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Palladium mediated one-pot synthesis of 3-aryl-cyclohexenones and 1,5-diketones from allyl alcohols and aryl ketones†‡

Shaikh Samser, Priyabrata Biswal, Sushanta Kumar Meher and Krishnan Venkatasubbaiah *

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One-pot synthesis of Robinson annulated 3-aryl-cyclohexenones from allyl alcohols and ketones using palladium is reported. Long chain aliphatic or aryl substitutions at the C1 position of allyl alcohol result in the formation of 1,5-diketone products. This simple one-pot method avoids the use of highly electrophilic vinyl ketones.

1. Introduction

There is considerable interest in the use of allylic alcohols as building blocks in organic synthesis since they react as alkylating or allylating compounds to yield diverse products.[1] As the hydroxyl group in allylic alcohols is considered to be a weak leaving group, usually they need a prefunctional transformation of allylic alcohols into esters, halides, sulfonates, carboxylates, *etc*.[2] A stoichiometric amount of Lewis acids such as BEt_3 or $Ti(O\text{-}i\text{-}Pr)_4$ may optionally be triggered to activate them, but all these approaches lead to the production of substantial wastes and affect the atom economy of the reaction, which can be prevented by direct catalytic activation.[2] Allylic alcohols can be used as enolate precursors in tandem reactions leading to the formation of a new C–C bond.[3] The enol formed during the reaction tautomerizes to the corresponding carbonyl compounds, which can be achieved by simple metal-catalysed isomerisation.[3] This isomerization reaction is green, effective, safe and environment friendly, and occurs in one step without generating by-products and without the need for toxic reagents, unlike the classical oxidation.[4]

Grée and co-workers coupled allyl alcohols with various aldehydes using an iron carbonyl complex resulting in aldol products.[5] The same group reported the synthesis of β-aminoketones from allyl alcohols and *N-tert*-butanesulfinimines using a tandem isomerisation-Mannich reaction approach.[6] The Martín-Matute group reported the *ortho*-alkylation of ketones using tandem isomerisation and C–H activation of allyl alcohols.[7] They also reported the synthesis of α-fluorinated ketones by combining the isomerisation of allyl alcohols to ketones followed by α-fluorination.[8] In addition, allylic alcohols also act as the enolate precursor as this moiety has a β-electrophilic centre that fosters nucleophilic addition (1,4-addition), which results in β-functionalised carbonyl compounds. In this regard, it is worth mentioning that Kapur and co-workers reported the coupling of allyl alcohols with various anilines using a Pd-catalyst to afford β-amino ketones.[9]

Herein, we report the synthesis of 3-aryl-2-cyclohexenones and 1,5-diketones by coupling allyl alcohols with a variety of ketones using a palladium–BINOL phosphoric acid system.

2. Results and discussion

We recently reported α-alkylation of ketones and *N*-alkylation of amines using alcohols as an alkylating agent.[10] We were curious to investigate the reactivity of allyl alcohols as an alkylating agent. The reaction of 3-buten-2-ol with propiophenone was studied using palladium acetate, BINOL phosphoric acid (BPA) and NaOH as the catalyst, ligand and base, respectively, with the expectation to obtain a *C*-alkylated product. To our surprise, we isolated 33% of 3-aryl-2-cyclohexenone (a Robinson annulated product[11]) from the reaction mixture (Table 1, entry 1). As 3-aryl-2-cyclohexenones[12] act as feedstock for the synthesis of substituted phenols apart from acting as structural motifs in bioactive molecules, we decided to explore this reaction. Changing the palladium source to Pd_2dba_3 did not yield any product (Table 1, entry 2); however, $PdCl_2$ resulted in 29% of the product (Table 1, entry 3). Upon the addition of 4 Å molecular sieves to the reaction mixture, the product was isolated in 71% yield (Table 1, entry 4). Little or

School of Chemical Sciences, National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar 752050, Odisha, India. E-mail: krishv@niser.ac.in

† Dedicated to Prof. T. K. Chandrashekar on his 65th birthday.

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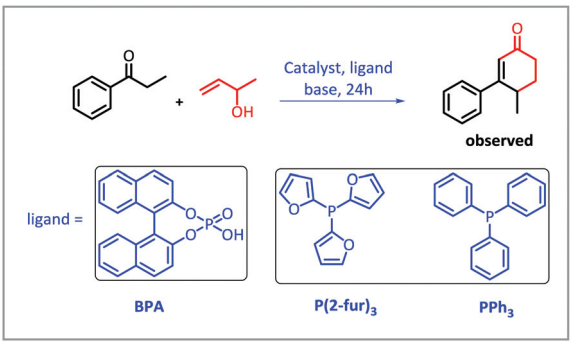
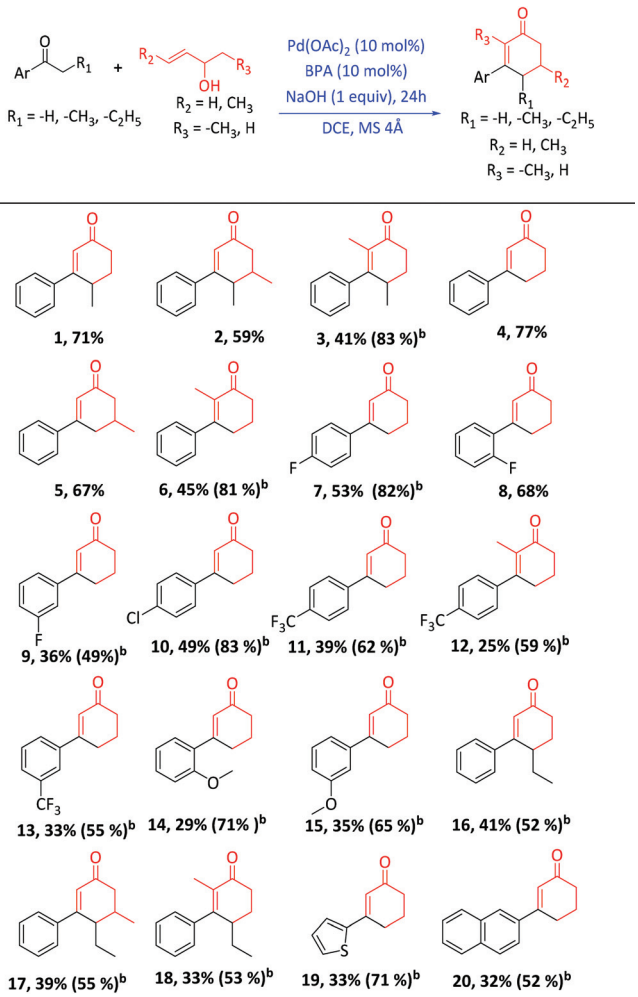
Table 1 Optimisation of Robinson's annulation using allyl alcohols[a]



S. no.	Palladium (mol%)	Ligand (mol%)	Base (equiv.)	Yield[c] (%)
1	$Pd(OAc)_2$(10)	BPA(10)	NaOH(1)	33
2	Pd_2dba_3(10)	BPA(10)	NaOH(1)	ND
3	$PdCl_2$(10)	BPA(10)	NaOH(1)	29
4[b]	$Pd(OAc)_2$(10)	BPA(10)	NaOH(1)	71
5[b]	$Pd(OAc)_2$(10)	BPA(20)	NaOH(1)	70
6[b]	$Pd(OAc)_2$(10)	BPA(10)	LiOH(1)	Trace
7[b]	$Pd(OAc)_2$(10)	BPA(10)	Cs_2CO_3(1)	70
8[b]	$Pd(OAc)_2$(10)	BPA(10)	LiO^{t}Bu(1)	25
9[b]	$Pd(OAc)_2$(10)	BPA(10)	KOH(1)	45
10[b]	$Pd(OAc)_2$(10)	PPh_3(10)	NaOH(1)	Trace
11[b]	$Pd(OAc)_2$(10)	P(2-fur)$_3$(10)	NaOH(1)	ND
12[b]	—	BPA(10)	NaOH(1)	Trace
13[b]	$Pd(OAc)_2$(10)	—	NaOH(1)	37
14[b]	$Pd(OAc)_2$(10)	dppe	NaOH(1)	Trace
15[b]	$Pd(OAc)_2$(10)	1,10-Phenanthroline	NaOH(1)	ND
16[b]	$Pd(OAc)_2$(5)	BPA(5)	NaOH(1)	53
17[b]	$Pd(OAc)_2$(7)	BPA(7)	NaOH(1)	61

[a] Reaction conditions: acetophenone (1 mmol), allyl alcohol (2 mmol) and 0.8 mL of DCE (solvent) were stirred at room temperature for 24 h. [b] 4 Å molecular sieves were used. [c] Isolated yield after column chromatography. ND = not detected.

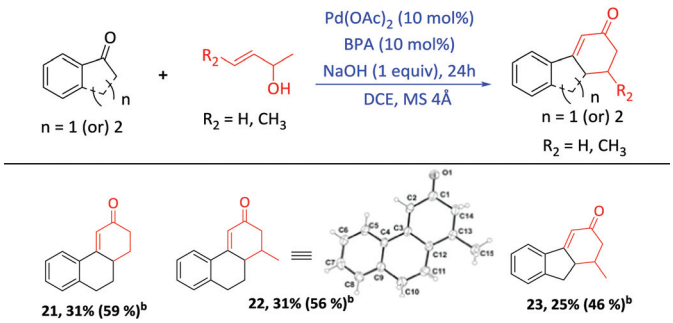
Table 2 Substrate scope of Robinson's annulation for aryl ketones[a]



[a] Reaction conditions: 1 mmol ketone, 2 mmol allylic alcohol, 1×10^{-1} mmol $Pd(OAc)_2$, 1×10^{-1} mmol of BINOL phosphoric acid, 1 mmol NaOH, 4 Å molecular sieves and 0.8 mL of DCE were stirred at room temperature for 24 h. [b] 6 mmol allylic alcohol – GC conversion.

no conversion was observed when phosphine or pyridine ligands were used instead of BPA (Table 1, entries 10, 11, 14 and 15). A further decrease of catalyst loading resulted in lower yields (Table 1, entries 16 and 17). With the optimised conditions in hand, we checked the substrate scope of Robinson annulation with different aryl ketones and allylic alcohols. Acetophenone reacted with 3-buten-2-ol, 3-penten-2-ol and 1-penten-3-ol to give the corresponding annulated products in 77%, 67% and 45% isolated yield, respectively (Table 2, entries **4**, **5** and **6**). Acetophenone bearing fluorine at the *para* and *ortho* positions yielded the corresponding products **7** and **8** in good yields. However, *meta* substituted acetophenone (3-fluoroacetophenone) resulted in a decrease in the product yield (Table 2, entry **9**). Our methodology has good tolerance towards $-CF_3$ and –Cl substitution on acetophenone (Table 2, entries **10–13**). Electron donating –OMe at the *ortho* and *meta* positions gave lower yields (Table 2, entries **14** and **15**). Butyrophenone with 3-buten-2-ol resulted in 41% yield (Table 2, entry **16**). Moreover, propiophenone and butyrophenone underwent annulation with 3-penten-2-ol to yield the corresponding products in 59% and 39% yields, respectively (Table 2, entries **2** and **17**). On careful examination of the products **2** and **17**, we noticed the presence of two isomers, as is evident by GC, GC-MS, and NMR. The peaks at RT 13.14 and RT 12.63 (Fig. S40 and S41‡) correspond to the molecular weight of 214 which is the molecular weight of the corresponding annulated product of butyrophenone with 3-penten-2-ol. From GC, the ratio of the two isomers was found to be 4 : 1 (compound **17**). Similarly, the ratio of isomers in the case of the annulated product of propiophenone and 3-penten-2-ol was 6.1 : 1 (compound **2**). A heteroaromatic compound, 2-acetylthiophene, produced the annulated compound in 33% yield (Table 2, entry **19**). A trace amount of conversion was observed in the case of 2-acetylpyridine possibly owing to the coordination of the palladium metal to the N-atom of the pyridine moiety. 2,6-Dimethoxyacetophenone failed to give the product, whereas 4-bromoacetophenone underwent electrophilic substitution. 2-Acetylnaphthalene gave a moderate yield of 32%

Table 3 Substrate scope of Robinson's annulation for cyclic aryl ketones[a]



[a] Reaction conditions: 1 mmol ketone, 2 mmol allylic alcohol, 1×10^{-1} mmol $Pd(OAc)_2$, 1×10^{-1} mmol of BINOL phosphoric acid, 1 mmol NaOH, 4 Å molecular sieves and 0.8 mL of DCE were stirred at room temperature for 24 h. [b] 6 mmol allylic alcohol – GC conversion.

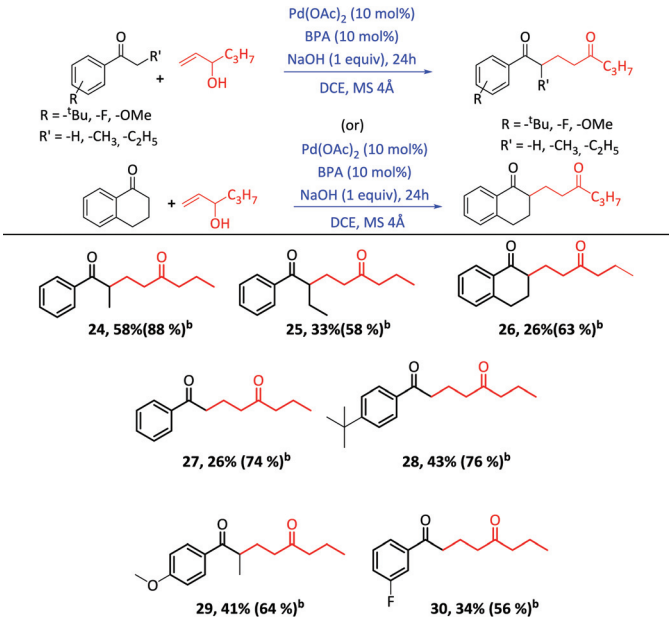
(Table 2, entry **20**). 1-Tetralone and 1-indanone with 3-penten-2-ol resulted in 31% and 25% of the isolated product, respectively (Table 3, entries **22** and **23**). To our delight, compound **22** crystallized in a monoclinic system with a space group $P2_1/n$ which was analysed using single crystal X-ray crystallography. The molecular structure of compound **22** is presented in Table 3 and also in the ESI.‡

Furthermore, 1-tetralone on reaction with 3-buten-2-ol gave the corresponding annulated product in moderate yield (Table 3, entry **21**). The reaction did not proceed with aliphatic and alicyclic systems such as 3-methylbutanone, acetone, cyclopropylmethyl ketone and cyclohexyl methyl ketone. Under the experimental conditions mentioned, a gram-scale experiment of propiophenone (10 mmol) was performed. The reaction proceeded smoothly and gave the desired product **1** in 58% yield (1.078 g).

To our surprise, increasing the alkyl chain from 1-penten-3-ol to 1-hexen-3-ol resulted in 1,5-diketone as the only product. Our attempts to make the annulated product from 1-hexen-3-ol failed (Table S2, ESI‡). As 1,5 diketones play a significant role in organic chemistry for the synthesis of many heterocycles,[13] we screened the potential of this methodology. Propiophenone and butyrophenone afforded the diketone in 58% and 33% yield respectively (Table 4, entries **24** and **25**). Interestingly, acetophenone gave a low yield of 26% (Table 4, entry **27**). Substitution with electron-withdrawing and electron-donating groups did not have much impact on the yield of the reaction (Table 4, entries **28–30**). 1-Tetralone resulted in 26% of the product with 1-hexen-3-ol (Table 4, entry **26**). Since cyclohexenones acted as precursors for phenols as mentioned *vide supra*, we attempted to prepare substituted phenols in one pot using our methodology. However, our methodology failed to yield aromatized phenols. A similar result was also observed by Liu and co-workers[14] when they used palladium acetate as a catalyst.

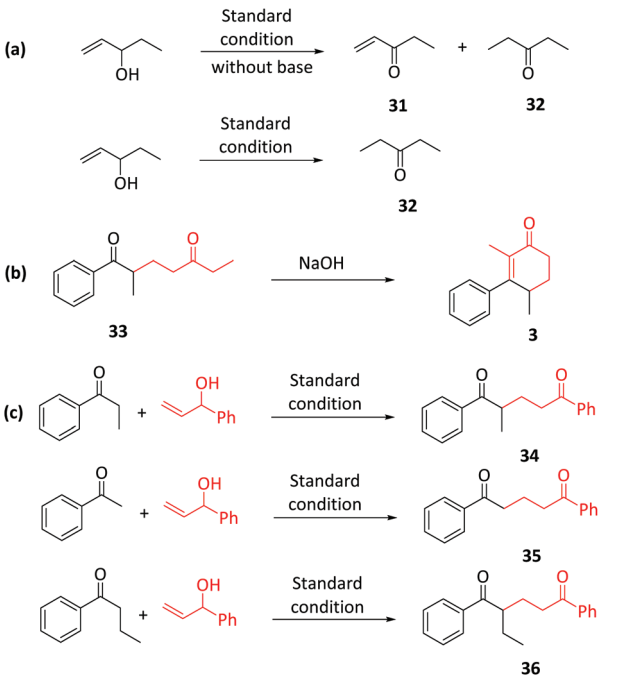
To gain insight into the mechanism of the reaction, control experiments were carried out. Under the optimized conditions,

Table 4 Substrates scope for the synthesis of 1,5-diketone[a]

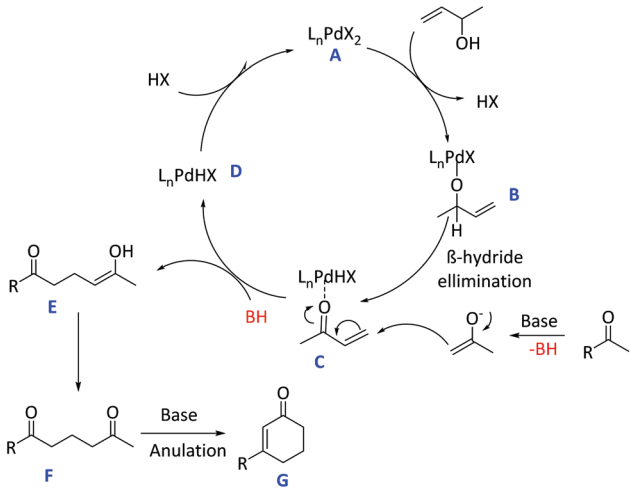


[a] Reaction conditions: 1 mmol ketone, 2 mmol allylic alcohol, 1×10^{-1} mmol $Pd(OAc)_2$, 1×10^{-1} mmol of BINOL phosphoric acid, 1 mmol NaOH, 4 Å molecular sieves and 0.8 mL of DCE were stirred at room temperature for 24 h. [b] 6 mmol allylic alcohol – GC conversion.

without a base, the reaction of 1-penten-3-ol (without acetophenone, using NMR) revealed the formation of 3-pentanone along with 3-pentenone.[15] (Scheme 1a). Yet another control reaction carried out in the presence of a base resulted in,



Scheme 1 Control experiments.



Scheme 2 Proposed mechanism.

exclusively, a saturated ketone. These results suggest that under the reaction conditions, the allyl alcohol is converted to the corresponding saturated ketone. The evolution of hydrogen gas was studied as reported in the literature.[16] As given in the ESI,‡ we have taken 1-penten-3-ol under standard conditions without the base and in another chamber, phenylacetylene and palladium charcoal were taken in methanol. The crude NMR of the reaction mixture of the second chamber showed the presence of styrene along with ethyl benzene which supports that dehydrogenation takes place during the course of the reaction. The base plays a major role in the conversion of diketone to the corresponding annulated product. In order to prove the role of the base, we stirred diketone (**33**) in the presence of NaOH which resulted in the annulated product **3** in quantitative yield[17] (crude NMR is given in the ESI‡). We repeated a few reactions using 6 equivalents of allylic alcohols under the optimized conditions. In most cases, we observed higher conversions (Tables 2–4), suggesting that the formation of species **32** limits the yield in these reactions.

Based on the findings from the control experiments and a recent study,[18] we propose the following mechanism (Scheme 2). The palladium complex reacts with an allyl alcohol to give the corresponding metal alkoxide **B**, which can undergo β-hydride elimination to form the intermediate **C**. The intermediate **C** can result in the formation of the corresponding enol[18a] which can either undergo keto–enol tautomerisation to form the observed species **32** or react with the ketone in the presence of a base to form the enolic species **E** which results in the diketone product **F**. The diketone in the presence of a base undergoes aldol condensation to form the annulated product. However, when we used 1-hexen-3-ol, the annulation did not proceed (ESI, Table S2‡). The presence of α-hydrogen is essential for the formation of an annulated product. To further support this hypothesis, we reacted propiophenone, acetophenone and butyrophenone with phenylallyl alcohol under the optimized reaction conditions, which resulted in 1,5-diketones (**34–36**) as the only product (Scheme 1c).

3. Conclusion

In summary, we have developed a new palladium-BINOL phosphoric acid system for the synthesis of 3-aryl substituted cyclohexenones or 1,5-diketones. The developed method has shown good tolerance to different functional groups. The reaction of aryl ketones with 3-buten-2-ol, 3-penten-2-ol or 1-penten-3-ol resulted in Robinson's annulated products; however, 1-hexen-3-ol yielded 1,5-diketones as the only product.

4. Experimental section

General information

All reagents and solvents were obtained from commercial sources. Solvents were purified according to standard procedures. BINOL phosphoric acid (BPA)[19] and 2-methyl-1-phenylheptane-1,5-dione (compound **33**)[20] were synthesized following the procedures reported in the literature. All 400 (or) 700 MHz ^{1}H and 100 (or) 176 MHz ^{13}C spectra were recorded on a spectrometer operating at 400 (or) 700 MHz. All ^{1}H and ^{13}C NMR spectra were referenced internally to solvent signals. ^{19}F NMR spectra were externally referenced to α,α,α-trifluorotoluene in $CDCl_3$ (δ = −63.73 ppm). ^{31}P spectra were referenced externally to H_3PO_4 in D_2O (δ = 0). High-resolution mass spectra (HRMS) were recorded using a Bruker microTOF-QII mass spectrometer. Single-crystal X-ray diffraction data were collected at 114 K using Cu Kα radiation (1.54184 Å). Crystallographic data for compound **22** (CCDC No. 2023107‡), and details of X-ray diffraction experiments and crystal structure refinements are given in Table S1.‡ The structures were solved and refined with the SHELX suite of programs or Olex. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and refined as riding atoms. Sodium hydroxide was ground to powder form using a mortar and pestle and kept under vacuum when not in use.

General procedure for annulations and the diketone reaction. Palladium acetate (0.022 g, 0.10 mmol), BINOL phosphoric acid (0.035 g, 0.10 mmol) and sodium hydroxide (0.039 g, 1.00 mmol) were taken in a scintillation vial. Aryl ketone (1.00 mmol), allyl alcohol (2.00 mmol) and 0.8 mL of dichloroethane (DCE) were added to it. Finally, 4 Å molecular sieves were added to the reaction mixture and stirred at room temperature for 24 hours. Then the reaction mixture was evaporated under vacuum and purified by flash column chromatography in ethyl acetate and *n*-hexane (1 : 4) as an eluent.

Analytical data for annulated compounds

6-Methyl-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one[21] (Table 2, entry 1). Prepared from propiophenone (0.134 g, 1.00 mmol) and 3-buten-2-ol (0.144 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.132 g, 71%). ^{1}H NMR (700 MHz, $CDCl_3$) δ = 7.49–7.48 (m, 2H), 7.41–7.37 (m, 3H), 6.25 (s, 1H), 3.18–3.13 (m, 1H), 2.60 (ddd, J = 17.7, 12.9, 5.0, 1H), 2.44 (ddd, J = 17.2,

4.6, 4.6, 1H), 2.34–2.29 (m, 1H), 2.04–1.90 (m, 1H), 1.18 (d, J = 7.2, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ = 199.84, 165.40, 138.41, 129.89, 128.91, 126.76, 125.22, 33.29, 31.27, 29.67, 18.44. HRMS (ESI): calculated for $C_{13}H_{14}O$ ($[M + H]^+$): 187.1117, found: 187.1126.

5,6-Dimethyl-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one (Table 2, entry 2). Prepared from propiophenone (0.134 g, 1.00 mmol) and 3-penten-2-ol (0.172 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.118 g, 59%). Data for the major isomer are given. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54–7.52 (m, 2H), 7.43–7.39 (m, 3H), 6.28 (s, 1H), 2.98 (dq, J = 8, 4, 1H), 2.54–2.41 (m, 2H), 2.37–2.29 (m, 2H), 1.13 (d, J = 6.8, 3H), 1.04 (d, J = 7.1, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.35, 166.64, 138.17, 130.08, 128.96, 126.78, 124.50, 40.11, 36.87, 32.90, 18.78, 12.13. HRMS (ESI): calculated for $C_{14}H_{16}O$ ($[M + H]^+$): 201.1274, found: 201.1268.

2,6-Dimethyl-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one (Table 2, entry 3). Prepared from propiophenone (0.134 g, 1.00 mmol) and 1-penten-3-ol (0.172 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as colorless oil (0.082 g, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (t, J = 7.4, 2H), 7.32 (t, J = 7.1, 1H), 7.12 (d, J = 7.2, 2H), 2.84–2.76 (m, 1H), 2.65 (ddd, J = 16.6, 11.4, 4.8, 1H), 2.46 (ddd, J = 16.9, 6.3, 4.8, 1H), 2.34–2.28 (m, 1H), 1.91–1.84 (m, 1H), 1.62 (s, 3H), 1.02 (d, J = 7.1, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.06, 161.53, 140.65, 131.23, 128.45, 127.74, 127.39, 35.73, 34.34, 29.95, 18.20, 13.14. HRMS (ESI): calculated for $C_{14}H_{16}O$ ($[M + Na]^+$): 223.1093, found: 223.1093.

5,6-Dihydro-[1,1′-biphenyl]-3(4*H*)-one[21] (Table 2, entry 4). Prepared from acetophenone (0.120 g, 1.00 mmol) and 3-buten-2-ol (0.142 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.132 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56–7.52 (m, 2H), 7.43–7.39 (m, 3H), 6.42 (s, 1H), 2.81–2.74 (m, 2H), 2.49 (t, J = 8.0, 2H), 2.19–2.13 (m, 6.2, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.08, 159.96, 130.12, 128.90, 126.22, 125.59, 37.41, 28.26, 22.96. HRMS (ESI): calculated for $C_{12}H_{12}O$ ($[M + H]^+$): 173.0961, found: 173.0962.

5-Methyl-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one[22] (Table 2, entry 5). Prepared from acetophenone (0.120 g, 1.00 mmol) and 3-penten-2-ol (0.172 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.124 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55–7.52 (m, 2H), 7.43–7.39 (m, 3H), 6.41 (s,1H), 2.84 (dd, J = 17.3, 3.8, 1H), 2.56 (dd, J = 16.1, 3.6, 1H), 2.49–2.42 (m, 1H), 2.38–2.26 (m, 1H), 2.17 (dd, J = 16.1, 12.1, 1H), 1.17 (d, J = 6.5, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.33, 159.24, 138.93, 130.10, 128.89, 126.26, 125.26, 45.59, 36.68, 30.47, 21.44. HRMS (ESI): calculated for $C_{13}H_{14}O$ ($[M + H]^+$): 187.1117, found: 187.1121.

2-Methyl-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one[23] (Table 2, entry 6). Prepared from acetophenone (0.120 g, 1.00 mmol) and 1-penten-3-ol (0.172 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.083 g, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (t, J = 7.5, 2H), 7.35–7.29 (m, 1H), 7.20 (d, J = 8.1, 2H), 2.63 (t, J = 4.0, 2H), 2.53 (t, J = 4.0, 2H), 2.10 (p, J = 4.0, 2H), 1.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.08, 156.61, 141.37, 131.88, 128.35, 127.85, 127.10, 37.80, 32.98, 22.83, 12.89. HRMS (ESI): calculated for $C_{13}H_{14}O$ ($[M + H]^+$): 187.1117, found: 187.1104.

4′-Fluoro-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one[24] (Table 2, entry 7). Prepared from 4-fluoroacetophenone (0.138 g, 1.00 mmol) and 3-buten-2-ol (0.144 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.10 g, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55–7.49 (m, 2H), 7.12–7.08 (m, 2H), 6.37 (s, 1H), 2.75 (t, J = 6.6, 2H), 2.48 (t, J = 6.7, 2H), 2.15 (p, J = 6.2, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.84, 163.91 (d, J = 251), 158.59, 134.99, 128.14 (d, J = 9), 125.41, 115.95 (d, J = 21), 37.28, 28.28, 22.89. HRMS (ESI): calculated for $C_{12}H_{11}FO$ ($[M + H]^+$): 191.0867, found: 191.0871.

2′-Fluoro-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one[25] (Table 2, entry 8). Prepared from 2-fluoroacetophenone (0.138 g, 1.00 mmol) and 3-buten-2-ol (0.144 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.129 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38–7.32 (m, 2H), 7.19–7.16 (m, 1H), 7.10 (dd, J = 11.1, 8.5, 1H), 6.28 (s, 1H), 2.76 (t, J = 5.8, 2H), 2.50 (t, J = 8.0, 2H), 2.14 (p, J = 6.2, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.71, 159.96 (d, J = 251), 157.36 (d, J = 3), 134.60, 131.07 (d, J = 8), 128.98, 124.56 (d, J = 4), 116.650 (d, J = 23), 37.54, 29.81, 23.28. HRMS (ESI): calculated for $C_{12}H_{11}FO$ ([M + H]): 191.0867, found: 191.0879.

3′-Fluoro-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one[25] (Table 2, entry 9). Prepared from 3-fluoroacetophenone (0.138 g, 1.00 mmol) and 3-buten-2-ol (0.144 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a colorless liquid (0.068 g, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41–7.36 (m, 1H), 7.33–7.30 (m, 1H), 7.23–7.20 (m, 1H), 7.10 (tdd, J = 8.2, 2.5, 1.1, 1H), 6.39 (s, 1H), 2.74 (td, J = 6.2, 2H), 2.52–2.44 (m, 2H), 2.21–2.10 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.81, 163.07 (d, J = 247), 158.36 (d, J = 2.6), 141.26 (d, J = 7.5), 130.44 (d, J = 8.4), 126.27, 121.89 (d, J = 2.9), 116.87 (d, J = 21.4), 113.23 (d, J = 22.3), 22.84, 28.21, 37.36. ^{19}F NMR (376 MHz, $CDCl_3$) δ = −112.15. HRMS (ESI): calculated for $C_{12}H_{11}FO$ ($[M + H]^+$): 191.0867, found: 191.0871.

4′-Chloro-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one[25] (Table 2, entry 10). Prepared from 4-chloroacetophenone (0.155 g, 1.00 mmol) and 3-buten-2-ol (0.144 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.10 g, 49%). ^{1}H NMR (700 MHz, $CDCl_3$) δ = 7.46 (d, J = 8.6, 2H), 7.38 (d, J = 8.6, 2H), 6.38 (s, 1H), 2.73 (t, J = 6, 2H), 2.48 (t, J = 6.8, 2H), 2.15 (p, J = 6.2, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ = 199.79, 158.43, 137.31, 136.16, 129.13, 127.49, 125.76, 37.30, 28.13, 22.85. HRMS (ESI): calculated for $C_{12}H_{11}ClO$ ($[M + Na]^+$): 229.0391, found: 229.0402.

4′-(Trifluoromethyl)-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one[25] (Table 2, entry 11). Prepared from 4′-(trifluoromethyl)acetophenone (0.188 g, 1.00 mmol) and 3-buten-2-ol (0.144 g, 2.00 mmol). After purification by column chromatography, the

compound was isolated as a yellow gel (0.094 g, 39%). ^{1}H NMR (700 MHz, $CDCl_3$) δ = 7.66 (d, J = 8.3, 2H), 7.62 (d, J = 8.2, 2H), 6.42 (s, 1H), 2.77 (t, J = 5.9, 2H), 2.50 (t, J = 6.8, 2H), 2.18 (p, J = 6.3, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ = 199.63, 158.20, 142.57, 131.71 (q, J = 32), 128.51, 127.03, 126.54, 125.85 (q, J = 3.5), 123.95 (q, J = 271), 37.32, 28.27, 22.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ = −62.58. HRMS (ESI): calculated for $C_{13}H_{11}F_3O$ ($[M + H]^+$): 241.0835, found: 241.0849.

2-Methyl-4′-(trifluoromethyl)-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one (Table 2, entry 12). Prepared from 4′-(trifluoromethyl)acetophenone (0.188 g, 1.00 mmol) and 1-penten-3-ol (0.172 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.063 g, 25%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (d, J = 8.3, 2H), 7.31 (d, J = 7.9, 2H), 2.63–2.58 (m, 2H), 2.54 (t, J = 8.0, 2H), 2.11 (p, J = 8.0, 2H), 1.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.66, 154.83, 145.08, 132.74, 130.08 (q, J = 33), 125.60 (q, J = 4), 124.04 (q, J = 273) 37.83, 32.84, 22.91, 12.94. ^{19}F NMR (376 MHz, $CDCl_3$) δ = −62.57. HRMS (ESI): calculated for $C_{14}H_{13}F_3O$ ($[M + H]^+$): 255.0991, found: 255.0987.

3′-(Trifluoromethyl)-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one[12b] (Table 2, entry 13). Prepared from 3′-(trifluoromethyl)acetophenone (0.188 g, 1.00 mmol) and 3-buten-2-ol (0.144 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a yellow gel (0.079 g, 33%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (s, 1H), 7.71 (d, J = 7.8, 1H), 7.66 (d, J = 7.8, 1H), 7.54 (t, J = 7.8, 1H), 6.43 (s, 1H), 2.79 (td, J = 6.1, 1.4, 2H), 2.51 (t, J = 8.0, 2H), 2.19 (p, J = 6.3, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.61, 158.10, 139.87, 129.49, 129.39, 126.71, 126.58 (q, J = 4), 123.029 (q, J = 4), 37.31, 28.23, 22.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ = −62.69. HRMS (ESI): calculated for $C_{13}H_{11}F_3O$ ($[M + Na]^+$): 263.0654, found: 263.0651.

2′-Methoxy-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one[25] (Table 2, entry 14). Prepared from 2′-methoxyacetophenone (0.15 g, 1.00 mmol) and 3-buten-2-ol (0.144 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a yellow gel (0.0586 g, 29%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37–7.30 (m, 1H), 7.20 (dd, J = 7.2, 1.7, 1H), 7.00–6.90 (m, 2H), 6.20 (s, 1H), 3.84 (s, 3H), 2.74 (td, J = 6.2, 1.2, 2H), 2.48 (t, J = 8.0, 2H), 2.10 (p, J = 8.0, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.35, 161.89, 156.74, 130.46, 129.79, 128.89, 128.34, 120.88, 111.29, 55.59, 37.69, 30.21, 23.45. HRMS (ESI): calculated for $C_{13}H_{14}O_2$ ($[M + H]^+$): 203.1067, found: 203.1087.

3′-Methoxy-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one[25] (Table 2, entry 15). Prepared from 3′-methoxyacetophenone (0.150 g, 1.00 mmol) and 3-buten-2-ol (0.144 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.070 g, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 (t, J = 8.0, 1H), 7.14–7.11 (m, 1H), 7.05–7.04 (m, 1H),6.41 (s, 1H), 3.83 (s, 3H), 2.76 (td, J = 6.1, 1.5, 2H), 2.49 (t, J = 8.0, 2H), 2.15 (p, J = 4.0, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.19, 159.90, 140.41, 129.89, 125.73, 118.69, 115.56, 111.83, 100.05, 55.48, 37.42, 28.33, 22.93. HRMS (ESI): calculated for $C_{13}H_{14}O_2$ ($[M + H]^+$): 203.1067, found: 203.1075.

6-Ethyl-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one[26] (Table 2, entry 16). Prepared from butyrophenone (0.148 g, 1.00 mmol) and 3-buten-2-ol (0.144 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.082 g, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52–7.49 (m, 2H), 7.41–7.38 (m, 3H), 6.24 (s, 1H), 2.94–2.88 (m, 1H), 2.54 (ddd, J = 17.9, 12.2, 6.1, 1H), 2.47–2.40 (m, 1H), 2.26–2.05 (m, 2H), 1.61–1.43 (m, 2H), 0.95 (t, J = 7.4, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.92, 165.07, 138.78, 129.88, 128.91, 126.74, 125.50, 38.11, 33.07, 29.84, 25.26, 24.71, 12.81. HRMS (ESI): calculated for $C_{14}H_{16}O$ ($[M + Na]^+$): 223.1093, found: 223.1076.

6-Ethyl-5-methyl-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one (Table 2, entry 17). Prepared from butyrophenone (0.148 g, 1.00 mmol) and 3-penten-2-ol (0.172 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.083 g, 39%). Only the major isomer data are presented. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51–7.46 (m, 2H), 7.42–7.39 (m, 3H), 6.24 (s, 1H), 2.91–2.79 (m, 1H), 2.58–2.46 (m, 1H), 2.36 (d, J = 9.9, 2H), 1.78–1.65 (m, 2H), 1.50–1.39 (m, 1H), 1.17 (d, J = 6.9, 3H), 0.75 (t, J = 7.5, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.60, 166.72, 139.87, 129.85, 128.89, 126.72, 125.49, 43.51, 41.30, 33.62, 21.42, 18.85, 13.64. HRMS (ESI): calculated for $C_{15}H_{18}O$ ($[M + Na]^+$): 237.1250, found: 237.1240.

6-Ethyl-2-methyl-5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one (Table 2, entry 18). Prepared from butyrophenone (0.148 g, 1.00 mmol) and 1-penten-3-ol (0.172 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.071 g, 33%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (t, J = 7.3, 2H), 7.32 (t, J = 7.3, 1H), 7.13 (d, J = 6.9, 2H), 2.64–2.52 (m, 2H), 2.46–2.39 (m, 1H), 2.28–2.19 (m, 1H), 2.07–2.00 (m, 1H), 1.63 (s, 3H), 1.45–1.35 (m, 2H), 0.85 (t, J = 7.4, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.17, 161.08, 140.80, 131.36, 128.39, 127.78, 127.62, 42.50, 33.87, 25.25, 23.94, 13.19, 12.64. HRMS (ESI): calculated for $C_{15}H_{18}O$ ($[M + Na]^+$): 237.1250, found: 237.1265.

3-(Thiophen-2-yl)cyclohex-2-en-1-one[23] (Table 2, entry 19). Prepared from 2-acetylthiophene (0.126 g, 1.00 mmol) and 3-buten-2-ol (0.144 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.0587 g, 33%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, J = 5.0, 1H), 7.38 (d, J = 3.7, 1H), 7.09 (dd, J = 5.1, 3.8, 1H), 6.43 (s, 1H), 2.79 (t, J = 6.0, 2H), 2.46 (t, J = 6.6, 2H), 2.14 (p, J = 6.3, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.59, 152.58, 131.42, 128.89, 128.40, 127.45, 122.87, 37.37, 28.17, 22.58. HRMS (ESI): calculated for $C_{10}H_{10}OS$ ($[M + H]^+$): 179.0525, found: 179.0537.

3-(Naphthalen-2-yl)cyclohex-2-en-1-one[23] (Table 2, entry 20). Prepared from 2-acetylnaphthalene (0.170 g, 1.00 mmol) and 3-buten-2-ol (0.144 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.071 g, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (s, 1H), 7.89–7.82 (m, 3H), 7.65 (dd, J = 8.7, 1.9, 1H), 7.55–7.49 (m, 2H), 6.57 (s, 1H), 2.94–2.87 (m, 2H), 2.56–2.49 (m, 2H), 2.24–2.18 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.05, 159.60, 136.09, 134.11, 133.22, 128.82, 128.63, 127.80, 127.33, 126.84, 126.27, 125.89, 123.44, 37.47, 28.23, 22.99. HRMS

(ESI): calculated for $C_{16}H_{14}O$ ($[M + H]^+$): 223.1117, found: 223.1119.

1,9,10,10a-Tetrahydrophenanthren-3(2*H*)-one[27] (Table 3, entry 21). Prepared from 1-tetralone (0.146 g, 1.00 mmol) and 3-buten-2-ol (0.144 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a yellow gel (0.061 g, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, J = 8.3, 1H), 7.33 (t, J = 7.4, 1H), 7.29–7.23 (m, 1H), 7.20 (t, J = 7.0, 1H), 6.66 (s, 1H), 3.05–2.87 (m, 2H), 2.71–2.42 (m, 3H), 2.24–2.18 (m, 1H), 2.10–2.04 (m, 1H), 1.88–1.77 (m, 1H), 1.62 (dq, J = 12.7, 5.3, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.37, 158.41, 139.93, 131.40, 130.68, 129.76, 126.72, 125.31, 120.52, 37.52, 37.27, 30.68, 30.44, 30.13. HRMS (ESI): calculated for $C_{14}H_{14}O$ ($[M + Na]^+$): 221.0937, found: 221.0944.

1-Methyl-1,9,10,10a-tetrahydrophenanthren-3(2*H*)-one (Table 3, entry 22). Prepared from 1-tetralone (0.146 g, 1.00 mmol) and 3-penten-2-ol (0.172 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.066 g, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, J = 8.0, 1H), 7.32 (t, J = 8.0, 1H), 7.26–7.18 (m, 2H), 6.66 (s, 1H), 2.96–2.92 (m, 2H), 2.52 (dd, J = 12.0, 4.0, 1H), 2.38–2.33 (m, 3H), 2.05–1.93 (m, 1H), 1.51–1.40 (m, 1H), 1.19 (d, J = 4.0, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.20, 158.23, 140.06, 131.68, 130.60, 129.61, 126.76, 125.67, 120.79, 46.08, 44.25, 35.35, 30.16, 27.38, 19.68. HRMS (ESI): calculated for $C_{15}H_{16}O$ ($[M + H]^+$): 213.1274, found: 213.1277.

1-Methyl-1,2,9,9a-tetrahydro-3*H*-fluoren-3-one (Table 3, entry 23). Prepared from 1-indanone (0.132 g, 1.00 mmol) and 3-penten-2-ol (0.172 g, 2 mmol). After purification by column chromatography, the compound was isolated as a yellow gel (0.0495 g, 25%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 (d, J = 7.7, 1H), 7.43–7.35 (m, 2H), 7.31 (t, J = 7.5, 1H), 6.33 (s, 1H), 3.30 (dd, J = 15.8, 7.7, 1H), 2.87–2.78 (m, 1H), 2.73 (dd, J = 15.8, 6.8, 1H), 2.24–2.04 (m, 2H), 1.18 (d, J = 6.4, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.37, 148.06, 138.37, 131.91, 127.54, 125.76, 123.13, 117.49, 100.07, 49.22, 46.90, 36.96, 35.95, 29.85, 20.11. HRMS (ESI): calculated for $C_{14}H_{14}O$ ($[M + Na]^+$): 221.0937, found: 221.0939.

Characterisation data for diketone compounds

2-Methyl-1-phenyloctane-1,5-dione (Table 4, entry 24). Prepared from propiophenone (0.134 g, 1.00 mmol) and 1-hexen-3-ol (0.200 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.135 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98–7.91 (m, 2H), 7.53–7.49 (m, 1H), 7.44–7.41 (m, 2H), 3.52 (sext, J = 8.0, 1H), 2.49–2.41 (m, 1H), 2.38–2.23 (m, 3H), 2.08–1.99 (m, 1H), 1.78–1.66 (m, 1H), 1.52 (sext, J = 8.0, 2H), 1.15 (d, J = 8.0, 3H), 0.85 (t, J = 8.0, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.70, 203.87, 136.42, 133.03, 128.68, 128.31, 77.40, 77.08, 76.77, 44.74, 39.82, 39.49, 27.17, 17.43, 17.26, 13.70. HRMS (ESI): calculated for $C_{15}H_{20}O_2$ ($[M + Na]^+$): 255.1356, found: 255.1365.

2-Ethyl-1-phenyloctane-1,5-dione (Table 4, entry 25). Prepared from butyrophenone (0.148 g, 1.00 mmol) and 1-hexen-3-ol (0.200 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a yellow liquid (0.081 g, 33%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00–7.97 (m, 2H), 7.15–7.10 (m, 3H), 2.97 (t, J = 8.0, 2H), 2.54–2.50 (m, 2H), 2.38 (t, J = 8.0, 2H), 2.00 (p, J = 8.0, 2H), 1.64–1.55 (m, 3H), 0.93–0.88 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.93, 204.13, 137.45, 133.17, 128.80, 128.32, 46.44, 44.84, 40.01, 25.59, 25.27, 17.35, 13.82, 11.82. HRMS (ESI): calculated for $C_{16}H_{22}O_2$ ($[M + H]^+$): 247.1693, found: 247.1688.

2-(3-Oxohexyl)-3,4-dihydronaphthalen-1(2*H*)-one (Table 4, entry 26). Prepared from 1-tetralone (0.146 g, 1.00 mmol) and 1-hexen-3-ol (0.200 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.0635 g, 26%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, J = 7.8, 1H), 7.48–7.40 (m, 1H), 7.32–7.26 (m, 1H), 7.22 (d, J = 7.7, 1H), 3.03–2.96 (m, 2H), 2.59 (t, J = 7.5, 2H), 2.55–2.46 (m, 1H), 2.40 (t, J = 7.3, 2H), 2.25–2.04 (m, 2H), 1.97–1.75 (m, 2H), 1.60 (sext, J = 7.4, 2H), 0.91 (t, J = 7.4, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.20, 200.25, 144.00, 133.39, 132.54, 128.84, 127.48, 126.73, 46.85, 44.88, 40.37, 29.20, 28.59, 24.17, 17.45, 13.90. HRMS (ESI): calculated for $C_{16}H_{20}O_2$ ($[M + Na]^+$): 267.1356, found: 267.1369.

1-Phenyloctane-1,5-dione[17] (Table 4, entry 27). Prepared from acetophenone (0.120 g, 1.00 mmol) and 1-hexen-3-ol (0.200 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.056 g, 26%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97–7.95 (m, 2H), 7.58–7.52 (m, 1H), 7.48–7.44 (m, 2H), 3.01 (t, J = 8.0, 2H), 2.53 (t, J = 8.0, 2H), 2.39 (t, J = 7.4, 2H), 2.02 (p, J = 4.0, 2H), 1.66–1.54 (m, 2H), 0.91 (t, J = 7.4, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 210.99, 200.00, 136.97, 133.21, 128.75, 128.20, 77.48, 77.16, 76.84, 44.91, 41.78, 37.66, 18.44, 17.45, 13.90. HRMS (ESI): calculated for $C_{14}H_{18}O_2$ ($[M + Na]^+$): 241.1199, found: 241.1205.

1-(4-(*tert*-Butyl)phenyl)octane-1,5-dione (Table 4, entry 28). Prepared from 4′-*tert*-butylacetophenone (0.176 g, 1.00 mmol) and 1-hexen-3-ol (0.200 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as colorless oil (0.118 g, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, J = 8.8, 2H), 7.47 (d, J = 8.8, 2H), 2.98 (t, J = 8.0, 2H), 2.52 (t, J = 8.0, 2H), 2.38 (t, J = 8.0, 2H), 2.02 (p, J = 8.0, 2H), 1.65–1.22 (m, 2H), 1.34 (s, 9H), 0.91 (t, J = 8.0, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.02, 199.70, 156.94, 139.26, 134.41, 128.18, 125.68, 44.90, 41.84, 37.57, 35.25, 31.23, 18.56, 17.45, 13.90. HRMS (ESI): calculated for $C_{18}H_{26}O_2$ ($[M + Na]^+$): 297.1825, found: 297.1818.

1-(4-Methoxyphenyl)-2-methyloctane-1,5-dione (Table 4, entry 29). Prepared from 4′-methoxypropiophenone (0.164 g, 1.00 mmol) and 1-hexen-3-ol (0.200 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a colorless oil (0.107 g, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, J = 8.8, 2H), 6.93 (d, J = 8.0, 2H), 3.86 (s, 3H), 3.50 (sext, J = 8.0, 1H), 2.51–2.43 (m, 1H), 2.38–2.30 (m, 2H), 2.09–2.00 (m, 2H), 1.76–1.68 (m, 1H), 1.55 (sext, J = 8.0, 2H), 1.15 (d, J = 8.0, 3H), 0.87 (t, J = 8.0, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 210.82, 202.40, 163.50, 130.62, 129.40, 113.83, 55.45, 44.73, 39.90, 39.08, 27.39, 17.59, 17.28, 13.72. HRMS

(ESI): calculated for $C_{16}H_{22}O_3$ ([M + H]$^+$): 263.1642, found: 263.1611.

1-(3-Fluorophenyl)octane-1,5-dione (Table 4, entry 30). Prepared from 3′-fluoroacetophenone (0.138 g, 1.00 mmol) and 1-hexen-3-ol (0.200 g, 2.00 mmol). After purification by column chromatography, the compound was isolated as a colorless oil (0.080 g, 34%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75–7.73 (m, 1H), 7.65–7.62 (m, 1H), 7.46–7.41 (m, 1H), 7.28–7.23 (m, 1H), 2.99 (t, J = 7.0, 2H), 2.53 (t, J = 7.0, 2H), 2.39 (t, J = 7.0, 2H), 2.01 (p, J = 7.0, 2H), 1.60 (sext, J = 7.0, 2H), 0.91 (t, J = 7.0, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 210.51, 202.30, 163.14 (d, J = 247), 139.03 (d, J = 7), 139.06 (d, J = 7), 124.27, 120.45 (d, J = 21), 115.22 (d, J = 23), 44.96, 44.21, 39.64, 25.44, 17.40, 13.84. ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.42. HRMS (ESI): calculated for $C_{14}H_{17}FO_2$ ([M + Na]$^+$): 259.1105, found: 259.1110.

2-Methyl-1,5-diphenylpentane-1,5-dione (Scheme 1C, entry 34).[27] Prepared from propiophenone (0.134 g, 1.00 mmol) and 1-phenylprop-2-en-1-ol (0.268 g, 2.00 mmol). The compound was isolated as a white solid (0.162 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00–7.98 (m, 2H), 7.94–7.92 (m, 2H), 7.58–7.52 (m, 2H), 7.48–7.42 (m, 3H), 3.66 (sext, J = 7.0, 1H), 3.14–3.06 (m, 1H), 2.95–2.87 (m, 1H), 2.32–2.24 (m, 1H), 1.97–1.89 (m, 1H), 1.25 (d, J = 7.0, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.05, 200.05, 136.94, 136.55, 133.20, 128.84, 128.73, 128.52, 128.19, 39.89, 35.99, 27.87, 17.78. HRMS (ESI): calculated for $C_{18}H_{18}O_2$ ([M + Na]$^+$): 289.1199, found: 289.1200.

1,5-Diphenylpentane-1,5-dione (Scheme 1C, entry 35). Prepared from acetophenone (0.120 g, 1.00 mmol) and α-vinylbenzyl alcohol (0.537 g, 4.00 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.108 g, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (d, J = 7.3, 4H), 7.56 (t, J = 7.4, 02H), 7.46 (t, J = 7.7, 4H), 3.13 (t, J = 7.0, 4H), 2.21 (p, J = 8.0, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 18.89, 37.76, 128.22, 128.76, 133.22, 137.01, 200.03. HRMS (ESI): calculated for $C_{17}H_{16}O_2$ ([M + Na]$^+$): 275.1043, found: 275.1024.

2-Ethyl-1,5-diphenylpentane-1,5-dione (Scheme 1C, entry 36). Prepared from butyrophenone (0.148 g, 1.00 mmol) and α-vinylbenzyl alcohol (0.537 g, 4.00 mmol). After purification by column chromatography, the compound was isolated as colorless oil (0.132 g, 47%). ^{1}H NMR (400 MHz, $CDCl_3$). δ = 8.00–7.94 (m, 2H), 7.93–7.86 (m, 2H), 7.57–7.52 (m, 2H), 7.48–7.40 (m, 4H), 3.62–3.49 (m, 1H), 3.10–3.02 (m, 1H), 2.89–2.81 (m, 1H), 2.27–2.17 (m, 1H), 2.07–1.95 (m, 1H), 1.90–1.79 (m, 1H), 1.67–1.50 (m, 1H), 0.92 (t, J = 7.4, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 11.84, 25.80, 36.08, 46.76, 128.18, 128.41, 128.71, 128.85, 133.18, 136.95, 137.48, 200.11, 204.10. HRMS (ESI): calculated for $C_{19}H_{20}O_2$ ([M + Na]$^+$): 303.1356, found: 303.1352.

Procedure for gram-scale annulation of propiophenone. Palladium acetate (0.224 g, 1.00 mmol), BINOL phosphoric acid (0.174 g, 1.00 mmol) and sodium hydroxide (0.39 g, 10.00 mmol) were taken in a scintillation vial. Propiophenone (1.32 g, 10.00 mmol), 3-buten-2-ol (1.44 g, 20.00 mmol) and 3.0 mL of dichloroethane (DCE) were added to it. Finally, 4 Å molecular sieves were added to the reaction mixture and stirred at room temperature for 24 hours. Then the reaction mixture was evaporated under vacuum and purified by flash column chromatography in ethyl acetate and *n*-hexane (1 : 4) as an eluent. Yield = 1.078 g, (58%).

Conflicts of interest

The authors declare no competing financial interest.

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