Palladium-Catalyzed Cyclopentenone Formation by Carbonylative Cycloaddition of Allylic Tosylates and Alkynes

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Abstract: Carbonylative cycloaddition of allyl tosylates and alkynes proceeded in the presence of palladium catalysts to afford a range of cyclopentenones. In the presence of methanol, five-component coupling reactions gave methyl cyclopentenyl acetates, whereas in the absence of methanol, (cyclopentenoylmethylidene)furanones were formed from six components. Allyl tosylate was found to be essential for these reactions, as allyl acetate and allyl bromide proved to be ineffective.

Key words: carbonylations, cycloadditions, palladium, alkynes, homogeneous catalysis

The development of methodologies for the synthesis of cyclopentenones from readily available substrates is one of the most active and challenging fields in organic synthesis due to their occurrence in a large number of natural products. Transition-metal-catalyzed cycloaddition of alkynes, alkenes and carbon monoxide (known as the Pauson–Khand reaction[1]) has been recognized as one of the most important methods for the construction of the cyclopentenone skeleton[2] and has been extensively utilized for the synthesis of a variety of natural compounds.[2b,2c,2e,2f,2h] A closely related reaction, the nickel carbonyl mediated carbonylative cycloaddition of allylic halides and alkynes via a η^3-allyl intermediate, was first reported by Chiusoli et al. in the 1960s.[3] This method has been the subject of continuous study by Moretó et al., and has been widely applied in organic synthesis.[4] However, most of the reactions require more than stoichiometric amounts of the hazardous nickel complex. Apart from the so-called 'metallocene-type' cyclization/carbonylation sequence, catalyzed by nickel or palladium complexes,[6] there have been few examples of catalytic versions of the cycloaddition reaction.[5] Chatani et al. reported palladium-catalyzed indanone formation from carbon monoxide, allyl acetate and benzyne, a highly reactive alkyne.[5a] Recently, Moretó et al. made the above, nickel-mediated cyclocarbonylation, catalytic by adding iron powder.[5b]

Previously, we reported that palladium-catalyzed benzannulation from alkynes and allyl tosylate led to penta- or tri-substituted benzenes.[7] In this cycloaddition, the use of allyl tosylate as an allylic compound was essential, and the key step was the insertion of an alkyne into a π-allylpalladium intermediate. As the insertion of an alkyne into π-allylnickel is also an essential step in Chiusolis carbonylative cycloaddition,[3,4] we anticipated that our strategy of using allyl tosylates as the allylic component[7,8] might be applicable to the palladium-catalyzed intermolecular carbonylative cycloaddition for unactivated alkynes. We report here the results of an investigation that focused on the synthesis of several cyclopentenones by the reaction of allylic tosylates, alkynes and carbon monoxide.

Treatment of allyl tosylate with 2-butyne and methanol in the presence of 5 mol% of $Pd_2(dba)_3{\cdot}CHCl_3$ and 10 mol% of phosphine ligands in 1,2-dichloroethane (DCE) at 80 °C for 6 hours under 5 atmospheres of carbon monoxide, afforded the cyclopentenone **1a** (Table 1), which is a key intermediate in the production of methylenomycin B.[4a] The cyclopentenone was obtained as a sole product, with neither benzenes **2**[7] nor **3** observed in the cycloaddition. Other typical allylic reagents, such as allyl acetate and allyl bromide, did not undergo any cycloaddition. When using triaryl- or trialkylphosphine as a ligand, the yield of **1a** was low (entries 1–3). The use of $P(OPh)_3$ increased the yield to 46% (entry 4). Other $P(OR)_3$ ligands were less reactive than $P(OPh)_3$ (entries 6 and 7). The use of either sub-stoichiometric or excess $P(OPh)_3$ per palladium, led to a decrease in yield. The cyclopentenone **1a** was obtained in 55% yield (entry 5) after optimizing the reaction temperature and the amount of methanol. The use of larger amounts of methanol decreased the yield of **1a**, whereas changes of carbon monoxide pressure scarcely affected the yield between 1 and 10 atmospheres, although higher pressure (40 atmospheres) decreased the yield.

Table 2 summarizes the results obtained from the reactions of allyl tosylate with several alkynes. The reactions of symmetrical alkynes, 3-hexyne and 4-octyne, gave the corresponding cyclopentenones **1b** and **1c** in 36% and 20% yield, respectively (entries 1 and 2). In the reactions of phenyl-substituted alkynes, 2-phenylcyclopentenones **1d** and **1e** were selectively obtained, although the yield was low (entries 3 and 4). The reaction of methyl 2-butynoate also proceeded regioselectively to afford **1f** alone (entry 5). Since, in most reactions, the alkynes were recovered with no other products observed, the low yield may be attributed to the low reactivity of the alkynes and/or the low stability of the allyl tosylate. Reactions with excess alkyne or excess allyl tosylate, however, did not improve the yields.

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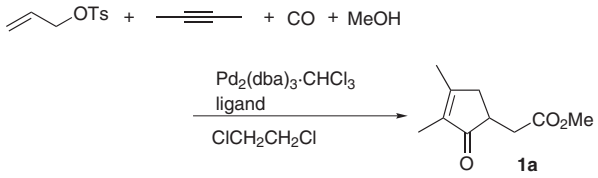
Table 1 Pd-Catalyzed Carbonylative Cycloaddition of Allyl Tosylate to 2-Butyne[a]



Entry	Ligand	Yield[b] (%)
1	PCy_3	7
2	PPh_3	22
3	$P(o\text{-Tol})_3$	21
4	$P(OPh)_3$	46
5[c]	$P(OPh)_3$	55
6	$P(O\text{-}o\text{-Tol})_3$	18
7	$P(OMe)_3$	32

[a] All reactions were carried out in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.025 mmol) and a ligand (0.05 mmol) with allyl tosylate (0.5 mmol), 2-butyne (0.6 mmol) and MeOH (2.0 mmol) in DCE (3 mL) at 80 °C for 6 h under 5 atm CO.
[b] GC yields.
[c] Reaction using 3.0 mmol of MeOH at 100 °C.

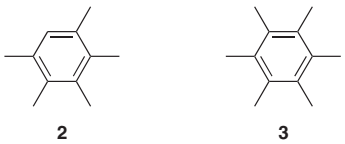
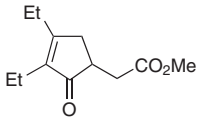
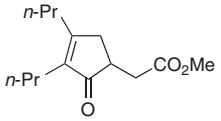
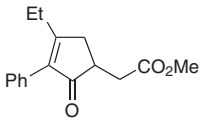
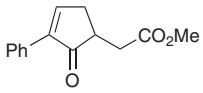
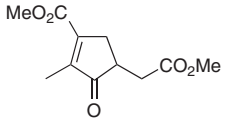


Figure 1

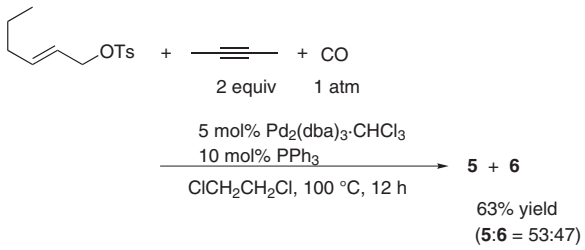
The reactions of 2-butyne and a range of substituted allyl tosylates were also investigated. The results are summarized in Table 3. Methallyl tosylate and 2-phenyl-2-propenyl tosylate also underwent carbonylative cycloaddition to give the corresponding cyclopentenones **1g** and **1h** (entries 1 and 2). The reaction of crotyl tosylate gave a mixture of isomers **1i** and **4** (entry 3). In the reaction of 2-hexenyl tosylate (entry 4), β-hydride elimination occurred instead of the second insertion of carbon monoxide, giving cyclopentenones **5** and **6** in 43% combined yield. Since these products include no methoxy group, the reaction did not require the addition of methanol. The yield was improved to 59% using PPh_3 as a ligand, and 63% after optimization of other reaction conditions (Equation 1).

Unexpectedly, the reaction of unsubstituted allyl tosylate, in the absence of methanol, did not give methylenecyclopentenones corresponding to the cyclopentenone **5**. Instead, the cyclopentenone **7a**, which consists of six components, was obtained from allyl tosylate and 3-hexyne. The amount of PPh_3 had a significant effect on the yield of **7a**. The reaction using 0.5 and 1 equivalents PPh_3 per palladium gave **7a** in 70% and 67% yield, respectively (entries 2 and 3).[9] In contrast, a dramatic decrease in yield occurred without PPh_3 (entry 1) or with two equivalents PPh_3 (entry 4). Since triphenylphosphite was less effective in this reaction, it seems that PPh_3 is better than $P(OPh)_3$ for the reaction without methanol. Higher temperature and higher pressure of carbon monoxide decreased the yield. Dialkylethynes, such as 2-butyne and 4-octyne, also underwent carbonylative cycloaddition to afford the corresponding cyclopentenones **7b** and **7c** (en-

Table 2 Pd-Catalyzed Carbonylative Cycloaddition of Allyl Tosylate to Alkynes[a]

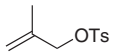
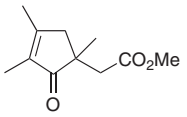
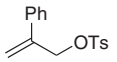
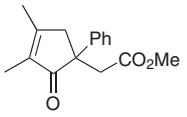
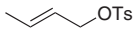
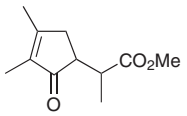
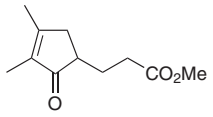
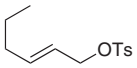
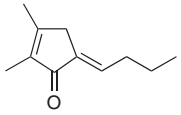
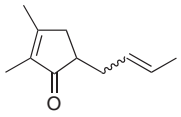
Entry	Alkyne	Product	Yield[b] (%)
1	Et—≡—Et	 **1b**	36
2	*n*-Pr—≡—Pr-*n*	 **1c**	20
3	Et—≡—Ph	 **1d**	14[c,d]
4	≡—Ph	 **1e**	11[c,d]
5	≡—CO_2Me	 **1f**	25[c]

[a] All reactions were carried out in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.025 mmol) and $P(OPh)_3$ (0.05 mmol) with allyl tosylate (0.5 mmol), alkyne (0.6 mmol) and MeOH (3.0 mmol) in DCE (3 mL) at 100 °C for 6 h under 5 atm CO.
[b] GC yields.
[c] Isolated yields.
[d] Contaminated with a small amount of an isomer.



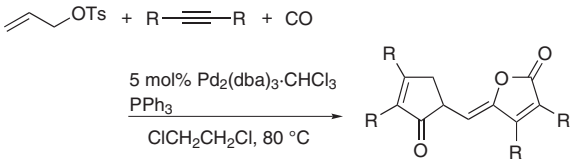
Equation 1

Table 3 Pd-Catalyzed Carbonylative Cycloaddition of 2-Butyne to Allyl Tosylates[a]

Entry	Allyl tosylate	Product	Yield[b] (%)
1		 **1g**	31
2		 **1h**	42
3		 **1i**  **4**	34[c] **1i**:**4** = 61:39
4		 **5**  **6**	43[c] **5**:**6** = 64:36

[a] All reactions were carried out in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.025 mmol) and $P(OPh)_3$ (0.05 mmol) with substituted allyl tosylate (0.5 mmol), 2-butyne (0.6 mmol) and MeOH (2.0 mmol) in DCE (3 mL) at 100 °C for 6 h under 5 atm CO.
[b] Isolated yields.
[c] Yields for a mixture of isomers.

Table 4 Pd-Catalyzed Carbonylative Cycloaddition of Allyl Tosylate and Alkynes in the Absence of Methanol[a]



7a (R = Et)
7b (R = Me)
7c (R = *n*-Pr)

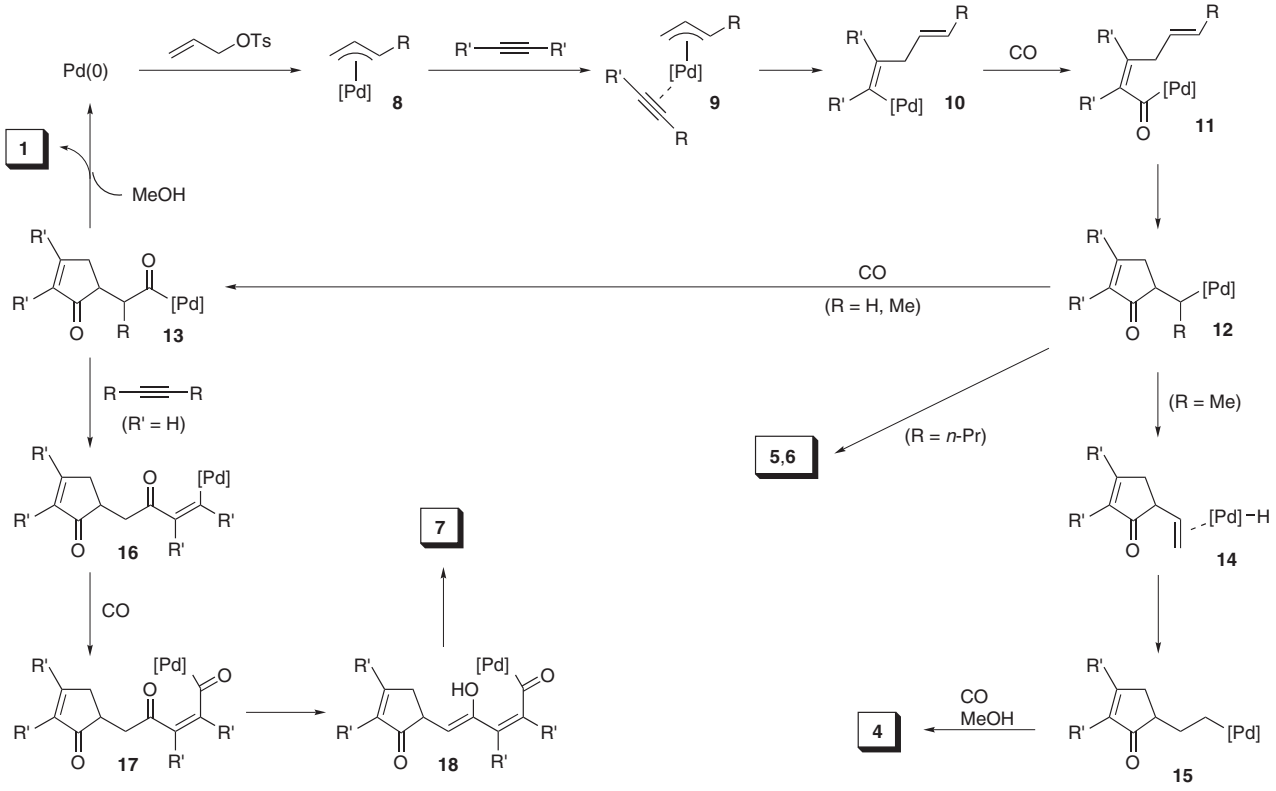
Entry	R	Amount of PPh_3 (mol%)	Product	Yield[b] (%)
1	Et	0	**7a**	12
2	Et	5	**7a**	70
3	Et	10	**7a**	67
4	Et	20	**7a**	6
5	Me	5	**7b**	48[c]
6[d]	*n*-Pr	5	**7c**	28[c]

[a] All reactions were carried out in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ 0.025 mmol) and PPh_3 with allyl tosylate (0.5 mmol) and an alkyne (2.0 mmol) in DCE (3 mL) at 80 °C for 1 h under 1 atm CO.
[b] GC yields.
[c] Isolated yields.
[d] Reaction time: 12 h.

tries 5 and 6), although the reaction of 4-octyne required prolonged reaction time. Diphenylacetylene and dimethyl acetylenedicarboxylate did not react under these conditions.

A plausible mechanism for the present palladium-catalyzed carbonylative cycloaddition is illustrated in Scheme 1. The insertion of an alkyne into the π-allylpalladium **8**, gives vinylpalladium **10**. This insertion reaction could be a key step in the cycloaddition. When typical allylic reagents, such as allyl acetate and allyl bromide, are employed instead of allyl tosylate, the acetate and bromide ligands on **8** coordinate firmly to palladium and hinder the coordination of an alkyne. Similarly, higher carbon monoxide pressure or excess phosphine ligands inhibit the coordination of an alkyne. Weak coordination of the tosylate ligand and the amount of phosphine ligands (one equivalent per palladium or less) are thus important for the reaction. The subsequent insertion of carbon monoxide into the vinylpalladium **10**, followed by the intramolecular insertion of a double bond, gives the cyclopentenone intermediate **12**.[6f] In the presence of methanol, the insertion of carbon monoxide into **12** is followed by termination by methanol to afford the cyclopentenone **1**. In the reaction of crotyl tosylate, β-hydride elimination also takes place on the intermediate **12**. Reinsertion of the double bond of **14** and insertion of carbon monoxide to **15** give the cyclopentenone **4**. In the reaction of 2-hexenyl tosylate, insertion of carbon monoxide into **12** does not take place. Elimination of palladium with a β-hydride affords the cyclopentenone **5** and 1-butenylcyclopentene **6**. The latter could be formed by isomerization of the double bond of the 1-butenylcyclopentenone. When the reaction is carried out in the absence of methanol, the insertion of carbon monoxide into **12** is followed by successive insertion of an alkyne and carbon monoxide, giving the acylpalladium **17**. Cyclization of the enol tautomer of **18** affords the cyclopentenone **7**.

In summary, we have found the Chiusoli carbonylative cycloaddition proceeded catalytically by using allyl tosylate instead of allyl halide and palladium complexes as catalyst. Although the yields were moderate, multiple carbon–carbon bond formation was achieved in a single operation.[10] In the presence of methanol, five-component coupling reactions gave methyl cyclopentenyl acetates. The reaction without methanol afforded (cyclopentenoylmethylidene)furanones from six components.



Scheme 1

Spectroscopic measurements were carried out with the following instruments: Bruker DPX-400 and DRX-500 (^{1}H NMR and ^{13}C NMR), JEOL FT/IR-350 (FT-IR). Alkynes were purchased from Aldrich or TCI and used without purification. Allyl tosylates were prepared by reaction of the corresponding allylic alcohol with excess TsCl and KOH. DCE was distilled from CaH_2 under a nitrogen atmosphere.

General Procedure

To a solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (26 mg, 0.025 mmol) and $P(OPh)_3$ (13.1 μL, 0.05 mmol) in DCE (3 mL) was added an allylic tosylate (0.5 mmol), an alkyne (0.6 mmol) and MeOH (2.0 mmol) under nitrogen atmosphere in a stainless autoclave. After the autoclave was pressurized with CO and heated at 100 °C for 6 h, the mixture was cooled and filtered through a short silica gel column using Et_2O as eluent. Solvent and excess alkyne were removed under reduced pressure, and cyclopentenones were purified by silica gel column chromatography. The structure and stereochemistry of products were determined by NMR spectra and NOE experiments.

5-(Methoxycarbonyl)methyl-2,3-dimethyl-2-cyclopentenone (1a)[4a]

IR (neat): 2949, 2920, 1739, 1700, 1650, 1437, 1388, 1330, 1219, 1173 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.68 (s, 3 H, OMe), 2.85 (m, 1 H, CH*H*CO_2Me), 2.80 (m, 1 H, C=CCH*H*), 2.71 (m, 1 H, C*H*COC=C), 2.35 (dd, *J* = 7.8, 13.2 Hz, 1 H, CH*H*CO_2Me), 2.25 (d, *J* = 17.8 Hz, 1 H, C=CCH*H*), 2.04 (s, 3 H, 2-Me), 1.70 (s, 3 H, 3-Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.79, 173.24, 169.01, 135.88, 52.23, 41.79, 39.19, 35.77, 17.57, 8.54.

2,3-Diethyl-5-(methoxycarbonyl)methyl-2-cyclopentenone (1b)[4c]

IR (neat): 2968, 2940, 1739, 1696, 1641, 1437, 1360, 1311, 1217, 1172 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.69 (s, 3 H, OMe), 2.86 (dd, *J* = 4.1, 16.4 Hz, 1 H, CH*H*CO_2Me), 2.82 (m, 1 H, C=CCH*H*) 2.69 (m, 1 H, C*H*COC=C), 2.44 (q, *J* = 7.7 Hz, 2 H, 2-C*H*$_2$CH$_3$), 2.34 (dd, *J* = 9.7, 16.4 Hz, 1 H, CH*H*CO_2Me), 2.24 (m, 1 H, C*H*COC=C), 2.20 (q, *J* = 7.5 Hz, 2 H, 3-C*H*$_2$CH$_3$), 1.13 (t, *J* = 7.7 Hz, 3 H, 2-CH$_2$C*H*$_3$), 0.98 (t, *J* = 7.5 Hz, 3 H, 3-CH$_2$*CH*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.34, 173.24, 172.83, 140.37, 51.75, 41.33, 35.76, 35.39, 23.97, 16.38, 13.29, 12.06.

5-(Methoxycarbonyl)methyl-2,3-propyl-2-cyclopentenone (1c)

IR (neat): 2959, 2871, 1739, 1698, 1638, 1437, 1364, 1214, 1170 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.68 (s, 3 H, OMe), 2.86 (dd, *J* = 4.1, 16.5 Hz, 1 H, CH*H*CO_2Me), 2.81 (dd, *J* = 6.8, 18.2 Hz, 1 H, C*H*COC=C) 2.69 (ddd, *J* = 4.1, 6.8, 9.6 Hz, 1 H, C*H*COC=C), 2.40 (t, *J* = 7.5 Hz, 2 H, 2-C*H*$_2$CH$_2$CH$_3$), 2.35 (dd, *J* = 9.6, 16.5 Hz, 1 H, CH*H*CO_2Me), 2.23 (d, *J* = 18.2 Hz, 1 H, C=CCH*H*), 2.16 (t, *J* = 7.7 Hz, 2 H, 3-C*H*$_2$CH$_2$CH$_3$), 1.56 (m, 2 H, 2-CH$_2$C*H*$_2$CH$_3$), 1.40 (m, 2 H, 2-CH$_2$*CH*$_2$CH$_3$), 0.96 (t, *J* = 7.4 Hz, 3 H, 2-CH$_2$CH$_2$C*H*$_3$), 0.89 (t, *J* = 7.4 Hz, 3 H, 2-CH$_2$CH$_2$C*H*$_3$).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 209.48, 172.78, 172.41, 139.55, 51.74, 41.24, 36.10, 35.37, 32.96, 25.18, 21.80, 20.77, 14.14, 14.08.

Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.58; H, 9.24.

3-Ethyl-5-(methoxycarbonyl)methyl-2-phenyl-2-cyclopentenone (1d)

IR (neat): 2926, 1737, 1697, 1355, 1175, 909, 733, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (m, 2 H, Ar), 7.32 (m, 1 H, Ar), 7.26 (m, 2 H, Ar), 3.71 (s, 3 H, OMe), 3.01 (dd, *J* = 7.0, 18.5 Hz, 1 H, C=CCH*H*), 2.96 (dd, 1 H, *J* = 4.0, 16.4 Hz, CH*H*CO_2Me), 2.89 (m, 1 H, C*H*COC=C), 2.57 (q, *J* = 7.6 Hz, 2 H, C*H*$_2$CH$_3$), 2.48 (dd, *J* = 9.4, 16.4 Hz, 1 H, CH*H*CO_2Me), 2.43 (dd, *J* = 2.8, 18.5 Hz, 1 H, C=CCH*H*), 1.17 (t, *J* = 7.6 Hz, 3 H, CH$_2$C*H*$_3$).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 207.45, 175.27, 172.64, 138.87, 131.76, 129.05, 128.25, 127.68, 51.79, 41.65, 35.77, 35.36, 24.70, 12.14.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{18}NaO_3$: 281.1154; found: 281.1147.

5-(Methoxycarbonyl)methyl-2-phenyl-2-cyclopentenone (1e)[11]
IR (neat): 2952, 1731, 1493, 1436, 1215, 884, 764, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (t, *J* = 2.9 Hz, 1 H, C=C*H*), 7.71 (m, 2 H, *m*-Ar), 7.39–7.32 (m, 3 H, *o*- and *m*-Ar), 3.70 (s, 3 H, OMe), 3.03 (ddd, *J* = 2.9, 6.8, 19.4 Hz, 1 H, C=CCH*H*), 2.97–2.87 (m, 2 H, CH*H*CO_2Me and C*H*COC=C), 2.54 (m, 1 H, CH*H*CO_2Me), 2.47 (dt, *J* = 19.4, 2.9 Hz, 1 H, C=CCH*H*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 207.27, 172.41, 157.08, 142.49, 131.45, 128.58, 128.44, 128.41, 126.96, 51.81, 47.58, 42.76, 35.04, 33.27.

3-Methoxycarbonyl-5-(methoxycarbonyl)methyl-2-methyl-2-cyclopentenone (1f)[4c]
IR (neat) 2953, 2912, 1717, 1438, 1229, 911, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, OMe), 3.69 (s, 3 H, OMe), 3.08 (ddq, *J* = 7.0, 18.5, 2.2 Hz, 1 H, C=CCH*H*), 2.85 (dd, *J* = 4.1, 16.7 Hz, 1 H, CH*H*CO_2Me), 2.76 (m, 1 H, C*H*COC=C), 2.56 (dd, *J* = 8.3, 16.7 Hz, 1 H, CH*H*CO_2Me), 2.50 (m, 1 H, C=CCH*H*), 2.08 (t, *J* = 2.2 Hz, 3 H, C=CMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.72, 172.03, 165.67, 152.62, 146.78, 52.12, 51.92, 41.04, 34.57, 33.44, 10.02.

5-(Methoxycarbonyl)methyl-2,3,5-trimethyl-2-cyclopentenone (1g)
IR (neat): 2953, 2924, 2252, 1737, 1699, 1655, 1437, 1204, 1018, 914, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.62 (s, 3 H, OMe), 2.72 (m, 1 H, C=CCH*H*), 2.52 (s, 2 H, C*H*$_2$$CO_2$Me), 2.32 (m, 1 H, C=CCH*H*), 2.03 (m, 3 H, 2-Me), 1.72 (m, 3 H, 3-Me), 1.12 (s, 3 H, COCMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.74, 171.91, 167.19, 133.47, 51.43, 45.81, 44.15, 41.00, 24.25, 16.98, 8.11.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.14; H, 8.59.

5-(Methoxycarbonyl)methyl-2,3-dimethyl-5-phenyl-2-cyclopentenone (1h)
IR (neat): 2968, 2921, 1740, 1702, 1653, 1437, 1330, 1172, 698 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29–7.27 (m, 4 H, Ph), 7.21 (m, 1 H, Ph), 3.59 (s, 3 H, OMe), 3.09 (d, *J* = 16.4 Hz, 1 H, C=CH*H*), 3.05 (m, 2 H, C*H*$_2$$CO_2$Me), 2.93 (d, *J* = 16.4 Hz, 1 H, C=CCH*H*), 2.09 (m, 3 H, 2-Me), 1.76 (m, 3 H, 3-Me).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 208.46, 171.61, 167.74, 141.80, 134.63, 128.64, 126.89, 126.05, 52.10, 51.65, 46.73, 41.48, 17.04, 8.38.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{18}NaO_3$: 281.1154; found: 281.1148.

5-[1-(Methoxycarbonyl)ethyl]-2,3-dimethyl-2-cyclopentenone (1i)
Isomer A

IR (neat): 2921, 1736, 1699, 1648, 1437, 1388, 1330, 1201, 1057 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.71 (s, 3 H, OMe), 3.03 (m, 1 H, C*H*Me), 2.83 (m, 1 H, C*H*COC=C), 2.58 (m, 1 H, C=CC*H*), 2.34 (m, 1 H, C=CC*H*), 2.05 (s, 3 H, 2-Me), 1.69 (s, 3 H, 3-Me), 0.97 (d, *J* = 7.0 Hz, 3 H, *Me*CCO_2Me).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 209.03, 175.80, 169.27, 136.31, 51.81, 46.58, 38.99, 34.48, 17.08, 11.56, 7.94.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.00; H, 8.29.

Isomer B

IR (neat): 2920, 1735, 1700, 1654, 1437, 1388, 1330, 1204, 1172, 1060 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.61 (s, 3 H, OMe), 3.03 (m, 1 H, C*H*Me), 2.62 (m, 1 H, C*H*COC=C), 2.52 (m, 1 H, C=CC*H*), 2.32 (m, 1 H, C=CC*H*), 2.03 (s, 3 H, 2-Me), 1.70 (s, 3 H, 3-Me), 1.28 (d, *J* = 7.3 Hz, 3 H, *Me*CCO_2Me).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 208.98, 174.80, 167.73, 135.84, 51.59, 47.57, 39.62, 35.82, 17.03, 15.02, 7.97.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.16; H, 8.66.

5-[2-(Methoxycarbonyl)ethyl]-2,3-dimethyl-2-cyclopentenone (4)
IR (neat): 2921, 1737, 1698, 1653, 1437, 1387, 1174, 1053, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67 (s, 3 H, OMe), 2.69 (m, 1 H, C=CCH*H*), 2.44 (m, 2 H, C*H*$_2$$CO_2$Me), 2.36 (m, 1 H, C*H*COC=C), 2.15 (m, 1 H, C=CCH*H*), 2.07 (m, 1 H, CH*H*CH_2CO_2Me), 2.03 (s, 3 H, 2-Me), 1.70 (m, 1 H, CH*H*CH_2CO_2Me), 1.68 (m, 3 H, 3-Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.60, 173.67, 168.14, 135.56, 51.57, 43.96, 38.42, 31.77, 26.78, 17.04, 7.93.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 66.92; H, 8.39.

(*E*)-5-Butylidene-2,3-dimethyl-2-cyclopentenone (5)[12]
IR (neat) 2960, 2930, 1697, 1670, 1640, 1389, 1330, 1094 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.54 (t, 1 H, *J* = 7.6 Hz, C=CH), 3.01 (s, 2 H, C=CCH_2C=C), 2.18 (q, *J* = 7.3 Hz. 2 H, $CH_3CH_2CH_2$), 2.07 (s, 3 H, 2-Me), 1.77 (s, 3 H, 3-Me), 1.51 (sext, *J* = 7.3 Hz, 2 H, $CH_3CH_2CH_2$), 0.94 (t, *J* = 7.3 Hz, 3 H, $CH_3CH_2CH_2$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.46, 162.28, 138.21, 134.82, 133.14, 35.17, 31.50, 21.84, 16.62, 13.88, 8.22.

5-(2-Butenyl)-2,3-dimethyl-2-cyclopentenone (6)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.56–5.43 (m, 1 H, C=CH), 5.39–5.27 (m, 1 H, C=CH), 2.67–2.35 (m, 3 H, two allyl protons and one methyne proton), 2.23–2.10 (m, 1 H, one allyl proton), 2.03 (s, 3 H, 2-Me), 2.03–1.94 (m, 1 H, one allyl proton), 1.69 (m, 3 H, 3-Me), 1.67–1.60 (m, 3 H, C=CMe).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 211.30, 168.82, 135.65, 135.50, 128.15, 127.13, 127.03, 125.86, 44.75, 37.82, 34.54, 28.50, 17.95, 17.14, 12.94, 7.99.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C. 80.46; H. 9.55.

(*Z*)-3,4-Diethyl-5-[(3,4-diethyl-2-oxo-3-cyclopentenyl)methylidene]-2-(5*H*)-furanone (7a)
IR (neat): 2973, 2921, 2874, 1764, 1699, 1637, 1459, 1029, 912, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.28 (d, *J* = 8.0 Hz, 1 H, C=C*H*), 3.59 (m, 1 H, C*H*COC=C), 3.03 (dd, *J* = 7.3, 18.3 Hz, 1 H, C=CCH*H*), 2.51–2.43 (m, 5 H, C=CCH*H* and 2 × CH_2CH$_3$), 2.35 (q, *J* = 7.6 Hz, 2 H, CH_2CH$_3$), 2.22 (q, *J* = 7.6 Hz, 2 H, CH_2CH$_3$), 1.19–1.12 (m, 9 H, 3 × Me), 1.01 (t, *J* = 7.6 Hz, 3 H, Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.74, 173.57, 170.25, 152.05, 150.89, 140.11, 129.50, 107.28, 43.62, 36.66, 24.05, 17.90, 17.10, 16.50, 14.38, 13.30, 13.05, 12.04.

Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.41; H, 7.89.

(*Z*)-3,4-Dimethyl-5-[(3,4-dimethyl-2-oxo-3-cyclopenten-yl)methylidene]-2-(5*H*)-furanone (7b)

Mp 160.8–161.2 °C.

IR (KBr): 2922, 1753, 1693, 1675, 1642, 1383, 1075, 1011, 854, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.22 (d, *J* = 7.8 Hz, 1 H, C=C*H*), 3.61 (dt, *J* = 3.0, 7.8 Hz, 1 H, C*H*COC=C), 2.99 (m, 1 H, C=CCH*H*), 2.48 (m, 1 H, C=CCH*H*), 2.07 (s, 3 H, Me on furanone), 2.03 (s, 3 H, Me on cyclopentenone), 1.91 (s, 3 H, Me on furanone), 1.74 (s, 3 H, Me on cyclopentenone).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.76, 170.57, 168.91, 151.98, 146.88, 135.20, 124.75, 107.00, 43.41, 39.41, 17.12, 9.91, 8.66, 8.19.

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.48; H, 6.92.

(*Z*)-3,4-Dipropyl-5-[(3,4-dipropyl-2-oxo-3-cyclopentenyl)methylidene]-2-(5*H*)-furanone (7c)

IR (neat): 2962, 2933, 2872, 2252, 1762, 1698, 1636, 1464, 910, 733 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.26 (d, *J* = 7.9 Hz, 1 H, C=C*H*), 3.60 (dt, *J* = 2.9, 7.9 Hz, 1 H, C*H*COC=C), 3.02 (dd, *J* = 7.9, 18.4 Hz, 1 H, C=CCH*H*), 2.49–2.36 (m, 5 H, C=CCH*H* and 2 × CH_2CH$_2$CH$_3$), 2.33–2.26 (m, 2 H, CH_2CH$_2$CH$_3$), 2.24–2.13 (m, 2 H, CH_2CH$_2$CH$_3$), 1.64–1.53 (m, 6 H, 3 × CH$_2$CH_2CH$_3$), 1.51–1.39 (m, 2 H, CH$_2$CH_2CH$_3$), 1.03–0.84 (m, 12 H, 4 × Me).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 207.66, 172.54, 170.09, 151.09, 150.85, 139.07, 128.37, 107.29, 43.41, 36.83, 28.28, 26.41, 25.64, 25.09, 21.83, 21.58, 21.39, 20.58, 13.99, 13.98, 13.90, 13.84.

Anal. Calcd for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36. Found: C, 76.96; H, 9.60.

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