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PAPER

Synthesis and characterization of bis-cyclopropanated 1,3,5-tricarbonyl compounds. A combined synthetic, spectroscopic and theoretical study†

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Bis-cyclopropanated 1,3,5-tricarbonyl compounds were prepared by a sequence of Claisen condensations and cyclopropanations. The optimization of the conditions proved to be very important to suppress retro-Claisen reactions. The conformation of these molecules was studied by experimental and computational methods. The *syn/syn;syn/syn* conformation is present for all derivatives. It is exclusively present in the case of the derivative containing a phenyl group located at the terminal carbon atom. In most cases, equilibria with other conformers are found.

Introduction

A great variety of pharmacologically important natural products are biosynthetically derived from poly(β-oxo)carboxylic acids (polyketides).[1] Polyketides also represent important synthetic building blocks.[2] Harris and coworkers reported the biomimetic synthesis of various 1,3,5-tricarbonyl compounds **A** based on condensations of 1,3-dicarbonyl dianions or 1,3,5-tricarbonyl trianions with carboxylic acid derivatives (Fig. 1).[3] 1,3,5-Tricarbonyl compounds also are available by reaction of 1,3-bis(silyloxy)-1,3-butadienes, masked 1,3-dicarbonyl dianions, with acid chlorides.[4] We were attracted by the beautiful and interesting structure of open-chained bis-cyclopropanated 1,3,5-tricarbonyl compounds **B**. Like their permethylated analogues **C**, they are lacking the CH-acidic methylene groups.[5,6] Cyclopropyl-based molecular architectures have recently gained considerable theoretical and structural interest.[7] For example, versatile synthetic approaches to open-chain oligocyclopropanes[8] and σ-[*n*]helicenes[9] have been developed.

Cyclic cyclopropanated 1,3,5-triketone **D** was prepared in low yield by a Zn/Cu mediated transformation of 1-bromocyclopropanecarboxylic acid chloride.[10] Open-chained 1,3,5-tricarbonyl compounds of type **B** had not been prepared until our recent short communication,[11] and their synthesis is a difficult task because 1,3,5-tricarbonyl compounds containing quaternary carbons easily undergo fragmentations (by means of retro-Claisen reactions). Herein, we report a comprehensive synthetic, structural and theoretical study. With regard to our preliminary communication, we greatly extended the scope for the synthesis of bis-cyclopropanated 1,3,5-triketones and also successfully extended our synthetic strategy to the preparation of various bis-cyclopropanated triketides (*i.e.*, bis-cyclopropanated 3,5-dioxoesters). In addition, we have found that the direct cyclopropanation of 3,5-dioxoesters resulted in the formation of cyclopropanated dihydrofurans which are interesting in their own right. The structure and the conformation of the products, containing different substitution patterns, were thoroughly analyzed by spectroscopic methods and by DFT calculations.

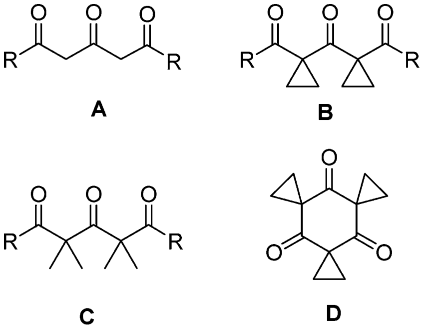

Fig. 1 Structures of 1,3,5-tricarbonyl compounds **A–D**.

Results and discussion

Synthesis

Our first target was the synthesis of bis-cyclopropanated 1,3,5-triketones. We chose a synthetic strategy based on a straightforward sequence of Claisen condensation and cyclopropanation (Scheme 1, Table 1). The K_2CO_3-mediated[12] cyclopropanation of 1-(cyclopropyl)butane-1,3-dione and benzoylacetone with 1,2-dibromoethane afforded the known cyclopropanes **2a** and **2b**.[13] The LDA-mediated reaction of **2a** with cyclopropanecarboxylic

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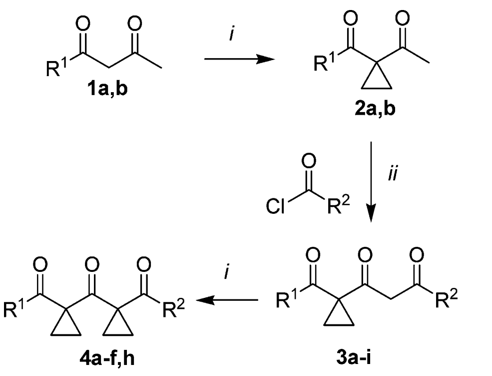
Table 1 Synthesis of cyclopropyl-triketones **4a–f,h**

2	3,4	R^1	R^2	% (**2**)[a]	% (**3**)[a]	% (**4**)[a]
a	**a**	*c*Pr	*c*Pr	70	65	30
b	**b**	Ph	*c*Pr	75	47	64
b	**c**	Ph	*t*Bu	75	31	42
b	**d**	Ph	Ph	75	22	30
b	**e**	Ph	4-MeC_6H_4	75	31	34
b	**f**	Ph	4-(MeO)C_6H_4	75	21	33
b	**g**	Ph	$4\text{-(ClCH}_2)C_6H_4$	75	18	0
b	**h**	Ph	4-*t*BuC_6H_4	75	25	30
b	**i**	Ph	3-ClC_6H_4	75	63	0

[a] Isolated yields.



Scheme 1 Synthesis of cyclopropyl-triketones **4a–f,h**. *Conditions*: *i*, 1,2-dibromoethane (2.0 equiv.), K_2CO_3 (4.0 equiv.), DMSO, 8 h, 20 °C; *ii*, 1) LDA (1.2 equiv.), THF, 1 h, −78 °C, 2) acid chloride, −78 → 20 °C, 12 h.

acid chloride gave **3a** in up to 65% yield. Subsequent cyclopropanation gave bis-cyclopropanated 1,3,5-triketone **4a**. Likewise, the condensation of **2b** with cyclopropanecarboxylic acid chloride or pivaloyl chloride afforded **3b** and **3c** which were transformed into **4b** and **4c**, respectively. The reaction of **2b** with various aroyl chlorides afforded products **3c–i**. The cyclopropanation of **3c–f** and **3h** afforded products **4c–f** and **4h**. The cyclopropanation of derivatives **3g** and **3i**, containing electron-withdrawing groups, failed.

As mentioned above, compounds **4** represent bis-cyclopropanated 1,3,5-triketones. Our next goal was to prepare bis-cyclopropanated 3,5-dioxoesters (triketides) which are, to the best of our knowledge, also unknown to date. The strategy depicted in Scheme 1 for the synthesis of 1,3,5-triketones **4** proved to be *not* applicable to the synthesis of triketides **8**, due to decomposition by retro-Claisen reaction. However, the synthesis of triketides **8** could be realized by a slightly different strategy (Scheme 2, Table 2). The Claisen condensation of dimethyl cyclopropane-1,1-dicarboxylate (**5**), which is readily available in large scale, with ketones **6a,b,d–h** afforded the mono-cyclopropanated triketides **7a,b,d–h** which were transformed by cyclopropanation into the desired bis-cyclopropanated triketides **8a,b,d–h**. Likewise, the reaction of **5** with methyl acetate (**6c**) and subsequent cyclopropanation afforded the symmetrical, hitherto unknown bis-cyclopropanated diester **8c**.

The best yields of mono-cyclopropanated triketides **7** were obtained when sodium methoxide and MTBE were used as base and solvent, respectively. The use of KO*t*Bu or LDA proved to be

Table 2 Synthesis of cyclopropyl-triketides **8a–h**

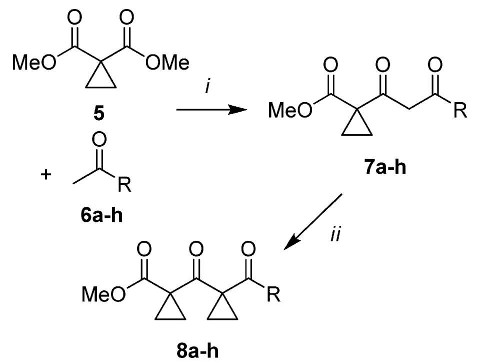
7,8	R	% (**7**)[a]	% (**8**)[a]
a	*c*Pr	40	18[b]
b	Me	58	37
c	OMe	44	67
d	Ph	51	37
e	1-Naphthyl	32	44
f	*c*Hex	40	34
g	4-(MeO)C_6H_4	48	67
h	η^5-Ferrocenyl	52	48

[a] Isolated yields. [b] Stirring for 8 h instead of 12 h.

Table 3 Optimization of the synthesis of cyclopropyl-triketide **7b**

T [°C]	*Time* (heating) + *time* (20 °C) [h][a]	% (**7b**)
30	3 + 0	24
30	5 + 12	28
45	5 + 12	58

[a] Reaction time: heating at the indicated temperature + stirring at 20 °C.



Scheme 2 Synthesis of cyclopropyl-triketides **8a–h**. *Conditions*: *i*, 1) NaOMe (2.0 equiv.), MTBE, 5 h, 50 °C, 2) 12 h, 22 °C, 3) HCl (10%), brine; *ii*, 1,2-dibromoethane (2.0 equiv.), K_2CO_3 (4.0 equiv.), DMSO, 12 h, 22 °C.

unsuccessful as it resulted in a retro-Claisen reaction. Moreover, we found that the reaction time and the temperature had a great effect on the yield. The best yields were obtained when the reaction was carried out at 45–50 °C for a minimum reaction time of 5 h (Table 3). A lower temperature or shorter reaction time led to a decrease in the yield.

Compounds **7a,b,d–h** exist as a mixture of keto and enol tautomers. According to the NMR experiments, the enol tautomer is generally preferred, except for **7c** which exclusively exists in the keto form. For compound **7e**, we were able to grow crystals and to study the molecular structure by X-ray crystal structure analysis (Fig. 2).

The NaOMe-mediated reaction of **5** with **2a** afforded the bis-cyclopropanated tetraketide **9** which represents a rare example of an open-chained tetraketide (Scheme 3). Unfortunately, the cyclopropanation of **9** proved to be unsuccessful under various conditions, due to decomposition by retro-Claisen reactions.

In an attempt to facilitate the synthesis of bis-cyclopropanated 1,3,5-tricarbonyl compounds, we studied the direct twofold cyclopropanation of 1,3,5-tricarbonyl derivatives (Scheme 4, Table 4). The cyclopropanation of 1,3,5-tricarbonyl compounds

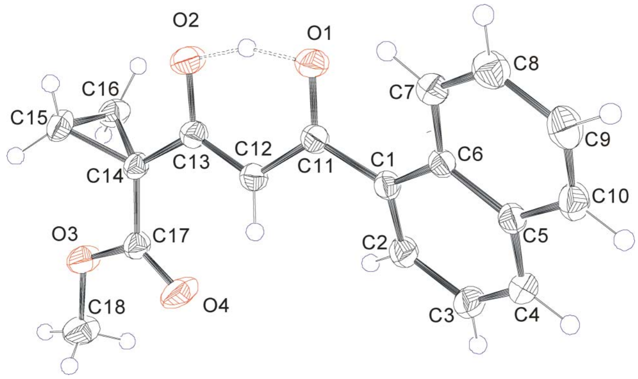
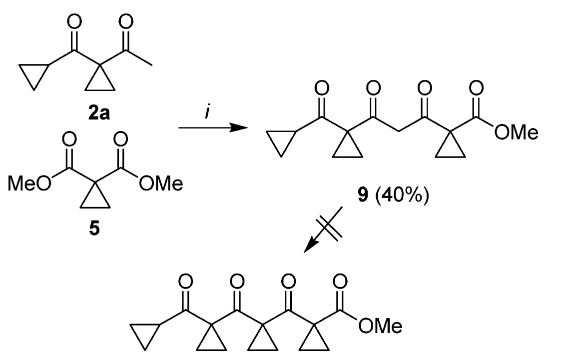
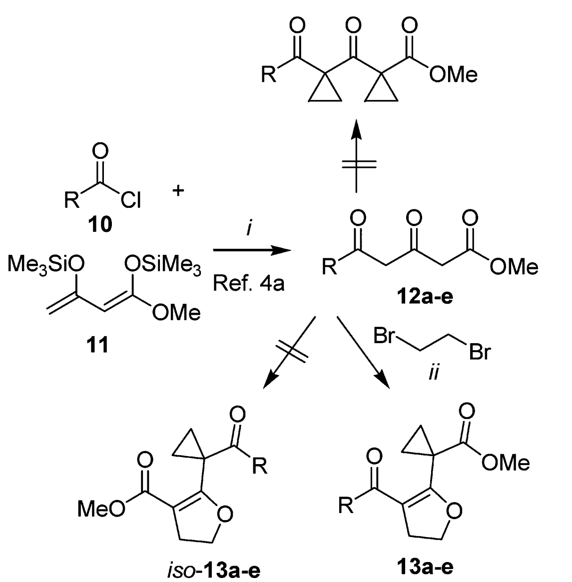


Fig. 2 Molecular structure of **7e**.



Scheme 3 Synthesis of cyclopropanated tetraketide **9**. Conditions: *i*, 1) NaOMe, MTBE, 3 h, 30 °C, 2) HCl (10%).



Scheme 4 Synthesis of dihydrofurans **13a–e**. *Conditions*: *i*, 1) CH_2Cl_2, $-87 \to 20$ °C; 2) $NaHCO_3$, H_2O; *ii*, 1,2-dibromoethane (2.5 equiv.), K_2CO_3 (5.0 equiv.), DMSO, 8 h, 20 °C.

has, to the best of our knowledge, not been studied so far. The methyl 3,5-dioxoalkanoates **12a–e** were prepared, using our previously reported procedure,[4a] by condensation of 1,3-bis(silyloxy)-1,3-butadiene **11** with acid chlorides **10**. The synthesis of derivatives **12a,b** has been previously reported.[4a] The reaction of **12a–e** with 2.5 equiv. of 1,2-dibromoethane afforded the cyclopropanated dihydrofurans **13a–e** rather than the bis-cyclopropanated triketides **8**. The relatively low yields can be explained by practical problems during the chromatographic purification and by partial decomposition, due to retro-Claisen reactions. The formation of products **13** was not unexpected, since a competition of cyclopropanation and dihydrofuran formation has been previously reported for the reaction of 1,2-dibromoethane with simple 1,3-dicarbonyl derivatives.[14] The synthesis of cyclopropanated dihydrofurans related to products **13** has, to the best of our knowledge, not been previously reported.

Table 4 Synthesis of dihydrofurans **13**

13	R	%^{a,b} (**12**)	%^{a} (**13**)
a	*c*Pr	91	32
b	Ph	63	35
c	4-(MeO)C_6H_4	42	15
d	4-MeC_6H_4	58	21
e	3-ClC_6H_4	64	17

^{a} Yields of isolated products. ^{b} Keto/enol = 0 : 100

A ^{1}H NOESY experiment was performed on **13a** to confirm the identity of compounds **13a–e** (Fig. 3). It is important to note that the cyclopropylidene moiety is located next to the ester group and the cyclopropyl adjacent to the keto group. The regioisomeric products iso-**13a–e** could not be isolated.

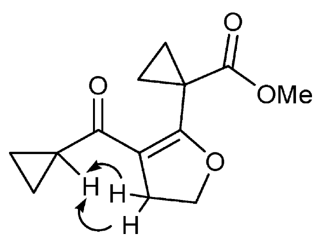


Fig. 3 Diagnostic NOESY interactions of compound **13a**.

Conformations

The conformations of bis-cyclopropanated 1,3,5-triketones **4a** and **4d** were already studied in our preliminary communication from both X-ray structural analysis and B3LYP/6-311+G(d,p) density functional theory computation.[11] For clarity and comparison, we herein refer to those findings. In the case of **4d**, only one conformer (*syn*/*syn*;*syn*/*syn*) is present in the solid state and in solution, and this is also confirmed by computation, and the second conformer (*syn*/*syn*; *anti*/*anti*) is found less stable by 9.32 kcal mol^{-1} (Fig. 4). In the more stable conformer, the two cyclopropyl rings possess a *syn* conformation to the central carbonyl group; and the carbonyl groups of the benzoyl groups also exist in a *syn* conformation to the cyclopropyl rings.

The predominance of the *syn*/*syn*;*syn*/*syn* conformer in the case of **4d** might be explained by the fact that the molecule contains two phenyl groups and a stabilizing intramolecular π-stacking effect might play a role. We tried to gain more insight by NMR. For the apparently C_{2v}-symmetric triketone **4a**, only one set of signals and thus no individual conformers were observed even at temperatures down to −100 °C.[11] For the non-symmetrical bis-cyclopropanated

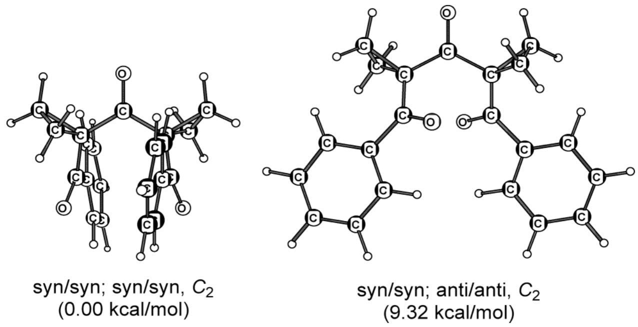


Fig. 4 Conformation and energy of **4d** (see ref. 11).

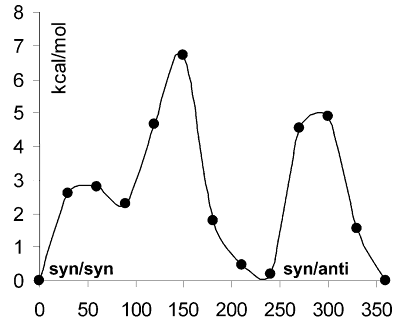


Fig. 6 Relaxed scan along the O1–C2–C3–C4 torsional angle at HF/6-31G(d) for **4c**.

1,3,5-triketones **4c**, **4e**, **4f** and **4h**, ^{1}H NOESY measurements were carried out in CD_2Cl_2. Here, individual observation of all molecular positions is possible and qualitative conclusions are straightforward. The following spectroscopic patterns were similar for all four derivatives. We find *four* signals (each of them representing two protons), two AA′XX′ patterns, for the cyclopropylidene groups. This proves averaged mirror symmetry for the molecules, however, the preferred conformation is not the planar (C_s) one. We find a positive NOE between the phenyl *ortho* protons and both types of protons at the adjacent three-membered ring (which is not surprising) and another positive NOE between the phenyl *ortho* protons and one type of proton at the remote cyclopropylidene. The latter indicates a significant contribution of a *syn*/*anti* conformation (with respect to the central carbonyl group). In such an arrangement, the substituents at both ends of the chain should be able to approach each other. This can in particular be observed for **4c** by a positive NOE between the phenyl *ortho* protons and the *tert*-butyl group (see ESI†). Unfortunately, the resonances of the aromatic proton at the terminal residues are insufficiently separated to observe this also for **4e**, **4f** and **4h**.

To elucidate the change of the conformations of compound **4c**, we carried out density functional theory computations using the B3LYP/6-311+G(d,p) method,[15,16] and used the same procedure for **4d**.[11] For **4c**, we have found an energy minimum structure with the phenyl and *tert*-butyl groups in *syn*/*syn*;*syn*/*syn* conformation (Fig. 5). To search for the potential energy surface, we have rotated the torsional angle of O1–C2–C3–C4 by 360° for a relaxed scan at the HF/6-31G(d) level (Fig. 6). Two minimum structures very close in energy are found: one corresponds to the *syn*/*syn*;*syn*/*syn* conformation and the other one to a *syn*/*anti*;*syn*/*syn* conformation (Fig. 5). The rotational barrier is lower than 7 kcal mol^{-1} which indicates a free rotation and equilibrium of both conformers. The structure of the *syn*/*anti*;*syn*/*syn* conformation was further refined at B3LYP/6-311+G(d,p) and characterized as a true energy minimum; the torsional angle of O1–C2–C3–C4 is −152.8°. At B3LYP/6-311+G(d,p), under the consideration of the thermal correction to Gibbs free energy at 298 K from frequency calculations, we have found that the *syn*/*syn*;*syn*/*syn* conformation (−962.82571 au) and the *syn*/*anti*;*syn*/*syn* conformation (−962.82577 au) of **4c** are nearly identical in Gibbs free energy. This reveals that both conformers are nearly equally populated in solution. All observed NOEs (*vide supra*) are compatible with the *syn*/*anti*;*syn*/*syn* conformation. The *syn*/*syn*;*syn*/*syn* conformation is characterized by large distances between the H-bearing groups and thus does not give rise to specific cross peaks in the NOESY spectrum.

Finally, the conformation of bis-cyclopropanated triketides **8** was studied. Unfortunately, NMR experiments remained inconclusive, due to signal overlap. However, we were able to study the structure of **8g** in the solid state by X-ray crystal structure analysis (Fig. 7). In the solid state, a *syn*/*syn*;*syn*/*syn* conformation is adopted (like in the case of compound **4d**). Of course, this result does not necessarily reflect the situation in solution and the conformation might be a result of crystal packing effects.

Conclusions

In conclusion, we have reported the synthesis of various symmetrical and unsymmetrical bis-cyclopropanated 1,3,5-tricarbonyl

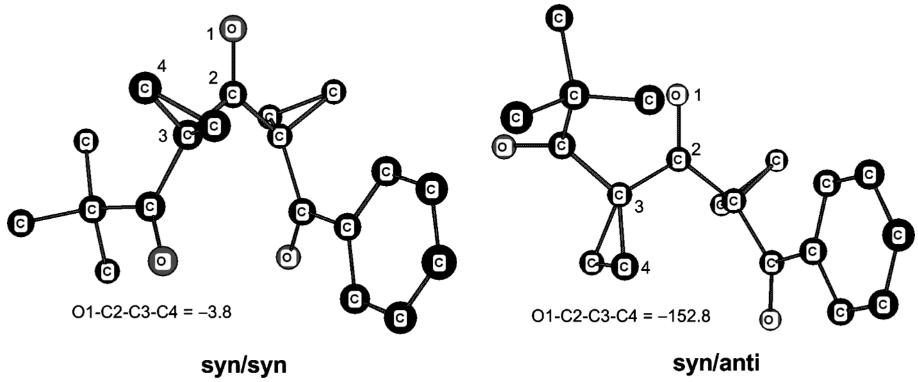


Fig. 5 The B3LYP/6-311+G(d,p) optimized energy minimum structures of **4c**.

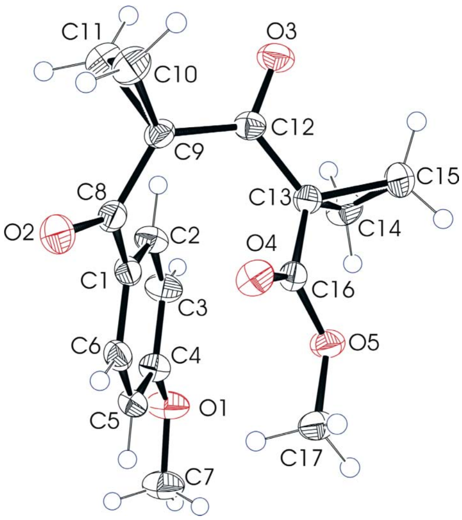


Fig. 7 Molecular structure of **8g**.

compounds. While the direct cyclopropanation of 3,5-dioxoesters resulted in the formation of mono-cyclopropanated dihydrofurans, the target molecules could be prepared by a stepwise strategy of Claisen condensation and cyclopropanation. The optimization of the reaction conditions played an important role in order to suppress the decomposition by retro-Claisen reactions. The conformations of these molecules were studied using a combined approach of X-ray crystal structure analysis, NOE-experiments and computational methods. In the solid state, only one conformation (*syn*/*syn*;*syn*/*syn*) was present in the case of the symmetrical bis-cyclopropanated 1,3,5-triketone **4d** and of the bis-cyclopropanated triketide **8g**. In the case of derivative **4d**, containing two phenyl groups located at the terminal positions of the chain, this conformation is by far more stable than the *syn*/*syn*;*anti*/*anti* conformation and is likely to be exclusively present in solution. In the case of **4a**, containing two cyclopropyl groups located at the terminal positions of the chain, two main conformations (*syn*/*syn*;*syn*/*syn* and *syn*/*syn*;*anti*/*anti*), which are similar in Gibbs free energy, were found to coexist in solution. Only one conformation (*syn*/*syn*;*syn*/*syn*) was present in the case of the bis-cyclopropanated 1,3,5-triketones **4a** and **4c**.

Experimental section

General comments

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^{1}H and ^{13}C NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane) or electrospray ionization (ESI). For preparative scale chromatography silica gel 60 (0.063-0.200 mm, 70–230 mesh) was used.

General procedure for the synthesis of cyclopropylketides 2

To a suspension of K_2CO_3 (4.0 equiv.) in DMSO (0.3–0.5 mL mmol^{-1}) was added **1** (1.0 equiv.). To the reaction mixture dibromoethane (2.0 equiv.) was added dropwise at 20 °C with vigorous stirring. After stirring at 20 °C for 8 h, K_2CO_3 was removed by filtration. The solid was thoroughly washed with diethyl ether. The filtrate was washed with water until the yellow colour disappeared, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc = 2 : 1) to give product **2**. The synthesis of **2a,b** has been previously reported.[13]

General procedure for the synthesis of cyclopropylketides 3

To a solution of LDA (1.2 equiv.) in THF (2 mL mmol^{-1}) was added **2** (1 equiv.) at −78 °C. The reaction mixture was stirred for 1 h and acid chloride (1.1 equiv.) was added dropwise at −78 °C. The reaction mixture was stirred for 12 h and allowed to warm to 20 °C. After aqueous workup with saturated NH_4Cl solution, the aqueous phase was extracted with diethyl ether. The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc = 2 : 1) to give product **3**.

1-(1-(Cyclopropanecarbonyl)cyclopropyl)-3-cyclopropylpropane-1,3-dione (3a)

Starting with **2a** (1.000 g, 6.57 mmol) dissolved in a solution of LDA (9.86 mmol) in THF (13 ml) and cyclopropanecarbonyl chloride (0.824 g, 7.89 mmol), **3a** was isolated as a yellow oil (0.94 g, 65%). ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 25 : 75): δ (enol) = 0.94–1.15 (m, 10H, CH/CH_2), 1.40–1.48 (m, 4H, CH_2), 5.90 (s, 1H, CH), 15.89 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ (enol) = 10.7, 12.6, 17.7 (CH_2), 18.5, 19.8 (CH), 38.9 (C), 99.7 (CH), 187.2, 196.9, 206.4 (CO). IR (neat., cm^{-1}) 2999 (m), 2970 (w), 1749 (m), 1683 (s), 1623 (s, br), 1443 (s), 1386 (s), 1296 (m), 1265 (m), 1197 (m), 1137 (s), 1106 (m), 1062 (s), 951 (m), 910 (m), 892 (m). MS (EI, 70 eV) m/z = 220 (M^+, 2.5), 205 (2.0), 192 (8.6), 152 (23.9), 137 (5.9), 69 (100). Anal. calcd. for $C_{13}H_{16}O_3$ (220.26): C, 70.89; H, 7.32. Found: C, 70.60; H, 7.71.

1-(1-Benzoylcyclopropyl)-3-cyclopropylpropane-1,3-dione (3b)

Starting with **2b** (1.000 g, 5.31 mmol) dissolved in a solution of LDA (6.38 mmol) in THF (11 ml) and cyclopropanecarbonyl chloride (0.611 g, 5.84 mmol), **3b** was isolated as a yellow oil (0.64 g, 47%). ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 50 : 50): δ (enol) = 0.82–1.02 (m, 4H, CH_2), 1.38 (m, 1H, CH), 1.50–1.58 (m, 4H, CH_2), 5.36 (s, 1H, CH), 7.34–8.00 (m, 5H, Ph), 15.91 (s, 1H, OH); δ (keto) = 0.82–1.02 (m, 4H, CH_2), 1.50–1.66 (m, 4H, CH_2), 1.69 (m, 1H, CH), 2.06 (s, 2H, CH_2), 7.34–8.00 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ (enol) = 10.0, 16.4 (CH_2), 17.2 (CH), 37.0 (C), 98.5 (CH), 128.6, 129.2, 133.3 (Ph), 136.3 (C), 191.0, 192.4, 196.2 (CO). IR (ATR, cm^{-1}) 3085 (w), 3061 (w) 3010 (w), 2970 (w), 2933 (w), 2873 (w), 1673 (s), 1596 (s), 1581 (s), 1449 (m), 1369 (m), 1321 (s), 1295 (s) 1195 (s), 1176 (s), 1133 (m), 1075 (m), 1028 (m), 1002 (s), 945 (m), 928 (s), 895 (m). MS (EI, 70 eV) m/z = 256 (M^+, 7.1), 187 (33.4), 145 (9.8), 105 (100), 77 (51.5), 69 (69.3). HRMS (EI, 70 eV): cacld. for $C_{16}H_{16}O_3$ (M^+) 256.1094, found 256.1096.

1-(1-Benzoylcyclopropyl)-4,4-dimethylpentane-1,3-dione (3c)

Starting with **2b** (2.000 g, 10.63 mmol) dissolved in a solution of LDA (12.76 mmol) in THF (20 ml) and acid chloride (1.44 ml, 11.69 mmol), **3c** was isolated as a yellow oil (0.90 g, 31%). ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 0 : 100): δ (enol) = 0.94 (s, 9H, $C(CH_3)_3$), 1.54–1.72 (m, 4H, CH_2), 5.24 (s, 1H, CH), 7.29–7.57 (m, 3H, Ph), 7.89–7.93 (m, 2H, Ph), 15.50 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ (enol) = 17.2 (CH_2), 27.2 (CH_3), 37.7, 38.6 (C), 96.3 (CH), 128.5, 129.0, 133.2 (Ar), 136.8 (C), 194.1, 196.2, 196.8 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3064 (w), 2968 (m), 2935 (w), 2908 (w), 2872 (w), 1748 (w), 1678 (m), 1596 (s), 1480 (m), 1449 (m), 1395 (w), 1363 (m), 1320 (m), 1294 (m, br), 1202 (m), 1178 (w), 1131 (s), 1075 (w), 1035 (m), 1001 (m), 964 (m), 916 (m), 877 (w), 785 (s). MS (EI, 70 eV) m/z = 272 (M$^+$, 1.8), 215 (65.0), 187 (9.7), 173 (70.4), 105 (100), 77 (34.4). Anal. calcd. for $C_{17}H_{20}O_3$ (272.34): C, 74.97; H, 7.40. Found: C, 75.13; H, 7.45.

1-(1-Benzoylcyclopropyl)-3-phenylpropane-1,3-dione (3d)

Starting with **2b** (1.000 g, 5.31 mmol) dissolved in a solution of LDA (6.38 mmol) in THF (11 ml) and benzoyl chloride (0.7 ml, 5.84 mmol), **3d** was isolated as a yellow oil (0.34 g, 22%). ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 0 : 100): δ = 1.59–1.77 (m, 4H, CH_2), 5.87 (s, 1H, CH), 7.34–8.01 (m, 10H, Ph), 15.85 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.5 (CH_2), 39.3 (C), 96.9 (CH), 127.1, 128.9, 129.1, 129.5, 132.6, 133.8, (Ph), 133.9, 136.9 (C), 178.5, 196.7, 197.2 (CO). IR (ATR, cm^{-1}) 3084 (w), 3062 (w) 3034 (w) 1719 (w, br), 1677 (m), 1596 (m), 1567 (s), 1492 (m), 1456 (m), 1421 (m) 1296 (m), 1249 (m), 1203 (m), 1177 (m), 1133 (m), 1097 (w), 1074 (m), 1026 (m), 998 (s), 930 (m, br), 901 (w), 868 (w), 795 (m). MS (EI, 70 eV) m/z = 392 (M$^+$, 8.3), 187 (32.0), 147 (8.1), 105 (100), 77 (41.9), 69 (16.2). HRMS (EI, 70 eV): cacld for $C_{19}H_{16}O_3$ (M$^+$) 292.1094, found 292.1096.

1-(1-Benzoylcyclopropyl)-3-*p*-tolylpropane-1,3-dione (3e)

Starting with **2b** (2.000 g, 10.63 mmol) dissolved in a solution of LDA (12.76 mmol) in THF (20 ml) and acid chloride (1.63 ml, 11.69 mmol), **3e** was isolated as a colourless solid (1.00 g, 31%); mp 89 °C. ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 0 : 100): δ (enol) = 1.58 (q, ^3J = 3.83 Hz, 2H, CH_2), 1.75 (q, ^3J = 3.83 Hz, 2H, CH_2), 2.42 (s, 3H, CH_3), 5.85 (s, 1H, CH), 7.13 (d, ^3J = 7.91 Hz, 2H, Ar), 7.41–7.53 (m, 5H, Ar/Ph), 7.98–8.01 (m, 2H, Ph), 15.94 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ (enol) = 17.1 (CH_2), 21.6 (CH_3), 38.9 (C), 96.2 (CH), 126.8, 128.7, 129.2, 129.4 (Ar), 130.8 (C), 133.4 (Ar), 136.6, 143.1 (C), 178.6, 196.4, 196.5 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3079 (w), 3060 (w), 3030 (w), 2966 (w), 2920 (w), 1716 (m), 1675 (m), 1596 (s), 1557 (s, br), 1508 (m), 1446 (m), 1342 (m), 1317 (m), 1290 (m), 1266 (s), 1207 (m), 1190 (m), 1178 (m), 1097 (s), 1066 (m), 1031 (m), 1017 (m), 1007 (m), 990 (m), 951 (m), 937 (m), 905 (m), 885 (m), 866 (m), 841 (m), 828 (m), 772 (s). MS (EI, 70 eV) m/z = 306 (M$^+$, 36.2), 187 (76.2), 161 (27.3), 145 (12.9), 119 (100), 105 (82.3), 91 (45.2), 77 (55.3), 69 (46.6). Anal. calcd. for $C_{20}H_{18}O_3$ (306.36): C, 78.41; H, 5.92. Found: C, 78.47; H, 5.95.

1-(1-Benzoylcyclopropyl)-3-(4-methoxyphenyl)propane-1,3-dione (3f)

Starting with **2b** (2.000 g, 10.63 mmol) dissolved in a solution of LDA (12.76 mmol) in THF (20 ml) and acid chloride (1.99 g, 11.69 mmol), **3f** was isolated as a yellow oil (0.72 g, 21%). ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 10 : 90): δ (enol) = 1.56–1.74 (m, 4H, CH_2), 3.77 (s, 3H, CH_3), 5.81 (s, 1H, CH), 6.82 (d, ^3J = 9.03 Hz, 2H, Ar), 7.40–7.49 (m, 3H, Ph), 7.56 (d, ^3J = 9.06 Hz, 2H, Ar), 8.00 (d, ^3J = 6.96 Hz, 2H, Ph), 16.13 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ (enol) = 16.8 (CH_2), 38.5 (C), 55.4 (CH_3), 95.4 (CH), 113.9 (Ar), 125.9 (C), 128.8, 128.9, 129.1, 133.3 (Ar), 136.5, 163.0 (C), 178.7, 195.4, 196.4 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3084 (w), 3061 (w), 3008 (w), 2978 (w), 2940 (w), 2910 (w), 2842 (w), 1675 (m), 1607 (s), 1588 (s), 1556 (s), 1505 (s), 1446 (s), 1435 (s), 1319 (m), 1300 (m), 1248 (s), 1201 (m), 1174 (s), 1133 (m), 1118 (s), 1074 (m), 1036 (m), 1018 (s), 1001 (s), 966 (m), 933 (m), 873 (m), 859 (w), 841 (s), 812 (m), 780 (s). MS (EI, 70 eV) m/z = 322 (M$^+$, 7.1), 187 (8.4), 177 (7.1), 135 (100), 105 (28.6), 77 (28.5), 69 (11.5). Anal. calcd. for $C_{20}H_{18}O_4$ (322.35): C, 74.52; H, 5.63. Found: C, 74.82; H, 5.58.

1-(1-Benzoylcyclopropyl)-3-(4-(chloromethyl)phenyl)propane-1,3-dione (3g)

Starting with **2b** (2.000 g, 10.63 mmol) dissolved in a solution of LDA (12.76 mmol) in THF (20 ml) and acid chloride (2.00 g, 11.63 mmol), **3g** was isolated as a yellow oil (0.65 g, 18%). ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 0 : 100): δ (enol) = 1.50–1.77 (m, 4H, CH_2), 2.06 (s, 2H, CH_2), 5.81 (s, 1H, CH), 7.34–7.59 (m, 7H, Ph/Ar), 7.91–8.00 (m, 2H, Ph/Ar), 15.80 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ (enol) = 17.1, 17.3 (CH_2), 39.0, 41.9 (C), 45.3 (CH_2), 96.8 (CH), 127.7, 128.4, 128.6, 133.5, 133.5 (Ar), 136.5, 136.8, 141.5, 177.2 (C), 196.3, 197.1, 203.9 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3084 (w), 3062 (w), 3010 (w), 2963 (w), 2871 (w), 1672 (s), 1597 (s), 1556 (s), 1508 (m), 1448 (m), 1359 (w), 1321 (s), 1296 (s, br), 1266 (s), 1204 (m), 1177 (m), 1135 (m), 1113 (m), 1074 (m), 1035 (m), 1002 (s), 898 (w), 854 (w), 785 (s). MS (EI, 70 eV) m/z = 340 (M$^+$, 34.5), 305 (23.0), 195 (17.5), 187 (99.7), 153 (100), 145 (18.8), 135 (11.8), 125 (16.0), 119 (15.4), 112 (12.9), 105 (81.8), 91 (15.5), 77 (74.4), 69 (26.4). HRMS (EI, 70 eV): cacld. for $C_{20}H_{17}ClO_3$ (M$^+$) 340.08607, found 340.085130.

1-(1-Benzoylcyclopropyl)-3-(4-tert-butylphenyl)propane-1,3-dione (3h)

Starting with **2b** (2.000 g, 10.63 mmol) dissolved in a solution of LDA (12.76 mmol) in THF (20 ml) and acid chloride (2.30 g, 11.69 mmol), **3h** was isolated as an orange oil (0.93 g, 25%). ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 0 : 100): δ (enol) = 1.29 (s, 9H, $C(CH_3)_3$), 1.59 (q, ^3J = 3.82 Hz, 2H, CH_2), 1.75 (q, ^3J = 3.83 Hz, 2H, CH_2), 5.85 (s, 1H, CH), 7.35–8.02 (m, 9H, Ar/Ph), 15.89 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ (enol) = 17.1 (CH_2), 31.1 (CH_3), 35.0, 38.9 (C), 96.4 (CH), 125.6, 126.7, 128.7, 129.2 (Ar), 130.8 (C), 133.4 (Ar), 136.6, 156.1 (C), 178.4, 180.0, 196.5 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3062 (w), 2963 (m), 2906 (w), 2869 (w), 1719 (w), 1676 (m), 1597 (s), 1557 (m), 1508 (m), 1448 (m), 1363 (m), 1320 (m), 1297 (m, br), 1268 (s), 1201 (m), 1178 (m), 1140 (w), 1112 (m), 1097 (m), 1071 (m), 1032 (m), 1015 (m), 1001 (m), 934 (m), 904 (m), 848 (m), 783 (s). MS (EI, 70 eV) m/z = 348 (M$^+$, 10.8), 187 (23.5), 161 (100), 145 (9.7), 105 (34.9), 77 (21.3), 69 (9.7). HRMS (EI, 70 eV): calcd. for $C_{23}H_{24}O_3$ (M$^+$) 348.17200, found 348.172840.

1-(1-Benzoylcyclopropyl)-3-(3-chlorophenyl)propane-1,3-dione (3i)

Starting with **2b** (2.000 g, 10.63 mmol) dissolved in a solution of LDA (12.76 mmol) in THF (20 ml) and acid chloride (1.50 ml, 11.69 mmol), **3i** was isolated as an orange oil (2.20 g, 63%); mp 89 °C. ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 0 : 100): δ (enol) = 1.60–1.79 (m, 4H, CH_2), 5.83 (s, 1H, CH), 7.24–7.57 (m, 6H, Ar/Ph), 7.97–8.00 (m, 2H, Ph), 15.74 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ (enol) = 17.5 (CH_2), 39.1 (C), 96.9 (CH), 124.8, 126.9, 128.8, 129.2, 129.9, 132.1, 133.6 (Ar/Ph), 134.8, 135.5, 136.5 (C), 176.5, 196.2, 197.3 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3068 (w), 3011 (w), 1724 (w), 1676 (m), 1598 (m), 1561 (s, br), 1448 (m), 1320 (m), 1292 (m), 1244 (m), 1202 (m), 1177 (m), 1132 (m), 1096 (m), 1075 (m), 1034 (m), 1000 (m), 933 (m), 907 (m), 843 (w), 804 (w), 776 (s). MS (EI, 70 eV) m/z = 326 (M$^+$, 5.8), 187 (49.5), 139 (78.7), 105 (100), 77 (55.6), 69 (24.3). HRMS (EI, 70 eV): calcd. for $C_{19}H_{15}ClO_3$ (M$^+$) 326.07042, found 326.06966.

Procedure for the synthesis of cyclopropylketides 4

To a suspension of K_2CO_3 (4.0 equiv.) in DMSO (0.3–0.5 mL mmol^{-1}) was added **3** (1.0 equiv.). To the reaction mixture dibromoethane (2.0 equiv.) was added dropwise at 20 °C with vigorous stirring. After stirring at 20 °C for 8 h, K_2CO_3 was removed by filtration. The solid was thoroughly washed with diethyl ether. The filtrate was washed with water until the yellow colour disappeared, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc = 2 : 1) to give product **4**.

1,1′-Carbonylbis(cyclopropane-1,1-diyl)bis(cyclopropylmethanone) (4a)

Starting with **3a** (0.500 g, 2.27 mmol) dissolved in a suspension of K_2CO_3 (0.784 g, 5.68 mmol) in DMSO (0.7 ml) and dibromoethane (0.2 ml, 2.27 mmol), **4a** was isolated as a colorless oil (0.17 g, 30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86–1.04 (m, 4H, CH_2), 1.63 (m, 4H, CH_2), 1.83–1.89 (m, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.3 (CH_2), 17.9 (CH), 19.6 (CH_2), 43.5 (C), 202.4, 205.8 (CO). IR (neat., cm^{-1}) 3096 (m), 3011 (s) 1681 (s, br), 1570 (m), 1444 (s), 1392 (s, br) 1319 (s), 1280 (s), 1198 (m), 1107 (s), 1085 (s), 1061 (s), 1006 (s), 953 (m), 936 (w), 922 (w), 893 (m), 841 (w). MS (EI, 70 eV) m/z = 246 (M$^+$, 0.3), 218 (82.9), 203 (17.7), 177 (19.4), 121 (15.0), 69 (100). Anal. calcd. for $C_{15}H_{18}O_3$ (246.30): C, 73.15; H, 7.37. Found: C, 73.30; H, 7.36.

(1-(1-Benzoylcyclopropanecarbonyl)cyclopropyl)(cyclopropyl)-methanone (4b)

Starting with **3b** (0.200 g, 0.78 mmol) dissolved in a suspension of K_2CO_3 (0.43 g, 3.12 mmol) in DMSO (0.5 ml) and dibromoethane (0.13 ml, 1.56 mmol), **4b** was isolated as a colorless oil (0.14 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80–0.97, (m, 4H, CH_2), 1.19–1.41 (m, 4H, CH_2), 1.62 (m, 1H, CH), 1.70–1.75 (m, 4H, CH_2), 7.27–7.72 (m, 5H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9 (CH_2), 18.3 (CH), 19.8, 20.7 (CH_2), 42.5, 44.1 (C), 128.6, 129.1, 133.1 (Ph), 138.5 (C), 197.1, 202.4, 205.2 (CO). IR (ATR, cm^{-1}) 3087 (w), 3063 (w), 3011 (w), 1731 (w), 1666 (s, br), 1598 (w), 1580, (w), 1449 (m), 1387 (m, br) 1320 (s), 1202 (m), 1165 (m), 1108 (w), 1078 (s), 1049 (s), 1008 (m), 993 (s), 906 (m, br). MS (EI, 70 eV) m/z = 282 (M$^+$, 4.3), 254 (22.4), 293 (10.7), 213 (11.4), 207 (11.4), 191 (18.5), 163 (14.4), 105 (100), 77 (60.7), 69 (45.0). HRMS (EI, 70 eV): cacld. for $C_{18}H_{18}O_3$ (M$^+$) 281.1172, found 281.1174.

1-(1-(1-Benzoylcyclopropanecarbonyl)cyclopropyl)-2,2-dimethylpropan-1-one (4c)

Starting with **3c** (0.24 g, 0.88 mmol) dissolved in a suspension of K_2CO_3 (0.49 g, 3.52 mmol) in DMSO (0.5 ml) and 1,2-dibromoethane (0.15 ml, 1.76 mmol) added dropwise, **4c** was isolated as an orange oil (0.11 g, 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.95 (m, 2H, CH_2), 1.14 (s, 9H, $C(CH_3)_3$), 1.25 (m, 2H, CH_2), 1.54 (q, ^3J = 3.79 Hz, 2H, CH_2), 1.71 (q, ^3J = 3.80 Hz, 2H, CH_2), 7.30–7.89 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.0, 18.1 (CH_2), 28.4 (CH_3), 41.1, 43.6, 45.5 (C), 128.5, 129.4, 133.4 (Ph), 137.3 (C), 195.6, 200.8, 211.0 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3063 (w), 2970 (w), 2935 (w), 2908 (w), 2872 (w), 1730 (w), 1666 (s), 1598 (m), 1480 (m), 1449 (m), 1395 (w), 1365 (w), 1320 (m), 1296 (m), 1202 (m), 1177 (m), 1146 (m, br), 1073 (s), 1049 (m), 1014 (m), 993 (s), 938 (m), 882 (m), 785 (m). MS (EI, 70 eV) m/z = 297 (M$^+$, 1.0), 241 (100), 213 (12.6), 173 (21.7), 105 (79.6), 77 (34.2). HRMS (ESI): cacld. for $C_{19}H_{23}O_3$ ([M+1]$^+$) 299.16417, found 299.16443.

1,1′-Carbonylbis(cyclopropane-1,1-diyl)bis(phenylmethanone) (4d)

Starting with **3d** (0.280 g, 0.96 mmol) dissolved in a suspension of K_2CO_3 (0.530 g, 3.83 mmol) in DMSO (0.5 ml) and dibromoethane (0.17 ml, 1.92 mmol), **4d** was isolated as a colorless solid (0.17 g, 30%). MP: 144–145 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18–1.41 (m, 4H, CH_2), 7.41–7.77 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1 (CH_2), 43.0 (C), 128.8, 129.4, 133.6 (Ph), 138.0 (C), 196.2, 202.2 (CO). IR (ATR, cm^{-1}) 3094 (w), 3054 (w) 3017 (w) 1723 (w, br), 1666 (m), 1647 (s), 1597 (m), 1579 (m), 1451 (m), 1416 (w) 1320 (s), 1295 (s), 1203 (m), 1173 (m), 1067 (s), 1037 (m), 1027 (m), 1001 (m), 985 (m), 929 (w), 866 (m), 841 (w), 805 (w). MS (EI, 70 eV) m/z = 318 (M$^+$, 5.3), 290 (12.4), 227 (5.6), 213 (10.2), 199 (13.4), 105 (100), 77 (62.3). Anal. calcd. for $C_{21}H_{18}O_3$ (318.37): C, 79.22; H, 5.70. Found: C, 79.04; H, 5.59.

(1-(1-Benzoylcyclopropanecarbonyl)cyclopropyl)(*p*-tolyl)-methanone (4e)

Starting with **3e** (0.27 g, 0.88 mmol) dissolved in a suspension of K_2CO_3 (0.49 g, 3.52 mmol) in DMSO (0.5 ml) and 1,2-Dibromoethane (0.15 ml, 1.76 mmol) added dropwise, **4e** was isolated as a colourless solid (0.10 g, 34%); mp 96 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15–1.23 (m, 4H, CH_2), 1.35–1.44 (m, 4H, CH_2), 2.42 (s, 3H, CH_3), 7.23 (d, ^3J = 8.06 Hz, 2H, Ar), 7.41–7.46 (m, 2H, Ph), 7.54–7.58 (m, 1H, Ph), 7.66 (d, ^3J = 8.16 Hz, 2H, Ar), 7.74–7.77 (m, 2H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.7, 18.8 (CH_2), 21.8 (CH_3), 42.5, 42.6 (C), 128.4, 129.1, 129.2, 129.2, 133.23 (Ar/Ph), 135.1, 137.8, 144.1 (C), 195.2, 195.9, 202.1 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3090 (w), 3053 (w), 3011 (w), 2923 (w), 2862 (w), 1722 (w), 1664 (s), 1650 (s), 1604 (s), 1578 (m), 1509 (w), 1450 (m), 1418 (w), 1317 (s), 1296 (s), 1202 (m), 1172 (s), 1119 (w), 1099 (m), 1069 (s), 1046 (m), 1001 (m), 988 (s), 914 (w), 864 (m), 840 (m), 819 (m), 782 (s). MS (EI, 70 eV) m/z = 332 (M$^+$, 22.5), 304 (61.9), 276 (9.0), 227 (36.4), 213 (34.8), 199 (19.5), 171 (11.3), 157

(10.2), 119 (100), 105 (96.4), 91 (71.2), 77 (52.6). HRMS (ESI): cacld. for $C_{22}H_{21}O_3$ ($[M+1]^+$) 333.14852, found 333.14868.

(1-(1-Benzoylcyclopropanecarbonyl)cyclopropyl)(4-methoxyphenyl)methanone (4f)

Starting with **3f** (0.31 g, 0.96 mmol) dissolved in a suspension of K_2CO_3 (0.53 g, 3.83 mmol) in DMSO (0.5 ml) and 1,2-dibromoethane (0.17 ml, 1.92 mmol) added dropwise, **4f** was isolated as a colourless solid (0.11 g, 33%); mp 105 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.15$ (q, $^3J = 3.86$ Hz, 2H, CH_2), 1.24 (q, $^3J = 3.86$ Hz, 2H, CH_2), 1.35 (q, $^3J = 3.86$ Hz, 2H, CH_2), 1.44 (q, $^3J = 3.86$ Hz, 2H, CH_2), 3.88 (s, 3H, CH_3), 6.91 (m, 2H, Ar), 7.41–7.60 (m, 4H, Ar/Ph), 7.73–7.77 (m, 3H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.5$, 18.7 (CH_2), 42.3, 42.6 (C), 55.5 (CH_3), 113.6 (Ar), 128.4, 129.1 (Ar/Ph), 130.5 (C), 131.3, 133.2 (Ar), 137.7, 163.6 (C), 193.9, 195.8, 202.2 (CO). IR (ATR, cm^{-1}): $\tilde{\nu} = 3088$ (w), 3054 (w), 3013 (w), 2966 (w), 2938 (w), 2912 (w), 1663 (m), 1648 (s), 1596 (s), 1573 (s), 1510 (m), 1450 (m), 1300 (s), 1253 (s), 1204 (s), 1168 (s), 1116 (m), 1069 (s), 1029 (s), 1000 (m), 985 (s), 864 (w), 844 (s), 807 (m), 781 (s). MS (EI, 70 eV) $m/z = 348$ (M^+, 30.6), 320 (64.8), 243 (20.2), 229 (18.1), 187 (23.4), 159 (12.3), 135 (100), 105 (79.9), 92 (25.3), 77 (77.6). Anal. calcd. for $C_{22}H_{20}O_4$ (348.39): C, 75.84; H, 5.79. Found: C, 75.81; H, 5.87.

(1-(1-Benzoylcyclopropanecarbonyl)cyclopropyl)(4-*tert*-butylphenyl)methanone (4h)

Starting with **3h** (0.31 g, 0.88 mmol) dissolved in a suspension of K_2CO_3 (0.49 g, 3.52 mmol) in DMSO (0.5 ml) and 1,2-Dibromoethane (0.15 ml, 1.76 mmol) added dropwise, **4h** was isolated as a pale yellow oil (0.10 g, 30%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.16$–1.21 (m, 4H, CH_2) 1.35 (s, 9H, $C(CH_3)_3$), 1.37–1.41 (m, 4H, CH_2), 7.34–7.41 (m, 2H, Ph), 7.45 (d, $^3J = 8.58$ Hz, 2H, Ar), 7.52–7.59 (m, 1H, Ph), 7.70 (d, $^3J = 8.58$ Hz, 2H, Ar), 7.74–7.77 (m, 1H, Ph), 7.99–8.01 (m, 1H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.5$, 18.6 (CH_2), 31.1 (CH_3), 35.2, 42.6, 42.7 (C), 125.4, 126.7, 128.4, 129.1, 133.2 (Ar/Ph), 135.1, 137.8, 157.1 (C), 195.4, 195.9, 202.1 (CO). IR (ATR, cm^{-1}): $\tilde{\nu} = 3061$ (w), 2963 (w), 2906 (w), 2869 (w), 1722 (w), 1665 (s), 1604 (m), 1507 (w), 1448 (m), 1409 (w), 1364 (w), 1319 (s), 1268 (s), 1202 (m), 1185 (m), 1111 (m), 1066 (s), 1039 (w), 989 (s), 878 (w), 847 (m), 836 (m), 785 (s). MS (EI, 70 eV) $m/z = 374$ (M^+, 14.7), 373 (27.3), 346 (31.8), 331 (27.0), 317 (17.0), 269 (11.9), 255 (17.8), 227 (15.3), 213 (19.1), 199 (16.2), 162 (12.7), 161 (100), 146 (16.6), 118 (23.4), 115 (17.9), 105 (99.5), 91 (16.8), 77 (57.0). Anal. calcd. for $C_{25}H_{26}O_3$ (374.47): C, 80.18; H, 7.00. Found: C, 80.23; H, 7.06.

Synthesis of methyl 1-(3-cyclopropyl-3-oxopropanoyl)cyclopropanecarboxylate (7a)

To a suspension of sodium methoxide (4.0 equiv.) in MTBE (1.0 mL mmol^{-1}) was added **6** (2.0 equiv.) at 30 °C. To the reaction mixture **5** (1.0 equiv.) was added dropwise at 30 °C with vigorous stirring. After stirring at 30 °C for 3 h and aqueous workup with 10% HCl solution with ice cooling, the organic layer was separated and washed with water. The aqueous phase was extracted with MTBE. The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc = 2 : 1) to give product **7**. Starting with **5** (3.95 g, 25.00 mmol) dissolved in a suspension of sodium methoxide (5.40 g, 100.00 mmol) in MTBE (25.0 ml) and **6** (4.20 g, 50.00 mmol), **7** was isolated as a orange oil (2.09 g, 40%). ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 45 : 55): δ (enol) = 0.98–1.18 (m, 4H, CH_2), 1.57 (m, 4H, CH_2), 1.68 (m, 1H, CH), 3.77 (s, 3H, CH_3), 6.27 (s, 1H, CH), 16.01 (s, 1H, OH); δ (keto) = 0.98–1.18 (m, 4H, CH_2), 1.63 (m, 4H, CH_2), 2.04 (m, 1H, CH), 3.74 (s, 3H, CH_3), 4.21 (s, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ (enol) = 10.4 (CH_2), 18.2 (CH), 18.7 (CH_2), 30.3 (C), 52.6 (CH_3), 99.4 (CH), 171.6, 187.1, 195.2 (CO); δ (keto) = 11.7 (CH_2), 21.4 (CH), 21.6 (CH_2), 35.1 (C), 52.5 (CH_3), 57.3 (CH_2), 171.6, 200.1, 205.0 (CO). IR (neat., cm^{-1}) 3011 (m), 2950 (m) 2848 (m) 1732 (s), 1653 (m), 1594 (m, br), 1559 (m), 1442 (m), 1382 (m), 1319 (m, br) 1201 (m), 1155 (m), 1119 (m), 1072 (m), 1027 (w), 967 (m), 944 (m), 915 (w), 900 (w). MS (EI, 70 eV) $m/z = 210$ (M^+, 5.4), 182 (19.8), 178 (11.5), 137 (9.5), 127 (15.1), 111 (10.5), 69 (100). Anal. calcd. for $C_{11}H_{14}O_4$ (210.23): C, 62.85; H, 6.71. Found: C, 63.23; H, 6.78.

General procedure for the synthesis of cyclopropylketides 7b–h

To a suspension of sodium methoxide (2.0 equiv.) in MTBE (0.75 mL mmol^{-1} ketone) was added **6** (1.0 equiv.) at 50 °C. After stirring for 10 min **5** (1.0 equiv.) was added dropwise over a period of 30 to 60 min at 45–50 °C with vigorous stirring. Then stirring was continued for 5 h at the same temperature and then for a further for 12 h at 22 °C. After neutralization with 10% HCl solution with ice cooling and addition of saturated NaCl solution, the organic layer was separated and washed with water. The aqueous phase was extracted with diethyl ether. The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (heptane/EtOAc = 100/1 → 20/1) to give product **7**.

Methyl 1-(3-oxobutanoyl)cyclopropanecarboxylate (7b)

Starting with **5** (6.90 mL, 50.00 mmol) dissolved in a suspension of sodium methoxide (5.402 g, 100 mmol) in MTBE (37.0 ml) and **6b** (2.904 g, 50 mmol), **7b** was isolated as a light-yellow oil (5.400 g, 58%). ^{1}H NMR (300 MHz, $CDCl_3$,keto/enol = 1: 2): δ (enol) = 1.52 (s, 4H, CH_2CH_2), 2.04 (s, 3H, CH_3), 3.70 (s, 3H, OCH_3), 6.10 (s, 1H, CH), 15.42 (s, 1H, OH); δ (keto) = 1.59 (s, 4H, CH_2CH_2), 2.23 (s, 3H, CH_3), 3.67 (s, 3H, OCH_3), 4.02 (s, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ (enol) = 18.8 (CH_2CH_2), 23.5 (CH_3), 31.2 (C_q), 52.2 (OCH_3), 99.8 (CH), 171.1 ($COOCH_3$), 186.2 (COH), 192.5 (CO); δ (keto) = 21.4 (CH_2CH_2), 30.4 (CH_3), 34.4 (C_q), 57.2 (CH_2), 171.1 ($COOCH_3$), 199.6 (CO), 202.4 (CO). IR (ATR, cm^{-1}): $\tilde{\nu} = 3116$ (w), 3011 (w), 2956 (m), 2848 (w), 1723 (s), 1692 (w), 1605 (s). MS (EI, 70 eV): $m/z = 184$ (M^+, 30), 156 (57), 127 (88), 85 (71), 43 (100). Anal. calcd. for $C_9H_{12}O_4$ (184.189): C, 58.69; H, 6.57; Found: C, 58.316; H, 6.338.

Methyl 1-(3-methoxy-3-oxopropanoyl)cyclopropanecarboxylate (7c)

Starting with **5** (6.90 mL, 50.00 mmol) dissolved in a suspension of sodium methoxide (5.402 g, 100 mmol) in MTBE (37.0 ml) and **6c** (2.904 g, 50 mmol), **7c** was isolated as a colourless liquid (5.400 g, 58%). ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 1: 0) δ (keto) = 1.61 (s, 4H, CH_2CH_2), 3.71, 3.72 (s, 3H, OCH_3), 3.94 (s, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ (keto) = 21.4 (CH_2), 34.3 (C_q), 48.7 (C[O]*C*H_2), 52.2, 52.2 (OCH_3), 168.1, 171.0 (*C*$OOCH_3$), 198.1 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3111 (w), 3006 (w), 2956 (m), 2848 (w), 1725 (s), 1694 (s). MS (EI, 70 eV): m/z = 200 (M^+, 2), 172 (24), 127 (100), 101 (24), 59 (43). HRMS (ESI, 70 eV) calcd. for $C_{16}H_{23}O_4$ (223.05769 $[M+Na]^+$): 223.05771.

Methyl 1-(3-phenyl-3-oxopropanoyl)cyclopropanecarboxylate (7d)

Starting with **5** (2.76 mL, 20.00 mmol) dissolved in a suspension of sodium methoxide (2.160 g, 40 mmol) in MTBE (15.0 ml) and **6d** (2.33 mL, 20 mmol), **7d** was isolated as a yellow liquid (2.488 g, 51%). ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 1: 5) δ (enol) = 1.59–1.69 (m, 4H, CH_2CH_2), 3.76 (s, 3H, OCH_3), 6.90 (s, 1H, C[O]CH), 7.42–7.59 (m, 3H, PhH), 7.88–7.96 (m, 2H, PhH), 16.04 (s, 1H, OH); δ (keto) = 1.59–1.69 (m, 4H, CH_2CH_2), 3.62 (s, 4H, OCH_3), 4.62 (s, 2H, C[O]CH_2), 7.42–7.59 (m, 3H, PhH), 7.88–7.96 (m, 2H, PhH).^{13}C NMR (75 MHz, $CDCl_3$) δ (enol) = 19.4 (CH_2CH_2), 31.8 (C_q), 52.3 (OCH_3), 96.6 (C[O]*C*H), 126.919 (Ph, Ph), 128.6 (Ph, Ph), 132.1 (Ph), 134.2 ($C_{q,Ar}$), 171.3 (*C*$OOCH_3$), 179.4 (COH), 194.1 (CO); δ (keto) = 21.7 (CH_2CH_2), 34.6 (C_q), 52.2 (OCH_3), 52.8 (C[O]CH_2), 128.3 (Ph, Ph), 128.7 (Ph, Ph), 133.5 (Ph), 136.4 (C_q), 171.3 (*C*$OOCH_3$), 194.7 (CO), 200.2 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3151 (w), 3062 (w), 3021 (w), 2953 (m), 2845 (w), 1724 (s), 1683 (w), 1598 (s), 1565 (s). MS (EI, 70 eV): m/z = 246 (M^+, 29), 147 (42), 105 (100), 77 (45), 69 (33). Anal. calcd. for $C_{14}H_{14}O_4$ (246.259): C, 68.28; H, 5.73; Found: C, 68.294; H, 5.678.

Methyl 1-(3-(1-napththyl)-3-oxopropanoyl)cyclopropanecarboxylate (7e)

Starting with **5** (2.76 mL, 20.00 mmol) dissolved in a suspension of sodium methoxide (2.160 g, 40 mmol) in MTBE (30.0 ml) and **6e** (2.33 mL, 20 mmol), **7e** was isolated as a yellow solid (1.667 g, 32%). mp 67–69 °C; ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 1: 5) δ (enol) = 1.62–1.73 (m, 4H, CH_2CH_2), 3.35 (s, 3H, OCH_3), 6.68 (s, 1H, C[O]CH), 7.48–7.60 (m, 3H, ArH), 7.75–7.97 (m, 3H, ArH), 8.46–8.49 (m, 1H, ArH), 16.07 (s, 1H, OH); δ (keto) = 1.62–1.73 (m, 4H, CH_2CH_2), 3.75 (s, 3H, OCH_3), 4.74 (s, 2H, C[O]CH_2), 7.48–7.60 (m, 3H, ArH), 7.75–7.97 (m, 3H, ArH), 8.46–8.49 (m, 1H, ArH).^{13}C NMR (75 MHz, $CDCl_3$) δ (enol) = 19.4 (CH_2CH_2), 31.8 (C_q), 52.4 (OCH_3), 101.8 (C[O]*C*H), 124.8 (Ph), 125.5 (Ph), 126.3 (Ph), 127.1 (Ph), 127.2 (Ph), 128.6 (Ph), 130.2 (C_q), 131.6 (Ph), 133.4 (C_q), 133.8 (C_q), 171.1 (*C*$OOCH_3$), 183.1 (COH), 193.6 (CO); δ (keto) = 21.8 (CH_2CH_2), 34.6 (C_q), 52.2 (OCH_3), 55.9 (C[O]CH_2), 124.3 (Ph), 125.8 (Ph), 126.5 (Ph), 128.2 (Ph), 128.4 (Ph), 128.5 (Ph), 128.6 (Ph), 130.2 (C_q), 134.0 (C_q), 134.6 (C_q), 171.4 ($COOCH_3$), 197.8 (CO), 200.2 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3048 (w), 3012 (w), 2951 (w), 2844 (w), 1723 (s), 1675 (w), 1598 (w), 1567 (s), 1508 (m). MS (EI, 70 eV): m/z = 296 (M^+, 21), 197 (20), 168 (22), 155 (100), 127 (64). Anal. calcd. for $C_{18}H_{16}O_4$ (296.317): C, 72.96; H, 5.44; Found: C, 73.005; H, 5.435.

Methyl 1-(3-cyclohexyl-3-oxopropanoyl)cyclopropanecarboxylate (7f)

Starting with **5** (1.40 mL, 10.00 mmol) dissolved in a suspension of sodium methoxide (1.800 g, 20 mmol) in MTBE (7.5 ml) and **6f** (1.262 g, 10 mmol), **7f** was isolated as a colourless liquid (1.008 g, 40%). ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 1: 3) δ (enol) = 1.23–1.89 (m, 14H, CH_2), 2.14–2.21 (m, 1H, $CHCH_2$), 3.71 (s, 3H, OCH_3), 6.13 (s, 1H, C[O]CH), 15.56 (s, 1H, OH); δ (keto) = 1.23–1.89 (m, 14H, CH_2), 2.45–2.71 (m, 1H, $CHCH_2$), 3.67 (s, 3H, OCH_3), 4.01 (s, 2H, C[O]CH_2).^{13}C NMR (75 MHz, $CDCl_3$) δ (enol) = 18.9, 25.7, 29.7 (CH_2), 31.3 (C_q), 45.4 (CH), 52.2 (OCH_3), 97.4 (CH), 171.3 (*C*$OOCH_3$), 192.8, 193.1 (CO); δ (keto) = 21.5, 25.5, 28.2 (CH_2), 34.5 (C_q), 51.0 (CH), 52.1 (OCH_3), 54.5 (CH_2), 171.4 (*C*$OOCH_3$), 200.4, 208.0 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3013 (w), 2929 (s), 2854 (m), 2668 (w), 1717 (s), 1693 (w), 1592 (s). MS (EI, 70 eV): m/z = 252 (M^+, 6), 169 (93), 127 (100), 83 (36), 69 (24). Anal. calcd. for $C_{14}H_{20}O_4$ (252.306): C, 66.65; H, 7.99; Found: C, 66.761; H, 8.061.

Methyl 1-(3-(4-methoxyphenyl)-3-oxopropanoyl)cyclopropanecarboxylate (7g)

Starting with **5** (3.50 mL, 25.00 mmol) dissolved in a suspension of sodium methoxide (2.701 g, 50 mmol) in MTBE (19 ml) and **6g** (3.754 g, 25 mmol), **7g** was isolated as a light-yellow oil (3.307 g, 48%). ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 1: 5) δ (enol) = 1.59–1.66 (m, 4H, CH_2CH_2), 3.75 (s, 3H, $ArOCH_3$), 3.87 (s, 3H, $COOCH_3$), 6.81 (s, 1H, C[O]CH), 6.93–6.96 (m, 2H, PhH), 7.86–7.94 (m, 2H, PhH), 16.27 (s, 1H, OH); δ (keto) = 1.59–1.66 (m, 4H, CH_2CH_2), 3.63 (s, 3H, $ArOCH_3$), 3.87 (s, 3H, $COOCH_3$), 4.57 (s, 2H, C[O]CH_2), 6.93–6.96 (m, 2H, PhH), 7.86–7.94 (m, 2H, PhH).^{13}C NMR (75 MHz, $CDCl_3$) δ (enol) = 19.0 (CH_2CH_2), 31.4 (C_q), 52.2, 55.3 (OCH_3), 95.5 (C[O]*CH*), 113.9 (PhH), 126.7 ($C_{Ar,q}$), 129.0 (PhH), 163.0 (C_q-OCH_3), 171.4 (*C*$OOCH_3$), 180.4, 192.2 (CO); δ (keto) = 21.4 (CH_2CH_2), 34.6 (C_q), 52.1 (OCH_3), 52.5 (C[O]CH_2), 55.4 (OCH_3), 113.8 (PhH), 129.4 ($C_{Ar,q}$), 130.6 (PhH), 163.8 (C_q-OCH_3), 171.3 (*C*$OOCH_3$), 193.1, 200.3 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3005 (w), 2953 (m), 2840 (m), 1723 (s), 1672 (m), 1599 (s), 1563 (m), 1507 (s). MS (EI, 70 eV): m/z = 276 (M^+, 15), 248 (11), 177 (12), 135 (100), 77 (11). Anal. calcd. for $C_{15}H_{16}O_5$ (276.285): C, 65.21; H, 5.84. Found: C, 65.530; H, 6.009.

Methyl 1-(3-(η^5-ferrocenyl)-3-oxopropanoyl)cyclopropanecarboxylate (7h)

Starting with **5** (1.582 g, 10.00 mmol) dissolved in a suspension of sodium methoxide (1.084 g, 20 mmol) in MTBE (7.5 mL) and **6h** (2.281 g, 10.00 mmol), **7h** was isolated as a dark-red oil (1.824 g, 52%). ^{1}H NMR (300 MHz, $CDCl_3$, keto/enol = 3: 5) δ (enol) = 1.58–1.64 (m, 4H, CH_2CH_2), 3.75 (s, 3H, OCH_3), 4.19 (s, 5H, CH), 4.49–4.50 (m, 2H, CH), 4.79–4.80 (m, 2H, CH), 6.39 (s, 1H, C[O]CH), 16.06 (s, 1H, OH); δ (keto) = 1.58–1.64 (m, 4H, CH_2), 3.68 (s, 3H, OCH_3), 4.24 (s, 5H, CH), 4.40 (s, 2H, C[O]CH_2), 4.52–4.53 (m, 2H, CH), 4.76–4.78 (m, 2H, CH).^{13}C NMR (75 MHz, $CDCl_3$) δ = 18.6 (CH_2), 30.5 (C_q), 52.2 (OCH_3), 68.5, 70.0, 70.3 (CH), 78.6 (C_q), 96.8 (C[O]*C*H), 171.4 (*C*$OOCH_3$), 187.6, 200.1 (CO); δ (keto) = 21.0 (CH_2), 34.9 (C_q), 52.1 (OCH_3), 53.4 (C[O]CH_2), 69.5, 71.9, 72.6 (CH), 77.2 (C_q), 170.1 (*C*$OOCH_3$), 188.8, 198.1 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3100 (w), 3014 (w), 2953 (w), 1725 (s), 1661 (m), 1651 (m), 1520 (s), 1504 (s). MS (EI, 70 eV): m/z = 253 ($[M-H]^+$, 3), 228 (100), 185 (56), 129 (28), 56 (17). HRMS (ESI, 70 eV) calcd. for $C_{18}H_{19}FeO_4$ ($[M+H]^+$, 355.0627): 355.0627.

Synthesis of methyl 1-(1-(cyclopropanecarbonyl)cyclopropane-carbonyl)-cyclopropanecarboxylate (8a)

To a suspension of K_2CO_3 (4.0 equiv.) in DMSO (0.3–0.5 mL mmol^{-1}) was added **7** (1.0 equiv.). To the reaction mixture dibromoethane (2.0 equiv.) was added dropwise at 20 °C with vigorous stirring. After stirring at 20 °C for 8 h, K_2CO_3 was removed by filtration. The solid was thoroughly washed diethyl ether. The filtrate was washed with water until the yellow colour disappears, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc = 2 : 1) to give product **8**. Starting with **7** (1.500 g, 7.14 mmol) dissolved in a suspension of K_2CO_3 (2.47 g, 17.84 mmol) in DMSO (2.1 ml) and dibromoethane (0.6 ml, 7.14 mmol), **8** was isolated as a colorless oil (0.30 g, 18%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81–0.98 (m, 4H, CH_2), 1.52–1.55 (m, 8H, CH_2), 1.75–1.80 (m, 1H, CH), 3.59 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.0 (CH_2), 17.7 (CH), 19.1, 21.3 (CH_2), 35.2, 43.5 (C), 52.4 (CH_3), 171.6, 201.2, 206.1 (CO). IR (neat., cm^{-1}) 3011 (m), 2954 (m) 1733 (s), 1674 (s), 1570 (w), 1540 (w), 1506 (w), 1437 (m), 1400 (m, br) 1324 (s), 1199 (m), 1164 (m), 1079 (s), 1048 (m), 1009 (m), 954 (w), 911 (w), 889 (w), 835 (w), 751 (w), 735 (w). MS (EI, 70 eV) m/z = 236 (M$^+$, 7.9), 208 (100), 193 (15.7), 179 (27.9), 177 (32.2), 167 (34.7), 149 (21.8), 137 (22.1), 109 (14.3), 95 (25.3), 69 (98.8). Anal. calcd. for $C_{13}H_{16}O_4$ (236.26): C, 66.09; H, 6.83. Found: C, 66.14; H, 6.78.

General procedure for the synthesis of cyclopropylketides 8b–h

To a suspension of K_2CO_3 (4.0 equiv.) in DMSO (1.2 mL mmol^{-1} tricarbonyl) was added **7** (1.0 equiv.). To the reaction mixture dibromoethane (2.0 equiv.) was dropwise added at 0 °C with vigorous stirring. After 30 min the mixture was warmed to 22 °C and then stirring was continued for 12 h. Subsequently K_2CO_3 was removed by filtration and the solid was thoroughly washed with diethyl ether. The filtrate was washed two times with saturated NaCl-solution, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (heptane/EtOAc = 30 : 1 → 5 : 1) to give products **8**.

Methyl 1-(1-acetylcyclopropanecarbonyl)-cyclopropanecarboxylate (8b)

Starting with **7b** (0.921 g, 5.00 mmol) dissolved in a suspension of K_2CO_3 (2.764 g, 20.00 mmol) in DMSO (6.0 ml) and dibromoethane (0.9 ml, 10.00 mmol), **8b** was isolated as a light-yellow oil (0.388 g, 37%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.46–1.50 (m, 4H, CH_2), 1.55–1.60 (m, 4H, CH_2), 2.08 (s, 3H, CH_3), 3.65 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 18.0, 20.6 (CH_2), 26.0 (CH_3), 34.2, 42.9 (C_q), 52.0 (OCH_3), 171.4 ($COOCH_3$), 200.8, 203.9 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3099 (w), 3013 (w), 2954 (m), 2848 (w), 1724 (s), 1681 (s), 1582 (s). MS (EI, 70 eV): m/z = 210 (M$^+$, 6), 182 (100), 127 (32), 69 (36), 43 (60). HRMS (ESI, 70 eV) calcd. for $C_{11}H_{15}O_4$ (211.0965 [M+H]$^+$): 211.0966.

Dimethyl 1,1′-carbonyldicyclopropanecarboxylate (8c)

Starting with **7c** (0.800 g, 4.00 mmol) dissolved in a suspension of K_2CO_3 (2.211 g, 16.00 mmol) in DMSO (3.0 ml) and dibromoethane (0.8 ml, 6.00 mmol), **8c** was isolated as a colourless liquid (0.597 g, 67%).^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.56 (s, 8H, CH_2), 3.67 (s, 6H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 20.2 (CH_2), 34.8 (C_q), 52.0 (OCH_3), 171.6 ($COOCH_3$), 199.4 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3111 (w), 3012 (w), 2958 (m), 2847 (w), 1723 (s), 1677 (s). MS (EI, 70 eV): m/z = 226 (M$^+$, 7), 198 (90), 127 (100), 95 (32), 59 (41). HRMS (ESI, 70 eV) calcd. for $C_{11}H_{14}O_5$ (226.08358): 226.083021.

Methyl 1-(1-benzoylcyclopropanecarbonyl)cyclopropanecarboxylate (8d)

Starting with **7d** (1.500 g, 6.00 mmol) dissolved in a suspension of K_2CO_3 (3.320 g, 24.00 mmol) in DMSO (5.0 ml) and dibromoethane (1.60 ml, 12.00 mmol), **8d** was isolated as a colourless oil (0.593 g, 37%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.15–1.40 (m, 4H, CH_2CH_2), 1.70–1.71 (m, 4H, CH_2CH_2), 3.59 (s, 3H, OCH_3), 7.39–7.44 (m, 2H, PhH), 7.50–7.56 (m, 1H, PhH), 7.67–7.70 (m, 2H, PhH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 19.5, 22.2 (CH_2), 35.1, 42.2 (C_q), 52.1 (OCH_3), 128.4, 128.4, 132.8 (Ph), 138.2 ($C_{q,Ph}$), 170.5 ($COOCH_3$), 196.9, 201.0 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3061 (w), 3011(w), 2952 (w), 2846 (w), 1728 (s), 1663 (s), 1598 (m), 1579 (w). MS (EI, 70 eV): m/z = 271 ([M-H]$^+$, 244 (29), 181 (42), 105 (100), 77 (59). Anal. calcd. for $C_{16}H_{16}O_4$ (272.296): C, 70.57; H, 5.92; Found: C, 70.723; H, 5.917.

Methyl 1-(1-(1-naphthoyl)cyclopropanecarbonyl)cyclopropane-carboxylate (8e)

Starting with **7e** (0.200 g, 0.67 mmol) dissolved in a suspension of K_2CO_3 (0.370 g, 2.68 mmol) in DMSO (1.0 ml) and dibromoethane (0.14 ml, 1.34 mmol), **8e** was isolated as a white solid (0.096 g, 44%). mp 98–100 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.96–1.22 (m, 4H, CH_2CH_2), 1.78–1.92 (m, 4H, CH_2CH_2), 3.32 (s, 3H, OCH_3), 7.41–7.71 (m, 3H, ArH), 7.85–7.88 (m, 1H, ArH), 7.95–7.97 (m, 1H, ArH), 8.39–8.42 (m, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 21.3, 22.1 (CH_2), 34.6, 44.0 (C_q), 51.7 (OCH_3), 124.0, 125.7, 126.5, 127.6, 128.1, 128.3 (Ar), 130.1 ($C_{q,Ar}$), 132.4 (Ar), 133.8, 135.8 ($C_{q,Ar}$), 170.6 ($COOCH_3$), 199.0, 201.1 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3089 (w), 3048 (w), 3011 (w), 2952 (w), 2848 (w), 1723 (s), 1661 (s), 1592 (w), 1574 (w), 1508 (m). MS (EI, 70 eV): m/z = 322(M$^+$, 33), 181 (14), 179 (10), 155 (100), 127 (78). Anal. calcd. for $C_{20}H_{18}O_4$ (322.355): C, 74.52; H, 5.63; Found: C, 74.249; H, 5.471.

Methyl 1-(1-(cyclohexanecarbonyl)cyclopropanecarbonyl)cyclo-propanecarboxylate (8f)

Starting with **7f** (0.757 g, 3.00 mmol) dissolved in a suspension of K_2CO_3 (1.658 g, 12.00 mmol) in DMSO (4.0 ml) and dibromoethane (0.60 ml, 6.00 mmol), **8f** was isolated as a colourless liquid (0.279 g, 34%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.18–1.79 (m, 18H, CH_2), 2.38–2.48 (m, 1H, CH), 3.65 (s, 3H, OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ = 17.7, 20.9, 25.7, 29.2 (CH_2), 34.7, 41.8 (C_q), 47.5 (CH), 52.2 (OCH_3), 171.1 ($COOCH_3$), 201.1, 208.5 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3096 (w), 3013 (w), 2931 (s), 2854 (m), 1728 (s), 1677 (s). MS (EI, 70 eV): m/z = 278 (M$^+$, 1), 195 (100), 127 (38), 83 (18), 55 (17). HRMS (ESI, 70 eV) calcd. for $C_{16}H_{23}O_4$ (279.1591 [M+H]$^+$): 279.1593.

Methyl 1-(1-(4-methoxybenzoyl)cyclopropanecarbonyl)cyclopropanecarboxylate (8g)

Starting with **7g** (1.381 g, 5.00 mmol) dissolved in a suspension of K_2CO_3 (2.764 g, 20.00 mmol) in DMSO (5.0 ml) and dibromoethane (1.20 ml, 7.50 mmol), **8g** was isolated as a light-yellow solid (0.909 g, 61%). mp 52–53 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.18–1.41 (m, 4H, CH_2), 1.63–1.67 (m, 4H, CH_2), 3.59 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.87–6.90 (m, 2H, PhH), 7.68–7.71 (m, 2H, PhH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 19.0, 21.7 (CH_2), 35.2, 41.8 (C_q), 52.1, 55.4 (OCH_3), 113.6 (Ph), 130.7 ($C_{q,Ph}$), 130.8 (Ph), 163.4 ($C_{q,Ph}$), 170.5 (*C*OOCH$_3$), 194.9, 201.3 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3054 (w), 3020 (w), 2968 (w), 2935 (w), 2843 (w), 1711 (s), 1677 (m), 1656 (s), 1596 (s), 1506 (s). MS (EI, 70 eV): m/z = 302 (M$^+$, 8), 274 (31), 172 (11), 135 (100), 77 (13). Anal. calcd. for $C_{17}H_{18}O_5$ (302.322): C, 67.54; H, 6.00. Found: C, 67.209; H, 5.990.

Methyl 1-(1-(η^5-ferrocenoyl)cyclopropanecarbonyl)cyclopropanecarboxylate (8h)

Starting with **7h** (0.708 g, 2.00 mmol) dissolved in a suspension of K_2CO_3 (1.106 g, 8.00 mmol) in DMSO (2.0 ml) and dibromoethane (0.40 ml, 4.00 mmol), **8h** was isolated as a red solid (0.361 g, 48%). mp 128–130 °C;^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.32–1.69 (m, 8H, CH_2), 3.54 (s, 3H, OCH_3), 4.13 (s, 5H, CH), 4.46–4.47 (m, 2H, CH), 4.72–4.73 (m, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 18.3, 22.0 (CH_2), 35.1, 42.6 (C_q), 52.0 (OCH_3), 70.1, 70.3, 71.7 (CH), 79.6 (C_q), 170.4 (*C*OOCH$_3$), 200.1, 201.1 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3097 (w), 3009 (w), 2956 (w), 1723 (s), 1673 (w), 1652 (s), 1569 (w), 1553 (w), 1537 (w), 1504 (w). MS (EI, 70 eV): m/z = 381 (24), 280 (M$^+$, 100), 283 (6), 257 (8), 247 (7), 121 (13). Anal. calcd. for $C_{20}H_{20}FeO_4$ (380.215): C, 63.18; H, 5.30. Found: C, 62.808; H, 5.447.

Synthesis of methyl 1-(3-(1-(cyclopropanecarbonyl)cyclopropyl)-3-oxopropanoyl)-cyclopropanecarboxylate (9)

To a suspension of sodium methoxide (2.0 equiv.) in MTBE (1.33 mL mmol^{-1}) was added **2a** (1.0 equiv.) at 30 °C. To the reaction mixture **5** (1.0 equiv.) was added dropwise at 30 °C with vigorous stirring. After stirring at 30 °C for 3 h and aqueous workup with 10% HCl-solution with ice cooling, the organic layer was separated and washed with water. The aqueous phase was extracted with MTBE. The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc = 2 : 1) to give product **9**. Starting with **5** (1.830 g, 12.00 mmol) dissolved in a suspension of sodium methoxide (1.30 g, 24.00 mmol) in MTBE (9.0 ml) and **2a** (1.90 g, 12.00 mmol), **9** was isolated as a orange oil (1.29 g, 39%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91–1.15 (m, 8H, CH_2), 1.47–1.50 (m, 4H, CH_2), 2.21 (m, 1H, CH), 3.77 (s, 3H, CH_3), 5.80 (s, 1H, CH), 15.50 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.6, 17.0, 17.9 (CH_2), 17.9 (CH), 28.1, 40.3 (C), 52.9 (CH_3), 100.3 (CH), 170.5, 188.3, 193.4, 206.3 (CO). IR (neat, cm^{-1}) 3101 (w), 3003 (m), 2954 (m), 1733 (s), 1684 (s), 1653 (m), 1616 (s), 1559 (m), 1540 (m), 1522 (m), 1507 (m), 1437 (s), 1419 (s), 1388 (s), 1321 (s), 1216 (m), 1135 (m), 1063 (s), 1009 (m), 948 (m), 885 (w), 783 (w), 754 (w). MS (EI, 70 eV) m/z = 278 (M$^+$, 8.7), 263 (20.8), 150 (23.0), 246 (15.1), 179 (11.3), 151 (12.6), 137 (33.0), 127 (100), 95 (19.7), 69 (100). Anal. calcd. for $C_{15}H_{18}O_5$ (278.30): C, 64.74; H, 6.52. Found: C, 64.99; H, 7.03.

General procedure for the synthesis of tricarbonyl compounds 12

To a suspension of **11** (2.0 equiv.) in CH_2Cl_2 (2 mL mmol^{-1}) **10** (1.0 equiv.) was added at −78 °C. The reaction mixture was allowed to warm to 20 °C and stirred for 12 h. After aqueous workup with saturated $NaHCO_3$-solution the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc = 2 : 1) to give product **9**. The synthesis of **12a,b** has been previously reported.[4a]

Methyl 5-(4-methoxyphenyl)-3,5-dioxopentanoate (12c)

Starting with *p*-anisoyl chloride (0.8 ml, 5.76 mmol) and 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (3.00 g, 11.52 mmol), dissolved in CH_2Cl_2 (10 mL), **12c** was isolated as an orange solid (0.60 g, 42%); mp 133 °C. ^{1}H-NMR (300 MHz, $CDCl_3$, keto/enol = 0 : 100): δ (enol) = 3.46 (s, 2H, CH_2), 3.76 (s, 3H, OCH_3), 3.86 (s, 3H, ArOC*H*$_3$), 6.21 (s, 1H, CH), 6.93 (d, ^3J = 8.97 Hz, 2H, Ar), 7.86 (d, ^3J = 9.00 Hz, 2H, Ar), 16.00 (s, 1H, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): enol: δ = 45.3 (CH_2), 52.5 (OCH_3), 55.5 (OCH_3), 95.9 (CH), 114.1 (Ar), 126.6 (C), 129.3 (Ar), 163.5 (CAr), 168.3, 183.4, 187.1 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3470 (w), 2981 (w), 2846 (w), 2629 (w, br), 2559 (w, br), 1751 (s), 1738 (m), 1675 (m, br), 1600 (s), 1577 (s), 1513 (m), 1465 (m), 1442 (m), 1427 (s), 1299 (s), 1254 (s), 1190 (s), 1178 (s), 1142 (s), 1118 (s), 1106 (s), 1010 (s), 953 (m), 934 (m), 874 (m), 845 (s), 822 (s), 783 (s), 766 (s). MS (EI, 70 eV): m/z (%) = 250 (M$^+$, 9.0), 218 (8.8), 190 (8.7), 177 (15.4), 152 (39.5), 135 (100), 107 (8.6), 92 (6.4), 77 (12.1), 69 (8.3). Anal. calcd. for $C_{13}H_{14}O_5$ (250.25): C, 62.39; H, 5.64. Found: C, 62.44; H, 5.44.

Methyl 3,5-dioxo-5-*p*-tolylpentanoate (12d)

Starting with *p*-methylbenzoyl chloride (0.89 g, 5.76 mmol) and 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (3.00 g, 11.52 mmol), dissolved in CH_2Cl_2 (10 mL), **12d** was isolated as a yellow oil (0.78 g, 58%). ^{1}H-NMR (300 MHz, $CDCl_3$, keto/enol = 0 : 100): δ (enol) = 2.41 (s, 3H, CH_3), 3.48 (s, 2H, CH_2), 3.76 (s, 3H, OCH_3), 6.26 (s, 1H, CH), 7.25 (d, ^3J = 8.46 Hz, 2H, Ar), 7.78 (d, ^3J = 8.28 Hz, 2H, Ar), 15.86 (s, 1H, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): enol: δ = 21.7 (CH_3), 45.6 (CH_2), 52.5 (OCH_3), 96.4 (CH), 127.2, 129.5 (Ar), 131.3, 143.6 (C), 168.1, 183.1, 188.5 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3032 (w), 2999 (w), 2953 (w), 2923 (w, br), 2846 (w, br), 1739 (s), 1606 (s), 1506 (m), 1435 (s), 1254 (s), 1184 (s), 1147 (s), 1076 (m), 1017 (s), 954 (m), 832 (m), 780 (s). MS (EI, 70 eV): m/z (%) = 234 (M$^+$, 46.0), 202 (22.4), 174 (68.1), 161 (81.5), 119 (100), 91 (57.4), 69 (75.5). HRMS (EI, 70 eV): calcd. for $C_{13}H_{14}O_4$ (M$^+$) 234.08866, found 234.088131.

Methyl 5-(3-chlorophenyl)-3,5-dioxopentanoate (12e)

Starting with *m*-chlorobenzoylchloride (0.7 ml, 5.76 mmol) and 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (3.00 g, 11.52 mmol), dissolved in CH_2Cl_2 (10 mL), **12e** was isolated as a yellow oil (0.94 g, 64%). ^{1}H-NMR (300 MHz, $CDCl_3$, keto/enol = 0 : 100): δ (enol) = 3.50 (s, 2H, CH_2), 3.77 (s, 3H, OCH_3), 6.26 (s, 1H, CH), 7.39 (dd, ^3J = 7.86 Hz, ^3J = 7.92 Hz, 1H, Ar), 7.50 (ddd, ^3J = 7.91 Hz, ^4J = 2.07 Hz, ^4J = 1.13 Hz, 1H, Ar), 7.74 (ddd, ^3J = 7.83 Hz, ^4J = 1.50 Hz, ^4J = 1.13 Hz, 1H, Ar), 7.74 (dd, ^4J = 1.86 Hz, ^4J = 1.88 Hz, 1H, Ar), 15.63 (s, 1H, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): enol: δ = 45.7 (CH_2), 52.6 (OCH_3), 97.1 (CH), 125.2, 127.2, 130.0, 132.6 (Ar), 135.0, 135.9 (C), 167.8, 181.0, 189.5 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3070 (w), 3002 (w), 2953 (w), 2844 (w, br), 1738 (s), 1602 (s), 1563 (s), 1503 (m), 1435 (s), 1324 (m), 1251 (s), 1198 (s), 1145 (s), 1099 (m), 1078 (m), 1011 (m), 954 (m), 897 (m), 768 (s). MS (EI, 70 eV): m/z (%) = 254 (M$^+$, 48.8), 222 (32.4), 196 (57.1), 195 (23.1), 194 (93.7), 183 (66.0), 182 (20.3), 181 (98.0), 141 (76.7), 140 (17.2), 139 (100), 111 (71.0), 101 (22.6), 89 (10.7), 75 (33.8), 69 (91.2). HRMS (EI, 70 eV): calcd. for $C_{12}H_{11}ClO_4$ (M$^+$) 254.03404, found 254.033453.

General procedure for the synthesis of dihydrofuranes 13

To a suspension of K_2CO_3 (5.0 equiv.) in DMSO (0.3-0.5 mL mmol^{-1}) **12** (1.0 equiv.) was added. To the reaction mixture was dibromoethane (2.5 equiv.) added dropwise at 20 °C with vigorous stirring. After stirring at 20 °C for 8 h, K_2CO_3 was removed by filtration. The solid was thoroughly washed with diethyl ether. The filtrate was washed with water until the yellow colour disappeared, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc = 2 : 1) to give product **13**.

Methyl 1-(3-(cyclopropanecarbonyl)-4,5-dihydrofuran-2-yl)cyclopropanecarboxylate (13a)

Starting with **12a** (1.70 g, 9.23 mmol) dissolved in a suspension of K_2CO_3 (6.38 g, 46.15 mmol) in DMSO (3 ml) and 1,2-dibromoethane (1.67 ml, 19.38 mmol), **13a** was isolated as an yellow oil (0.70 g, 32%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.76 (m, 2H, $(CH_aH_b)_2$CH), 0.99 (m, 2H, $(CH_aH_b)_2$CH), 1.25 (m, 2H, $(CH_aH_b)_2$C), 1.55 (m, 2H, $(CH_aH_b)_2$C), 2.03 (m, 1H $(CH_2)_2CH$), 3.01 (t, ^3J = 9.69 Hz, 2H, CH_2), 3.62 (s, 3H, CH_3), 4.37 (t, ^3J = 9.69 Hz, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.5 (CH_2), 17.7 (CH_2), 19.2 (CH), 23.5 (C), 31.0 (CH_2), 52.7 (CH_3), 70.3 (OCH_2), 115.6 (C), 165.4, 172.0, 196.1 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3095 (w), 3007 (w), 2954 (w), 2903 (w), 2871 (w), 1726 (s), 1659 (m), 1615 (m), 1589 (m), 1436 (m), 1402 (s), 1305 (s), 1200 (s), 1174 (s), 1129 (s), 1098 (m), 1070 (m), 1029 (m), 990 (w), 958 (s), 904 (m), 866 (m), 843 (w), 751 (w). MS (EI, 70 eV) m/z = 236 (M$^+$, 83.0), 221 (19.1), 208 (100), 195 (70.3), 189 (50.0), 177 (54.1), 163 (24.4), 135 (22.6), 127 (23.3), 107 (28.6), 95 (26.1), 91 (25.6), 79 (38.6), 77 (32.6), 69 (96.2). Anal. calcd. for $C_{13}H_{16}O_4$ (236.26): C, 66.09; H, 6.83. Found: C, 66.04; H, 6.88.

Methyl 1-(3-benzoyl-4,5-dihydrofuran-2-yl)cyclopropanecarboxylate (13b)

Starting with **12b** (0.3 g, 1.36 mmol) dissolved in a suspension K_2CO_3 (0.94 g, 6.81 mmol) in DMSO (0.4 ml) and 1,2-dibromoethane (0.29 ml, 3.41 mmol), **13b** was isolated as a colourless oil (0.13 g, 35%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45 (m, 2H, $(CH_aH_b)_2$C), 1.71 (m, 2H, $(CH_aH_b)_2$C), 2.76 (t, ^3J = 9.66 Hz, 2H, CH_2), 3.53 (s, 3H, CH_3), 4.41 (t, ^3J = 9.70 Hz, 2H, CH_2), 7.34–7.39 (m, 2H, Ph), 7.43–7.46 (m, 1H, Ph), 7.73–7.77 (m, 2H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.1 (CH_2), 29.6 (C), 30.3 (CH_2), 50.6 (CH_3), 70.5 (OCH_2), 105.5 (C), 127.8, 127.9, 131.9 (Ph), 137.8 (C), 165.1, 168.4, 197.4 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3061 (w), 3013 (w), 2949 (w), 2904 (w), 2870 (w), 1693 (s), 1628 (m), 1598 (w), 1581 (w), 1437 (m), 1387 (m), 1355 (w), 1321 (w), 1289 (m), 1208 (m), 1189 (m), 1155 (m), 1108 (s), 1045 (s), 991 (s), 939 (m), 882 (w), 849 (w, br), 795 (m), 783 (m), 763 (m). MS (EI, 70 eV) m/z = 272 (M$^+$, 33.0), 271 (34.2), 240 (9.9), 239 (10.5), 213 (14.2), 212 (14.3), 185 (6.4), 181 (10.2), 105 (100), 77 (55.2). Anal. calcd. for $C_{16}H_{16}O_4$ (272.30): C, 70.57; H, 5.92. Found: C, 70.14; H, 5.90.

Methyl 1-(3-(4-methoxybenzoyl)-4,5-dihydrofuran-2-yl)cyclopropanecarboxylate (13c)

Starting with **12c** (0.34 g, 1.36 mmol) dissolved in a suspension K_2CO_3 (0.94 g, 6.81 mmol) in DMSO (0.4 ml) and 1,2-dibromoethane (0.29 ml, 3.41 mmol), **13c** was isolated as a colourless oil (0.06 g, 15%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (m, 2H, $(CH_aH_b)_2$C), 1.67 (m, 2H, $(CH_aH_b)_2$C), 2.80 (t, ^3J = 9.67 Hz, 2H, CH_2), 3.52 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 4.42 (t, ^3J = 9.67 Hz, 2H, CH_2), 6.86 (d, ^3J = 9.04 Hz, 2H, Ar), 7.76 (d, ^3J = 9.00 Hz, 2H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.6 (CH_2), 29.3 (C), 30.4 (CH_2), 50.5, 55.4 (CH_3), 70.5 (OCH_2), 105.2 (C), 113.2, 130.0 (Ar), 130.4, 162.6 (C), 165.1, 168.6, 195.6 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2950 (w), 2904 (w), 2841 (w), 1695 (m), 1673 (m), 1630 (m), 1599 (s), 1576 (m), 1510 (m), 1436 (m), 1419 (w), 1387 (w), 1354 (w), 1295 (m), 1253 (s), 1213 (m), 1167 (s), 1108 (s), 1029 (s), 986 (s), 937 (m), 884 (w), 839 (m), 817 (m), 794 (m), 757 (m). MS (EI, 70 eV) m/z = 302 (M$^+$, 13.7), 301 (23.6), 271 (14.2), 181 (6.7), 135 (100), 107 (7.0), 92 (10.6), 77 (15.6). Anal. calcd. for $C_{17}H_{18}O_5$ (302.32): C, 67.54; H, 6.00. Found: C, 67.38; H, 6.03.

Methyl 1-(3-(4-methylbenzoyl)-4,5-dihydrofuran-2-yl)cyclopropanecarboxylate (13d)

Starting with **12d** (0.31 g, 1.36 mmol) dissolved in a suspension K_2CO_3 (0.94 g, 6.81 mmol) in DMSO (0.4 ml) and 1,2-dibromoethane (0.29 ml, 3.41 mmol), **13d** was isolated as a pale yellow oil (0.08 g, 21%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (m, 2H, $(CH_aH_b)_2$C), 1.69 (m, 2H, $(CH_aH_b)_2$C), 2.36 (s, 3H, CH_3), 2.78 (t, ^3J = 9.66 Hz, 2H, CH_2), 3.52 (s, 3H, CH_3), 4.41 (t, ^3J = 9.70 Hz, 2H, CH_2), 7.16 (d, ^3J = 8.27 Hz, 2H, Ar), 7.66 (d, ^3J = 8.28 Hz, 2H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.9 (CH_2), 21.6 (CH_3), 29.5 (C), 30.4 (CH_2), 50.5 (CH_3), 70.5 (OCH_2), 105.3 (C), 127.9, 128.7 (Ar), 135.1, 142.5 (C), 165.1, 168.5, 196.8 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2949 (w), 2903 (w), 1695 (m), 1677 (m), 1627 (m), 1607 (m), 1437 (m), 1387 (m), 1355 (w), 1316 (w), 1293 (m), 1204 (m), 1179 (s), 1153 (w), 1108 (s), 1043 (s), 995 (s), 938 (m), 916 (m), 886 (w), 817 (m), 794 (w), 763 (w). MS (EI, 70 eV) m/z = 286 (M$^+$, 22.6), 271 (76.0), 239 (9.3), 226 (16.6), 181 (6.7), 119 (100), 91 (68.2). HRMS (EI, 70 eV): calcd. for $C_{17}H_{18}O_4$ (M$^+$) 286.11996, found 286.120056.

Methyl 1-(3-(3-chlorobenzoyl)-4,5-dihydrofuran-2-yl)cyclopropanecarboxylate (13e)

Starting with **12e** (0.35 g, 1.36 mmol) dissolved in a suspension K_2CO_3 (0.94 g, 6.81 mmol) in DMSO (0.4 ml) and

1,2-dibromoethane (0.29 ml, 3.41 mmol), **13e** was isolated as a pale yellow oil (0.07 g, 17%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (m, 2H, $(CH_aH_b)_2C$), 1.21 (m, 2H, $(CH_aH_b)_2C$), 3.12 (t, ^3J = 9.57 Hz, 2H, CH_2), 3.70 (s, 3H, CH_3), 4.51 (t, ^3J = 9.51 Hz, 2H, CH_2), 7.34 (dd, ^3J = 7.53 Hz, ^3J = 7.62 Hz, 1H, Ar), 7.45 (ddd, ^3J = 7.76 Hz, ^4J = 1.20 Hz, ^4J = 1.20 Hz, 1H, Ar), 7.55 (ddd, ^3J = 7.65 Hz, ^4J = 1.26 Hz, ^4J = 1.44 Hz, 1H, Ar), 7.67 (dd, ^4J = 1.69 Hz, ^4J = 1.68 Hz, 1H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.2 (CH_2), 23.7 (C), 32.0 (CH_2), 52.8 (CH_3), 70.5 (OCH_2), 114.5 (C), 125.9, 128.3, 129.7, 131.4 (Ar), 134.2, 142.4 (C), 167.3, 171.5, 191.1 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3066 (w), 2953 (w), 2902 (w), 1727 (m), 1605 (s), 1566 (m), 1474 (w), 1435 (m), 1418 (w), 1383 (m), 1357 (m), 1298 (s), 1262 (m), 1199 (s), 1173 (s), 1125 (s), 1076 (m), 1040 (w), 1026 (w), 999 (w), 954 (w), 901 (m), 858 (m), 802 (m), 737 (s). MS (EI, 70 eV) m/z = 306 (M^+, 74.4), 291 (25.7), 280 (38.7), 279 (15.1), 278 (91.5), 275 (30.0), 249 (17.0), 248 (8.2), 247 (30.4), 239 (17.1), 222 (11.5), 221 (7.2), 220 (38.5), 211 (11.8), 195 (19.5), 163 (13.3), 141 (50.6), 140 (10.4), 139 (100), 127 (26.6), 113 (20.9), 112 (5.9), 111 (70.0), 75 (19.5). HRMS (EI, 70 eV): calcd. for $C_{16}H_{15}ClO_4$ (M^+) 306.06400, found 306.064482.

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