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Cerium-Catalyzed α-Hydroxylation Reactions of α-Cyclopropyl β-Dicarbonyl Compounds with Molecular Oxygen

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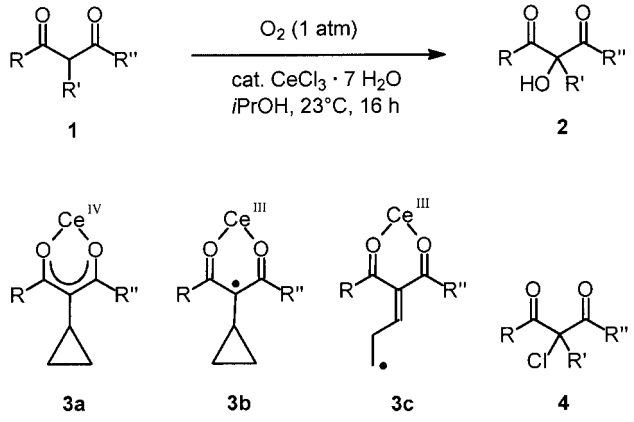
Three α-cyclopropyl β-dicarbonyl compounds have been used as probes for α-radicals as electrophilic reaction intermediates in a cerium-catalyzed α-hydroxylation reaction with molecular oxygen. Since the cyclopropyl group did not ring-open to products with a butenyl moiety, but was retained in the products, a localized unpaired electron at the α position can be excluded during the course of the reaction. The α-cyclopropyl-substituted substrates were prepared by aldol or Claisen reactions. Other substrates with α-methyl, α-isopropyl, and α-*tert*-butyl substituents were prepared and converted under the α-hydroxylation conditions in order to estimate steric influences on the yield of the reaction.

Introduction

We have recently reported on a new α-hydroxylation reaction of β-dicarbonyl compounds **1** catalyzed by cerium chloride in 2-propanol (Scheme 1).[1] The key feature of this reaction is the utilization of dioxygen as oxidant, which can be regarded as optimal in terms of economic and ecological considerations. Moreover, the precatalyst $CeCl_3 \cdot 7H_2O$ is inexpensive and nontoxic. We have meanwhile further developed this method towards oxidative C–C bond forming reactions yielding 1,2-dioxane[2] derivatives or 1,4-diketones.[3] This development was actually based on the assumption that an α-radical species was formed as a reactive intermediate.

The exact stoichiometry of this reaction could be established from oxygen-uptake measurements with half an equivalent of O_2 taken up per equivalent of product **2** formed. In some cases the formation of α-chlorinated byproducts **4** was observed, presumably resulting from a nucleophilic attack of the chloride counterion of the catalyst on an electrophilic reaction intermediate. With regard to the mechanism of the catalysis we have made the following proposal: The role of dioxygen might only be to oxidize the Ce^{III} species to Ce^{IV} under the reaction conditions. The hydroxy group in product **2** could result from a nucleophilic attack of water on an electrophilic reaction intermediate.



Scheme 1. Cerium-catalyzed α-hydroxylation of β-dicarbonyl compounds **1**, possible reaction intermediates **3a**–**3c** (co-ligands at cerium cannot be specified and are omitted for clarity), and chlorinated byproducts **4**.

Ce^{IV} ions, for example, as hydrate or chloro complexes in solution, readily form Ce^{IV}–diketonate species **3a** (Scheme 1) under the reaction conditions. As known from the stoichiometric use of Ce^{IV} reagents, for example, CAN, for the formation of α-radicals,[4] we propose ligand-to-metal electron transfer generating species **3b**. In this complex the central metal formally has the oxidation state +III and a neutral β-diketone ligand with an unpaired electron localized in the α-position. This radical species might then be the electrophilic reaction intermediate[5] that forms the hydroxylation products **2** or the byproducts **4** upon reaction with water or chloride as nucleophiles.

As a probe for spin density at the α-position and, thus, to support our mechanistic proposal, we decided to prepare α-cyclopropyl-substituted β-dicarbonyl compounds and study them under the conditions of α-hydroxylation. If an

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unpaired electron is localized in this α-position, rapid fragmentation to a butenyl radical species **3c** will occur. Hence, the cyclopropane ring should not be retained in any isolable reaction product. This "radical clock" concept has proved to be very effective in studies of radical intermediates in oxygenation[6] and other reactions described in the literature.[7]

Results and Discussion

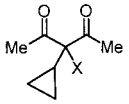
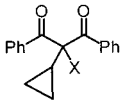
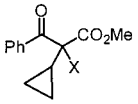
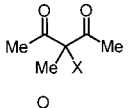
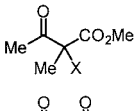
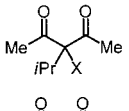
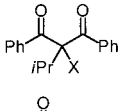
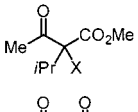
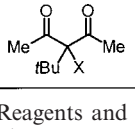
Hydroxylation Reactions

Three cyclopropane derivatives **1a**–**1c** were prepared as radical probes. These were then allowed to react for 16 h under standard conditions for α-hydroxylation reactions, employing 2-propanol as the solvent and 5 mol-% $CeCl_3 \cdot 7H_2O$ as the catalyst under oxygen (1 atm). In the case of acetylacetone derivative **1a** and benzoyl acetate (**1c**) the respective acyloins **2a** and **2c** were isolated by chromatography on silica as the major components of the reaction mixtures in 47 and 45% yields, respectively (Table 1). With the β-keto ester **2c** the chloro compound **4c** was obtained as a byproduct in 15% yield. In contrast, dibenzoylmethane derivative **1b** was not oxidized to the respective alcohol **2b**. The only isolable material in this case was the chloro compound **4b** (5%). However, the crude reaction mixture contained several species with an intact cyclopropane moiety, as clearly indicated by characteristic signals in the ^{13}C (<12 ppm) and ^{1}H NMR spectra (<1 ppm). The total integral of cyclopropane protons is about 4 H relative to the aromatic protons (10 H), indicating, that in approx. 80% of the material the cyclopropane rings were retained. We presume decomposition of the β-dicarbonyl unit of compounds **1b**, **2b**, or **4b** occurs by a retro-Claisen reaction before or after α-oxidation due to the high steric congestion of these compounds.

From these results we can conclude that a localized unpaired electron at the α position, as depicted in structure **3b**, can definitely be excluded. Therefore, we need to revise our mechanistic picture of the overall reaction.

Since the yields of products **2a** and **2c** were relatively low, we investigated the reactions of other aliphatic β-dicarbonyl compounds **1d**–**1i** under α-hydroxylation conditions in order to obtain an estimate of the influence of the steric bulk of the α-substituent on the yield of the respective product. In particular, we investigated α-methyl-, α-isopropyl-, and α-*tert*-butyl substitution. In the cases of an α-methyl residue, oxidation products **2d**[8] and **2e**[9] were isolated in moderate yields, similar to those of cyclopropyl derivatives **2a** and **2c**. For the isopropyl congeners **2f** and **2h** the yields drop significantly to about 10% and some starting materials **1f** and **1h** could be reisolated. Therefore, we conclude that the steric requirement of a cyclopropyl group is comparable to that of a methyl group, which are both smaller than an isopropyl group. Similar to the cyclopropyl derivative **1b**, the isopropylated dibenzoylmethane **1g** partly decomposed under the reaction conditions. The amount of starting material reisolated was 88%. Bulking up the substrate sterically with a *tert*-butyl group, as in compound **1i**, completely prevents conversion under the standard reaction conditions.

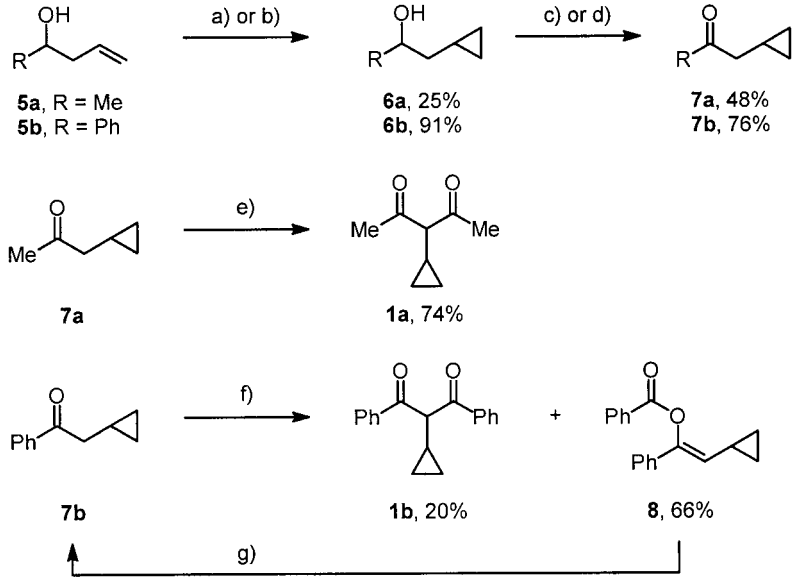
Table 1. α-Hydroxylation of β-dicarbonyl compounds **1a**–**1i**.[a]

Starting material **1** X = H		Product **2** X = OH	Byproduct **4** X = Cl	Reisolated **1** X = H
	**1a**	**2a** (47%)	–	–
	**1b**	**2b** (< 1%)	**4b** (5%)	–
	**1c**	**2c** (45%)[b]	**4c** (15%)	–
	**1d**	**2d** (34%)	–	–
	**1e**	**2e** (52%)	–	**1e** (25%)
	**1f**	**2f** (11%)	–	**1f** (38%)
	**1g**	–	–	**1g** (88%)
	**1h**	**2h** (8%)	–	**1h** (69%)
	**1i**	–	–	**1i** (100%)[b, c]

[a] Reagents and conditions: Approx. 3 mol dm^{-3} *i*PrOH, 5 mol-% $CeCl_3 \cdot 7H_2O$, 23 °C, 16 h. [b] Reagents and conditions: 10 mol-% $CeCl_3 \cdot 7H_2O$, 22 h. [c] Yield determined by GC-MS.

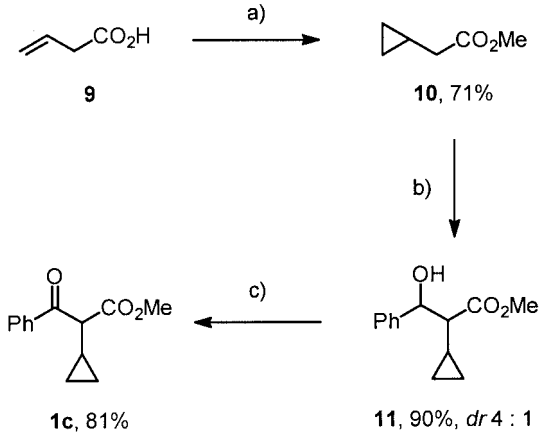
Synthesis of Cyclopropane Derivatives

Since compounds **1a**, **1b** (Scheme 2), and **1c** (Scheme 3) were not accessible by direct α-alkylation of β-dicarbonyl compounds, we decided to build up the β-dicarbonyl moiety by Claisen or aldol reactions. For this purpose, homoallylic alcohols **5a**[10] and **5b**[11] were prepared by the reaction of vinyl Grignard reagents with the corresponding aldehydes according to literature procedures and subsequently cyclopropanated[12] by the Simmons–Smith protocol[13] or its Furukawa modification[14] to furnish the alcohols **6a**[15] and **6b**,[16] respectively (Scheme 2). Oxidation with PCC[17] or $Na_2Cr_2O_7/H_2SO_4$[18] gave ketones **7a**[15,19] and **7b**.[16a,19a,19b,20] Lewis acid mediated Claisen condensation[21] of methyl ketone **7a** with Ac_2O regioselectively gave the new β-diketone **1a** in a good yield. Claisen condensation of phenyl ketone **7b** was more problematic, but could be



Scheme 2. Preparation of α-cyclopropyl β-diketones **1a** and **1b**. Reagents and conditions: a) Zn, CuCl, CH_2I_2, Et_2O, 35 °C, 16 h; 25% (**6a**), 91% (**6b**); b) Et_2Zn, CH_2I_2, toluene, 23 °C, 1.5 h; 83% (**6b**); c) PCC, CH_2Cl_2, 23 °C, 1.5 h; 48% (**7a**); d) $Na_2Cr_2O_7$, H_2SO_4/H_2O, Et_2O, 23 °C, 5 h; 76% (**7b**); e) Ac_2O, $BF_3{\cdot}OEt_2$, 50 °C, 16 h; 74% (**1a**); f) 1. LDA, THF, –78 °C, 0.5 h; 2. $(PhCO)_2O$, THF, 60 °C, 5 h; 66% (**8**), 20% (**1b**); g) NaOH, cat. H_2O_2, MeOH/H_2O, 16 h, 50 °C; 82% (**7b**).

achieved with benzoic anhydride after stoichiometric deprotonation with LDA.[22] However, *O*-acylation was the predominant process and enol ester **8** was isolated as the major product, which could be recycled to the starting material **7b** in 82% yield by saponification[23]. The new *C*-acylation product **1b** was obtained in preparatively useful amounts by repeated conversion of ketone **7b**.

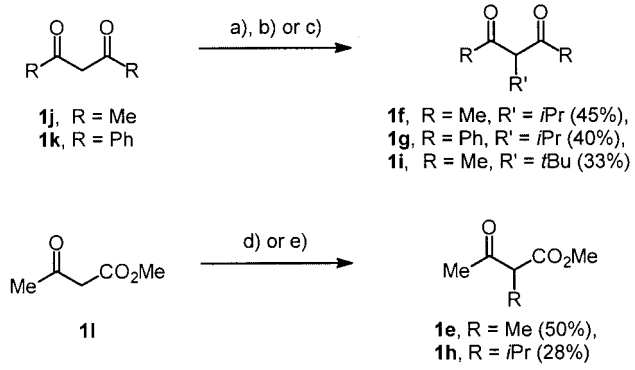


Scheme 3. Synthesis of α-cyclopropyl β-keto ester **1c**. Reagents and conditions: a) CH_2N_2, cat. $Pd(OAc)_2$, Et_2O, 23 °C, 5 h; 71% (**10**); b) 1. LDA, THF, –78 °C, 40 min; 2. PhCHO, –78 °C, 15 min; 90% (**11**), *dr* = 4:1; c) NMO, cat. TPAP, CH_2Cl_2, mol. sieves (4 Å), 23 °C, 45 min; 81% (**1c**).

In order to synthesize β-keto ester **1c**, vinylacetic acid **9** was first cyclopropanated[24] and esterified with diazomethane[25] in a Pd-catalyzed reaction (Scheme 3) to furnish compound **10**. Subsequent aldol reaction of the ester enolate of **10**, prepared by stoichiometric deprotonation with LDA, gave hydroxy ester **11** as a mixture of two diastereoisomers, which were oxidized according to the Ley procedure[26] to give cyclopropane derivative **1c** in 52% yield over three steps.

α-Alkylation of β-Dicarbonyl Compounds

α-Isopropylation of acetylacetone (**1j**)[27] and dibenzoylmethane (**1k**)[28] was achieved only in moderate yields in acetone at higher temperatures and with an excess of isopropyl iodide and K_2CO_3 (Scheme 4). Acetylacetone (**1j**) was alkylated with *tert*-butyl alcohol and sulfuric acid to give β-diketone **1i**; the still moderate yield of this process was significantly increased compared with the literature procedure by changing the solvent to CH_2Cl_2.[29] Com-



Scheme 4. α-Alkylation of β-dicarbonyl compounds. Reagents and conditions: a) *i*PrI, K_2CO_3, acetone, 120 °C, 2.5 d; 45% (**1f**); b) *i*PrI, K_2CO_3, acetone, 60 °C, 16 h; 40% (**1g**), 51% (starting material **1k**); c) *t*BuOH, H_2SO_4, CH_2Cl_2, 23 °C, 16 h; 33% (**1i**); d) MeI, DBU, Et_2O, 16 h, 23 °C; 50% (**1e**); e) NaOMe, *i*PrI, MeOH, 65 °C, 16 h; 28% (**1h**).

pounds **1e**[30] and **1f**[27] were prepared by α-alkylation of acetoacetate **1l** with MeI/DBU and *i*PrI/NaOMe, respectively.

Conclusion

An electrophilic reaction intermediate with an unpaired electron was proposed in the cerium-catalyzed α-hydroxylation of β-dicarbonyl compounds. Three α-cyclopropyl β-dicarbonyl compounds **1a**–**1c** were prepared by aldol or Claisen condensation reactions as probes for this α-radical. However, under the standard reaction conditions of the oxidation process, the cyclopropyl moieties of these substrates were retained rather than being converted to the ring-opened product with a butenyl moiety. Therefore we conclude that the spin density in a long-lived paramagnetic intermediate cannot be localized at the α position, but must be highly delocalized among the six-membered chelate ring.

For comparison of steric influences on the yields of this α-hydroxylation process, six β-dicarbonyl compounds with α-methyl, α-isopropyl, or α-*tert*-butyl substituents were prepared and exposed to the conditions of the α-hydroxylation reaction.

Experimental Section

General Methods: Procedures using Grignard reagents, Et_2Zn, CuCl, LDA, $BF_3{\cdot}Et_2O$, TPAP–NMO, or NaOMe were performed in flame-dried glassware and with absolute solvents under nitrogen. Column chromatography was carried out using Merck SiO_2 60 with hexanes (= PE, boiling range 40–60 °C) and ethyl acetate (= EA) as eluents. ^{1}H NMR spectra were recorded with a Bruker ARX 500 (500 MHz), Bruker ARX 300 (300 MHz), or Bruker AC 250 (250 MHz) spectrometer. ^{13}C NMR spectra were recorded with a Bruker ARX 500 (125 MHz), Bruker ARX 300 (75 MHz) or Bruker AC 250 (62 MHz) instrument. Multiplicities were determined by DEPT experiments. IR spectra were recorded with a Bruker Vector 22 instrument with a Diamond ATR unit. Mass spectra were recorded with Varian MAT 711 (EI, HRMS) and Finnigan MAT 95 (EI, CI) instruments. Melting points were measured with a Büchi 510 and are uncorrected. The starting material **1d** was commercially available. Compounds **5a**,[10] **5b**,[11] and diazomethane[25] were prepared according to literature procedures.

3-Cyclopropyl-2,4-pentanedione (1a): $BF_3{\cdot}Et_2O$ (0.66 mL, 0.74 g, 5.6 mmol) was added dropwise to a solution of the ketone **7a** (200 mg, 2.04 mmol) in Ac_2O (0.42 g, 4.1 mmol). The reaction mixture was then stirred for 16 h at 50 °C, a solution of NaOAc (0.67 g, 8.2 mmol) in H_2O (6 mL) was added, and the mixture refluxed for 3 h. After cooling to ambient temperature the organic layer was separated and the aqueous phase extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution, dried with $MgSO_4$, filtered, and the solvent removed in vacuo. The residue was purified by chromatography (SiO_2, PE/EA, 5:1, R_f = 0.51) to provide compound **1a** (212 mg, 1.51 mmol, 74%) as a colorless oil as a mixture of keto-enol tautomer (keto:enol = 2:1, determined by ^{1}H NMR). ^{1}H NMR (500 MHz, $CDCl_3$), ketone: δ = 0.25–0.28 (m, 2 H), 0.70–0.74 (m, 2 H), 1.30–1.35 (m, 1 H), 2.26 (s, 6 H), 2.72 (d, J = 10.5 Hz, 1 H) ppm; enol: δ = 0.36–0.39 (m, 2 H), 0.87–0.92 (m, 2 H), 1.36–1.43 (m, 1 H), 2.25 (s, 6 H), 16.45 (s, 1 H, OH) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), keto: δ = 4.42 (CH_2), 10.23 (CH), 29.06 (CH_3), 72.97 (CH), 204.90 (C=O) ppm; enol: δ = 8.58 (CH), 8.92 (CH_2), 23.68 (CH_3), 112.92 (C), 192.92 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3413 (s, br), 1710 (m), 1687 (s), 1463 (m), 1252 (m), 1097 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_8H_{12}O_2$: 140.0837; found 140.0837 [M]$^+$.

2-Cyclopropyl-1,3-diphenyl-1,3-propanedione (1b): A solution of LDA (4.2 mL, 8.4 mmol, c = 2.0 mol dm^{-3} in THF) was added at –78 °C to a stirred solution of ketone **7b** (1.22 g, 7.62 mmol) in THF (5 mL). After stirring the mixture for 30 min at –78 °C, benzoic anhydride (2.58 g, 11.4 mmol) was added, the mixture was stirred for a further 5 h at 60 °C, and then diluted with a saturated aqueous NH_4Cl solution (5 mL). The aqueous layer was extracted with THF (4 × 20 mL), the combined organic layers dried with Na_2SO_4, and after filtration, concentrated in vacuo. The product mixture was separated by column chromatography (SiO_2, PE/EA, 10:1) to give enol ester **8** (R_f = 0.30, 1.49 g, 5.66 mmol, 66%) in the first fraction as a brown oil and the title compound **1b** (R_f = 0.15, 439 mg, 1.66 mmol, 20%) in the second fraction as a brownish oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.33–0.36 (m, 2 H), 0.69–0.75 (m, 2 H), 1.61–1.70 (m, 1 H), 4.34 (d, J = 9.7 Hz, 1 H), 7.42–7.45 (m, 4 H), 7.53–7.56 (m, 2 H), 7.94–7.99 (m, 4 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 4.85 (2 CH_2), 11.36 (CH), 63.67 (CH), 128.82 (8 CH), 133.46 (2 CH), 136.32 (2 C), 195.99 (2 C) ppm. IR (ATR): $\tilde{\nu}$ = 1721 (m), 1694 (s), 1659 (s), 1595 (m), 1580 (m), 1447 (m), 1320 (m), 1270 (s), 1204 (m), 1021 (m), 1001 (m), 946 (m) cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_{18}H_{16}O_2$: 264.1150; found 264.1142 [M]$^+$.

Methyl 2-Cyclopropyl-3-oxo-3-phenylpropanoate (1c): Molecular sieves (6.7 g, 4 Å) and NMO (2.300 g, 17.02 mmol) were added at 23 °C to a solution of alcohol **11** (2.500 g, 11.35 mmol) in CH_2Cl_2 (23 mL). After stirring for 8 min at 23 °C, TPAP (597 mg, 1.70 mmol) was added and the reaction mixture was stirred for a further 45 min, then filtered through a pad of SiO_2 to yield the title compound **1c** (1.997 g, 9.150 mmol, 81%) as a brown oil. R_f (SiO_2, PE/EA, 5:1) = 0.32. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.16–0.24 (m, 1 H), 0.36–0.46 (m, 1 H), 0.60–0.77 (m, 2 H), 1.62–1.50 (m, 1 H), 3.54 (d, J = 9.9 Hz, 1 H), 3.70 (s, 3 H), 7.45–7.51 (m, 2 H), 7.56–7.62 (m, 1 H), 7.94–7.98 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 3.95 (CH_2), 4.51 (CH_2), 10.61 (CH), 52.51 (CH_3), 59.12 (CH), 128.62 (CH), 128.78 (CH), 133.54 (CH), 136.29 (C), 170.30 (C=O), 194.79 (C=O) ppm. MS (CI, CH_4): m/z (%) = 219 (5) [MH]$^+$, 187 (5) [M – MeOH]$^+$, 105 (100). IR (ATR): $\tilde{\nu}$ = 1743 (vs), 1686 (vs), 1442 (m), 1290 (m) cm^{-1}. $C_{13}H_{14}O_3$ (218.25): calcd. C 71.54, H 6.47; found C 71.24, H 6.50.

Methyl 2-Methyl-3-oxobutanoate (1e): MeI (4.31 g, 30.4 mmol) was added to a suspension of keto ester **1l** (2.89 g, 24.9 mmol) and DBU (3.79 g, 24.9 mmol) in Et_2O (35 mL). The reaction mixture was stirred for 16 h at 23 °C and then diluted with H_2O (20 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried with $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was purified by chromatography (SiO_2, PE/EA, 2:1, R_f = 0.33) to give the title compound **1e** (1.61 g, 12.4 mmol, 50%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (d, J = 7.5 Hz, 3 H), 2.27 (s, 3 H), 3.55 (q, J = 7.3 Hz, 1 H), 3.77 (s, 3 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 12.20 (CH_3), 28.48 (CH_3), 52.47 (CH_3), 53.46 (CH), 171.02 (C=O), 203.66 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 2990 (m), 2954 (m), 1746 (s), 1718 (s), 1456 (m), 1436 (m), 1360 (m), 1210 (m) cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_6H_{10}O_3$: 130.0629; found 130.0628 [M]$^+$.

3-Isopropyl-2,4-pentanedione (1f): A mixture of diketone **1j** (7.34 g, 73.3 mmol), 2-iodopropane (37.4 g, 220 mmol), and K_2CO_3 (30.4 g,

220 mmol) in acetone (30 mL) was stirred in an autoclave for 2.5 d at 120 °C. After cooling to ambient temperature and filtration the solvent was removed in vacuo and the residue purified by chromatography [SiO_2, PE/EA, 10:1, R_f = 0.21] to give the title compound **1f** as a colorless oil (4.66 g, 32.8 mmol, 45%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92 (d, J = 6.6 Hz, 6 H), 2.16 (s, 6 H), 2.48 (dsept, J = 10.5, J = 6.6 Hz, 1 H), 3.41 (d, J = 10.5 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 20.54 (CH_3), 29.28 (CH), 29.60 (CH_3), 77.80 (CH), 204.49 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 1690 (s), 1098 (m) cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_8H_{14}O_2$: 142.0994; found 142.0994 [M]$^+$.

2-Isopropyl-1,3-diphenyl-1,3-propanedione (1g): A mixture of diketone **1k** (245 mg, 1.09 mmol), 2-iodopropane (537 mg, 3.28 mmol), K_2CO_3 (435 mg, 3.28 mmol), and acetone (1 mL) was heated for 16 h at 60 °C and then cooled to ambient temperature, filtered, and the residue washed with acetone. The filtrate was concentrated in vacuo and purified by chromatography (SiO_2, PE/EA, 10:1) to give the starting material **1k** (44 mg, 0.20 mmol, 18%) in the first fraction (R_f = 0.41), while the second fraction was a mixture, which was submitted to another chromatography (SiO_2, PE/EA, 10:1) to yield again the starting material **1k** (96 mg, 0.36 mmol, 33%) in the first fraction and the title compound **1g** (118 mg, 0.44 mmol, 40%) in the second fraction [R_f(PE/EA, 10:1) = 0.21] as a colorless solid, m.p. 80 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.02 (d, J = 6.6 Hz, 6 H), 2.92 (dsept, J = 9.3, J = 6.6 Hz, 1 H), 5.06 (d, J = 9.3 Hz, 1 H), 7.41–7.45 (m, 4 H), 7.51–7.56 (m, 2 H), 7.98–8.01 (m, 4 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 21.35 (CH_3), 30.29 (CH), 65.13 (CH), 128.72 (CH), 128.79 (CH), 133.38 (CH), 137.14 (C), 195.65 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 2963 (m), 1692 (s), 1655 (s), 1594 (m), 1579 (m), 1447 (m), 1330 (m), 1307 (s), 1278 (s), 1202 (s), 1178 (s), 1158 (m), 1119 (m), 995 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 266 (2) [M]$^+$, 105 (100) [PhCO]$^+$. $C_{18}H_{18}O_2$ (266.34): calcd. C 81.17, H 6.81; found C 81.31, H 6.80.

Methyl 2-Isopropyl-3-oxobutanoate (1h): NaOMe (0.930 g, 17.2 mmol) and 2-iodopropane (4.39 g, 25.8 mmol) were added to a stirred solution of keto ester **1l** (2.00 g, 17.2 mmol) in MeOH (12 mL) and the resulting mixture was refluxed for 16 h. Then the solvent was mostly evaporated under reduced pressure and the residue dissolved in water (8 mL) and extracted with Et_2O (4 × 10 mL). The combined organic layers were dried with $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was purified by chromatography [SiO_2, PE/EA, 5:1 gradient to 2:1, R_f (PE/EA, 2:1) = 0.54] to give the title compound **1h** (757 mg, 4.79 mmol, 28%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (d, J = 6.7 Hz, 3 H), 0.90 (d, J = 6.7 Hz, 3 H), 2.15 (s, 3 H) 2.40 (dsept, J = 9.5, J = 6.7 Hz, 1 H), 3.13 (d, J = 9.5 Hz, 1 H) 3.66 (s, 3 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 20.47 (CH_3), 20.48 (CH_3), 28.75 (CH_3), 29.26 (CH), 52.21 (CH_3), 67.47 (CH), 169.72 (C=O), 203.24 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 2963 (m), 2876 (m), 1736 (s), 1709 (s), 1434 (m), 1358 (m), 1284 (m), 1197 (s), 1144 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 158 (2) [M]$^+$, 127 (15) [M – CH_3]$^+$, 116 (70) [M – C_3H_6]$^+$, 101 (100). $C_8H_{14}O_3$ (158.20): calcd. C 60.74, H 8.92; found C 60.64, H 8.84.

3-*tert*-Butyl-2,4-pentanedione (1i): Conc. H_2SO_4 (76.4 g, 779 mmol) was slowly added to a cooled (ice/water bath) and stirred solution of acetylacetone (**1j**) (40.0 g, 400 mmol) in CH_2Cl_2 (80 mL). During this addition the reaction temperature should not rise above 10 °C. Then *t*BuOH (47.4 g, 639 mmol) was added dropwise and the mixture stirred for 16 h at 23 °C. Water (200 mL) was added slowly and the mixture extracted with PE (5 × 200 mL). The combined organic layers were washed with a saturated aqueous $MgSO_4$ solution (480 mL) and dried with $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the residue purified by distillation (b.p. 80 °C, 20 mbar) to give the title compound **1i** (20.5 g, 131 mmol, 33%) as a yellowish oil. R_f (PE/EA, 2:1) = 0.55. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.08 (s, 9 H), 2.22 (s, 6 H), 3.65 (s, 1 H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ = 28.42 (3 CH_3), 32.44 (2 CH_3), 35.42 (C), 76.45 (CH), 204.59 (2 C) ppm. IR (ATR): $\tilde{\nu}$ = 2959 (m), 1720 (s), 1693 (vs), 1356 (s), 1148 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 156 (1) [M]$^+$, 114 (8) [M – C_2H_3O]$^+$, 99 (100) [M – C_4H_9]$^+$. $C_9H_{16}O_2$ (156.22): calcd. C 69.20, H 10.32; found C 68.90, H 10.11.

General Procedure for the α-Hydroxylation Reaction: The respective β-dicarbonyl compound **1** (1 equiv.) was added to a suspension of $CeCl_3 \cdot 7H_2O$ (5 mol-%) in *i*PrOH (approx. 3 mol dm^{-3} of **1**). The flask was evacuated twice to approx. 500 mbar, each time flushed with O_2, and the mixture then stirred for 16 h at 23 °C while a slow stream of O_2 (approx. 50 cm^3 h^{-1}) was passed through. Finally, the solvent was evaporated and the residue purified by column chromatography (SiO_2, PE/EA) to yield the products **2** and **4** as specified below.

3-Cyclopropyl-3-hydroxy-2,4-pentanedione (2a): Diketone **1a** (250 mg, 1.78 mmol) and $CeCl_3 \cdot 7H_2O$ (33 mg, 0.088 mmol) were converted in *i*PrOH (1 mL) according to the general procedure. Chromatography (SiO_2, PE/EA, 10:1, R_f = 0.32) furnished the α-hydroxy compound **2a** (131 mg, 0.840 mmol, 47%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.40 (d, J = 6.9 Hz, 4 H), 1.64 (quint, J = 6.7 Hz, 1 H), 2.32 (s, 6 H), 4.25 (s, 1 H, OH) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = –0.23 (CH), 15.34 (CH_2), 25.49 (CH_3), 86.82 (C), 207.68 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3435 (w), 3011 (m), 1702 (s), 1418 (m), 1353 (m), 1236 (m), 1191 (m), 1154 (s), 1050 (s), 1025 (s), 971 (s) cm^{-1}. HRMS (CI, CH_4): calcd. for $C_8H_{13}O_3$: 157.0865; found 157.0856 [MH]$^+$.

Methyl 2-Cyclopropyl-2-hydroxy-3-oxo-3-phenylpropanoate (2c): The keto ester **1c** (251 mg, 1.15 mmol) and $CeCl_3 \cdot 7H_2O$ (45 mg, 0.12 mmol) were converted in *i*PrOH (0.5 mL) according to the general procedure. After chromatography (SiO_2, PE/EA, 10:1) the chloro compound **4c** [46 mg, 0.18 mmol, 15%, R_f (PE/EA, 5:1) = 0.42] was obtained in the first fraction as a colorless oil (data vide infra). In the second fraction [R_f (SiO_2, PE/EA, 5:1) = 0.28] the title compound **2c** (120 mg, 0.512 mmol, 45%) was obtained as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.33–0.40 (m, 2 H), 0.53–0.59 (m, 1 H), 0.68–0.73 (m, 1 H), 1.65–1.70 (m, 1 H), 3.78 (s, 3 H), 4.28 (s, 1 H, OH), 7.45–7.49 (m, 2 H), 7.58–7.61 (m, 1 H), 8.01–8.04 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 0.12 (CH_2), 0.99 (CH_2), 15.40 (CH), 53.28 (CH_3), 79.82 (C), 128.69 (CH), 129.53 (CH), 133.35 (C), 133.75 (CH), 172.48 (C=O), 195.66 (C=O) ppm. MS (CI, CH_4): m/z (%) = 235 (4) [MH]$^+$, 217 (62) [MH – H_2O]$^+$, 203 (5) [MH – MeOH]$^+$, 105 (100). IR (ATR): $\tilde{\nu}$ = 3064 (w), 3010 (w), 2954 (w), 1741 (s), 1694 (s), 1274 (m), 1235 (m), 1170 (m) cm^{-1}. $C_{13}H_{14}O_4$ (234.25): calcd. C 66.66, H 6.02; found C 66.46, H 6.04.

3-Hydroxy-3-methyl-2,4-pentanedione (2d): Diketone **1d** (300 mg, 2.62 mmol) and $CeCl_3 \cdot 7H_2O$ (48 mg, 0.13 mmol) were converted in *i*PrOH (0.9 mL) according to the general procedure. Chromatography (SiO_2, PE/EA, 2:1, R_f = 0.38) furnished the α-hydroxy compound **2d** (115 mg, 0.884 mmol, 34%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.54 (s, 3 H), 2.24 (s, 6 H), 4.70 (br. s, 1 H, OH) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 22.59 (CH_3), 24.72 (CH_3), 87.61 (C), 207.43 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3351 (m), 2973 (m), 2925 (m), 2854 (m), 1708 (s), 1417 (m), 1356 (m), 1237 (m), 1148 (m) cm^{-1}. HRMS (CI, CH_4): calcd. for $C_6H_{11}O_3$: 131.0708; found 131.0708 [MH]$^+$.

Methyl 2-Hydroxy-2-methyl-3-oxobutanoate (2e): Dicarbonyl compound **1e** (200 mg, 1.54 mmol) and $CeCl_3 \cdot 7H_2O$ (29 mg, 0.078 mmol) were converted in *i*PrOH (0.5 mL) according to the general procedure. Chromatography (SiO_2, PE/EA, 5:1, R_f = 0.38) furnished the acyloin **2e** (117 mg, 0.802 mmol, 52%) as a colorless oil in the second fraction and the remaining starting material **1e** (R_f = 0.49, 49 mg, 0.38 mmol, 25%) in the first fraction. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.61 (s, 3 H), 2.29 (s, 3 H), 3.81 (s, 3 H), 4.21 (br. s, 1 H, OH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 21.97 (CH_3), 24.18 (CH_3), 53.40 (CH_3), 81.04 (C), 171.76 (C=O), 204.90 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3460 (m, br), 1726 (s), 1438 (m), 1360 (m), 1269 (m), 1156 (m) cm^{-1}. HRMS (CI, CH_4): calcd. for $C_6H_{11}O_4$: 147.0657; found 147.0657 $[MH]^+$.

3-Hydroxy-3-isopropyl-2,4-pentanedione (2f): Diketone **1f** (303 mg, 2.13 mmol) and $CeCl_3 \cdot 7H_2O$ (40 mg, 0.11 mmol) were converted in *i*PrOH (0.7 mL) according to the general procedure. Chromatography (SiO_2, PE/EA, 10:1, R_f = 0.35) furnished the α-hydroxy compound **2f** (37 mg, 0.23 mmol, 11%) as a colorless oil in the first fraction and the starting material **1f** (115 mg, 0.809 mmol, 38%) in the second fraction (R_f = 0.21). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.80 (d, J = 6.7 Hz, 6 H), 2.24 (s, 6 H), 2.76 (sept, J = 6.7 Hz, 1 H), 4.55 (s, 1 H, OH) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 16.31 (CH_3), 25.84 (CH), 34.73 (CH), 94.28 (C), 208.22 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3448 (s, br), 2668 (m), 2937 (m), 2879 (m), 1700 (s), 1416 (m), 1388 (m), 1353 (s), 1190 (m), 1173 (m), 1147 (s), 1043 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_8H_{14}O_3$: 158.0943; found 158.0948 $[M]^+$.

Methyl 2-Hydroxy-2-isopropyl-3-oxobutanoate (2h): Diketone **1h** (300 mg, 1.90 mmol) and $CeCl_3 \cdot 7H_2O$ (35 mg, 0.094 mmol) were converted in *i*PrOH (0.6 mL) according to the general procedure. Chromatography (SiO_2, PE/EA, 10:1, R_f = 0.14) furnished the acyloin **2h** (28 mg, 0.16 mmol, 8%) as a colorless oil in the second fraction and the starting material **1h** (R_f = 0.25, 208 mg, 1.31 mmol, 69%) in the first fraction. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.78 (d, J = 6.8 Hz, 3 H), 0.94 (d, J = 6.7 Hz, 3 H), 2.33 (s, 3 H), 2.72 (sept, J = 6.8 Hz, 1 H), 3.81 (s, 3 H), 4.13 (s, 1 H, OH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62 MHz): δ = 15.87 (CH_3), 16.92 (CH_3), 25.09 (CH), 34.01 (CH_3), 53.32 (CH_3), 87.90 (C), 171.34 (C=O), 205.74 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3467 (s, br), 2966 (m), 1720 (vs), 1357 (m), 1263 (m), 1154 (m) cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_8H_{14}O_4$: 174.0892; found 174.0892 $[M]^+$.

2-Chloro-2-cyclopropyl-1,3-diphenyl-1,3-propanedione (4b): Diketone **1b** (296 mg, 1.12 mmol) and $CeCl_3 \cdot 7H_2O$ (20 mg, 0.054 mmol) were converted in *i*PrOH (1.0 mL) according to the general procedure. Chromatography (SiO_2, PE/EA, 10:1, R_f = 0.40) furnished the α-chloro compound **4b** (18 mg, 0.060 mmol, 5%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.74–0.77 (m, 4 H), 1.90–1.94 (m, 1 H), 7.34–7.39 (m, 4 H), 7.46–7.49 (m, 2 H), 7.92–7.97 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 3.31 (CH_2), 13.31 (CH_2), 17.46 (CH), 81.22 (C), 128.59 (CH), 130.17 (CH), 133.47 (CH), 191.73 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3062 (w), 3012 (w), 2929 (w), 1766 (w), 1678 (s), 1596 (m), 1580 (m), 1448 (m), 1218 (s) cm^{-1}. GCMS (CI, CH_4): m/z (%) = 299 (3) $[MH]^+$, 263 (66) $[MH - Cl]^+$, 176 (21), 105 (100). HRMS (EI, 70 eV): calcd. for $C_{18}H_{15}ClO_2$: 298.0761; found 298.0775 $[M]^+$.

Methyl 2-Chloro-2-cyclopropyl-3-oxo-3-phenylpropanoate (4c): The title compound **4c** (46 mg, 0.18 mmol, 15%) was obtained as a colorless oil as a byproduct in the synthesis of acyloin **2c**. R_f (SiO_2, PE/EA, 5:1) = 0.42. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.59–0.84 (m, 4 H), 1.78–1.87 (m, 1 H), 3.75 (s, 3 H, CH_3), 7.42–7.47 (m, 2 H), 7.51–7.59 (m, 1 H), 7.95–7.99 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 1.53 (CH_2), 2.95 (CH_2), 16.80 (CH), 53.76 (CH_3), 74.12 (C), 128.50 (CH), 129.40 (CH), 133.34 (CH), 133.66 (C), 168.96 (C=O), 189.33 (C=O) ppm. MS (CI, CH_4): m/z (%) = 253 (4) $[MH]^+$, 217 (12) $[MH - HCl]^+$, 193 (8), 185 (10), 105 (100). IR (ATR): $\tilde{\nu}$ = 3056 (w), 3017 (w), 2954 (w), 1759 (vs), 1730 (vs), 1697 (s), 1258 (m), 1221 (m) cm^{-1}. $C_{13}H_{13}ClO_3$ (252.70): calcd. C 61.79, H 5.19; found C 61.85, H 5.29.

1-Cyclopropyl-2-propanol (6a): A suspension of Zn dust (15.9 g, 242 mmol) and CuCl (24.0 g, 242 mmol) in Et_2O (47 mL) was stirred for 30 min at 35 °C. The olefin **5a** (8.04 g, 93.4 mmol) and CH_2I_2 (50.0 g, 187 mmol) were added and the mixture stirred for a further 16 h at 35 °C. After filtration and washing of the residue with 5% hydrochloric acid (2 × 50 mL), the filtrate was washed with a saturated aqueous $NaHCO_3$ solution (50 mL) and brine (50 mL). The organic layer was dried with $MgSO_4$, filtered, and the solvent evaporated under reduced pressure. Chromatography (SiO_2, PE/EA, 5:1, R_f = 0.11) afforded the product **6a** (1.40 g, 13.9 mmol, 25%) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.03–0.08 (m, 1 H), 0.09–0.13 (m, 1 H), 0.43–0.52 (m, 2 H), 0.68–0.77 (m, 1 H), 1.22 (d, J = 6.2 Hz, 3 H), 1.36 (t, J = 6.6 Hz, 2 H), 1.66 (s, 1 H, OH), 3.91 (sext, J = 6.2 Hz, 1 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 3.74 (CH_2), 4.36 (CH_2), 7.48 (CH), 23.19 (CH_3), 44.07 (CH_2), 68.71 (CH) ppm. IR (ATR): $\tilde{\nu}$ = 3343 (s, br), 2967 (m), 2914 (m), 1460 (m), 1372 (m), 1119 (m), 1085 (s), 1041 (m), 1015 (m), 929 (m) cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_6H_{12}O$: 100.0888; found 100.0890 $[M]^+$.

2-Cyclopropyl-1-phenyl-1-ethanol (6b): a) Simmons–Smith protocol: A suspension of CuCl (14.7 g, 148 mmol) and Zn dust (9.66 g, 148 mmol) in Et_2O (84 mL) was refluxed for 30 min. The olefin **5b** (8.44 g, 56.9 mmol) and CH_2I_2 (39.7 g, 148 mmol) were added and the mixture was stirred for 16 h at 35 °C. After filtration through Florisil (Et_2O) the solvent was evaporated in vacuo and after chromatography (bas. Al_2O_3, PE/EA, 10:1) the product **6b** (8.39 g, 52.4 mmol, 91%) was obtained as a yellowish oil. b) Furukawa modification: A solution of Et_2Zn (33.3 mL, 36.7 mmol, c = 1.1 mol dm^{-3} in toluene) was quickly dropped at 0 °C into a mixture of the alcohol **5b** (1.81 g, 12.2 mmol) and CH_2I_2 (9.82 g, 36.7 mmol). The mixture was warmed to room temperature and stirred for 1.5 h. Subsequently, air was blown through the mixture (15 min) which was then stirred overnight at ambient temperature. Toluene (20 mL) was added and the mixture washed with an aqueous NaOH solution (3 mol dm^{-3}, 20 mL). The aqueous layer was separated and extracted with Et_2O (3 × 50 mL). The combined organic extracts were dried with Na_2SO_4 and filtered. After evaporation of the solvent under reduced pressure, chromatography (SiO_2, PE/E, 10:1, R_f = 0.10) yielded the product **6b** (1.65 g, 10.1 mmol, 83%) as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.01–0.07 (m, 1 H), 0.09–0.19 (m, 1 H), 0.36–0.55 (m, 2 H), 0.64–0.79 (m, 1 H), 1.59–1.75 (m, 2 H), 1.93 (s, 1 H), 4.79 (dd, J = 7.4, J = 5.9 Hz, 1 H), 7.24–7.39 (m, 5 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 3.92 (CH_2), 4.50 (CH), 7.65 (CH_2), 44.18 (CH_2), 75.05 (CH), 125.89 (CH), 127.44 (CH), 128.36 (CH), 144.68 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3219 (m), 3076 (m), 2999 (m), 2905 (m), 1491 (s), 1454 (m), 1335 (s), 1064 (s), 1040 (m), 1012 (s), 964 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 162 (10) $[M]^+$, 107 (100). $C_{11}H_{14}O$ (162.23): calcd. C 81.44, H 8.70; found C 80.94, H 8.85.

1-Cyclopropyl-2-propanone (7a): A solution of the alcohol **6a** (1.77 g, 17.8 mmol) and PCC (5.73 g, 26.6 mmol) in CH_2Cl_2 (35 mL) was stirred at 23 °C for 1.5 h, then diluted with Et_2O (26 mL), and decanted from the solid. The solid was extracted with Et_2O (4 × 50 mL) and the combined organic extracts were filtered (SiO_2, Et_2O, R_f = 0.65). After removing the solvent in vacuo ketone **7a** (839 mg, 8.55 mmol, 48%) was obtained as a brownish oil. ^{1}H

NMR (500 MHz, $CDCl_3$): δ = 0.11–0.14 (m, 2 H), 0.55–0.59 (m, 2 H), 0.94–1.02 (m, 1 H), 2.18 (s, 3 H), 2.30 (d, J = 7.0 Hz, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 4.50 (CH_2), 6.43 (CH), 29.61 (CH_3), 48.98 (CH_2), 209.15 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3410 (s, br), 2953 (m), 2857 (m), 1686 (s), 1463 (s), 1406 (m), 1251 (m), 1218 (s), 1098 (s), 1004 (m), 905 (m) cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_6H_{10}O$: 98.0731; found 98.0727 $[M]^+$.

2-Cyclopropyl-1-phenyl-1-ethanone (7b): a) By oxidation of alcohol **6b**: A solution of $Na_2Cr_2O_7$ (24.0 g, 80.7 mmol) in conc. H_2SO_4 (18.3 mL) and H_2O (120 mL) was added over a period of 5 h to a solution of alcohol **6b** (14.5 g, 89.5 mmol) in Et_2O (40 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (5 × 50 mL). The combined organic layers were washed with a saturated aqueous $NaHCO_3$ solution, dried (Na_2SO_4), filtered, and all volatile materials were removed in vacuo. The residue was purified by chromatography (SiO_2, PE/EA, 10:1, R_f = 0.36) to afford the diketone **7b** (11.0 g, 68.7 mmol, 76%) as a colorless oil. b) By saponification of enol ester **8**: Solid NaOH (3.10 g, 77.4 mmol) and one drop of H_2O_2 (30%) was added to a solution of ester **8** (1.84 g, 6.96 mmol) in MeOH (15.5 mL) and H_2O (12.5 mL). The mixture was heated to 50 °C for 16 h, then diluted with a saturated aqueous $NaHCO_3$ solution (25 mL), and extracted with Et_2O (4 × 50 mL). The combined organic layers were dried with $MgSO_4$ and filtered. The solvent was evaporated to give a residue, which was purified by chromatography (SiO_2, PE/EA, 10:1, R_f = 0.36) to give diketone **7b** as a colorless oil (0.980 g, 6.14 mmol, 82%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.17–0.22 (m, 2 H), 0.57–0.64 (m, 2 H), 1.11–1.24 (m, 1 H), 2.89 (d, J = 6.8 Hz, 2 H), 7.42–7.52 (m, 2 H), 7.52–7.59 (m, 1 H), 7.91–7.98 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 4.53 (CH_2), 6.64 (CH), 43.78 (CH_2), 128.12 (CH), 128.55 (CH), 132.91 (CH), 136.96 (C), 200.03 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3078 (w), 3003 (w), 1680 (s), 1448 (m), 1286 (m), 1211 (s), 1178 (m), 1101 (m), 1070 (m), 1047 (m), 1018 (m), 964 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 160 (8) $[M]^+$, 105 (100). $C_{11}H_{12}O$ (160.21): calcd. C 82.46, H 7.55; found C 82.06, H 7.57.

(*Z*)-2-Cyclopropyl-1-phenyl-1-ethenyl Benzoate (8): Compound **8** was obtained as the major product in the preparation of diketone **1b** [R_f (PE/EA, 10:1) = 0.30]. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.55–0.60 (m, 2 H), 0.81–0.88 (m, 2 H), 1.58–1.68 (m, 1 H), 5.37 (d, J = 9.9 Hz, 1 H), 7.22–7.25 (m, 1 H), 7.27–7.31 (m, 2 H), 7.40–7.42 (m, 2 H), 7.51–7.54 (m, 2 H), 7.62–7.66 (m, 1 H), 8.24–8.29 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 7.36 (CH_2), 9.26 (CH), 122.71 (CH), 123.88 (CH), 127.78 (CH), 128.51 (CH), 128.63 (CH), 129.43 (C), 130.22 (CH), 133.54 (CH), 134.91 (C), 145.80 (C), 164.55 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 1734 (s), 1243 (s), 1088 (m), 1067 (m) 1025 (m), 989 (s), 955 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 264 (3) $[M]^+$, 212 (3) $[M - C_4H_4]^+$, 159 (12) $[M - C_7H_5O]^+$, 143 (10), 105 (100) $[M - C_{11}H_{11}O]^+$, 77 (29). $C_{18}H_{16}O_2$ (264.32): calcd. C 81.79, H 6.10; found C 81.33, H 6.15.

Methyl 2-Cyclopropylacetate (10): A solution of diazomethane (approx. 13.5 g, approx. 321 mmol) in Et_2O (1200 mL) was slowly added dropwise to a solution of vinylacetic acid (**9**) (4.000 g, 46.46 mmol) in Et_2O (30 mL) until the reaction mixture became yellow. Then the speed of addition was increased. Subsequently, a suspension of $Pd(OAc)_2$ (200 mg, 0.891 mmol) in Et_2O (10 mL) was added carefully (***CAUTION:*** vigorous gas evolution). The mixture was stirred for 10 min and further $Pd(OAc)_2$ (100 mg, 0.445 mmol) was added. After stirring the reaction mixture for 5 h at 23 °C, brine (300 mL) was added and the aqueous layer extracted with Et_2O (2 × 200 mL). The combined organic layers were washed with brine (200 mL) and dried with $MgSO_4$. After filtration, the solvent was removed in vacuo and the residue purified by distillation (b.p. 93–95 °C, 304 mbar) to yield the title compound **10** (3.743 g, 32.79 mmol, 71%) as a colorless liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = –0.06 to +0.08 (m, 2 H), 0.32–0.48 (m, 2 H), 0.83–0.97 (m 1 H), 2.06 (d, J = 7.1 Hz, 2 H), 3.54 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 4.39 (CH_2), 6.89 (CH), 39.22 (CH_2), 51.55 (CH_3), 173.73 (C=O) ppm. MS (EI, 70 eV): m/z (%) = 114 (18) $[M]^+$, 99 (9) $[M - Me]^+$, 83 (24) $[M - OMe]^+$. IR (ATR): $\tilde{\nu}$ = 1737 (vs), 1193 (m), 1173 (m) cm^{-1}. $C_6H_{10}O_2$ (114.14): calcd. C 63.14, H 8.83; found C 63.13, H 8.93.

Methyl 2-Cyclopropyl-3-hydroxy-3-phenylpropanoate (11): A solution of ester **10** (608 mg, 5.33 mmol) in THF (2.0 mL) was added dropwise to a solution of LDA (3.0 mL, 6.0 mmol, c = 2 mol dm^{-3} in THF, heptane, and ethylbenzene) diluted with THF (10 mL) at –78 °C. The reaction mixture was stirred for 40 min at –78 °C, then benzaldehyde (585 mg, 5.51 mmol) was added, and the mixture was stirred for a further 15 min at –78 °C. A saturated NH_4Cl solution (5.0 mL) was added, the mixture warmed to 23 °C, then H_2O (20 mL) was added, and the mixture extracted with Et_2O (3 × 20 mL). The combined organic layers were dried with $NaSO_4$. After filtration, all volatiles were removed in vacuo and the residue purified by chromatography (SiO_2, PE/EE = 5:1) to yield the title compound **11** (1.051 g, 4.771 mmol, 90%) in two fractions as two diastereomers (A/B, 80:20). The first fraction (R_f = 0.22) contained isomer A as a yellow oil, the second fraction contained isomer B (R_f = 0.14) as a yellow solid, m.p. 72–73 °C. The relative configuration was not assigned. ^1H NMR (300 MHz, $CDCl_3$), isomer A: δ = –0.09 to –0.01 (m, 1 H), 0.15–0.27 (m, 1 H), 0.43–0.53 (m, 2 H), 1.07–1.89 (m, 1 H), 2.00 (dd, J = 10.0, J = 5.4 Hz, 1 H), 3.18 (d, J = 2.9 Hz, 1 H; OH), 3.63 (s, 3 H), 5.09 (dd, J = 5.4, J = 2.9 Hz, 1 H), 7.27–7.38 (m, 5 H) ppm; isomer B: δ = –0.36 to –0.25 (m, 1 H), 0.18–0.31 (m, 2 H), 0.37–0.48 (m, 1 H), 0.87–0.99 (m, 1 H), 1.99 (dd, J = 9.0, J = 8.0 Hz, 1 H), 3.04 (d, J = 4.9 Hz, 1 H, OH), 3.70 (s, 3 H), 4.94 (dd, J = 7.8, J = 4.5 Hz, 1 H), 7.27–7.37 (m, 5 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), isomer A: δ = 2.16 (CH_2), 5.42 (CH_2), 9.91 (CH), 51.75 (CH_3), 57.59 (CH), 74.69 (CH), 126.27 (CH), 127.65 (CH), 128.11 (CH), 141.31 (C), 174.82 (C=O) ppm; isomer B: δ = 2.87 (CH_2), 5.20 (CH_2), 11.14 (CH), 51.79 (CH_3), 57.86 (CH), 75.74 (CH), 126.48 (CH), 127.78 (CH), 128.24 (CH), 142.40 (C), 175.17 (C=O) ppm. MS (EI, 70 eV): m/z (%) = 220 (3) $[M]^+$, 202 (1) $[M - H_2O]^+$, 114 (100). IR (ATR): $\tilde{\nu}$ = 1719 (vs), 1329 (m), 1250 (m), 1194 (m), 1191 (m), 1021 (m) cm^{-1}. $C_{13}H_{16}O_3$ (220.27): calcd. C 70.89, H 7.32; C 70.62, H 7.41.

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