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PAPER

Preparation of a Microsized Cerium Chloride-Based Catalyst and its Application in Michael Addition of β-Diketones to Vinyl Ketones

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A facile method, which does not require special equipment, was developed for the preparation of microsized cerium chloride by the thermal treatment of $CeCl_3 \times 7H_2O$ or evaporation of its alcoholic solutions. The way of the preparation of the cerium chloride-based catalyst plays a decisive role in its catalytic activity. This catalyst is efficient in the Michael addition of β-diketones to vinyl ketones giving β,δ-triketones.

Introduction

The Michael reaction provides the commonly used and efficient synthetic route to the C-C bond formation. The synthesis involves the coupling of C-nucleophiles with unsaturated compounds activated by an electron-withdrawing group. β-Dicarbonyl compounds comprise one of the largest groups of C-nucleophiles. The latter are used to prepare products that are widely used in organic synthesis.

In the present study, we found that microsized cerium chloride prepared from cerium chloride heptahydrate catalyzes the coupling of β-diketones with vinyl ketones. The reaction products, β,δ-triketones, are used in the synthesis of cyclic peroxides exhibiting antiparasitic activity [1] and a wide range of nitrogen-containing heterocyclic compounds, [2] as well as oxabicyclic systems, which are natural product analogues with antiparasitic activity. [3]

According to the literature data, the conditions of the coupling of β-diketones with vinyl ketones may vary in a wide range. The nature of the catalyst is the main factor responsible for the successful synthesis. Traditional alkaline catalysts are of little use for this purpose because in the presence of these catalysts, the condensation of diketones and the polymerization of vinyl ketones become the dominant reactions. When searching for catalysts, it was found that the reaction of β-diketones with vinyl ketones is catalyzed by complexes and salts of nickel [4, 2a] and copper,[5] aluminum compounds,[6] cerium compounds,[7] ionic liquids,[8] and iron,[9] indium,[10] zirconium,[11] bismuth,[12] and europium [13] chlorides.

In the past decades, cerium salts have found wide application in organic synthesis. Cerium(IV) compounds, particularly, ammonium cerium nitrate, are actively used as one-electron oxidants.[14] Cerium(III) chloride heptahydrate [15] has emerged as a very cheap, water-tolerant, and friendly reagent, which is able to promote a variety of selective functional group transformations.[16] About twenty years ago it was found that $CeCl_3 \cdot 7H_2O$ in combination with sodium iodide can act as a more active Lewis acid promoter that is able to facilitate a variety of useful organic transformations, whereby no precautions need to be taken to exclude moisture or oxygen from the reaction system.[17] It is supposed that the efficiency of the $CeCl_3 \cdot 7H_2O$ - NaI system is associated with the generation of a cerium-chlorine-iodine-containing catalyst.

Cerium compounds are used also in redox processes. Thus, the $CeCl_3 \times 7H_2O$ - $NaBH_4$ system, in which cerium chloride acts as a Lewis acid, selectively reduces the carbonyl group in enones, with the C=C bond remaining intact.[18] The cerium salt ($CeCl_3 \times 7H_2O$) catalyzes α-hydroxylation of β-dicarbonyl compounds with oxygen.[19]

Since anhydrous $CeCl_3$ can be used both as a Lewis acid and the starting compound for the synthesis of organocerium reagents,[16d, 20] considerable attention has been given to procedures for the dehydration of commercially available $CeCl_3 \times 7H_2O$. It was found that the heating above 90 °C is accompanied by the partial hydrolysis to form CeOCl, about 80 % of water can be removed at temperatures below 90 °C, and residual water can be removed at 140-150 °C in vacuo.[21]

In the present study, we propose a facile method for the preparation of microsized cerium chloride from $CeCl_3 \times 7H_2O$ and consider the effect of the surface structure on the efficiency of the catalyst in the addition reaction of β-diketones to vinyl ketones giving β,δ-triketones. When used as-is, commercial $CeCl_3 \times 7H_2O$ does not catalyze this reaction. In the study, [7a] this salt acted as the catalyst only under solvent-free conditions when subjected to microwave radiation, which requires special equipment. Besides, the authors did not report the reaction temperature and the radiation power; the absence of these parameters does not allow one to obtain reproducible results. More recently, it was found that $CeCl_3 \times 7H_2O$, in combination with NaI catalyzes this reaction at room

temperature.[7b]

The microsized $CeCl_3$-based catalyst proposed in the present study can be prepared without the use of additional reagents and special equipment. This catalyst is efficient in the addition reaction of β-diketones to vinyl ketones to form β,δ-triketones.

Results and Discussion

The work on the preparation of microsized cerium chloride and its application in the synthesis of β,δ-triketones was performed in two steps. In the first step, we developed a procedure for the preparation of the active catalyst because the commercial salt $CeCl_3\times7H_2O$ is a poor catalyst for the addition reaction. In the second step, the microsized catalyst was used in the Michael addition of β-diketones to vinyl ketones.

With the aim of developing a reproducible, facile, and scaled-up procedure, we proposed several ways of the preparation of the catalyst. The catalyst **A** was commercial $CeCl_3\times7H_2O$ (Fig. 1). The catalyst **B** was prepared as follows: $CeCl_3\times7H_2O$ was dissolved in MeOH, the solvent was evaporated, and the resulting precipitate was heated at 150 °C for 2 h. The catalyst **C** was prepared by dissolving $CeCl_3\times7H_2O$ in EtOH followed by the evaporation of the solvent and heating of the resulting precipitate at 150 °C for 2 h (Fig. 2). The catalyst **D** was prepared by heating $CeCl_3\times7H_2O$ at 150 °C for 2 h (Fig. 3). The catalyst **E** was prepared as follows: $CeCl_3\times7H_2O$ was heated at 150 °C for 2 h and dissolved in MeOH, then silica gel was added (85 wt. % SiO_2 / (SiO_2 + $CeCl_3\times7H_2O$)), the reaction mixture was sonicated for 10 min, and the solvent was evaporated at 80 °C for 1 h at 10-15 mm Hg. The catalyst **F** was prepared as follows: $CeCl_3\times7H_2O$ was dissolved in MeOH, silica gel was added (85 wt. % SiO_2 / (SiO_2 + $CeCl_3\times7H_2O$)), the reaction mixture was sonicated for 10 min, and the solvent was evaporated at 60 °C for 0.5 h at 10-15 mm Hg (Fig. 4).

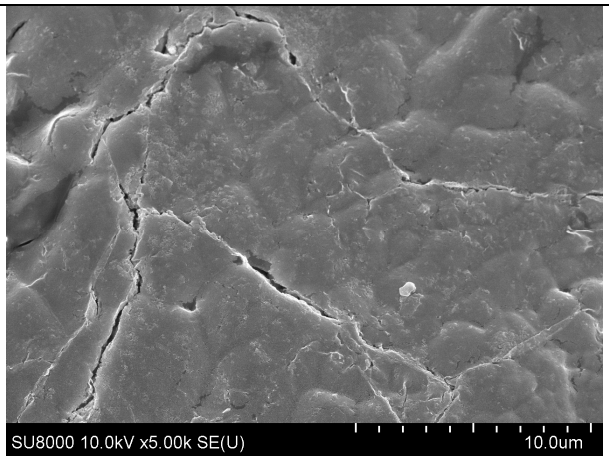


Fig. 1. Micrograph of the commercial sample A $CeCl_3\times7H_2O$

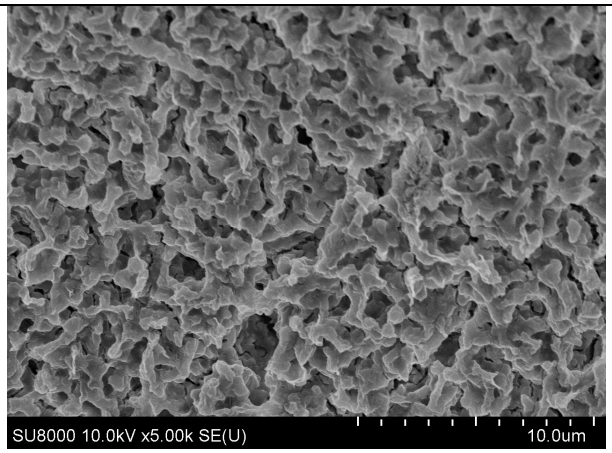


Fig. 2. Micrograph of the catalyst C

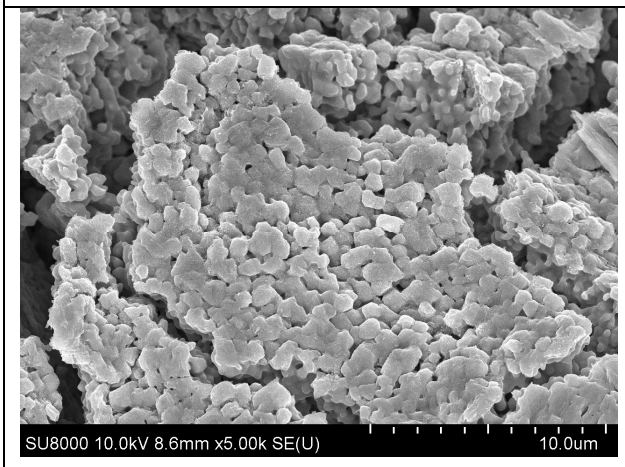


Fig. 3. Micrograph of the catalyst D

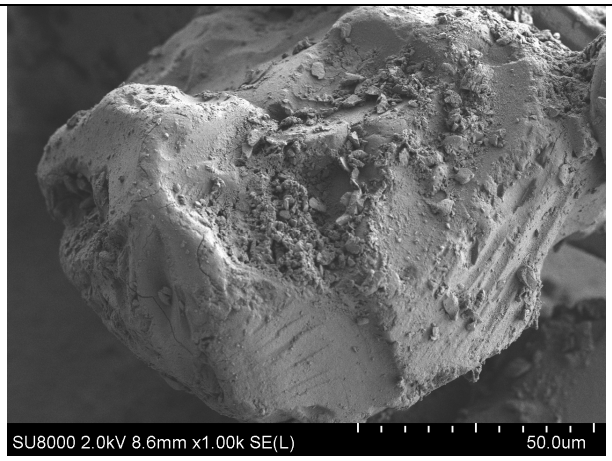


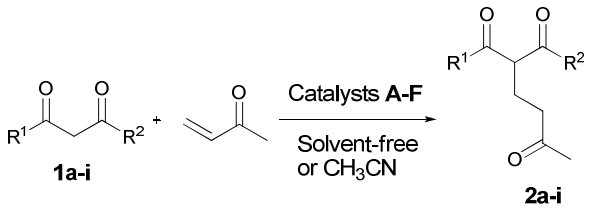
Fig. 4. Micrograph of the catalyst F

The X-ray powder diffraction study showed that the catalysts **B**, **C**, and **D** prepared by the thermal treatment of $CeCl_3\times7H_2O$ were anhydrous $CeCl_3$ with different morphology. The preparation of the catalyst **D** from commercial cerium chloride heptahydrate resulted in the weight loss corresponding to the practically complete dehydration of $CeCl_3\times7H_2O$. According to the literature data, a small amount of CeOCl probably formed.[21] The X-ray powder diffraction also revealed that the anhydrous catalysts **B**, **C**, and **D** rapidly took up atmospheric moisture during storage in air and were transformed into the crystalline phase of $CeCl_3\times7H_2O$ within one hour.

The field-emission scanning electron microscopy (FE-SEM) study

of the samples of cerium chloride showed that its structure substantially depends on the way of the treatment. The commercial sample **A** of $CeCl_3 \times 7H_2O$ does not have a pronounced microstructure (Fig. 1). The catalyst **C** has a porous microstructure formed by particles with a size of about 1 μm (Fig. 2). The catalyst **D** is composed of particle aggregates with a particle size of about 1 μm (Fig. 3). The catalyst **F** apparently contains small particles of cerium chloride on the surface of large silica gel grains (Fig. 4). It should be noted that the immobilization of cerium chloride onto silica gel with the aim of preparing the active catalyst was described earlier. Thus, silica gel-supported $CeCl_3 \times 7H_2O$-NaI was used [22] for the conjugate addition of amines to α,β-enones.

The above-described catalysts **A – F** were used in the reaction of β-diketones **1a-i** with methyl vinyl ketone (Scheme 1).



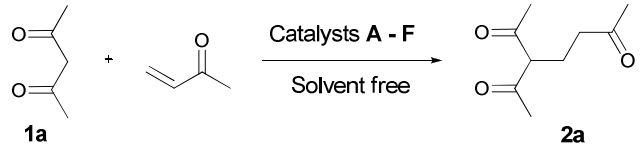
1a-i **2a-i**

a: $R^1 = CH_3$, $R^2 = CH_3$; **b:** $R^1 = CH_3$, $R^2 = CH_2CH(CH_3)_2$;
c: $R^1 = CH_2CH_3$, $R^2 = CH_2CH(CH_3)_2$; **d:** $R^1 = C_6H_5$, $R^2 = CH_3$
e: $R^1 = 4\text{-}CH_3\text{-}C_6H_4$, $R^2 = CH_3$; **f:** $R^1 = 4\text{-}CH_3O\text{-}C_6H_4$, $R^2 = CH_3$
g: $R^1 = 4\text{-Br-}C_6H_4$, $R^2 = CH_3$; **h:** $R^1 = C_6H_5$, $R^2 = C_6H_5$
i: R^1 = Adamantyl, $R^2 = CH_3$

Scheme 1. Synthesis of β,δ-triketones **2a-i** from β-diketones **1a-i** and methyl vinyl ketone.

The conditions for the synthesis of β,δ-triketones were optimized by investigating the preparation of 3-acetylheptane-2,6-dione **2a** from methyl vinyl ketone and pentane-2,4-dione **1a**. The influence of the preparation procedure, the amount of the catalysts **A - F**, and the reaction time on the yield of **2a** was studied (Table 1).

Table 1. Synthesis of 3-acetylheptane-2,6-dione **2a** from methyl vinyl ketone and pentane-2,4-dione **1a**.



1a **2a**

Run	Catalyst **A – F**	Amount of **A - F** (mol. %)	Reaction time, h	Yield of **2a** based on NMR (isolated product), %
1	A	20	6	3
2	B	20	6	71 (65)
3	C	20	6	85 (77)
4	D	20	6	91 (84)
5	D	10	6	91 (83)
6	D	5	6	94 (89)
7	D	1	6	15
8	D	20	12	89 (82)
9	D	10	24	93 (87)
10	D [a]	10	24	87 (82)
11	D [b]	10	24	33
12	E [c]	10	24	69 (61)
13	F [c]	10	24	83 (79)

General reaction conditions: the catalyst (372.6 mg (**A**); 246.5 mg (**B-C**); 12.3-246.5 mg (**D**); 1.179 g (**E**); or 1.242 g (**F**)) was added to pentane-2,4-dione **1a** (0.5 g, 5 mmol), the reaction mixture was stirred at room temperature for 5 min, and then methyl vinyl ketone (385 mg, 5.5 mmol, 1.1 mole per mole of **1a**) was added. The mixture was stirred at 20 – 25 °C for 6, 12, or 24 h.

[a] $CeCl_3 \times 7H_2O$ was heated at 70 °C for 1 h.

[b] After the mixing of all reagents, H_2O (7 mole per mole of $CeCl_3$) was added.

[c] The catalyst **E** or **F** was added to a solution of pentane-2,4-dione **1a** (0.5 g, 5 mmol) in CH_3CN (5 mL).

In run 1, commercial $CeCl_3 \times 7H_2O$ proved to be a poor catalyst for this reaction. Only the specially prepared catalyst (runs 2-13) is suitable for the synthesis of the target product, 3-acetylheptane-2,6-dione **2a**. An increase in the surface area of the catalyst and changes in its properties have a decisive effect of the yield of the product. The simple procedure for the dissolution of $CeCl_3 \times 7H_2O$ followed by the evaporation of the liquid phase (runs 2 with **B** and 3 with **C**) resulted in a strong increase in the activity of the catalyst. Thus, the yield of **2a** was 71 and 85%, respectively. In runs 4-6 (the catalyst **D** was used), the yield of **2a** was even 6-9 % higher.

The amount of the catalyst also has a substantial effect on the result of the reaction. In the range from 5 to 20 mol. %, the yield of **2a** changed only slightly, whereas in the presence of 1 % of the catalyst (run 7), the yield decreased to 15 %.

The reaction time (6, 12, or 24 h) is of no importance. In runs 4-6 and 8, 9, the yields of 3-acetylheptane-2,6-dione **2a** differ only slightly.

Among the catalysts **B**, **C**, and **D**, the latter exhibits the highest activity, its preparation does not require preliminary preparation of solutions, and the simple treatment of the catalyst at 150 °C ensures the reproducibility of its composition.

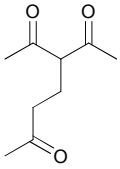
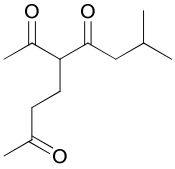
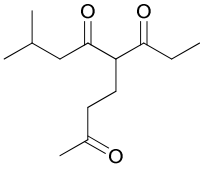
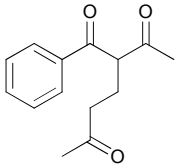
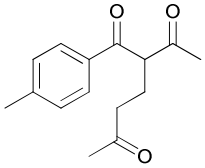
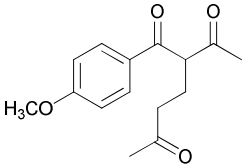
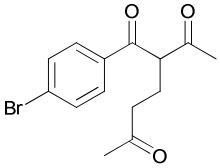
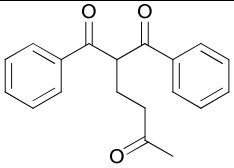
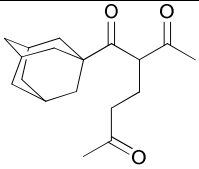
A decrease in the temperature of the treatment of the catalyst to 70 °C, at which the water loss from $CeCl_3 \times 7H_2O$ is very low, has no significant effect on the yield of the target product (run 10). These experiments showed that the structure of the catalyst rather than its composition is mainly responsible for the activity. In run 11, water (7 moles of H_2O per mole of $CeCl_3$) was added to the reaction mixture containing the anhydrous catalyst **D**. In this case, the target product **2a** was obtained in lower yield. Therefore, although the presence of water decreases the activity of the catalyst, it is not fully suppressed.

The use of silica gel as the substrate for cerium chloride (runs 12 and 13) led to a decrease in the yield of 3-acetylheptane-2,6-dione **2a**. The reaction with the use of the thermally pre-treated $CeCl_3 \times 7H_2O$ (run 12, **E**) afforded **2a** in lower yield compared to that obtained in the reaction catalyzed by thermally untreated SiO_2-immobilized $CeCl_3 \times 7H_2O$ (run 13, **F**).

Taking into account the data on the optimization of the reaction conditions (Table 1, run 9, catalyst **D**), β,δ-triketones **2a-i** were synthesized from β-diketones **1a-i** and methyl vinyl ketone, including unsymmetrical β-diketones **1b**,**c** and β-diketones containing bulky aryl and adamantly moieties **1d-i**, in yields up to 89% (Table 2).

Table 2. β,δ-Triketones **2a-i** synthesized from β-diketones **1a-i** and methyl vinyl ketone.

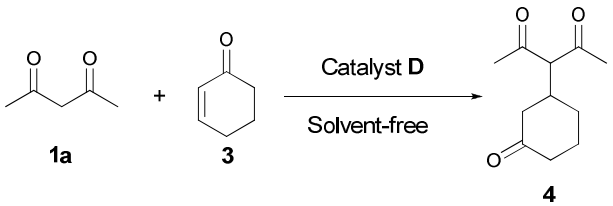
Structures of β,δ-triketones **2a-i** and yields, %

 **2a**, 87	 **2b**, 65	 **2c**, 49
 **2d**, 81	 **2e**, 82	 **2f**, 89
 **2g**, 32 (27[a])	 **2h**, 42 (55[a])	 **2i**, 72

General reaction conditions: the catalyst **D** (123.1-51.1 mg, 0.207-0.5 mmol, 0.1 mole of $CeCl_3$ per mole of diketone **1a-i**) was added with stirring to solution of diketone **1a-i** (0.5 g, 2.074-5.0 mmol) in 3 mL of CH_3CN (in the case of **1a-c**, the solvent was not used), the reaction mixture was stirred at room temperature for 5 min, methyl vinyl ketone (160-385 mg, 2.281-5.50 mmol, 1.1 mole per mole of diketone **1a-i**) was added, and the mixture was stirred at 20–25 °C for 24 h.

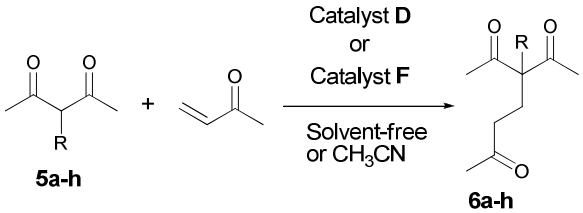
[a] The catalyst sample **F** was used.

The addition of pentane-2,4-dione **1a** to 2-cyclohexen-1-one **3** catalyzed by the catalyst **D** gave β,δ-triketone **4** in 76 % yield (Scheme 2).



Scheme 2. Synthesis of 3-(3-oxocyclohexyl)pentane-2,4-dione **4** from pentane-2,4-dione **1a** and 2-cyclohexen-1-one **3**.

The addition of α-substituted β-diketones **5a-h** to methyl vinyl ketone occurs most efficiently in the presence of the catalysts **D** and **F** under conditions similar to runs 9 and 13, respectively, in Table 1 (Table 3, Scheme 3).



a: R = CH_3; **b:** R = Bu; **c:** R = Hexyl;
d: R = CH_2CH_2COOEt; **e:** R = CH_2CH_2CN; **f:** R = $CH_2C_6H_5$;
g: R = CH_2-C_6H_4-(4)Cl; **h:** R = CH_2-C_6H_4-(4)NO_2

Scheme 3. Synthesis of α-substituted-3-acetyl-2,6-diones **6a-h.**

Table 3. Synthesis of α-substituted-3-acetyl-2,6-diones **6a-h** from methyl vinyl ketone and α-substituted β-diketones **5a-h**.

Run	Substituent R	Yield of **6a-h** based on the isolated product, %	
		Catalyst **D**	Catalyst **F**
1	Me (**5a**)	71	42
2	Bu (**5b**)	32	51
3	Hexyl (**5c**)	34	27
4	CH_2CH_2COOEt (**5d**)	25	34
5	CH_2CH_2CN (**5e**)	66	62
6	CH_2Ph (**5f**)	57	77
7	CH_2-C_6H_4-(4)Cl (**5g**)	48	70
8	CH_2-C_6H_4-(4)NO_2 (**5h**)	39 [a]	62[a]

General reaction conditions: the catalyst **D** or **F** (10 mol. %; 52.4–108.0 mg (**D**) or 0.527-1.088 g (**F**)) was added with stirring to β-diketone **5a-h** (0.5 g, 2.125 - 4.381 mmol) or a solution of β-diketone **5a-h** in CH_3CN (2 mL), respectively, and then methyl vinyl ketone (2.338–4.819 mmol, 163.9 – 337.8 mg, 1.1 mole per mole of β-diketone **5a-h**) was added. The reaction mixture was stirred at room temperature for 24 h.

[a] THF (2 mL) was added.

According to the above-described data, structurally different β,δ-triketones **2a-i**, **4**, and **6a-h** are produced in yields from satisfactory to good in the reactions catalyzed by the **D** and **F**. The yield of the products depends on the type of the catalyst. Thus, the sample **D** proved to be the most efficient catalyst for the synthesis of unsymmetrical β,δ-triketones **2b,c**, β,δ-triketones containing bulky aryl and adamantly moieties **2d-i**, and β,δ-triketone **4**, whereas the catalyst **F** was efficient in the synthesis of α-substituted β,δ-triketones **6f-h** with large benzyl substituents. For β,δ-triketones **6a-e** no clear dependence of the yield on the nature of the catalyst was observed.

Conclusions

It was found that the catalytic activity of cerium chloride widely used in organic chemistry depends on the preliminary thermal treatment. The results of the present study suggest that this effect can play a substantial role in the synthesis with the use of organocerium reagents.

Procedures were developed for the preparation of the structured microsized catalyst $CeCl_3$ from commercial $CeCl_3{\times}7H_2O$ by evaporation of its alcoholic solutions followed by the heating of the residue at 150 °C or only by heating commercial $CeCl_3{\times}7H_2O$ at this temperature. The efficiency of the catalysts was estimated in the addition reaction of β-diketones to vinyl ketones. The yields of the corresponding β,δ-triketones reach 89 %.

Experimental

General materials and methods.

NMR spectra were recorded on a commercial instrument (300.13 MHz for ^1H, 75.48 MHz for ^{13}C) in $CDCl_3$. High-resolution mass spectra (HRMS) were measured using electrospray ionization (ESI).[23] The measurements were done in positive ion mode (interface capillary voltage 4500 V); the spectra were acquired in the mass-to-charge ratio (m/z) range of 50−3000; the external/internal calibration was done with Electrospray Calibrant Solution. Solutions in MeCN were injected with a syringe (flow rate 3 μL min^{-1}). Nitrogen was applied as a dry gas; the interface temperature was set at 180 °C.

For scanning electron microscopy observations,[24] samples were mounted on a 25 mm aluminum stub using conductive glue and coated with a 10 nm thick metal layer (Pt/Pd, 80/20) by magnetron sputtering. The microstructure was studied by field-emission scanning electron microscopy (FE-SEM) on a Hitachi SU8000 electron microscope. The images were taken using a secondary electron detector at an accelerating voltage of 10 kV and the working distance of 8 - 10 mm. The morphology of the samples was studied taking into account the correction for surface effects of the conductive layer sputtering.

The TLC analysis was carried out on standard silica gel chromatography plates. The melting points were determined on a Kofler hot-stage apparatus. The chromatography and the catalyst preparation were performed on silica gel (0.060–0.200 mm, 60 A, CAS 7631-86-9, Acros). Ultrasonic bath with an operating frequency of 22 kHz was used; the power of the generator was 85 W.

Ethanol, methanol, petroleum ether (PE) (40/70), MeCN, ethyl acetate (EA), pentane-2,4-dione, methyl vinyl ketone, dibenzoylmethane and 2-cyclohexen-1-one were purchased from Acros. Cerium(III) chloride heptahydrate was purchased from Alfa Aesar.

Synthesis of diketones 1b-g, i and 5a-h.

Diketones **1b**,[25] **1c**,[26] **1d**,[27] **1e**,[27] **1f**,[28] **1g**,[28] **1i**,[29] **5a**,[30] **5b**,[31] **5c**,[32] **5d**,[33] **5e**,[34] **5f**,[35] **5g**,[35] **5h**[35] were synthesized according to the literature.

6-Methylheptane-2,4-dione, 1b.[25]

Colorless oil.

^1H NMR (300.13 MHz, $CDCl_3$, δ): 0.87-0.91 (m, 6H), 2.01-2.19 (m, 6H), 2.34 (d, 0.25H, J = 7.34 Hz), 3.51 (s, 0.25H), 5.43 (s, 0.75H), 15.5 (br.s., 0.75H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 22.4, 24.2, 25.1, 26.2, 47.1, 52.6, 58.2, 100.5, 192.2, 192.7.

7-Methyloctane-3,5-dione, 1c.[26]

Colorless oil.

^1H NMR (300.13 MHz, $CDCl_3$, δ): 0.86-0.91 (m, 6H), 1.01 (t, 0.6H, J = 7.34 Hz), 1.09 (t, 2.4H, J = 7.34 Hz), 1.92-2.10 (m, 2.8H), 2.24-2.36 (m, 1.8H), 2.48 (q, 0.4H, J = 7.34 Hz), 3.50 (s, 0.4H), 5.43 (s, 0.8H), 15.47 (br.s., 0.8H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 7.4, 9.5, 22.4, 24.2, 26.2, 31.7, 37.0, 47.2, 52.6, 57.2, 99.1, 192.4, 196.4, 204.0.

1-Phenylbutane-1,3-dione, 1d.[27]

White crystals, m.p. = 58-60 °C (m.p. = 60 °C [36]).

^1H NMR (300.13 MHz, $CDCl_3$, δ): 2.18 (s, 2.75H), 2.28 (s, 0.25H), 4.08 (s, 0.25H), 6.16 (s, 1H), 7.40-7.50 (m, 3H), 7.85-7.94 (m, 2H), 16.16 (br.s., 0.75H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 25.7, 54.6, 96.6, 126.9, 128.5, 128.7, 132.2, 134.8, 183.3, 193.7.

1-(4-Methylphenyl)butane-1,3-dione, 1e.[27]

Colorless oil.

^1H NMR (300.13 MHz, $CDCl_3$, δ): 2.15 (s, 2.7H), 2.26 (s,0.3H), 2.37 (s, 3H), 4.04 (s, 0.2H), 6.12 (s, 0.9H), 7.22 (d, 2H, J = 8.07 Hz), 7.74-7.82 (m, 2H), 16.20 (br.s., 0.9H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 21.5, 25.6, 54.6, 96.2, 127.0,

129.3, 132.1, 143.0, 183.7, 193.0.

1-(4-Methoxyphenyl)butane-1,3-dione, 1f.[28]
White crystals, m.p. = 57-59 °C (m.p. = 53 °C [36]).
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 2.16 (s, 3H), 3.85 (s, 3H), 6.10 (s, 1H), 6.92 (d, 2H, *J* = 8.81 Hz), 7.83-7.93 (m, 2H), 16.30 (br.s., 1H).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 25.2, 26.2, 55.4, 95.7, 113.6, 113.8, 127.7, 129.0, 130.5, 163.0, 163.4, 184.0, 191.5, 196.6.

1-(4-Bromophenyl)butane-1,3-dione, 1g.[28]
White crystals, m.p. = 91-92 °C (m.p. = 96.5 °C [36]).
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 2.18 (s, 3H), 4.05 (s, 0.12H), 6.12 (s, 0.94H), 7.55 (d, 2H, *J* = 8.81 Hz), 7.71 (d, 2H, *J* = 8.81 Hz), 16.07 (br.s., 0.94H).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 25.8, 54.6, 96.6, 127.0, 128.4, 130.1, 131.8, 133.7, 182.2, 193.8.

1-(1-Adamantyl)butane-1,3-dione, 1i.[29]
Light yellow crystals, m.p. = 57-58 °C (m.p. = 55-57 °C [29]).
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.71-2.19 (m, 18H), 3.58 (s, 0.2H), 5.53 (s, 0.9H), 15.85 (br.s., 0.9H).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 25.7, 27.7, 28.0, 36.5, 37.8, 38.9, 40.7, 51.9, 95.5, 193.7, 198.5.

3-Methylpentane-2,4-dione, 5a.[30]
Oil.
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.27 (d, 2.2H, *J* = 7.31 Hz), 1.78 (s, 1.6H), 2.06 (s, 2.2H), 2.14 (s, 3H), 3.62 (q, 0.6H, *J* = 7.31 Hz), 16.37 (br.s., 0.4H).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 12.9, 21.1, 22.4, 23.3, 24.6, 28.6, 61.9, 104.8, 190.4, 205.1, 207.3.

3-Butylpentane-2,4-dione, 5b.[31]
Oil.
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.80-0.89 (m, 3H), 1.11-1.32 (m, 4H), 1.77 (q, 1.4H, *J* = 7.32 Hz), 2.01-2.16 (m, 6.6H), 3.55 (t, 0.7H, *J* = 7.32 Hz), 16.61 (br.s., 0.3H).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 13.6, 13.7, 22.4, 22.5, 22.7, 25.1, 27.2, 27.9, 28.9, 29.6, 32.7, 35.9, 68.8, 110.5, 190.8, 204.5.

3-Hexylpentane-2,4-dione, 5c.[32]
Oil.
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.83 (t, 3H, *J* = 7.34 Hz), 1.22-1.26 (m, 8H), 1.78 (q, 1.5H, *J* = 7.34 Hz), 2.02-2.17 (m, 6.5H), 3.56 (t, 0.6H, *J* = 7.34 Hz), 16.63 (br.s., 0.4H).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 13.9, 22.4, 22.6, 22.8, 23.6, 27.5, 27.5, 28.3, 28.9, 29.0, 29.2, 29.7, 30.3, 30.6, 31.4, 31.6, 69.0, 110.6, 190.8, 204.4.

Ethyl 4-acetyl-5-oxohexanoate, 5d.[33]
Oil.
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.18 (t, 3H, *J* = 7.33 Hz), 1.77-1.86 (m, 1.4H), 2.01-2.28 (m, 7H), 2.42-2.55 (m, 1.6H), 3.68 (t, 0.3H, *J* = 7.33 Hz), 4.02-4.10 (m, 2H), 16.68 (br.s., 0.7H).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 14.1, 18.8, 22.7, 22.9, 29.2, 29.8, 31.5, 33.1, 34.7, 42.3, 60.2, 60.5, 67.0, 172.5, 173.1, 191.2, 203.7, 208.1.

4-Acetyl-5-oxohexanenitrile, 5e.[34]
Oil.
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 2.07-2.21 (m, 7H), 2.34-2.44 (m, 2.3H), 2.63 (t, 0.7H, *J* = 7.34 Hz), 3.82 (t, 0.6H, *J* = 7.33 Hz), 16.88 (br.s., 0.4H).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 15.1, 18.1, 22.9, 23.1, 23.6, 29.5, 65.7, 107.1, 118.5, 118.7, 191.6, 202.3.

3-Benzylpentane-2,4-dione, 5f.[35]
Oil.
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 2.07 (s, 2H), 2.12 (s, 4H), 3.14 (d, 1.5H, *J* = 7.34 Hz), 3.65 (s, 0.5H), 4.00 (t, 0.6H, *J* = 7.34 Hz), 7.13-7.32 (m, 5H), 16.82 (br.s., 0.4H).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 23.2, 29.7, 32.8, 34.2, 69.8, 108.2, 126.2, 126.7, 127.3, 128.5, 128.6, 128.6, 137.9, 139.6, 191.8, 203.5.

3-(4-Chlorobenzyl)pentane-2,4-dione, 5g.[35]
Oil.
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 2.04 (s, 3H), 2.11 (s, 2.7H), 2.19 (s, 0.3H), 3.09 (d, 1H, *J* = 7.34 Hz), 3.61 (s, 1H), 3.95 (t, 0.5H, *J* = 7.34 Hz), 7.05-7.09 (m, 2H), 7.21-7.27 (m, 2H), 16.79 (br.s., 0.5H).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 23.2, 29.7, 32.3, 33.4, 69.8, 107.9, 128.4, 128.5, 128.7, 128.8, 128.8, 129.7, 130.0, 131.4, 132.1, 132.6, 136.5, 138.1, 191.9, 203.1.

3-(4-Nitrobenzyl)pentane-2,4-dione, 5h.[35]
Yellow crystals, m.p. = 89-90 °C (m.p. = 90-91 °C [37]).
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 2.04 (s, 4.8H), 2.15 (s, 1.2H), 3.22 (d, 0.4H, *J* = 7.34 Hz), 3.75 (s, 1.6H), 4.01 (t, 0.2H, *J* = 7.34 Hz), 7.31 (d, 2H, *J* = 8.07 Hz), 8.10-8.16 (m, 2H), 16.84 (br.s., 0.8H).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 23.3, 29.6, 33.0, 33.5, 69.2, 107.1, 123.8, 123.9, 128.2, 129.6, 146.7, 147.5, 191.9, 202.3.

Catalysts preparation.

Catalyst B.
$CeCl_3 \times 7H_2O$ (1 g) was dissolved in MeOH (10 mL), followed by the evaporation of the solvent and heating of the resulting precipitate at 150 °C for 2 h; 669 mg of the catalyst were obtained.

Catalyst C.
$CeCl_3 \times 7H_2O$ (1 g) was dissolved in EtOH (10 mL), followed by the evaporation of the solvent and heating of the resulting precipitate at 150 °C for 2 h; 665 mg of the catalyst were obtained.

Catalyst D.
$CeCl_3 \times 7H_2O$ (1 g) was heated at 150 °C for 2 h; 671 mg of the catalyst were obtained.

Catalyst E.
$CeCl_3 \times 7H_2O$ (1 g) was heated at 150 °C for 2 h, the resulting powder was dissolved in MeOH (10 mL), silica gel (5.67 g) was added (85 wt. % SiO_2 / (SiO_2 + $CeCl_3 \times 7H_2O$)), the mixture was sonicated for 10 min, and the solvent was evaporated at 80 °C for 1 h at 10-15 mm Hg; 6.38 g of the catalyst were obtained.

Catalyst F.
$CeCl_3 \times 7H_2O$ (1 g) was dissolved in MeOH (10 mL), silica gel (5.67 g) was added (85 wt. % SiO_2 / (SiO_2 + $CeCl_3 \times 7H_2O$)), the mixture

was sonicated for 10 min, and the solvent was evaporated at 60 °C for 0.5 h at 10-15 mm Hg; 6.65 g of the catalyst were obtained.

Experiment for Table 1.

Synthesis of 3-acetylheptane-2,6-dione 2a from methyl vinyl ketone and pentane-2,4-dione 1a using catalysts A - F.

The catalyst (372.6 mg (**A**); 246.5 mg (**B-C**); 12.3-246.5 mg (**D**); 1.179 g (**E**); and 1.242 g (**F**); 1 - 20 mol. %) was added to pentane-2,4-dione **1a** (0.5 g, 5 mmol). The mixture was stirred at room temperature for 5 min, and then methyl vinyl ketone (385 mg, 5.5 mmol) was added. The mixture was stirred at 20–25 °C for 6, 12, or 24 h and then filtered. The precipitate was washed with a PE : EA mixture (1 : 2, v/v). The solvent was evaporated using a water-jet vacuum pump. The product was isolated by silica gel column chromatography using gradient elution with 30 % to 80 % (v/v) of ethyl acetate in petroleum ether.

In run 10, the catalyst was prepared by heating $CeCl_3 \times 7H_2O$ at 70 °C for 1 h.

In run 11, after the mixing of all reagents, H_2O (63 mg, 7 moles per mole of $CeCl_3$) was added.

In the case of the catalysts **E** and **F**, the reagents were added to a solution of pentane-2,4-dione **1a** (0.5 g, 5 mmol) in CH_3CN (5 mL).

3-Acetylheptane-2,6-dione, 2a.[7b]

Colorless oil, $n_D^{20} = 1.4658$.

$R_f = 0.65$ (PE : EA = 2 : 1).

^1H NMR (300.13 MHz, $CDCl_3$, δ): 1.96-2.12 (m, 10H), 2.37 (t, 2H, $J = 7.34$ Hz), 2.45-2.46 (m, 1H), 3.61 (t, 0.8H, $J = 7.33$ Hz), 16.62 (br.s., 0.2H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 21.3, 21.3, 22.8, 29.1, 29.8, 29.9, 40.4, 43.8, 66.7, 108.8, 191.0, 204.0, 207.3.

Experiment for Table 2.

Synthesis of β,δ-triketones 2a-i from β-diketones 1a-i and methyl vinyl ketone.

The catalyst **D** (123.1-51.1 mg, 0.207-0.5 mmol, 10 mol. %) or, in the case of **1g** and **1h**, the catalyst **F** (367.0-394.5 mg, 10 mol.%) was added with vigorous stirring to β-diketone **1a-i** (0.5 g, 2.07-5.0 mmol) (in the case of solid β-diketones **1d-i**, CH_3CN (3 mL) was also added). The mixture was stirred at room temperature for 5 min, and then methyl vinyl ketone (160-385 mg, 2.281-5.50 mmol, 1.1 mole per mole of **1a-i**) was added. The reaction mixture was stirred at room temperature for 24 h and filtered. The precipitate was washed with a PE : EA mixture (1 : 2, v/v). The solvent was evaporated using a water-jet vacuum pump. The product was isolated by silica gel column chromatography using gradient elution with 30 % to 80 % (v/v) of ethyl acetate in petroleum ether. The following products were obtained: **2a**, 740 mg (4.35 mmol, 87 %); **2b**, 485 mg (2.28 mmol, 65 %); **2c**, 354 mg (1.57 mmol, 49 %); **2d**, 582 mg (2.51 mmol, 81 %); **2e**, 570 mg (2.32 mmol, 82 %); **2f**, 607 mg (2.32 mmol, 89 %); **2g**, 206 mg (0.66 mmol, 32 %); **2h**, 270 mg (0.89 mmol, 42 %); **2i**, 474 mg (1.63 mmol, 72 %).

Analytical data for β,δ-triketones 2b-i.

5-Acetyl-8-methylnonane-2,6-dione, 2b.

Yellow oil, $n_D^{20} = 1.4450$.

$R_f = 0.42$ (PE : EA = 5 : 1).

^1H NMR (300.13 MHz, $CDCl_3$, δ): 0.85-0.92 (m, 6H), 2.00-2.48 (m, 13H), 3.62 (t, 0.8H, $J = 7.34$ Hz), 16.85 (br.s, 0.2H).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 20.9, 21.5, 22.3, 22.3, 22.6, 23.3, 23.9, 25.9, 29.0, 29.9, 30.0, 40.5, 43.6, 44.3, 51.2, 66.6, 109.0, 192.2, 203.9, 205.7, 207.3.

HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{12}H_{20}NaO_3]^+$: 235.1305. Found: 235.1305.

Calculated for $C_{12}H_{20}O_3$ C: 67.89 %, H: 9.5 %. Found C: 67.61 %, H: 9.69 %.

IR (thin layer): 2960, 2936, 2874, 1716, 1593, 1468, 1414, 1365, 1168 cm^{-1}.

8-Methyl-5-propionylnonane-2,6-dione, 2c.

Colorless oil, $n_D^{20} = 1.4557$.

$R_f = 0.40$ (PE : EA = 5 : 1).

^1H NMR (300.13 MHz, $CDCl_3$, δ): 0.84-1.06 (m, 9H), 1.98-2.18 (m, 6H), 2.29-2.52 (m, 6H), 3.64 (t, 0.9H, $J = 7.34$ Hz), 16.88 (br.s., 0.1H)

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 7.5, 21.6, 22.7, 24.0, 29.8, 35.4, 40.6, 50.9, 65.8, 205.7, 206.6, 207.4.

Calculated for $C_{13}H_{22}O_3$ C: 68.99 %, H: 9.80 %. Found C: 68.68 %, H: 10.21 %.

HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{13}H_{22}NaO_3]^+$: 249.1461. Found: 249.1462.

IR (thin layer): 2960, 2940, 2874, 1717, 1594, 1463, 1410, 1367, 1166, 1037 cm^{-1}.

3-Benzoylheptane-2,6-dione, 2d. [7b]

Yellow oil, $n_D^{20} = 1.5278$.

$R_f = 0.56$ (PE : EA = 2 : 1).

^1H NMR (300.13 MHz, $CDCl_3$, δ): 2.07-2.25 (m, 8H), 2.38-2.59 (m, 2H), 4.53 (t, 1H, $J = 7.33$ Hz), 7.43-7.59 (m, 3H), 7.98 (d, 2H, $J = 7.34$ Hz).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 22.4, 28.5, 29.9, 40.4, 61.0, 128.6, 128.8, 133.8, 136.1, 196.5, 203.8, 207.7.

3-(4-Methylbenzoyl)heptane-2,6-dione, 2e.[1c]

Yellow oil, $n_D^{20} = 1.5309$.

$R_f = 0.54$ (PE : EA = 2 : 1).

^1H NMR (300.13 MHz, $CDCl_3$, δ): 2.08-2.22 (m, 8H), 2.39 (s, 3H), 2.44-2.54 (m, 2H), 4.50 (t, 1H, $J = 7.34$ Hz), 7.27 (d, 2H, $J = 8.07$ Hz), 7.89 (d, 2H, $J = 8.07$ Hz).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 21.6, 22.4, 28.4, 29.9, 40.5, 61.0, 128.8, 129.6, 133.7, 144.9, 196.1, 204.0, 207.8.

3-(4-Methoxybenzoyl)heptane-2,6-dione, 2f. [1c]

Oil, $n_D^{20} = 1.5451$.

$R_f = 0.44$ (PE : EA = 2 : 1).

^1H NMR (300.13 MHz, $CDCl_3$, δ): 2.09-2.25 (m, 8H), 2.39-2.61 (m, 2H), 3.86 (s, 3H), 4.48 (t, 1H, $J = 7.34$ Hz), 6.94 (d, 2H, $J = 8.81$ Hz), 7.99 (d, 2H, $J = 8.80$ Hz).

^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 22.5, 28.3, 30.0, 40.6, 55.5, 61.0, 114.1, 129.2, 131.2, 164.2, 194.9, 204.2, 207.9.

3-(4-Bromobenzoyl)heptane-2,6-dione, 2g.[1c]

White crystals, m.p. = 74-76 °C (m.p. = 70-71 °C [1c]).

$R_f = 0.64$ (PE : EA = 2 : 1).

^1H NMR (300.13 MHz, $CDCl_3$, δ): 2.11-2.22 (m, 8H), 2.48-2.60 (m, 2H), 4.49 (t, 1H, $J = 6.60$ Hz), 7.62 (d, 2H, $J = 8.80$ Hz), 7.88

(d, 2H, J = 8.80 Hz).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 22.3, 28.5, 29.9, 40.3, 61.0, 129.2, 130.2, 132.2, 134.7, 195.6, 203.7, 207.8.

2-Benzoyl-1-phenylhexane-1,5-dione, 2h. [9a]
White crystals, m.p. = 70-72 °C (m.p. = 60 °C [9a]).
R_f = 0.80 (PE : EA = 2 : 1).
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 2.10 (s, 3H), 2.31 (q, 2H, J = 6.60 Hz), 2.68 (t, 2H, J = 6.60 Hz), 5.47 (t, 1H, J = 6.60 Hz), 7.44 (t, 4H, J = 7.34 Hz), 7.55 (t, 2H, J = 7.34 Hz), 8.02 (d, 4H, J = 7.34 Hz).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 23.2, 30.0, 40.8, 54.8 (, 128.6, 128.9, 133.6, 135.8, 196.2, 208.6.

3-(Adamant-1-ylcarbonyl)-2,6-heptanedione, 2i.
White crystals, m.p. = 53-55 °C.
R_f = 0.27 (PE : EA = 5 : 1).
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.61-1.74 (m, 10H), 1.96-2.09 (m, 11H), 2.36 (q, 2H, J = 6.60 Hz), 4.06 (t, 1H, J = 6.60 Hz).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 23.3, 27.7, 27.9, 29.9, 36.3, 37.6, 40.6, 47.7, 59.6, 204.0, 207.4, 210.6.
Calculated for $C_{18}H_{26}O_3$ C: 74.45 %, H: 9.02 %. Found C: 74.29 %, H: 9.30 %.
HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{18}H_{26}NaO_3]^+$: 313.1774. Found: 313.1761.
IR (KBr): 3434, 3412, 2921, 2905, 2850, 1722, 1687, 1355, 1255, 1152, 1012 cm^{-1}.

Synthesis of 3-(3-oxocyclohexyl)pentane-2,4-dione 4 from pentane-2,4-dione 1a and 2-cyclohexen-1-one 3 (Scheme 2).
The catalyst **D** (123.2 mg, 10 mol. %, 0.5 mmol) was added with vigorous stirring to pentane-2,4-dione (500 mg, 5 mmol). The mixture was stirred at room temperature for 5 min, and then 2-cyclohexen-1-one (528.6 mg, 5.5 mmol) was added. The reaction mixture was stirred at room temperature for 24 h and filtered. The precipitate was washed with a PE : EA mixture (1 : 2, v/v). The solvent was evaporated using a water-jet vacuum pump. The product was isolated by silica gel column chromatography using gradient elution with 30 % to 80 % (v/v) of ethyl acetate in petroleum ether. 3-(3-Oxocyclohexyl)pentane-2,4-dione **4** was obtained in 66 % yield (643 mg, 3.28 mmol).

3-(3-Oxocyclohexyl)pentane-2,4-dione, 4. [9d]
White crystals, m.p. = 51-52 °C (m.p. = 53-54 °C [5]).
R_f = 0.71 (PE : EA = 1 : 1).
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.28-1.41 (m, 1H), 1.65-1.79 (m, 2H), 1.97-2.05 (m, 2H), 2.13-2.39 (m, 9H), 2.59-2.70 (m, 1H), 3.60 (d, 1H, J = 10.27 Hz).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 24.4, 28.8, 29.6, 29.7, 38.3, 41.0, 45.2, 74.8, 202.6, 202.8, 208.9.

Experiment for Table 3.
Synthesis of α-substituted-3-acetyl-2,6-diones 6a-h from methyl vinyl ketone and α-substituted β-diketones 5a-h.
The catalyst **D** or **F** (52.4–108.0 mg (**D**) or 0.527-1.088 g (**F**), 10 mol. %) was added with stirring to β-diketone **5a-h** (0.5 g, 2.125–4.381 mmol) or a solution of **5a-h** in CH_3CN (2 mL), respectively (in the case β-diketone **5h**, THF (2 mL) was added). Then methyl vinyl ketone (163.9–337.8 mg, 2.338–4.819 mmol, 1.1 mole per mole of **5a-h**) was added. The reaction mixture was stirred at room temperature for 24 h and filtered. The precipitate was washed with a PE : EA mixture (1 : 2, v/v). The solvent was evaporated using a water-jet vacuum pump. Products **6a-h** were isolated by silica gel column chromatography using gradient elution with 30 % to 80 % (v/v) of ethyl acetate in petroleum ether. The following products were obtained: **6a**, 573.0 mg (3.110 mmol, 71 %); **6b**, 369.4 mg (1.632 mmol, 51 %); **6c**, 234.7 mg (0.923 mmol, 34 %); **6d**, 229.5 mg (0.849 mmol, 34 %); **6e**, 481 mg (2.154 mmol, 66 %); **6f**, 526.9 mg (2.024 mmol, 77 %); **6g**, 459.2 mg (1.558 mmol, 70 %), and **6h**, 402.4 mg (1.318 mmol, 62 %).

Analytical data for α-substituted-3-acetyl-2,6-diones 6a-h.
3-Acetyl-3-methylheptane-2,6-dione, 6a. [9a]
Oil.
R_f = 0.51 (PE : EA = 2 : 1).
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.27 (s, 3H), 2.02-2.06 (m, 11H), 2.29 (t, 2H, J = 7.32 Hz).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 18.5, 26.4, 27.5, 29.8, 38.3, 65.2, 207.2.

3-Acetyl-3-butylheptane-2,6-dione, 6b. [1c]
White crystals, m.p. = 42-43 °C (m.p. = 45-46 °C [1c]).
R_f = 0.76 (PE : EA = 2 : 1).
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.86 (t, 3H, J = 7.34 Hz), 0.94-1.05 (m, 2H), 1.26-1.33 (m, 2H), 1.81 (t, 2H, J = 7.34 Hz), 2.07-2.11 (m, 11H), 2.22 (t, 2H, J = 7.34 Hz).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 13.6, 23.0, 24.2, 25.8, 26.9, 29.8, 31.3, 38.0, 69.2, 207.1.

3-Acetyl-3-hexylheptane-2,6-dione, 6c.
Oil.
R_f = 0.28 (PE : EA = 5 : 1).
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.82 (t, 3H, J = 5.95 Hz), 0.96-1.04 (m, 2H), 1.22-1.33 (m, 7H), 1.47-1.56 (m, 1H), 1.76-1.82 (m, 2H), 2.05-2.23 (m, 11H).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 13.9, 22.5, 23.7, 24.2, 26.9, 29.7, 29.9, 31.4, 31.7, 38.1, 62.9, 207.2.
Calculated for $C_{15}H_{26}O_3$ C: 70.83 %, H: 10.30 %. Found C: 70.79 %, H: 10.29 %.
HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{15}H_{26}NaO_3]^+$: 277.1774. Found: 277.1778.
IR (thin layer): 2956, 2930, 2859, 1176, 1697, 1459, 1423, 1358, 1169 cm^{-1}.

Ethyl 4,4-diacetyl-7-oxo-octanoate, 6d. [1c]
Oil.
R_f = 0.39 (PE : EA = 5 : 1).
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.19 (t, 3H, J = 7.34 Hz), 1.97-2.28 (m, 17H), 4.05 (q, 2H, J = 7.34 Hz).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 14.0, 24.1, 26.1, 26.9, 28.8, 29.9, 37.7, 60.7, 68.4, 172.5, 206.5, 206.9.

4,4-Diacetyl-7-oxooctanenitrile, 6e. [1c]
Yellow crystals, m.p. = 76-78 °C (m.p. = 74-75 °C [1c]).
R_f = 0.24 (PE : EA = 2 : 1).

^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 2.10-2.26 (m, 17H).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 12.4, 24.0, 26.7, 26.9, 29.9, 37.3, 68.2, 118.7, 205.6, 206.2.

3-Acetyl-3-benzylpentane-2,4-dione, 6f. [1c]
White crystals, m.p. = 77-79 °C (m.p. = 79-80 °C [1c]).
R_f = 0.58 (PE : EA = 2 : 1).
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 2.08-2.12 (m, 11H), 2.30 (t, 2H, *J* = 7.34 Hz), 3.16 (s, 2H), 6.98 (d, 2H, *J* = 7.34 Hz), 7.20-7.24 (m, 3H).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 24.2, 27.7, 29.9, 37.5, 37.9, 70.0, 127.0, 128.5, 129.5, 135.5, 206.9.

3-Acetyl-3-[(4-chlorophenyl)methyl]heptane-2,6-dione, 6g.
White crystals, m.p. = 128-130 °C.
R_f = 0.53 (PE : EA = 2 : 1).
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 2.06-2.13 (m, 11H), 2,28 (t, 2H, *J* = 7.78 Hz), 3,11 (s, 2H), 6,92 (d, 2H, *J* = 8.24 Hz), 7,19 (d, 2H, *J* = 8.24 Hz).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 24.2, 27.8, 29.9, 36.8, 37.9, 69.9, 128.7, 130.9, 133.0, 134.1, 206.6.
Calculated for $C_{16}H_{19}ClO_3$ C: 65.19 %, H: 6.50 %, Cl: 12.03 %. Found C: 65.16 %, H: 6.65 %, Cl: 12.17 %.
HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{16}H_{19}ClNaO_3]^+$: 317.0915. Found: 317.0905.
IR (KBr): 3416, 3390, 1720, 1691, 1492, 1370, 1360, 1167, 1147, 816 cm^{-1}.

3-Acetyl-3-[(4-nitrophenyl)methyl]heptane-2,6-dione, 6h.[1c]
Yellow crystals, m.p. = 110-112 °C (m.p. = 113-114 °C [1c]).
R_f = 0.33 (PE : EA = 2 : 1).
^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 2.09-2.13 (m, 11H), 2.31 (t, 2H, *J* = 8.24 Hz), 3.24 (s, 2H), 7.17 (d, 2H, *J* = 8.24 Hz), 8.07 (d, 2H, *J* = 8.24 Hz).
^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 24.4, 27.7, 30.0, 37.1, 37.7, 70.0, 123.6, 130.6, 143.6, 206.1.

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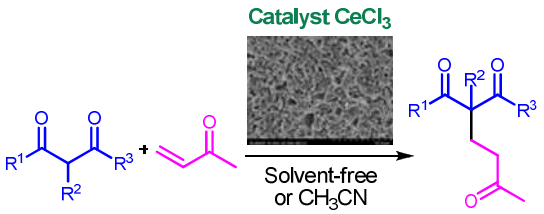

A facile method was developed for the preparation of microsized cerium chloride, which is efficient catalyst in the Michael addition reaction.