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# Cationic Vanadium(IV) Complexes as Efficient Catalysts for Nazarov Cyclizations

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Vanadium(IV) species generated in situ from V(salen)$Cl_2$ complexes (**1**) by reaction with 2 equiv. of $AgSbF_6$ are effective catalysts for Nazarov cyclizations. Thus, dialkenyl ketones bearing α-ester groups are efficiently converted to corresponding cyclopentenones in good yields at room temperature, in the presence of 2 mol-% catalyst. Under such conditions full conversion takes place within minutes for substrates bearing an electron-donating group at position 1 of the 1,4-dien-3-one system.



## Introduction

Five-membered carbocycles are useful building blocks in synthetic chemistry. One of the most versatile approaches to their synthesis is the Nazarov cyclization,[1] a pericyclic reaction involving a conratotory 4π process of a pentadienyl cation (Figure 1). This reaction has witnessed increasing interest in the past decade.

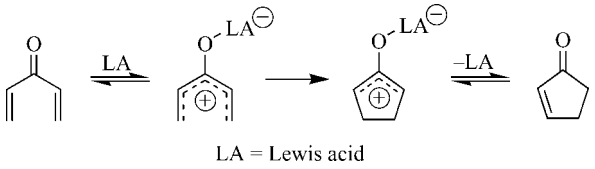


Figure 1. Nazarov cyclization pathway.

In general, to promote the reaction high temperature and/or strong Lewis acids are required, one or more molar equiv. of which are necessary. Searching for milder alternatives, such as reactions at ambient temperature and Lewis acids that can be used in catalytic amounts,[2] several research groups have recently reported new developments in Nazarov chemistry, including a few enantioselective variants of the reaction using either catalytic or stoichiometric amounts of metal complexes bearing chiral ligands.[3] However, this approach still remains quite rare. The stepwise nature of the Nazarov cyclization has been discussed in early mechanistic works.[4]

## Results and Discussion

Previous studies have shown that coordinatively unsaturated cationic complexes bearing $C_2$ symmetric ligands, often formed by chloride abstraction from a suited corresponding precursor, are required for both good conversion and enantioselectivity in the Nazarov cyclization.[5] With this in mind, we prepared the new achiral dichloridovanadium(IV) complex **1a** as well as the analogous chiral derivative **1b** shown in Figure 2.

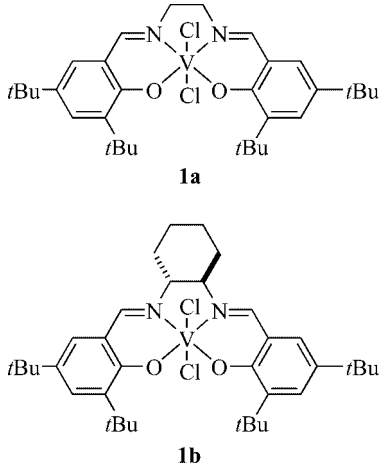


Figure 2. Vanadium salen complexes **1a** and **1b**.

The chemistry of vanadium(IV) is dominated by the stable $VO^{2+}$ entity and a large amount of data on vanadyl complexes containing tetradentate salen ligands are available.[6] The synthetic applications of oxovanadium derivatives are basically limited to oxidation reactions[7] and only few examples of other C–C or C–O bond-forming reactions catalyzed by oxovanadium(IV) complexes are known.[8] Surprisingly, even though a large number of dichloridovanadium complexes have been described, as obtained by known deoxygenation reactions of oxovanadium species,[9] it appears that $V^{IV}Cl_2$ complexes have not been used as catalysts or catalyst precursors before.

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Our rationale for using dichlorido(salen)vanadium complexes for Nazarov cyclization is based on the following reasons. i. Treatment of the dichloridovanadium complex with a chloride abstracting agent should form an extremely reactive dicationic species, which can serve as a Lewis-acidic catalyst. ii. Many metal salen complexes displaying the *cis*-β configuration are known.[10] This configuration, which should also be accessible for the $[V(salen)]^{2+}$ fragment, provides two coordination sites in mutual *cis* position, suited for the coordination of the two carbonylic oxygen atoms of a Nazarov substrate in a bidentate manner.[11]

It has been previously reported that the electronic properties of the Nazarov substrate has a strong influence on both cyclization rates and efficiency of the reaction.[2a,12] With this in mind, we have prepared and tested three different types of substrates (Figure 3) representing different polarization states of the basic dialkenyl ketone structure. All substrates were obtained by standard synthetic procedures and have been partly reported before.

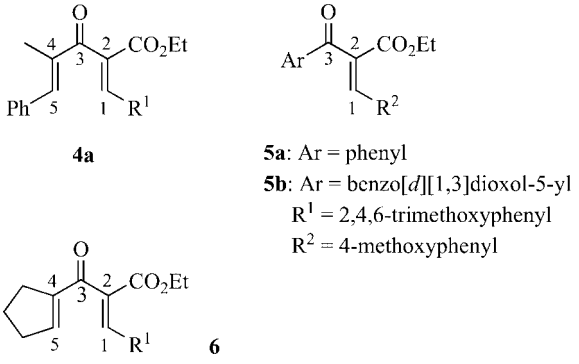
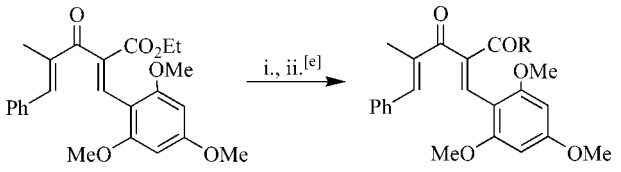



Figure 3. The types of dialkenyl ketones tested in this study.

Thus, substrates **4** were obtained by the addition of the enolate of ethyl acetate to either an aldehyde or an acyl chloride. In the case of the addition to the aldehyde,[13] the resulting alcohol was oxidized with $MnO_2$[14] or DMP (Dess–Martin periodane).[15] Subsequent Knoevenagel condensation of the β-keto ester **3** with the appropriate aldehyde gave the desired dialkenyl ketones[16] with overall yields of 29–71% (Table 1).

In order to introduce bulkier ester or amide groups at the C2 position of the dialkenyl ketone system, the ethyl ester **4a** was saponified to give the corresponding acid, which was then treated with the appropriate alcohol or amine to afford the desired products in overall yields of 34–62% (Table 2).

Table 2. Modification of substrate **4a**.[a]

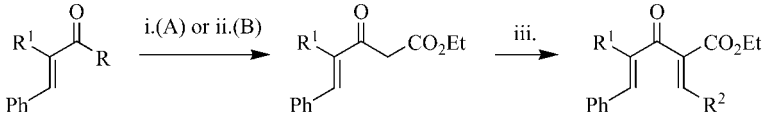



| Compound | R | % Yield[b] |
|---|---|---|
| **4j** | OBn | 59 |
| **4k** | OMES[c] | 34 |
| **4l** | ONp[d] | 55 |
| **4m** | $NBn_2$ | 62 |

[a] Reagents and conditions: i. KOH, EtOH, $H_2O$, 55 °C. ii. ROH, DMAP, DCC, $CH_2Cl_2$, 0 °C; ii. (amide synthesis): $Bn_2NH$, DMAP, DCC, DMF, room temp. [b] Isolated overall yields of **4j**–**m**. [c] MES = 2,4,6-trimethylphenyl. [d] Np = 1-naphthyl.

Initial experiments with the vanadium system **1a**, after in-situ activation with two equiv. of $AgSbF_6$, were carried out with Nazarov substrates of type **5**. However, compound **5a** did not give any cyclized product even not after eleven days at room temperature in $CH_2Cl_2$ with 2 mol-% of the vanadium complex. For comparison, the more polarized

Table 1. Synthesis of dialkenyl ketones.[a]




| Compound | $R^1$ | $R^2$ | % Yield[b] |
|---|---|---|---|
| **4a** | Me | 2,4,6-trimethoxyphenyl | 71 |
| **4b** | Me | 4-methoxyphenyl | 64 |
| **4c** | Me | 2,4,6-trimethoxyphenyl | 59 |
| **4d** | Me | phenyl | 71 |
| **4e** | Me | 4-nitrophenyl | 57 |
| **4f** | Ph | 2,4,6-trimethoxyphenyl | 58 |
| **4g** | Ph | 4-methoxyphenyl | 64 |
| **4h** | H | 4-methoxyphenyl | 29 |
| **4i** | H | 2,4,6-trimethoxyphenyl | 25 |

[a] **3a**–**g** were prepared starting from **2a**–**b**. Reagents and conditions i. (A): (1) LDA, THF, EtOAc, –78 °C. (2) $MnO_2$, $CH_2Cl_2$; or DMP, $CH_2Cl_2$. **3c** was prepared from **2c**. Reagents and conditions ii. (B): (1) $(COCl_2)_2$, DMF, $CH_2Cl_2$, 0 °C; (2) LDA, THF, EtOAc, –78 °C. iii. (a) $TiCl_4$, $CCl_4$, THF, $R^2CHO$, pyridine, 0 °C; (b) $R^2CHO$, AcOH, piperidine, benzene, 100 °C. [b] Isolated overall yields of **4a**–**i**.

substrate **5b** cyclized within three days under the same conditions. Even though the corresponding product was obtained in very good yield, the reaction is still very slow. Moreover, substrate **6** was cyclized within twenty minutes affording the product in good yield, however, as a mixture of regioisomers.[17]

We therefore focused on substrates of type **4**, which turned out to be the most reactive with respect to our vanadium catalyst. Initial experiments addressed the nature of the activating reagent and were carried out by using substrate **4a** in dichloromethane at room temperature. These experiments showed that only $AgSbF_6$ was able to generate a catalytically active species, whereas the other common chloride abstracting agents $[Et_3O]PF_6$, $TlPF_6$, $AgPF_6$, and $AgBF_4$ did not. This may be due to two main reasons: i. $Ag^+$ is usually a more efficient chloride scavenger than triethyloxonium and $Tl^+$.[18] ii. The possible coordinating properties of the anion play a crucial role. Only the least coordinating $SbF_6^-$ is compatible with the postulated interaction of the substrate with the $V^{IV}$ metal center.[19] Therefore, we assume that a dicationic vanadium complex is the active catalytic species. The formation of a white precipitate (AgCl) and a color change of the solution from dark blue to dark purple followed the addition of $AgSbF_6$ to the dichloridovanadium complex **1a**. No noticeable effect of the AgCl precipitate present in the reaction mixture could be discerned. Removal of AgCl by filtration did not change neither the reaction time nor the yield. We also took the precaution of verifying that any soluble silver salt *alone* would be able to catalyze the reaction and found that 1 equiv. of $AgSbF_6$ led to only ca. 17% conversion of **4a** in 2 d. This means that the Ag-catalyzed reaction constitutes only a very weak and therefore negligible background.

Using the dialkenyl ketone **4a** we also tested different solvents and found that in $CH_2Cl_2$ the reaction is fastest, affording the best yield at room temperature (Table 3). Indeed, when working with 2 mol-% of the catalyst precursor **1a** the reaction reaches complete conversion within ca. 2 min, as shown by TLC monitoring. Coordinating solvents drastically reduce the reaction rate.

Under these optimized conditions a number of dialkenyl ketones of type **4** was subjected to the V-catalyzed cyclization and the results are reported in Table 4.

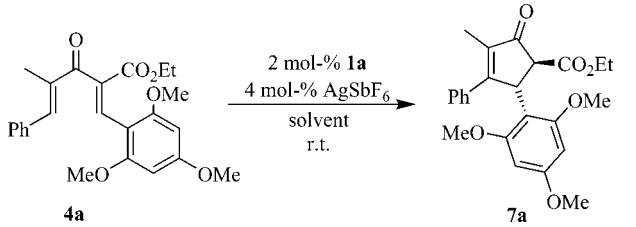
From these data it is apparent that the electronic properties of the substituent at C1 of the 3-oxopentadiene system considerably influences the reactivity of compounds **4** in this V-catalyzed cyclization. Thus, dialkenyl ketone **4a**, bearing the electron-rich trimethoxyphenyl group, cyclize within two minutes, whereas the cyclization of the simple phenyl derivative **4d** takes three hours. Moreover, the reaction of dialkenyl ketone **4e**, having a 4-nitrophenyl group at C1, requires about six hours for full conversion.

Nearly all dialkenyl ketones **4** give the expected cyclopentenone derivatives as products with an endocyclic double bond. Surprisingly, however, **4b** affords the cyclic enol **7b** in which the olefinic double bond is exocyclic (Scheme 1).

Furthermore, substrates **4c** react within minutes, but give an only modest yield of a mixture of endocyclic and exocyclic double bond isomers. Cyclization of dialkenyl ketones **4j**–**l**, bearing relatively bulky ester groups, results in slightly lower reaction rates, whereas dialkenyl ketone **4m**, having an amide instead of an ester group, do not show any appreciable conversion after two days at room temperature.

Dialkenyl ketones **4h**–**i** and **8** (Figure 4) were also subjected to optimized reaction conditions. Substrate **8** was synthesized similarly to ketones **4** via Knoevenagel condensation of β-keto ester **3a** with 4,6-dimethoxysalicylaldehyde,

Table 3. Influence of different solvents on the cyclization of **4a**.

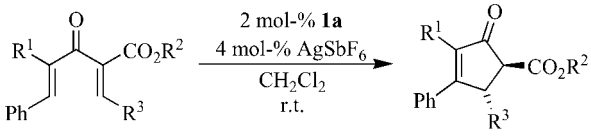



**4a** **7a**

| Entry | Solvent | Time [min] | % Yield |
|---|---|---|---|
| 1 | $CH_2Cl_2$ | 2 | 94 |
| 2 | toluene | 5 | 85 |
| 3 | THF | 10 | 41[a] |
| 4 | $CH_3CN$ | 3 d | 20 |

[a] Mixture of regioisomers.

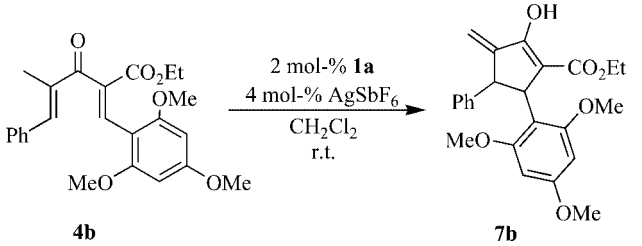
Table 4. Nazarov cyclization under optimized conditions.




**4a–l** **7a–l**

| Compound | $R^1$ | $R^2$ | $R^3$ | Time | % Yield |
|---|---|---|---|---|---|
| **7a** | Me | Et | TMP[a] | 2 min | 94 |
| **7b** | Me | Et | MES | 5 min | 63[b] |
| **7c** | Me | Et | PMP[c] | 10 min | 37 |
| **7d** | Me | Et | Ph | 3 h | 87 |
| **7e** | Me | Et | 4-$NO_2$Ph | 6 h | 80 |
| **7f** | Ph | Et | TMP | 10 min | 98 |
| **7g** | Ph | Et | PMP | 10 min | 97 |
| **7j** | Me | Bn | TMP | 5 min | 65 |
| **7k** | Me | MES[d] | TMP | 15 min | 99 |
| **7l** | Me | Np[e] | TMP | 1.5 h | 80 |

[a] TMP = 2,4,6-trimethoxyphenyl. [b] Cyclization of **4b** gave an exocyclic double bond isomer, see Scheme 1. [c] PMP = 4-methoxyphenyl. [d] MES = 2,4,6-trimethylphenyl. [e] Np = 1-naphthyl.

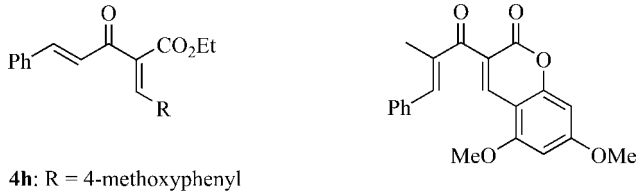



**4b** **7b**

Scheme 1. Cyclization of **4b**.

followed by lactonization with concomitant loss of ethanol.[20] In the cases of **4h–i** no cyclization could be observed, even not after two days at room temperature. We tentatively ascribe this lack of reactivity to the preferred *s-cis* conformation of the C3–C4 bond in these two substrates favored by the absence of substituents at C4. The failure of the cyclization in the case of **8** can be rationalized in terms of rigidity of the lactone, detrimental in view of the required conrotatory movement.



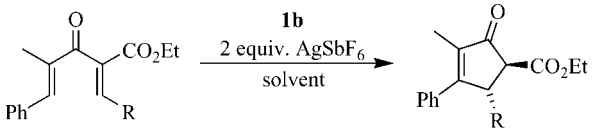

**4h**: R = 4-methoxyphenyl
**4i**: R = 2,4,6-trimethoxyphenyl

**8**

Figure 4. Conformations of divinyl ketones.

Because of their propensity to act as bidentate ligands (two-points binding), we reckon that dialkenyl ketones **4** can be suitable substrates for a catalytic asymmetric process. However, our attempts to develop an asymmetric version of the Nazarov cyclization using the chiral vanadium salen precursor **1b** were unsuccessful. In fact, when the reaction of **4a** was carried out using a catalyst generated in situ from complex **1b**, in different solvents, with different catalyst loadings, and at various temperatures, the product was invariably isolated in racemic form (Table 5).

Table 5. Attempted asymmetric Nazarov cyclization of **4a**.[a]




**4a** R = 2,4,6-trimethoxyphenyl **7a**

| Entry | Solvent | **1b** [mol-%] | *T* [°C] | % Yield |
|---|---|---|---|---|
| 1 | $CH_2Cl_2$ | 2 | 20 | 93 |
| 2 | $CH_2Cl_2$ | 100 | –78 | 92 |
| 3 | toluene | 2 | 20 | 80 |
| 4 | THF | 2 | 20 | 38 |
| 5 | $CH_3CN$ | 2 | 20 | 25 |

[a] All cyclizations afforded racemic cyclopentenone **7a**.

## Conclusions

In conclusion, we have developed the first vanadium(IV)-catalyzed Nazarov cyclization. Good to excellent yields can be obtained for substrates displaying 1,2,4,5-tetrasubstitution pattern of the dialkenyl ketone system. The short reaction times of just a few minutes when working at room temp. with 2 mol-% of the vanadium complex and therefore average TOF's of up to 25 $min^{-1}$ are unprecedented for transition-metal-catalyzed Nazarov cyclizations. Despite the first unsuccessful attempts towards an asymmetric variant of the reaction using a catalyst derived from complex **1b**, we will further explore chiral enantiopure catalysts.

## Experimental Section

**General:** All catalysis experiments were conducted under an atmosphere of argon or nitrogen using standard Schlenk techniques or in a glove box. All vanadium-promoted Nazarov cylizations were carried out at ambient temperature in the glove box, due to the air sensitivity of the involved dicationic species. All solvents were stored over activated molecular sieves (4 Å) unless otherwise indicated. In the case of freshly distilled solvents, the following drying agents were used: Na/benzophenone for THF and $Et_2O$; Na for toluene; $CaH_2$ for $CH_2Cl_2$. Chromatography was carried out with Merck silica gel 60. The NMR spectra were recorded at 25 °C on Bruker Avance 250 (250.1 MHz, $^1H$; 62.9 MHz, $^{13}C$), 300 (300.1 MHz, $^1H$; 75.5 MHz, $^{13}C$) spectrometers. $^1H$ and $^{13}C$ chemical shifts (δ) were referenced internally by the residual solvent signal. High-resolution MALDI mass spectra were measured by the analytical service of the Organic Chemistry Laboratory of the ETH Zürich on an IonSpec ultima FT MALDI mass spectrometer. Elemental analyses were obtained on a Leco CHN-900 analyzer. All commercially available chemicals were used without further purification. {*N*,*N*′-Bis[3,5-bis(*tert*-butyl)salicylidene]ethylene-1,2-diamino}vanadium(IV) oxide[21] and {(1*R*,2*R*)-*N*,*N*′-bis[3,5-bis(*tert*-butyl)salicylidene]cyclohexane-1,2-diamino}vanadium(IV) oxide[22] were prepared according to the literature procedures.

**{*N*,*N*′-Bis[3,5-bis(*tert*-butyl)salicylidene]ethylene-1,2-diamino}vanadium(IV) Dichloride (1a):**[23] {*N*,*N*′-Bis[3,5-bis(*tert*-butyl)salicylidene]ethylene-1,2-diamino}vanadium(IV) oxide (2 g, 3.59 mmol. 1 equiv.) was dissolved in dry toluene (50 mL) under argon atmosphere and $SOCl_2$ (0.33 mL, 4.56 mmol, 1.3 equiv.) was added to the reaction mixture. The green reaction solution turned immediately to dark blue and a precipitate was formed. The reaction mixture was refluxed for 30 min. After cooling to ambient temperature, the solvent was removed to dryness; the black residue was washed with cold toluene. The crude complex was recrystallized by dissolution in a small volume of EtOH (1 mL) followed by the addition of *n*-hexane (3 mL) and subsequent slow evaporation. The black solid was washed with cold *n*-hexane (2 × 3 mL) to afford (2.2 g, 100%) the title compound. IR (KBr): ṽ = 2956.6, 1605.1, 1541.4, 1435.5, 1363.6, 1269.9, 1248.1, 917.1, 873.6, 843.7, 758.4, 597.1, 582.7 $cm^{-1}$. $C_{32}H_{46}Cl_2N_2O_2V$ (612.57): calcd. C 62.74, H 7.57, N 4.57, O 5.22, Cl 11.57; found C 62.46, H 7.54, N 4.59, Cl 11.29. MS (HR MALDI): *m*/*z* 576.2687 (calcd. for $C_{32}H_{46}ClN_2O_2V$); found 575.2682 [$M^+$ – Cl].

**{(1*R*,2*R*)-*N*,*N*′-Bis[3,5-bis(*tert*-butyl)salicylidene]cyclohexane-1,2-diamino}vanadium(IV) Dichloride (1b):** This compound was synthesized analogously to **1a**; reaction time 30 min, yield 86%, black solid. IR (KBr): ṽ = 2953.2, 1605.4, 1642.2, 1542.2, 1464.2, 1364.1, 1271.1, 1243.6, 919.8, 868.9, 850.8, 760.1, 568.0 $cm^{-1}$. $C_{36}H_{52}Cl_2N_2O_2V$ (666.67): calcd. C 64.86, H 7.86, N 4.20, O 4.80, Cl 10.64; found C 64.83, H 7.83, N 4.12, O 5.02, Cl 10.51. MS (HR MALDI): *m*/*z* 630.3157 (calcd. for $C_{36}H_{52}ClN_2O_2V$), found 630.3164 [$M^+$ – Cl].

Knoevenagel condensations were carried out by **Method A**, a representative procedure of which is given below.

**Method A.**[24] **Ethyl 4-Methyl-3-oxo-5-phenyl-2-(2,4,6-trimethoxybenzylidene)pent-4-enoate (4a):** To a stirred solution of ethyl 4-methyl-3-oxo-5-phenylpent-4-enoate (2 g, 8.61 mmol, 1 equiv.) in

benzene (50 mL) AcOH (0.25 mL, 4.3 mmol, 0.5 equiv.), piperidine (0.08 mL, 0.86 mmol, 0.1 equiv.) and 2,4,6-trimethoxybenzaldehyde (1.69 g, 8.61 mmol, 1 equiv.) were added. The yellow solution was refluxed in a Dean–Stark apparatus at 100 °C. After 4 h, the reaction was complete, the orange solution was cooled down to ambient temperature and diluted with water and diethyl ether (each 50 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether (50 mL). The combined organic layers were washed with 1 N HCl (2 × 50 mL), $NaHCO_3$ (2 × 50 mL), dried with $MgSO_4$ and the solvent removed under reduced pressure. The residue was purified by column chromatography eluting with cyclohexane/ethyl acetate (7:3), $R_f$ = 0.35 to give the title compound as a yellow solid (3.4 g, 96%) and as an *E*/*Z* mixture (1:9). $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 1.17 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $OCH_2CH_3$, minor isomer), 1.25 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $OCH_2CH_3$, major isomer), 2.16 (d, $^4J_{H,H}$ = 1.2 Hz, 3 H, $CH_3$, major isomer), 2.28 (d, $^4J_{H,H}$ = 1.2 Hz, 3 H, $CH_3$, minor isomer), 3.68 (s, 6 H, 2 $OCH_3$, major isomer), 3.76 (s, 3 H, $OCH_3$, major isomer), 3.82 (s, 3 H, $OCH_3$, minor isomer), 4.16 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, $OCH_2CH_3$, minor isomer), 4.24 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, $OCH_2CH_3$, major isomer), 6.02 (s, 2 H, C*H*Ar, major isomer), 6.10 (s, 2 H, C*H*Ar, minor isomer), 7.25–7.40 (m, 5 H, C*H*Ar), 7.45 (s, 1 H, C*H*, minor isomer), 8.06 (s, 1 H, C*H*, major isomer) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 13.02, 14.08, 14.25, 14.32, 55.05, 55.35, 55.40, 55.44, 60.39, 60.89, 90.31, 90.34, 105.38, 105.75, 128.22, 128.30, 128.35, 128.38, 129.34, 129.51, 129.64, 133.38, 135.43, 135.58, 135.96, 136.33, 136.80, 137.67, 139.16, 139.71, 159.53, 159.54, 163.27, 163.39, 166.86, 167.41, 196.20, 196.73 ppm. $C_{24}H_{26}O_6$ (410.47): calcd. C 70.23, H 6.38; found C 70.20, H 6.48. MS (HR MALDI): *m*/*z* 433.1627 (calcd. for $C_{24}H_{26}O_6Na$), found 433.1622 [$MNa^+$].

**Ethyl 2-(4-Methoxybenzylidene)-4-methyl-3-oxo-5-phenylpent-4-enoate (4b):** This compound was prepared according to method A, yield 86%, cyclohexane/ethyl acetate (8:2), yellow oil, $R_f$ = 0.37. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 1.29 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_2CH_3$), 2.24 (s, 3 H, $CH_3$), 3.82 (s, 3 H, $OCH_3$), 4.28 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, $CH_2CH_3$), 6.85 (d, $^4J_{H,H}$ = 8.4 Hz, 2 H, C*H*Ar), 7.34–7.42 (m, 7 H, C*H*Ar), 7.51 (s, 1 H, C*H*), 7.85 (s, 1 H, C*H*) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 12.65, 14.23, 55.29, 61.28, 114.33, 125.81, 128.46, 128.98, 129.03, 129.94, 132.05, 135.59, 137.12, 141.79, 142.69, 161.30, 165.49, 198.55 ppm. $C_{22}H_{22}O_4$ (350.41): calcd. C 75.41, H 6.33; found C 75.67, H 6.39. MS (HR MALDI): *m*/*z* 373.1416 (calcd. for $C_{22}H_{22}O_4Na$), found 373.1410 [$MNa^+$].

**Ethyl 4-Methyl-3-oxo-5-phenyl-2-(2,4,6-trimethylbenzylidene)pent-4-enoate (4c):** This compound was prepared according to method A, yield 80%, *E*/*Z* (4:6), cyclohexane/ethyl acetate (9.5:0.5), yellow oil, $R_f$ = 0.26. $^1$H NMR (250.1 MHz, $CDCl_3$): $\delta$ = 1.05 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_2CH_3$, minor isomer), 1.36 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, $CH_2CH_3$, major isomer), 1.89 (d, $^4J_{H,H}$ = 3.0 Hz, 3 H, $CH_3$, major isomer), 2.23 (s, major isomer, 6 H, $CH_3$Ar), 2.25 (s, major isomer, 3 H, $CH_3$Ar), 2.28 (d, $^4J_{H,H}$ = 3.0 Hz, 3 H, $CH_3$, minor isomer), 2.31 (s, 6 H, $CH_3$Ar, minor isomer), 2.33 (s, 3 H, $CH_3$Ar, minor isomer), 4.10 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, $CH_2CH_3$, minor isomer), 4.36 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, $CH_2CH_3$, minor isomer), 6.81 (s, 1 H, C*H*Ar, major isomer), 6.92 (s, 1 H, C*H*Ar, minor isomer), 7.28–7.57 (m, 6 H, C*H*Ar, C*H*, both isomers), 8.07 (s, 1 H, C*H*) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 12.62, 13.74, 13.77, 14.23, 20.37, 20.42, 20.98, 21.08, 60.92, 61.49, 128.10, 128.32, 128.46, 128.63, 128.72, 128.93, 129.57, 129.84, 130.37, 131.35, 134.83, 135.37, 135.38, 135.53, 135.56, 136.19, 137.34, 137.48, 137.51, 137.74, 137.80, 141.22, 141.37, 143.90, 143.95, 164.82, 165.00, 195.53, 196.27 ppm. $C_{24}H_{26}O_3$ (362.47): calcd. C 79.53, H 7.23; found C 79.76, H 7.31. MS (HR MALDI): *m*/*z* 363.1960 (calcd. for $C_{24}H_{27}O_3$), found 363.1955 [$MH^+$].

**Ethyl Benzylidene-4-methyl-3-oxo-5-phenyl-4-pentenoate (4d)** and **Ethyl 4-Methyl-2-(4-nitrobenzylidene)-3-oxo-5-phenyl-4-enoate (4e)** were synthesized according to the procedure given in ref.[3b]

**Ethyl 3-Oxo-4,5-diphenyl-2-(2,4,6-trimethoxybenzylidene)pent-4-enoate (4f):** This compound was prepared according to method A, yield 90%, *E*/*Z* (1:9); cyclohexane/TBME (3:2); yellow foam; $R_f$ = 0.25. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 1.30 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $OCH_2CH_3$), 3.76 (s, 6 H, 2 x $OCH_3$), 3.86 (s, 3 H, $OCH_3$), 4.21 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, $OCH_2CH_3$), 6.13 (s, 2 H, C*H*Ar), 7.01–7.05 (m, 2 H, C*H*Ar), 7.17–7.21 (m, 5 H, C*H*Ar), 7.35–7.38 (m, 3 H, C*H*Ar), 7.61 (s, 1 H, C*H*), 7.99 (s, 1 H, C*H*) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 14.29, 55.06, 55.40, 61.00, 90.34, 105.52, 127.56, 128.16, 128.25, 128.74, 130.20, 130.46, 135.24, 135.61, 135.99, 139.83, 140.57, 159.63, 163.38, 166.68, 194.36 ppm. $C_{29}H_{28}O_6$ (472.53): calcd. C 73.71, H 5.97; found C 73.54, H 6.03. MS (HR MALDI): *m*/*z* 473.1964 (calcd. for $C_{29}H_{29}O_6$), found 473.1959 [$MH^+$].

**Ethyl 2-(4-Methoxybenzylidene)-3-oxo-4,5-diphenylpent-4-enoate (4g):** This compound was prepared according to method A, yield 98%) *E*/*Z* (1:9); cyclohexane/TBME (3:2), yellow viscous oil, $R_f$ = 0.28 cyclohexane/ethyl acetate (8:2). $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 1.34 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_2CH_3$, minor isomer), 1.35 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_2CH_3$, major isomer), 3.79 (s, 3 H, $OCH_3$, minor isomer), 3.85 (s, 3 H, $OCH_3$, major isomer) 4.30 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, $CH_2CH_3$, major isomer), 4.38 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, $CH_2CH_3$, minor isomer), 6.82–7.59 (m, 10 H, C*H*Ar, both isomers), 7.69 (s, 1 H, C*H*), 7.83 (s, 1 H, C*H*) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 14.01, 14.29, 55.37, 55.41, 61.37, 61.62, 114.17, 114.37, 125.31, 125.92, 126.38, 128.13, 128.31, 128.61, 128.88, 128.92, 129.11, 129.43, 129.67, 129.70, 129.88, 130.35, 130.67, 130.98, 132.06, 132.22, 132.46, 134.44, 135.23, 135.45, 137.77, 137.88, 139.48, 140.66, 141.71, 142.84, 144.37, 161.45, 162.12, 165.37, 167.50, 196.88, 197.03 ppm. $C_{27}H_{24}O_4$ (412.48): calcd. C 78.62, H 5.86; found C 78.35, H 5.91. MS (HR MALDI): *m*/*z* 413.1453 (calcd. for $C_{27}H_{25}O_4$), found 413.1747 [$MH^+$].

**Ethyl 2-(4-Methoxybenzylidene)-3-oxo-5-phenylpent-4-enoate (4h):** This compound was prepared according to ref.[3b], yield 96%, cyclohexane/ethyl acetate (9.5:0.5), yellow oil, $R_f$ = 0.21. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 1.28 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_2CH_3$, major isomer), 1.34 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_2CH_3$, minor isomer), 3.75 (s, 3 H, $OCH_3$, major isomer), 3.83 (s, 3 H, $OCH_3$, minor isomer), 4.28 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, $CH_2CH_3$, major isomer), 4.41 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, $CH_2CH_3$, major isomer), 6.81–6.93 (m, 2 H, C*H*Ar, both isomers), 7.19–7.81 (m, 9 H, C*H*Ar, C*H*, both isomers), 7.86 (s, 1 H, C*H*, major isomer) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 14.04, 14.22, 55.29, 55.39, 61.37, 61.66, 114.34, 11437, 121.59, 125.51, 125.70, 127.20, 128.49, 128.56, 128.95, 129.02, 130.60, 130.90, 131.94, 132.26, 132.50, 134.26, 134.76, 141.33, 142.08, 144.44, 146.08, 161.46, 161.82, 165.29, 168.42, 186.25, 190.73, 196.18 ppm. $C_{21}H_{20}O_4$ (336.39): calcd. C 74.98, H 5.99; found C 74.88, H 6.15. MS (HR MALDI): *m*/*z* 337.1440 (calcd. for $C_{21}H_{22}O_4$), found 337.1434 [$MH^+$].

**(1*Z*,4*E*)-4-Methyl-3-oxo-5-phenyl-2-(2,4,6-trimethoxybenzylidene)-pent-4-enoic Acid (S1):** To a stirred solution of KOH (3.38 g, 55.3 mmol, 10 equiv.) in EtOH/water (150:75 mL) ethyl (1*Z*,4*E*)-4-methyl-3-oxo-5-phenyl-2-(2,4,6-trimethoxybenzylidene)pent-4-enoate (2.27 g, 5.53 mmol, 1 equiv.) was added and the mixture was heated quickly to 55 °C. After 9 h at this temperature, it was cooled to ambient temperature, and $CH_2Cl_2$ (100 mL) was added. The reaction mixture was then quenched with 0.5 M HCl (180 mL). The

two layers were separated; the aqueous layer was extracted with $CH_2Cl_2$ (2 × 100 mL). The combined organic layers were dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure to give 2.11 g (quant.) of orange foam. The carboxylic acid was subjected to esterification without further purification. $^1$H NMR (250.1 MHz, $CDCl_3$): $\delta$ = 2.01 (d, $^4J_{H,H}$ = 1.0 Hz, 3 H, *CH*$_3$), 3.74 (s, 6 H, 2 O*CH*$_3$), 3.78 (s, 3 H, O*CH*$_3$), 5.99 (s, 2 H, C*H*Ar), 7.05–7.12 (m, 2 H, C*H*Ar), 7.23–7.33 (m, 4 H, C*H*Ar, C*H*), 8.37 (s, 1 H, C*H*) ppm. $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ = 13.01, 55.41, 55.44, 90.31, 105.89, 125.89, 128.27, 128.41, 129.46, 135.92, 135.94, 140.44, 141.57, 159.51, 163.91, 168.98, 199.02 ppm.

The esterifications of (1*Z*,4*E*)-4-methyl-3-oxo-5-phenyl-2-(2,4,6-trimethoxybenzylidene)pent-4-enoic acid were carried out by method B as given below.

**Benzyl 4-Methyl-3-oxo-5-phenyl-2-(2,4,6-trimethoxybenzylidene)-pent-4-enoate (Method B) (4j):** To a stirred solution of benzylic alcohol (262 μL, 2.53 mmol, 1.5 equiv.), (1*Z*,4*E*)-4-methyl-3-oxo-5-phenyl-2-(2,4,6-trimethoxybenzylidene)pent-4-enoic acid (646.27 mg, 1.69 mmol, 1 equiv.) DMAP (31 mg, 253 μmol, 0.15 equiv.) and dichloromethane (15 mL) at 0 °C DCC (383 mg, 1.86 mmol, 1.1 equiv.) was added, giving a yellow reaction solution. After 10 min at this temperature, a white precipitate was formed and the reaction mixture was warmed to ambient temperature. After 10 h, the reaction mixture was filtered, dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure. The residue was purified by column chromatography eluting with cyclohexane/ethyl acetate (8:2), $R_f$ = 0.3 to give 641 mg (80%) of an yellow foam. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 2.13 (s, 3 H, *CH*$_3$), 3.72 (s, 6 H, 2 O*CH*$_3$), 3.82 (s, 3 H, O*CH*$_3$), 5.26 (s, 2 H, O*CH*$_2$), 6.04 (s, 2 H, C*H*Ar), 7.23–7.41 (m, 11 H, C*H*Ar, *CH*), 8.14 (s, 1 H, C*H*) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 13.09, 55.07, 55.39, 66.52, 90.28, 105.39, 127.82, 127.94, 128.18, 128.31, 128.37, 128.86, 129.63, 136.02, 136.24, 136.35, 136.90, 139.90, 159.70, 163.46, 166.72, 196.16 ppm. $C_{29}H_{28}O_6$ (472.53): calcd. 73.71, H 5.97; found C 73.46, H 6.16. MS (HR MALDI): *m*/*z* 473.1964 (calcd. for $C_{29}H_{29}O_6$), found 473.1959 [MH$^+$].

**Mesityl 4-Methyl-3-oxo-5-phenyl-2-(2,4,6-trimethoxybenzylidene)-pent-4-enoate (4k):** This compound was prepared according to method B, yield 46%, cyclohexane/ethyl acetate (8:2), yellow foam, $R_f$ = 0.2. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 2.1 (s, 6 H, *CH*$_3$), 2.18 (s, 3 H, *CH*$_3$), 2.30 (s, 3 H, *CH*$_3$), 3.76 (s, 6 H, 2 O*CH*$_3$), 3.78 (s, 3 H, O*CH*$_3$), 6.12 (s, 2 H, *CH*Ar), 6.90 (s, 2 H, C*H*Ar), 7.32–7.42 (m, 5 H, C*H*Ar), 7.55 (s, 1 H, C*H*), 8.26 (s, 1 H, C*H*) ppm. $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ = 13.08, 16.51, 20.79, 55.11, 55.43, 90.32, 105.35, 127.59, 128.32, 128.42, 129.06, 129.62, 130.01, 135.08, 136.29, 136.32, 137.23, 140.24, 146.15, 160.03, 163.79, 165.11, 196.25 ppm. $C_{31}H_{32}O_6$ (500.58): calcd. C 74.38, H 6.44; found C 74.53, H 6.56. MS (HR MALDI): *m*/*z* 501.2277 (calcd. for $C_{31}H_{33}O_6$), found 501.2272 [MH$^+$].

**Naphthalen-1-yl 4-Methyl-3-oxo-5-phenyl-2-(2,4,6-trimethoxybenzylidene)pent-4-enoate (4l):** This compound was prepared according to method B, yield 74%, cyclohexane/ethyl acetate (8:2), yellow foam, $R_f$ = 0.28. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 2.23 (d, $^3J_{H,H}$ = 1.2 Hz, 3 H, *CH*$_3$), 2.26 (d, $^4J_{H,H}$ = 0.9 Hz, 3 H, *CH*$_3$), 2.31 (d, $^4J_{H,H}$ = 1.2 Hz, 3 H, *CH*$_3$), 3.58 (s, 6 H, O*CH*$_3$), 3.77 (s, 3 H, O*CH*$_3$), 3.78 (s, 6 H, O*CH*$_3$), 3.80 (s, 3 H, O*CH*$_3$), 3.83 (s, 3 H, O*CH*$_3$), 3.85 (s, 6 H, O*CH*$_3$), 3.88 (s, 3 H, O*CH*$_3$), 6.04 (s, 2 H, C*H*Ar), 6.07 (s, 2 H, C*H*Ar), 6.15 (s, 2 H, C*H*Ar), 7.13–8.41 (m, 14 H, C*H*Ar, *CH*) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 13.2, 14.4, 21.3, 22.7, 22.9, 25.0, 25.6, 33.9, 49.0, 55.1, 55.2, 55.4, 55.5, 55.6, 55.7, 90.2, 90.4, 90.6, 90.7, 105.4, 105.5, 105.7, 105.8, 117.2, 118.0, 118.1, 121.8, 122.1, 122.3, 125.2, 123.2, 125.3, 125.3, 125.4, 125.6, 125.8, 126.0, 126.0, 126.2, 126.3, 126.3, 126.4, 126.8, 126.8, 126.9, 127.1, 127.2, 127.3, 127.5, 127.6, 127.6, 127.6, 127.7, 127.7, 127.8, 128.2, 128.2, 128.4, 128.5, 128.5, 128.8, 129.2, 129.7, 129.8, 129.9, 131.0, 131.7, 132.6, 134.6, 134.6, 134.6, 135.9, 135.9, 136.2, 136.5, 136.9, 136.9, 137.2, 137.4, 137.5, 137.6, 137.8, 138.2, 138.8, 140.4, 140.5, 146.8, 146.9, 146.9, 156.9, 159.6, 159.7, 160.0, 160.2, 163.6, 163.7, 164.0, 164.2, 164.6, 164.7, 165.0, 165.8, 194.7, 196.1, 196.9, 199.2 ppm. $C_{32}H_{28}O_6$ (508.57): calcd. C 75.58, H 5.55; found C 75.55, H 5.73. MS (HR MALDI): *m*/*z* 531.1784 (calcd. for $C_{32}H_{28}O_6Na$), found 531.1778 [MNa$^+$].

**(2*Z*,4*E*)-*N*,*N*-Dibenzyl-4-methyl-3-oxo-5-phenyl-2-(2,4,6-trimethoxybenzylidene)pent-4-enamide (4m):** To a stirred solution of (1*Z*,4*E*)-4-methyl-3-oxo-5-phenyl-2-(2,4,6-trimethoxybenzylidene)-pent-4-enoic acid (139 mg, 365 μmol, 1 equiv.) in DMF (15 mL) dibenzylamine (71 μL, 365 μmol, 1 equiv.), HOBT (49 mg, 365 μmol, 1 equiv.) and DCC (82 mg, 397 μmol, 1.09 equiv.) were added in this order. After 19 h the solvent was evaporated to dryness. The residue was taken up in $CH_2Cl_2$, and the organic layer was washed with $H_2O$, dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure. The residue was purified by column chromatography eluting with cyclohexane/MTBE (1:1), to 180 mg (88%) of an white foam. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 1.96 (d, $^4J_{H,H}$ = 1.2 Hz, 3 H, *CH*$_3$), 3.69 (s, 6 H, O*CH*$_3$), 3.75 (s, 3 H, O*CH*$_3$), 4.62 (br., 2 H, C(O)N*CH*$_2$), 4.73 (br., 2 H, C(O)-N*CH*$_2$), 6.01 (s, 2 H, *CH*Ar), 7.09–7.13 (m, 2 H, *CH*Ar), 7.22–7.39 (m, 14 H, *CH*Ar, *CH*), 7.41–7.44 (m, 1 H, *CH*Ar) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 12.97, 55.31, 55.34, 90.18, 106.35, 127.17, 127.42, 127.87, 127.99, 128.05, 128.47, 128.60, 129.42, 135.12, 135.87, 136.42, 136.92, 141.65, 158.41, 162.08, 170.66, 196.75 ppm. $C_{36}H_{35}NO_5$ (561.68): calcd. C 76.98, H 6.28, N 2.49; found C 76.74, H 6.40, N 2.59. MS (HR MALDI): *m*/*z* 562.2593 (calcd. for $C_{36}H_{36}NO_5$), found 562.2588 [MH$^+$].

**Ethyl 2-Benzoyl-3-(4-methoxyphenyl)acrylate (5a):** This compound was prepared according to method A, yield quant.), reaction time 12 h, hexane/ethyl acetate (8:2), yellow oil, $R_f$ = 0.26. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 1.18 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_2CH_3$), 3.77 (s, 3 H, O*CH*$_3$), 4.22 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, $CH_2CH_3$), 6.77 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, *CH*Ar), 7.32–7.60 (m, 5 H, *CH*Ar), 7.92 (s, 1 H, *CH*), 7.98 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, *CH*Ar) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 14.04, 55.28, 61.31, 114.28, 125.49, 128.65, 128.80, 129.15, 132.25, 133.77, 136.37, 142.307, 161.36, 165.30, 196.18 ppm. CAS number 25364-67-4.

**Ethyl 2-(Benzo[*d*][1,3]dioxol-5-ylcarbonyl)-3-(4-methoxyphenyl)-acrylate (5b):** This compound was prepared according to method B, yield 94%, reaction time 12 h, hexane/ethyl acetate (9:1), yellow oil, $R_f$ = 0.19. $^1$H NMR (250.1 MHz, $CDCl_3$): $\delta$ = 1.23 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, $CH_2CH_3$), 3.79 (s, 3 H, O*CH*$_3$), 4.25 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, $CH_2CH_3$), 6.07 (s, 2 H, OC*CH*$_2$CO), 6.77–6.82 (m, 3 H, *CH*Ar), 7.32–7.36 (m, 2 H, *CH*Ar), 7.51–7.56 (m, 2 H, *CH*Ar), 7.88 (s, 1 H, *CH*) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 14.12, 55.27, 61.31, 101.99, 108.18, 108.24, 114.28, 125.52, 126.34, 128.67, 131.32, 132.22, 141.85, 148.46, 152.54, 161.31, 165.33, 194.16 ppm. $C_{20}H_{18}O_6$ (354.35): calcd. C 67.79, H 5.12; found C 67.73, H 5.22. MS (HR MALDI): *m*/*z* 355.1182 (calcd. for $C_{20}H_{19}O_6$), found 355.1176 [MH$^+$].

**Ethyl 2-(Cyclopent-1-enylcarbonyl)-3-(2,4,6-trimethoxyphenyl)acrylate (6):** This compound was prepared according to method A, yield 40%, cyclohexane/ethyl acetate (7:3); yellow solid; $R_f$ = 0.28. $^1$H NMR (250.1 MHz, $CDCl_3$) (one isomer given): $\delta$ = 1.28 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, $CH_2CH_3$), 1.85–2.0 (m, 2 H, *CH*$_2$), (m, 2 H, *CH*$_2$), (m, 2 H, *CH*$_2$), 3.72 (s, 6 H, O*CH*$_3$), 3.83 (s, 3 H, O*CH*$_3$), 4.26 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, *CH*$_2$), 6.02 (s, 2 H, *CH*Ar), 6.45 (m,

1 H, *CH*), 7.95 (s, 1 H, *CH*) ppm. $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ = 14.25, 23.22, 30.54, 33.75, 55.03, 55.37, 60.89, 90.15, 105.55, 129.75, 134.37, 144.19, 145.22, 159.49, 163.21, 166.84, 191.66 ppm. $C_{20}H_{24}O_6$ (360.41): calcd. C 66.65, H 6.71; found C 66.72, H 6.83. MS (HR MALDI): *m*/*z* 383.1471 (calcd. for $C_{20}H_{24}O_6Na$), found 383.1482 [$MNa^+$].

**(*E*)-5,7-Dimethoxy-3-(2-methyl-3-phenylacryloyl)-2*H*-chromen-2-one (8):** This compound was prepared according to method A, yield 95%, recrystallized from $CH_2Cl_2$/*n*-hexane, yellow solid, cyclohexane/ethyl acetate (8:2), $R_f$ = 0.28. $^1$H NMR (250.1 MHz, $CDCl_3$): $\delta$ = 2.23 (d, $^4J_{H,H}$ = 1.2 Hz, 3 H, $CH_3$), 3.89 (s, 3 H, $OCH_3$), 3.90 (s, 3 H, O$CH_3$), 6.31 (d, $^4J_{H,H}$ = 2.2 Hz, 1 H, *CH*Ar), 6.46 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H, *CH*Ar), 7.26 (s, 1 H, *CH*), 7.33–7.46 (m, 5 H, *CH*Ar), 8.28 (s, 1 H, *CH*) ppm. $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ = 13.65, 56.01, 56.10, 92.77, 95.16, 103.64, 121.63, 128.45, 128.80, 129.95, 135.67, 137.12, 140.32, 142.20, 157.57, 158.0, 159.06, 165.30, 194.82 ppm. $C_{21}H_{18}O_5$ (350.36): calcd. C 71.99, H 5.18; found C 71.72, H 5.26. MS (HR MALDI): *m*/*z* 373.1052 (calcd. for $C_{21}H_{18}O_5Na$), found 373.1046 [$MNa^+$].

**General Procedure for the Nazarov Cyclization Catalyzed by $V^{IV}$-(salen) Complex (Method C):** The vanadium salen complex **1a** (0.6 mg, 1 μmol, 0.02 equiv.) was treated with a solution of $AgSbF_6$ (0.7 mg, 2 μmol, 0.04 equiv.) in dry $CH_2Cl_2$ (2 mL) turning the blue solution to purple. A white precipitate of AgCl was formed immediately. After 10 min, the substrate (0.05 mmol, 1 equiv.) was treated with this suspension, whereby the reaction mixture changed from purple to brown and then black, which indicates complete conversion. The reaction was quenched with water (1 mL), the layers were separated and the aqueous phase was extracted with $CH_2Cl_2$ (2 × 1 mL), the combined organic layers were dried with $MgSO_4$, filtered, the solvent was evaporated in vacuo and the resulting residue was purified by flash column chromatography to give the cyclized product.

**Ethyl 3-Methyl-2-oxo-4-phenyl-5-(2,4,6-trimethoxyphenyl)-cyclopent-3-ene-1-carboxylate (7a):** This compound was synthesized by using method C, reaction time 2 min, yield 94%, cyclohexane/ethyl acetate (7:3); yellowish solid; $R_f$ = 0.33. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 1.31 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_2CH_3$), 1.96 (d, $^4J_{H,H}$ = 2.2 Hz, 3 H, $CH_3$), 3.55 (s, 1 H, O$CH_3$), 3.69 (d, $^3J_{H,H}$ = 3.3 Hz, 1 H, C(O)*CH*C(O)), 3.72 (s, 1 H, O$CH_3$), 3.84 (s, 1 H, O$CH_3$), 4.18–4.32 (m, 2 H, $CH_2CH_3$), 5.42 (t, $^3J_{H,H}$ = 2.5 Hz, 1 H, *CH*), 5.89 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H, *CH*Ar), 6.06 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H, *CH*Ar), 7.25–7.35 (m, 5 H, *CH*Ar) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 10.03, 14.25, 40.50, 55.14, 55.17, 56.13, 58.31, 61.18, 90.62, 90.87, 108.14, 127.90, 127.91, 128.85, 133.17, 135.11, 158.77, 159.41, 160.34, 170.13, 171.50, 202.86 ppm. $C_{24}H_{26}O_6$ (410.47): calcd. C 70.23, H 6.38; found C 70.42, H 6.49. MS (HR MALDI): *m*/*z* 411.1808 (calcd. for $C_{24}H_{27}O_6$), found 411.1802 [$MH^+$].

**Ethyl 2-Hydroxy-5-mesityl-3-methylene-4-phenylcyclopent-1-ene-1-carboxylate (7b):** This compound was synthesized by using method C, reaction time 10 min, yield 63%, cyclohexane/diethyl ether (9.8:0.2); yellowish oil; $R_f$ = 0.2. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 0.99 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, $CH_2CH_3$), 1.92 (s, 3 H, $CH_3$Ar), 2.24 (s, 3 H, $CH_3$Ar), 2.26 (s, 3 H, $CH_3$Ar), 3.92 (d, $^3J_{H,H}$ = 3.3 Hz, 1 H, *CH*), 4.01–4.10 (m, 2 H, $CH_2CH_3$), 4.49 (d, $^3J_{H,H}$ = 3.9 Hz, 1 H, *CH*), 5.10 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H, *CH*Ar), 5.82 (d, $^4J_{H,H}$ = 3.0 Hz, 1 H, *CH*Ar), 6.75 (s, 1 H, *CH*Ar), 6.80 (s, 1 H, *CH*Ar), 7.13–7.15 (m, 2 H, *CH*Ar), 7.25–7.33 (m, 3 H, *CH*Ar), 10.23 (s, 1 H, O*H*) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 13.84, 20.39, 20.85, 21.25, 49.84, 52.85, 60.18, 109.16, 112.01, 126.72, 127.96, 128.74, 128.87, 131.10, 135.34, 135.85, 136.22, 137.07, 144.77, 149.38, 167.26, 169.81 ppm. $C_{24}H_{26}O_3$ (362.47): calcd. C 79.53, H 7.23; found C 79.39, H 7.32. MS (HR MALDI): *m*/*z* 363.4694 (calcd. for $C_{24}H_{27}O_3$), found 363.4682 [$MH^+$].

**Ethyl 5-(4-Methoxyphenyl)-3-methyl-2-oxo-4-phenylcyclopent-3-ene-1-carboxylate (7c):** This compound was synthesized by using method C, reaction time 10 min, yield 37%) keto and enol forms mixture (9:1), cyclohexane/ethyl acetate (9:1), colorless oil, $R_f$ = 0.4. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 1.34 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_2CH_3$), 2.03 (d, $^4J_{H,H}$ = 1.8 Hz, 3 H, $CH_3$), 3.45 (d, $^3J_{H,H}$ = 2.7 Hz, 1 H, C(O)*CH*C(O)), 3.73 (s, 3 H, O$CH_3$), 4.24–4.32 (m, 2 H, $CH_2CH_3$), 4.86 (t, $^3J_{H,H}$ = 1.8 Hz, 1 H, *CH*), 6.75 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, *CH*Ar), 7.00 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, *CH*Ar), 7.30–7.36 (m, 5 H, *CH*Ar) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 10.21, 14.23, 50.34, 55.15, 61.79, 61.88, 113.68, 114.30, 127.59, 127.90, 128.31, 128.38, 128.65, 129.32, 132.72, 134.64, 135.72, 158.57, 168.69, 169.19, 201.72 ppm. $C_{22}H_{22}O_4$ (350.41): calcd. C 75.41, H 6.33; found C 74.86, H 6.20. MS (HR MALDI): *m*/*z* 351.1596 (calcd. for $C_{22}H_{23}O_4$), found 351.1591 [$MH^+$].

**Ethyl 2-Methyl-2-oxo-4,5-diphenylcyclopent-3-ene-1-carboxylate (7d):** This compound was synthesized by using method C, yield 87%, cyclohexane/ethyl acetate (9:1), yellowish oil, $R_f$ = 0.24. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 1.34 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_2CH_3$), 2.05 (d, $^4J_{H,H}$ = 1.8 Hz, 3 H, $CH_3$), 3.49 (d, $^3J_{H,H}$ = 2.7 Hz, 1 H, C(O)*CH*C(O)), 4.25–4.32 (m, 2 H, $CH_2CH_3$), 4.91 (d, $^3J_{H,H}$ = 2.1 Hz, 1 H, *CH*), 7.08–7.40 (m, 10 H, *CH*Ar) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 10.28, 14.25, 51.01, 61.73, 61.84, 127.16, 127.67, 128.33, 128.43, 128.93, 129.42, 134.53, 135.93, 140.77, 168.62, 169.00, 201.61 ppm. CAS number 650605-56-4.

**Ethyl 3-Methyl-5-(4-nitrophenyl)-2-oxo-4-phenylcyclopent-3-ene-1-carboxylate (7e):** This compound was synthesized by using method C, reaction time 6 h, yield 80%, cyclohexane/ethyl acetate (8:2), beige solid, $R_f$ = 0.24. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 1.33 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_2CH_3$), 2.06 (d, $^4J_{H,H}$ = 2.1 Hz, 3 H, $CH_3$), 3.43 (d, $^3J_{H,H}$ = 3.3 Hz, 1 H, C(O)*CH*C(O)), 4.24–4.34 (m, 2 H, $CH_2CH_3$), 5.07 (t, $^3J_{H,H}$ = 2.7 Hz, 1 H, *CH*), 7.27 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, *CH*Ar), 7.30–7.38 (m, 5 H, *CH*Ar), 8.07 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, *CH*Ar) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 10.31, 14.21, 50.36, 61.09, 62.18, 124.24, 128.17, 128.63, 128.75, 129.90, 133.78, 136.73, 147.08, 148.36, 167.26, 167.97, 200.27 ppm. CAS number 650605-47-3.

**Ethyl 2-Oxo-3,4-diphenyl-5-(2,4,6-trimethoxyphenyl)cyclopent-3-ene-1-carboxylate (7f):** This compound was synthesized by using method C, reaction time 10 min, yield 98%, cyclohexane/ethyl acetate (7:3), yellowish solid, $R_f$ = 0.23. $^1$H NMR (250.1 MHz, $CDCl_3$): $\delta$ = 1.30 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_2CH_3$), 3.61 (s, 3 H, O$CH_3$), 3.74 (s, 3 H, O$CH_3$), 3.79 (d, $^3J_{H,H}$ = 3.2 Hz, 1 H, *CH*), 3.90 (s, 3 H, O$CH_3$), 4.13–4.31 (m, 2 H, $CH_2CH_3$), 5.53 (d, $^3J_{H,H}$ = 3.2 Hz, 1 H, C(O)*CH*C(O)), 5.94 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H, *CH*Ar), 6.12 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H, *CH*Ar), 7.09–7.33 (m, 1 H, *CH*Ar) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 14.27, 40.45, 55.17, 55.23, 56.20, 59.17, 61.31, 90.70, 90.87, 107.98, 127.58, 127.72, 128.20, 128.52, 129.07, 129.72, 132.21, 134.61, 136.62, 158.78, 159.37, 160.49, 169.77, 173.05, 200.57 ppm. $C_{29}H_{28}O_6$ (472.53): calcd. C 73.71, H 5.97; found C 73.56, H 6.07. MS (HR MALDI): *m*/*z* 473.1964 (calcd. for $C_{29}H_{29}O_6$), found 473.1963 [$MH^+$].

**Ethyl 2-Oxo-3,4-diphenyl-5-(4-methoxyphenyl)cyclopent-3-ene-1-carboxylate (7g):** This compound was synthesized by using method C, reaction time 10 min, yield 97%, cyclohexane/ethyl acetate (8:2), yellowish oil, $R_f$ = 0.25. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 1.34 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, $CH_2CH_3$), 3.64 (d, $^3J_{H,H}$ = 3.0 Hz, 1 H, *CH*), 3.74 (s, 3 H, O$CH_3$), 4.21–4.38 (m, 2 H, $CH_2CH_3$), 4.99 (d, $^3J_{H,H}$ = 2.7 Hz, 1 H, C(O)*CH*C(O)), 6.79 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H,

*CH*Ar), 7.10 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, *CH*Ar), 7.12–7.37 (m, 10 H, *CH*Ar) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 14.24, 50.35, 55.17, 61.87, 62.71, 114.46, 128.20, 128.23, 128.37, 128.78, 128.97, 129.57, 129.90, 131.31, 132.44, 134.21, 138.57, 158.70, 168.44, 170.28, 199.61 ppm. $C_{27}H_{24}O_4$ (412.48): calcd. C 78.62, H 5.86; found C 78.27, H 5.93. MS (HR MALDI): *m*/*z* 413.1753 (calcd. for $C_{27}H_{25}O_4$), found 413.1747 [$MH^+$].

**Benzyl 3-Methyl-2-oxo-4-phenyl-5-(2,4,6-trimethoxyphenyl)cyclopent-3-ene-1-carboxylate (7j):** This compound was synthesized by using method C, reaction time 5 min, yield 65%, cyclohexane/ethyl acetate (8:2), beige solid, $R_f$ = 0.19. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 1.97 (d, $^4J_{H,H}$ = 2.4 Hz, 3 H, *CH*$_3$), 3.54 (s, 3 H, O*CH*$_3$), 3.72 (s, 3 H, O*CH*$_3$), 3.75 (s, 3 H, O*CH*$_3$), 3.79 (d, $^3J$ = 3.3 Hz, 1 H, *CH*), 5.19 (d, $^2J_{H,H}$ = 12.6 Hz, 1 H, C(O)*CH*$_2$Ph), 5.30 (d, $^2J_{H,H}$ = 12.6 Hz, 1 H, C(O)*CH*$_2$Ph), 5.42–5.47 (m, 1 H, C(O)-*CH*C(O)), 5.87 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H, *CH*Ar), 6.03 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H, *CH*Ar), 7.25–7.46 (m, 10 H, *CH*Ar) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 10.05, 40.49, 55.15, 56.07, 58.24, 66.82, 90.61, 90.83, 108.03, 127.90, 127.91, 127.93, 127.99, 128.00, 128.44, 128.86, 133.22, 135.08, 136.01, 158.74, 159.39, 160.35, 170.00, 202.59 ppm. MS (HR MALDI): *m*/*z* 473.1964 (calcd. for $C_{29}H_{29}O_6$), found 473.1959 [$MH^+$]; no elemental analysis is available because the compound is unstable.

**Mesityl 3-Methyl-2-oxo-4-phenyl-5-(2,4,6-trimethoxyphenyl)cyclopent-3-enecarboxylate (7k):** This compound was synthesized by using method C, reaction time 15 min, yield 99%, cyclohexane/ethyl acetate (8:2), beige solid, $R_f$ = 0.2. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 2.03 (d, $^4J_{H,H}$ = 2.1 Hz, 3 H, *CH*$_3$), 2.19 (s, 3 H, *CH*$_3$), 2.19 (s, 3 H, *CH*$_3$), 2.28 (s, 3 H, *CH*$_3$), 3.60 (s, 3 H, O*CH*$_3$), 3.74 (s, 3 H, O*CH*$_3$), 3.84 (s, 3 H, O*CH*$_3$), 3.98 (d, $^3J_{H,H}$ = 3.3 Hz, 1 H, *CH*), 5.57–5.64 (m, 1 H, C(O)*CH*C(O)), 5.93 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H, *CH*Ar), 6.08 (d, $^4J_{H,H}$ = 2.0 Hz, 1 H, *CH*Ar), 6.89 (s, 2 H, *CH*Ar), 7.26–7.43 (m, 5 H, *CH*Ar) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 10.09, 16.19, 20.77, 40.99, 55.15, 55.24, 55.76, 58.24, 90.33, 90.79, 107.79, 127.92, 127.99, 128.97, 129.14, 129.99, 133.45, 135.04, 135.27, 145.96, 158.57, 159.52, 160.48, 168.40, 171.86, 202.61 ppm. $C_{31}H_{32}O_6$ (500.59): calcd. C 74.38, H 6.44; found C 74.53, H 6.56. MS (HR MALDI): *m*/*z* 501.2277 (calcd. for $C_{31}H_{33}O_6$), found 501.2272 [$MH^+$].

**Naphthalen-1-yl 3-Methyl-2-oxo-4-phenyl-5-(2,4,6-trimethoxyphenyl)cyclopent-3-ene-1-carboxylate (7l):** This compound was synthesized by using method C, reaction time 5 h, yield 76%, cyclohexane/ethyl acetate (8:2), beige solid, $R_f$ = 0.37. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 2.07 (s, 3 H, *CH*$_3$), 3.62 (s, 3 H, O*CH*$_3$), 3.76 (s, 3 H, O*CH*$_3$), 3.91 (s, 3 H, O*CH*$_3$), 4.14 (s, 1 H, *CH*), 5.69–5.74 (m, 1 H, C(O)*CH*C(O)), 5.95 (d, $^4J_{H,H}$ = 1.5 Hz, 1 H, *CH*Ar), 6.14 (s, 1 H, *CH*Ar), 7.22–7.58 (m, 10 H, *CH*Ar), 7.77 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, *CH*Np), 7.88 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, *CH*Np), 8.16 (d, $^3J_{H,H}$ = 7.2 Hz, 1 H, *CH*Np) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 10.15, 40.87, 55.21, 55.27, 56.16, 58.54, 90.62, 90.94, 107.79, 118.14, 121.87, 125.31, 126.09, 126.40, 126.52, 126.97, 127.77, 127.96, 127.99, 129.03, 133.31, 134.65, 134.97, 146.90, 158.82, 159.49, 160.58, 168.85, 172.03, 202.41 ppm. $C_{32}H_{28}O_6$ (508.56): calcd. C 75.57, H 5.55; found C 75.34, H 5.55. MS (HR MALDI): *m*/*z* 509.1964 (calcd. for $C_{32}H_{29}O_6$), found 509.1959 [$MH^+$].

**Ethyl 5-(4-Methoxyphenyl)-7-oxo-6,7-dihydro-5*H*-indeno[5,6-*d*][1,3]dioxole-6-carboxylate (S2):** This compound was synthesized by using method C, reaction time 72 h, yield 99%, cyclohexane/ethyl acetate (7:3), beige solid, $R_f$ = 0.5. $^1$H NMR (250.1 MHz, $CDCl_3$): $\delta$ = 1.29 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_2CH_3$), 3.60 (d, $^3J_{H,H}$ = 4.2 Hz, 1 H, *CH*), 3.79 (s, 3 H, O*CH*$_3$), 4.19–4.29 (m, 2 H, $CH_2CH_3$), 4.79 (d, $^3J_{H,H}$ = 4.0 Hz, 1 H, *CH*), 6.06 (s, 2 H, OC*CH*$_2$CO), 6.59 (s, 1 H, *CH*Ar), 6.85 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, *CH*Ar), 7.05 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, *CH*Ar), 7.12 (s, 1 H, *CH*Ar) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 14.21, 47.71, 55.30, 61.72, 64.06, 102.29, 102.53, 105.72, 114.43, 128.85, 129.64, 133.78, 148.97, 154.61, 155.08, 158.98, 168.63, 196.57 ppm. $C_{20}H_{18}O_6$ (354.35): calcd. C 67.79, H 5.12; found C 67.44, H 4.89. MS (HR MALDI): *m*/*z* 361.1651 (calcd. for $C_{20}H_{25}O_6$), found 361.1646 [$MH^+$].

**Ethyl 1-Oxo-3-(2,4,6-trimethoxyphenyl)-1,2,3,4,5,6-hexahydropentalene-2-carboxylate (S3):** This compound was synthesized by using method C, reaction time 2 h, yield 61%, cyclohexane/ethyl acetate (7:3), yellowish solid, $R_f$ = 0.39. $^1$H NMR (250.1 MHz, $CDCl_3$): $\delta$ = 1.29 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_2CH_3$), 2.26–2.37 (m, 4 H, $CH_2$), 2.43–2.45 (m, 2 H, $CH_2$), 3.73 (s, 6 H, O*CH*$_3$), 3.82 (s, 3 H, O*CH*$_3$), 3.84 (d, $^3J_{H,H}$ = 3.0 Hz, 1 H, C(O)*CH*C(O)), 4.14–4.30 (m, 2 H, $CH_2CH_3$), 4.89 (br., 1 H, *CH*), 6.11 (s, 2 H, *CH*Ar) ppm. $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ = 14.26, 24.81, 27.85, 30.61, 37.84, 55.34, 55.71, 61.10, 64.85, 90.76, 106.69, 145.09, 159.32, 160.56, 170.13, 191.14, 191.14, 196.57 ppm. $C_{20}H_{24}O_6$ (360.41): calcd. C 66.65, H 6.71; found C 66.43, H 6.59. MS (HR MALDI): *m*/*z* 361.1651 (calcd. for $C_{20}H_{25}O_6$), found 361.1646 [$MH^+$].

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[1] a) K. L. Habermas, S. E. Denmark, T. K. Jones, *Org. React.* **1994**, *45*, 1–159; b) M. A. Tius, *Eur. J. Org. Chem.* **2005**, 2193–2206.
[2] a) W. He, X. Sun, A. J. Frontier, *J. Am. Chem. Soc.* **2003**, *125*, 14278–14279; b) C. Bee, E. Leclerc, M. Tius, *Org. Lett.* **2003**, *5*, 4927–4930; c) G. Liang, S. N. Grandl, D. Trauner, *Org. Lett.* **2003**, *5*, 4931–4934; d) M. Janka, W. He, A. J. Frontier, R. Eisenberg, *J. Am. Chem. Soc.* **2004**, *126*, 6864–6865.
[3] a) G. Liang, D. Trauner, *J. Am. Chem. Soc.* **2004**, *126*, 9544–9545; b) V. K. Aggarwal, A. J. Belfield, *Org. Lett.* **2003**, *5*, 5075–5078.
[4] a) C. W. Shopee, R. E. Lack, *J. Chem. Soc. C* **1969**, 1346–1349; b) C. W. Shopee, B. J. Cooke, *J. Chem. Soc., Perkin Trans. 1* **1972**, 2271–2276; c) C. W. Shoppee, B. J. Cooke, *J. Chem. Soc., Perkin Trans. 1* **1973**, 1026–1032; d) R. D. Woodward, *Chem. Soc. Special Publication No. 21* **1967**, 237–239.
[5] H. Pellissier, *Tetrahedron* **2005**, *61*, 6479–6517.
[6] T. R. J. Achard, L. A. Clutterbuck, M. North, *Synlett* **2005**, *12*, 1828–1847.
[7] C. Bolm, *Coord. Chem. Rev.* **2003**, *237*, 245–256.
[8] a) A. Togni, *Organometallics* **1990**, *9*, 3113–3121; b) C.-T. Chen, S.-W. Hon, S.-S. Weng, *Synlett* **1999**, *6*, 816–818; c) Y. N. Belokon, M. North, T. Parsons, *Org. Lett.* **2000**, *2*, 1617–1619.
[9] M. Pasquali, A. Torres-Filho, C. Floriani, *J. Chem. Soc., Chem. Commun.* **1975**, 534–535.
[10] T. Katsuki, *Chem. Soc. Rev.* **2004**, *33*, 437–444.
[11] V. Vergopoulos, S. Jantzen, D. Rodewald, D. Rehder, *J. Chem. Soc., Chem. Commun.* **1995**, 377–378.
[12] M. Janka, W. He, A. J. Frontier, C. Flaschenriem, R. Eisenberg, *Tetrahedron* **2005**, *61*, 6193–7606.
[13] R. Zibuck, J. M. Streiber, *J. Org. Chem.* **1989**, *54*, 4717–4719.
[14] A. Aoyama, N. Sodona, M. Yamauchi, K. Toriyama, A. Ando, T. Shioiri, *Synlett* **1998**, 35–36.
[15] D. B. Dess, J. C. Martin, *J. Org. Chem.* **1983**, *48*, 4155–4156.
[16] Divinyl ketones are drawn as the *Z*-isomer, although most of them were isolated as *E*/*Z* mixtures.

  

[17] Three double bond isomers were isolated, but only one of them was characterized. See experimental section.
[18] *CRS Handbook of Chemistry and Physics 1984–1985* (Ed.: R. C. Weast), CRS Press, Boca Raton, Florida, 65th ed.
[19] D. A. Evans, J. A. Murry, P. Matt, R. D. Norcross, S. J. Miller, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 798–800.
[20] J. A. M. Van den Goorbergh, M. Van der Steeg, A. Van Der Gen, *Synthesis* **1984**, 859–860.
[21] I. A. Fallis, D. M. Murphy, D. J. Willock, R. J. Tucker, R. D. Farley, R. Jenkins, R. R. Strevens, *J. Am. Chem. Soc.* **2004**, *126*, 15660–15661.
[22] Y. N. Belokon, P. Carta, A. V. Gutnov, V. Maleev, M. A. Moskalenko, L. V. Yashkina, N. S. Ikonnikov, N. V. Voskoboev, V. N. Khrustalev, M. North, *Helv. Chim. Acta* **2002**, *85*, 3301–3312.
[23] a) M. Pasquali, F. Marchetti, C. Floriani, *Inorg. Chim. Acta* **1979**, *18*, 2401–2404; b) H. Schmidt, D. Reheder, *Inorg. Chim. Acta* **1998**, *267*, 229–238.
[24] R. Anonioletti, P. Bovicelli, S. Malancona, *Tetrahedron* **2002**, *58*, 589–596.

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