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Pd(0) or Pd(II)-catalyzed ring-opening reactions of benzylidene- and alkylidenecyclopropyl ketones and aldehydes

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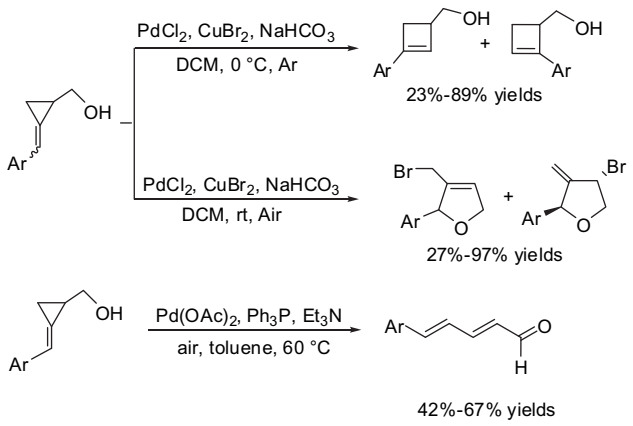
ABSTRACT

Pd(0) catalyzed reactions of methylenecyclopropyl carbonyl compounds afforded a convenient method for the synthesis of conjugate (*E*,*E*)-1,3-diene derivatives **2** in good to excellent yields. Moreover, we also found that Pd(II)-catalyzed reactions of methylenecyclopropyl carbonyl compounds with water gave 1,5-diketones in good to high yields via a carbene–palladium intermediate. The plausible reaction mechanisms have also been provided on the basis of control and ^{18}O-labeling experiments.

1. Introduction

Methylenecyclopropanes (MCPs) are generally used as building blocks in organic synthesis for their ready accessibility as well as diverse reactivity driven by the relief of ring strain.[1] The ring-opening reactions of MCPs are synthetically useful protocols in the construction of complex product structures that have been studied extensively thus far.[2] Over the past decades, transition metal catalysts, now one of the most powerful tools for synthetic chemists, have played an increasingly important role in these transformations involving ring-opening of MCPs.[3,4] Previously, we reported Pd(II)-catalyzed ring enlargement of 2-(arylmethylene)cyclopropylcarbinols to afford (arylcyclobutenyl)carbinols in 23–89% yields or hydrogenated furans in 27–97% yields, respectively. In addition, we also found that Pd(0) and Pd(II)-cocatalyzed ring-opening and oxidation reactions of 2-(arylmethylene)cyclopropylcarbinols provided a novel method to synthesize (2*E*,4*E*)-5-arylpenta-2,4-dienals in 42–67% yields under mild conditions.[5] However, this research area should be further investigated because the mechanism about the formation of dienals was not very clear and the achieved yields for the preparation of (2*E*,4*E*)-5-arylpenta-2,4-dienals were moderate. In addition, we also hypothesized that a new transformation might occur by changing the employed palladium catalyst. Herein, we wish to report the ring-opening reactions of methylenecyclopropyl carbonyl compounds **1** catalyzed by Pd(0) or Pd(II) catalyst to furnish (*E*,*E*)-1,3-diene or 1,5-dikeone derivatives in good to excellent yields (66–95% yields and 62–94% yields), respectively, under mild conditions (Scheme 1).



Scheme 1. Previous studies on the ring-opening reactions of 2-(arylmethylene) cyclopropylcarbinols (MCPs) catalyzed by Pd catalysts.

2. Results and discussion

We started our work by using (*E*)-1-(2-benzylidenecyclopropyl)-2-phenylethanone **1a** as the substrate upon treatment with $Pd(OAc)_2$ and Ph_3P at 110 °C in toluene.[6] To our delight, we found that the starting material **1a** disappeared quickly within 30 min

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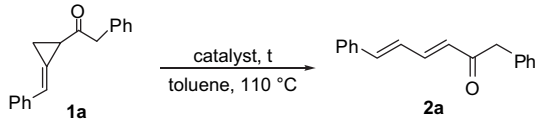
and (3*E*,5*E*)-1,6-diphenylhexa-3,5-dien-2-one **2a** was obtained in 95% yield (Table 1, entry 1). Further investigation revealed that the reaction did not take place in the presence of Pd(0) complexes such as $Pd_2(dba)_3$ and $Pd(Ph_3P)_4$ along with the recovery of the starting materials under the identical conditions (Table 1, entries 2 and 3). Using 1.0 equiv of CH_3CO_2Na as the additive afforded **2a** in 8% yield within 30 min in the presence of $Pd_2(dba)_3$, suggesting that the acetate might work as a base to initiate the reaction (Table 1, entry 4). The configuration of **2a** was unambiguously determined by X-ray diffraction (Fig. 1) and its CIF data are presented in Supplementary data.[7]

Table 1
The ring-opening reaction of **1a** catalyzed by several palladium catalysts



Entry[a]	Catalyst	*T* (min)	Yield[b] (%) of **2a**
1	*Pd(OAc)₂ (5 mol%), Ph₃P (10 mol%)*	*30*	*95*
2	$Pd_2(dba)_3$ (5 mol%)	60	N.R.
3	$Pd(Ph_3P)_4$ (5 mol%)	60	N.R.
4	$Pd_2(dba)_3$ (5 mol%)	30	8[c]

[a] Reaction scale: 0.2 mmol of **1a**.
[b] Isolated yields.
[c] CH_3CO_2Na (0.2 mmol) was added.

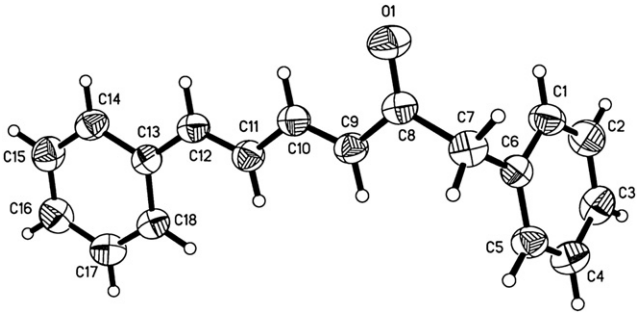
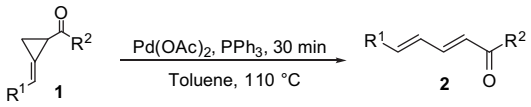


Figure 1. ORTEP drawing of **2a**.

With these optimized reaction conditions in hand, we next attempted to study the scope and limitations of this reaction by using a variety of other MCP carbonyl compounds. The results are outlined in Table 2. As for MCP phenylethanones **1a–d** (R^2=Bn), the corresponding conjugate diene ketone derivatives **2a–d** were obtained in 66–95% yields whether electron-withdrawing or electron-donating group substituted aryl group or phenyl group was introduced as R^1 in MCPs **1** (Table 2, entries 1–4). Only in the case of substrate **1e** in which the aryl group R^1 has an *ortho*-Br atom, the reaction became disordered and complex product mixtures were formed without the formation of the desired compound (Table 2, entry 5). When R^1 was phenyl group and R^2 was phenyl, H, CH_3, CH_2=$CHCH_2$ or CH_2=$CHCH_2CH_2$ group, the reactions proceeded smoothly to give the corresponding products **2f–h** and **2j–k** in 77–94% yields (Table 2, entries 6–8 and 10, 11). In the case of substrate **1j**, R^2 group of CH_2=$CHCH_2$ has rearranged to CH_3CH=CH_2 group under the standard reaction conditions (Table 2, entry 11). As for aliphatic substrate **1i** (R^1=C_7H_{15}, R^2=H), the corresponding conjugate diene ketone **2i** was also formed in 75% yield, indicating wide substrate scope of this reaction (Table 2, entry 9).

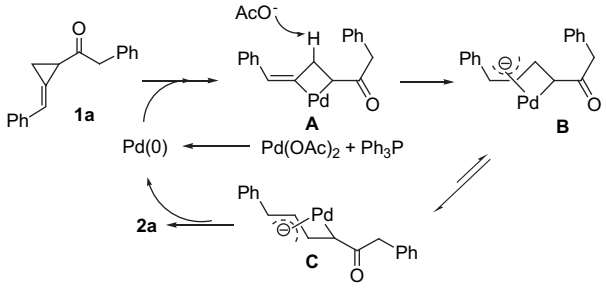
A more reasonable mechanism was proposed in Scheme 2. First, Pd(0), generated from $Pd(OAc)_2$ and PPh_3,[6] inserts into the cyclopropane to generate the corresponding palladacycle intermediate **A**, in which a proton is deprived by the base AcO^- and intermediate

Table 2
Reaction generality of the ring-opening reaction of various MCP carbonyl compounds **1** catalyzed by Pd(0)



Entry[a]	R^1	R^2	Yield[b] (%) of **2**
1	C_6H_5, **1a**	Bn	**2a**, 95
2	3,4,5-$(MeO)_3C_6H_2$, **1b**	Bn	**2b**, 88
3	*p*-BrC_6H_4, **1c**	Bn	**2c**, 66
4	*p*-ClC_6H_4, **1d**	Bn	**2d**, 84
5	*o*-BrC_6H_4, **1e**	Bn	Complex
6	C_6H_5, **1f**	Ph	**2f**, 90
7	C_6H_5, **1g**	H	**2g**, 89
8	C_6H_5, **1h**	CH_3	**2h**, 79
9	*E* and *Z* isomers, C_7H_{15}, **1i**	H	**2i**, 75
10	C_6H_5, **1j**	CH_2=$CHCH_2$	**2j**, 77[c]
11	C_6H_5, **1k**	CH_2=$CHCH_2CH_2$	**2k**, 94

[a] Reaction conditions: **1a** (0.2 mmol), Pd(OAc)2 (5 mol%), PPh_3 (10 mol%).
[b] Isolated yield.
[c] R^2 has rearranged to CH_3CH=CH_2.

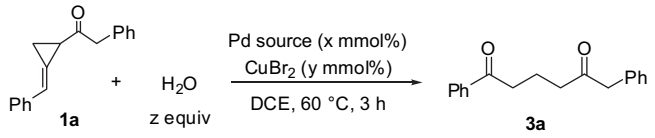


Scheme 2. A plausible reaction mechanism.

B is formed.[8] Intermediate **C**, a much more stable isomer of **B**, is produced, which can be more easily transformed to product **2a** via reductive elimination and regenerates the Pd(0) catalyst.

Since MCP carbonyl compounds could undergo a ring-opening process in the presence of Pd(0) catalyst, we next attempted to extend the reaction scope by using a Pd(II) complex. We first used $Pd(OAc)_2$ and $CuBr_2$ as the co-catalyst to examine the reaction outcome, to our delight, a 1,5-diketone product **3a** was obtained in 55% yield in 1,2-dichloroethane (DCE) (Table 3, entry 1). Further investigation revealed that $Pd(OAc)_2$ itself could not catalyze the reaction in the absence of $CuBr_2$ and when 2.0 equiv of $CuBr_2$ was used as the additive, the reaction became disordered to give complex product mixtures (Table 3, entries 2 and 3). It was also found that if the reaction was conducted under a O_2 atmosphere (1.0 atm), the desired 1,5-diketone product was formed only in 36% yield in DCE (Table 3, entry 4). We were pleased to find that using $PdBr_2$ as the catalyst, **3a** was obtained in 64% yield (Table 3, entry 5). On the basis of above results, we envisaged that one molecule of water might participate in this reaction to give the final product. After adding 2.0 equiv of water into the reaction system, we found that $PdBr_2$ was the best catalyst and the yield of **3a** increased to 80% in the presence of 20 mol% of $PdBr_2$ in anhydrous DCE, although $Pd(OAc)_2$ did not catalyze the reaction under identical conditions (Table 3, entries 6–8). It should be noted that adding 1.0 equiv of water into the reaction system, **3a** was produced in 68% yield (Table 3, entry 6). Using $PdCl_2$ as the catalyst under the standard conditions gave **3a** in 76% yield (Table 3, entry 9).

Table 3
Optimized the conditions of the ring-opening reaction of **1a** with H_2O catalyzed by Pd(II)

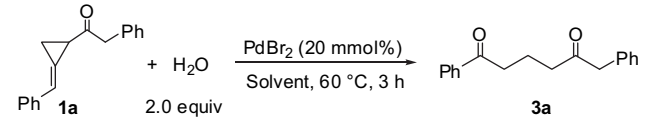


Entry[a]	Pd source	X	Y	Z	Yield[b] (%) of **3a**
1	$Pd(OAc)_2$	5	7	—	55
2	$Pd(OAc)_2$	5	—	—	NR
3	$Pd(OAc)_2$	5	200	—	Complex
4	$Pd(OAc)_2$	5	—	—	36[c]
5	$PdBr_2$	5	—	—	64[d]
6	$PdBr_2$	10	—	2 (1)	70[e] (68)[e]
7	$PdBr_2$	20	—	2	80[e]
8	$Pd(OAc)_2$	10	—	2	NR[e]
9	$PdCl_2$	20	—	2	76

[a] Reaction conditions: **1a** (0.2 mmol), 2.0 mL of DCE.
[b] Isolated yield.
[c] The reaction was conducted under 1.0 atm of O_2.
[d] DCE is not dried by CaH_2.
[e] Anhydrous DCE was used as the solvent.

Our next purpose came to investigate the solvent effects in this reaction under the tentatively optimized conditions established above. It was found that tetrahydrofuran (THF) and CH_3CN benefited this reaction significantly, producing **3a** in 94% and 79% yields, respectively (Table 4, entries 1 and 2). Using toluene as the solvent provided **3a** in only 34% yield, presumably due to that water was relatively insoluble in toluene (Table 4, entry 3). When a mixed solvent CH_3OH/THF (1:10) was used, **3a** was formed in 68% yield under otherwise identical conditions (Table 4, entry 4). Moreover, decreasing the catalyst loading to 10 mol % in THF, the yield of **3a** dropped to 80% (Table 4, entry 5). Under argon atmosphere, **3a** was produced in 94% yield similarly (Table 4, entry 6).

Table 4
Solvent effects in the ring-opening reaction of **1a** with H_2O catalyzed by $PdBr_2$

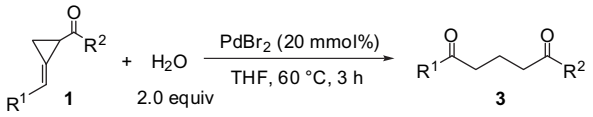


Entry[a]	Solvent	Yield[b] (%) of **3a**
1	*THF*	*94*
2	CH_3CN	79
3	Toluene	34
4	CH_3OH/THF (1:10)	68
5	THF	80[c]
6	THF	94[d]

[a] Reaction conditions: **1a** (0.2 mmol), 2 mL of DCE.
[b] Isolated yield.
[c] $PdBr_2$ (10 mmol %) was used.
[d] Under argon atmosphere.

With these optimized reaction conditions being identified, we next turned our interest to examine the reaction generality by using a variety of MCPs **1** under these optimal conditions. When R^2 was a benzyl group, the corresponding 1,5-diketone derivatives **3b–e** were obtained in 76–84% yields whether aromatic R^1 group has electron-withdrawing or electron-donating substituent (Table 5, entries 2–5). For MCPs **1f–h** and **1k**, in which R^1 was phenyl group and R^2 was phenyl, H, CH_3 or CH_2=$CHCH_2CH_2$ group, the corresponding 1,5-diketone derivatives **3f–h** and **3j** were formed in 62–83% yields (Table 5, entries 6–8 and 11). Using (*Z*)-2-benzylidenecyclopropanecarbaldehyde *Z*-**1g**, the geometric isomer of **1g**, as the substrate, the reaction also proceeded smoothly to afford **3g** in 65% yield (Table 5, entry 9). However, in the case of aliphatic MCP

Table 5
Reaction generality of the ring-opening reaction of various MCPs **1** with H_2O catalyzed by $PdBr_2$

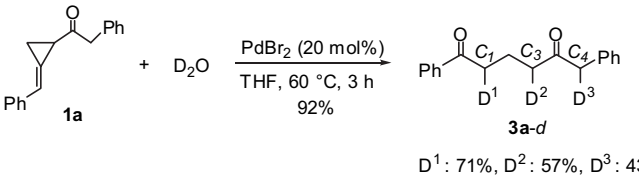


Entry[a]	Substrate	R^1	R^2	Yield[b] (%) of **3**
1	**1a**	C_6H_5	Bn	**3a**, 94
2	**1b**	3,4,5-$(MeO)_3C_6H_2$	Bn	**3b**, 76
3	**1c**	*p*-BrC_6H_4	Bn	**3c**, 81
4	**1d**	*p*-ClC_6H_4	Bn	**3d**, 84
5	**1e**	*o*-BrC_6H_4	Bn	**3e**, 79
6	**1f**	C_6H_5	Ph	**3f**, 71
7	**1g**	C_6H_5	H	**3g**, 74
8	**1h**	C_6H_5	CH_3	**3h**, 83
9	*Z*-**1g**	C_6H_5	H	**3g**, 65
10	**1i**	*E* and *Z* isomers, C_7H_{15}	H	Complex
11	**1k**	C_6H_5	CH_2=$CHCH_2CH_2$	**3j**, 62

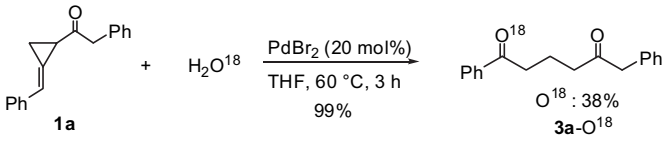
[a] Reaction conditions: **1a** (0.2 mmol) and $PdBr_2$ (20 mol %).
[b] Isolated yield.

1j (R^1 was C_7H_{15} group), the reaction became disordered and complex product mixtures were obtained (Table 5, entry 10).

To get more insight into the mechanism of this reaction, two control experiments were conducted. As shown in Scheme 2, when 2 equiv of D_2O was used instead of H_2O, the corresponding product **3a**-*d* was obtained in 92% yield and the deuterium incorporation occurred at the three protons of C_1, C_2, and C_3 positions along with D contents of 71%, 57%, and 43%, respectively (Scheme 3).[9] On the other hand, if 2 equiv of $H_2{}^{18}O$ was added to this reaction, we found the product **3a**–^{18}O was formed in 99% yield along with 38% of ^{18}O content on the basis of EI-Mass spectrum (Scheme 4). These results suggest that water indeed participates in this palladium(II)-catalyzed reaction and one oxygen atom of carbonyl group is derived from water (H_2O).



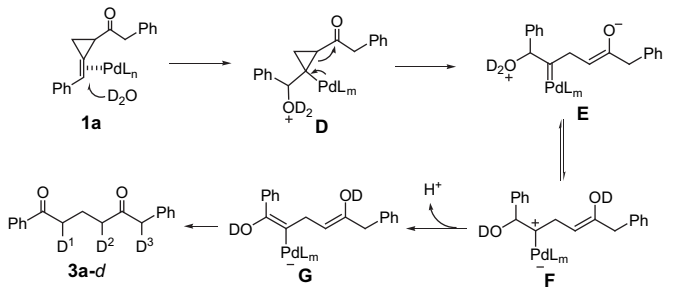
Scheme 3. Deuterium labeling experiment.



Scheme 4. ^{18}O-labeling experiment.

On the basis of above results, a plausible reaction mechanism for the formation of the 1,5-dicarbonyl compound is outlined in Scheme 5 using **1a** as a model. First, **1a** undergoes a process similar to the Wacker–Smidt oxidation to generate intermediate **D**, in which the ring-opening of cyclopropane takes place to give the carbene–palladium intermediate **E**. Intermediate **F**, the resonance-stabilized isomer of **E**, can release a proton to give an enol intermediate **G**, followed by a isomerization to produce product **3a**-*d*.

In summary, we have developed the ring-opening reaction of MCP carbonyl compounds catalyzed by Pd(0) catalyst, which affords an efficient synthetic protocol for the preparation of conjugate diene carbonyl derivatives in good to excellent yields. In



Scheme 5. A plausible reaction mechanism.

addition, a more detailed overview of the reaction mechanism was provided. Furthermore, a convenient access to 1,5-diketones was established via the ring-opening reaction of MCP carbonyl compounds with water catalyzed by Pd(II) catalyst. The potential utilization and extension of the scope of the methodology are currently under investigation in our group.

3. Experimental section

3.1. General procedure for the Pd(0) catalyzed reaction of (*E*)-1-(2-benzylidenecyclopropyl)-2-phenylethanone 1a

(*E*)-1-(2-Benzylidenecyclopropyl)-2-phenylethanone **1a** (0.2 mmol), $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), and toluene (2.0 mL) were added to a Schlenk tube under Ar. The reaction mixture was stirred at 110 °C for 30 min. The solvent was removed under reduced pressure and then the residue was purified by a flash column chromatography.

3.2. General procedure for the Pd(II) catalyzed reaction of (*E*)-1-(2-benzylidenecyclopropyl)-2-phenylethanone 1a

1-Cyclopropyl-2-phenylethanones **1** (0.2 mmol), $PdBr_2$ (20 mol %), and THF (2.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at 60 °C for 3 h. The solvent was removed under reduced pressure and then the residue was purified by a flash column chromatography.

3.2.1. (E)-1-(2-Benzylidenecyclopropyl)-2-phenylethanone ***1a****.* A white solid. Mp 68–70 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.90–1.95 (m, 1H), 2.17–2.21 (m, 1H), 2.64–2.68 (m, 1H), 3.74 (s, 2H, CH_2), 6.50–6.52 (m, 1H), 7.22–7.37 (m, 8H, Ar), 7.46 (d, J=8.0 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.3, 24.1, 48.5, 119.2, 124.6, 127.0, 127.1, 127.5, 128.5, 128.7, 129.5, 134.0, 136.4, 205.0; IR (CH_2Cl_2): ν 3084, 3061, 3028, 2968, 1783, 1703, 1600, 1495, 1453, 1404, 1366 cm^{-1}; MS (EI) m/z (%): 248 [M$^+$] (36.1), 157 (100.0), 129 (79.6), 128 (84.8), 127 (31.8), 91 (63.7), 77 (26.0), 44 (22.1); HRMS (EI) calcd for $C_{18}H_{16}O$ (M$^+$) requires 248.1201, found: 248.1198.

3.2.2. (E)-1-(2-(3,4,5-Trimethoxybenzylidene)cyclopropyl)-2-phenylethanone ***1b****.* A white solid. Mp 86–88 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.91–1.95 (m, 1H), 2.17–2.21 (m, 1H), 2.67–2.70 (m, 1H), 3.76 (s, 2H, CH_2), 3.85 (s, 3H, CH_3), 3.88 (s, 6H, $2CH_3$), 6.44–6.46 (m, 1H), 6.70 (s, 2H, Ar), 7.24–7.31 (m, 3H, Ar), 7.34–7.38 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.1, 24.0, 48.7, 56.0, 60.9, 104.1, 119.1, 124.1, 127.0, 128.7, 129.5, 132.2, 134.0, 137.8, 153.2, 204.9; IR (CH_2Cl_2): ν 3061, 2998, 2939, 2838, 1784, 1703, 1584, 1505, 1462, 1424 cm^{-1}; MS (EI) m/z (%): 338 [M$^+$] (74.6), 323 (26.0), 247 (100.0), 235 (28.0), 221 (35.2), 219 (30.5), 216 (83.0), 91 (68.8); HRMS (EI) calcd for $C_{21}H_{22}O_4$ (M$^+$) requires 338.1518, found: 338.1519.

3.2.3. (E)-1-(2-(4-Bromobenzylidene)cyclopropyl)-2-phenylethanone ***1c****.* A white solid. Mp 110–112 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.87–1.92 (m, 1H), 2.14–2.18 (m, 1H), 2.64–2.68 (m, 1H), 3.76 (s, 2H, CH_2), 6.41–6.42 (m, 1H), 7.23–7.25 (m, 2H, Ar), 7.29–7.32 (m, 3H, Ar), 7.35–7.38 (m, 2H, Ar), 7.42–7.45 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.2, 23.9, 49.1, 118.0, 121.3, 125.7, 127.1, 128.5, 128.7, 129.5, 131.6, 133.9, 135.4, 204.7; IR (CH_2Cl_2): ν 3062, 3028, 2923, 1787, 1703, 1587, 1488, 1454, 1409, 1362 cm^{-1}; MS (EI) m/z (%): 326 [M$^+$] (8.4), 185 (28.0), 129 (34.0), 128 (62.3), 105 (100.0), 91 (93.6), 77 (67.8), 51 (35.0); HRMS (EI) calcd for $C_{18}H_{15}OBr$ (M$^+$) requires 326.0306, found: 326.0310.

3.2.4. (E)-1-(2-(4-Chlorobenzylidene)cyclopropyl)-2-phenylethanone ***1d****.* A white solid. Mp 66–68 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.89–1.93 (m, 1H), 2.16–2.20 (m, 1H), 2.66–2.69 (m, 1H), 3.77 (s, 2H, CH_2), 6.43–6.45 (m, 1H), 7.23–7.31 (m, 5H, Ar), 7.34–7.39 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.2, 23.9, 49.1, 118.0, 125.5, 127.1, 128.2, 128.7, 128.8, 129.5, 133.2, 134.0, 135.0, 204.8; IR (CH_2Cl_2): ν 3085, 3062, 3029, 2969, 1785, 1703, 1592, 1491, 1454, 1414, 1363 cm^{-1}; MS (EI) m/z (%): 282 [M$^+$] (70.5), 284 (24.1), 193 (33.5), 191 (100.0), 156 (40.1), 128 (93.7), 127 (50.5), 91 (77.0); HRMS (EI) calcd for $C_{18}H_{15}OCl$ (M$^+$) requires 282.0811, found: 282.0809.

3.2.5. (E)-1-(2-(2-Bromobenzylidene)cyclopropyl)-2-phenylethanone ***1e****.* A white solid. Mp 98–102 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.87–1.92 (m, 1H), 2.20–2.24 (m, 1H), 2.68–2.72 (m, 1H), 3.79 (d, J=1.6 Hz, 2H, CH_2), 6.87–6.89 (m, 1H), 7.08 (td, J=7.6, 1.6 Hz, 1H, Ar), 7.24–7.31 (m, 4H, Ar), 7.35–7.39 (m, 2H, Ar), 7.54 (dd, J=7.6, 1.6 Hz, 1H, Ar), 7.71 (dd, J=7.6, 1.6 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 12.7, 24.1, 49.1, 117.6, 123.6, 127.1, 127.3, 127.6, 127.7, 128.8, 129.5, 133.0, 133.8, 135.7, 204.5; IR (CH_2Cl_2): ν 3062, 3028, 2970, 1788, 1700, 1587, 1495, 1470, 1454, 1438 cm^{-1}; MS (EI) m/z (%): 326 [M$^+$] (10.8), 237 (29.9), 235 (30.5), 156 (57.8), 128 (87.1), 91 (63.6), 58 (36.6), 43 (100.0); HRMS (EI) calcd for $C_{18}H_{15}OBr$ (M$^+$) requires 326.0306, found: 326.0308.

3.2.6. (E)-(2-Benzylidenecyclopropyl)(phenyl)methanone ***1f****.* A white solid. Mp 70–72 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.04–2.09 (m, 1H), 2.43–2.47 (m, 1H), 3.34–3.38 (m, 1H), 6.73–6.75 (m, 1H), 7.22–7.26 (m, 1H, Ar), 7.31–7.36 (m, 2H, Ar), 7.50–7.54 (m, 4H, Ar), 7.58–7.63 (m, 1H, Ar), 8.07–8.10 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 12.7, 20.9, 118.6, 125.8, 127.0, 127.4, 128.4, 128.5, 128.6, 133.1, 136.6, 137.5, 196.7; IR (CH_2Cl_2): ν 3060, 3027, 2928, 1673, 1596, 1491, 1449, 1366, 1332, 1214 cm^{-1}; MS (EI) m/z (%): 234 [M$^+$] (48.3), 128 (42.9), 105 (56.9), 91 (34.6), 77 (68.4), 55 (32.7), 44 (100.0), 43 (46.6); HRMS (EI) calcd for $C_{17}H_{14}O$ (M$^+$) requires 234.1045, found: 234.1047.

3.2.7. (E)-1-(2-Benzylidenecyclopropyl)ethanone ***1h****.* A colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.97–2.02 (m, 1H), 2.08 (s, 3H, CH_3), 2.09–2.14 (m, 1H), 2.57–2.61 (m, 1H), 6.78–6.79 (m, 1H), 7.23–7.28 (m, 1H, Ar), 7.33–7.37 (m, 2H, Ar), 7.52 (d, J=8.0 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.3, 25.3, 26.7, 119.6, 124.0, 127.0, 127.6, 128.5, 136.4, 206.0; IR (CH_2Cl_2): ν 3060, 3027, 3003, 1785, 1692, 1559, 1578, 1493, 1453, 1368 cm^{-1}; MS (EI) m/z (%): 172 [M$^+$] (22.6), 145 (100.0), 131 (62.6), 129 (69.1), 128 (76.2), 127 (30.9), 115 (37.2), 91 (33.1); HRMS (EI) calcd for $C_{12}H_{12}O$ (M$^+$) requires 172.0888, found: 172.0890.

3.2.8. (E) and (Z)-2-Octylidenecyclopropanecarbaldehyde ***1i*** *(6:4).* A colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.85–0.96 (m, 4H), 1.27–1.33 (m, 7H), 1.36–1.41 (m, 1H), 1.45–1.52 (m, 1H), 1.73–1.83 (m, 2H), 2.11–2.17 (m, 1H), 2.20–2.28 (m, 1H), 2.35–2.41 (m, 1H), 5.99–6.08 (m, 1H), 8.58 (d, J=6.8 Hz, 0.6H), 8.61 (d, J=6.8 Hz, 0.4H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 9.5, 9.7, 14.1, 22.5, 22.6, 27.8, 28.8, 29.04, 29.06, 29.08, 29.13, 29.16, 31.64, 31.66, 31.76, 31.80, 117.9, 118.2, 123.5, 124.0, 198.4; IR (CH_2Cl_2): ν 2957, 2927, 2856, 2714, 1715,

1638, 1465, 1378, 1149, 1092, 1053 cm^{-1}; MS (EI) *m/z* (%): 180 [M^+] (0.8), 109 (18.2), 96 (11.4), 95 (100.0), 82 (47.2), 81 (32.9), 67 (22.3), 55 (15.9); HRMS (EI) calcd for $C_{12}H_{20}O$ (M^+) requires 180.1514, found: 180.1515.

3.2.9. (E)-1-(2-Benzylidenecyclopropyl)but-3-en-1-one ***1j***. A white solid. Mp 65–67 °C. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.98–2.05 (m, 1H), 2.16–2.20 (m, 1H), 2.65–2.68 (m, 1H), 3.20–3.23 (m, 1H), 5.14–5.30 (m, 2H), 5.90–5.99 (m, 1H), 6.75–6.77 (m, 1H), 7.24–7.34 (m, 1H, Ar), 7.35–7.37 (m, 2H, Ar), 7.52 (d, *J*=8.0 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.4, 24.2, 45.6, 118.9, 119.5, 124.3, 127.1, 127.6, 128.6, 130.5, 136.5, 205.5; IR (CH_2Cl_2): ν 3062, 3029, 2926, 1785, 1711, 1638, 1496, 1452, 1421, 1390 cm^{-1}; MS (EI) *m/z* (%): 198 [M^+] (17.9), 157 (99.8), 156 (19.4), 149 (16.5), 129 (99.5), 128 (100.0), 127 (45.1), 41 (16.1); HRMS (EI) calcd for $C_{14}H_{14}O$ (M^+) requires 198.1045, found: 198.1043.

3.2.10. (E)-1-(2-Benzylidenecyclopropyl)pent-4-en-1-one ***1k***. A colorless oil. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.95–2.00 (m, 1H), 2.13–2.19 (m, 1H), 2.34–2.39 (m, 2H), 2.51–2.57 (m, 2H), 2.61–2.64 (m, 1H), 4.97–5.07 (m, 2H), 5.76–5.86 (m, 1H), 6.75–6.76 (m, 1H), 7.23–7.28 (m, 1H, Ar), 7.32–7.37 (m, 2H, Ar), 7.51 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.2, 24.5, 27.9, 39.6, 115.3, 119.3, 124.3, 127.1, 127.6, 128.5, 136.5, 137.0, 207.1; IR (CH_2Cl_2): ν 3085, 3062, 3029, 2969, 1785, 1703, 1592, 1491, 1454, 1414, 1363 cm^{-1}; MS (EI) *m/z* (%): 212 [M^+] (27.8), 171 (47.5), 157 (42.9), 129 (88.8), 128 (100.0), 127 (33.1), 115 (26.8), 55 (33.2); HRMS (EI) calcd for $C_{15}H_{16}O$ (M^+) requires 212.1201, found: 212.1203.

3.2.11. (3E,5E)-1,6-Diphenylhexa-3,5-dien-2-one ***2a***. A known compound.[10] ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.85 (s, 2H, CH_2), 6.31 (d, *J*=15.6 Hz, 1H), 6.77–6.95 (m, 2H), 7.23–7.44 (m, 11H); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 48.3, 126.5, 126.9, 127.2, 128.4, 128.7, 128.8, 129.2, 129.4, 134.5, 135.9, 141.7, 143.3, 197.3.

3.2.12. (3E,5E)-1-Phenyl-6-(3,4,5-trimethoxyphenyl)hexa-3,5-dien-2-one ***2b***. A white solid. Mp 90–92 °C. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.85 (s, 2H, CH_2), 3.86 (s, 3H, CH_3), 3.87 (s, 6H, $2CH_3$), 6.32 (d, *J*=15.2 Hz, 1H), 6.67 (s, 2H, Ar), 6.71–6.87 (m, 2H), 7.24–7.28 (m, 3H), 7.32–7.42 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 48.4, 56.0, 60.8, 104.2, 125.9, 126.8, 128.0, 128.6, 129.4, 131.5, 134.5, 139.1, 141.6, 143.2, 153.3, 197.2; IR (CH_2Cl_2): ν 3061, 2998, 2939, 2838, 1784, 1703, 1584, 1505, 1462, 1424 cm^{-1}; MS (EI) *m/z* (%): 338 [M^+] (27.5), 248 (15.7), 247 (100.0), 219 (12.4), 216 (18.7), 188 (13.1), 115 (8.2), 91 (24.0); HRMS (EI) calcd for $C_{21}H_{22}O_4$ (M^+) requires 338.1518, found: 338.1528.

3.2.13. (3E,5E)-6-(4-Bromophenyl)-1-phenylhexa-3,5-dien-2-one ***2c***. A yellow solid. Mp 92–94 °C. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.86 (s, 2H, CH_2), 6.32 (d, *J*=15.2 Hz, 1H), 6.76–6.87 (m, 2H), 7.23–7.42 (m, 8H), 7.44–7.47 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 48.4, 123.2, 126.9, 127.2, 128.5, 128.7, 128.8, 129.4, 131.9, 134.4, 134.8, 140.1, 142.8, 197.2; IR (CH_2Cl_2): ν 3028, 2891, 1763, 1736, 1718, 1683, 1612, 1594, 1580, 1487 cm^{-1}; MS (EI) *m/z* (%): 326 [M^+] (4.0), 238 (12.3), 237 (97.3), 235 (100.0), 156 (23.4), 128 (76.4), 127 (18.5), 102 (9.2); HRMS (EI) calcd for $C_{18}H_{15}OBr$ (M^+) requires 326.0306, found: 326.0305.

3.2.14. (3E,5E)-6-(4-Chlorophenyl)-1-phenylhexa-3,5-dien-2-one ***2d***. A yellow solid. Mp 88–90 °C. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.85 (s, 2H, CH_2), 6.30 (d, *J*=15.2 Hz, 1H), 6.74–6.88 (m, 2H), 7.23–7.39 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 48.4, 126.9, 127.1, 128.3, 128.7, 128.8, 129.0, 129.4, 134.3, 134.4, 134.8, 140.1, 142.8, 197.2; IR (CH_2Cl_2): ν 3086, 3062, 3028, 2924, 1683, 1615, 1597, 1583, 1491, 1453, 1406, 1344 cm^{-1}; MS (EI) *m/z* (%): 282 [M^+] (8.1), 193 (32.2), 192 (13.2), 191 (100.0), 156 (7.4), 128 (38.0), 127 (24.8), 91 (13.4); HRMS (EI) calcd for $C_{18}H_{15}OCl$ (M^+) requires 282.0811, found: 282.0810.

3.2.15. (2E,4E)-1,5-Diphenylpenta-2,4-dien-1-one ***2f***. A known compound.[11] ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.02–7.04 (m, 2H), 7.10 (d, *J*=15.0 Hz, 1H), 7.32–7.41 (m, 4H, Ar), 7.46–7.62 (m, 5H), 7.97–7.99 (m, 2H, Ar).

3.2.16. (2E,4E)-5-Phenylpenta-2,4-dienal ***2g***. A known compound.[12] ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 6.24–6.31 (m, 1H), 7.00–7.02 (m, 2H), 7.23–7.42 (m, 4H), 7.50–7.52 (m, 2H, Ar), 9.61 (d, *J*=6.6 Hz, 1H, CHO); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 126.1, 127.5, 128.9, 129.7, 131.5, 135.5, 142.5, 152.2, 193.7.

3.2.17. (3E,5E)-6-Phenylhexa-3,5-dien-2-one ***2h***. A known compound.[13] ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.31 (s, 3H, CH_3), 6.26 (d, *J*=15.2 Hz, 1H), 6.85–6.97 (m, 2H), 7.26–7.38 (m, 4H), 7.46–7.48 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 126.1, 127.5, 128.9, 129.7, 131.5, 135.5, 142.5, 152.2, 193.7.

3.2.18. (2E,4E)-Dodeca-2,4-dienal ***2i***. A colorless oil. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.87–0.90 (m, 3H), 1.25–1.33 (m, 8H), 1.42–1.48 (m, 2H), 2.19–2.25 (m, 2H), 6.08 (dd, *J*=15.2, 7.6 Hz, 1H), 6.24–6.36 (m, 2H), 7.05–7.12 (m, 2H), 9.54 (d, *J*=7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 22.6, 28.5, 29.0, 29.1, 31.7, 33.2, 128.6, 130.0, 147.5, 152.9, 194.0; IR (CH_2Cl_2): ν 2957, 2927, 2856, 2714, 1715, 1686, 1640, 1465, 1378, 1050, 1115 cm^{-1}; MS (EI) *m/z* (%): 180 [M^+] (1.9), 109 (18.7), 95 (100.0), 82 (46.0), 81 (46.4), 67 (24.2), 55 (18.6), 41 (26.8); HRMS (EI) calcd for $C_{12}H_{20}O$ (M^+) requires 180.1514, found: 180.1516.

3.2.19. (2E,5E,7E)-8-Phenylocta-2,5,7-trien-4-one ***2j***. A white solid. Mp 112–114 °C. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.95 (dd, *J*=6.8, 1.6 Hz, 3H, CH_3), 6.41 (dq, *J*=15.2, 1.6 Hz, 1H), 6.51 (d, *J*=15.2 Hz, 1H), 6.89–7.01 (m, 3H), 7.30–7.49 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.5, 126.9, 127.2, 128.3, 128.8, 129.1, 130.8, 136.1, 141.2, 143.0, 143.1, 189.2; IR (CH_2Cl_2): ν 3028, 2925, 2852, 1660, 1627, 1582, 1494, 1447, 1350, 1293 cm^{-1}; MS (EI) *m/z* (%): 198 [M^+] (100.0), 197 (29.9), 155 (26.9), 129 (34.4), 128 (59.2), 127 (22.2), 121 (20.9), 91 (18.8); HRMS (EI) calcd for $C_{14}H_{14}O$ (M^+) requires 198.1045, found: 198.1049.

3.2.20. (1E,3E)-1-Phenylnona-1,3,8-trien-5-one ***2k***. A colorless oil. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.38–2.44 (m, 2H, CH_2), 2.68–2.72 (m, 2H, CH_2), 4.99–5.09 (m, 2H), 5.81–5.91 (m, 1H), 6.29 (d, *J*=15.2 Hz, 1H), 6.84–6.97 (m, 2H), 7.29–7.38 (m, 4H), 7.46–7.48 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 28.2, 39.7, 115.2, 126.6, 127.2, 128.8, 129.1, 129.5, 136.0, 137.2, 141.3, 142.5, 199.6; IR (CH_2Cl_2): ν 3079, 3028, 3002, 2919, 1785, 1681, 1588, 1495, 1449, 1406, 1362 cm^{-1}; MS (EI) *m/z* (%): 212 [M^+] (24.5), 171 (22.1), 157 (100.0), 131 (23.0), 130 (34.7), 129 (52.4), 128 (76.2), 127 (27.6); HRMS (EI) calcd for $C_{15}H_{16}O$ (M^+) requires 212.1201, found: 212.1199.

3.2.21. 1,6-Diphenylhexane-1,5-dione ***3a***. A known compound.[14] ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.95–2.04 (m, 2H, CH_2), 2.60 (t, *J*=7.2 Hz, 2H, CH_2), 2.95 (t, *J*=7.2 Hz, 2H, CH_2), 3.70 (s, 2H, CH_2), 7.19–7.34 (m, 5H, Ar), 7.42–7.47 (m, 2H, Ar), 7.53–7.58 (m, 1H, Ar), 7.92 (dd, *J*=7.2, 1.5 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.1, 37.3, 40.8, 50.2, 127.0, 128.0, 128.5, 128.7, 129.4, 133.0, 134.1, 136.7, 199.7, 208.0.

3.2.22. 6-Phenyl-1-(3,4,5-trimethoxyphenyl)hexane-1,5-dione ***3b***. A yellow oil. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.95–2.02 (m, 2H, CH_2), 2.60 (t, *J*=7.2 Hz, 2H, CH_2), 2.91 (t, *J*=7.2 Hz, 2H, CH_2), 3.70 (s, 2H, CH_2), 3.91 (s, 9H, $3CH_3$), 7.19–7.21 (m, 4H, Ar), 7.24–7.27 (m, 1H, Ar),

7.29–7.33 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.4, 37.1, 40.7, 50.2, 56.2, 60.9, 105.5, 127.0, 128.7, 129.3, 131.9, 134.1, 142.5, 153.0, 198.5, 208.0; IR (CH_2Cl_2): ν 3059, 2940, 2837, 1713, 1678, 1580, 1504, 1455, 1413, 1361 cm^{-1}; MS (EI) *m*/*z* (%): 356 [M$^+$] (37.2), 266 (16.0), 265 (100.0), 237 (74.9), 210 (13.3), 195 (85.5), 91 (21.7), 55 (16.8); HRMS (EI) calcd for $C_{21}H_{24}O_5$ (M$^+$) requires 356.1624, found: 354.1623.

3.2.23. 1-(4-Bromophenyl)-6-phenylhexane-1,5-dione ***3c***. A yellow solid. Mp 70–72 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.94–2.01 (m, 2H, CH_2), 2.59 (t, *J*=6.8 Hz, 2H, CH_2), 2.89 (t, *J*=6.8 Hz, 2H, CH_2), 3.69 (s, 2H, CH_2), 7.19–7.21 (m, 2H, Ar), 7.24–7.26 (m, 1H, Ar), 7.29–7.33 (m, 2H, Ar), 7.58 (d, *J*=8.4 Hz, 2H, Ar), 7.77 (d, *J*=8.4 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.0, 37.2, 40.6, 50.2, 127.0, 128.1, 128.7, 129.3, 129.5, 131.8, 134.0, 135.4, 198.6, 207.9; IR (CH_2Cl_2): ν 3085, 3061, 3029, 2933, 1712, 1688, 1616, 1584, 1495, 1486, 1453 cm^{-1}; MS (EI) *m*/*z* (%): 344 [M$^+$] (4.5), 255 (99.4), 253 (100.0), 237 (59.8), 235 (59.4), 227 (68.8), 225 (74.4), 183 (72.7); HRMS (EI) calcd for $C_{18}H_{17}O_2Br$ (M$^+$) requires 344.0412, found: 344.0416.

3.2.24. 1-(4-Chlorophenyl)-6-phenylhexane-1,5-dione ***3d***. A yellow solid. Mp 48–50 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.94–2.01 (m, 2H, CH_2), 2.59 (t, *J*=7.2 Hz, 2H, CH_2), 2.89 (t, *J*=7.2 Hz, 2H, CH_2), 3.69 (s, 2H, CH_2), 7.18–7.20 (m, 2H, Ar), 7.21–7.26 (m, 1H, Ar), 7.29–7.33 (m, 2H, Ar), 7.39–7.42 (m, 2H, Ar), 7.83–7.86 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.0, 37.2, 40.6, 50.2, 127.0, 128.7, 128.8, 129.3, 129.4, 134.0, 135.0, 139.4, 198.4, 207.9; IR (CH_2Cl_2): ν 3062, 3029, 2931, 1782, 1712, 1589, 1494, 1453, 1401, 1365 cm^{-1}; MS (EI) *m*/*z* (%): 300 [M$^+$] (5.3), 211 (33.3), 209 (100.0), 191 (68.0), 183 (27.9), 181 (83.6), 141 (27.2), 139 (79.8); HRMS (EI) calcd for $C_{18}H_{17}O_2Cl$ (M$^+$) requires 300.0917, found: 300.0916.

3.2.25. 1-(2-Bromophenyl)-6-phenylhexane-1,5-dione ***3e***. A yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.93–2.00 (m, 2H, CH_2), 2.59 (t, *J*=6.8 Hz, 2H, CH_2), 2.88 (t, *J*=6.8 Hz, 2H, CH_2), 3.69 (s, 2H, CH_2), 7.19–7.23 (m, 2H, Ar), 7.24–7.56 (m, 6H, Ar), 7.77 (d, *J*=6.4 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 17.8, 40.6, 41.3, 50.1, 118.4, 127.0, 127.4, 128.2, 128.7, 129.3, 131.4, 133.6, 134.1, 141.5, 203.7, 207.7; IR (CH_2Cl_2): ν 3062, 3028, 2936, 1709, 1587, 1563, 1496, 1454, 1428, 1405 cm^{-1}; MS (EI) *m*/*z* (%): 344 [M$^+$] (3.8), 255 (94.3), 253 (100.0), 227 (67.8), 225 (69.2), 185 (78.3), 183 (79.1), 91 (48.7); HRMS (EI) calcd for $C_{18}H_{17}O_2Br$ (M$^+$) requires 344.0412, found: 344.0416.

3.2.26. 1,5-Diphenylpentane-1,5-dione ***3f***. A known compound.[15] ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.16–2.25 (m, 2H, CH_2), 3.13 (t, *J*=6.9 Hz, 2H, CH_2), 7.44–7.49 (m, 4H, Ar), 7.54–7.59 (m, 2H, Ar), 7.98 (d, *J*=7.2 Hz, 4H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.7, 37.5, 128.0, 128.6, 133.0, 136.8, 199.8.

3.2.27. 5-Oxo-5-phenylpentanal ***3g***. A known compound.[16] ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.04–2.14 (m, 2H, CH_2), 2.61 (t, *J*=7.2 Hz, 2H, CH_2), 3.06 (t, *J*=7.2 Hz, 2H, CH_2), 7.45–7.50 (m, 2H, Ar), 7.55–7.60 (m, 1H, Ar), 7.96 (d, *J*=7.2 Hz, 2H, Ar), 9.82 (s, 1H, CHO).

3.2.28. 1-Phenylhexane-1,5-dione ***3h***. A known compound.[17] ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.98–2.05 (m, 2H, CH_2), 2.15 (s, 3H, CH_3), 2.58 (t, *J*=7.2 Hz, 2H, CH_2), 3.02 (t, *J*=7.2 Hz, 2H, CH_2), 7.44–7.48 (m, 2H, Ar), 7.54–7.58 (m, 1H, Ar), 7.96 (dd, *J*=7.2, 1.2 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.1, 29.9, 37.3, 42.5, 128.0, 128.5, 133.0, 136.7, 199.7, 208.5.

3.2.29. 1-Phenylnon-8-ene-1,5-dione ***3j***. A yellow solid. Mp 33–35 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.99–2.06 (m, 2H, CH_2), 2.30–2.36 (m, 2H, CH_2), 2.50–2.57 (m, 4H, $2CH_2$), 3.01 (t, *J*=7.2 Hz, 2H, CH_2), 4.96–5.05 (m, 2H, CH_2), 5.75–5.85 (m, 1H, CH), 7.44–7.48 (m, 2H, Ar), 7.54–7.58 (m, 1H, Ar), 7.96 (d, *J*=7.2 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.1, 27.7, 37.4, 41.6, 41.7, 115.2, 128.0, 128.5, 133.0, 136.7, 137.0, 199.7, 209.8; IR (CH_2Cl_2): ν 3065, 3028, 2925, 1712, 1687, 1641, 1597, 1581, 1448, 1410 cm^{-1}; MS (EI) *m*/*z* (%): 230 [M$^+$] (3.8), 175 (25.3), 147 (33.4), 133 (18.4), 120 (28.5), 105 (100.0), 77 (37.9), 55 (28.0); HRMS (EI) calcd for $C_{15}H_{18}O_2$ (M$^+$) requires 230.1307, found: 230.1306.

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Supplementary data

Spectroscopic data of all the new compounds and the detailed descriptions of experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.08.044.

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