Efficient Synthesis of Functionalised 4-Hydroxycyclopent-2-en-1-ones by Cyclisation of 1,3-Bis(silyl) Enol Ethers and 1,3-Dicarbonyl Dianions with 1,2-Diketones

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The cyclisation of 1,3-bis(silyl) enol ethers and 1,3-dicarbonyl dianions with 1,2-diketones provides convenient access to functionalised 4-hydroxycyclopent-2-en-1-ones.

Introduction

Despite their simplicity, the synthetic applicability of cyclisation reactions of 1,3-dicarbonyl dianions[1,2] with dielectrophiles is often limited by side reactions such as polymerisation, decomposition,[3] formation of open-chain products,[4] elimination[5] or SET reactions.[6] Lewis acid mediated reactions of 1,3-bis(silyl) enol ethers, which can be regarded as masked 1,3-dicarbonyl dianions, have been developed to overcome these problems.[7,8] During the past years, we have studied cyclisation reactions[9] of free and masked 1,3-dicarbonyl dianions with a variety of 1,2-dielectrophiles.[10] In this context, reactions of 1,2-dicarbonyl derivatives such as 1,2-diketones, 2-formylketones, glyoxal or 2-formylketals are of special synthetic relevance. Base-mediated cyclisation reactions of ketones with 1,2-diketones have been studied for a long time[11] but they are often limited to the use of nonenolisable (e.g. aromatic) substrates. Molander et al. developed the Lewis acid mediated cyclisation of an electroneutral equivalent of the trimethylenemethane dianion with enolisable 1,2-diketones to give 1,2-dihydroxy-4-methylenecyclopentanes[12] and we have recently reported[13] the cyclisation of enolisable 1,2-diketones with 1,3-bis(silyl) enol ethers. These reactions allow the chemoselective synthesis of a variety of functionalised 4-hydroxycyclo-2-penten-1-ones. Herein, we wish to report full details of this methodology. With regards to our preliminary report, we have extended the preparative scope to the use of 1,2-formylketals. In addition, we report what are, to the best of our knowledge, the first cyclisations of free 1,3-dicarbonyl dianions with enolisable 1,2-diketones to give cyclopentenones.

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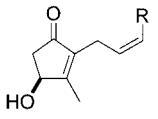
Functionalised 4-hydroxycyclo-2-penten-1-ones are of pharmacological relevance and are present in a number of natural products such as prostaglandins[14,15] and industrial compounds for crop protection.[14,16] For example, (+)-pyrethrolon, (+)-cinerolon and (+)-jasmolon represent the active compounds of the insecticide pyrethrum isolated from *Chrysanthemum* plants.[14] The development of methods for the synthesis of analogues, which are less harmful towards humans and animals, is of considerable interest.



Pyrethrolon: R = Vinyl
Cinerolon: R = Me
Jasmolon: R = Et

One-Pot Cyclisation of 1,3-Bis(silyl) Enol Ethers with 1,2-Diketones

The reaction of 1,3-bis(silyl) enol ether **1a** with butane-2,3-dione (**2a**) afforded the 4-hydroxycyclo-2-penten-1-one **3a** (Scheme 1). The best yields were obtained when the Lewis acid $TiCl_4$ (2 equiv.) was employed. The use of Me_3SiOTf or $BF_3{\cdot}OEt_2$ proved unsuccessful. The presence of molecular sieves (4 Å) and a proper tuning of the concentration, reaction time and temperature also proved extremely important during the optimisation. The success of the reaction depended very much on the reaction conditions and on the quality of the reagents and solvents.

The formation of **3a** can be explained by the occurrence of a double Mukaiyama−aldol-reaction[17] and subsequent elimination of water. The reaction proceeds by regioselective attack of the terminal carbon of the diene on **2a** and subsequent cyclisation via the central carbon atom. In contrast, a cyclisation via the carbon and the oxygen atom was observed in the reactions of **1a** with oxalyl chloride due to stereoelectronic effects (Baldwin rules). The change from C,O- to C,C-cyclisation in the reaction of **1a** with **2a** can be explained by reversible formation of a labile hemiketal

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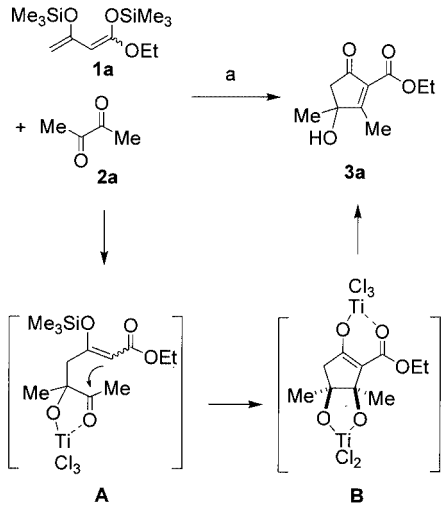
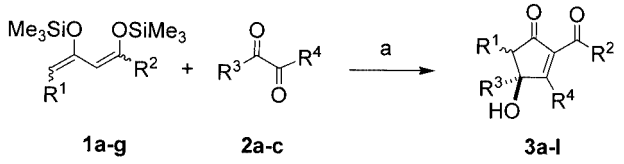


Scheme 1. Cyclisation of 1,3-bis(silyl) enol ether **1a** with 2,3-butanedione, a: 2.0 $TiCl_4$, CH_2Cl_2, 4-Å mol. sieves, −78 − 20 °C, 6−12 h, 20 °C, 2−6 h

(C,O-cyclisation) which was subsequently opened and irreversibly transformed into **3a**.

To study the preparative scope of the reaction, the substituents were systematically varied (Scheme 2, Table 1). The reaction of **2a** with 1,3-bis(trimethylsilyloxy)-1,3-butadienes **1a**−**c**, prepared from ethyl acetoacetate, acetylacetone and 1-methoxyacetylacetone, afforded the cyclopent-2-en-1-ones **3a**−**c**. The cyclisation of **2a** with dienes **1d**−**e**, derived from methyl 3-oxopentanoate and ethyl 3-oxohexanoate, gave the cyclopentenones **3d**−**e**. The reaction of **2a** with **1f**−**g**, prepared from methyl 4-methoxyacetoacetate and 1-methoxyacetylacetone, afforded the methoxy-substituted cyclopent-2-en-1-ones **3f** and **3g**, respectively. The 1,2-stereoselectivities observed for **3d** and **3f**−**g** were low. A moderate 1,2-stereoselectivity was observed in the case of **3e**.



Scheme 2. Synthesis of 4-hydroxycyclopent-2-en-1-ones **3**, a: 2.0 $TiCl_4$, CH_2Cl_2, 4-Å mol. sieves, −78 °C − 20 °C, 12 h, 20 °C, 2 h

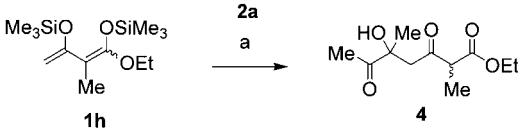
Table 1. Products and yields

3	R^1	R^2	R^3	R^4	(%)[a]	δ (multiplicity)[b]		*ds*[c]
a	H	OEt	Me	Me	50	2.24 (s)	1.47 (s)	−
b	H	Me	Me	Me	38	2.25 (s)	1.45 (s)	−
c	H	CH_2OMe	Me	Me	40	2.29 (s)	1.46 (s)	−
d	Me	OMe	Me	Me	32	2.26 (s)	1.45 (s)	1.2:1
e	Et	OEt	Me	Me	34	2.30 (s)	1.49 (s)	3.5:1
f	OMe	OMe	Me	Me	42	2.28 (s)	1.46 (s)	1:1.4
g	OMe	Me	Me	Me	25	2.36 (s)	1.36 (s)	1:1.2
h	H	OEt	Et	Et	28	2.60 (m)	1.78 (m)	−
i	H	Me	Et	Et	16	2.60 (m)	1.70 (m)	−
j	Me	OMe	Et	Et	21	2.68 (m)	1.79 (m)	5:1
k	H	OEt	Me	Et	45	2.67 (m)	1.53 (s)	5:1
l	H	CH_2OMe	Me	Et	35	2.76 (m)	1.52 (s)	4:1

[a] Isolated yields. [b] chemical shifts (^{1}H NMR) of the CH_3 and CH_2 groups attached to carbons C-3 and C-4; for **3d**−**g** and **3j**−**l** the signals of the major isomers are given. [c] for **3d**−**g** and **3j**: diastereomeric ratio (by ^{1}H NMR), for **3k**−**l**: regioisomeric ratio (by ^{1}H NMR spectroscopy).

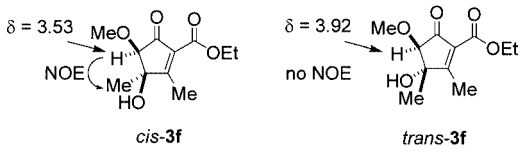
The reaction of 3,4-hexanedione (**2b**) with 1,3-bis(trimethylsilyloxy)-1,3-butadienes **1a** and **1b** afforded the cyclopentenones **3h** and **3i**, respectively. Cyclopentenone **3j** was prepared from diene **1d** with good diastereoselectivity (5:1). The structure of the major component could not be unambiguously assigned, however, due to signal overlap. The yields obtained from the reactions of **2b** were lower than those obtained from the reactions of the respective cyclisations of **2a**. In addition, longer reaction times were required (6 + 12 h). The reactions of **1a** and **1c** with the unsymmetrical pentane-2,3-dione (**2c**) afforded the cyclo-2-penten-1-ones **3k**−**l** with good and moderate regioselectivities, respectively.

The reaction of 1-ethoxy-2-methyl-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**1h**) with butane-2,3-dione afforded the open-chained product **4** as a mixture of diastereomers (Scheme 3). No cyclisation could be induced, presumably due to the steric effect of the methyl group.



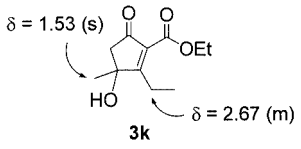
Scheme 3. Reaction of **1h** with **2a**, a: 2.0 $TiCl_4$, CH_2Cl_2, 4-Å mol. sieves, −78 °C − 20 °C, 12 h, 20 °C, 2 h, 53%

The diastereomers of **3f** were separated and analysed by NOESY measurements. For one of the isomers, an interaction was detected between hydrogen atom 5-H and the methyl group attached to C-4. This supports the presence of a *cis* relationship between the hydroxy and the methoxy groups which is also supported by a comparison of the chemical shifts of the CH groups of the isomers. For one isomer, the corresponding resonance at δ = 3.92 ppm appears at significantly lower field than for the other (δ = 3.53 ppm). This can be explained by deshielding of the proton located *cis* to the neighbouring hydroxy group.

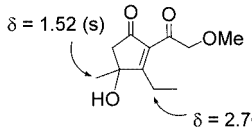


The configurations of the isomers of **3d**−**e** could not be established by NOESY experiments due to a severe signal overlap. However, comparisons of the chemical shifts of the endocyclic CH-signals and of the alkyl groups R^1 (Me, Et) of the isomers and comparisons with the signals of compounds with known configurations[18] supported the exist-

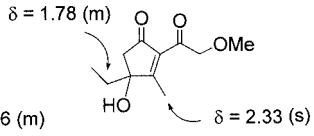
ence of a *trans* configuration in the main isomers of **3d**−**e**. The configurations of the unsymmetrically substituted compounds **3k**−**l** were established by analysis of the chemical shifts: the signals of the CH_3 and CH_2 groups of substituent R^4 generally appear at lower field than those of R^3 (Table 1). Characteristic singlets and multiplets were observed for the CH_3 and the CH_2 groups, respectively.



3k



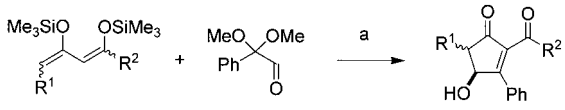
3l (main isomer)



3l (minor isomer)

2,2-Dimethoxy-2-phenylacetaldehyde

The cyclisations of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 2-ketoaldehydes were studied next although the use of 2-oxo-2-phenylacetaldehyde proved unsuccessful. Based on the pioneering work of Chan et al., the desired cyclisation could be induced when 2,2-dimethoxy-2-phenylacetaldehyde (**5**)[19] was employed.[20] The reaction of diene **1a** with **5** afforded the 4-hydroxycyclo-2-penten-1-one **6a** with very good regioselectivity (Scheme 4). The reaction proceeded by chemo- and regioselective attack of the terminal carbon of the diene on the aldehyde and subsequent cyclisation by attack of the central carbon atom on the ketal. The cyclisation of **5** with dienes **1i**−**m**, prepared from methyl, methoxyethyl, isobutyl, benzyl and isopropyl acetoacetate, afforded the cyclopentenones **6a**−**e** (Scheme 4, Table 2). The cyclisation of 1-phenyl-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**1n**) with **5** afforded the corresponding product **6f**. The 4-hydroxycyclopent-2-en-1-ones **6g**−**h** were prepared from dienes **1d** and **1e** with good *trans*-diastereoselectivities. The relative configurations were established from spectroscopic data (comparison of chemical shifts as outlined above).[21]



1 **5** **6a-h**

Scheme 4. Cyclisation of dienes **1** with 2,2-dimethoxy-2-phenylacetaldehyde, a: 2.0 $TiCl_4$, CH_2Cl_2, 4-Å mol. sieves, −78 °C − 20 °C, 12 h, 20 °C, 2 h

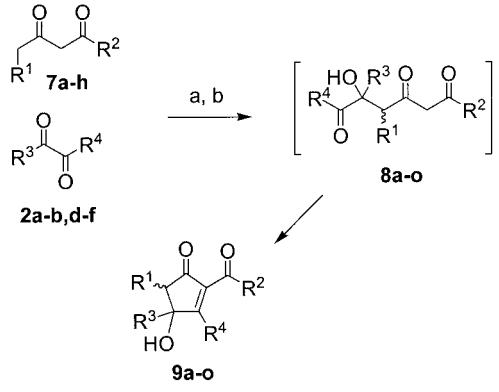
Table 2. Synthesis of 4-hydroxycyclopent-2-en-1-ones **6a**−**h**

6	R^1	R^2	Yield (%)[a]	*ds*[b]
a	H	OMe	17	−
b	H	$O(CH_2)_2OMe$	16	−
c	H	O(*i*Bu)	16	−
d	H	OCH_2Ph	5	−
e	H	O(*i*Pr)	10	−
f	H	Ph	14	−
g	Me	OMe	55	3:1
h	Et	OEt	48	15:1

[a] Isolated yields. [b] Diastereoselectivity in favour of the *trans*-isomer.

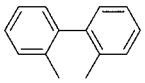
One-Pot Cyclisation of 1,3-Dicarbonyl Dianions with 1,2-Diketones

The reaction of the dianion of ethyl acetoacetate (**7a**) with butane-2,3-dione (**2a**) and subsequent aqueous workup afforded the open-chained β-keto ester **8a** as the crude product (Scheme 5, Table 3). All attempts to induce a cyclisation by heating a solution of **8a** failed. Interestingly, chromatographic purification (silica gel) of **8a** resulted in complete cyclisation and formation of the 4-hydroxycyclo-2-penten-1-one **9a** in 92% yield. Based on this observation, a one-pot cyclisation was developed for the reaction of the dianion of **7a** with hexane-3,4-dione (**2b**). After warming the reaction mixture to 20 °C, silica gel (0.5 g/1 mmol of **2b**) was added and the mixture was stirred for 19 h at reflux. Aqueous workup and chromatographic purification afforded the desired cyclopentenone **9b**. The one-pot procedure outlined above allowed the synthesis of **9b** in a significantly higher yield (61%) than by the use of 1,3-bis(silyl) enol ether **1a** (Table 1, 28%). The open-chained product **8b** could be isolated in 37% yield when no silica gel was added to the reaction mixture. The one-pot reaction presumably proceeded by initial condensation of the dianion with **2** to give a dilithiated intermediate. The latter then became protonated upon addition of the (slightly acidic) silica gel and the cyclopentenone **9** was subsequently formed by silica gel mediated cyclisation.

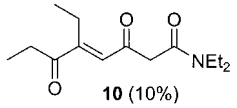


Scheme 5. Cyclisation of 1,3-dicarbonyl dianions with 1,2-diketones, a: 1) 2.3 LDA, THF, 0 °C, **7**, 1 h, 2) **2**, −78 °C − 20 °C, 12 h, b: addition of SiO_2, THF, reflux, 19−26 h

Table 3. Products and yields

9	R^1	R^2	R^3	R^4	(%)[a]
a	H	OEt	Me	Me	92[b]
b	H	OEt	Et	Et	61
c	H	OEt	–$(CH_2)_4$–		25
d	H	OEt	Me	Pr	37[c]
e	H	OEt	Ph	Ph	73
f	H	OMe	Et	Et	44
g	H	$O(CH_2)_2OMe$	Et	Et	42
h	H	O*t*Bu	Et	Et	31
i	H	O*t*Bu	Ph	Ph	45
j	H	O*t*Bu			31
k	H	OBn	Et	Et	13
l	Et	OEt	Et	Et	49[d]
m	OMe	OMe	Et	Et	33+12[e]
n	H	NEt_2	Me	Me	65
o	H	NEt_2	Et	Et	32+10[f]

[a] Isolated yields. [b] Formed from pure **8a** during chromatographic purification. [c] Mixture of regioisomers: *r*s = 3:1. [d] Mixture of diastereomers: *d*s = 4:1. [e] Diastereomers were separated. [f]



10 (10%)

The cyclisation of the dianion of **7a** with cyclohexane-1,2-dione (**2d**) afforded the desired bicyclic product **9c** in up to 25% yield. During optimisation of this reaction, the use of an excess of **7a** (2 equiv.) and removal of the silica gel by filtration proved to be important. The addition of water to the suspension of silica gel also proved unsuccessful. The cyclisation of dilithiated **7a** with (unsymmetrical) hexane-2,3-dione (**2e**) afforded **9d** as a 3:1 mixture of its regioisomers. The major product was formed by attack of the terminal carbon of the dianion on the sterically less encumbered side of the diketone. The cyclisation of dilithiated **7a** with benzile (**2f**) afforded the phenyl-substituted cyclopentenone **9e** in 69% yield. The reaction of the dianion of **7a** with 3,4,5,6-tetrachloro-1,2-benzoquinone, acenaphtenequinone and 1,2-naphthoquinone resulted in the formation of complex mixtures due to competing SET-processes. The cyclopentenones **9f**–**h** were prepared by cyclisation of the dianions of methyl, methoxyethyl and *tert*-butoxy acetoacetate (**7b**–**d**) with hexane-3,4-dione (**2b**). The cyclisation of dilithiated *tert*-butoxy acetoacetate with benzile and phenanthrene-9,10-dione afforded the cyclopentenones **9i** and **9j**, respectively. The cyclisation of the dianions of benzyloxy acetoacetate with **2b** afforded the cyclopentenone **9k**, albeit in low yield. The cyclisation of dilithiated ethyl 3-oxohexanoate with **2b** gave **9l** as a mixture of diastereomers. The reaction of the dianion of methyl 4-methoxyacetoacetate with **2b** afforded **9m** as a separable mixture of diastereomers. The cyclisation of the dianion of *N*,*N*-diethylacetylacetamide with **2a** and **2b** afforded the cyclopentenones **9n** and **9o**, respectively. In the case of **9o**, the open-chained product **10** was isolated as a side product.

A brief comparison of the two reported methods for the synthesis of cyclopentenones seems to be appropriate. Similar yields were obtained for cyclisations of **2a** with dianions or 1,3-bis(silyl) enol ethers derived from simple β-keto esters. The aryl-substituted cyclopentenones **9e** and **9j** could not be prepared by application of the $TiCl_4$-mediated cyclisation reaction. The amide-substituted products **9n** and **9o** are also not available by $TiCl_4$-mediated cyclisations since β-ketoamide-derived 1,3-bis(silyl) enol ethers undergo a rapid 1,5-silyl migration.[22] The cyclisations of hexane-3,4-dione (**2b**) generally proceeded in higher yields when the dianion method was employed. Similar regio- and diastereoselectivities were observed for both the dianion and the silyl enol ether methodologies. For both methods, the yields decreased for cyclopentenones containing a substituent at carbon C-5.

In summary, we have reported two convenient methods for the synthesis of cyclopentenones. Each method offers specific advantages.

Experimental Section

General Procedure for the Cyclisation of 1,2-Diketones with 1,3-Bis(trimethylsilyloxy)-1,3-butadienes: To a CH_2Cl_2 solution (40 mL) of 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (**1a**) (0.52 g, 1.9 mmol) and 2,3-butanedione (0.17 mL, 0.17 g, 2.0 mmol, 1.0 equiv.) was added $TiCl_4$ (0.42 mL, 0.72 g, 2.0 equiv.) at −78 °C in the presence of molecular sieves (4 Å). The reaction mixture was warmed to 20 °C over 6–12 h. After stirring for 2–6 h at 20 °C, a saturated aqueous $NaHCO_3$ solution (20 mL) was added, the organic layer was separated and the aqueous layer was extracted with diethyl ether (4 × 50 mL). The combined organic layers were dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, diethyl ether/petroleum ether, 1:1) to give **3a** as a colourless oil (188 mg, 50%). The results of our earlier work are substituted by the results reported herein.

Ethyl 3-Hydroxy-2,3-dimethyl-5-oxocyclopent-1-enecarboxylate (3a): ^{1}H NMR ([D$_6$]acetone, 250 MHz, ppm): δ = 1.27 (t, J = 7.1 Hz, 3 H, CH_3CH$_2$), 1.47 (s, 3 H, 3-CH$_3$), 2.24 (s, 3 H, 2-CH$_3$), 2.53 (s, 2 H, 4-H), 4.22 (q, J = 7.1 Hz, 2 H, CH$_2$O), 4.62 (s, 1 H, OH). ^{13}C NMR ([D$_6$]acetone, 62.9 MHz, ppm): δ = 11.68, 13.62 (*C*H$_3$CH$_2$, 3-CH$_3$), 25.31 (2-CH$_3$), 51.07 (C-4), 60.22 (CH$_3$*C*H$_2$), 75.02 (C-3), 131.57 (C-1), 162.97 (CO$_2$Et), 182.60 (C-2), 198.45 (C=O). MS (70 eV, EI): *m*/*z* (%) = 198 (43) [M$^+$], 183 (60), 154 (46), 152 (64), 137 (100); the exact molecular mass for $C_{10}H_{14}O_4$ *m*/*z* = 198.0892±2 ppm [M$^+$] was confirmed by HRMS (EI, 70 eV).

2-Acetyl-4-hydroxy-3,4-dimethylcyclopent-2-enone (3b): Following the general procedure, 2,3-butanedione (0.20 mL, 0.19 g, 2.2 mmol, 1 equiv.) was treated with 2,4-bis(trimethylsilyloxy)-1,3-pentadiene (0.53 g, 2.2 mmol, 1 equiv.) and $TiCl_4$ (0.48 mL, 0.82 g, 4.3 mmol, 2 equiv.). The product was purified by chromatography to give **3b** as a colourless solid (140 mg, 38%). ^{1}H NMR ([D$_6$]acetone,

250 MHz, ppm): δ = 1.45 (s, 3 H, 4-CH_3), 2.25 (s, 3 H, 3-CH_3), 2.34 (s, 3 H, CH_3C=O), 2.56 (s, 2 H, 5-H), 4.61 (s, 1 H, OH). ^{13}C NMR ([D$_6$]acetone, 50.3 MHz, ppm): δ = 12.72, 26.22, 30.89 (4-*C*H_3, 3-CH_3, *C*H_3C=O), 51.97 (C-5), 75.76 (C-4), 137.56 (C-2), 185.17 (C-3), 197.63, 202.00 (2 × C=O). MS (70 eV, EI): *m*/*z* (%) = 168 (65) [M$^+$], 153 (22), 125 (22), 85 (59), 43 (100). $C_9H_{12}O_3$ (168.2): calcd. C 64.26, H 7.20; found C 64.01, H 7.11.

4-Hydroxy-2-(2-methoxyethanoyl)-3,4-dimethylcyclopent-2-enone (3c): Following the general procedure, 2,3-butanedione (0.18 g, 0.18 mL, 2.1 mmol) was treated with 2,4-bis(trimethylsilyloxy)-5-methoxy-1,3-pentadiene (0.56 g, 2.0 mmol) and $TiCl_4$ (0.45 mL, 0.78 g, 4.1 mmol, 2 equiv.). The product was purified by chromatography to give **3c** as a colourless oil (160 mg, 40%). ^{1}H NMR ([D$_6$]acetone, 250 MHz, ppm): δ = 1.46 (s, 3 H, 4-CH_3), 2.29 (s, 3 H, 3-CH_3), 2.56 (s, 2 H, 5-H), 3.33 (s, 3 H, CH_3O), 4.39 (s, 2 H, CH_2O), 4.66 (s, 1 H, OH). ^{13}C NMR ($CDCl_3$, 62.9 MHz, ppm): δ = 12.05, 25.42 (3-CH_3, 4-CH_3), 50.99 (C-5), 58.28 (CH_3O), 75.43 (C-4), 135.21 (C-2), 186.26 (C-3), 196.19, 201.13 (C=O). MS (70 eV, EI): *m*/*z* (%) = 198 (10) [M$^+$]; the exact molecular mass for $C_{10}H_{14}O_4$ *m*/*z* = 198.0892±2 ppm [M$^+$] was confirmed by HRMS (EI, 70 eV).

Methyl 3-Hydroxy-2,3,4-trimethyl-5-oxocyclopent-1-enecarboxylate (3d): Following the general procedure, 2,3-butanedione (0.18 g, 0.18 mL, 2.1 mmol) was treated with 1,3-bis(trimethylsilyloxy)-1-methoxypenta-1,3-diene (0.56 g, 2.0 mmol, 1 equiv.) and $TiCl_4$ (0.45 mL, 0.78 g, 2 equiv.). The product was purified by chromatography to give **3d** as a colourless oil (128 mg, 32%, *ds* = 1.2:1). ^{1}H NMR ([D$_6$]acetone, 250 MHz, ppm): δ = 1.00−1.10 (d, *J* = 7.4 Hz, 3 H, 4-CH_3), overlapped by 1.05 (d, *J* = 7.4 Hz, 3 H, 4-CH_3), 1.25 (s, 3 H, 3-CH_3), 1.45 (s, 3 H, 3-CH_3), 2.26 (s, 3 H, 2-CH_3), 2.29 (s, 3 H, 2-CH_3), overlapped by 2.32 (q, *J* = 7.4 Hz, 1 H, 4-CH_3), 2.54 (q, *J* = 7.4 Hz, 1 H, 4-H), 3.74 (s, 3 H, CH_3O), overlapped by 3.74 (s, 3 H, CH_3O), 4.32 (s, 1 H, OH), 4.64 (s, 1 H, OH). ^{13}C NMR ($CDCl_3$, 62.9 MHz, ppm): δ = 8.25, 9.38, 11.88, 11.99 (2 × 4-CH_3, 2 × 3-CH_3), 22.07, 24.58 (2 × 2-CH_3), 50.90, 50.93, 51.41, 54.39 (2 × C-4, 2 × CH_3O), 76.48, 78.18 (2 × C-3), 129.85, 130.50 (2 × C-1), 163.42, 163.73 (2 × CO_2Me), 181.37, 183.53 (2 × C-2), 199.44, 202.13 (2 × C=O). IR (neat): $\tilde{\nu}$ = 3446 (br), 2978 (m), 2954 (m), 2940 (m), 1720 (s), 1632 (m), 1438 (s), 1376 (s), 1347 (s), 1330 (m), 1234 (s), 1106 (m), 1053 (s) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 198 (12) [M$^+$], 183 (22), 166 (100), 151 (72); the exact molecular mass for $C_{10}H_{14}O_4$ *m*/*z* = 198.0892±2 ppm [M$^+$] was confirmed by HRMS (EI, 70 eV).

Ethyl 4-Ethyl-3-hydroxy-2,3-dimethyl-5-oxocyclopent-1-enecarboxylate (3e): Following the general procedure, 2,3-butanedione (0.16 mL, 0.16 g, 1.9 mmol) was treated with 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-hexadiene (0.56 g, 1.8 mmol) and $TiCl_4$ (0.41 mL, 0.70 g, 3.7 mmol, 2 equiv.). The product was purified by chromatography to give **3e** as a colourless oil (104 mg, 34%, *ds* = 3.5:1). ^{1}H NMR ($CDCl_3$, 250 MHz, ppm): δ = 1.10 (t, *J* = 7.4 Hz, 3 H, CH_3CH$_2$CH), 1.32 (t, *J* = 7.1 Hz, 3 H, CH_3CH$_2$O), 1.49 (s, 3 H, 3-CH_3), 1.51−1.79 (m, 4 H, 4-H, CH_3CH_2CH), 2.30 (s, 3 H, 2-CH_3), 4.29 (q, *J* = 7.1 Hz, 2 H, CH_3CH_2O). ^{13}C NMR ($CDCl_3$, 62.9 MHz, ppm): δ = 12.69, 12.80, 14.09 (*C*H_3CH$_2$CH, *C*H_3CH$_2$O, 2-CH_3), 20.08 (*C*H$_2$CH), 26.41 (3-CH_3), 58.01 (C-4), 60.99 (CH$_2$O), 77.26 (C-3), 130.66 (C-1), 163.42 (CO_2Et), 182.42 (C-2), 202.71 (C=O). MS (70 eV, EI): *m*/*z* (%) = 226 (5) [M$^+$], 211 (12), 197 (10), 184 (18), 180 (100); the exact molecular mass for $C_{12}H_{18}O_4$ *m*/*z* = 226.1205±2 ppm [M$^+$] was confirmed by HRMS (EI, 70 eV).

Methyl 3-Hydroxy-4-methoxy-2,3-dimethyl-5-oxocyclopent-1-enecarboxylate: (*cis*-3f, *trans*-3f) Following the general procedure, 2,3-butanedione (0.16 g, 0.16 mL, 1.9 mmol) was treated with 1,3-bis(trimethylsilyloxy)-1,4-dimethoxybuta-1,3-diene (0.55 g, 1.9 mmol, 1 equiv.) and $TiCl_4$ (0.42 mL, 0.72 g, 2 equiv.). The product was purified by chromatography to give **3f** as a colourless oil (171 mg, 42%, *ds* = 1:1.4). The diastereomers could be separated by repeated chromatography to give (*cis*-**3f**) (46 mg, 11%) and (*trans*-**3f**) (19 mg, 5%) as yellowish solids.

***cis*-3f:** ^{1}H NMR ([D$_6$]acetone, 250 MHz, ppm): δ = 1.46 (s, 3 H, 3-CH_3), 2.28 (s, 3 H, 2-CH_3), 3.53 (s, 1 H, 4-H), 3.59 (s, 3 H, CH_3OCH), 3.75 (s, 3 H, CH_3OC=O), 4.12 (s, 1 H, OH). ^{13}C NMR ([D$_6$]acetone, 50.3 MHz, ppm): δ = 13.10 (3-CH_3), 24.77 (2-CH_3), 51.85 (*C*H_3OC=O), 59.63 (*C*H_3OCH), 75.53 (C-3), 85.24 (C-4), 130.59 (C-1), 164.04 (CO_2Me), 182.99 (C-2), 197.82 (C=O). IR (neat): $\tilde{\nu}$ = 3469 (br), 2956 (m), 2936 (m), 1746 (s), 1721 (s), 1629 (m), 1438 (s), 1377 (s), 1348 (m), 1323 (m), 1232 (s), 1127 (s), 1102 (s). MS (70 eV, EI): *m*/*z* (%) = 214 (16) [M$^+$], 199 (10), 184 (12), 182 (100); the exact molecular mass for $C_{10}H_{14}O_5$ *m*/*z* = 214.0841±2 ppm [M$^+$] was confirmed by HRMS (EI, 70 eV).

***trans*-3f:** ^{1}H NMR ([D$_6$]acetone, 250 MHz, ppm): δ = 1.27 (s, 3 H, 3-CH_3), 2.30 (s, 3 H, 2-CH_3), 3.63 (s, 3 H, CH_3OCH), 3.74 (s, 3 H, CH_3OC=O), 3.92 (s, 1 H, 4-H), 4.96 (s, 1 H, OH). ^{13}C NMR ([D$_6$]acetone, 75.5 MHz, ppm): δ = 12.79 (3-CH_3), 22.30 (2-CH_3), 51.79 (CH_3OC=O), 59.91 (*C*H_3OCH), 78.92 (C-3), 91.23 (C-4), 129.27 (C-1), 163.76 (CO_2Me), 182.49 (C-2), 196.14 (C=O). MS (70 eV, EI): *m*/*z* (%) = 214 (32) [M$^+$], 199 (16), 182 (100).

2-Acetyl-4-hydroxy-5-methoxy-3,4-dimethylcyclopent-2-enone (3g): Following the general procedure, 2,3-butanedione (0.15 g, 0.15 mL, 1.8 mmol) was treated with 2,4-bis(trimethylsilyloxy)-1-methoxy-1,3-pentadiene (0.50 g, 1.8 mmol) and $TiCl_4$ (0.69 g, 0.40 mL, 3.6 mmol). The product was purified by chromatography to give **3g** as a colourless oil (88 mg, 25%, *ds* = 1:1.2). ^{1}H NMR ($CDCl_3$, 250 MHz, ppm): δ = 1.36 (s, 3 H, 4-CH_3), 2.36 (s, 3 H, 3-CH_3), 2.45 (s, 3 H, CH_3C=O), 3.72 (s, 3 H, CH_3O), 3.96 (s, 1 H, 5-H). ^{13}C NMR ($CDCl_3$, 62.9 MHz, ppm): δ = 12.15, 21.64, 29.99 (4-CH_3, 3-CH_3, *C*H_3C=O), 59.11 (CH_3O), 78.20 (C-4), 90.32 (C-5), 134.05 (C-2), 182.17 (C-3), 195.90, 198.08 (2 × C=O). MS (70 eV, EI): *m*/*z* (%) = 198 (4) [M$^+$]; the exact molecular mass for $C_{10}H_{14}O_4$ *m*/*z* = 198.0892±2 ppm [M$^+$] was confirmed by HRMS (EI, 70 eV).

Ethyl 2,3-Diethyl-3-hydroxy-5-oxocyclopent-1-enecarboxylate (3h): Following the general procedure, 3,4-hexanedione (0.24 g, 0.26 mL, 2.1 mmol) was treated with 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (0.55 g, 2.0 mmol, 1 equiv.) and $TiCl_4$ (0.44 mL, 0.76 g, 4.0 mmol, 2 equiv.). The product was purified by chromatography to give **3h** as a colourless oil (125 mg, 28%). ^{1}H NMR ([D$_6$]acetone, 250 MHz, ppm): δ = 0.85 (t, *J* = 7.3 Hz, 3 H, CH_3CH$_2$COH), 1.19 (t, *J* = 7.6 Hz, 3 H, CH_3CH$_2$C=C), 1.28 (t, *J* = 7.0 Hz, 3 H, CH_3CH$_2$O), AB-signal (δ_A = 1.68, δ_B = 1.91, $J_{A,B}$ = 14.6, $J_{A,X}$ = $J_{B,X}$ = 7.3 Hz, 2 H, CH_3CH_2COH), AB-signal (δ_A = 2.41, δ_B = 2.60, $J_{A,B}$ = 18.3 Hz, 2 H, 4-H), overlapped by 2.48−2.74 (m, 2 H, CH$_2$C=C), 4.23 (q, *J* = 7.0 Hz, 2 H, CH$_2$O), 4.54 (s, 1 H, OH). ^{13}C NMR ([D$_6$]acetone, 62.9 MHz, ppm): δ = 8.64, 13.54, 14.39 (*C*H_3CH$_2$COH, *C*H_3CH$_2$C=C, *C*H_3CH$_2$O), 20.65, 31.62 (*C*H$_2$COH, *C*H$_2$C=C), 48.96 (C-4), 61.16 (CH$_2$O), 79.86 (C-3), 133.69 (C-1), 164.13 (CO_2Et), 185.76 (C-2), 199.68 (C=O). MS (70 eV, EI): *m*/*z* (%) = 226 (12) [M$^+$], 197 (59), 181 (14), 151 (100); the exact molecular mass for $C_{12}H_{18}O_4$ *m*/*z* = 226.1205±2 ppm [M$^+$] was confirmed by HRMS (EI, 70 eV).

2-Acetyl-3,4-diethyl-4-hydroxycyclopent-2-enone (3i): Following the general procedure 3,4-hexanedione (0.28 mL, 0.26 g, 2.2 mmol, 1 equiv.) was treated with 2,4-bis(trimethylsilyloxy)-1,3-pentadiene

(0.53 g, 2.3 mmol, 1 equiv.) and $TiCl_4$ (0.48 mL, 0.83 g, 2 equiv.). The product was purified by chromatography to give **3i** as a colourless oil (70 mg, 16%). ^1H NMR ($CDCl_3$, 250 MHz, ppm): δ = 0.88 (t, J = 7.5 Hz, 3 H, CH_3CH$_2$COH), 1.22 (t, J = 7.5 Hz, 3 H, CH_3CH$_2$C=C), 1.70, 1.94 (2 × m, 2 × 1 H, CH_2COH), overlapped by 1.98 (s, 1 H, OH), 2.47 (s, 3 H, CH_3CO), 2.54, 2.66 (2 × m, 2 × 1 H, CH$_3$CH$_2$C=C), overlapped by AB-signal (δ_A = 2.52, δ_B = 2.69, $J_{A,B}$ = 18.4 Hz, 2 H, 5-H). ^{13}C NMR ($CDCl_3$, 62.9 MHz, ppm): δ = 8.31, 13.48 (*C*H$_3$CH$_2$COH, *C*H$_3$CH$_2$C=C), 20.51, 31.24, 31.34 (*C*H$_2$C=C, *C*H$_2$COH, *C*H$_3$CO), 48.63 (CH_2), 79.71 (COH), 137.82 (CH$_2$C=*C*), 188.00 (CH$_2$*C*=C), 197.47, 201.56 (2 × C=O). IR (Film): $\tilde{\nu}$ = 3428 (br), 2974 (m), 2940 (m), 2882 (m), 1711 (s), 1692 (s), 1601 (m), 1463 (m), 1361 (m), 1331 (m), 1299 (m), 1189 (m), 1034 (m) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 196 (10) [M^+]; the exact molecular mass for $C_{11}H_{16}O_3$ *m*/*z* = 196.1099±2 ppm [M^+] was confirmed by HRMS (EI, 70 eV).

Methyl 2,3-Diethyl-3-hydroxy-4-methyl-5-oxocyclopent-1-enecarboxylate (3j): Following the general procedure, 3,4-hexanedione (0.27 mL, 0.25 g, 2.1 mmol, 1 equiv.) was treated with 1,3-bis(trimethylsilyloxy)-1-methoxy-1,3-pentadiene (0.55 g, 2.1 mmol, 1 equiv.) and $TiCl_4$ (0.46 mL, 0.79 g, 4.2 mmol, 2 equiv.). The product was purified by chromatography to give **3j** as a colourless oil (100 mg, 21%, *ds* = 5:1). The main isomer **3j** could be separated by a second chromatographic procedure as a colourless oil (19 mg, 4%). ^1H NMR ($CDCl_3$, 250 MHz, ppm): δ = 0.90 (t, J = 7.4 Hz, 3 H, CH_3CH$_2$COH), 1.16 (d, J = 7.6 Hz, 3 H, 4-CH$_3$), 1.23 (t, J = 7.6 Hz, 3 H, CH_3CH$_2$C=C), AB-signal (δ_A = 1.66, δ_B = 1.92, $J_{A,B}$ = 14.8, $J_{A,X}$ = $J_{B,X}$ = 7.4 Hz, 2 H, CH$_3$CH_2COH), 2.48 (q, J = 7.6 Hz, 1 H, 4-H), 2.56−2.82 (m, 2 H, CH$_3$CH_2C=C), 3.84 (s, 3 H, CH_3O). Besides **3j** an open-chain minor component was isolated (22 mg, 4%). **Methyl 5-ethyl-5-hydroxy-4-methyl-3,6-dioxooctanoate:** ^1H NMR ($CDCl_3$, 250 MHz, ppm): δ = 0.74 (t, J = 7.4 Hz, 3 H, CH_3CH$_2$COH), 1.06 (d, J = 7.2 Hz, 3 H, CH_3CH), overlapped by 1.08 (t, J = 7.2 Hz, 3 H, 8-H), AB-signal (δ_A = 1.61, δ_B = 1.80, $J_{A,B}$ = 14.8, $J_{A,X}$ = $J_{B,X}$ = 7.4 Hz, 2 H, CH$_3$CH_2COH), 2.53 (q, J = 7.2 Hz, 1 H, 7-H), overlapped by 2.54 (q, J = 7.2 Hz, 1 H, 7-H), 3.01 (q, J = 7.2 Hz, 1 H, 4-H), AB-signal (δ_A = 3.57, δ_B = 3.68, $J_{A,B}$ = 16.4 Hz, 2 H, 2-H), overlapped by 3.73 (s, 3 H, CH_3O), 4.04 (s, 1 H, OH). ^{13}C NMR ($CDCl_3$, 62.9 MHz, ppm): δ = 7.28, 7.55, 11.65 (C-8, *C*H$_3$CH$_2$COH, 4-CH$_3$), 30.44, 30.78 (C-7, *C*H$_2$COH), 47.93 (C-2), 52.14, 53.00 (C-4, CH_3O), 82.59 (C-5), 167.44 (CO_2Me), 206.38, 213.57 (2 × C=O). MS (DCI, NH_3): *m*/*z* (%) = 279 (99) [M + NH_4^+ + NH_3], 262 (100) [M + NH_4^+]. $C_{12}H_{20}O_5$ (244.3): calcd. C 58.98, H 8.26; found C 59.32, H 8.12.

Ethyl 2-Ethyl-3-hydroxy-3-methyl-5-oxocyclopent-1-enecarboxylate (3k) and Ethyl 3-Ethyl-3-hydroxy-2-methyl-5-oxocyclopent-1-enecarboxylate (3k′): Following the general procedure, 2,3-pentanedione (0.24 mL, 0.23 g, 2.2 mmol, 1 equiv.) was treated with 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (0.60 g, 2.2 mmol, 1 equiv.) and $TiCl_4$ (0.48 mL, 0.83 g, 4.4 mmol, 2 equiv.). The product was purified by chromatography to give **3k** as a colourless oil and as a mixture of regioisomers (210 mg, 45%, **3k**/**3k′**, 5:1, crude product: 9:1). ^1H NMR ($CDCl_3$, 250 MHz, ppm): δ = 1.24 (t, J = 7.6 Hz, 3 H, CH_3CH$_2$C=C), 1.33 (t, J = 7.2 Hz, 3 H, CH_3CH$_2$O), 1.53 (s, 3 H, 3-CH$_3$), 2.54−2.79 (2 × m, 2 × 2 H, CH$_2$C=C, 4-H), 4.30 (q, J = 7.2 Hz, 2 H, CH_2O). ^{13}C NMR ($CDCl_3$, 62.9 MHz, ppm): δ = 13.37, 13.86 (*C*H$_3$CH$_2$C=C, *C*H$_3$CH$_2$O), 20.36 (*C*H$_2$C=C), 26.01 (3-CH$_3$), 51.24 (C-4), 60.90 (CH_2O), 76.02 (C-3), 130.74 (C-1), 163.11 (CO_2Et), 188.30 (C-2), 200.48 (C=O). MS (70 eV, EI): *m*/*z* (%) = 212 (44) [M^+], 197 (8), 183 (40), 167 (46), 166 (100); the exact molecular mass for $C_{11}H_{16}O_4$ *m*/*z* = 212.1049±2 ppm [M^+] was confirmed by HRMS (EI, 70 eV).

3-Ethyl-4-hydroxy-2-(2-methoxyethanoyl)-4-methylcyclopent-2-enone (3l) and 4-Ethyl-4-hydroxy-2-(2-methoxyethanoyl)-3-methylcyclopent-2-enone (3l′): Following the general procedure, 2,3-pentanedione (0.26 mL, 0.25 g, 2.4 mmol, 1 equiv.) was treated with 2,4-bis(trimethylsilyloxy)-5-methoxy-1,3-pentadiene (0.65 g, 2.4 mmol, 1 equiv.) and $TiCl_4$ (0.52 mL, 0.90 g, 4.8 mmol, 2 equiv.). The product was purified by chromatography to give **3l** as a colourless oil (180 mg, 35%, **3l**/**3l′** = 4:1). **3 *l*:** ^1H NMR ($CDCl_3$, 250 MHz, ppm): δ = 1.22 (t, J = 7.5 Hz, 3 H, CH_3CH$_2$C=C), 1.52 (s, 3 H, 4-CH$_3$), 1.60−1.95 (m, 2 H, CH_2COH), 2.65 (s, 2 H, 5-H), overlapped by 2.65−2.87 (m, 2 H, *C*H$_2$C=C), 3.44 (s, 3 H, OCH_3), 4.40−4.60 (m, 2 H, 2 × CH_2OMe). ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ = 13.43 (*C*H$_3$CH$_2$C=C), 20.77 (*C*H$_2$C=C), 26.12 (4-CH$_3$), 51.23 (C-5), 59.01 (CH_3O), 76.32 (C-4), 78.05 (CH_2OMe), 133.95 (C-2), 193.04 (C-3), 195.50, 202.26 (C=O).

3l′: ^1H NMR ($CDCl_3$, 250 MHz, ppm): δ = 0.83 (t, J = 7.4 Hz, 3 H, CH_3CH$_2$COH), 1.60−1.95 (m, 2 H, CH_2COH), 2.33 (s, 3 H, 3-CH$_3$), 2.64 (s, 2 H, 5-H), overlapped by 3.44 (s, 3 H, CH_3O), 4.40−4.60 (m, 2 H, CH_2OMe). ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ = 8.02, 13.15 (*C*H$_3$CH$_2$COH, 3-CH$_3$), 30.63 (CH$_2$COH), 47.95 (C-5), 59.01 (CH_3O), 77.98 (CH_2OMe), 79.00 (C-4), 135.47 (C-2), 187.81 (C-3), 195.43, 201.77 (C=O). MS (70 eV, EI): *m*/*z* (%) = 212 (48) [M^+], 183 (29), 167 (92), 99 (100); the exact molecular mass for $C_{11}H_{16}O_4$ *m*/*z* = 212.1049±2 ppm [M^+] was confirmed by HRMS (EI, 70 eV).

Ethyl 5-Hydroxy-2,5-dimethyl-3,6-dioxoheptanoate (4): Following the general procedure, 2,3-butanedione (0.18 mL, 0.18 g, 2.0 mmol, 1 equiv.) was treated with 1,3-bis(trimethylsilyloxy)-1-ethoxy-2-methyl-1,3-butadiene (0.57 g, 2.0 mmol, 1 equiv.) and $TiCl_4$ (0.44 mL, 0.76 g, 4.0 mmol, 2 equiv.). The product was purified by chromatography to give **4** as a colourless oil (0.22 g, 53%, *ds*: A/B = 1:1). ^1H NMR ($CDCl_3$, 250 MHz, ppm): δ = 1.24−1.32 (diastereomer A, 2 × t, 2 × 3 H, 2 × CH_3CH$_2$O, 2 × d, 2 × 3 H, 2 × 2-CH$_3$, 2 × s, 2 × 3 H, 2 × 5-CH$_3$), 2.26 (diastereomer B, s, 3 H, CH$_3$C=O), overlapped by 2.27 (A, s, 3 H, CH$_3$C=O), AB-signal (A, δ_A = 2.81, δ_B = 2.88, $J_{A,B}$ = 5.4 Hz, 2 H, 4-H), AB-signal (B, δ_A = 3.25, δ_B = 3.28, $J_{A,B}$ = 16.1 Hz, 2 H, 4-H), 3.51 (B, q, J = 7.1 Hz, 1 H, 2-H), overlapped by 3.55 (A, q, J = 7.2 Hz, 1 H, 2-H), 4.14−4.24 (A and B, m, 2 × H, 2 × CH$_3$CH_2). **Diastereomer B:** ^{13}C NMR ($CDCl_3$, 62.9 MHz, ppm): δ = 13.91, 23.86, 25.16 (*C*H$_3$CH$_2$, 2-CH$_3$, 5-CH$_3$), 49.37 (C-4), 61.47 (CH$_2$O), 77.61 (C-5), 169.82 (CO_2Et), 206.01, 211.59 (CH$_3$*C*=O, C-3). **Diastereomer A:** ^3C NMR ($CDCl_3$, 62.9 MHz, ppm): δ = 12.23, 23.75, 24.79 (*C*H$_3$CH$_2$, 2-CH$_3$, 5-CH$_3$), 49.65 (C-4), 61.47 (CH$_2$O), 78.08 (C-5), 169.78 (CO_2Et), 207.00, 212.46 (CH$_3$*C*=O, C-3). MS (70 eV, EI): *m*/*z* (%) = 214 (12) [M^+]; the exact molecular mass for $C_{11}H_{18}O_4$ *m*/*z* = 214.1205±2 ppm [M^+] was confirmed by HRMS (EI, 70 eV).

General Procedure for the Cyclisation of 1,3-Bis(trimethylsilyloxy)-1,3-butadienes with 2,2-Dimethoxy-2-phenylethanal: To a CH_2Cl_2 solution of 2,2-dimethoxy-2-phenylethanal (0.9 equiv.) was added the 1,3-bis(trimethylsilyloxy)-1,3-butadiene **1** (1.0 equiv.) at −78 °C. A CH_2Cl_2 solution (5 mL) of $TiCl_4$ (3.0 equiv.) was then added to the reaction mixture. The solution was stirred for the required time and at the temperature indicated and was subsequently poured into a saturated aqueous solution of sodium hydrogencarbonate (150 mL). The organic layer was separated and the aqueous layer was repeatedly extracted with diethyl ether (4 × 80 mL). The combined organic layers were dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by repeated chromatography.

Methyl 3-Hydroxy-5-oxo-2-phenylcyclopent-1-enecarboxylate (6a): To a CH_2Cl_2 solution (25 mL) of 2,2-dimethoxy-2-phenylethanal (292 mg, 1.62 mmol) was added 1,3-bis(trimethylsilyloxy)-1-methoxy-1,3-butadiene (482 mg, 1.85 mmol) at −78 °C. A solution of $TiCl_4$ (1.15 g, 6.06 mmol) in CH_2Cl_2 (5 mL) was then added and the reaction mixture was stirred for 75 min at −78 °C. The temperature was raised to 0 °C within 20 min. The product was purified by chromatography (50 g silica gel, column 2.5 × 25 cm, petroleum ether/diethyl ether, 3:1) to give **6a** as an orange oil (62 mg, 17%). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 2.56 (dd, ^2J = 12, ^3J = 2 Hz, 1 H, 4-H), 2.68 [m, 1 H, CH(O*H*)], 2.98 (dd, ^2J = 12, ^3J = 4 Hz, 1 H, 3-H), 3.73 (s, 3 H, OCH_3), 5.42 (dd, ^3J = 2, ^3J = 4 Hz, 1 H, CH_2−C*H*(OH)), 7.42−7.56 (m, 5 H, Ph). ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT, ppm): δ = 44.42 (C-4), 52.43 (CH_3, OCH_3), 69.49 (C-3), 128.41, 128.84, 131.42 (5 × CH, 5 × Ph-CH), 131.34 (Ph-C), 133.10 (C-2), 164.76 (CO_2), 172.186 (C-1), 200.07 (C-5). IR (neat): $\tilde{\nu}$ = 3445 (br, OH), 2953 (m, Ar-H), 1738 (s, C=O), 1707 (s), 1620 (s), 1495 (w), 1436 (m), 1350 (s), 1238 (s), 1062 (s), 1017 (m), 928 (w), 800 (w), 780 (m), 728 (m), 694 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 232 (100) [M$^+$], 200 (58), 198 (20), 172 (44), 171 (22), 145 (18), 144 (42), 129 (71); the exact molecular mass for $C_{13}H_{12}O_4$ *m*/*z* = 232.0735±2 ppm [M$^+$] was confirmed by HRMS (EI, 70 eV).

2-Methoxyethyl 3-Hydroxy-5-oxo-2-phenylcyclopent-1-enecarboxylate (6b): To a CH_2Cl_2 solution (10 mL) of 2,2-dimethoxy-2-phenylethanal (438 mg, 2.43 mmol) was added 1,3-bis(trimethylsilyloxy)-1-(2-methoxyethoxy)-1,3-butadiene (822 mg, 2.70 mmol) at −78 °C. A CH_2Cl_2 solution (5 mL) of $TiCl_4$ (1.67 g, 8.80 mmol) was then added and the solution was stirred for 75 min at −78 °C. The temperature was raised to 0 °C within 20 min. The product was purified by chromatography (50 g silica gel, 2.5 × 25 cm, petroleum ether/diethyl ether, 3:1 to pure ether) to give **6b** as a deep yellow oil (112 mg, 16%). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 2.46 (dd, ^2J = 12, ^3J = 2 Hz, 1 H, 4-H), 2.91 (dd, ^2J = 12, ^3J = 4 Hz, 1 H, 4-H), 3.21 (s, 3 H, OCH_3), 3.48 (m, 2 H, C*H*$_2$-OCH_3), 4.32 (m, 2 H, CO_2CH_2), 5.54 (dd, ^3J = 2, ^3J = 4 Hz, 1 H, 3-H), 7.36−7.58 (m, 5 H, Ph). ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT, ppm): δ = 44.45 (C-4), 58.62 (CH_3, OCH_3), 64.11 (CH_2, *C*H$_2$-OCH_3), 69.37 (CO_2*C*H$_2$), 69.80 (C-3), 128.54, 128.68, 131.18 (5 × CH, 5 × Ph-CH), 131.45 (Ph-C), 133.13 (C-2), 164.25 (CO_2), 171.90 (C-1), 199.97 (C-5). IR (neat): $\tilde{\nu}$ = 3429 (br, OH), 2932 (w, Ar-H), 1737 (s, C=O), 1707 (s), 1621 (m), 1447 (m), 1734 (m), 1339 (m), 1236 (m), 1196 (m), 1128 (m), 1031 (m), 864 (w), 757 (m), 695 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 276 (2) [M$^+$].

Isobutyl 3-Hydroxy-5-oxo-2-phenylcyclopent-1-enecarboxylate (6c): To a CH_2Cl_2 solution (10 mL) of 2,2-dimethoxy-2-phenylethanal (483 mg, 2.68 mmol) was added 1,3-bis(trimethylsilyloxy)-1-isobutoxy-1,3-butadiene (958 mg, 3.17 mmol) at −78 °C. A solution of $TiCl_4$ (1.84 g, 9.70 mmol) was then added and the reaction mixture was stirred for 1.5 h at −78 °C. The temperature was raised within 20 min to 0 °C. The product was purified by chromatography (50 g silica gel, 2.5 × 25 cm, petroleum ether/diethyl ether, 1:2) to give **6c** (120 mg, 16%, R_f = 0.45 in petroleum ether/diethyl ether, 1:2) as an orange oil. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 0.78 (d, ^3J = 3 Hz, 6 H, 2 × CH_3), 1.68−1.89 [m, 1 H, C*H*$(CH_3)_2$], 2.46 (dd, ^2J = 12, ^3J = 2 Hz, 1 H, 4-H), 2.92 (dd, ^2J = 12, ^3J = 4 Hz, 1 H, 4-H), 3.42−3.78 (br. s, 1 H, OH), 3.88 [d, ^3J = 3 Hz, 2 H, C*H*$_2$−CH$(CH_3)_2$], 5.34 (dd, ^3J = 2, ^3J = 4 Hz, 1 H, 3-H), 7.38−7.54 (m, 5 H, Ph). ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT, ppm): δ = 18.70, 18.71 (CH_3, 2 × CH_3), 27.24 [*C*H$(CH_3)_2$], 44.45 (C-4), 69.38 (C-3), 71.56 (CO_2*C*H$_2$), 128.28, 128.68, 131.04 (5 × Ph-CH), 131.64 (Ph-C), 133.40 (C-2), 164.44 (*C*O$_2$CH$_2$), 172.06 (C, C-1), 200.18 (C-5). IR (neat): $\tilde{\nu}$ = 3436 (br, OH), 2962 (w, Ar-H), 2876 (w), 1733 (s, C=O), 1621 (m), 1469 (m), 1446 (m), 1379 (m), 1348 (m), 1236 (s), 1199 (m), 1014 (s), 798 (w), 729 (m). 695 (w). MS (EI, 70 eV): *m*/*z* (%) = 274 (3) [M$^+$], 256 (5), 220 (6), 219 (33), 201 (100); the exact molecular mass for $C_{16}H_{18}O_4$ *m*/*z* = 274.1205±2 ppm [M$^+$] was confirmed by HRMS (EI, 70 eV).

Benzyl 3-Hydroxy-5-oxo-2-phenylcyclopent-1-enecarboxylate (6d): To a CH_2Cl_2 solution (10 mL) of 2,2-dimethoxy-2-phenylethanal (535 mg, 2.97 mmol) was added 1-benzyloxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (1.11 g, 3.30 mmol) at −78 °C. A solution of $TiCl_4$ (2.04 g, 10.8 mmol) was then added and the mixture was stirred for 2 h at −78 °C. The temperature was raised within 20 min to 0 °C. The product was purified by chromatography (50 g silica gel, 2.5 × 25 cm, petroleum ether/diethyl ether, 1:2) to give **6d** (43 mg, 5%) as a slightly brownish solid. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 2.54 (dd, ^2J = 12, ^3J = 2 Hz, 1 H, 4-H), 2.98 (dd, ^2J = 12, ^3J = 4 Hz, 1 H, 4-H), 5.22 (s, 2 H CH_2-Ph), 5.38 (dd, ^3J = 2, ^3J = 4 Hz, 1 H, 3-H), 7.16−7.51 (m, 10 H, Ph). ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT, ppm): δ = 44.43 (C-4), 67.32 (CH_2, CH_2-Ph), 69.67 (C-3), 128.39, 128.49, 131.62, 128.91 (Ph-CH), 131.28 (C, Ph*C*−C=C), 133.86 (C, Ph*C*−CH_2), 134.70 (C-2), 164.02 (CO_2), 171.64 (C-1), 199.56 (C-5). IR (neat): $\tilde{\nu}$ = 3450 (br), 2925 (w, Ar-H), 1731 (s, C=O), 1695 (m), 1621 (w), 1456 (w), 1381 (m), 1227 (m), 1188 (m), 1058 (w), 903 (m), 750 (m), 696 (w), 602 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 308 (1) [M$^+$], 280 (2), 235 (1), 217 (2), 202 (39), 184 (78), 91 (100).

Isopropyl 3-Hydroxy-5-oxo-2-phenylcyclopent-1-enecarboxylate (6e): To a CH_2Cl_2 solution (10 mL) of 2,2-dimethoxy-2-phenylethanal (498 mg, 2.76 mmol) was added 1,3-bis(trimethylsilyloxy)-1-isopropyloxy-1,3-butadiene (627 mg, 2.17 mmol) at −78 °C. A solution of $TiCl_4$ (1.39 g, 7.33 mmol) was then added and the mixture was stirred for 105 min at −78 °C. The temperature was raised within 20 min to 0 °C. The product was purified by chromatography (50 g silica gel, 2.5 × 25 cm, petroleum ether/diethyl ether, 1:2) to give **6e** (51 mg, 10%) as a yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 1.14 [d, ^3J = 8 Hz, 3 H, CH$(CH_3)_2$], 1.16 [d, ^3J = 8 Hz, 3 H, CH$(CH_3)_2$], 2.49 (dd, ^2J = 12, ^3J = 2 Hz, 1 H, 4-H), 2.96 (dd, ^2J = 12, ^3J = 4 Hz, 1 H, 4-H), 3.15−3.41 (br. s, 1 H, OH), 5.12 [m, 1 H, C*H*$(CH_3)_2$], 5.38 (dd, ^3J = 2, ^3J = 4 Hz, 1 H, 3-H), 7.22−7.58 (m, 5 H, Ph). ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT, ppm): δ = 21.23, 21.53 (2 × CH_3, 2 × CH_3), 44.49 (C-4), 69.50 (C-3), 128.46, 128.70, 131.14 (3 × CH, 3 × Ph-CH), 131.57 (Ph-C), 134.29 (C-2), 163.93 (CO_2), 171.01 (C-1), 200.07 (C-5). IR (neat): $\tilde{\nu}$ = 3437 (br, OH), 2982 (w, Ar-H), 1732 (s, C=O), 1621 (m), 1447 (w), 1372 (m), 1238 (m), 1202 (m), 1104 (m), 1004 (w), 910 (w), 833 (w), 695 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 260 (22) [M$^+$], 246 (3), 218 (100), 201 (52).

2-Benzoyl-4-hydroxy-3-phenylcyclopent-2-enone (6f): To a CH_2Cl_2 solution (10 mL) of 2,2-dimethoxy-2-phenylethanal (178 mg, 0.99 mmol) was added 1,3-bis(trimethylsilyloxy)-1-phenyl-1,3-butadiene (336 mg, 1.10 mmol) at −78 °C. A solution of $TiCl_4$ (686 mg, 3.61 mmol) was then added and the mixture was stirred for 1 h at −78 °C. The temperature was raised to 0 °C within 30 min. The product was purified by chromatography (50 g silica gel, 2.5 × 25 cm, petroleum ether/diethyl ether, 1:2) to give **6f** (37 mg, 14%, R_f = 0.38 in petroleum ether/diethyl ether, 1:1) as a yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 2.56 (dd, ^2J = 12, ^3J = 2 Hz, 1 H, 5-H), 2.98 (dd, ^2J = 12, ^3J = 4 Hz, 1 H, 5-H), 3.24−3.82 (br. s, 1 H, OH), 5.42 (dd, ^3J = 2, ^3J = 4 Hz, 1 H, 4-H), 7.18−7.84 (m, 10 H, Ph). ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT, ppm): δ = 44.81 (C-5), 69.43 (C-4), 128.72, 128.84, 128.92, 129.29, 131.20, 134.27 (6 × CH, 6 × Ph-CH), 131.37 (C, Ph*C*−C=O), 135.36 (C,

Ph*C*−C=C), 139.81 (C-3), 170.17 (C-2), 194.59 (O=CPh), 201.94 (C-1). IR (neat): $\tilde{\nu}$ = 3430 (br), 3061 (w, Ar-H), 2926 (w, Ar-H), 1710 (s, C=O), 1660 (s), 1597 (s), 1579 (s), 1494 (w), 1448 (s), 1344 (w), 1238 (s), 1177 (s), 1160 (m), 1060 (m), 1001 (m), 980 (w), 912 (w), 841(w), 779 (m), 736 (s), 689 (m), 647 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 278 (23) [M^+], 122 (38), 105 (100), 86 (65), 84 (100), 77 (68).

Methyl 3-Hydroxy-4-methyl-5-oxo-2-phenylcyclopent-1-enecarboxylate (6g): To a CH_2Cl_2 solution (10 mL) of 2,2-dimethoxy-2-phenylethanal (269 mg, 1.49 mmol) was added 1,3-bis(trimethylsilyloxy)-1-methoxy-4-methyl-1,3-butadiene (455 mg, 1.66 mmol) at −78 °C. A solution of $TiCl_4$ (1.04 g, 5.48 mmol) was then added and the mixture was stirred for 1 h at −78 °C. The temperature was raised within 30 min to 0 °C and the mixture was stirred for 30 min at 0°. The product was purified by chromatography (40 g silica gel, 3 × 20 cm, petroleum ether/diethyl ether, 1:2) to give **6g** (201 mg, 55%, *trans*/*cis* = 3:1) as a yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 1.22 (d, ^3J = 4 Hz, 3 H, CH_3), 1.31 (d, ^3J = 4 Hz, 1 H, C*H*CH_3), 2.62−2.81 (m, 1 H, OH), 3.78 (s, 3 H, OCH_3), 5.32 (d, ^3J = 4 Hz, 1 H, 3-H), 7.24−7.60 (m, 5 H, Ph). ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT, ppm): δ = 10.06 (CH_3, CH_3), 45.47 (C-4), 52.43 (CH_3, OCH_3), 71.83 (C-3), 128.46, 128.51, 128.82 (3 × CH, 3 × Ph-CH), 131.25 (Ph-C), 131.89 (C-2), 165.11 (CO_2), 170.29 (C-1), 203.78 (C-5). IR (KBr): $\tilde{\nu}$ = 3373 (br, OH-stretching), 3062 (m), 2924 (w, Ar-H), 1736 (s, C=O), 1707 (s), 1622 (m), 1437 (m), 1350 (m), 1234 (m), 1120 (m), 1033 (m), 846 (w), 696 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 246 (36) [M^+], 214 (25), 129 (19), 121 (90), 105 (100), 77 (42).

Ethyl 4-Ethyl-3-hydroxy-5-oxo-2-phenyl-1-enecarboxylate (6h): To a CH_2Cl_2 solution (10 mL) of 2,2-dimethoxy-2-phenylethanal (339 mg, 1.88 mmol) was added 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-hexadiene (617 mg, 2.04 mmol) at −78 °C. A solution of $TiCl_4$ (1.19 mg, 6.27 mmol) was then added and the mixture was stirred for 1 h at −78 °C. The temperature was raised within 20 min to 0 °C. The product was purified by chromatography (50 g silica gel, 2.5 × 25 cm, petroleum ether/diethyl ether, 1:2) to give **6h** (250 mg, 48%, *trans*/*cis* = 15:1) as a slight yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 1.12−1.38 (m, 6 H, 2 × CH_3), 1.52 (m, 2 H, 4-H_2), 2.56 (m, 1 H, 4-H), 3.42−3.53 (m, 1 H, OH), 4.18−4.30 (m, 2 H, O*C*$H_2$$CH_3$), 5.39 (d, ^3J = 3 Hz, 1 H, 3-H), 7.31−7.64 (m, 5 H, Ph). ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT, ppm): δ = 12.46 (C−CH_2*C*H_3), 13.87 (CH_3, O−CH_2*C*H_3), 18.74 (C−*C*$H_2$$CH_3$), 52.33 (C-4), 61.62 (O*C*H_2), 71.64 (C-3), 128.46, 128.79, 130.07 (3 × CH, 3 × Ph-CH), 131.17 (Ph-C), 134.24 (C-2), 164.64 (CO_2), 169.33 (C-1), 203.02 (C-5). IR (neat): $\tilde{\nu}$ = 3444 (br), 3062 (m), 3029 (m), 2974 (w, Ar-H), 1734 (s, C=O), 1706 (s), 1624 (m), 1496 (w), 1449 (m), 1372 (m), 1343 (m), 1230 (m), 1113 (m), 1023 (m), 860 (w), 763 (w), 698 (m) cm^{-1}. MS (CI, NH_3, 70 eV): *m*/*z* (%) = 566 (12) [2 M + NH_4^+], 292 (100) [M + NH_4^+].

General Procedure for the One-Pot Cyclisation of 1,3-Dicarbonyl Dianions with 1,2-Diketones: A THF solution (15 mL, 25 mL for liquid starting materials) of diisopropylamine (2.3 equiv.) and *n*-butyllithium (2.3 equiv., solution in *n*-hexane) was stirred at 0 °C for 30 min. The 1,3-dicarbonyl compound **7** was added (1.1 equiv., solids were dissolved in 10 mL of THF) and the mixture was stirred for 1 h. To the solution was added the 1,2-diketone (1.0 equiv., solids were dissolved in 10 mL of THF) at −78 °C. The solution was stirred for 1 h and was then slowly warmed to 20 °C. To the solution was added silica gel (0.5 g/ 1 mmol of 1,2-diketone) and the mixture heated to refluxed (TLC control). After cooling the mixture, hydrochloric acid (5 mL, 10%), a saturated aqueous solution of sodium chloride (10 mL) and diethyl ether (50 mL) were added and the aqueous layer was repeatedly extracted with diethyl ether. The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo.

Ethyl 5-Ethyl-5-hydroxy-3,6-dioxooctanoate (8b): Starting with ethyl acetoacetate (143 mg, 1.1 mmol, 1.1 equiv.), diisopropylamine (253 mg, 2.5 mmol, 2.5 equiv.), *n*-butyllithium (2.5 mmol, 2.5 equiv.) and hexane-3,4-dione (114 mg, 1.0 mmol), **8b** was isolated by chromatography (petroleum ether /diethyl ether, 1.5:1, R_f = 0.30, 40 g silica gel, Ø = 2.0 cm) as a yellow oil (91 mg, 37%). Reaction time: 35 min. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 0.74 (t, ^3J = 7 Hz, 3 H, CH_3), 1.01 (t, ^3J = 7 Hz, 3 H, CH_3), 1.21 (t, ^3J = 7 Hz, 3 H, CH_3), 1.57 (q, ^3J = 7 Hz, 2 H, CH_2), 2.55 (q, ^3J = 7 Hz, 2 H, CH_2), 2.88 (d, ^2J = 17 Hz, 1 H, CH_2), 3.13 (d, ^2J = 17 Hz, 1 H, CH_2), 3.41 (s, 2 H, CH_2), 4.12 (q, ^3J = 7 Hz, 2 H, O−CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm): δ = 7.10, 7.41, 13.93 (CH_3), 29.64, 31.42 (CH_2, ethyl), 49.84, 49.94 (CH_2, HOC−*C*H_2, O−CH_2), 61.38 (CH_2, CO−*C*H_2−CO), 80.32 (C, COH), 166.62 (C, CO, ester), 203.03, 214.09 (C, CO, ketone). IR (neat): $\tilde{\nu}$ = 3466 (w) cm^{-1}, 2979 (m), 2940 (m), 1742 (s), 1713 (s), 1650 (m), 1461 (m), 1372 (m), 1180 (m), 1142 (m), 1031 (m), 808 (w). MS (EI, 70 eV): 187 (39), 141 (68), 99 (35), 57 (100). MS (CI, NH_3, 70 eV): *m*/*z* (%) = 506 (84) [2M + NH_4]$^+$, 262 (100) [M + NH_4]$^+$. $C_{12}H_{20}O_5$ (244.29): calcd. C 59.00, H 8.25; found C 59.18, H 7.97.

One-Pot Synthesis of Ethyl 2,3-Diethyl-3-hydroxy-5-oxocyclopent-1-enecarboxylate (9b): The reaction was carried out following the general procedure vide infra. Starting with ethyl acetoacetate (140 mg, 1.1 mmol), diisopropylamine (273 mg, 2.7 mmol), *n*-butyllithium (2.7 mmol) and hexane-3,4-dione (1.0 mmol), **9b** was isolated by chromatography as a colourless oil (61%). For spectroscopic data, see **3h**.

Ethyl 3-Hydroxy-2,3-dimethyl-5-oxocyclopent-1-enecarboxylate (9a): For spectroscopic data of **9a**, see **3a** (vide supra).

Ethyl 3,3a,4,5,6,7-Hexahydro-3a-hydroxy-2-oxoinden-1-carboxylate (9c): Starting with ethyl acetoacetate (281 mg, 2.2 mmol, 2.0 equiv.), diisopropylamine (546 mg, 5.4 mmol, 5.0 equiv.), *n*-butyllithium (5.4 mmol, 5.0 equiv.) and cyclohexane-1,2-dione (121 mg, 1.1 mmol), **9c** was isolated by chromatography (petroleum ether/diethyl ether, 1:2, R_f = 0.20, Ø = 2.0 cm) as a yellow oil (62 mg, 25%). Reaction time: 20 h. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 1.34 (t, ^3J = 7 Hz, 3 H, CH_3), 1.45 (dt, ^2J = 13, ^3J = 4 Hz, 1 H, CH_2), 1.57 (dd, ^2J = 13, ^3J = 4 Hz, 1 H, CH_2), 1.60−1.75 (m, 2 H, CH_2), 1.87 (ddt, ^2J = $^3J_{trans}$ = 13, $^3J_{cis}$ = 4 Hz, 1 H, CH_2), 2.00−2.15 (m, 1 H, CH_2), 2.20−2.40 (m, 1 H, CH_2), 2.51 (d, ^2J = 19 Hz, 1 H, *H*−HC−CO), 2.51 (d, ^2J = 19 Hz, 1 H, H−*H*C−CO), 3.20−3.35 (m. 1 H, =C−CH_2), 4.31 (q, ^3J = 7 Hz, 2 H, O−CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm): δ = 14.04 (CH_3), 20.68, 26.33, 27.05, 39.99, 50.32 (CH_2), 61.01 (O−CH_2), 74.13 (C, COH), 128.88 (C, C=*C*−CO), 162.94 (C, CO, ester), 186.30 (C, *C*=C−CO), 200.51 (C, CO, ketone). IR (neat): $\tilde{\nu}$ = 3423 (m) cm^{-1}, 2934 (s), 2859 (m), 1740 (s), 1719 (s), 1645 (s), 1447 (m), 1375 (s), 1318 (s), 1263 (s), 1207 (s), 1132 (m), 1028 (s), 854 (w), 619 (w), 591 (w). MS (EI, 70 eV): *m*/*z* (%) = 224 (34) [M^+], 178 (95), 151 (45), 150 (100), 43 (62), 41 (46); the exact molecular mass for $C_{12}H_{16}O_4$ *m*/*z* = 224.1049±2 ppm [M^+] was confirmed by HRMS (EI, 70 eV). $C_{12}H_{16}O_4$ (224.26): calcd. C 64.27, H 7.19; found C 63.95, H 6.97.

Ethyl 3-hydroxy-3-methyl-3-propylcyclopent-1-ene-1-carboxylate and Ethyl 3-Hydroxy-3-methyl-5-oxo-2-propylcyclopent-1-ene-1-carboxylate (9d): Starting with ethyl acetoacetate (143 mg, 1.1 mmol, 1.1 equiv.), diisopropylamine (253 mg, 2.5 mmol, 2.5 equiv.), *n*-bu-

tyllithium (2.5 mmol, 2.5 equiv.) and hexane-2,3-dione (114 mg, 1.0 mmol), 9d was isolated by chromatography (petroleum ether/diethyl ether, 1:3, R_f = 0.29, 40 g silica gel, Ø = 2.0 cm) as a yellow oil (86 mg, 37%). Reaction time: 26 h. Isomeric ratio: 4-methyl isomer (major)/3-methyl isomer (minor), 3:1. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 0.95 (t, ^3J = 7 Hz, 3 H, CH_3, minor), 1.03 (t, ^3J = 7 Hz, 3 H, CH_3, major), 1.10−1.30 (m, 1 H, minor and major), 1.34 (t, ^3J = 7 Hz, 2 H, CH_3, minor and major), 1.53 (s, 3 H, CH_3, major), 1.55−1.75 (m, 2 H, major), 1.75−1.90 (m, 2 H, minor), 2.29 (s, 3 H, CH_3, minor), 2.45−2.75 (m, 3 H, minor and major), 4.31 (q, ^3J = 7 Hz, 2 H, O−CH_2, minor and major). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm): δ = 13.02, 14.15, 14.26 (CH_3, minor), 14.08, 14.82, 26.27 (CH_3, major), 17.45, 40.14 (CH_2, minor), 22.91, 29.48 (CH_2, major), 48.75 (CO−CH_2, minor), 51.43 (CO−CH_2, major), 61.13 (O−CH_2, minor and major) 76.27 (C, COH, major), 78.38 (C, COH, minor), 131.41 (C, C=*C*−CO, major), 131.95 (C, C=*C*−CO, minor), 163.06 (C, CO, ester, minor), 163.35 (C, CO, ester, major), 184.07 (C, *C*=C−CO, minor), 186.49 (C, *C*=C−CO, major), 200.07 (C, CO, ketone, minor), 200.43 (C, CO, ketone, major). IR (neat): $\tilde{\nu}$ = 3439 (m) cm^{-1}, 2971 (s), 2945 (m), 2876 (m), 1741 (s), 1629 (m) 1463 (m), 1375 (s), 1304 (m), 1201 (s), 1102 (m), 1032 (s), 955 (w), 598 (w). MS (EI, 70 eV): *m*/*z* (%) = 226 (28) [M$^+$], 183 (69), 181 (52), 180 (98), 162 (45), 137 (100), 43 (41); the exact molecular mass for $C_{12}H_{18}O_4$ *m*/*z* = 226.1205±2 ppm [M$^+$] was confirmed by HRMS (EI, 70 eV).

Ethyl 3-Hydroxy-5-oxo-2,3-diphenylcyclopent-1-ene-1-carboxylate (9e): Starting with ethyl acetoacetate (159 mg, 1.2 mmol, 1.1 equiv.), diisopropylamine (280 mg, 2.8 mmol, 2.5 equiv.), *n*-butyllithium (2.8 mmol, 2.5 equiv.) and benzil (232 mg, 1.1 mmol), **9e** was isolated by chromatography (petroleum ether/diethyl ether, 1.5:1, R_f = 0.20, 40 g silica gel, Ø = 2.0 cm) as a yellow solid (263 mg, 73%). Reaction time: 26 h. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 1.16 (t, ^3J = 7 Hz, 3 H, CH_3), 3.00 (d, ^2J = 18 Hz, 1 H, *H*−HC−CO), 3.12 (d, ^2J = 18 Hz, 1 H, H−*H*C−CO), 4.24 (q, ^3J = 7 Hz, 2 H, O−CH_2), 7.10−7.50 (m, 10 H, Ph). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm): δ = 13.83 (CH_3), 55.05 (CO−CH_2), 61.61 (O−CH_2), 80.84 (C, COH), 124.50, 128.35, 128.63, 128.91 (CH, Ph, *ortho* and *meta*), 127.78, 130.48 (CH, Ph, *para*), 131.24, 134.31, 142.56 (C, Ph, C=*C*−CO), 163.84 (C, CO, ester), 173.82 (C, *C*=C−CO), 199.86 (C, CO, ketone). IR (neat): $\tilde{\nu}$ = 3463 (s) cm^{-1}, 3062 (w), 2979 (m), 2931 (m), 1737 (s), 1712 (s), 1618 (m), 1447 (m), 1373 (m), 1336 (s), 1211 (s), 1102 (m), 1026 (m), 772 (m), 701 (m). MS (EI, 70 eV): *m*/*z* (%) = 322 (59) [M$^+$], 276 (100), 105 (59); the exact molecular mass for $C_{20}H_{18}O_4$ *m*/*z* = 322.1205±2 ppm [M$^+$] was confirmed by HRMS (EI, 70 eV). Analysis: calcd. for: $C_{20}H_{18}O_4$ (322.36): calcd. C 74.52, H 5.63; found C 74.43, H 5.36.

Compound 9f: Starting with methyl acetoacetate (128 mg, 1.1 mmol, 1.1 equiv.), diisopropylamine (253 mg, 2.5 mmol, 2.5 equiv.), *n*-butyllithium (2.5 mmol, 2.5 equiv.) and hexane-3,4-dione (114 mg, 1.0 mmol), **9f** was isolated by chromatography (petroleum ether/diethyl ether, 1:3, R_f = 0.25, 40 g silica gel, Ø = 2.0 cm) as a yellow oil (91 mg, 44%). Reaction time: 19 h. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 0.92 (t, ^3J = 7 Hz, 3 H, CH_3), 1.24 (t, ^3J = 8 Hz, 3 H, CH_3), 1.50−2.10 (AB system, additional splitting by ^3J-coupling, 2 H, HOC−CH_2), 2.40−2.80 (m. 2 H, =C−CH_2), partly overlapped by 2.52 (d, ^2J = 19 Hz, 1 H, *H*−HC−CO) and 2.72 (d, ^2J = 19 Hz, 1 H, H−*H*C−CO), 3.85 (s, 3 H, O−CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm): δ = 8.28, 13.26 (CH_3), 20.50, 30.98 (CH_2), 48.41 (CO−CH_2), 51.99 (O−CH_3), 79.63 (C, COH), 131.71 (C, C=*C*−CO), 163.71 (C, CO, ester), 188.43 (C, *C*=C−CO), 200.24 (C, CO, ketone). IR (neat): $\tilde{\nu}$ = 3440 (s) cm^{-1}, 2945 (s), 2884 (m), 1741 (s), 1718 (s), 1627 (s), 1439 (s), 1355 (s), 1308 (s), 1221 (s), 1152 (m), 1028 (s), 794 (w), 591 (w). MS (EI, 70 eV): *m*/*z* (%) = 212 [M$^+$] (12), 183 (79), 151 (100), 125 (40).

Compound 9g: Starting with 2-(methoxyethyl)acetoacetate (176 mg, 1.1 mmol, 1.1 equiv.), diisopropylamine (253 mg, 2.5 mmol, 2.5 equiv.), *n*-butyllithium (2.5 mmol, 2.5 equiv.) and hexane-3,4-dione (114 mg, 1.0 mmol), **9g** was isolated by chromatography (pentane/diethyl ether, 1:3, R_f = 0.22, 40 g silica gel, Ø = 2.0 cm) as a yellow oil (109 mg, 42%). Reaction time: 25 h. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ = 0.90 (t, ^3J = 7 Hz, 3 H, CH_3), 1.25 (t, ^3J = 8 Hz, 3 H, CH_3), 1.72 (dq, ^3J = 7, ^2J = 14 Hz, 1 H, H−*H*C−COH), 1.91 (dq, ^3J = 8, ^2J = 14 Hz, 1 H, *H*−HC−COH), 2.52 (d, ^2J = 18 Hz, 1 H, *H*−HC−CO), partly overlapped by 2.45−2.80 (m. 2 H, C=C−CH_2), overlapped by 2.70 (d, ^2J = 18 Hz, 1 H, H−*H*C−CO), 3.39 (s, 3 H, O−CH_3), 3.67 (dd, $^3J_1$ = $^3J_2$ = 5 Hz, 2 H, O−CH_2), 4.40 (dd, $^3J_1$ = $^3J_2$ = 5 Hz, 2 H, COO−CH_2). (dd, $^3J_1$ = $^3J_2$ = 5 Hz, 2 H, O−CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm): δ = 8.36, 13.37 (CH_3), 20.50, 31.10 (CH_2), 48.49 (CO−CH_2), 58.85 (O−CH_3), 63.79, 70.14 (O−CH_2), 79.51 (C, O−C), 132.11 (C, C=*C*−CO), 163.01 (C, CO, ester), 187.11 (C, *C*=C−CO), 199.69 (C, CO, ketone). IR (neat): $\tilde{\nu}$ = 3436 (s) (cm^{-1}), 2974 (s), 2940 (s), 1742 (s), 1721 (s), 16.29 (m), 1461 (s), 1380 (s), 1305 (s), 1198 (s), 1131 (s), 1097 (s), 1036 (s), 864 (w), 590 (w). MS (EI, 70 eV): *m*/*z* (%) = 256 (50) [M$^+$], 181 (63), 180 (70), 151 (100), 59 (79), 58 (77), 45 (55), 43 (42); the exact molecular mass for $C_{13}H_{20}O_5$ *m*/*z* = 256.1311±2 ppm [M$^+$] was confirmed by HRMS (EI, 70 eV). $C_{13}H_{20}O_5$ (256.30): calcd. C 60.92, H 7.87; found C 60.72, H 7.64.

Compound 9h: Starting with *tert*-butyl acetoacetate (174 mg, 1.1 mmol, 1.1 equiv.), diisopropylamine (253 mg, 2.5 mmol, 2.5 equiv.), *n*-butyllithium (2.5 mmol, 2.5 equiv.) and hexane-3,4-dione (114 mg, 1.0 mmol), **9h** was isolated by chromatography (petroleum ether/diethyl ether, 1:1.5, R_f = 0.29, 40 g silica gel, Ø = 2.0 cm) as a yellow oil (78 mg, 31%). Reaction time: 25 h. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 0.90 (t, ^3J = 7 Hz, 3 H, CH_3), 1.25 (t, ^3J = 7 Hz, 3 H, CH_3), 1.55 (s, 9 H CH_3), overlapped by 1.50−2.00 (AB system, additional splitting by ^3J-coupling, 2 H, HOC−CH_2), 2.47 (d, ^2J = 18 Hz, 1 H, *H*−HC−CO), partly overlapped by 2.45−2.80 (m, 2 H, =C−CH_2), partly overlapped by 2.68 (d, ^2J = 18 Hz, 1 H, H−*H*C−CO). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm): δ = 8.38, 13.49 (CH_3), 20.23, 31.08 (CH_2), 48.46 (CO−CH_2), 28.09 (3 × CH_3, C(*C*H_3) $_3$), 79.64, 82.34 (C, O−C), 133.77 (C, C=*C*−CO), 162.01 (C, CO, ester), 184.28 (C, *C*=C−CO), 200.04 (C, CO, ketone). IR (neat): $\tilde{\nu}$ = 3438 (s) (cm^{-1}), 2976 (s), 2938 (s), 1735 (s), 1714 (s), 1621 (s), 1461 (s), 1369 (s), 1158 (s), 1095 (s), 1016 (s), 896 (m), 843 (s), 810 (m), 736 (w), 589 (m). MS (EI, 70 eV): *m*/*z* (%) = 86 (100), 58 (51), 57 (65), 44 (58), 43 (52). MS (CI, NH_3, 70 eV): *m*/*z* (%) = 526 [2M + NH_4^+] (56), 272 (71) [M + NH_4^+], 216 (100). $C_{14}H_{22}O_4$ (254.33): calcd. C 66.12, H 8.72; found C 65.86, H 8.45.

Compound 9i: Starting with *tert*-butyl acetoacetate (178 mg, 1.1 mmol, 1.1 equiv.), diisopropylamine (259 mg, 2.6 mmol, 2.5 equiv.), *n*-butyllithium (2.6 mmol, 2.5 equiv.) and benzil (316 mg, 1.0 mmol), **9i** was isolated by chromatography (petroleum ether/diethyl ether, 3:1, R_f = 0.22, Ø = 1.5 cm) as a slight yellow solid 163 mg (45%). Reaction time: 19 h. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 1.37 (s, 9 H, CH_3), 2.85 (br, 1 H, OH), 2.99 (d, ^2J = 18 Hz, 1 H, *H*−HC−CO), 3.08 (d, ^2J = 18 Hz, 1 H, H−*H*C−CO), 7.10−7.45 (m, 10 H, Ph). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm): δ = 27.79 (CH_3), 54.96 (CH_2), 80.70, 82.98 (C, O−C), 124.58, 128.17, 128.56, 128.81 (CH, Ph, *ortho* and *meta*),

127.68, 130.11 (CH, Ph, *para*), 131.64 (C, C=*C*−CO), 135.39, 142.65 (C, Ph), 162.93 (C, CO, ester), 172.81 (C, *C*=C−CO), 200.10 (C, CO, ketone). IR (KBr): $\tilde{\nu}$ = 3465 (m) (cm^{-1}), 2975 (m), 1748 (s), 1450 (m), 1361 (s), 1250 (m), 1160 (s), 1057 (m), 702 (m), 538 (w). MS (CI, NH_3, 70 eV): *m*/*z* (%) = 368 $[M + NH_4]^+$ (42), 312 (100).

Compound 9j: Starting with *tert*-butylacetoacetate (178 mg, 1.1 mmol, 1.1 equiv.), diisopropylamine (259 mg, 2.6 mmol, 2.5 equiv.), *n*-butyllithium (2.6 mmol, 2.5 equiv.) and phenanthrene-9,10-dione (213 mg, 1.0 mmol), **9j** was isolated by chromatography (petroleum ether/diethyl ether, 1:1, R_f = 0.33, 40 g silica gel, Ø = 1.5 cm) as a colourless solid (109 mg, 31%). Reaction time: 18 h. ^{1}H NMR (250 MHz, [D$_6$]DMSO, ppm): δ = 0.60 (s, 9 H, CH_3), 1.63 (s, 1 H, OH), 2.05 (d, ^2J = 18 Hz, 1 H, CH_2), 2.45 (d, ^2J = 18 Hz, 1 H, CH_2), 6.50−6.70 (m, 4 H, CH, Ar), 6.70−6.80 (m, 2 H, CH, Ar), 7.17 (d, ^3J = 7 Hz, 1 H, CH, Ar), 7.27 (d, ^3J = 7 Hz, 1 H, CH, Ar). ^{13}C NMR (50.3 MHz, [D$_6$]DMSO, ppm): δ = 27.59 (CH_3), 47.63 (CH_2), 73.51 (C, *C*−O−C=O), 82.64 (C, COH), 124.44, 124.68, 127.50, 128.01, 128.46, 128.99. 129.10, 132.40 (CH, Ar), 126.43 (C, C=*C*−CO), 131.39, 131.52, 133.48, 137.70 (C, Ar), 163.40 (C, CO, ester), 166.34 *C*=C−CO), 200.40 (C, CO, ketone). IR (KBr): $\tilde{\nu}$ = 3466 (s) (cm^{-1}), 2983 (w), 1716 (s), 1701 (s), 1637 (s), 1451 (m), 1353 (s), 1228 (s), 1159 (s), 1051 (m), 998 (m), 759 (m), 734 (m). MS (EI, 70 eV): *m*/*z* (%) = 248 (75) $[M^+]$, 292 (96), 275 (100), 274 (70), 202 (50), 57 (50); the exact molecular mass for $C_{22}H_{20}O_4$ *m*/*z* = 348.1362±2 ppm $[M^+]$ was confirmed by HRMS (EI, 70 eV).

Compound 9k: Starting with benzyl acetoacetate (212 mg, 1.1 mmol, 1.1 equiv.), diisopropylamine (253 mg, 2.5 mmol, 2.5 equiv.), *n*-butyllithium (2.5 mmol, 2.5 equiv.) and hexane-3,4-dione (114 mg, 1.0 mmol), **9k** was isolated by chromatography (petroleum ether/diethyl ether, 1:2, R_f = 0.28, 40 g silica gel, Ø = 1.5 cm) as a yellow oil (38 mg, 13%). Reaction time: 25 h. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ = 0.89 (t, ^3J = 7 Hz, 3 H, CH_3), 1.17 (t, ^3J = 8 Hz, 3 H, CH_3), 1.60−2.00 (AB system, additional splitting by ^2J−coupling, 2 H, HOC−CH_2), 2.51 (d, ^2J = 18 Hz, 1 H, *H*−HC−CO), partly overlapped by 2.50−2.80 (m, 2 H, =C−CH_2), partly overlapped by 2.68 (d, ^2J = 18 Hz, 1 H, H−*H*C−CO), 5.30 (s, 2 H, O−CH_2), 7.30−7.50 (m, 5 H, CH, Ph). ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm): δ = 8.34, 13.39 (CH_3), 20.43, 31.07 (CH_2), 48.46 (CO−CH_2), 66.74 (O−CH_2), 79.71 (C, O−C), 128.23, 128.50 (CH, Ph, *ortho* and *meta*), 128.26 (CH, Ph, *para*), 131.96, 135.28 (C, Ph, C=*C*−CO), 162.87 (C, CO, ester), 187.47 (C, *C*=C−CO), 199.78 (C, CO, ketone). IR (neat): $\tilde{\nu}$ = 3441 (s) (cm^{-1}), 3037 (w), 2976, (m), 2939 (m), 1736 (s), 1715 (s), 1633 (m), 1458 (m), 1384 (m), 1305 (m), 1196 (m), 1097 (m), 1024 (m), 749 (w), 699 (w). MS (EI, 70 eV): *m*/*z* (%) = 288 (2) $[M^+]$, 164 (35), 91 (100); the exact molecular mass for $C_{16}H_{18}O_4$ *m*/*z* = 288.1362±2 ppm $[M^+]$ was confirmed by HRMS (EI, 70 eV).

Compound 9l: Starting with ethyl 3-oxohexanoate (174 mg, 1.1 mmol, 1.1 equiv.), diisopropylamine (253 mg, 2.5 mmol, 2.5 equiv.), *n*-butyllithium (2.5 mmol, 2.5 equiv.) and hexane-3,4-dione (114 mg, 1.0 mmol), **9l** was isolated by chromatography (pentane/diethyl ether, 2:1, R_f = 0.21, 40 g silica gel, Ø = 2.0 cm) as a yellow oil (124 mg, 49%, two diastereomers, *dr* = 4:1). Reaction time: 25 h. ^{1}H NMR (300 MHz, $CDCl_3$, major, ppm): δ = 0.82 (t, ^3J = 8 Hz, 3 H, CH_3), 1.03 (t, ^3J = 7 Hz, 3 H, CH_3), 1.18 (t, ^3J = 8 Hz, 3 H, CH_3), 1.30 (t, ^3J = 7 Hz, 3 H, CH_3), 1.50−1.70 (m, 2 H, CH_2), 1.70−1.95 (m, 2 H, CH_2), 2.25 (t, ^3J = 7 Hz, 1 H, CH), 2.40−2.60 (m, 1 H, CH_2), 2.60−2.80 (m, 1 H, CH_2), 4.26 (q, ^3J = 7 Hz, 2 H, O−CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm): δ = 8.29 (CH_3, major, minor), 9.55, 13.19, 13.20 (CH_3, minor) 12.47, 13.47, 14.06 (CH_3, major), 17.21, 20.25, 29.09 (CH_2, minor), 20.50, 21.35, 32.13 (CH_2, major), 54.96 (CH, major), 60.88 (O−CH_2, minor), 61.01 (O−CH_2, major), 61.20 (CH, minor), 81.22 (C, O−C, major), 83.00 (C, O−C, minor), 131.28 (C, C=*C*−CO, minor), 131.66 (C, C=*C*−CO, major), 163.09 (C, CO, ester, minor), 163.40 (C, CO, ester, major), 184.70 (C, *C*=C−CO, minor), 185.82 (C, *C*=C−CO, major), 199.51 (C, CO, ketone, minor), 203.4 (C, CO, ketone, major). IR (neat): $\tilde{\nu}$ = 3467 (s) (cm^{-1}), 2974 (s), 2939 (s), 1736 (s), 1715 (s), 1630 (m), 1463 (s), 1375 (s), 1306 (s), 1211 (s), 1096 (m), 1025 (s), 895 (w), 797 (w), 592(w). MS (EI, 70 eV): *m*/*z* (%) = 254 (3) $[M^+]$, 225 (67), 179 (100), 57 (37); the exact molecular mass for $C_{14}H_{22}O_4$ *m*/*z* = 254.1518±2 ppm $[M^+]$ was confirmed by HRMS (EI, 70 eV).

Compound 9m: Starting with methyl 4-methoxyacetoacetate (161 mg, 1.1 mmol, 1.1 equiv.), diisopropylamine (253 mg, 2.5 mmol, 2.5 equiv.), *n*-butyllithium (2.5 mmol, 2.5 equiv.) and hexane-3,4-dione (114 mg, 1.0 mmol), **9m** was isolated by chromatography (40 g silica gel, Ø = 2.0 cm). Reaction time: 22 h. Diastereomer 1 (petroleum ether/diethyl ether, 2:1, R_f = 0.29): Yield: 29 mg (12%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.83 (t, ^3J = 8 Hz, 3 H, CH_3), 1.19 (t, ^3J = 8 Hz, 3 H, CH_3), 1.55 (dq, ^3J = 8, ^2J = 14 Hz, 1 H, H−*H*C−COH), 1.91 (dq, ^3J = 8, ^2J = 14 Hz, 1 H, *H*−HC−COH), 2.57 (dq, ^3J = 8, ^2J = 12 Hz, 1 H, H−*H*C−C=), 2.81 (dq, ^3J = 8, ^2J = 12 Hz, 1 H, *H*−HC−C=), 3.37 (s, 1 H, CH), 3.62 (s, 3 H, O−CH_3), 3.81 (s, 3 H, O−CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm): δ = 7.99, 13.55 (CH_3), 21.20, 29.92 (CH_2), 51.98, 59.07 (O−CH_3), 78.00 (C, O−C), 81.12 (CH), 129.66 (C, C=*C*−CO), 163.15 (C, CO, ester), 189.63 (C, *C*=C−CO), 197.41 (C, CO, ketone). IR (neat): $\tilde{\nu}$ = 3486 (m) (cm^{-1}), 2971 (m), 2940 (m), 1744 (s), 1722 (s), 1626 (m), 1461 (m), 1439 (m), 1308 (m), 1220 (s), 1105 (m), 1024 (m), 790 (w). MS (EI, 70 eV): *m*/*z* (%) = 213 (40), 210 (55), 57 (100), 43 (48). MS (CI, NH_3, 70 eV): *m*/*z* (%) = 502 (100) $[2M + NH_4^+]$, 260 (45) $[M + NH_4^+]$. Diastereomer 2 (petroleum ether/diethyl ether, 1:1.5, R_f = 0.29): Yield: 79 mg (33%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.65 (t, ^3J = 8 Hz, 3 H, CH_3), 1.20 (t, ^3J = 8 Hz, 3 H, CH_3), 1.72 (dq, ^3J = 8, ^2J = 14 Hz, 1 H, H−*H*C−COH), 1.99 (dq, ^3J = 8, ^2J = 14 Hz, 1 H, *H*−HC−COH), 2.54 (dq, ^3J = 8, ^2J = 12 Hz, 1 H, H−*H*C−C=), 2.83 (dq, ^3J = 8, ^2J = 12 Hz, 1 H, *H*−HC−C=), 3.68 (s, 3 H, O−CH_3), 3.81 (s, 3 H, O−CH_3), 3.91 (s, 1 H, CH). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm): δ = 9.16, 13.16 (CH_3), 20.57, 29.55 (CH_2), 52.00, 60.29 (O−CH_3), 82.57 (C, O−C), 90.00 (CH), 129.52 (C, C=*C*−CO), 162.84 (C, CO, ester), 183.65 (C, *C*=C−CO), 196.27 (C, CO, ketone). IR (neat): $\tilde{\nu}$ = 3460 (s) (cm^{-1}), 2977 (s), 2943 (s), 1741 (s), 1726 (s), 1618 (m), 1440 (s), 1310 (s), 1221 (s), 1129 (s), 1028 (s), 841 (w), 787 (w), 732 (m). MS (EI, 70 eV): *m*/*z* (%) = 242 (24) $[M^+]$, 213 (97), 210 (100); the exact molecular mass for $C_{12}H_{18}O_5$ *m*/*z* = 242.1154±2 ppm $[M^+]$ was confirmed by HRMS (EI, 70 eV).

Compound 9n: Starting with *N*,*N*-diethylacetylacetamide (173 mg, 1.1 mmol, 1.1 equiv.), diisopropylamine (253 mg, 2.5 mmol, 2.5 equiv.), *n*-butyllithium (2.5 mmol, 2.5 equiv.) and butane-2,3-dione (86 mg, 1.0 mmol), **9n** was isolated by chromatography (diethyl ether/acetone, 10:1, R_f = 0.21, 40 g silica gel, Ø = 2.0 cm) as a yellow oil (146 mg, 65%). Reaction time: 19 h. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 1.08 (t, ^3J = 7 Hz, 3 H, CH_3), 1.18 (t, ^3J = 7 Hz, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 2.06 (s, 3 H, CH_3), 2.58 (d, ^2J = 18 Hz, 1 H, CH_2), 2.68 (d, ^2J = 18 Hz, 1 H, CH_2), 3.14 (q, ^3J = 7 Hz, 2 H, CH_2), 3.46 (q, ^3J = 7 Hz, 2 H, CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm): δ = 11.18, 13.01, 14.36, 25.67 (CH_3), 39.21, 42.88 (CH_2), 51.19 (CO−*C*H_2), 77.63 (C, COH), 137.76 (C,

C=*C*−CO), 164.39 (C, CO, ester), 175.76 (C, *C*=C−CO), 200.65 (C, CO, ketone). IR (neat): $\tilde{\nu}$ = 3397 (s), 2978 (s), 2937 (s), 1711 (s), 1611 (s), 1442 (s), 1379 (s), 1326 (s), 1273 (s), 1226 (s), 1200 (s), 1089 (s), 949 (m), 651 (w), 589 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 225 (6) [M^+], 72 (100); the exact molecular mass for $C_{12}H_{19}NO_3$ *m/z* = 225.1365±2 ppm [M^+] was confirmed by HRMS (EI, 70 eV).

Compound 9o and *E*-10: Starting with *N*,*N*-diethylacetylacetamide (173 mg, 1.1 mmol, 1.1 equiv.), diisopropylamine (253 mg, 2.5 mmol, 2.5 equiv.), *n*-butyllithium (2.5 mmol, 2.5 equiv.) and hexane-3,4-dione (114 mg, 1.0 mmol), **9o** was isolated by chromatography (diethyl ether, 40 g silica gel, Ø = 2.0 cm). Reaction time: 20 h. Yield of **10**: 26 mg (10%) of a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.78 (t, ^3J = 8 Hz, 6 H, CH_3), 1.09 (t, ^3J = 7 Hz, 3 H, CH_3), 1.19 (t, ^3J = 7 Hz, 3 H, CH_3), 1.74 (q, ^3J = 8 Hz, 4 H, CH_2), 3.31 (q, ^3J = 7 Hz, 2 H, CH_2), 3.37 (q, ^3J = 7 Hz, 2 H, CH_2), 3.56 (s, 2 H, CO−CH_2−CO), 5.54 (s, 1 H, HC=C). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm): δ = 7.14 (2 X CH_3), 12.74, 14.29 (CH_3), 28.76 (2 × CH_2), 36.30, 40.41, 42.59 (CH_2), 95.23 (C, C=), 106.09 (CH), 165, 07 (C, CO, amide), 186.07, 206.72 (C, CO, ketone). IR (neat): $\tilde{\nu}$ = 2974 (m) (cm^{-1}), 1699 (m), 1649 (s), 1595 (m), 1460 (m), 1439 (m), 1382 (m), 1259 (w), 1138 (m), 1100 (m), 975 (w), 802 (w). MS (EI, 70 eV): 253 [M^+] (2), 225 (46), 100 (91), 72 (50), 58 (100), 43 (54). MS (CI, NH_3, 70 eV): *m/z* (%) = 507 (37) [2M + NH_4^+], 271 (52) [M + NH_4]$^+$, 254 (100) [M + H]$^+$; the exact molecular mass for $C_{14}H_{23}NO_3$ *m/z* = 253.1678±2 ppm [M^+] was confirmed by HRMS (EI, 70 eV). Yield of **9o** (R_f = 0.16): 80 mg (32%) of a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.83 (t, ^3J = 7 Hz, 3 H, CH_3), 1.00−1.40 (m, 9 H, CH_3), 1.66 (dq, ^3J = 8, ^2J = 14 Hz, 1 H, H−*H*C−COH), 1.88 (dq, ^3J = 8, ^2J = 14 Hz, 1 H, *H*−HC−COH), 2.30−2.55 (m, 2 H, C=C−*C*H_2), partly overlapped by 2.49 (d, ^2J = 18 Hz, 1 H, *H*−HC−CO), 2.60 (d, ^2J = 18 Hz, 1 H, H−*H*C−CO), 3.14 (q, ^3J = 7 Hz, 2 H, NCH_2), 3.25−3.50 (m, 2 H, NCH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm): δ = 8.46, 12.06, 12.54, 14.01 (CH_3), 20.21, 30.70 (CH_2), 38.84, 42.89 (N−CH_2), 48.21 (CO−CH_2), 79.95 (C, O−C), 138.16 (C, C=*C*−CO), 164.84 (C, CO, ester), 179.36 (C, *C*=C−CO), 201.26 (C, CO, ketone). IR (KBr): $\tilde{\nu}$ = 3269 (m) (cm^{-1}), 2977 (m), 2936 (m), 1707 (s), 1653 (m), 1603 (s), 1466 (m), 1383 (m), 1322 (m), 1174 (m), 1043 (m), 822 (w), 718 (w), 677 (w). MS (EI, 70 eV): 253 (15) [M^+], 72 (100). $C_{14}H_{23}NO_3$ (253.34): calcd. C 66.37, H 9.15, N 5.53; found C 66.39, H 8.95, N 5.37.

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