Hz, −C*H*(E)−C(O)−].

Dimethyl 6-Methoxy-2-oxabicyclo[3.2.0]hept-6-ene-1,7-dicarboxylate (43): The treatment of **41** (67 mg; 0.30 mmol) with DAM (3.0 mmol) led to the corresponding enol ether **43** (54 mg; 0.22 mmol; 68%) as white crystals after concentration (15 Torr) and purification by silica gel chromatography (ethyl acetate/hexane, 50:50). −M.p. 92 °C. − UV (CH_3CN): λ_{max} = 238 nm (ε = 11244). − IR (CCl_4): $\tilde{\nu}$ = 2952, 1714 (C=O), 1651, 1451 (C=C) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.64−1.89 (m, 2 H, −C*H*$_2$−CH$_2$−O−), 3.46−3.49 [d, 1 H, *J* = 7.4 Hz, −C*H*−C(OCH$_3$)=C(E)−], 3.64 (s, 3 H, −CO$_2$C*H*$_3$), 3.77 (s, 3 H, −CO$_2$C*H*$_3$), 3.83−4.02 (m, 1 H,−C*H*H−O−), 4.20 (s, 3 H, −OC*H*$_3$), 4.19−4.33 (m, 1 H, −CH*H*−O−). − ^{13}C NMR

(50 MHz, $CDCl_3$): δ = 24.8 (*C*H_2), 51.4 (O*C*H_3), 52.6 (O*C*H_3), 53.5 (O*C*H_3), 61.1 (*C*H), 67.7 (O*C*H_2), 81.5 [−*C*(O−)(E)−], 101.8 [−*C*(E)=C(OMe)−], 160.5 [−C(E)=*C*(OMe)−], 165.0 (*C*=O), 170.8 (*C*=O). − MS (EI); *m/z* (%): 242 (79), 211 (18), 183 (100), 179 (24), 151 (65). − $C_{11}H_{14}O_6$ (242.23): calcd. C 54.54, H 5.83; found C 54.38, H 5.63.

Dimethyl 7-Oxo-2-oxabicyclo[4.2.0]octane-1,8-dicarboxylate (44): To a stirred solution of cyclobutene **16** (1 equiv.; 100 mg; 0.32 mmol) in Et_2O (5 mL) was added, at 0° C, boron trifluoride−diethyl ether (9 equiv.; 0.29 mL; 2.88 mmol). The cooling bath was removed and the reaction mixture was allowed to reach room temperature. After 1 h of stirring at room temperature, the solution was hydrolyzed with water (8 mL), extracted with Et_2O (3 × 10 mL), washed with saturated solutions of $NaHCO_3$ (10 mL), and saturated NaCl (10 mL), dried with $MgSO_4$ and filtered. Concentration under reduced pressure in a rotary evaporator (15 Torr) provided **44** (68 mg; 0.27 mmol; 88%) as a colourless oil. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.49−2.20 (m, 4 H, −C*H*$_2$−C*H*$_2$−), 3.75 (s, 3 H, −CO_2C*H*$_3$), 3.84 (s, 3 H, −CO_2C*H*$_3$), 3.80−3.95 [m, 3 H,−C*H*$_2$−O + −C*H*−C(O)−C(E)−], 4.62 (d, 1 H, *J* = 2.9 Hz, −C*H*−CO_2Me).

Dimethyl 7-Methoxy-2-oxabicyclo[4.2.0]oct-7-ene-1,8-dicarboxylate (45): Treatment of **44** (56 mg; 0.23 mmol) with DAM (3.0 mmol) led to the corresponding enol ether **45** (43 mg; 0.16 mmol; 50%) as a colourless oil after purification by silica gel chromatography (ethyl acetate/hexane, 50:50). − UV (CH_3CN): λ_{max} = 239 nm (ε = 13054). − IR (CCl_4): ṽ = 2952, 1714 (C=O), 1645, 1451 (C=C) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.39−2.01 (m, 4 H, −C*H*$_2$−C*H*$_2$−), 3.14 [t, 1 H, *J* = 6.1 Hz, −C*H*−C(OMe)=C(E)−], 3.65 (s, 3 H, −CO_2C*H*$_3$), 3.76 (s, 3 H, −CO_2C*H*$_3$), 3.93 (t, 2 H, *J* = 6.9 Hz,−C*H*$_2$−O−), 4.20 (s, 3 H, −OC*H*$_3$). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.3 (*C*H_2), 21.2 (*C*H_2), 46.1 (*C*H), 51.4 (O*C*H_3), 52.5 (O*C*H_3), 60.9 (O*C*H_3), 62.5 (O*C*H_2), 72.7 [−C(O−)(E)−], 105.7 [−*C*(E)=C(OMe)−], 160.7 [−C(E)=*C*(OMe)−], 168.1 (*C*=O), 172.5 (*C*=O). − $C_{12}H_{16}O_6$ (256.25): calcd. C 56.25, H 6.29; found C 56.19, H 6.10.

Dimethyl 6-Methoxy-2-thiabicyclo[3.2.0]hept-6-ene-1,7-dicarboxylate (48): Same reaction conditions as for cyclobutene **13**: **21** (103 mg; 0.32 mmol); THF (6 mL); H_2O (2 mL); HCl 10% (0.2 mL); product formed: β-oxo ester **47** (77 mg; 0.31 mmol, 98%). Treatment with DAM (4.0 mmol), followed by concentration (15 Torr) and silica gel chromatography (ethyl acetate/hexane, 50:50) led to **48** (24 mg; 0.09 mmol; 41%). − UV (CH_3CN): λ_{max} = 241 nm (ε = 8174). − IR (CCl_4): ṽ = 1733, 1716 (C=O), 1651 (C=C) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.73 (dddd, 1 H, *J* = 13.3 Hz, 12.3 Hz, 7.2 Hz, 6.1 Hz, −C*H*H−CH_2−O−), 2.15 (ddt, 1 H, *J* = 13.3 Hz, 4.7 Hz, 1.0 Hz, −CH*H*−CH_2−O−), 2.78 (td, 1 H, *J* = 12.3 Hz, 4.7 Hz, −C*H*H−S−), 2.98 (ddt, 1 H, *J* = 12.3 Hz, 6.1 Hz, 1.0 Hz, −CH*H*−S−), 3.62 [dd, 1 H, *J* = 7.2 Hz, 1.0 Hz, −C*H*−C(OMe)=C(E)−], 3.69 (s, 3 H, −CO_2C*H*$_3$), 3.77 (s, 3 H, −CO_2C*H*$_3$), 4.17 (s, 3 H, −OC*H*$_3$). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.7 (*C*H_2), 31.6 (S*C*H_2), 51.8 (O*C*H_3), 53.0 (O*C*H_3), 56.4 (O*C*H_3), 60.9 (*C*H), 103.4 [−*C*(S-)(E)−], 115.8 [−*C*(E)=C(OMe)−], 160.3 [−C(E)=*C*(OMe)−], 162.2 (*C*=O), 171.3 (*C*=O). − $C_{11}H_{14}O_5S$ (258.29): calcd. C 51.15, H 5.46; found C 51.37, H 5.22.

Preparation of Furan Derivatives 40 and 42, Pyran Derivative 46 and Thiophene Derivative 49

Furan Derivative 40: To a stirred solution of cyclobutene **13** (1 equiv.; 80 mg; 0.27 mmol) in Et_2O (5 mL) was added, at 0 °C, boron trifluoride−diethyl ether (9 equiv.; 0.24 mL; 2.40 mmol). The cooling bath was removed and the reaction mixture was allowed to reach room temperature, and stirred for 48 h. The solution was then hydrolyzed with H_2O (15 mL), extracted with Et_2O (3 × 10 mL), dried with $MgSO_4$ and filtered. Concentration in a rotary evaporator (15 Torr) afforded furan derivative **40** (65 mg; 0.26 mmol; 98%) as a colourless oil. − IR (CCl_4): ṽ = 2955 (OH, br.), 1749 (C=O) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.21−2.42 (m, 2 H, −C*H*$_2$−CH_2−O−), δ_A = 2.85, δ_B = 3.15 (AB, *J* = 16.0 Hz, −C*H*$_2$−E), 3.39 (dd, 1 H, *J* = 7.8 Hz, 6.3 Hz, −C*H*−COOH), 3.68 (s, 3 H, −CO_2C*H*$_3$), 3.83 (s, 3 H, −CO_2C*H*$_3$), 4.03−4.31 (m, 2 H, −C*H*$_2$−O−), 7.60−7.90 (s, br., 1 H, −COO*H*). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.1 (*C*H_2), 39.4 (*C*H_2), 50.6 (*C*H), 52.1 (O*C*H_3), 53.0 (O*C*H_3), 68.9 (O*C*H_2), 84.6 [−*C*(O-)(E)−], 170.2 (O*C*H_3), 173.0 (*C*=O), 176.1 (*C*O_2 H).

Furan Derivative 42. − Method A: Treatment of **40** (65 mg; 0.26 mmol) with DAM (3.0 mmol) led to the corresponding furan derivative **42** (41 mg; 0.16 mmol; 61%) as a colourless oil, after purification by silica gel chromatography (ethyl acetate/hexane, 20:80). − **Method B:** The β-oxo ester **41** (63 mg; 0.27 mmol) was dissolved in MeOH (2 mL) with added 10% HCl (5 drops). After stirring overnight, MeOH was removed in vacuo (15 Torr). The residue was hydrolyzed with H_2O (5 mL) and extracted with Et_2O (3 × 10 mL), washed with a saturated solution of NaCl (10 mL), then dried with $MgSO_4$, filtered and concentrated in a rotary evaporator (15 Torr). Chromatography on silica gel (ethyl acetate/hexane, 20:80) afforded furan **42** (63 mg; 0.24 mmol, 90%). − IR (CCl_4): ṽ = 1746 (C=O) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.15−2.37 (m, 2 H,−C*H*$_2$−CH_2−O−), δ_A = 2.76, δ_B = 3.05 (AB, *J* = 16.0 Hz, −C*H*$_2$−E), 3.33−3.41 [dd, 1 H, *J* = 7.8 Hz, 6.3 Hz, −C*H*(R)−E], 3.67 (s, 3 H, −CO_2C*H*$_3$), 3.73 (s, 3 H, −CO_2C*H*$_3$), 3.80 (s, 3 H, −CO_2C*H*$_3$), 4.01−4.34 (m, 2 H, −C*H*$_2$−O−). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.3 (*C*H_2), 39.4 (*C*H_2), 50.6 (*C*H), 52.0 (O*C*H_3), 52.3 (O*C*H_3), 52.9 (O*C*H_3), 69.0 (O*C*H_2), 84.8 [−*C*(O-)(E)−], 170.2 (*C*=O), 171.9 (*C*=O), 172.9 (*C*=O). − MS (CI, isobutane); *m/z* (%): 261 (100) [M + 1], 229 (48) [M − OMe], 201 (27) [M − CO_2Me], 169 (17) [M − CO_2Me − OMe − 1]. − $C_{11}H_{16}O_7$ (260.2): calcd. C 50.60, H 6.17; found C 50.80, H 6.20.

Pyran Derivative 46: Same reaction conditions as for β-oxo ester **41**: **44** (68 mg; 0.27 mmol); MeOH (2 mL); 10% HCl (5 drops); product formed: pyran **46** (60 mg; 0.21 mmol, 80%) as a colourless oil. − IR (CCl_4): ṽ = 1746 (C=O) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.50−2.03 (m, 4 H, −C*H*$_2$−C*H*$_2$−), 3.00 (dd, 1 H, *J* = 8.2 Hz, 4.7 Hz, −C*H*−E), δ_A = 3.09, δ_B = 3.14 (AB, *J* = 15.6 Hz, −C*H*$_2$−E), 3.65 (s, 3 H, −CO_2C*H*$_3$), 3.67 (s, 3 H, −CO_2C*H*$_3$), 3.80 (s, 3 H, −CO_2C*H*$_3$), 3.80−3.88 (m, 2 H, −C*H*$_2$−O−). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.5 (*C*H_2), 23.1 (*C*H_2), 37.6 (*C*H), 45.7 (O*C*H_3), 51.9 (O*C*H_3), 52.8 (O*C*H_3), 63.1 (O*C*H_2), 77.1 [−*C*(O-)(E)−], 169.8 (*C*=O), 171.9 (*C*=O), 172.5 (*C*=O). − $C_{12}H_{18}O_7$ (274.27): calcd. C 52.55, H 6.61; found C 52.79, H 6.66.

Thiophene Derivative 49: Same reaction conditions as for β-oxo ester **41**: **47** (77 mg, 0.31 mmol); MeOH (2 mL); 10% HCl (5 drops); product formed: thiophene derivative **49** (34 mg, 0.12 mmol, 40%) as a colourless oil after purification by silica gel chromatography. − IR (CCl_4): ṽ = 1747 (C=O) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.29−2.64 (m, 2 H, −C*H*$_2$−CH_2−S−), 2.82−3.05 (m, 1 H, −C*H*H−S−), 3.11−3.20 (m, 1 H, −CH*H*−S−), δ_A = 2.99, δ_B = 3.16 (AB, *J* = 17.5 Hz, −C*H*$_2$−E), 3.66 (s, 3 H, −CO_2C*H*$_3$), 3.67 (s, 3 H, −CO_2C*H*$_3$), 3.68−3.72 (m, 1 H, −C*H*−E), 3.76 (s, 3 H, −CO_2C*H*$_3$). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.4 (*C*H_2), 34.8 (*C*H_2), 41.0 (S*C*H_2), 51.7 (O*C*H_3), 51.8 (O*C*H_3), 53.0 (O*C*H_3), 58.8 (CH), 120.1 [−*C*(O-)(E)−], 170.9

Table 3. Crystallographic details

	16	**43**	**49**
Empirical formula	$C_{14}H_{22}O_6Si$	$C_{11}H_{14}O_6$	$C_{11}H_{16}O_6S$
Molecular mass	314.41	242.23	276.31
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P12_1/c1$	$P\bar{1}$
a [Å]	6.5640(5)	8.5220(5)	6.7585(4)
b [Å]	8.7700(5)	14.0970(9)	9.3735(4)
c [Å]	15.164(1)	10.4440(5)	10.8744(5)
α [°]	89.802(4)	90	98.121(5)
β [°]	80.656(4)	112.188(3)	103.911(5)
γ [°]	74.681(4)	90	100.649(5)
V [Å]	830.0(2)	1161.8(2)	644.6(1)
Z	2	4	2
Colour	colourless	colourless	colourless
Crystal size [mm]	0.20×0.16×0.08	0.25×0.20×0.18	0.20×0.18×0.14
$D_{calcd.}$ [g cm^{-3}]	1.26	1.38	1.42
$F000$	336	512	292
μ [mm^{-1}]	0.164	0.114	0.268
Temperature (K)	294	173	173
Wavelength (Å)	0.71073	0.71073	0.71073
Radiation	Mo-K_α graphite-monochromated	Mo-K_α graphite-monochromated	Mo-K_α graphite-monochromated
Diffractometer	Kappa CCD	Kappa CCD	Kappa CCD
Scan mode	φ scans	φ scans	φ scans
hkl limits	0.8/−10, 11/−19, 19	0.11/−18, 18/−13, 11	−8/8, −12/12, −14/13
φ limits [°]	2.5/27.54	2.5/27.49	2.5/27.50
Number of data meas.	8890	7236	4150
Number of data with $I > 3\sigma(I)$	2403	1916	2333
Weighting scheme	4 $F_o^2/[\sigma^2(F_o^2) + 0.0064\ F_o^4]$	4 $F_o^2/[\sigma^2(F_o^2) + 0.0064\ F_o^4]$	4 $F_o^2/[\sigma^2(F_o^2) + 0.0064\ F_o^4]$
Number of variables	190	154	163
R	0.042	0.043	0.036
R_w	0.069	0.069	0.066
GOF	1.317	1.298	1.215
Largest peak in final difference [e Å^{-3}]	0.273	0.363	0.295

(*C*=O), 172.2 (*C*=O), 173.2 (*C*=O). − $C_{11}H_{16}O_6S$ (276.2): calcd. C 47.83, H 5.84; found C 48.01, H 5.74.

X-ray Crystallographic Study: Crystal data, data collection parameters and results are summarized in Table 3. Data were collected at room temperature for **16** and at 173 K for **43** and **49**, corrected for Lorentz and polarization factors. Absorption corrections are included in the scaling procedure for data collected using the Kappa CCD. The structures were determined using direct methods and refined against $|F|$ using the OpenMoleN package on a DEC Alpha workstation. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (**16**: CCDC-130653; **43**: -130654; **49**: -144428). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax:(internat) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

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