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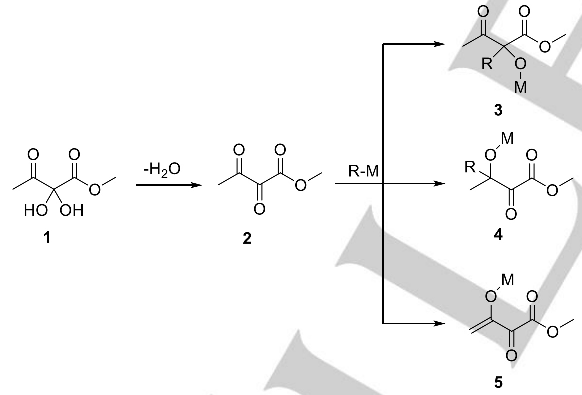
Addition of Mixed Alkenyl-Dialkyl Zincates to Vicinal Diketoesters

Lars Selter,[a] Klaus Harms,[a] and Ulrich Koert*[a]

Abstract: Methods for the regioselective alkylation, arylation and alkenylation of α,β-diketoesters using organozinc reagents are reported. Alkylation and arylation in α-position is possible using diorgano zinc compounds. Alkenylation can be achieved using mixed alkenyl-dineopentyl zincates.

Introduction

Vicinal tricarbonyl compounds (VTC) offer three sites for nucleophilic attack and are interesting building blocks for organic synthesis due to their high density of functional groups.[1,2,3] Given a coplanar structure of the three carbonyl groups the central keto group is most reactive. The high electrophilicity of the central carbonyl group results in the formation of stable hydrates. Deviation from the coplanar structure of the three carbonyl groups can result in attack of the nucleophile at one of the flanking ones as it was observed with the crotylboration of α,β-diketoamides.[4] The addition of organometallic reagents to vic-tricarbonyl compounds is complicated by enolate formation. For vic-diketoesters the situation is the following (Scheme 1): upon chemical (P_2O_5 or molecular sieves) or physical (thermic) dehydration of the hydrate **1** the tricarbonyl compound **2** is formed which can react with an organometallic reagent by attack at the α–position (→ **3**), attack at the β–position (→ **4**), or in formation of enolate **5**.

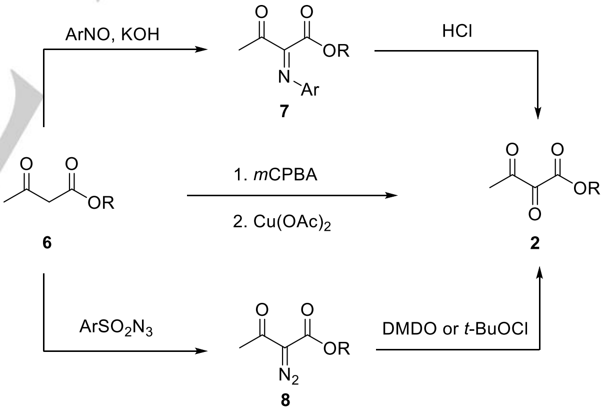


Scheme 1. Reactivity of vic-diketoester with organometallic reagents.

Organozinc reagents combine temperate reactivity with low basicity.[5] They should be good candidates for transferring alkyl, alkenyl and aryl groups to vic-tricarbonyl compounds. Here we report on the addition of organozinc reagents in particular zincates to vic-diketoesters.

Results and Discussion

A number of procedures have been developed for the preparation of vic-diketoester **2**, typically starting from easily accessible β-ketoester **6** (Scheme 2). Normally the hydrate is isolated, stored and converted to the vic-diketoester prior to use. In contrast to most other procedures the Sachs method avoids oxidative conditions.[6] Thereby nitrosobenzene derivatives are condensed with the β-ketoester followed by hydrolysis of the imino intermediate **7**. Alternatively stepwise oxidation first with *m*CPBA and then copper acetate gives access to the vic-diketoester **2**.[7] Probably the most common method, which is also used in this work, is the generation of a diazo compound **8** via Regitz diazo transfer and subsequent oxidation with DMDO or *t*-BuOCl.[8]



Scheme 2. Methods for the preparation of vic-diketoester **2**.

The synthesis of vic-diketoesters started from carboxylic acids **9** (Scheme 3), which were activated by CDI based on Masmune's procedure.[9] Reaction with potassium monomethyl malonate and subsequent decarboxylation gave access to β-keto methyl ester **10**. Cyclohexyl ester **11** was prepared by transesterification with cyclohexanol in toluene. Regitz diazo transfer to the corresponding α-diazo-β-ketoester and subsequent oxidation with *t*-BuOCl yielded the desired hydrates **12** and **13** in good overall yield (Table 1).

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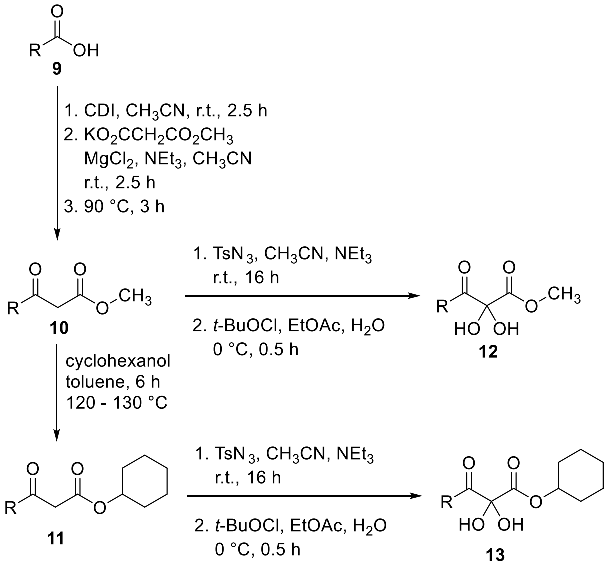


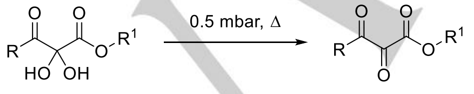
Scheme 3. Preparations of hydrates **12** and **13**.

Table 1. Syntheses of hydrates **12** and **13** according to Scheme 3.

Rest R =	Suffix	Yield **10**	Yield **11**	Yield **12**	Yield **13**
Ph	**a**	93%	99%	79%	66%
PhCH(CH2CH3)	**b**	89%	[b]	64%	[b]
Ph(CH2)3	**c**	93%	97%	50%	63%
CH(CH3)2	**d**	[a]	[b]	64%	[b]
p-methoxybenzene	**e**	89%	[b]	59%	[b]
3,5-dinitrobenzene	**f**	78%	[b]	65%	[b]

[a] commercially available, [b] not prepared.

The α,β-diketoesters **14** and **15** were freshly prepared prior to use by bulb-to-bulb distillation (90 to 180 ˚C) of hydrates **12** or **13** respectively (Scheme 4). Yields for the dehydration step were > 90% for all cases.

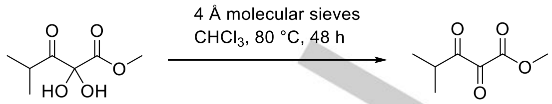


12
13

14, R^1 = Me
15, R^1 = cyclohexyl

Scheme 4. Preparation of the α,β-diketoesters **14** and **15**.

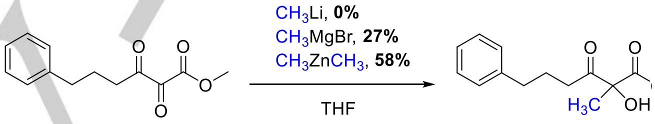
For the volatile α,β-diketoester **14d** dehydration was achieved by refluxing a solution of **12d** in chloroform in the presence of molecular sieves (4 Å) for 48 h (Scheme 5).



12d **14d**

Scheme 5. Dehydration of **12d** by molecular sieves.

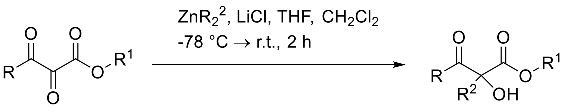
With α,β-diketoesters in hand, addition reactions with different organometallic compounds such as methyl lithium and methyl magnesium bromide were investigated (Scheme 6). For the reaction of methyl lithium with α,β-diketoester **14c** no methyl transfer was observed obviously due to enolate formation and subsequent side reactions. TLC control showed mainly decomposition. For the reaction with the corresponding Grignard reagent the α-methylated product **16c** was obtained in 27% yield only. Switching to ZnMe$_2$ gave a higher yield (58%) indicating that enolate formation could be reduced with the less basic dialkylzinc reagent.



14c **16c**

Scheme 6. Reaction of α,β-diketoester **14c** with different organometallic reagents.

For the reaction of diorgano zinc reagents with α,β-diketoesters **14** and **15** it was found that two equiv. of the diorgano zinc reagent and one equiv. of LiCl in THF/dichloromethane as solvents proved to be the optimal condition (Scheme 7, Table 2). ZnPh$_2$ was prepared from phenyl lithium and ZnCl$_2$.[10]



14, R^1 = Me
15, R^1 = cyclohexyl

16, R^1 = Me, R^2 = Me
17, R^1 = Me, R^2 = Et
18, R^1 = Me, R^2 = Ph
19, R^1 = cyclohexyl, R^2 = Me
20, R^1 = cyclohexyl, R^2 = Et
21, R^1 = cyclohexyl, R^2 = Ph

Scheme 7. Alkylation and arylation of vic-diketoesters **14** and **15** by dialkyl and diaryl zinc reagents.

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Table 2. Alkylation and arylation of vic-diketoester **14** according to Scheme 7.

Entry	R =	Suffix	Yield **16**	Yield **17**	Yield **18**
1	Ph	**a**	77%	85%	98%
2	PhCH(CH$_2$CH$_3$)	**b**	67% d.r. 1:1	64% d.r. 1.2:1	82% d.r. 10:1
3	Ph(CH$_2$)$_3$	**c**	65%	55%	63%
4	CH(CH$_3$)$_2$	**d**	66%[a]	52%[a]	14%[a]
5	*p*-methoxybenzene	**e**	74%	64%	80%
6	3,5-dinitrobenzene	**f**	20%	5%	-

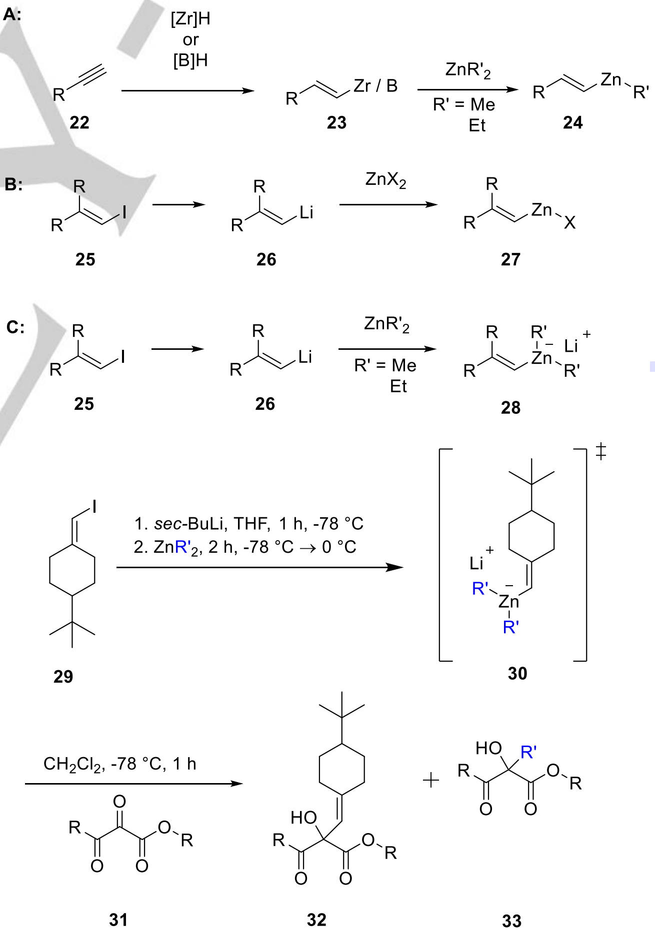
Table 2b. Alkylation and arylation of vic-diketoester **15** according to Scheme 7.

Entry	R =	Suffix	Yield **19**	Yield **20**	Yield **21**
7	Ph	**a**	79%	65%	73%
8	Ph(CH$_2$)$_3$	**c**	67%	59%	53%

[a] prepared from hydrate **12d**, yields given over 2 steps.

Depending on the substituent in γ-position of the α,β-diketoesters **14** and **15** moderate to very good yields were obtained for the alkylation and arylation products **16**-**21** using dialkyl/diaryl zinc reagents. In cases without acidic protons in γ-position excellent yields were obtained. (Table 2a, entry 1) With a branched chain in γ-position good yields were obtained and in case of **18b** even high diastereomeric ratios (entry 2). Electron rich aromatic substituents gave good yields (entry 5), while electron deficient aromatics (entry 6) had a negative impact on the reaction and only low yields were obtained. In this case the electrophilicity of the β-keto position is increased and therefore double alkylation (in α- and in β-position) was observed. For small branched chains (entry 4) and long linear chains (entry 3) yields between 52-66% were obtained. Comparison between methyl esters (Table 2a, entries 1 and 3) and the corresponding cyclohexyl esters (Table 2b, entries 7 and 8) showed no significant change in yield.

Mixed alkenyl zinc reagents provide an opportunity to transfer an alkenyl group to a carbonyl group.[5] Depending on the alkenyl substitution there are three paths to mixed alkenyl zinc reagents (Scheme 8). 2-Monosubstituted (*E*)-1-alkenyl zinc reagents **24** can be obtained via path A starting from alkynes **22** by hydrozirconation[11] or hydroboration[12] to give the corresponding alkenyl zircon or boron reagents **23** which are treated with diethyl or dimethyl zinc to get the mixed alkenyl-alkyl zinc reagent. 2,2-Disubstituted 1-alkenyl zinc reagents are accessible from 2,2-disubstitued alkenyl iodides **25** by iodine-lithium exchange to the corresponding alkenyl lithium intermediate **26** and subsequent transmetallation to zinc. This transmetallation can be accomplished either by treatment with ZnX$_2$ leading to an alkenyl-zinc halogenide reagent **27** (path B)[13] or by reaction of the alkenyl lithium intermediate **26** with a dialkyl zinc reagent resulting in a mixed dialkyl-alkenyl zincate **28** (path C)[14]. With the goal to study the transfer of alkenyl groups via mixed zincates the reaction of 2,2-disubstituted 1-alkenyl zinc reagents **30** with vic-diketoester **31** to yield the allylic alcohols **32** was carried out. The precursor for the mixed zincate **30**, the iodide **29**, was prepared from the corresponding ketone via Takai olefination.[15]



Scheme 8. General methods for the preparation of alkenyl-zinc reagents and alkenyl addition of mixed alkyl-alkenyl zincates **30** to α,β-diketoester **31**.

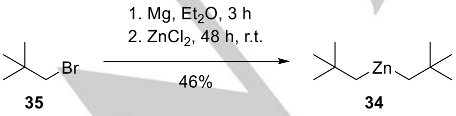
Attempts to add an alkenyl zinc bromide reagent of type **27** prepared from iodide **29** to vic-diketoesters **31** (path B) were unsuccessful. Therefore we turned our attention to path C using mixed dialkyl-alkenyl zinc reagents of type **28**/**30**. Following pathway C it was found that *in situ* formation of a mixed dimethyl-alkenyl zincate **30** and reaction with the α,β-diketoester **31** resulted in the formation of the desired α-alkenylated product **32** together with the undesired α-alkylated product **33** (Scheme 8). The mixed dimethyl alkenyl zincate was prepared by iodide-lithium exchange of vinyl iodide **29** with *sec*-BuLi at -78 °C and subsequent reaction with $ZnMe_2$ (Scheme 8). For complete zincate formation an increase of the reaction temperature to 0 °C after addition of $ZnMe_2$ was necessary. The mixed zincate was allowed to react with vic-diketoester **31** at low temperature (-78 °C). The overall yield for the addition of the mixed zincate was low and the amount of alkenyl transfer to **32** versus alkyl transfer to **33** was in a comparable range (Table 3). Attempts to repress alkyl transfer by lowering the reaction temperature were not successful.

Table 3. Addition of dimethyl-alkenyl zincate **30** to α,β-diketoester **31** results in transfer of the alkenyl group to **32** and the alkyl group to **33**.

Entry	α,β-Diketoester	Alkenyltransfer **32**[a]	Alkyltransfer **33**[b]
1	**15a**	8%	27%
2	**14c**	36%	13%
3	**15c**	20%	17%

[a] yield refers to applied vinyl iodide. [b] yield refers to applied VTC.

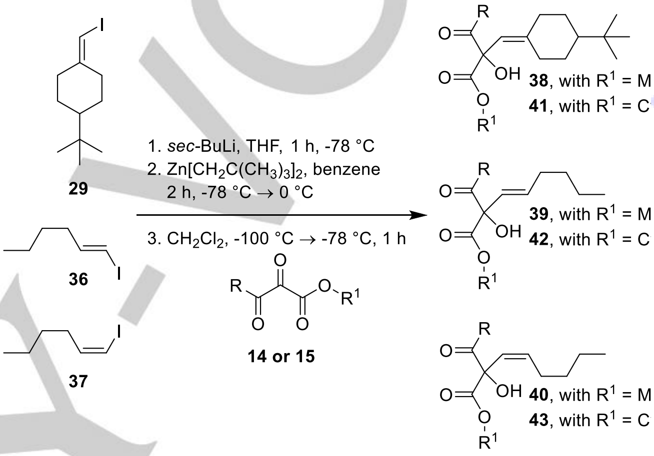
The undesired alkyl transfer should be less favourable when sterically demanding alkyl groups were introduced. A study on the addition of mixed dineopentyl zincates to enones reported that the neopentyl group is transferred very slowly.[16a] The trimethylsilylmethyl group[16b] and N,N-dimethylbenzylamine[16c] have also been used as dummy ligands with organozinc reagents. Therefore we decided to investigate the addition of alkenyl-dineopentyl zincates to α,β-diketoester **31**. Dineopentyl zinc **34** was prepared from neopentyl bromide **35** by transmetallation of neopentylmagnesium bromide in a variation of Schrock's procedure.[17]



Scheme 9. Preparation of dineopentyl zinc **34**.

In addition to iodide **29**, two other alkenyl iodides were prepared and used: *E*-alkenyl iodide **36** by hydroalumination of 1-hexyne[18], followed by iodolysis in 58% yield and *Z*-alkenyl iodide **37** by Stork-Zhao-olefination[19] from the corresponding aldehyde in 56% yield (Scheme 10).

A series of alkenylations (**29** + **14** → **38**, **36** + **14** → **39, 37** + **14** → **40, 29** + **15** → **41, 36** + **15** → **42, 37** + **15** → **43)** was examined using mixed alkyl-alkenyl zincates derived from dineopentyl zinc following Scheme 10 and the obtained results are summarized in Table 4.



Scheme 10. Alkenylation with vinyliodides **29**, **36**, **37** using dineopentyl zinc.

Table 4a. Synthesis of **38**, **39** and **40** with α,β-diketoester **14** according to Scheme 10.

Entry	α,β-Diketoester	Yield[a] of **38**	Yield of **39**	Yield of **40**
1	**14a**	82%	50%	15%
2	**14b**	45%	46%	40%
3	**14c**	60%	26%	20%
4	**14e**	61%	66%	13%
5	**14f**	-	-	-

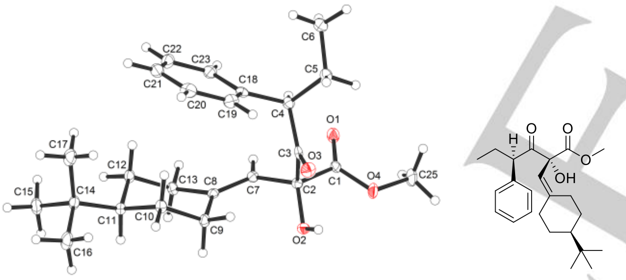
Table 4b. Synthesis of **41**, **42** and **43** with α,β-diketoester **15** according to Scheme 10.

Entry	α,β-Diketoester	Yield[a] of **41**	Yield of **42**	Yield of **43**
6	**15a**	75%	46%	15%
7	**15c**	44%	46%	-

[a] Yields refer to mixtures of diastereomers.

For the alkenylation of α,β-diketoesters using alkenyl dineopentyl zincates substituents in γ-position have an impact on the reaction and the best results were obtained for derivatives without enolizable protons in this position (Table 4a entry 1 and Table 4b entry 6). With the 2,2-disubstituted iodide **29** good results were obtained. In these cases two diastereomers were obtained, which could sometimes be separated (depending on the substituents). Notably the diastereomeric ratio differs from 1:1. Products **38** and **41** were obtained in very good yields for diketoester **14a** (82%) and **15a** (75%) respectively, showing again no significant difference between methyl ester (Table 4a entry 1) and the corresponding cyclohexyl ester (Table 4b entry 6).

The reaction is stereospecific with regard to the double bond configuration. With *E*-iodide **36** moderate yields of **39** or **42** (45-50%) were obtained, while *Z*-iodide **37** gave only low yields of **40** or **43** respectively. In case of a branched chain in γ-position (Table 4a entry 2) yields of 40-46% were obtained. The highest yield obtained with the Z-iodide **37** was observed for **40b** (40%). Alkenylation product **38b** was prepared in 45% overall yield. In this case, two diastereomers were obtained and separated by chromatography on silica. The main diastereomer could be crystallized and its stereostructure is shown together with the crystal structure[20] in Figure 1.



38b (main diastereomer)

Figure 1. Crystal structure of the main diastereomer of **38b**.

With an electron deficient aromatic substituent in γ-position no product could be obtained due to side reactions (Table 4a, entry 5). In case of an electron rich derivative (Table 4a, entry 4) a yield of 66% was obtained for product **39**. Reaction of **29** with diketoester **14e** gave access to **38** in 61% yield (d.r. 1.2:1), however some neopentyl transfer (17%) was observed as side reaction.

Conclusion

In summary a regioselective alkylation/arylation of a variety of α,β-diketo esters with dialkyl- and diarylzinc reagents was achieved in moderate to good yields for most examples. Limitations are observed for electron withdrawing groups in γ-position, because the β-position is activated resulting in double alkylation. Mixed alkenyl dineopentyl zincates were applied for alkenyl transfer to the α-carbonyl group of vic-diketo esters. Zincates prepared from a 2,2-disubsituted alkenyl iodide gave good results. In case of an *E*-alkenyl iodide moderate to good yields of the respective alkenylation products were obtained while a *Z*-vinyl iodide gave lower yields.

Experimental Section

General Methods:

All non-aqueous reactions were carried out using Schlenk technique with freshly dried and distilled solvents. Other solvents were distilled by rotary evaporation prior to use. ^{1}H-NMR spectra were recorded at 300 or 500 MHz, ^{13}C-NMR at 75 or 126 MHz, the solvent residue signals were used as internal standard and all spectra are reported in ppm. Mass spectra were recorded on a LTQ-FT or AccuTOF-GCv mass spectrometer. Melting points were recorded on a Mettler Toledo MP70 using one side open capillary tubes.

Complete experimental data for the synthesis of α,β-diketoesters (**General procedures 1-6**) is given in the Supporting information (SI). Complete experimental data for the addition reactions of organo zinc reagents (**General procedures 7, 8**) is given below. The SI consists of experimental procedures, experimental data and NMR-spectra of all new compounds.

General procedure 1 (GP1): preparation of methyl β-ketoesters
Under argon atmosphere to a solution of potassium monomethyl malonate (1.50 equiv.) in CH_3CN (8.5 mL/ mmol of $MgCl_2$) were added $MgCl_2$ (1.00 equiv.) and NEt_3 (3.20 equiv.). In a separate flask the respective acid (1.00 equiv.) was dissolved in CH_3CN (3.3 mL/ mmol of acid) and CDI (1.10 equiv.) was added. Both mixtures were stirred at r.t. for 2.5 h before the CDI-acid solution was added slowly to the malonate. The resulting reaction mixture was stirred at r.t. for 16 h before it was heated to 90 °C for 3 h. After cooling to r.t. it was filtered through a glass frit, rinsed with CH_3CN (3.5 mL/ mmol of acid) and solvent was removed under reduced pressure. The residue was taken up in CH_2Cl_2 (5 mL/ mmol of acid) and H_2O (2 mL/ mmol of acid) before citric acid was added (until two layers had been formed) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL/ mmol of acid), the combined organic layers were washed with H_2O (3 mL/ mmol of acid) dried with $MgSO_4$ and solvent was removed under reduced pressure. After silica gel column chromatography SCC (mixture of solvents given in the SI) the pure β-ketoester was obtained.

General procedure 2 (GP2): transesterification to cyclohexyl esters
Under argon atmosphere to a solution of the respective β–keto-methyl ester (1.00 equiv.) in dry toluene (1.6 mL/ mmol) was added cyclohexanol (1.20 equiv.). The reaction mixture was stirred at 130 °C while the solvent was slowly distilled off. The remaining solvent was removed under reduced pressure, the residue was purified by SCC (mixture of solvents given in the SI) to obtain the corresponding cyclohexyl ester.

General procedure 3 (GP3): preparation of α-diazo-β-ketoester with tosylazide

To a solution of the respective β-ketoester (1.00 equiv.) in CH_3CN (2 mL/ mmol), were added NEt_3 (1.00 equiv.) as well as tosylazide (1.00 equiv.) and it was stirred at r.t. for 16 h. The reaction mixture was concentrated and after SCC (mixture of solvents given in the SI) the pure α-diazo-β-ketoester was obtained.

General procedure 4 (GP4): preparation of α-diazo-β-ketoester with *p*ABSA

To a solution of the respective β-ketoester (1.00 equiv.) in CH_3CN (4.8 mL/ mmol), were added NEt_3 (1.50 equiv.) as well as *p*ABSA (1.50 equiv.) and the reaction mixture was stirred at r.t. for 16 h. It was filtered through sea sand and rinsed with CH_3CN (2 mL/ mmol of β-ketoester). The solvent was removed under reduced pressure and after SCC (mixture of solvents given in the SI) the pure α-diazo-β-ketoester was obtained.

General procedure 5 (GP5): Preparation of α-dihydroxy-β-ketoester

The respective α-diazo-β-ketoester (1.00 equiv.) was dissolved in EtOAc (7.0 mL/ mmol of α-diazo-β-ketoester), H_2O (2.20 equiv.) was added and the reaction mixture was cooled to 0 °C. *t*-BuOCl (1.50 equiv.) was added slowly and it was stirred at 0 °C for 30 min. Solvent was removed under reduced pressure and after SCC (mixture of solvents given in the SI) as well as crystallisation from *n*-pentane/ Et_2O for 16 h at -20 °C the α-dihydroxy-β-ketoester was obtained as colourless to slightly yellow solid or wax-like compound.

General procedure 6 (GP6): preparation of α,β-diketoester

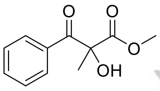
The respective α-dihydroxy-β-ketoester (1.00 equiv.) was distilled in a bulb-to-bulb-still at 0.5 mbar and the appropriate temperature (given in the SI) for 1.5-4.0 h, yielding the corresponding α,β-diketoester as yellow oil.

General procedure 7 (GP7): reaction of α,β-diketoesters with ZnR_2

Under argon atmosphere to a freshly prepared solution of the respective α,β-diketoester (0.5 M in CH_2Cl_2, 1.00 equiv.) was added a solution of LiCl (0.5 M in THF, 1.00 equiv.), it was cooled to -78 °C and a solution of the respective diorganozinc reagent (2.00 equiv.; $ZnMe_2$ 1.2 M in toluene, $ZnEt_2$ 1.0 M in heptane or $ZnPh_2$ 1.0 M in THF) was added. The reaction mixture was stirred for 2 h while slowly warming to r.t., poured into a separatory funnel containing H_2O (10 mL), aq. HCl (2 M, 1.0 mL) and Et_2O (10 mL). The layers were separated; the aqueous layer was extracted with Et_2O (2 x 10 mL), the combined organic layers were washed with brine (10 mL), dried with $MgSO_4$ and solvent was removed under reduced pressure. After SCC (mixture of solvents given below) the corresponding addition product was obtained.

Methyl 2-hydroxy-2-methyl-3-oxo-3-phenylpropanoate (16a)

Following **GP7** starting from α,β-diketoester **14a** (0.5 M in CH_2Cl_2, 0.80 mL, 0.40 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 0.80 mL, 0.40 mmol, 1.0 equiv.) and reaction with $ZnMe_2$ (1.2 M in toluene, 0.67 mL, 0.80 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 10:1) **16a** (160 mg, 0.77 mmol, 77%) as colourless oil.

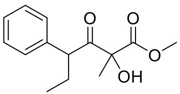


16a

TLC: R_f= 0.20 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 1.74 (s, 3H, Me), 3.75 (s, 3H, OCH_3), 4.51 (s, 1H, OH), 7.41-7.49 (m, 2H, 3-H-Ph), 7.54-7.62 (m, 1H, 4-H-Ph), 7.93-8.00 (m, 2H, 2-H-Ph) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 23.7 (Me), 53.4 (OMe), 79.6 (2-C), 128.8 (2-C-Ph), 129.6 (3-C-Ph), 133.1 (1-C-Ph), 133.9 (4-C-Ph), 172.8 (1-C), 196.1 (3-C) ppm. **HRMS:** ESI^+ calcd. for $C_{11}H_{12}O_4Na$ $[M+Na]^+$: 231.0628; found: 231.0628. **IR** (ATR): ν = 3464 (br, w), 3066 (w), 3003 (w), 2954 (w), 1737 (m), 1687 (s), 1597 (w), 1580 (w), 1449 (m), 1370 (w), 1270 (w), 1232 (s), 1150 (m), 1120 (w), 1026 (w), 1001 (w), 968 (m), 939 (w), 921 (w), 855 (w), 791 (w), 751 (w), 704 (s), 669 (w), 541 (w) cm^{-1}.

Methyl 2-hydroxy-2-methyl-3-oxo-4-phenylhexanoate (16b)

Following **GP7** starting from α,β-diketoester **14b** (0.5 M in CH_2Cl_2, 1.76 mL, 0.88 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 1.76 mL, 0.88 mmol, 1.0 equiv.) and reaction with $ZnMe_2$ (1.2 M in toluene, 1.47 mL, 1.76 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 25:1 → 10:1) **16b** (150 mg, 0.59 mmol, 67%,d.r. 1:1) as colourless oil.



16b

HRMS: ESI^+ calcd. for $C_{14}H_{18}O_4Na$ $[M+Na]^+$: 273.1097; found: 273.1099. **IR** (ATR): ν = 3489 (br, w), 3062 (w), 3030 (w), 2965 (w), 2876 (w), 1742 (w), 1720 (s), 1600 (w), 1492 (w), 1452 (w) 1347 (w), 1257 (m), 1160 (m), 1121 (w), 1031 (w), 979 (w), 902 (w), 876 (w), 744 (w), 701 (w) cm^{-1}.

1. diastereomer

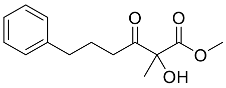
TLC: R_f= 0.23 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 0.78 (t, *J* = 7.4 Hz, 3H, 6-H), 1.44 (s, 3H, Me), 1.68-1.77 (m, 1H, 5-H_a), 1.96-2.04 (m, 1H, 5-H_b), 3.47 (s, 3H, OCH_3), 4.06 (s, 1H, OH), 4.15 (t, *J* = 7.5 Hz, 1H, 4-H), 7.19-7.30 (m, 5H, Ph) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 12.0 (6-C), 22.4 (Me), 27.4 (5-C), 53.2 (OCH_3), 54.3 (4-C), 81.1 (2-C), 127.6 (Ph), 128.7 (Ph), 128.9 (Ph), 138.0 (Ph), 172.3 (1-C), 206.7 (3-C) ppm.

2. diastereomer

TLC: R_f= 0.19 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 0.79 (t, *J* = 7.4 Hz, 3H, 6-H), 1.57 (s, 3H, Me), 1.69-1.78 (m, 1H, 5-H_a), 1.96-2.04 (m, 1H, 5-H_b), 3.31 (s, 3H, OCH_3), 4.03 (s, 1H, OH), 4.13 (t, *J* = 7.5 Hz, 1H, 4-H), 7.18-7.21 (m, 3H, Ph), 7.24-7.28 (m, 2H, Ph) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 12.3 (6-C), 22.3 (Me), 28.0 (5-C), 52.9 (OCH_3), 54.3 (4-C), 81.4 (2-C), 127.5 (Ph), 128.4 (Ph), 128.7 (Ph), 138.1 (Ph), 171.4 (1-C), 207.3 (3-C) ppm.

Methyl 2-hydroxy-2-methyl-3-oxo-6-phenylhexanoate (16c)

Following **GP7** starting from α,β-diketoester **14c** (0.5 M in CH_2Cl_2, 1.50 mL, 0.75 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 1.50 mL, 0.75 mmol, 1.0 equiv.) and reaction with $ZnMe_2$ (1.2 M in toluene, 1.25 mL, 1.50 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 10:1) **16c** (121 mg, 0.48 mmol, 65%) as colourless oil.

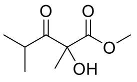


16c

TLC: R_f= 0.52 (*n*-pentane/EtOAc 3:1). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 1.57 (s, 3H, Me), 1.90-1.98 (m, 2H, 5-H), 2.46-2.80 (m, 4H, 4-H, 6-H), 3.76 (s, 3H, OCH_3), 4.20 (s, 1H, OH), 7.14-7.22 (m, 3H Ph), 7.26-7.31 (m, 2H, Ph) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 22.1 (Me), 25.1 (5-C), 34.9 (6-C), 35.7 (4-C), 53.4 (OCH_3), 81.0 (2-C), 126.2 (4-C-Ph), 128.5, 128.5 (2-C-Ph, 3-C-Ph), 141.3 (1-C-Ph), 172.0 (1-C), 207.0 (3-C) ppm. **HRMS:** ESI^+ calcd. for $C_{14}H_{18}O_4Na$ $[M+Na]^+$: 273.1097; found: 273.1099. **IR** (ATR): ν = 3478 (br, w), 3026 (w), 2952 (w), 1717 (s) 1496 (w), 1451 (m), 1402 (w), 1367 (w), 1258 (s), 1154 (m), 1114 (w), 1013 (w), 978 (m), 875 (w), 801 (w), 746 (m), 699 (s), 490 (w) cm^{-1}.

Methyl 2-hydroxy-2,4-dimethyl-3-oxopentanoate (16d)

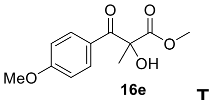
The solution of the respective tricarbonyl compound was prepared by stirring the hydrate **12d** (157 mg, 0.89 mmol, 1.0 equiv.) in $CHCl_3$ with 3 Å molecular sieves at 85 °C for 48 h. The title compound was then prepared following **GP7**with LiCl (0.5 M in THF, 1.78 mL, 0.89 mmol, 1.0 equiv.) and reaction with $ZnMe_2$ (1.2 M intoluene, 1.48 mL, 1.78 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 10:1) **16d** (102 mg, 0.59 mmol, 66% over 2 steps) as colourless oil.



16d **TLC:** R_f= 0.32 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ =1.07 (d, *J* = 5.2 Hz, 3H, $CH(CH_3)_2$), 1.09 (d, *J* = 5.2 Hz, 3H, $CH(CH_3)_2$), 1.59 (s, 3H, Me), 3.12 (hept, *J* = 6.8 Hz, 1H $CH(CH_3)_2$), 3.78 (s, 3H, OCH_3), 4.20 (s, 1H, OH) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 19.6, 19.7 ($CH(CH_3)_2$), 22.1 (Me), 35.0 ($CH(CH_3)_2$), 53.3 (OCH_3), 81.0 (2-C), 172.1 (1-C), 211.4 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_8H_{14}O_4Na$ [M+Na]$^+$: 197.0784, found: 197.0786. **IR** (ATR): ν =3478 (br, w), 2977 (w), 2878 (w), 1718 (s), 1450 (m), 1381 (w), 1257 (s), 1159 (w), 1108 (m), 1019 (s), 983 (w), 933 (w), 875 (w), 795 (w), 670 (w) cm^{-1}.

Methyl 2-hydroxy-3-(4-methoxyphenyl)-2-methyl-3-oxopropanoate (16e)

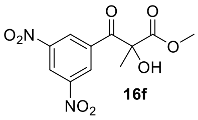
Following **GP7** starting from α,β-diketoester **14e** (0.5 M in CH_2Cl_2, 2.50 mL, 1.25 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 2.50 mL, 1.25 mmol, 1.0 equiv.) and reaction with $ZnMe_2$ (1.2 M in toluene, 2.08 mL, 2.50 mmol, 2.0 equiv.) gave SCC (*n*-pentane/EtOAc 15:1) **16e** (220 mg, 0.92 mmol, 74%) as colourless oil.



16e **TLC:** R_f= 0.30 (*n*-pentane/EtOAc 5:1). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 1.74 (s, 3H, CH_3), 3.74 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 4.65 (s, 1H, OH), 6.91-6.94 (m, 2H, 3-H-Ph), 7.98-8.01 (m, 2H, 2-H-Ph) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 29.4 (CH_3), 53.3 (OCH_3), 55.7 (OCH_3), 79.3 (2-C) 114.1 (3-C-Ph), 125.6 (1-C-Ph), 132.2 (2-C-Ph), 164.3 (4-C-Ar), 172.9 (1-C), 194.5 (3-C). **HRMS:** ESI$^+$ calcd. for $C_{13}H_{17}O_5Na$ [M+Na]$^+$: 261.0733; found: 261.0734. **IR** (ATR): ν = 3438 (w), 2931 (w), 2848 (w), 2063 (w), 1924 (w), 1737 (m), 1672 (m), 1598 (s), 1573 (w), 1510 (m), 1446 (m), 1421 (w), 1372 (w), 1311 (w), 1242 (s), 1174 (w), 1148 (s), 1121 (w), 1026 (m), 968 (m), 922 (w), 844 (m), 802 (w), 787 (w), 773 (w), 736 (w), 695 (w), 640 (w), 616 (m), 540 (w), 478 (w), 435 (w) cm^{-1}.

Methyl 2-hydroxy-3-(3,5-dinitrophenyl)-2-methyl-3-oxopropanoate (16f)

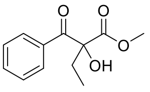
Following **GP7** starting from α,β-diketoester **14f** (0.5 M in CH_2Cl_2, 1.00 mL, 0.50 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 1.00 mL, 0.50 mmol, 1.0 equiv.) and reaction with $ZnMe_2$ (1.2 M in toluene, 0.83 mL, 1.00 mmol, 2.0 equiv.) gave SCC (*n*-pentane/EtOAc 3:1) **16f** (30 mg, 0.10 mmol, 77%) as colourless oil.



16f **TLC:** R_f= 0.41 (*n*-pentane/EtOAc 3:1). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 1.79 (s, 3H, Me), 3.86 (s, 3H, OCH_3), 4.02 (s, 1H, OH), 9.18 (d, *J* = 2.1 Hz, 2H, 2-H-Ph), 9.20 (t, *J* = 2.1 Hz, 1H, 4-H-Ph) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 23.8 (Me), 54.3 (OCH_3), 80.8 (2-C), 122.4 (4-C-Ph), 129.6 (2-C-Ph), 137.0 (1-C-Ph), 148.8 (3-C-Ph), 172.7 (1-C), 191.6 (3-C) ppm. **HRMS:** EI$^+$ calcd. for $C_{10}H_{10}N_2O_8$ [M+H]$^+$: 299.05096; found: 299.05154. **IR** (ATR): ν = 3481 (br, w), 3101 (w), 2959 (w), 1742 (w), 1709 (m), 1625 (w), 1593 (w), 1544 (s), 1452 (w), 1346 (s), 1273 (w), 1237 (m), 1157 (w), 1114 (w), 1025 (w), 974 (w), 920 (w), 727 (m), 695 (w) cm^{-1}.

Methyl 2-hydroxy-2-ethyl-3-oxo-3-phenylpropanoate (17a)

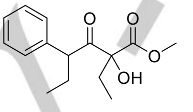
Following **GP7** starting from α,β-diketoester **14a** (0.5 M in CH_2Cl_2, 0.90 mL, 0.45 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 0.90 mL, 0.45 mmol, 1.0 equiv.)and reaction with $ZnEt_2$ (1.0 M in heptane, 0.90 mL, 0.90 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 10:1) **17a** (80 mg, 0.38 mmol, 85%) as colourless oil.



17a **TLC:** R_f= 0.34 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 0.82 (t, *J* = 7.5 Hz, 3H, CH_2CH_3), 2.11-2.34 (m, 2H, CH_2CH_3), 3.74 (s, 3H, OCH_3), 4.49 (s, 1H, OH), 7.38-7.49 (m, 2H, 3-H-Ph), 7.53-7.62 (m, 1H, 4-H-Ph), 7.93-8.00 (m, 2H, 2-H-Ph) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 7.0 (CH_2CH_3), 29.2 (CH_2CH_3), 53.2 (OCH_3), 82.7 (2-C), 128.7 (3-C-Ph), 129.3 (2-C-Ph), 133.6 (1-C-Ph), 133.7 (4-C-Ph), 172.5 (1-C), 196.2 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{12}H_{14}O_4Na$ [M+Na]$^+$: 245.0784; found: 245.0786. **IR** (ATR): ν = 3464 (br, w), 3066 (w), 2956 (w), 2882 (w), 1737 (m), 1683 (s), 1597 (w), 1580 (w), 1447 (m), 1384 (w), 1292 (w), 1225 (s), 1184 (w), 1149 (m), 1119 (w), 1090 (w), 1037 (w), 1020 (m), 969 (w), 920 (w), 865 (w), 809 (w), 777 (w), 743 (w), 694 (s), 666 (w), 559 (w), 425 (w) cm^{-1}.

Methyl 2-hydroxy-2-ethyl-3-oxo-4-phenylhexanoate (17b)

Following **GP7** starting from α,β-diketoester **14b** (0.5 M in CH_2Cl_2, 1.50 mL, 0.75 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 1.50 mL, 0.75 mmol, 1.0 equiv.)and reaction with $ZnEt_2$ (1.0 M in heptane, 1.50 mL, 1.50 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 25:1 → 10:1) **17b** (126 mg, 0.48 mmol, 64%,d.r. 1.2:1 detected by ^{1}H-NMR of crude product) as colourless oil.

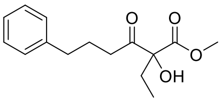


17b *Analytical data of main diastereomer:*

TLC: R_f= 0.48 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 0.69 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 0.77 (t, *J* = 7.4 Hz, 3H, 6-H), 1.60-2.14 (m, 4H, 5-H, CH_2CH_3), 3.46 (s, 3H, OCH_3), 3.97 (s, 1H, OH), 4.23 (dd, *J* = 6.6, 14.0 Hz, 1H, 4-H), 7.15-7.32 (m, 5H, Ph) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 7.4 (CH_2CH_3), 12.0 (6-C), 27.2 (CH_2CH_3), 28.7 (5-C), 53.2 (OCH_3), 54.4 (4-C), 127.5, 128.8, 128.9, 137.9 (Ph), 171.9 (1-C), 206.9 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{15}H_{20}O_4Na$ [M+Na]$^+$= 287.1254; found: 287.1254. **IR** (ATR): ν = 3492 (br, w), 3029 (w), 2966 (w), 2878 (w), 1717 (s), 1600 (w), 1492 (w), 1454 (m), 1439 (w), 1381 (w), 1346 (w) 1285 (w), 1243 (s), 1157 (m), 1076 (w), 1049 (w), 1010 (w), 975 (w), 928 (w), 894 (w), 829 (w), 802 (w), 741 (m), 700 (s), 658 (w), 549 (w), 509 (w) 430 (w) cm^{-1}.

Methyl 2-hydroxy-2-ethyl-3-oxo-6-phenylhexanoate (17c)

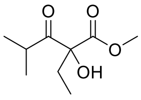
Following **GP7** starting from α,β-diketoester **14c** (0.5 M in CH_2Cl_2, 0.80 mL, 0.40 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 0.80 mL, 0.40 mmol, 1.0 equiv.) and reaction with $ZnEt_2$ (1.0 M in heptane, 0.80 mL 0.80 mmol, 2.0 equiv.) gave SCC (*n*-pentane/EtOAc 10:1) **17c** (51 mg, 0.19 mmol, 48%) as colourless oil.



17c **TLC:** R_f= 0.27 (*n*-pentane/EtOAc 3:1). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 0.86 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 1.85-2.01 (m, 3H 5-H, CH_2CH_3), 2.04-2.19 (m, 1H, CH_2CH_3), 2.47-2.80 (m, 4H, 4-H, 6H), 3.77 (s, 3H, OCH_3), 4.13 (s, 1H, OH), 7.12-7.33 (m, 5H, Ph) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 7.6 (CH_2CH_3), 25.1 (5-C), 28.8 (CH_2CH_3), 35.0 (4-C), 36.2 (6-C), 53.4 (OCH_3), 84.6 (2-C), 126.2 (4-C-Ph), 128.5, 128.6 (2-C-Ph, 3-C-Ph), 141.5 (1-C-Ph), 171.7 (1-C), 207.1 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{15}H_{20}O_4Na$ [M+Na]$^+$: 287.1254; found: 287.1255. **IR** (ATR): ν = 3484 (br, w), 3027 (w), 2952 (w), 1717 (s), 1496 (w), 1454 (w), 1439 (w), 1402 (w), 1364 (w), 1245 (s), 1160 (m), 1094 (w), 1028 (w), 1007 (w), 805 (w), 747 (w), 701 (m), 492 (w) cm^{-1}.

Methyl 2-ethyl-2-hydroxy-4-methyl-3-oxopentanoate (17d)

The solution of the respective tricarbonyl compound was prepared by stirring the hydrate **12d** (157 mg, 0.89 mmol, 1.0 equiv.) in $CHCl_3$ with 3 Å molecular sieves at 85 °C for 48 h. The title compound was then prepared following **GP7**with LiCl (0.5 M in THF, 1.78 mL, 0.89 mmol, 1.0 equiv.) and reaction with $ZnEt_2$ (1.0 M in heptane, 1.78 mL, 1.78 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 10:1) **17d** (87 mg, 0.46 mmol, 52% over 2 steps) as colourless oil.

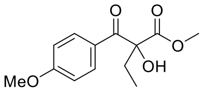


17d

TLC: R_f= 0.32 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 0.86 (t, *J* = 7.4 Hz, 3H, $CH_2C\mathit{H}_3$), 1.03-1.08 (m, 6H, $CH(C\mathit{H}_3)_2$), 1.93 (dq, *J* = 7.3, 14.5 Hz, 1H, $C\mathit{H}_2CH_3$), 2.13 (dq, *J* = 7.5, 14.8 Hz, 1H, $C\mathit{H}_2CH_3$), 3.13-3.28 (m, 1H, $C\mathit{H}(CH_3)_2$), 3.78 (s, 3H, OCH_3), 4.12 (s, 1H, OH) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 7.66 ($CH_2\mathit{C}H_3$), 19.2, 19.7 ($CH(\mathit{C}H_3)_2$), 28.6 ($\mathit{C}H_2CH_3$), 35.0 ($\mathit{C}H(CH_3)_2$), 53.3 (OCH_3), 84.5 (2-C), 171.9 (1-C), 211.5 (3-C) ppm. **HRMS:** ESI^+ calcd. for $C_{19}H_{26}O_4Na$ $[M+Na]^+$: 341.1723, found: 341.1724. **IR** (ATR): v = 3380 (br, w), 2977 (m), 2939 (w), 2881 (w), 1808 (w), 1747 (w), 1726 (s), 1463 (w), 1441 (w), 1387 (w), 1306 (w), 1248 (w), 1124 (m), 1068 (w), 1044 (w), 1008 (w), 967 (w), 898 (w), 814 (w) cm^{-1}.

Methyl 2-hydroxy-3-(4-methoxyphenyl)-2-ethyl-3-oxopropanoate (17e)

Following **GP7** starting from α,β-diketoester **14e** (0.5 M in CH_2Cl_2, 1.00 mL, 0.50 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 1.00 mL, 0.50 mmol, 1.0 equiv.) and reaction with $ZnEt_2$ (1.0 M in heptane, 1.00 mL, 1.60 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 10:1) **17e** (81 mg, 0.32 mmol, 64%) as colourless oil.

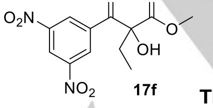


17e

TLC: R_f= 0.22 (*n*-pentane/EtOAc 5:1). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 0.82 (t, *J* = 7.43 Hz, 3H, $CH_2C\mathit{H}_3$), 2.15-2.32 (m, 2H, $C\mathit{H}_2CH_3$), 3.74 (s, 3H, $COOCH_3$) 3.87 (s, 3H, OCH_3), 4.64 (s, 1H, OH), 6.91-6.94 (m, 2H, 3-H-Ph), 7.99-8.02 (m, 2H, 2-H-Ph) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 7.0 ($CH_2\mathit{C}H_3$), 29.4 ($\mathit{C}H_2CH_3$), 53.1 ($COO\mathit{C}H_3$), 55.5 (OCH_3), 82.4 (2-C) 113.9 (3-C-Ph), 126.1 (1-C-Ph), 131.9 (2-C-Ph), 164.1 (4-C-Ph), 172.5 (1-C), 194.3 (3-C) ppm. **HRMS:** ESI^+ calcd. for $C_{13}H_{17}O_5$ $[M+H]^+$: 253.1071; found: 253.1071. **IR** (ATR): v = 3432 (w), 2926 (m), 2847 (w), 1736 (m), 1706 (w), 1670 (m), 1598 (s), 1573 (w), 1511 (m), 1441 (m), 1384 (w), 1296 (w), 1234 (s), 1174 (w), 1149 (s), 1120 (w), 1091 (w), 1024 (m), 970 (w), 921 (w), 871 (w), 844 (m), 807 (w), 792 (w), 778 (w), 731 (w), 684 (w), 641 (w), 617 (m), 557 (w), 511 (w) cm^{-1}.

Methyl 2-hydroxy-3-(3,5-dinitrophenyl)-2-ethyl-3-oxopropanoate (17f)

Following **GP7** starting from α,β-diketoester **14f** (0.5 M in CH_2Cl_2, 0.80 mL, 0.40 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 0.80 mL, 0.40 mmol, 1.0 equiv.) and reaction with $ZnEt_2$ (1.0 M in heptane, 0.67 mL, 0.80 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 3:1) **17f** (10 mg, 32.0 µmol, 5%) as colourless oil.

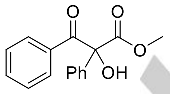


17f

TLC: R_f= 0.61 (*n*-pentane/EtOAc 3:1). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 0.97 (t, *J* = 7.4 Hz, 3H, $CH_2C\mathit{H}_3$), 2.16-2.25 (m, 2H, $C\mathit{H}_2CH_3$), 3.87 (s, 3H, OCH_3), 4.06 (s, 1H, OH), 9.16 (d, *J* = 2.1 Hz, 2H, 5-H-Ph), 9.20 (t, *J* = 2.1 Hz, 1H, 4-H-Ph) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 7.4 ($CH_2\mathit{C}H_3$), 29.7 ($\mathit{C}H_2CH_3$), 54.3 (OCH_3), 84.2 (2-C), 122.3 (2-C-Ph), 129.5 (4-C-Ph), 137.7 (1-C-Ph), 148.7 (3-C-Ph), 172.2 (1-C), 192.0 (3-C) ppm. **HRMS:** ESI^- calcd. for $C_{12}H_{11}N_2O_8Na[M-H]^-$: 311.0521; found: 311.0515. **IR** (ATR): v = 3482 (br, w), 3102 (w), 2961 (w), 2883 (w), 1739 (w), 1710 (m), 1625 (w), 1593 (w), 1545 (s), 1458 (w), 1346 (s), 1256 (w), 1235 (m), 1159 (w), 1082 (w), 1052 (w), 1011 (w), 970 (w), 919 (w), 806 (w), 727 (w), 692 (w) cm^{-1}.

Methyl 2-hydroxy-3-oxo-2,3-diphenylpropanoate (18a)

Following **GP7** starting from α,β-diketoester **14a** (0.5 M in CH_2Cl_2, 1.10 mL, 0.55 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 1.10 mL, 0.55 mmol, 1.0 equiv.) and reaction with $ZnPh_2$ (1.0 M in THF, 1.10 mL, 1.10 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 15:1) **18a** (145 mg, 0.54 mmol, 98%) as colourless solid.

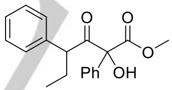


18a

TLC: R_f= 0.44 (*n*-pentane/EtOAc 10:1). **M.p.:** 90.3 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 3.86 (s, 3H, OCH_3), 4.83 (s, 1H, OH), 7.27-7.50 (m, 6H, Ph), 7.56 (dd, *J* = 1.7, 7.8 Hz, 2H, Ph), 7.88 (d, *J* = 7.4 Hz, 2H, Ph) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 54.1 (OCH_3), 84.7 (2-C) 126.6 (2-C-Ph), 128.3 (3-C-Ph), 128.6 (2-C-Ph'), 128.7 (4-C-Ph), 130.9 (3-C-Ph'), 133.3 (4-C-Ph'), 133.4 (1-C-Ph), 137.1 (1-C-Ph'), 172.4 (1-C), 195.2 (3-C) ppm. **HRMS:** ESI^+ calcd. for $C_{16}H_{14}O_4Na$ $[M+Na]^+$: 293.0784; found: 293.0785. **IR** (ATR): v = 3464 (br, w), 3062 (w), 3031 (w), 2954 (w), 1729 (m), 1680 (s), 1597 (w), 1580 (w), 1494 (w), 1448 (m), 1357 (w), 1320 (w), 1240 (s), 1182 (m), 1121 (m), 1072 (m), 1027 (w), 1003 (w), 972 (w), 952 (w), 883 (w), 808 (w), 747 (m), 700 (s), 608 (m), 557 (w), 505 (w) cm^{-1}.

Methyl 2-hydroxy-3-oxo-2,4-diphenylhexanoate (18b)

Following **GP7** starting from α,β-diketoester **14b** (0.5 M in CH_2Cl_2, 1.80 mL, 0.90 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 1.80 mL, 0.90 mmol, 1.0 equiv.) and reaction with $ZnPh_2$ (1.0 M in THF, 1.80 mL, 1.80 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 10:1) **18b** (231 mg, 0.74 mmol, 82%,d.r. 10:1) as colourless oil.



18b

Analytical data for mixture of diastereomers:

HRMS: ESI^+ calcd. for $C_{19}H_{20}O_4$ $[M+Na]^+$= 335.1254; found: 335.1255. **IR** (ATR): v = 3471 (br, w), 3062 (w), 3029 (w), 2964 (w), 2932 (w), 2875 (w), 1719 (s), 1600 (w), 1492 (w), 1451 (m), 1436 (w), 1345 (w), 1257 (s), 1178 (w), 1126 (m), 1070 (w), 1031 (w), 1013 (w), 982 (w), 939 (w), 892 (w), 825 (w), 796 (w), 734 (m), 696 (s), 626 (w), 581 (w), 545 (w), 507 (w) cm^{-1}.

Analytical data of major diastereomer:

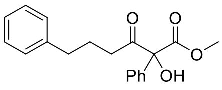
TLC: R_f= 0.30 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 0.68 (t, *J* = 7.4 Hz, 3H, 6-H), 1.70-1.81 (m, 1H, 5-H_a), 1.88-1.99 (m, 1H, 5-H_b), 3.68 (s, 3H, OCH_3), 4.10-4.16 (m, 1H, 4-H), 4.41 (s, 1H, OH), 7.07-7.11 (m, 2H, Ph), 7.15-7.25 (m, 3H, Ph), 7.29-7.32 (m, 3H, Ph), 7.51-7.56 (m, 2H, Ph) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 11.8 (6-C), 27.4 (5-C), 53.6 (OCH_3), 55.0 (4-C), 84.8 (2-C), 127.0, 127.1, 128.2, 128.5, 128.5, 128.7 (4-C-Ph, 4-C-Ph', 3-C-Ph, 3-C-Ph', 2-C-Ph, 2-C-Ph'), 135.4 (1-C-Ph'), 138.4 (1-C-Ph), 171.0 (1-C), 205.8 (3-C) ppm.

Analytical data of minor diastereomer:

TLC: R_f= 0.27 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 0.67 (t, *J* = 7.4 Hz, 3H, 6-H), 1.66-1.82 (m, 1H, 5-H_a), 1.82-2.00 (m, 1H, 5-H_b), 3.68 (s, 3H, OCH_3), 4.12 (dd, *J* = 6.6, 8.3 Hz, 1H, 4-H), 4.37 (s, 1H, OH), 7.03-7.22 (m, 5H, Ph), 7.28-7.56 (m, 5H, Ph) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 11.9 (6-C), 27.5 (5-C), 53.6 (OCH_3), 55.1 (4-C), 84.9 (2-C), 127.0, 128.3, 128.5, 128.6, 128.7 (4-C-Ph, 4-C-Ph', 3-C-Ph, 3-C-Ph', 2-C-Ph, 2-C-Ph'), 135.4 (1-C-Ph'), 138.5 (1-C-Ph), 171.0 (1-C), 205.8 (3-C) ppm.

Methyl 2-hydroxy-3-oxo-2,6-diphenylhexanoate (18c)

Following **GP7** starting from α,β-diketoester **14c** (0.5 M in CH_2Cl_2, 1.31 mL, 0.66 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 1.31 mL, 0.66 mmol, 1.0 equiv.) and reaction with $ZnPh_2$ (1.0 M in THF, 1.32 mL, 1.32 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 10:1) **18c** (128 mg, 0.41 mmol, 63%) as colourless oil.

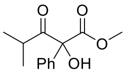


18c

TLC: R_f= 0.27 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 1.72-1.93 (m, 2H, 5-H), 2.44-2.74 (m, 4H, 4-H, 6-H), 3.85 (s, 3H, OCH_3), 4.72 (s, 1H, OH), 7.04-7.10 (m, 2H, Ph), 7.33-7.43 (m, 3H, Ph), 7.56-7.69 (m, 3H, Ph), 7.51-7.57 (m, 2H, Ph) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 25.6 (5-C), 35.0 (4-C), 36.7 (6-C), 53.7 (OCH_3), 84.7 (2-C), 126.0 (4-C-Ph), 126.5 (2-C-Ph), 128.5, 128.5 (2-C-Ph, 3-C-Ph), 128.6 (3-C-Ph), 128.9 (4-C-Ph), 136.1 (1-C-Ph), 141.6 (1-C-Ph), 171.1 (1-C), 205.9 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{19}H_{20}O_4Na$ $[M+Na]^+$: 335.1254; found: 335.1256. **IR** (ATR): ν = 3475 (br, w), 3062 (w), 3027 (w), 2953 (w), 2861 (w), 1722 (s), 1602 (w), 1495 (w), 1451 (w), 1437 (w), 1402 (w), 1362 (w), 1260 (s), 1191 (w), 1125 (w), 1070 (w), 1030 (w), 1006 (w), 976 (w), 748 (m), 700 (s), 492 (w) cm^{-1}.

Methyl 2-hydroxy-4-methyl-3-oxo-2-phenylpentanoate (18d)

The solution of the respective tricarbonyl compound was prepared by stirring the hydrate **12d** (68 mg, 0.43 mmol, 1.0 equiv.) in $CHCl_3$ with 3 Å molecular sieves at 85 °C for 48 h. The title compound was then prepared following **GP7**with LiCl (0.5 M in THF, 0.86 mL, 0.43 mmol, 1.0 equiv.) and reaction with $ZnPh_2$ (1.0 M in benzene, 0.86 mL, 0.86 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 10:1) **18d** (14 mg, 59.3 µmol, 14% over 2 steps) as colourless oil.

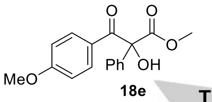


18d

TLC: R_f= 0.32 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 0.83 (d, *J* = 6.8 Hz, 3H, $CH(CH_3)_2$), 1.04 (d, *J* = 6.7 Hz, 3H, $CH(CH_3)_2$), 3.15 (hept, *J* = 6.7 Hz, 1H, $CH(CH_3)_2$), 3.86 (s, 3H, OCH_3), 4.78 (s, 1H, OH), 7.31-7.46 (m, 3H, Ph), 7.49-7.61 (m, 2H, Ph) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 19.8, 20.6 ($CH(CH_3)_2$), 36.1 ($CH(CH_3)_2$), 53.6 (OCH_3), 84.8 (2-C), 126.7, 128.5, 128.9, 135.9 (Ph), 171.2 (1-C), 210.3 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{13}H_{16}O_4Na$ $[M+Na]^+$: 259.0941; found: 259.0943. **IR** (ATR): ν = 3472 (br, w), 3063 (w), 2975 (w), 2875 (w), 1715 (s), 1600 (w), 1494 (w), 1467 (w), 1449 (m), 1437 (w), 1382 (w), 1348 (w), 1256 (s), 1190 (w), 1174 (w), 1125 (m), 1068 (w), 1037 (w), 1006 (w), 979 (w), 938 (w), 804 (w), 750 (m), 700 (s), 624 (w), 542 (w), 489 (w) cm^{-1}.

Methyl 2-hydroxy-3-(4-methoxyphenyl)-3-oxo-2-phenylpropanoate (18e)

Following **GP7** starting from α,β-diketoester **14e** (0.5 M in CH_2Cl_2, 1.70 mL, 0.85 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 1.70 mL, 0.85 mmol, 1.0 equiv.) and reaction with $ZnPh_2$ (1.0 M in THF, 1.70 mL, 1.70 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 15:1) **18e** (205 mg, 0.68 mmol, 80%) as yellow oil.

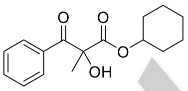


18e

TLC: R_f= 0.23 (*n*-pentane/EtOAc 5:1). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 3.79 (s, 3H, $COOCH_3$) 3.84 (s, 3H, OCH_3), 4.86 (s, 1H, OH), 6.78 (d, *J* = 9.1 Hz, 2H, 3-H-Ph), 7.29-7.41 (m, 3H, 4-H-Ph‘, 3-H-Ph‘), 7.54-7.56 (m, 2H, 2-H-Ph‘), 7.97-8.00 (d, *J* = 9.1 Hz, 2H, 2-H-Ph) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 54.1 ($COOCH_3$), 55.6 (OCH_3), 84.79 (2-C), 113.7 (3-C-Ph), 126.1 (1-C-Ph), 126.7 (2-C-Ph‘), 128.5 (3-H-Ph‘), 128.6 (4-H-Ph‘), 133.5 (2-C-Ph), 137.7 (1-C-Ph‘), 163.8 (4-C-Ph), 172.7 (1-C), 194.0 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{17}H_{16}O_5Na$ $[M+Na]^+$: 323.0890; found: 323.0892. **IR** (ATR): ν = 3416 (w), 2963 (w), 2933 (w), 2843 (w), 1733 (m), 1682 (s), 1601 (s), 1572 (w), 1512 (w), 1446 (w), 1429 (m), 1315 (w), 1263 (s), 1234 (w), 1171 (s), 1104 (m), 1075 (w), 1040 (w), 1013 (m), 934 (w), 862 (w), 846 (m), 823 (w), 799 (w), 772 (m), 745 (m), 724 (m), 694 (m), 647 (w), 631 (w), 606 (m), 528 (m), 498 (w), 458 (w) cm^{-1}.

Cyclohexyl 2-hydroxy-2-methyl-3-oxo-3-phenylpropanoate (19a)

Following **GP7** starting from α,β-diketoester **15a** (0.5 M in CH_2Cl_2, 1.00 mL, 0.50 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 1.00 mL, 0.50 mmol, 1.0 equiv.) and reaction with $ZnMe_2$ (1.2 M in toluene, 0.83 mL, 1.0 mmol, 2.00 equiv.) gave after SCC (*n*-pentane/EtOAc 10:1) **19a** (109 mg, 0.39 mmol, 79%) as colourless oil.

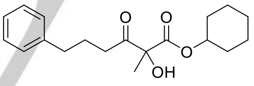


19a

TLC: R_f= 0.25 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 1.10-1.62 (m, 8H, 4'-H, 3'-H, 2'-H_a), 1.64-1.70 (m, 2H, 2'-H_b), 1.72 (s, 3H, CH_3), 4.36 (s, 1H, OH), 4.79-4.92 (m, 1H, 1'-H), 7.44 (t, *J* = 7.6 Hz, 2H, 3-H-Ph), 7.56 (t, *J* = 7.4 Hz, 4-H-Ph), 7.98 (d, *J* = 7.8 Hz, 2H, 2-H-Ph) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 23.3, 23.3 (3'-C), 23.6 (Me), 25.2 (4'-C), 31.0, 31.1 (2'-C), 75.1 (1'-C), 79.6 (2-C), 128.7 (3-C-Ph), 129.5 (2-C-Ph), 133.6 (1-C-Ph), 133.6 (4-C-Ph), 172.1 (1-C), 196.0 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{16}H_{20}O_4Na$ $[M+Na]^+$: 299.1254; found: 299.1254. **IR** (ATR): ν = 3463 (br, w), 3065 (w), 2936 (m), 2860 (w), 1733 (m), 1692 (s), 1598 (w), 1580 (w), 1450 (m), 1371 (w), 1273 (w), 1230 (s), 1150 (s), 1117 (w), 1034 (w), 1008 (m), 982 (w), 950 (w), 908 (w), 863 (w), 844 (w), 812 (w), 751 (w), 707 (m), 672 (w), 543 (w), 513 (w), 481 (w), 444 (w) cm^{-1}.

Cyclohexyl 2-hydroxy-2-methyl-3-oxo-6-phenylhexanoate (19c)

Following **GP7** starting from α,β-diketoester **15c** (0.5 M in CH_2Cl_2, 0.70 mL, 0.35 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 0.70 mL, 0.35 mmol, 1.0 equiv.) and reaction with $ZnMe_2$ (1.2 M in toluene, 0.58 mL, 0.70 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 10:1) **19c** (75 mg, 0.24 mmol, 67%) as colourless oil.

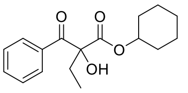


19c

TLC: R_f= 0.29 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 1.22-1.51 (m, 6H, 2'-H_a, 3'-H_a, 4'-H), 1.55 (s, 3H, Me), 1.61-1.78 (m, 4H, 2'-H_b, 3'-H_b), 1.87-2.00 (m, 2H, 5-H), 2.44-2.77 (m, 4H, 4-H, 6-H), 4.12 (s, 1H, OH), 4.81 (td, *J* = 3.83, 8.62 Hz, 1H, 1'-H), 7.12-7.32 (m, 5H, Ph) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 21.8 (Me), 23.5 (3'-C), 25.2 (4'-C), 25.3 (5-C), 31.25, 31.32 (2'-C), 35.1 (4-C), 35.8 (6-C), 75.3 (1'-C), 81.0 (2-C), 126.2 (4-C-Ph), 128.5 (2-C-Ph, 3-C-Ph), 141.5 (1-C-Ph), 171.2 (1-C), 206.9 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{21}H_{22}O_4Na$ $[M+Na]^+$: 341.1723; found: 341.1727. **IR** (ATR): ν = 3490 (br, w), 3026 (w), 2936 (m), 2860 (w), 1715 (s), 1603 (w), 1496 (w), 1451 (m), 1405 (w), 1368 (w), 1257 (s), 1162 (m), 1117 (w), 1032 (w), 1009 (m), 952 (w), 927 (w), 908 (w), 825 (w), 746 (m), 700 (s), 490 (w) cm^{-1}.

Cyclohexyl 2-hydroxy-2-ethyl-3-oxo-3-phenylpropanoate (20a)

Following **GP7** starting from α,β-diketoester **15a** (0.5 M in CH_2Cl_2, 0.80 mL, 0.40 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 0.80 mL, 0.40 mmol, 1.0 equiv.) and reaction with $ZnEt_2$ (1.0 M in heptane, 0.80 mL 0.80 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 15:1) **20a** (75 mg, 0.26 mmol, 65%) as colourless oil.

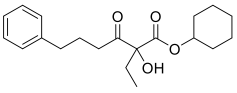


20a

TLC: R_f= 0.49 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 0.85 (t, *J* = 7.45 Hz, 3H, CH_2CH_3), 1.10-1.76 (m, 10H, 2'-H, 3'-H, 4'-H), 2.10-2.31 (m, 2H, $C\mathit{H}_2CH_3$), 4.33 (s, 1H, OH), 4.78-4.93 (m, 1H, 1'-H), 7.37-7.49 (m, 2H, 3-H-Ph), 7.50-7.62 (m, 1H, 4-H-Ph), 7.89-8.14 (m, 2H, 2-H-Ph) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 23.3, 23.4 (3'-C), 25.2 (4'-C), 29.1 (CH_2CH_3), 31.0, 31.2 (2'-C), 75.0 (1'-C), 82.7 (2-C), 128.6 (3-C-Ph), 129.3 (2-C-Ph), 133.5 (4-C-Ph), 134.2 (1-C-Ph), 171.7 (1-C), 196.1 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{17}H_{24}O_4Na$ $[M+Na]^+$: 313.1410; found: 313.1413. **IR** (ATR): v = 3463 (br, w), 3065 (w), 2936 (m), 2860 (w), 1733 (m), 1692 (s), 1598 (w), 1580 (w), 1450 (m), 1371 (w), 1273 (w), 1230 (s), 1150 (s), 1117 (w), 1034 (w), 1008 (m), 982 (w), 950 (w), 908 (w), 863 (w), 844 (w), 812 (w), 751 (w), 707 (m), 672 (w), 543 (w), 513 (w), 481 (w), 444 (w) cm^{-1}.

Cyclohexyl 2-hydroxy-2-ethyl-3-oxo-6-phenylhexanoate (20c)

Following **GP7** starting from α,β-diketoester **15c** (0.5 M in CH_2Cl_2, 0.56 mL, 0.28 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 0.56 mL, 0.28 mmol, 1.0 equiv.) and reaction with $ZnEt_2$ (1.0 in heptane, 0.56 mL, 0.56 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 10:1) **20c** (54 mg, 0.16 mmol, 59%) as colourless oil.

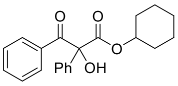


20c

TLC: R$_f$= 0.38 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 1.20-1.30 (m, 1H, 4'-H$_a$), 1.26 (t, *J* = 7.01 Hz, 3H, $CH_2C\mathit{H}_3$), 1.30-1.48 (m, 4H, 2'-H$_a$, 3'-H$_a$), 1.49-1.58 (m, 1H, 4'-H$_b$), 1.65-1.75 (m, 2H, 3'-H$_b$), 1.77-1.86 (m, 2H, 2'-H$_b$), 1.88-1.95 (m, 2H, 5-H), 2.59-2.67 (m, 4H, 4-H, 6-H), 3.47-3.55 (m, 1H, $C\mathit{H}_2$-CH_3), 3.62-3.70 (m, 1H, $C\mathit{H}_2$-CH_3), 4.32 (s, 1H, OH), 4.83-4.90 (m, 1H, 1'-H), 7.15-7.22 (m, 3H, Ph), 7.24-7.30 (m, 2H, Ph) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 15.2 ($CH_2\mathit{C}H_3$), 23.6, 23.7 (3'-C), 24.7 (5-C), 25.3 (4'-C), 31.4, 31.5 (2'-C), 35.1 (6-C), 37.9 (4-C), 66.8 ($\mathit{C}H_2CH_3$), 74.5 (1'-C), 85.5 (2-C), 126.1 (4-C-Ph), 128.5, 128.6 (2-C-Ph, 3-C-Ph), 141.6 (1-C-Ph), 167.0 (1-C), 204.2 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{20}H_{28}O_4Na$ $[M+Na]^+$: 355.1880; found: 355.1881. **IR** (ATR): v = 3027 (br, w), 2936 (s), 2860 (w), 1742 (w), 1723 (s), 1651 (w), 1604 (w), 1496 (w), 1452 (m), 1400 (w), 1367 (w), 1328 (w), 1253 (w), 1190 (w), 1119 (s), 1036 (w), 1012 (w), 956 (w), 910 (w), 893 (w), 747 (w), 700 (m) cm^{-1}.

Cyclohexyl 2-hydroxy-3-oxo-2,3-diphenylpropanoate (21a)

Following **GP7** starting from α,β-diketoester **15a** (0.5 M in CH_2Cl_2, 1.50 mL, 0.75 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 1.50 mL, 0.75 mmol, 1.0 equiv.) and reaction with $ZnPh_2$ (1.0 M in THF, 1.50 mL, 1.50 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 15:1) **21a** (184 mg, 0.54 mmol, 73%) as colourless solid.

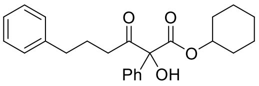


21a

TLC: R$_f$= 0.50 (*n*-pentane/EtOAc 10:1). **M.p.:** 80.6 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 1.19-1.50 (m, 6H, 4'-H, 3'H$_a$, 2'-H$_a$), 1.52-1.92 (m, 4H, 2'-H$_b$, 3'-H$_b$), 4.81(s, 1H, OH), 4.94 (tt, *J* = 3.4, 7.1 Hz, 1H, 1'-H), 7.22-7.48 (m, 6H, Ph', 4-H-Ph), 7.53-7.60 (m, 2H, 3-H-Ph), 7.85-7.92 (m, 2H, 2-H-Ph) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 23.0, 23.1 (3'-C), 25.3 (4'-C), 30.9, 31.0 (2'-C), 76.0 (1'-C), 84.3 (2-C), 126.6 (3-C-Ph), 128.2 (3-C-Ph'), 128.3 (2-C-Ph'), 128.5 (4-C-Ph'), 130.8 (2-C-Ph), 133.1 (4-C-Ph), 133.8 (1-C-Ph'), 137.6 (1-C-Ph), 171.2 (1-C), 195.0 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{21}H_{22}O_4Na$ $[M+Na]^+$: 361.1410; found: 361.1413. **IR** (ATR): v = 3461 (br, w), 3062 (w), 2936 (m), 2859 (w), 1718 (w), 1681 (s), 1597 (w), 1580 (w), 1494 (w), 1448 (m), 1335 (w), 1318 (w), 1235 (s), 1180 (m), 1118 (m), 1071 (w), 1030 (w), 1006 (m), 967 (w), 929 (w), 908 (m), 862 (w), 822 (w), 800 (w), 747 (w), 697 (s), 607 (m), 539 (w), 505 (w), 462 (w), 439 (w) cm^{-1}.

Cyclohexyl 2-hydroxy-3-oxo-2,6-diphenylhexanoate (21c)

Following **GP7** starting from α,β-diketoester **15c** (0.5 M in CH_2Cl_2, 1.00 mL, 0.50 mmol, 1.0 equiv.) with LiCl (0.5 M in THF, 1.00 mL, 0.50 mmol, 1.0 equiv.) and reaction with $ZnPh_2$ (1.0 M in THF, 1.00 mL, 1.00 mmol, 2.0 equiv.) gave after SCC (*n*-pentane/EtOAc 10:1) **21c** (66 mg, 0.17 mmol, 53%) as colourless oil.



21c

TLC: R$_f$= 0.42 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 1.14-1.58 (m, 7H, 4'-H, 3'-H$_a$, 3'-H$_b$, 2'-H$_a$), 1.60-1.69 (m, 2H, 3-H$_b$, 2'-H$_b$), 1.70-1.80 (m, 3H, 2'-H$_b$, 5-H), 2.39-2.58 (m, 4H, 4-H, 6-H), 4.57 (s, 1H, OH), 4.80-4.86 (m, 1H, 1'-H), 6.97 (d, *J* = 7.1 Hz, 2H, Ph), 7.06 (t, *J* = 7.4 Hz, 1H, Ph), 7.11-7.17 (m, 2H, Ph), 7.24-7.31 (m, 3H, Ph), 7.47 (dd, *J* = 1.5, 8.0 Hz, 2H, Ph) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 23.4, 23.4 (3'-C), 25.3 (4'-C), 25.6 (5-C), 31.2, 31.2 (2'-C), 35.0 (6-C), 36.8 (4-C), 76.0 (1'-C), 84.4 (2-C), 126.0 (4-Ph-C), 126.6 (4''-C), 128.1, 128.4, 128.5, 128.7 (2-C-Ph, 3-C-Ph, 2-C-Ph', 3-C-Ph'), 136.3 (1-C-Ph), 141.6 (1-C-Ph'), 170.1 (1-C), 205.8 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{24}H_{28}O_4Na$ $[M+Na]^+$: 403.1880; found: 403.1879. **IR** (ATR): v = 3465 (br, w), 3027 (w), 2935 (m), 2859 (w), 1714 (s), 1601 (w), 1494 (w), 1450 (m), 1402 (w), 1359 (w), 1257 (s), 1191 (w), 1119 (m), 1069 (w), 1032 (w), 1008 (m), 905 (w), 824 (w), 746 (m), 697 (s), 491 (w) cm^{-1}.

General procedure 8 (GP8) alkenylation with $Zn[CH_2C(CH_3)_3]_2$

Under argon atmosphere a solution of the respective alkenyl iodide (0.5 M in THF, 1.00 equiv.) in THF was cooled to -78 °C and a solution of *sec*-BuLi (2.00 equiv.) in cyclohexane was added. The reaction mixture was stirred at -78 °C for 1 h, a solution of $Zn[CH_2C(CH_3)_3]_2$ (1.0 M in benzene, 2.00 equiv.) was added, the reaction mixture was warmed to r.t and stirred for 2 h. The mixture was cooled to -100 °C and a freshly prepared solution of the respective tricarbonyl compound (0.5 M in CH_2Cl_2, 2.00 equiv.) was added. It was stirred for 1 h while slowly warming to -78 °C, the mixture was poured into a separatory funnel containing H_2O (10 mL), aq. HCl (2 M, 2.0 mL) and Et_2O (10 mL). The layers were separated; the aqueous layer was extracted with Et_2O (2 x 10 mL), the combined organic layers were washed with brine (10 mL), dried with $MgSO_4$ and solvent was removed under reduced pressure. After SCC (mixture of solvents given below) the corresponding addition product was obtained.

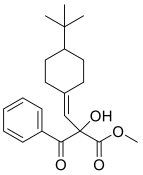
Dineopentylzinc (34)

Under argon atmosphere to a mixture of Mg (2.12 g, 87.4 mmol, 1.10 equiv.) in Et_2O (22 mL) was added dropwise neopentyl bromide (12.0 mL, 79.4 mmol, 1.00 equiv.) and the reaction mixture was stirred for 3 h. It was cooled to 0 °C, $ZnCl_2$ (5.41 g, 39.7 mmol, 0.50 equiv.) was added and the reaction mixture was stirred for 48 h. It was filtered, the solvent was removed in vacuo and after vacuum distillation **34** (3.84 g, 18.5 mmol, 47%) was obtained as colourless liquid.

b.p.: 60 °C at 10 mbar. **^{1}H-NMR** (300 MHz, C_6D_6) δ = 0.46 (s, 2H, $C\mathit{H}_2$), 1.08 (s, 9H, $C(C\mathit{H}_3)_3$) ppm. **^{13}C-NMR** (75 MHz, C_6D_6) δ = 35.7 ($\mathit{C}(CH_3)_3$), 35.8 ($C(\mathit{C}H_3)_3$), 37.1 ($\mathit{C}H_2$) ppm.

Methyl 2-((4-*tert*-butyl)cyclohexylidene)methyl)-2-hydroxy-3-oxo-3-phenylpropanoate (38a)

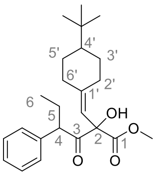
The title compound was prepared from alkenyl iodide **29** (0.3 M in THF, 1.00 mL, 0.30 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.43 mL, 0.60 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 0.60 mL, 0.60 mmol, 2.0 equiv.) and α,β-diketoester **14a** (0.5 M in CH_2Cl_2, 1.20 mL, 0.60 mmol, 2.0 equiv.) according to **GP8** to afford **38a** (68 mg, 0.25 mmol, 82%, d.r. 5:1) as colourless oil after SCC (*n*-pentane/ EtOAc 10:1).



38a **TLC:** R_f= 0.36 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 0.26 (ddd, *J* = 3.7, 12.8, 25.7 Hz, 1H, Cy), 0.64 (s, 9H, $C(CH_3)_3$), 0.81-0.92 (m, 2H, Cy), 0.98-1.12 (m, 1H, Cy), 1.36-1.85 (m, 3H, Cy), 2.24-2.43 (m, 2H, Cy), 3.73 (s, 3H, OCH_3), 5.00 (s, 1H, OH), 6.16 (s, 1H, C=C*H*), 7.39-7.47 (m, 2H, Ph), 7.56 (t, *J* = 7.42 Hz, 1H, Ph), 8.06-8.12 (m, 2H, Ph) ppm. Signals of major diastereomer are reported only. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ =27.0 (Cy), 27.5 ($C(CH_3)_3$), 27.9 (Cy), 28.9 (Cy), 29.9 (Cy), 32.3 ($C(CH_3)_3$), 47.5 (4'-C), 53.5 (OCH_3), 80.8 (2-C), 118.3 (C=*C*H), 128.4 (Ph), 130.8 (Ph), 132.2 (Ph), 134.1 (Ph), 149.5 (*C*=CH), 171.5 (1-C), 196.8 (3-C) ppm. Signals of major diastereomer are reported only. **HRMS:** ESI$^+$ calcd. for $C_{21}H_{28}O_4Na$ $[M+Na]^+$: 367.1880, found: 367.1881. **IR** (ATR): v =3462 (br, w), 3062 (w), 2947 (m), 2864 (w), 1742 (m), 1681 (s), 1598 (w), 1581 (w), 1448 (m), 1392 (w), 1365 (m), 1260 (w), 1223 (s), 1167 (m), 1130 (m), 1087 (w), 1068 (w), 1031 (w), 1012 (w), 988 (w), 940 (w), 911 (w), 833 (w), 806 (w), 749 (w), 690 (m), 631 (w), 549 (w) cm^{-1}.

Methyl 2-((4-(*tert*-butyl)cyclohexylidene)methyl)-2-hydroxy-3-oxo-4-phenylhexanoate (38b)

The title compound was prepared from alkenyl iodide**29** (0.3 M in THF, 1.00 mL, 0.30 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.43 mL, 0.60 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 0.60 mL, 0.60 mmol, 2.0 equiv.) and α,β-diketoester **14a** (0.5 M in CH_2Cl_2, 1.20 mL, 0.60 mmol, 2.0 equiv.) according to **GP8** to afford **38b** (fist diastereomer 25 mg, 65 µmol, 22%) as colourless foam and **38b** (second diastereomer 27 mg, 70 µmol, 23%) as colourless solid after SCC (*n*-pentane/ EtOAc 25:1).



38b *Mixture of diastereomers:* **HRMS:** ESI$^+$ calcd. for $C_{24}H_{34}O_4Na$ $[M+Na]^+$: 409.2349, found: 409.2352. **IR** (ATR): v = 3477 (br, w), 3062 (w), 3030 (w), 2948 (s), 2869 (w), 2840 (w), 1744 (w), 1716 (s), 1659 (w), 1600 (w), 1453 (m), 1438 (w), 1365 (w), 1252 (w), 1237 (s), 1174 (w), 1145 (w), 1121 (w), 1073 (w), 1032 (w), 992 (w), 925 (w), 899 (w), 855 (w), 831 (w), 752 (w), 700 (m), 574 (w), 502 (w) cm^{-1}.

1. diastereomer:

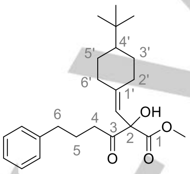
TLC: R_f= 0.44 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 0.50 (m, 1H, 2'-H_a), 0.71-0.75 (m, 12H, 6-H, $C(CH_3)_3$), 0.80-0.87 (m, 2H, 4'-H, 3'-H_a), 0.94-1.04 (ddd, *J* = 3.8, 12.8, 25.3 Hz, 1H, 5'-H_a), 1.53-1.64 (m, 2H, 3'-H_b, 5'-H_b), 1.70-1.80 (m, 2H, 6'-H_a, 5-H_a), 1.90-1.98 (m, 1H, 5-H_b), 2.10-2.20 (m, 2H, 2'-H_b, 6'-H_b), 3.70 (s, 3H, OCH_3), 4.03 (t, *J* = 7.5 Hz, 1H, 4-H), 4.39 (s, 1H, OH), 5.78 (br s, 1H, C=CH), 7.11-7.45 (m, 5H, Ph) ppm.**^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 12.0 (6-C), 27.7 ($C(CH_3)_3$), 27.9 (3'-C), 28.3 (5-C), 28.9 (5'-C), 29.3 (2'-C), 32.5 ($C(CH_3)_3$), 37.2 (6'-C), 47.8 (4'-C), 53.4 (OCH_3), 55.4 (4-C), 83.4 (2-C), 115.3 (C=*C*H), 127.2 (4-C-Ph), 128.4 (2-C-Ph), 128.6 (3-C-Ph), 138.9 (1-C-Ph), 151.4 (1'-C), 171.1 (1-C), 206.6 (3-C) ppm.

2. diastereomer:

TLC: R_f= 0.42 (*n*-pentane/EtOAc 10:1). **M.p.:** 99.5 °C. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 0.13 (ddd, *J* = 3.8, 12.8, 25.7 Hz, 1H, 3'-H_a), 0.65 (ddd, *J* = 3.9, 12.5, 25.5 Hz, 1H, 5'-H_a), 0.71 (s, 9H, $C(CH_3)_3$), 0.75 (m, 3H, 6-H), 0.89-0.94 (m, 1H, 4'-H), 1.43-1.49 (m, 1H, 3'-H_b), 1.60-1.66 (m, 2H, 5'-H_b, 2'-H_a), 1.71-1.78 (m, 1H, 5-H_a), 1.87-1.95 (m, 2H, 5-H_b, 6'-H_a), 2.17 (ddd, J = 3.0, 5.3, 13.7 Hz, 1H, 6'-H_b), 2.41 (ddd, J = 3.0, 5.2, 14.3 Hz, 1H, 2'-H_b), 3.66 (s, 3H, OCH_3), 4.07-4.11 (m, 1H, 4-H), 4.35 (s, 1H, OH), 5.73 (br s, 1H, C=CH), 7.17-7.23 (m, 2H, Ph), 7.26-7.29 (m, 3H, Ph) ppm.**^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 12.0 (6-C), 26.9 (3'-C), 27.8 ($C(CH_3)_3$), 28.1 (5'-C), 28.6 (5-C), 29.7 (2'-C), 32.3 ($C(CH_3)_3$), 37.5 (6'-C), 47.9 (1'-C), 53.4 (OCH_3), 54.9 (4-C), 83.6 (2-C), 115.6 (C=*C*H), 127.6 (4-C-Ph), 128.5 (2-C-Ph), 128.8 (3-C-Ph), 138.7 (1-C-Ph), 149.4 (1'-C), 171.2 (1-C), 206.0 (3-C) ppm.

Methyl 2-((4-*tert*-butyl)cyclohexylidene)methyl)-2-hydroxy-3-oxo-6-phenylhexanoate (38c)

The title compound was prepared from alkenyl iodide**29** (0.3 M in THF, 1.00 mL, 0.30 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.43 mL, 0.60 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 0.60 mL, 0.60 mmol, 2.0 equiv.) and α,β-diketoester **14c** (0.5 M in CH_2Cl_2 1.20 mL, 0.60 mmol, 2.0 equiv.) according to **GP8** to afford **38c** (50 mg, 181 µmol, 60%, d.r. 1.2:1) as colourless oil after SCC (*n*-pentane/ EtOAc 15:1).



38c *Mixture of diastereomers:***HRMS:** ESI$^+$ calcd. for $C_{24}H_{34}O_4Na$ $[M+Na]^+$: 409.2349, found: 409.2352. **IR** (ATR): v = 3472 (w) 3026 (w), 2945 (m), 2865 (w), 2841 (w), 1717 (s), 1660 (w), 1496 (w), 1451 (w), 1437 (w), 1394 (w), 1364 (m), 1253 (w), 1237 (s), 1172 (w), 1142 (w), 1098 (w), 1030 (w), 1011 (w), 990 (w), 925 (w), 830 (w), 744 (m), 700 (s), 652 (w), 491 (w) cm^{-1}.

1. diastereomer

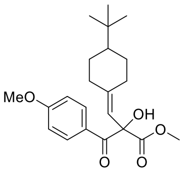
TLC: R_f= 0.26 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 0.83 (s, 9H, $C(CH_3)_3$), 0.97-1.08 (m, 1H, 3'-H_a), 1.08-1.17 (m, 2H, 5'-H_a, 4'-H), 1.53 (td, *J* = 4.3, 13.1 Hz, 1H, 6'-H_a), 1.77-1.83 (m, 1H, 3'-H_b), 1.83-1.88 (m, 1H, 5'-H_b), 1.91 (dt, *J* = 7.3, 14.7 Hz, 2H, 5-H), 1.98-2.06 (m, 1H, 2'-H_a), 2.26-2.32 (m, 1H, 2'-H_b), 2.56-2.61 (m, 3H, 6'-H_b, 6-H), 2.64 (t, *J* = 7.2 Hz, 2H, 4-H), 3.76 (s, 3H, OCH_3), 4.43 (s, 1H, OH), 5.74 (s, 1H, C=C*H*), 7.13-7.21 (m, 3H, Ph), 7.26-7.30 (m, 2H, Ph) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 25.6 (5-C), 27.7 ($C(CH_3)_3$), 28.2 (2'-C), 29.2 (3'-C), 29.9 (6'-C), 32.6 ($C(CH_3)_3$), 35.0 (6-C), 36.5 (4-C), 37.6 (5'-C), 48.0 (4'-C), 53.5 (OCH_3), 82.9 (2-C), 116.6 (C=*C*H), 126.2 (4-C-Ph), 128.5 (3-C-Ph), 128.5 (2-C-Ph), 141.5 (1-C-Ph), 150.0 (1'-C), 171.4 (1-C) 206.4 (3-C) ppm.

2. diastereomer

TLC: R_f= 0.21 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 0.91 (s, 9H, $C(CH_3)_3$), 0.94-1.00 (m, 1H, 3'-H_a), 1.09-1.19 (m, 1H, 5'-H_a), 1.19-1.28 (m, 1H, 4'-H),1.80-1.91 (m, 2H, 3'-H_b, 6'-H_a), 1.94-2.07 (m, 3H, 5'-H_b), 2.12-2.19 (m, 1H, 2'-H_a), 2.37-2.43 (m, 1H, 2'-H_b), 2.65-2.86 (m, 5H, 6'-H_b, 6-H, 4-H), 3.86 (s, 3H, OCH_3), 4.51 (s, 1H, OH), 5.81 (s, 1H, C=C*H*), 7.24-7.31 (m, 3H, Ph), 7.35-7.39 (m, 2H, Ph) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 25.8 (5-C), 27.6 ($C(CH_3)_3$), 27.9 (2'-C), 29.1 (3'-C), 29.7 (6'-C), 32.5 ($C(CH_3)_3$), 35.1 (6-C), 36.5 (4-C), 37.6 (5'-C), 47.8 (4'-C) 53.5 (OCH_3), 83.0 (2-C), 116.7 (C=*C*H), 126.2 (4-C-Ph), 128.5 (3-C-Ph), 128.5 (2-C-Ph), 141.4 (1-C-Ph), 149.7 (1'-C), 171.4 (1-C), 206.3 (3-C) ppm.

Methyl 2-((4-(tert-butyl)cylohexylidene)methyl)-2-hydroxy-3-(4-methoxyphenyl)-3-oxopropanoate (38e)

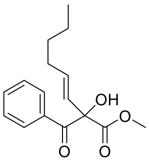
The title compound was prepared from alkenyl iodide**29** (0.3 M in THF, 1.00 mL, 0.30 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.43 mL, 0.60 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 0.60 mL, 0.60 mmol, 2.0 equiv.) and α,β-diketoester **14e** (0.5 M in CH_2Cl_2, 1.20 mL, 0.60 mmol, 2.0 equiv.) according to **GP8** to afford **38e** (69 mg, 184 µmol, 61%, d.r. 1.2:1) as colourless oil after SCC (*n*-pentane/ EtOAc 20:1 → *n*-pentane/ EtOAc 15:1).



38e **TLC:** R$_f$= 0.21 (*n*-pentane/EtOAc 10:1). Signals of the minor diastereomer are indicated by *. **^{1}H-NMR:** (500 MHz, CDCl$_3$) δ = 0.14-0.30 (m, 1H, 3-H$_a$), 0.64 (s, 9H, C(CH$_3$)$_3$), 0.78* (s, C(CH$_3$)$_3$), 0.80-0.86 (m, 1H, 4'-H), 0.87-1.14 (m, 2H, 4'-H*, 3'-H$_b$, 5'-H$_a$), 1.31-1.43 (m, 1H, 6'-H$_a$), 1.46-1.51 (m, 3-H$_a$*), 1.62-1.84 (m, 2H, 3'-H$_b$, 6-H$_a$*), 1.88-2.08 (m, 1H, 2'-H$_a$, 2'-H$_a$*), 2.26-2.52 (m, 2H, 2'-H$_b$, 2'-H$_b$*, 6'-H$_b$, 6'-H$_b$*), 3.69*, 3.70 (2 s, 3H, COOCH$_3$), 3.84, 3.85* (2 s, 3H, OCH$_3$), 5.07*, 5.16 (2 s, 1H, OH), 6.13*, 6.20 (2 s, 1H, C=CH), 6.89*, 6.90 (2 d, 2H, 3-H-Ph), 8.05*, 8.09 (2 d, 2H, 2-H-Ph) ppm. **^{13}C-NMR:** (125 MHz, CDCl$_3$) δ = 26.9, 27.9* (3'-C), 27.5, 27.7* (C(CH$_3$)$_3$), 28.9, 29.0* (5'-C), 29.7*, 29.9 (6'-C), 32.3, 32.5* (C(CH$_3$)$_3$), 37.5*, 37.7 (2'-C), 47.4, 47.8* (4'-C), 53.4*, 53.4 (COOCH$_3$), 55.6*, 55.6 (OCH$_3$), 80.5, 80.5* (2-C), 113.6, 113.7* (3-C-Ph), 118.4*, 118.7 (C=*C*H), 124.7, 124.8* (1-C-Ph), 133.1*, 133.5 (2-C-Ph), 149.2*, 149.2 (*C*=CH), 164.2*, 164.3 (4-C-Ph), 171.7, 171.9* (1-C), 194.6*, 195.1 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{22}H_{30}O_5Na$ [M+Na]$^+$: 397.1985; found: 397.1976. **IR(ATR):** ν = 3434 (br, w), 2946 (m), 2865 (w), 2842 (w), 1740 (m), 1669 (m), 1598 (s), 1574 (w), 1511 (m), 1439 (w), 1392 (w), 1365 (w), 1311 (w), 1257 (s), 1227 (w), 1165 (s), 1129 (m), 1087 (w), 1064 (w), 1027 (m), 988 (w), 941 (w), 911 (m), 846 (m), 801 (w), 731 (s), 633 (w), 610 (m), 553 (w), 511 (w), 452 (w) cm^{-1}.

Methyl (*E*)-2-benzoyl-2-hydroxyoct-3-enoate (39a)

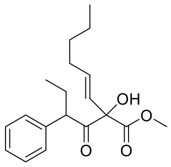
The title compound was prepared from *E*-alkenyl iodide **36** (0.5 M in THF, 1.00 mL, 0.50 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.71 mL, 1.00 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 1.00 mL, 1.00 mmol, 2.0 equiv.) and α,β-diketoester **14a** (0.5 M in CH$_2$Cl$_2$, 2.00 mL, 1.00 mmol, 2.0 equiv.) according to **GP8** to afford **39a** (69 mg, 249 µmol, 50%) as colourless oil after SCC (*n*-pentane/ EtOAc 12:1).



39a **TLC:** R$_f$= 0.35 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (300 MHz, CDCl$_3$) δ = 0.84 (t, *J* = 7.12 Hz, 3H, 8-H), 1.13-1.46 (m, 4H, 6-H, 7-H), 2.01-2.27 (m, 2H, 5-H), 3.77 (s, 3H, OCH$_3$), 4.70 (s, 1H, OH), 5.98 (dt, *J* = 6.63, 15.6 Hz, 1H, 4-H), 6.13 (d, *J* = 15.6 Hz, 1H, 3-H), 7.39-7.50 (m, 2H, 3-H-Ph), 7.52-7.71 (m, 1H, 4-H-Ph), 7.89-8.09 (m, 2H, 2-H-Ph) ppm. **^{13}C-NMR** (75 MHz, CDCl$_3$) δ = 13.9 (8-C), 22.2 (7-C), 30.9 (6-C), 32.1 (5-C), 53.5 (OCH$_3$), 82.1 (2-C), 126.3 (3-C), 128.6 (3-C-Ph), 130.2 (2-C-Ph), 132.3 (1-C-Ph), 133.8 (4-C-Ph), 135.4 (4-C), 171.8 (1-C), 194.8 (Ph*C*O) ppm. **HRMS:** ESI$^+$ calcd. for $C_{16}H_{20}O_4Na$ [M+Na]$^+$: 299.1254; found: 299.1253. **IR** (ATR): ν =3468 (br, w), 2956 (w), 2928 (w), 2857 (w), 1739 (m), 1682 (s), 1597 (w), 1580 (w), 1448 (m), 1365 (w), 1260 (w), 1229 (s), 1183 (w), 1154 (m), 1121 (w), 1075 (w), 1016 (w), 970 (m), 923 (w), 889 (w), 802 (m), 751 (w), 690 (s), 646 (w) cm^{-1}.

Methyl (*E*)-2-hydroxy-2-(2-phenylbutanoyl)oct-3-enoate (39b)

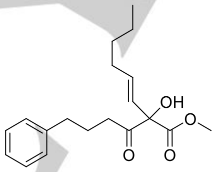
The title compound was prepared from *E*-alkenyl iodide**36** (0.5 M in THF, 1.00 mL, 0.50 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.71 mL, 1.00 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 1.00 mL, 1.00 mmol, 2.0 equiv.) and α,β-diketoester **14b** (0.5 M in CH$_2$Cl$_2$, 2.00 mL, 1.00 mmol, 2.0 equiv.) according to **GP8** to afford **39b** (73 mg, 229 µmol, 46%, d.r. 1.5:1) as colourless oil after SCC (*n*-pentane/ EtOAc 20:1 → 10:1).



39b **TLC:** R$_f$= 0.36 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, CDCl$_3$) δ = 0.82 (t, *J* = 7.3 Hz, 3H, 4'-H), 0.88 (t, *J* = 7.1 Hz, 3H, 8-H), 1.19-1.30 (m, 4H, 6-H, 7-H), 1.72-1.82 (m, 1H, 3'-H$_a$), 1.94-2.07 (m, 3H, 3'-H$_b$, 5-H), 3.64 (s, 3H, OCH$_3$), 4.19 (s, 1H, OH), 4.25 (t, *J* = 7.5 Hz, 1H, 2'-H), 5.88-5.96 (m, 2H, 3-H, 4-H), 7.24-7.28 (m, 3H, Ph), 7.30-7.34 (m, 2H, Ph) ppm. Signals of major diastereomer are reported only. **^{13}C-NMR** (125 MHz, CDCl$_3$) δ = 12.0 (4'-C), 14.0 (8-C), 22.3 (7-C), 27.3 (3'-C), 30.9 (6-C), 31.9 (5-C), 53.4 (OCH$_3$), 54.4 (2'-C), 83.8 (2-C), 124.7 (3-C), 127.4 (4-C-Ph), 128.7 (3-C-Ph, 2-C-Ph), 133.8 (4-C), 138.2 (1-C-Ph), 170.8 (1-C), 205.7 (1'-C) ppm. Signals of major diastereomer are reported only. **HRMS:** ESI$^+$ calcd. for $C_{19}H_{26}O_4Na$ [M+Na]$^+$: 341.1723, found: 341.1731. **IR** (ATR): ν = 3482 (br, w), 3029 (w), 2958 (m), 2929 (w), 2873 (w), 1718 (s), 1600 (w), 1492 (w), 1454 (m), 1436 (w), 1378 (w) 1346 (w), 1248 (s), 1203 (w), 1167 (w), 1121 (w), 1080 (w), 1024 (w), 973 (m), 934 (w), 899 (w), 831 (w), 743 (w), 699 (s), 656 (w), 562 (w), 506 (w), 431 (w) cm^{-1}.

Methyl (*E*)-2-hydroxy-2-(4-phenylbutanoyl)oct-3-enoate (39c)

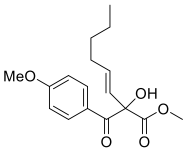
The title compound was prepared from *E*-alkenyl iodide**36** (0.5 M in THF, 0.60 mL, 0.30 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.43 mL, 0.60 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 1.00 mL, 1.00 mmol, 2.0 equiv.) and α,β-diketoester **14c** (0.5 M in CH$_2$Cl$_2$ 1.20 mL, 0.60 mmol, 2.0 equiv.) according to **GP8** to afford **39c** (25 mg, 78.5 µmol, 26%) as colourless oil after SCC (*n*-pentane/ EtOAc 10:1).



39c **TLC:** R$_f$= 0.60 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, CDCl$_3$) δ = 0.89 (t, *J* = 7.2 Hz, 3H, 8-H), 1.25-1.38 (m, 4H, 6-H 7-H), 1.88-1.95 (m, 2H, 3'-H), 2.08 (dt, *J* = 4.0, 7.9 Hz, 2H, 5-H), 2.57-2.62 (m, 2H, 4'-H), 2.63-2.75 (m, 2H, 2'-H), 3.78 (s, 3H, OCH$_3$), 4.32 (s, 1H, OH), 5.98 (dt, *J* = 1.4, 15.4 Hz, 1H, 4-H), 6.13 (dt, *J* = 6.8, 15.4 Hz, 1H, 3-H), 7.13-7.21 (m, 3H, 4-H-Ph, 3-H-Ph), 7.25-7.31 (m, 2H, 2-H-Ph) ppm. **^{13}C-NMR** (125 MHz, CDCl$_3$) δ = 14.0 (8-C), 22.3 (7-C), 25.4 (3'-C), 31.1 (6-C), 31.9 (5-C), 35.0 (4'-C), 36.3 (2'-C), 53.5 (OCH$_3$), 83.8 (2-C), 124.7 (3-C), 126.2 (4-C-Ph), 128.5 (2-C-Ph, 3-C-Ph), 134.5 (4-C), 141.5 (1-C-Ph), 170.9 (1-C), 205.4 (2'-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{19}H_{26}O_4Na$ [M+Na]$^+$: 341.1723; found: 341.1724. **IR** (ATR): ν =3483 (br, w), 3027 (w), 2955 (w), 2928 (m), 2859 (w), 1718 (s), 1603 (w), 1496 (w), 1454 (w), 1437 (w), 1401 (w), 1365 (w), 1251 (s), 1204 (w), 1167 (w), 1097 (w), 1075 (w), 1027 (w), 974 (m), 930 (w), 820 (w), 745 (m), 699 (s) 563 (w), 491 (w), 434 (w) cm^{-1}.

Methyl (*E*)-2-hydroxy-2-(4-methoxybenzoyl)oct-3-enoate (39e)

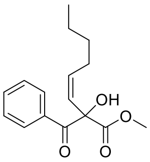
The title compound was prepared from *E*-alkenyl iodide **36** (0.5 M in THF, 1.00 mL, 0.50 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.71 mL, 1.00 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 1.00 mL, 1.00 mmol, 2.0 equiv.) and α,β-diketoester **14e** (0.5 M in CH$_2$Cl$_2$, 2.00 mL, 1.00 mmol, 2.0 equiv.) according to **GP8** to afford **39e** (101 mg, 330 µmol, 66%) as colourless oil SCC (*n*-pentane/ EtOAc 10:1).



39e **TLC:** R_f= 0.26 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR:** (500 MHz, CDCl$_3$) δ **=** 0.83 (t, *J* = 7.1 Hz, 3H, 8-H), 1.18-1.27 (m, 2H, 7-H), 1.29-1.36 (m, 2H, 6-H), 2.02-2.11 (m, 2H, 5-H), 3.74 (s, 3H, COOCH$_3$), 3.86 (s, 3H, OCH$_3$), 4.88 (s, 1H, OH), 5.94 (dt, *J* = 6.9, 15.5 Hz, 1H, 4-H), 6.15 (dt, *J* = 1.4, 15.5 Hz, 1H, 3-H), 6.91 (d, *J* = 9.0 Hz, 2H, 3-H-Ph), 8.02 (d, *J* = 9.0 Hz, 2H, 2-H-Ph) ppm. **^{13}C-NMR:** (125 MHz, CDCl$_3$) δ **=** 14.0 (8-C), 22.2 (7-C), 30.9 (6-C), 32.1 (5-C), 53.4 (COOCH$_3$), 55.7 (OCH$_3$), 81.7 (2-C), 113.9 (3-C-Ph), 125.6 (1-C-Ph), 126.6 (3-C), 132.7 (2-C-Ph), 135.1 (4-C), 164.2 (4-C-Ph), 171.9 (1-C), 192.9 (C=O) ppm. **HRMS:** ESI$^+$ calcd. for C$_{17}$H$_{22}$O$_5$Na [M+Na]$^+$: 329.1359; found: 329.1340. **IR** (ATR): v = 3465 (br, w), 2956 (w), 2929 (w), 2856 (w), 1738 (m), 1674 (m), 1598 (s), 1574 (w), 1511 (m), 1460 (w), 1437 (w), 1375 (w), 1311 (w), 1238 (s), 1155 (m), 1120 (w), 1063 (w), 1023 (m), 970 (w), 922 (w), 892 (w), 845 (m), 792 (w), 731 (w), 639 (w), 610 (m), 513 (w) cm^{-1}.

Methyl (*Z*)-2-benzoyl-2-hydroxyoct-3-enoate (40a)

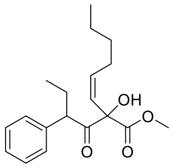
The title compound was prepared from *Z*-alkenyl iodide**37** (0.5 M in THF, 1.00 mL, 0.50 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.71 mL, 1.00 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 1.00 mL, 1.00 mmol, 2.0 equiv.) and α,β-diketoester **14a** (0.5 M in CH$_2$Cl$_2$, 2.00 mL, 1.00 mmol, 2.00 equiv.) according to **GP8** to afford **40a** (21 mg, 76.0 µmol, 15%) as colourless oil after SCC (*n*-pentane/ EtOAc 11:1).



40a **TLC:** R_f= 0.35 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, CDCl$_3$) δ =0.78 (t, *J* = 7.1 Hz, 3H, 8-H), 1.07-1.25 (m, 4H, 6-H, 7-H), 1.82-1.97 (m, 1H, 5-H$_a$), 2.01-2.12 (m, 1H, 5-H$_b$), 3.73 (s, 3H, OCH$_3$), 4.98 (s, 1H, OH), 5.69 (dt, *J* = 7.6, 11.4 Hz, 1H, 4-H), 6.34 (dt, *J* = 1.7, 11.4 Hz, 1H, 3-H), 7.41-7.47 (m, 2H, 3-H-Ph), 7.54-7.61 (m, 1H, 4-H-Ph), 8.00-8.08 (m, 2H, 2-H-Ph) ppm. **^{13}C-NMR** (125 MHz, CDCl$_3$) δ = 14.0 (8-C), 22.4 (7-C), 28.4 (5-C), 31.2 (6-C), 53.5 (OCH$_3$), 81.2 (2-C), 125.4 (3-C), 128.6 (3-C-Ph), 130.4 (2-C-Ph), 132.1 (1-C-Ph), 134.2 (4-C-Ph), 138.9 (4-C), 171.4 (1-C), 195.5 (Ph*C*O) ppm. **HRMS:** ESI$^+$ calcd. for C$_{16}$H$_{20}$O$_4$Na [M+Na]$^+$: 299.1254, found: 299.1253. **IR** (ATR): v = 3455 (br, w), 2956 (m), 2928 (w), 2860 (w), 1741 (m), 1681 (s), 1597 (w), 1580 (w), 1449 (m), 1436 (w), 1362 (w), 1225 (s), 1184 (w), 1145 (m), 1101 (m), 1063 (w), 1020 (w), 961 (w), 920 (w), 890 (w), 813 (w), 732 (w), 690 (s) cm^{-1}.

Methyl (*Z*)-2-hydroxy-2-(2-phenylbutanoyl)oct-3-enoate (40b)

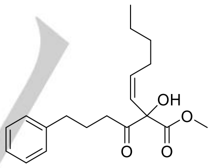
The title compound was prepared from *Z*-alkenyl iodide**37** (0.5 M in THF, 1.00 mL, 0.50 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.71 mL, 1.00 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 0.83 mL, 1.00 mmol, 2.0 equiv.) and α,β-diketoester **14b** (0.5 M in CH$_2$Cl$_2$, 2.00 mL, 1.00 mmol, 2.0 equiv.) according to **GP8** to afford **40b** (45 mg, 0.14 mmol, 40%, d.r. 4:1) as colourless oil after SCC (*n*-pentane/ EtOAc 25:1).



40b **TLC:** R_f= 0.37 (*n*-pentane/EtOAc 10:1). *Mixture of diastereomers 4:1. Signals of minor diastereomer indicated by *, if separated:* **^{1}H-NMR:** (300 MHz, CDCl$_3$) δ **=** 0.77 (dd, *J* = 6.9, 13.4 Hz, 6H, 8-H, 4'-H), 0.96-1.35 (m, 4H, 5-H, 7-H), 1.63-1.84 (m, 2H, 6-H$_a$, 3'-H$_a$), 1.88-2.06 (m, 2H, 6-H$_b$, 3'-H$_b$), 3.20* (s, OCH$_3$), 3.60 (s, 3H, OCH$_3$), 3.99* (t, *J* = 7.5 Hz, 2'-H), 4.14 (t, *J* = 7.5 Hz, 1H, 2'-H), 4.29 (s, 1H, OH), 4.42* (s, OH), 5.49 (dt, *J* = 7.4, 11.4 Hz, 1H, 4-H), 5.71-7.84* (m, 4-H), 5.93 (d, *J* = 11.4 Hz, 1H, 3-H), 6.14* (d, *J* = 11.4 Hz, 3-H), 7.16-7.30 (m, 5H, Ph) ppm. **^{13}C-NMR:** (75 MHz, CDCl$_3$) δ = 11.9 (8-C), 13.9 (4'-C), 14.0* (4'-C), 22.4 (7-C), 22.5* (7-C), 28.0 (6-C), 28.2 (3'-C), 28.2* (6-C), 28.3* (3'-C), 31.3 (5-C), 31.6* (5-C), 52.8* (OCH$_3$), 53.4 (OCH$_3$), 54.9 (2'-C), 55.1* (2'-C), 83.7* (2-C), 83.8 (2-C), 123.0* (3-C), 123.4 (3-C), 127.4 (4-C-Ph), 127.5* (4-C-Ph), 128.6* (2-C-Ph), 128.6* (3-C-Ph), 128.7 (2-C-Ph), 128.7 (3-C-Ph), 138.1* (1-C-Ph), 138.5 (1-C-Ph), 138.9 (4-C), 139.3* (4-C), 170.3* (1-C), 171.0 (1-C), 204.4* (1'-C), 205.6 (1'-C) ppm. **HRMS:** ESI$^+$ calcd. for C$_{19}$H$_{26}$O$_4$Na [M+Na]$^+$: 341.1723; found: 341.1726. **IR** (ATR): v = 3480 (w), 3030 (w), 2958 (m), 2929 (w), 2873 (w), 1717 (s), 1650 (w), 1600 (w), 1492 (w), 1454 (m), 1436 (w), 1378 (w), 1347 (w), 1246 (s), 1158 (m), 1123 (w), 1077 (w), 1056 (w), 1028 (w), 938 (w), 897 (w), 847 (w), 828 (w), 797 (w), 744 (m), 699 (s), 585 (w), 509 (w) cm^{-1}.

Methyl (*Z*)-2-hydroxy-2-(4-phenylbutanoyl)oct-3-enoate (40c)

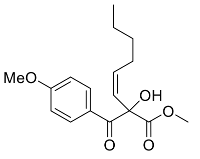
The title compound was prepared from *Z*-alkenyl iodide**37** (0.5 M in THF, 0.60 mL, 0.30 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.43 mL, 0.60 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 1.00 mL, 1.00 mmol, 2.0 equiv.) and α,β-diketoester **14c** (0.5 M in CH$_2$Cl$_2$ 1.20 mL, 0.60 mmol, 2.0 equiv.) according to **GP8** to afford **40c** (32 mg, 101 µmol, 20%) as colourless oil after SCC (*n*-pentane/ EtOAc 10:1).



40c **TLC:** R_f= 0.40 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR:** (500 MHz, CDCl$_3$) δ **=** 0.87 (t, *J* = 7.1 Hz, 3H, 8-H), 1.25-1.33 (m, 4H, 7-H 6-H), 1.92 (dt, *J* = 1.4, 9.0 Hz, 2H, 3'-H), 1.97-2.21 (m, 2H, 5-H), 2.58-2.63 (m, 2H, 4'-H), 2.67 (t, *J* = 7.2 Hz, 2H, 2'-H), 3.77 (s, 3H, OCH$_3$), 4.43 (s, 1H, OH), 5.70 (dt, *J* = 7.5, 11.4 Hz, 1H, 4-H), 5.93 (dt, *J* = 1.7, 11.4 Hz 1H, 3-H), 7.14-7.21 (m, 3H, Ph), 7.26-7.30 (m, 2H, Ph) ppm. **^{13}C-NMR:** (125 MHz, CDCl$_3$) δ = 14.0 (8-C), 22.5 (7-C), 25.6 (3'-C), 28.2 (5-C), 31.6 (6-C), 35.0 (4'-C), 36.4 (2'-C), 53.5 (OCH$_3$), 83.7 (2-C), 124.0 (3-C), 126.2 (4-C-Ph), 128.5 (3-C-Ph), 128.6 (2-C-Ph), 138.8 (4-C), 141.4 (1-C-Ph), 171.1 (1-C), 205.5 (1'-C) ppm. **HRMS:** ESI$^+$ calcd. for C$_{19}$H$_{26}$O$_4$Na [M+Na]$^+$: 341.1723; found: 341.1716. **IR** (ATR): v =3474 (br, w), 3027 (w) 2955 (m), 2928 (w), 2860 (w), 1718 (s), 1496 (w), 1454 (w), 1436 (w), 1403 (w), 1362 (w), 1246 (s), 1210 (w), 1159 (w), 1091 (w), 1014 (w), 975 (w), 911 (w), 801 (w), 744 (m), 699 (s), 491 (w) cm^{-1}.

Methyl (*Z*)-2-hydroxy-2-(4-methoxybenzoyl)oct-3-enoate (40e)

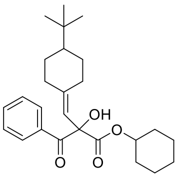
The title compound was prepared from *Z*-alkenyl iodide **37** (0.5 M in THF, 1.00 mL, 0.50 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.71 mL, 1.00 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 1.00 mL, 1.00 mmol, 2.0 equiv.) and α,β-diketoester **14e** (0.5 M in CH$_2$Cl$_2$, 2.00 mL, 1.00 mmol, 2.00 equiv.) according to **GP8** to afford **40e** (40 mg, 131 µmol, 13%) as colourless oil after SCC (*n*-pentane/ EtOAc 11:1).



40e **TLC:** R$_f$= 0.26 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR:** (500 MHz, $CDCl_3$) δ = 0.77 (t, *J* = 7.1 Hz, 3H, 8-H), 1.08-1.23 (m, 4H, 7-H, 6-H), 1.80-1.89 (m, 1H, 5-H$_a$), 2.01-2.10 (m, 1H, 5-H$_b$), 3.70 (s, 3H, $COOCH_3$), 3.86 (s, 3H, OCH_3), 5.14 (s, 1H, OH), 5.67 (dt, *J* = 7.5, 11.3 Hz, 1H, 4-H), 6.38 (dt, *J* = 1.7, 11.3 Hz, 1H, 3-H), 6.91 (d, *J* = 9.1 Hz, 2H, 3-H-Ph), 8.04 (d, *J* = 9.1 Hz, 2H, 2-H-Ph) ppm. **^{13}C-NMR:** (125 MHz, $CDCl_3$) δ = 14.0 (8-C), 22.4 (7-C), 28.2 (5-C), 31.2 (6-C), 53.4 (COO*C*H$_3$), 55.7 (OCH_3), 80.8 (2-C), 113.9 (3-C-Ph), 124.7 (1-C-Ph), 125.9 (3-C), 133.0 (2-C-Ph), 138.6 (4-C), 164.4 (4-C-Ph), 171.6 (1-C), 193.8 (C=O) ppm. **HRMS:** ESI$^+$ calcd. for $C_{17}H_{22}O_5Na$ [M+Na]$^+$: 329.1359; found: 329.1358. **IR(ATR):** ν = 3421 (br, w), 2956 (w), 2929 (w), 2859 (w), 1740 (m), 1671 (m), 1598 (s), 1574 (w), 1511 (m), 1460 (w), 1438 (w), 1362 (w), 1312 (w), 1255 (w), 1233 (s), 1173 (s), 1144 (w), 1102 (w), 1062 (w), 1024 (m), 962 (w), 920 (w), 891 (w), 845 (m), 789 (w), 728 (w), 656 (w), 612 (m), 514 (w) cm^{-1}.

Cyclohexyl 2-((4-*tert*-butyl)cyclohexylidene)methyl)-2-hydroxy-3-oxo-3-phenylpropanoate (41a)

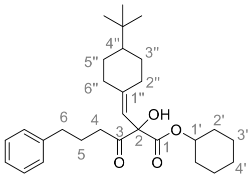
The title compound was prepared from alkenyl iodide**29** (0.3 M in THF, 1.00 mL, 0.30 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.43 mL, 0.60 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 0.60 mL, 0.60 mmol, 2.0 equiv.) and α,β-diketoester **15a** (0.5 M in CH_2Cl_2, 1.20 mL, 0.60 mmol, 2.0 equiv.) according to **GP8** to afford **41a** (78 mg, 230 µmol, 75%, d.r. 2:1) as colourless oil after SCC (*n*-pentane/ EtOAc 11:1).



41a **TLC:** R$_f$= 0.76 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 0.33 (ddd, *J* = 3.7, 12.8, 25.7 Hz, 1H, Cy), 0.65 (s, 9H, C(C*H*$_3$)$_3$), 0.77* (s, C(C*H*$_3$)$_3$), 0.78-0.91 (m, 1H, Cy-Hex), 0.98-1.12 (m, 1H, Cy), 1.17-1.38 (m, 4H, Cy), 1.38-1.85 (m, 10H, Cy), 1.89-2.08 (m, 1H, Cy), 2.28-2.60 (m, 2H, Cy), 4.77-4.84 (m, 1H, Cy), 4.81* (s, 1H, OH), 4.91 (s, 1H, OH), 6.06* (br s, C=C*H*), 6.13 (br s, 1H, C=C*H*), 7.39-7.44 (m, 2H, Ph), 7.51-7.56 (m, 1H, Ph), 8.02-8.09 (m, 2H, Ph) ppm. Signals of major diastereomer are reported only, accept for two signals of the minor diastereomer, which are indicated with *. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 23.4 (Cy), 25.3 (Cy), 27.1 (Cy), 27.5 (C(*C*H$_3$)$_3$), 27.7 (Cy), 28.9 (Cy), 29.9 (Cy), 31.0 (Cy), 31.1 (Cy), 32.3 (*C*(CH$_3$)$_3$), 37.7 (Cy), 47.6 (4''-C), 75.0 (1'-C), 80.9 (2-C), 118.3 (C=*C*H), 128.3 (Ph), 130.6 (Ph), 132.6 (Ph), 133.8 (Ph), 149.3 (*C*=CH), 170.3 (1-C), 196.9 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{26}H_{36}O_4Na$ [M+Na]$^+$: 435.2506, found: 435.2513. **IR** (ATR): ν = 3456 (br, w), 3061 (w), 2938 (s), 2861 (w), 2125 (w), 1735 (m), 1681 (s), 1597 (w), 1581 (w), 1449 (m), 1365 (m), 1317 (w), 1258 (w), 1240 (w), 1221 (s), 1167 (m), 1124 (m), 1088 (w), 1067 (w), 1034 (w), 1009 (m), 985 (w), 957 (w), 934 (m), 915 (w), 830 (w), 810 (w), 744 (w), 689 (s), 631 (w), 595 (w), 564 (w), 541 (w), 439 (w) cm^{-1}.

Cyclohexyl 2-((4-*tert*-butyl)cyclohexylidene)methyl)-2-hydroxy-3-oxo-6-phenylhexanoate (41c)

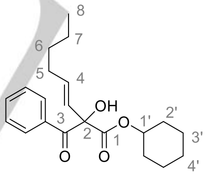
The title compound was prepared from alkenyl iodide**29** (0.3 M in THF, 1.00 mL, 0.30 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.43 mL, 0.60 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 0.60 mL, 0.60 mmol, 2.0 equiv.) and α,β-diketoester **15c** (0.5 M in CH_2Cl_2, 1.20 mL, 0.60 mmol, 2.0 equiv.) according to **GP8** to afford **41c** (60 mg, 0.13 mmol, 44%,d.r. 1:1) as colourless oil after SCC (*n*-pentane/ EtOAc 20:1).



41c **TLC:** R$_f$= 0.68 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 0.82, 0.83 (2 s, 9H, C(C*H*$_3$)$_3$), 1.00-1.17 (m, 2H, 4''-H, 5''-H$_a$), 1.23-1.60 (m, 7H, 4'-H$_a$, 4'-H$_b$, 2'-H$_a$, 3'-H$_a$, 3''-H$_a$), 1.63-1.83 (m, 6H, 2'-H$_b$, 3'-H$_b$, 3''H$_b$, 5''-H$_b$), 1.84-1.96 (m, 3H, 5-H, 2''-H$_a$), 1.98-2.10 (m, 1H, 6''-H$_a$), 2.27-2.34 (m, 1H, 6''-H$_b$), 2.56-2.73 (m, 5H, 4-H 6-H, 2''-H$_b$), 4.36, 4.37 (2 s, 1H, OH), 4.75-4.90 (m, 1H, 1'-H), 5.72, 5.75 (2 s, 1H, C=C*H*), 7.13-7.20 (m, 3H, Ph), 7.25-7.29 (m, 2H, Ph) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 23.6, 23.7 (3'-C), 25.3 (4'-C), 25.7, 25.8 (C(*C*H$_3$)$_3$), 27.7, 27.7 (5-C), 27.9 (3''-C), 28.2 (5''-C), 29.8, 29.9 (2''-C), 31.3, 31.3 (2'-C), 31.3, 31.4 (6''-C), 32.5, 32.6 (*C*(CH$_3$)$_3$), 35.1, 35.2 (6-C), 36.6 (4-C), 37.5, 37.6 (6''-C), 47.8, 48.0 (4''-C), 75.3, 75.3 (1'-C), 82.8, 82.9 (2-C), 116.7, 116.8 (C=CH), 126.1, 126.1 (1-C-Ph), 128.5, 128.5, 128.5 (2-C-Ph, 3-C-Ph), 141.5, 141.5 (4-C-Ph), 149.4, 149.7 (*C*=CH), 170.3, 170.3 (1-C), 206.4, 206.5 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{29}H_{42}O_4Na$ [M+Na]$^+$: 477.2975, found: 477.2977. **IR** (ATR): ν = 3475 (br, w), 3026 (w), 2937 (s), 2861 (w), 1714 (s), 1661 (w), 1496 (w), 1451 (m), 1393 (w), 1364 (m), 1253 (w), 1233 (s), 1172 (w), 1142 (w), 1121 (w), 1099 (w), 1034 (w), 1010 (m), 983 (w), 927 (w), 908 (w), 839 (w), 745 (w) 699 (s), 668 (w), 491 (w), 443 (w) cm^{-1}.

Cyclohexyl (*E*)-2-benzoyl-2-hydroxyoct-3-enoate (42a)

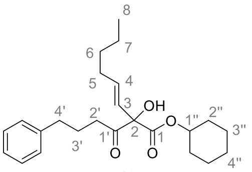
The title compound was prepared from *E*-alkenyl iodide**36** (0.5 M in THF, 0.48 mL, 0.24 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.34 mL, 0.48 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 1.00 mL, 1.00 mmol, 2.0 equiv.) and α,β-diketoester **15a** (0.5 M in CH_2Cl_2 2.00 mL, 1.00 mmol, 2.0 equiv.) according to **GP8** to afford **42a** (38 mg, 0.11 mmol, 46%) as colourless oil after SCC (*n*-pentane/ EtOAc 20:1).



42a **TLC:** R$_f$= 0.67 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 0.84 (t, *J* = 7.26 Hz, 3H, 8-H), 1.16-1.79 (m, 14H, 2'-H, 3'-H, 4'-H, 6-H, 7-H), 2.09 (dt, *J* = 6.23, 7.33 Hz, 2H, 5-H), 4.60 (s, 1H, OH), 4.85 (m, 1H, 1'-H), 5.96 (dt, *J* = 6.87, 15.6 Hz, 1H, 4-H), 6.13 (dt, *J* = 1.41, 15.6 Hz, 1H, 3-H), 7.40-7.46 (m, 2H, 3-H-Ph), 7.52-7.59 (m, 1H, 4-H-Ph), 7.97-8.04 (m, 2H, 2-H-Ph) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ = 14.0 (8-C), 22.2 (3'-C), 23.3 (4'-C), 25.3 (2'-C), 31.0, 31.1 (6-C, 7-C), 32.1 (5-C), 75.2 (1'-C), 82.0 (2-C), 126.5 (3-C), 128.5 (3-C-Ph), 130.0 (2-C-Ph), 133.5 (1-C-Ph), 133.7 (4-C-Ph), 135.0 (4-C), 170.7 (1-C), 194.9 (Ph*C*O) ppm. **HRMS:** ESI$^+$ calcd. for $C_{21}H_{28}O_4Na$ [M+Na]$^+$: 367.1880, found: 367.1881. **IR** (ATR): ν = 3467 (br, w), 2932 (s), 2859 (w), 1728 (s), 1686 (m), 1598 (w), 1581 (w), 1450 (m), 1375 (w), 1259 (w), 1228 (s), 1159 (m), 1121 (w), 1072 (w), 1034 (w), 1009 (m), 972 (w), 932 (w), 908 (w), 832 (w), 708 (w), 691 (m), 649 (w) cm^{-1}.

Cyclohexyl (*E*)-2-hydroxy-2-(-4-phenylbutanoyl)oct-3-enoate (42c)

The title compound was prepared from *E*-alkenyl iodide**36** (0.5 M in THF, 1.00 mL, 0.50 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.71 mL, 1.00 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 1.00 mL, 1.00 mmol, 2.0 equiv.) and α,β-diketoester **15c** (0.5 M in CH_2Cl_2, 2.00 mL, 1.00 mmol, 2.0 equiv.) according to **GP8** to afford **42c** (89 mg, 0.23 mmol, 46%) as colourless oil after SCC (*n*-pentane/ EtOAc 20:1).

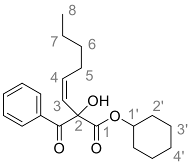


42c

^{1}H-NMR (500 MHz, CDCl$_3$) δ = 0.98 (t, *J* = 7.2 Hz, 3H, 8-H), 1.35-1.50 (m, 6H, 3''-H$_a$, 4''-H$_a$, 6-H, 7-H), 1.50-1.60 (m, 2H, 2''-H$_a$), 1.59-1.65 (m, 1H, 4''-H$_b$), 1.76-1.83 (m, 2H, 3''-H$_b$), 1.87-1.93 (m, 2H, 2''-H$_b$), 1.96-2.06 (m, 2H, 3'-H), 2.16-2.21 (m, 2H, 5-H), 2.67-2.84 (m, 4H, 2'-H, 4'-H), 4.35 (s, 1H, OH), 4.90-4.97 (m, 1H, 1''-H), 5.97 (d, *J* = 15.4 Hz, 1H, 3-H), 6.09 (dt, *J* = 6.8, 15.4 Hz, 1H, 4-H), 7.23-7.31 (m, 3H, Ph), 7.34-7.41 (m, 2H, Ph) ppm. **^{13}C-NMR** (125 MHz, CDCl$_3$) δ = 14.0 (8-C), 22.3 (7-C), 23.6 (3''-C), 25.3 (4''-C), 25.4 (3'-C), 31.1 (6-C), 31.3 (2''-C), 31.9 (5-H), 35.1 (4'-C), 36.4 (2'-C), 75.5 (1''-C), 83.7 (2-C), 124.9 (3-C), 126.1 (4-C-Ph), 128.5, 128.6 (2-C-Ph, 3-C-Ph), 134.1 (4-C), 141.5 (1-C-Ph), 169.9 (1-C), 205.5 (1'-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{24}H_{34}O_4Na$ [M+Na]$^+$: 409.2349; found: 409.2352. **IR** (ATR): ν = 3482 (br, w), 3027 (w), 2932 (s), 2859 (w), 1717 (s), 1604 (w), 1496 (w), 1452 (m), 1363 (w), 1255 (s), 1199 (w), 1170 (w), 1120 (w), 1097 (w), 1033 (w), 1011 (w), 976 (w), 928 (w), 908 (w), 838 (w), 804 (w), 745 (w), 700 (m), 491 (w) cm^{-1}.

Cyclohexyl (*Z*)-2-benzoyl-2-hydroxyoct-3-enoate (43a)

The title compound was prepared from *Z*-alkenyl iodide **37** (0.5 M in THF, 1.00 mL, 0.50 mmol, 1.0 equiv.), *sec*-butyl lithium (1.4 M in cyclohexane, 0.71 mL, 1.00 mmol, 2.0 equiv.), dineopentylzinc (1.0 M in benzene, 1.00 mL, 1.00 mmol, 2.0 equiv.) and α,β-diketoester **15a** (0.5 M in CH$_2$Cl$_2$, 2.00 mL, 1.00 mmol, 2.0 equiv.) according to **GP8** to afford **43a** (25 mg, 72.6 µmol, 15%) as colourless oil after SCC (*n*-pentane/ EtOAc 30:1).



43a

TLC: R$_f$= 0.68 (*n*-pentane/EtOAc 10:1). **^{1}H-NMR** (500 MHz, CDCl$_3$) δ = 0.78 (t, *J* = 7.1 Hz, 3H, 8-H), 1.10-1.25 (m, 7H, 7-H, 3'-H$_a$, 4'-H$_a$, 2'-H$_a$, 6-H), 1.27-1.36 (m, 1H, 3'-H$_a$), 1.38-1.48 (m, 3H, 2'-H$_a$, 3'-H$_b$, 4'-H$_b$), 1.54-1.60 (m, 1H, 2'-H$_b$), 1.61-1.67 (m, 1H, 3-H$_b$), 1.73-1.80 (m, 1H, 2-H$_b$), 1.86-1.96 (m, 1H, 5-H$_a$), 2.05-2.14 (m, 1H, 5-H$_b$), 4.78-4.85 (m, 1H, 1'-H), 4.88 (s, 1H, OH), 5.69 (dt, *J* = 7.5, 11.4 Hz, 1H, 4-H), 6.32 (dt, *J* = 1.7, 11.4 Hz, 1H, 3-H), 7.40-7.45 (m, 2H, 3-H-Ph), 7.52-7.59 (m, 1H, 4-H-Ph), 8.03 (dd, *J* = 1.2, 8.5 Hz, 2H, 2-H-Ph) ppm. **^{13}C-NMR** (125 MHz, CDCl$_3$) δ = 14.0 (8-C), 22.4 (7-C), 23.3, 23.4 (3'-C), 25.3 (4'-C), 28.3 (5-C), 31.0, 31.1 (2'-C), 31.3 (6-C), 75.1 (1'-C), 81.4 (2-C), 125.5 (3-C), 128.5 (3-C-Ph), 130.3 (2-C-Ph), 132.6 (1-C-Ph), 133.9 (4-C-Ph), 138.7 (4-C), 170.3 (1-C), 195.7 (3-C) ppm. **HRMS:** ESI$^+$ calcd. for $C_{21}H_{28}O_4Na$ [M+Na]$^+$: 367.1880, found: 367.1879. **IR** (ATR): ν = 3459 (br, w), 2933 (m), 2859 (w), 1735 (m), 1682 (s), 1597 (w), 1580 (w), 1450 (m), 1359 (w), 1318 (w), 1257 (w), 1223 (s), 1184 (w), 1146 (w), 1122 (w), 1100 (w), 1060 (w), 1034 (w), 1010 (m), 964 (w), 925 (m), 827 (w), 802 (w), 690 (s) cm^{-1}.

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Keywords: vic-tricarbonyl compounds•organo zinc reagents• zincates•ketones•chemoselectivity

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[20] CCDC-1522383 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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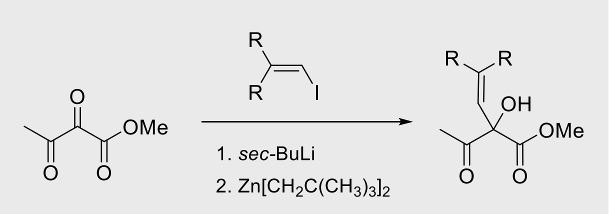

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Addition of Mixed Alkenyl-Dialkyl Zincates to Vicinal Diketoester

The reaction of α,β-diketoesters with various organozinc reagents is described. Diorganozinc reagents are suitable for alkylation and arylation while alkenyl-dineopentyl zincates transfer the alkenyl group to the central.
carbonyl group of α,β-diketoester.

Key Topic: mixed triorganozincates