This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Alkylation/1,2-Aryl Migration of α-Aryl Allylic Alcohols with α-Carbonyl Alkyl Bromides Using Visible-Light Photoredox Catalysis

Yang Li,† Bang Liu,† Xuan-Hui Ouyang,† Ren-Jie Song*,† and Jin-Heng Li*,†,‡

† State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China
‡ State Key Laboratory of Applied Organic Chemistry Lanzhou University, Lanzhou 730000, China

srj0731@hnu.edu.cn and jhli@hnu.edu.cn

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

Abstract

A novel visible-light-induced alkene difunctionalization strategy is described for the synthesis of 1,5-dicarbonyl compounds from two reaction partners, α-aryl allylic alcohols and α-carbonyl alkyl bromides. This method is successful by sequential alkylation of an alkene C-C double bond and intramolecular 1,2-aryl migration, and shows a broad substrate scope, excellent functional group tolerance and good selectivity.

Introduction

Alkenes represent an important class of chemical feedstock with broad utility in organic synthesis for the construction of more complex molecular entities. Thus, methods for the efficient functionalization of alkenes at the C-C double bond positions are of intense interest.1-2 Particularly attractive are the alkene
difunctionalization transformations wherein two functional groups are introduced across alkenes in a
catalytic and selectivity-controlled manner.\textsuperscript{2-7} Despite remarkable progress in the alkene
difunctionalization field, the dicarbofunctionalization of alkenes involving the simultaneous
incorporation of an arene group and an alkyl group has been more limited\textsuperscript{3-7} and mostly restricted to the
requirement of a stoichiometric amount of oxidants (often hypervalent iodine reagents or peroxides) and
the synthesis of oxindoles and related heterocycles.\textsuperscript{3-5,7} Liu group has first reported the alkylarylation of
activated alkenes with aryl C(sp\textsuperscript{2})-H bonds and alkyl C(sp\textsuperscript{3})-H bonds adjacent to a CN group in the
presence of Pd(II) catalysts and hypervalent iodine reagents to assemble CN-containing oxindoles.\textsuperscript{3}
Later, our group illustrated an oxidative alkylarylation of activated alkenes with aryl C(sp\textsuperscript{2})-H bonds
and alkyl C(sp\textsuperscript{3})-H bonds adjacent to a heteroatom (O, S or N atom) for the synthesis of functionalized
3-(2-oxoethyl)indolin-2-ones using the Fe catalyst/peroxide system.\textsuperscript{4} The group of Liu\textsuperscript{5a}, the group of
Cheng\textsuperscript{5b} and our groups\textsuperscript{5c} have independently described that similar transformations could be achieved
using hypervalent iodine reagents or peroxides as the alkyl resources. The group of Xu/Ji developed a
metal-free peroxide-mediated alkylarylation of alkenes (\(\alpha,\alpha\)-diaryl allylic alcohols) with alkyl C(sp\textsuperscript{3})-H
bonds adjacent to an oxygen atom through intramolecular 1,2-aryl migration.\textsuperscript{6} A Pd-catalyzed oxidative
Heck-type insertion strategy for the alkylarylation of activated alkenes with aryl C(sp\textsuperscript{2})-H bonds and
\(\alpha\)-C(sp\textsuperscript{3})-Br bonds in \(\alpha\)-carbonyl alkyl bromides, which has very recently been reported by our group,
appears to be a good alternative; however, such process is limited to activated system, thus only
enabling intramolecular aryl C(sp\textsuperscript{2})-H functionalization to access oxindoles and related heterocycles.\textsuperscript{7}
Thus, further discovery of a new mild strategy for general alkylarylation of alkenes leading to diverse
complex molecules is highly desirable.

Recently, visible-light photoredox catalysis has proven to be a powerful and environmentally benign
methodology for the construction of various C-C bonds in synthesis.\textsuperscript{8-11} In the field, alkene
functionalization initiated by the in-situ generation of alkyl radicals from alkyl halides through atom
transfer radical addition (alkylation-halogenation),\textsuperscript{9} hydroalkylation (Scheme 1a)\textsuperscript{10} and alkenylation
(Scheme 1b)\textsuperscript{11} have been well explored. Herein, we report a novel visible-light photoredox catalysis
strategy for the alkylarylation of α-aryl allylic alcohols with α-carbonyl alkyl bromides through alkylation/1,2-aryl migration (Scheme 1c). This visible-light photoredox catalysis is applicable to a wide range of α-carbonyl alkyl bromides, including primary-, secondary- and tertiary-α-bromoalkyl esters, ketones and amide, and even more challenging 2-bromo-2,2-difluoroacetate.


Results and discussion

We started optimization studies by investigating the reaction between 1,1-diphenylprop-2-en-1-ol (1a) and 2-bromoacetophenone (2a), a primary alkyl bromide, using the visible-light photoredox catalysis strategy (Table 1). The results demonstrated that among three photocatalysts [Ir(ppy)₃] was the most efficient than [Ru(bpy)₃Cl₂] and Eosin (entries 1-3). In the presence of 2 mol % [Ir(ppy)₃], 1.2 equiv Ag₂CO₃ and 36 W compact fluorescent light, the desired alkylation/1,2-phenyl migration product 3aa was formed from substrate 1a and alkyl bromide 2a in 90% yield (entry 1). Notably, a photocatalyst was necessary for successful alkylation/1,2-aryl migration, as its absence resulted in no detectable product 3aa (entry 4). The amount of [Ir(ppy)₃] was found to affect the reaction, as 2 mol % [Ir(ppy)₃] was preferred (entry 1 versus entries 4 and 5). However, the yield of 3aa decreased to 55% using 5 W blue LED light instead of 36 W compact fluorescent light (entry 1 versus entry 6). In addition, the reaction
did not take place without additional visible light (entry 7). It should be noted that the reaction could occur without bases, albeit with a lower yield (23% yield, entry 8). Extensive screening on the effect of bases revealed that adding a base, such as Ag₂CO₃, Ag₂O, AgOAc, Na₂CO₃ and NaOH, improved the reaction, and using 1.2 equiv Ag₂CO₃ was the best choice (entry 1 versus entries 8-14). After varying reaction temperatures and solvents, we found that this reaction in MeCN at 50 °C gave the best results (entry 1 versus entries 15-18). We were delighted to find that a reaction on 1 gram scale of substrate 1a was successfully performed in good yield (entry 19).

Table 1. Screening of the reaction conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>[M] (mol %)</th>
<th>Base (equiv)</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Ir(ppy)₃] (2)</td>
<td>Ag₂CO₃ (1.2)</td>
<td>MeCN</td>
<td>50</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>[Ru(bpy)₃Cl₂] (2)</td>
<td>Ag₂CO₃ (1.2)</td>
<td>MeCN</td>
<td>50</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>Eosin Y (2)</td>
<td>Ag₂CO₃ (1.2)</td>
<td>MeCN</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>—</td>
<td>Ag₂CO₃ (1.2)</td>
<td>MeCN</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>[Ir(ppy)₃] (5)</td>
<td>Ag₂CO₃ (1.2)</td>
<td>MeCN</td>
<td>50</td>
<td>91</td>
</tr>
<tr>
<td>6</td>
<td>[Ir(ppy)₃] (2)</td>
<td>Ag₂CO₃ (1.2)</td>
<td>MeCN</td>
<td>50</td>
<td>55</td>
</tr>
<tr>
<td>7</td>
<td>[Ir(ppy)₃] (2)</td>
<td>—</td>
<td>MeCN</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>[Ir(ppy)₃] (2)</td>
<td>Ag₂CO₃ (2)</td>
<td>MeCN</td>
<td>50</td>
<td>90</td>
</tr>
<tr>
<td>9</td>
<td>[Ir(ppy)₃] (2)</td>
<td>Ag₂CO₃ (1)</td>
<td>MeCN</td>
<td>50</td>
<td>85</td>
</tr>
<tr>
<td>10</td>
<td>[Ir(ppy)₃] (2)</td>
<td>Ag₂O (1.2)</td>
<td>MeCN</td>
<td>50</td>
<td>52</td>
</tr>
<tr>
<td>11</td>
<td>[Ir(ppy)₃] (2)</td>
<td>AgOAc (1.2)</td>
<td>MeCN</td>
<td>50</td>
<td>62</td>
</tr>
<tr>
<td>12</td>
<td>[Ir(ppy)₃] (2)</td>
<td>Na₂CO₃ (1.2)</td>
<td>MeCN</td>
<td>50</td>
<td>75</td>
</tr>
<tr>
<td>13</td>
<td>[Ir(ppy)₃] (2)</td>
<td>NaOH (1.2)</td>
<td>MeCN</td>
<td>50</td>
<td>35</td>
</tr>
<tr>
<td>14</td>
<td>[Ir(ppy)₃] (2)</td>
<td>Ag₂CO₃ (1.2)</td>
<td>MeCN</td>
<td>rt</td>
<td>60</td>
</tr>
<tr>
<td>15</td>
<td>[Ir(ppy)₃] (2)</td>
<td>Ag₂CO₃ (1.2)</td>
<td>MeCN</td>
<td>80</td>
<td>45</td>
</tr>
<tr>
<td>16</td>
<td>[Ir(ppy)₃] (2)</td>
<td>Ag₂CO₃ (1.2)</td>
<td>toluene</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>17</td>
<td>[Ir(ppy)₃] (2)</td>
<td>Ag₂CO₃ (1.2)</td>
<td>DMF</td>
<td>50</td>
<td>13</td>
</tr>
<tr>
<td>18</td>
<td>[Ir(ppy)₃] (2)</td>
<td>Ag₂CO₃ (1.2)</td>
<td>MeCN</td>
<td>50</td>
<td>92</td>
</tr>
</tbody>
</table>

* Reaction conditions: 1a (0.2 mmol), 2a (0.4 mmol), [M], base and solvent (2 mL) with 36 W compact fluorescent light under argon atmosphere for 16 h.  
  * 5 W blue LED light instead of 36 W compact fluorescent light.
Having established the optimal reaction conditions, we turned our attention to investigate the scope of this alkylation/1,2-aryl migration protocol with respect to α-aryl allylic alcohols 1 and α-carbonyl alkyl bromides 2 (Tables 2 and 3). First, we explore this new transformation by using different α-carbonyl alkyl bromides 2b-m, including primary-, secondary- and tertiary-α-bromoalkyl ketones, esters and amides, and 2-bromo-2,2-difluoroacetate, to react with 1,1-diphenylprop-2-en-1-ol (1a), [Ir(ppy)₃], Ag₂CO₃ and 36 W compact fluorescent light (Table 2). The optimal conditions proved to be compatible with both primary-α-bromoalkyl ketones 2b-e and ester 2f, giving the corresponding alkylation/1,2-aryl migration products 3ab-af in moderate to excellent yields. In addition, in ketones 2b-e the electronic properties of the substituted aryl groups affected the reaction, and their reactive order is as follow: electron-rich > electron-deficient. A number of secondary-α-bromoalkyl ketone 2g, ester 2h and amides 2i-j also worked well and led to the desired products 3ag-aj in moderate to good yields, although ketone 2g had the least reactivity. The alkylation/1,2-aryl migration of 1,1-diphenylprop-2-en-1-ol (1a) with tertiary-α-bromoalkyl esters 2k and 2l successfully afforded 3ak and 3al in high yields with excellent levels of regioselective control. Interestingly, 2-bromo-2,2-difluoroacetate (2m) also had high reactivity and delivered two fluoro atom-containing product 3am in 88% yield.

Table 2. Variation of the α-carbonyl alkyl bromides (2)°

**Organic Chemistry Frontiers Accepted Manuscript**
We next set out to apply the optimal conditions to the alkylation/1,2-aryl migration of various α-aryl allylic alcohols 1 with 2-bromoacetophenone (2a), methyl 2-bromopropanoate (2h), diethyl 2-bromo-2-methylmalonate (2l) or 2-bromo-2,2-difluoroacetate (2m) (Table 3). In the presence of 2-bromoacetophenone (2a), [Ir(ppy)$_3$], Ag$_2$CO$_3$ and 36 W compact fluorescent light, alcohols 1b-d, which contain two same substituted aryl groups, including two 4-MePh, two 4-ClPh and 4-BrPh groups, on the α-position chemospecifically furnished 3ba-3da in moderate to good yields. Alcohols 1e-s, which contain two different substituted aryl groups, were also viable substrates for the alkylation/1,2-aryl migration reaction, and selectivity of their products 3ea-3sa toward the migrating aryl group relied on the electronic and steric hindrance properties of the α-substituted aryl groups.

Alcohols 1e-f, the Ph group was the major migration group in alcohol 1e and 1f (product 3ea and 3fa$_{12c,12j}$) (product 3ea, two regioisomers are not separated by silica gel column chromatography).

Alcohols 1g-h, containing other two substituents – a α-Ph group and a α-4-substituted Ph group – provided the α-4-substituted Ph migrating products 3ga-3ha$_{12c,12j}$ as the major isomers in high yield.

While α-Ph group and α-3-MePh group in alcohol 1i had the same migrating chance (product 3ia), in
alcohol 1j the migration of α-3-CF₃Ph group had precedence over α-Ph group (product 3ja_{6a,12f,h}). For α-Ph group vs. α-3,4-disubstituted Ph groups, the former was a major migration group (Product 3ka_{6a,12f,h}) and the later was a major migration group (Product 3la_{12c,12j}). Notably, the sterically hindered α-2-substituted Ph groups were not good migrating groups: the migration of α-Ph group or α-4-ClPh group was found to be preferred during the reaction of alcohols 1m-q (Products 3ma-qa)_{12c,12j}. Using 1-(naphthalen-2-yl)-1-phenylprop-2-en-1-ol (1r) to react with 2-bromoacetophenone (2a) delivered the α-Naphthalen group migrating product 3ra_{12p} as the major in 58% yield. The α-Ph- and α-thiophen-2-yl-substituted alcohol 1s also worked well and mainly provided the thiophen-2-yl-migrating product 3sa in 85% yield. Interestingly, the reaction was applicable to 2-phenylbut-3-en-2-ol (1t), exclusively giving the Ph-migrating product 3ta in 75% yield.

The rule of α-substituted aryl group migration applied to alcohols 1 with other α-carbonyl alkyl bromides. For example, the α-Ph- and α-2-Cl-substituted alcohol 1n reacted with methyl 2-bromopropanoate (2h), diethyl 2-bromo-2-methylmalonate (2l) or 2-bromo-2,2-difluoroacetate (2m) mainly delivered the Ph-migrating products 3nh, 3nl and 3nm in 75-85% yield. Notably, the reaction with diethyl 2-bromo-2-methylmalonate (2l) was finished quickly (18 h) in contrast with the results of Yang and Xia group (143 h)._{12p}

Table 3. Variation of the α-aryl allylic alcohols (1)ᵦ

![Table 3](image-url)
Reaction conditions:

1 (0.2 mmol), 2 (0.4 mmol), [Ir(ppy)₃] (2 mol %), Ag₂CO₃ (1.2 equiv) and MeCN (2 mL) with 36 W compact fluorescent light at 50 °C under argon atmosphere for 18 h. The ratio of product its isomer is given in parenthesis determined by GC-MS or ¹H NMR analysis of the crude product.

As shown in Scheme 2, a control experiment using a mixture of two different α-aryl allylic alcohols 1a and 1c reacted with 2-bromoacetophenone (2a) under the optimal conditions was conducted to gain some mechanistic insight for the alkylation/1,2-aryl migration protocol. The results demonstrated that no cross aryl-migrating product 3ga was observed, suggesting that the 1,2-aryl migration proceeds via an intramolecular process. Notably, three radical inhibitors (2.5 equiv), TEMPO, hydroquinone and
BHT, were added to the reaction of alcohol $1a$ with 2-bromoacetophenone ($2a$) and resulted in no detectable product $3aa$, implying that this current reaction includes a radical process.

![Scheme 2](image)

**Scheme 2.** Control Experiment.

An off/on light profile over time was also illustrated to understand the mechanism of this photoredox alkylation/1,2-aryl migration insertion (Figure S1 in Supporting Information). The results show that the additional visible light is necessary for the current reaction: the reaction successfully proceeds upon irradiation with light, but the absence of the additional visible light results in no further conversion. These results suggest that the current reaction follows a photoredox mechanism.

Consequently, a possible mechanism outlined in Scheme 3 was proposed on the basis of the above results as well as pervious studies, $8^{-12}$. Initially, the active Ir$^{3+}$ species is irradiated to the excited state Ir$^{3+*}$ species by visible light.$8^{-11}$ Single-electron transfer (SET) between the Ir$^{3+*}$ species and 2-bromoacetophenone ($2a$) readily takes place to form alkyl radical $A$ and the Ir$^{4+}$ species. Subsequently, the addition of alkyl radical $A$ to the C-C double bond of 1,1-diphenylprop-2-en-1-ol ($1a$) leads to new alkyl radical intermediate $B$. Within intermediate $B$, 1,2-migration of aryl group occurs via spiro$^{2,5}$octadienyl radical $C$, giving intermediate $D$.$^{12}$ Finally, intermediate $D$ is oxidized by the Ir$^{4+}$ species to afford the cationic intermediate $E$ and regenerate the active Ir$^{3+}$ species, followed by deprotonation of the cationic intermediate $E$ gives the desired product $3aa$. 
Scheme 3. Possible Mechanism.

Conclusions

In summary, we have illustrated a highly efficient and practical alkylation/1,2-aryl migration of $\alpha$-aryl allylic alcohols with $\alpha$-carbonyl alkyl bromides through the visible-light photoredox catalysis. This new method successfully works with primary, secondary and tertiary $\alpha$-bromoalkyl carbonyl compounds or 2-bromo-2,2-difluoroacetate to produce 1,5-dicarbonyl compounds with different substitution patterns in good yields, which represents the first visible-light-induced alkylarylation of alkenes using the 1,2-aryl migration strategy with the broad substrate scope, excellent selectivity and mild reaction conditions.

Experimental Section

General Considerations:

The $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ solvent on a NMR spectrometer using TMS as internal standard. LRMS was performed on a GC-MS instrument and HRMS was measured on an
electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected.

**Typical Experimental Procedure for Alkylation/1,2-Aryl Migration of α-Aryl Allylic Alcohols with α-Carbonyl Alkyl Bromides Using Visible-Light Photoredox Catalysis:**

To a Schlenk tube were added α-aryl allylic alcohols 1 (0.2 mmol), α-carbonyl alkyl bromides 2 (0.4 mmol), [Ir(ppy)₃] (2 mol %), Ag₂CO₃ (1.2 equiv), and MeCN (2 mL). Then the tube was charged with argon, and was stirred at 50 °C (oil bath temperature) with 36 W compact fluorescent light under argon atmosphere for the indicated time until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted in diethyl ether, and washed with brine. The aqueous phase was re-extracted with diethyl ether. The combined organic extracts were dried over Na₂SO₄ and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products 3.

**1,2,5-Triphenylpentane-1,5-dione (3aa):** 59.0 mg, 90%; White solid; mp 81.1-82.3 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.98 (d, J = 7.2 Hz, 2H), 7.90 (d, J = 7.6 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.47 (m, 5H), 7.29 (d, J = 7.2 Hz, 4H), 7.21 (d, J = 6.8 Hz, 1H), 4.78 (t, J = 6.8 Hz, 1H), 3.05-2.89 (m, 2H), 2.63-2.55 (m, 1H), 2.32-2.24 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 199.9, 199.6, 139.1, 136.7, 136.6, 133.0, 132.9, 129.0, 128.7, 128.5, 128.5, 128.3, 128.0, 127.2, 52.4, 39.5, 28.2; IR (KBr, cm⁻¹): 1686, 1674; LRMS (EI, 70 eV) m/z (%): 329 (M⁺+1, 18), 328 (M⁺, 11), 223 (10), 105 (100); HRMS m/z (ESI) calcd for C₂₃H₂₁O₂ ([M+H]+) 329.1536, found 329.1523.

**1,2-Diphenyl-5-(p-tolyl)pentane-1,5-dione (3ab):** 56.1 mg, 82%; White solid; mp 87.8-88.6 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 7.97 (d, J = 7.2 Hz, 2H), 7.80 (d, J = 7.6 Hz, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 7.2 Hz, 2H), 7.29 (t, J = 8.0 Hz, 4H), 7.21 (d, J = 7.6 Hz, 3H), 4.77 (t, J = 7.2 Hz, 1H), 3.02-2.85 (m, 2H), 2.62-2.54 (m, 1H), 2.38 (s, 3H), 2.31-2.22 (m, 1H); ¹³C NMR (100
5-[(4-Methoxyphenyl)-1,2-diphenylpentane-1,5-dione (3ac): 51.6 mg, 72%; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.97 (d, $J = 7.2$ Hz, 2H), 7.89 (d, $J = 7.6$ Hz, 2H), 7.47 (t, $J = 7.2$ Hz, 1H), 7.37 (t, $J = 7.2$ Hz, 2H), 7.30 (s, 1H), 6.89 (d, $J = 7.6$ Hz, 2H), 4.77 (t, $J = 6.8$ Hz, 1H), 3.84 (s, 3H), 3.00-2.83 (m, 2H), 2.62-2.54 (m, 1H), 2.30-2.22 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 199.7, 199.5, 198.5, 163.4, 139.2, 136.6, 132.9, 130.3, 129.9, 129.0, 128.7, 128.5, 128.3, 127.2, 113.6, 55.4, 52.5, 35.6, 28.5; IR (KBr, cm$^{-1}$): 1686, 1649; LRMS (EI, 70 eV) m/z (%): 359 (M$^{++1}$, 10), 358 (M$^+$, 6), 209 (8), 105 (100); HRMS m/z (ESI) calcd for C$_{24}$H$_{23}$O$_3$ ([M$^+$H$^+$]$^+$) 359.1642, found 359.1655.

5-[(4-Fluorophenyl)-1,2-diphenylpentane-1,5-dione (3ad): 38.7 mg, 56%; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.98-7.91 (m, 4H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.38 (t, $J = 7.6$ Hz, 2H), 7.30-7.27 (m, 4H), 7.24-7.18 (m, 1H), 7.09 (t, $J = 8.6$ Hz, 2H), 4.76 (t, $J = 7.6$ Hz, 1H), 3.02-2.85 (m, 2H), 2.62-2.53 (m, 1H), 2.31-2.23 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 199.5, 198.3, 167.2 (d, $J = 253.1$ Hz), 139.1, 136.6, 133.2, 133.0, 130.7, 129.0, 128.8, 128.5, 128.3, 127.3, 115.6, 52.4, 35.9, 28.3; $^{19}$F NMR (375 MHz, CDCl$_3$) $\delta$: -105.3 (m); IR (KBr, cm$^{-1}$): 1686, 1649; LRMS (EI, 70 eV) m/z (%): 347 (M$^{++1}$, 16), 346 (M$^+$, 14), 209 (8), 105 (100); HRMS m/z (ESI) calcd for C$_{23}$H$_{20}$FO$_2$ ([M$^+$H$^+$]$^+$) 347.1442, found 347.1448.

4-(5-Oxo-4,5-diphenylpentanoyl)benzonitrile (3ae): 40.9 mg, 58%; White solid; mp 101.7-102.5 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.97 (t, $J = 7.2$ Hz, 4H), 7.74 (d, $J = 7.6$ Hz, 2H), 7.49 (t, $J = 7.2$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 2H), 7.29 (s, 1H), 7.22 (s, 1H), 4.74 (t, $J = 7.2$ Hz, 1H), 3.07-2.90 (m, 2H), 2.62-2.55 (m, 1H), 2.33-2.26 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 199.3, 198.5, 139.6, 138.9, 136.4, 133.1, 132.5, 129.2, 128.8, 128.6, 128.4, 128.2, 127.4, 117.9, 116.3, 52.4, 36.4, 28.1; IR
(KBr, cm\textsuperscript{-1}): 1686, 1653; LRMS (EI, 70 eV) m/z (%): 354 (M\textsuperscript{+}+1, 20), 353 (M\textsuperscript{+}, 11), 246 (16), 105 (100); HRMS m/z (ESI) calcd for C\textsubscript{24}H\textsubscript{20}NO\textsubscript{2} ([M+H]\textsuperscript{+}) 354.1488, found 354.1489.

**Ethyl 5-oxo-4,5-diphenylpentanoate (3af):** 56.8 mg, 96%; Yellow oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 7.94 (d, \(J = 7.2\) Hz, 2H), 7.45 (t, \(J = 7.6\) Hz, 1H), 7.36 (t, \(J = 7.6\) Hz, 2H), 7.29-7.25 (m, 4H), 7.23-7.17 (m, 1H), 4.68 (t, \(J = 7.2\) Hz, 1H), 4.13-4.07 (m, 2H), 2.50-2.42 (m, 1H), 2.31-2.73 (m, 2H), 2.21-2.13 (m, 1H), 1.21 (t, \(J = 7.2\) Hz, 3H); 13C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 199.2, 173.2, 138.7, 136.5, 132.9, 129.0, 128.6, 128.4, 128.2, 127.2, 60.3, 52.3, 31.8, 28.7, 14.1; IR (KBr, cm\textsuperscript{-1}): 1708, 1686; LRMS (EI, 70 eV) m/z (%): 297 (M\textsuperscript{+}+1, 19), 296 (M\textsuperscript{+}, 13), 117 (21), 105 (100); HRMS m/z (ESI) calcd for C\textsubscript{19}H\textsubscript{21}O\textsubscript{3} ([M+H]\textsuperscript{+}) 297.1497, found 297.1485.

4-Methyl-1,2-diphenylhexane-1,5-dione (3ag): d.r. = 3:2; 26.9 mg, 48%; Colorless oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 7.97-7.92 (m, 2.0H), 7.48 (t, \(J = 7.2\) Hz, 1.0H), 7.38 (t, \(J = 7.2\) Hz, 2.0H), 7.30-7.21 (m, 5.0H), 4.66-4.61 (m, 1.0H), 2.49-2.39 (m, 1.3H), 2.19 (t, \(J = 6.8\) Hz, 1.0H), 2.13 (s, 1.8H), 2.03 (s, 1.2H), 1.90-1.82 (m, 0.7H), 1.16 (d, \(J = 5.6\) Hz, 1.2H), 1.09 (d, \(J = 6.0\) Hz, 1.8H); 13C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 212.4, 212.3, 199.5, 199.4, 139.2, 138.9, 136.6, 136.5, 133.0 (2C), 129.1, 129.0, 128.7, 128.6, 128.5, 128.3, 128.1, 127.3, 127.2, 51.1, 50.8, 45.1, 44.4, 36.7, 36.2, 28.4, 28.2, 17.2, 16.9; IR (KBr, cm\textsuperscript{-1}): 1686, 1660; LRMS (EI, 70 eV) m/z (%): 381 (M\textsuperscript{+}+1, 8), 380 (M\textsuperscript{+}, 3), 176 (21), 105 (100); HRMS m/z (ESI) calcd for C\textsubscript{19}H\textsubscript{21}O\textsubscript{2} ([M+H]\textsuperscript{+}) 281.1549, found 281.1536.

Methyl 2-methyl-5-oxo-4,5-diphenylpentanoate (3ah): d.r. = 3:2; 41.4 mg, 70%; Yellow oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 7.95 (t, \(J = 6.8\) Hz, 2.0H), 7.47 (d, \(J = 6.8\) Hz, 1.0H), 7.39 (d, \(J = 7.6\) Hz, 2.0H), 6.31 (d, \(J = 10.0\) Hz, 2.0H), 7.28 (s, 4.0H), 7.21 (s, 1.0H), 4.67 (s, 1.0H), 3.67 (s, 1.8H), 3.57 (s, 1.2H), 2.52-2.45 (m, 0.8H), 2.34 (m, 1.2H), 2.16-2.10 (m, 0.4H), 2.02-1.96 (m, 0.6H), 1.21 (d, \(J = 6.8\) Hz, 1.2H), 1.15 (d, \(J = 6.8\) Hz, 1.8H); 13C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 199.2 (2C), 176.8, 176.7, 143.5, 139.1, 138.7, 136.7, 136.4, 132.9, 129.0, 128.7, 128.6, 128.5, 128.4, 128.1 (2C), 127.2 (2C), 126.9, 51.6, 51.5, 51.3, 51.2, 37.9, 37.6, 37.4, 36.9, 18.0, 17.6; IR (KBr, cm\textsuperscript{-1}): 1728, 1686; LRMS (EI, 70 eV) m/z
(%) 297 (M^+1, 16), 296 (M^+, 8), 209 (8), 105 (100); HRMS m/z (ESI) calcd for C_10H_{21}O_3 ([M+H]^+) 297.1497, found 297.1485.

**N,2-Dimethyl-5-oxo-N,4,5-triphenylpentanamide (3ai):** d.r. = 3:1; 54.2 mg, 73%; Colorless oil; \(^1\)H NMR (400 MHz, CDCl_3) \(\delta\): 8.03 (d, \(J = 7.6\) Hz, 1.5H), 7.94 (d, \(J = 7.6\) Hz, 0.5H), 7.49 (t, \(J = 6.8\) Hz, 0.5H), 7.41 (t, \(J = 6.8\) Hz, 1.5H), 7.31-7.24 (m, 4.5H), 7.20 (s, 3.5H), 7.17-7.11 (m, 1.0H), 6.74 (s, 2.0H), 4.82-4.78 (m, 0.8H), 4.63-4.59 (m, 0.3H), 3.25 (s, 2.2H), 3.18 (s, 0.8H), 2.50-2.43 (m, 1.0H), 2.36-2.28 (m, 1.0H), 2.02-1.95 (m, 1.0H), 1.07 (d, \(J = 6.8\) Hz, 0.8H), 0.96 (d, \(J = 6.8\) Hz, 2.3H); \(^{13}\)C NMR (100 MHz, CDCl_3) \(\delta\): 199.9, 199.0, 176.2, 175.7, 143.4, 143.4, 139.4, 138.6, 136.7, 136.5, 136.4, 133.0, 132.8, 129.5, 129.3, 128.8 (2C), 128.7 (2C), 128.5 (2C), 127.9, 127.6, 127.5, 127.2, 127.0, 126.9 (2C), 50.9, 50.6, 38.5 (2C), 37.4, 36.8, 34.7, 34.2, 18.8, 18.5; IR (KBr, cm\(^{-1}\)) 1686, 1640; LRMS (EI, 70 eV) m/z (%): 372 (M^++1, 13), 371 (M^+, 18), 256 (32), 105 (100); HRMS m/z (ESI) calcd for C_{25}H_{26}NO_2 ([M+H]^+) 372.1946, found 372.1958.

**2-Methyl-4,5-diphenyl-1-(piperidin-1-yl)pentane-1,5-dione (3aj):** d.r. = 5:1; 50.3 mg, 72%; White solid; mp 115.1-116.3 °C (uncorrected); \(^1\)H NMR (400 MHz, CDCl_3) \(\delta\): 8.00 (d, \(J = 7.2\) Hz, 2.0H), 7.95 (d, \(J = 7.6\) Hz, 0.4H), 7.46 (t, \(J = 6.8\) Hz, 1.2H), 7.40-7.33 (m, 3.0H), 7.30-7.24 (m, 4.6H), 7.20 (t, \(J = 6.0\) Hz, 1.2H), 4.73 (t, \(J = 4.8\) Hz, 1.2H), 3.67 (t, \(J = 6.8\) Hz, 1.0H), 3.53 (t, \(J = 6.8\) Hz, 1.2H), 3.37 (t, \(J = 7.6\) Hz, 0.2H), 3.22 (d, \(J = 4.8\) Hz, 2.0H), 3.08 (d, \(J = 4.8\) Hz, 0.4H), 2.78-2.73 (m, 0.2H), 2.52-2.46 (m, 2.0H), 2.30-2.14 (m, 0.5H), 1.98 (t, \(J = 8.8\) Hz, 1.0H), 1.63-1.57 (m, 4.4H), 1.43 (s, 2.8H), 1.14 (d, \(J = 6.8\) Hz, 0.6H), 1.08 (d, \(J = 6.0\) Hz, 3.0H); \(^{13}\)C NMR (100 MHz, CDCl_3) \(\delta\): 199.8, 173.8, 139.6, 138.9, 136.5, 133.0, 132.8, 128.8, 128.6, 128.5 (2C), 128.4, 128.1, 127.1, 50.9, 50.7, 46.2, 42.8, 38.7, 37.3, 33.1, 32.7, 26.3, 25.7, 25.5, 24.6, 24.4, 18.1; IR (KBr, cm\(^{-1}\)) 1686, 1651; LRMS (EI, 70 eV) m/z (%): 350 (M^++1, 19), 349 (M^+, 23), 243 (16), 105 (100); HRMS m/z (ESI) calcd for C_{23}H_{26}NO_2 ([M+H]^+) 350.2128, found 350.2115.

**Methyl 2-acetyl-2-ethyl-5-oxo-4,5-diphenylpentanoate (3ak):** d.r. = 2:1; 35.2 mg, 52%; Colorless oil; \(^1\)H NMR (400 MHz, CDCl_3) \(\delta\): 7.90 (d, \(J = 8.4\) Hz, 3.0H), 7.49-7.43 (m, 2.0H), 7.39-7.34 (m, 3.0H),
7.30-7.23 (m, 6.0H), 7.21-7.15 (m, 1.5H), 4.74-4.71 (m, 0.5H), 4.68-4.65 (m, 1.0H), 3.60 (s, 3.0H), 3.41 (s, 1.5H), 2.33-2.19 (m, 3.0H), 2.09 (d, \( J = 4.8 \) Hz, 4.5H), 2.06-1.95 (m, 2.0H), 1.90-1.81 (m, 1.0H), 0.80-0.76 (m, 4.6H); \(^{13}\)C NMR (100 MHz, CDCl \(_3\)) \( \delta \): 206.0, 205.2, 198.9, 198.7, 172.8, 172.7, 140.0, 139.7, 136.4, 132.9, 132.8, 129.1, 129.0, 128.7 (2C), 128.5 (2C), 128.3, 128.2, 127.2, 127.1, 63.3, 63.2, 52.2, 52.1, 49.3, 48.9, 35.1, 34.8, 26.9, 26.8, 26.4, 25.9, 8.4, 8.3; IR (KBr, cm \(^{-1}\)): 1721, 1686, 1668; LRMS (EI, 70 eV) \( m/z \) (%): 353 (M\(^{++}\)+1, 19), 352 (M\(^+\), 14), 248 (18), 105 (100); HRMS \( m/z \) (ESI) calcd for C\(_{14}\)H\(_{18}\)NO\(_3\) ([M+H]\(^+\)) 353.1747, found 353.1742.

Diethyl 2-methyl-2-(3-oxo-2,3-diphenylpropyl)malonate (3al): 61.1 mg, 80%; Colorless oil; \(^1\)H NMR (400 MHz, CDCl \(_3\)) \( \delta \): 7.94 (d, \( J = 7.2 \) Hz, 2H), 7.46 (t, \( J = 7.2 \) Hz, 1H), 7.37 (t, \( J = 7.2 \) Hz, 2H), 7.32-7.24 (m, 4H), 7.19-7.15 (m, 1H), 4.94-4.91 (m, 1H), 4.17-4.11 (m, 2H), 4.10-4.03 (m, 1H), 3.80-3.72 (m, 1H), 3.06-3.00 (m, 1H), 2.31-2.27 (m, 1H), 1.41 (s, 3H), 1.21 (t, \( J = 7.2 \) Hz, 3H), 1.03 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl \(_3\)) \( \delta \): 198.5, 172.3, 171.6, 139.9, 136.3, 132.8, 129.0, 128.7, 128.5, 127.0, 61.3, 61.2, 53.3, 49.6, 39.3, 21.6, 13.94 13.6; IR (KBr, cm \(^{-1}\)): 1726, 1686; LRMS (EI, 70 eV) \( m/z \) (%): 383 (M\(^{++}\)+1, 29), 382 (M\(^+\), 17), 277 (21), 105 (100); HRMS \( m/z \) (ESI) calcd for C\(_{23}\)H\(_{27}\)O\(_5\) ([M+H]\(^+\)) 383.1853, found 383.1865.

Ethyl 2,2-difluoro-5-oxo-4,5-diphenylpentanoate (3am): 58.4 mg, 88%; Colorless oil; \(^1\)H NMR (400 MHz, CDCl \(_3\)) \( \delta \): 7.95 (d, \( J = 7.6 \) Hz, 2H), 7.48 (t, \( J = 7.6 \) Hz, 1H), 7.38 (t, \( J = 7.6 \) Hz, 2H), 7.29-7.25 (m, 4H), 7.22-7.18 (m, 1H), 4.97-4.94 (m, 1H), 4.20-4.12 (m, 1H), 4.09-4.01 (m, 1H), 3.35-3.21 (m, 1H), 2.61-2.47 (m, 1H), 1.21 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl \(_3\)) \( \delta \): 197.3, 163.7 (t, \( J = 32.4 \) Hz), 137.8, 135.8, 133.2, 129.2, 128.8, 128.6, 128.2, 127.6, 115.3 (t, \( J = 249.1 \) Hz), 62.9, 46.8 (t, \( J = 3.85 \) Hz), 38.1 (d, \( J = 23.3 \) Hz, 1C), 13.7; \(^{19}\)F NMR (375 MHz, CDCl \(_3\)) \( \delta \): -104.3 (m), -104.4 (m); IR (KBr, cm \(^{-1}\)): 1770, 1686; LRMS (EI, 70 eV) \( m/z \) (%): 333 (M\(^{++}\)+1, 221), 332 (M\(^+\), 12), 132 (17), 105 (100); HRMS \( m/z \) (ESI) calcd for C\(_{19}\)H\(_{19}\)F\(_2\)O\(_2\) ([M+H]\(^+\)) 333.1297, found 333.1315.

5-Phenyl-1,2-di-p-tolylpentane-1,5-dione (3ba): 35.6 mg, 50%; White solid; mp 97.8-98.5 °C (uncorrected); \(^1\)H NMR (400 MHz, CDCl \(_3\)) \( \delta \): 7.91-7.86 (m, 4H), 7.53 (d, \( J = 7.6 \) Hz, 1H), 7.42 (t, \( J = 8.8 \) Hz, 2H), 7.30-7.25 (m, 1H), 7.15 (t, \( J = 8.8 \) Hz, 2H), 7.00-6.95 (m, 4H), 6.85-6.80 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl \(_3\)) \( \delta \): 197.4, 132.8, 129.2, 128.8, 128.6, 128.2, 127.6, 115.3 (t, \( J = 249.1 \) Hz), 62.9, 46.8 (t, \( J = 3.85 \) Hz), 38.1 (d, \( J = 23.3 \) Hz, 1C), 13.7; \(^{19}\)F NMR (375 MHz, CDCl \(_3\)) \( \delta \): -104.3 (m), -104.4 (m); IR (KBr, cm \(^{-1}\)): 1770, 1686; LRMS (EI, 70 eV) \( m/z \) (%): 333 (M\(^{++}\)+1, 221), 332 (M\(^+\), 12), 132 (17), 105 (100); HRMS \( m/z \) (ESI) calcd for C\(_{19}\)H\(_{19}\)F\(_2\)O\(_2\) ([M+H]\(^+\)) 333.1297, found 333.1315.
7.6 Hz, 2H), 7.19-7.16 (m, 4H), 7.08 (d, J = 8.0 Hz, 2H), 4.70 (t, J = 7.2 Hz, 1H), 3.10-2.85 (m, 2H), 2.60-2.49 (m, 1H), 2.34 (s, 3H), 2.29-2.18 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 200.0, 199.3, 143.6, 136.8, 136.8, 136.3, 134.1, 133.0, 129.7, 129.2, 128.9, 128.5, 128.1, 128.0, 51.9, 36.1, 28.3, 21.6, 21.0; IR (KBr, cm\(^{-1}\)): 1692, 1674; LRMS (EI, 70 eV) \(m/z\) (%): 357 (M\(^{+}+1\), 14), 356 (M\(^+\)), 252 (17), 105 (100); HRMS \(m/z\) (ESI) calcd for C\(_{25}\)H\(_{25}\)O\(_2\) ([M\(^+\)+H\(^+\)]\(^+\)) 357.1873, found 357.1849.

1,2-Bis(4-chlorophenyl)-5-phenylpentane-1,5-dione (3ca): 55.4 mg, 70%; White solid; mp 82.9-83.8 °C (uncorrected); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.89 (d, J = 8.4 Hz, 4H), 7.54 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 7.27-7.20 (m, 4H), 4.74 (t, J = 7.2 Hz, 1H), 3.03-2.90 (m, 2H), 2.60-2.53 (m, 1H), 2.28-2.19 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 199.7, 198.1, 139.6, 137.3, 136.6, 134.6, 133.3, 133.2, 130.1, 129.6, 129.3, 128.9, 128.6, 127.9, 51.5, 35.5, 28.0; IR (KBr, cm\(^{-1}\)): 1708, 1674; LRMS (EI, 70 eV) \(m/z\) (%): 398 (M\(^{+}+2\), 13), 396 (M\(^+\)), 207 (6), 105 (100); HRMS \(m/z\) (ESI) calcd for C\(_{23}\)H\(_{19}\)Cl\(_2\)O\(_2\) ([M\(^+\)+H\(^+\)]\(^+\)) 397.0762, found 397.0751.

1,2-Bis(4-bromophenyl)-5-phenylpentane-1,5-dione (3da): 53.5 mg, 55%; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.89 (d, J = 8.4 Hz, 4H), 7.55 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.28-7.20 (m, 4H), 4.73 (t, J = 7.6 Hz, 1H), 2.98-2.94 (m, 2H), 2.60-2.52 (m, 1H), 2.28-2.19 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 199.7, 198.1, 139.6, 137.3, 136.6, 134.6, 133.3, 133.2, 130.1, 129.6, 129.3, 128.9, 128.6, 127.9, 51.5, 35.5, 28.0; IR (KBr, cm\(^{-1}\)): 1697, 1674; LRMS (EI, 70 eV) \(m/z\) (%): 488 (M\(^{+}+2\), 10), 486 (M\(^+\)), 303 (12), 207 (24), 105 (100); HRMS \(m/z\) (ESI) calcd for C\(_{23}\)H\(_{19}\)Br\(_2\)O\(_2\) ([M\(^+\)+H\(^+\)]\(^+\)) 486.9731, found 486.9745.

2,5-Diphenyl-1-\((\rho\text{-}toly1)\)pentane-1,5-dione (3ea): d.r. = 2:1; 42.4 mg, 62%; White solid; mp 88.3-89.6 °C (uncorrected); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.97 (d, J = 7.6 Hz, 1H), 7.91-7.87 (m, 3H), 7.57-7.50 (m, 1H), 7.48-7.34 (m, 4H), 7.32-7.25 (m, 2H), 7.21-7.16 (m, 2H), 7.08 (d, J = 8.0 Hz, 1H), 4.77-4.71 (m, 1H), 3.05-2.88 (m, 2H), 2.60-2.54 (m, 1H), 2.33 (s, 2H), 2.31-2.22 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 200.0, 199.9, 199.7, 199.2, 143.7, 139.4, 136.8, 136.8, 136.6, 136.0, 134.1, 133.0, 132.8, 129.7, 129.2, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5 (2C), 128.4, 128.3, 128.1, 128.0, 127.1, 126.8,
52.3, 52.0, 36.0, 36.0, 28.3, 28.2, 21.5, 21.0; IR (KBr, cm\(^{-1}\)): 1690, 1674; LRMS (EI, 70 eV) m/z (%): 343 (M\(^{+1}\), 16), 342 (M\(^{+}\), 12), 223 (9), 119 (100); HRMS m/z (ESI) calcd for C\(_{24}\)H\(_{23}\)O\(_2\) ([M+H]\(^{+}\)) 343.1689, found 343.1691.

1-(4-Methoxyphenyl)-2,5-diphenylpentane-1,5-dione (3fa): 58.7 mg, 82%; White solid; mp 84.7-85.5 °C (uncorrected); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.97 (d, \(J = 9.2\) Hz, 2H), 7.90 (d, \(J = 7.6\) Hz, 2H), 7.53 (t, \(J = 7.2\) Hz, 1H), 7.42 (t, \(J = 7.6\) Hz, 2H), 7.32-7.26 (m, 4H), 7.22-7.18 (m, 1H), 6.85 (d, \(J = 8.8\) Hz, 2H), 4.72 (t, \(J = 7.2\) Hz, 1H), 3.80 (s, 3H), 3.05-2.88 (m, 2H), 2.62-2.53 (m, 1H), 2.31-2.22 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 200.0, 198.1, 163.3, 139.6, 136.8, 133.0, 131.1, 129.6, 129.0, 128.5, 128.2, 128.0, 127.1, 113.7, 55.4, 52.0, 36.1, 28.3; IR (KBr, cm\(^{-1}\)): 1692, 1674; LRMS (EI, 70 eV) m/z (%): 359 (M\(^{+2}\), 21), 358 (M\(^{+}\), 16), 135 (100); HRMS m/z (ESI) calcd for C\(_{24}\)H\(_{23}\)O\(_3\) ([M+H]\(^{+}\)) 359.1642, found 359.1651.

2-(4-Chlorophenyl)-1,5-diphenylpentane-1,5-dione (3ga): 50.7 mg, 70%; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.96 (d, \(J = 7.2\) Hz, 2H), 7.89 (d, \(J = 7.2\) Hz, 2H), 7.56-7.48 (m, 2H), 7.45-7.37 (m, 4H), 7.25 (s, 4H), 4.79 (t, \(J = 7.2\) Hz, 1H), 3.04-2.89 (m, 2H), 2.62-2.53 (m, 1H), 2.29-2.20 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 199.7, 199.3, 137.6, 136.8, 136.4, 133.1, 129.7, 129.2, 129.1, 128.8, 128.7, 128.6 (2C), 128.0, 51.5, 35.7, 28.1; IR (KBr, cm\(^{-1}\)): 1691, 1674; LRMS (EI, 70 eV) m/z (%): 364 (M\(^{+2}\), 8), 362 (M\(^{+}\), 21), 224 (8), 105 (100); HRMS m/z (ESI) calcd for C\(_{23}\)H\(_{20}\)ClO\(_2\) ([M+H]\(^{+}\)) 363.1152, found 363.1167.

1,5-Diphenyl-2-(4-(trifluoromethyl)phenyl)pentane-1,5-dione (3ha): 55.4 mg, 70%; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.98 (d, \(J = 7.6\) Hz, 2H), 7.89 (d, \(J = 7.2\) Hz, 2H), 7.56-7.49 (m, 4H), 7.46-7.38 (m, 6H), 4.90 (t, \(J = 7.2\) Hz, 1H), 3.06-2.92 (m, 2H), 2.67-2.58 (m, 1H), 2.33-2.24 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 199.6, 199.0, 143.2, 136.7, 136.3, 133.3, 133.2, 129.5 (q, \(J = 32.3\) Hz), 128.7 (2C), 128.6, 128.0, 125.9 (q, \(J = 3.7\) Hz), 125.3, 122.6, 51.9, 35.7, 28.2; \(^{19}\)F NMR (375 MHz, CDCl\(_3\)) \(\delta\): -62.5; IR (KBr, cm\(^{-1}\)): 1688, 1674; LRMS (EI, 70 eV) m/z (%): 397 (M\(^{+1}\), 13), 396 (M\(^{+}\), 10), 224 (11), 105 (100); HRMS m/z (ESI) calcd for C\(_{24}\)H\(_{20}\)F\(_3\)O\(_4\) ([M+H]\(^{+}\)) 397.1415, found 397.1436.
1,5-Diphenyl-2-(m-tolyl)pentane-1,5-dione (3ia): The $^1$H NMR spectrum of the crude product showed a 1:1 mixture of 3ia and a compound tentatively assigned as 3ia' based on the methyl peak at $\delta$ 2.34 for 3ia and at $\delta$ 2.28 for 3ia'. 35.6 mg, 52%; White solid; mp 92.7-94.1 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.98 (d, $J = 7.2$ Hz, 1.0H), 7.90 (d, $J = 7.6$ Hz, 2.0H), 7.77 (t, $J = 6.4$ Hz, 1.0H), 7.53 (t, $J = 7.2$ Hz, 1.0H), 7.48-7.35 (m, 3.5H), 7.32-7.25 (m, 3.0H), 7.23-7.17 (m, 1.0H), 7.11 (s, 1.0H), 7.01 (d, $J = 7.2$ Hz, 0.5H), 4.79-4.71 (m, 1.0H), 3.05-2.87 (m, 2.0H), 2.63-2.53 (m, 1.0H), 2.31-2.22 (m, 2.5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 200.0, 199.9, 199.8, 199.6, 139.2, 139.0, 138.7, 138.3, 136.8, 136.6, 133.7, 133.0, 132.9, 129.2, 129.0, 128.8 (2C), 128.5 (2C), 128.3 (2C), 128.0, 127.2, 126.0, 125.5, 52.4 (2C), 36.0, 28.3, 21.4, 21.3; IR (KBr, cm$^{-1}$): 1688, 1674; LRMS (EI, 70 eV) m/z (%): 343 (M$^+$+1, 33), 342 (M$^+$, 15), 223 (13), 119 (100); HRMS m/z (ESI) calcd for C$_{24}$H$_{23}$O$_2$ ([M+H]$^+$) 343.1689, found 343.1693.

(1,5-Diphenyl-2-(3-(trifluoromethyl)phenyl)pentane-1,5-dione (3ja): 51.5 mg, 65%; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.98 (d, $J = 7.2$ Hz, 2H), 7.89 (d, $J = 7.2$ Hz, 2H), 7.60 (s, 1H), 7.56-7.48 (m, 4H), 7.45-7.40 (m, 5H), 4.90 (t, $J = 7.2$ Hz, 1H), 3.06-2.90 (m, 2H), 2.67-2.58 (m, 1H), 2.33-2.24 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 199.6, 199.1, 140.1, 136.7, 136.3, 133.3, 133.2, 131.7, 131.5, 131.2, 129.5, 128.7, 128.6, 128.0, 125.1 (q, $J = 3.8$ Hz), 124.2 (q, $J = 3.7$ Hz), 122.5, 51.8, 35.8, 28.4; $^{19}$F NMR (375 MHz, CDCl$_3$) $\delta$: -62.5; IR (KBr, cm$^{-1}$): 1693, 1674; LRMS (EI, 70 eV) m/z (%): 397 (M$^+$+1, 18), 396 (M$^+$, 11), 224 (12), 105 (100); HRMS m/z (ESI) calcd for C$_{24}$H$_{20}$F$_3$O$_4$ ([M+H]$^+$) 397.1415, found 397.1428.

1-(3,4-Dimethylphenyl)-2,5-diphenylpentane-1,5-dione (3ka): The $^1$H NMR spectrum of the crude product showed a 2:1 mixture of 3ka and a compound tentatively assigned as 3ka' based on the methyl peak at $\delta$ 2.16 for 3ka and at $\delta$ 2.10 for 3ka'. 32.8 mg, 46%; White solid; mp 98.4-99.3 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.06 (d, $J = 7.2$ Hz, 0.5H), 7.89 (d, $J = 7.2$ Hz, 1.0H), 7.81 (d, $J = 7.6$ Hz, 2.0H), 7.68 (s, 1.0H), 7.63 (d, $J = 7.6$ Hz, 1.0H), 7.55-7.51 (m, 1.0H), 7.44 (t, $J = 7.2$ Hz, 2.0H), 7.35-7.29 (m, 5.0H), 7.24-7.16 (m, 4.0H), 7.12-7.07 (m, 2.0H), 7.03 (d, $J = 7.6$ Hz, 1.0H), 6.96
(d, J = 7.2 Hz, 1.0H), 4.67 (t, J = 7.2 Hz, 1.0H), 4.61 (t, J = 7.2 Hz, 0.5H), 2.98-2.89 (m, 2.0H), 2.86-2.79 (m, 2.0H), 2.54-2.45 (m, 2.0H), 2.16 (d, J = 2.0 Hz, 6.0H), 2.10 (d, J = 3.6 Hz, 3.0H); 13C NMR (100 MHz, CDCl3) δ: 200.0 (2C), 199.7, 199.4, 142.5, 139.5, 136.8 (2C), 136.4, 134.5, 133.0, 132.8, 130.2, 129.9 (2C), 129.7, 129.3, 128.9 (2C), 128.8, 128.5 (2C), 128.4, 128.2, 128.0, 127.8, 127.1, 126.8, 126.5, 125.8, 52.2, 52.0, 48.2, 36.1, 34.3, 29.7, 28.3, 19.9, 19.7, 19.3; IR (KBr, cm−1): 1696, 1674; LRMS (EI, 70 eV) m/z (%): 357 (M++1, 19), 356 (M+, 10), 223 (3), 133 (100); HRMS m/z (ESI) calcd for C25H25O2 ([M+H]+) 357.1873, found 357.1861.

2-(3,4-Dichlorophenyl)-1,5-diphenylpentane-1,5-dione (3la): 64.9 mg, 82%; White solid; mp 84.1-85.3 °C (uncorrected); 1H NMR (400 MHz, CDCl3) δ: 7.96 (d, J = 7.2 Hz, 2H), 7.89 (d, J = 7.2 Hz, 2H), 7.56-7.50 (m, 2H), 7.45-7.39 (m, 5H), 7.35 (d, J = 8.0 Hz, 1H), 7.18-7.15 (m, 1H), 4.80 (t, J = 7.6 Hz, 1H), 3.05-2.90 (m, 2H), 2.62-2.54 (m, 1H), 2.28-2.20 (m, 1H); 13C NMR (100 MHz, CDCl3) δ: 199.5, 198.8, 139.3, 136.6, 136.1, 133.4, 133.2, 133.0, 131.4, 130.9, 130.2, 128.7, 128.6, 127.9, 127.7, 51.1, 35.6, 28.1; IR (KBr, cm−1): 1694, 1674; LRMS (EI, 70 eV) m/z (%): 398 (M++2, 10), 396 (M+, 15), 264 (8), 173 (100); HRMS m/z (ESI) calcd for C23H19Cl2O2 ([M+H]+) 397.0762, found 397.0769.

2,5-Diphenyl-1-(o-tolyl)pentane-1,5-dione (3ma): 51.3 mg, 75%; White solid; mp 90.6-91.8 °C (uncorrected); 1H NMR (400 MHz, CDCl3) δ: 7.89 (d, J = 7.2 Hz, 2H), 7.58-7.51 (m, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.28-7.22 (m, 5H), 7.21-7.12 (m, 3H), 4.61 (t, J = 7.6 Hz, 1H), 3.05-2.90 (m, 2H), 2.66-2.57 (m, 1H), 2.33-2.25 (m, 4H); 13C NMR (100 MHz, CDCl3) δ: 203.7, 199.8, 138.5, 138.2, 137.9, 136.8, 133.0, 131.6, 130.9, 128.9, 128.5, 128.4, 128.0, 127.2, 125.4, 55.4, 35.9, 27.5, 20.7; IR (KBr, cm−1): 1710, 1674; LRMS (EI, 70 eV) m/z (%): 343 (M++1, 13), 342 (M+, 8), 223(7), 119 (100); HRMS m/z (ESI) calcd for C24H23O2 ([M+H]+) 343.1689, found 343.1695.

1-(2-Chlorophenyl)-2,5-diphenylpentane-1,5-dione (3na): 59.4 mg, 82%; Colorless oil; 1H NMR (400 MHz, CDCl3) δ: 7.90 (d, J = 7.6 Hz, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 8.0 Hz, 2H), 7.32-7.20 (m, 7H), 7.15-7.08 (m, 2H), 4.59 (t, J = 7.6 Hz, 1H), 3.09-2.95 (m, 2H), 2.70-2.61 (m, 1H),
2.36-2.27 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 203.0, 199.7, 139.4, 137.3, 136.7, 133.0, 131.1, 130.4, 130.1, 128.9 (2C), 128.7, 128.5, 128.0, 127.5, 126.5, 56.8, 35.9, 26.9; IR (KBr, cm\(^{-1}\)): 1704, 1674; LRMS (EI, 70 eV) \(m/z\) (%): 364 (M\(^{++}\)2, 5), 362 (M\(^+\), 14), 223 (53), 105 (100); HRMS \(m/z\) (ESI) calcd for C\textsubscript{23}H\textsubscript{20}ClO\textsubscript{2} ([M+H]\(^+\)) 363.1152, found 363.1171.

2,5-Diphenyl-1-(2-(trifluoromethyl)phenyl)pentane-1,5-dione (3oa): 43.6 mg, 55%; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 7.81 (d, \(J = 7.6\) Hz, 2H), 7.58 (d, \(J = 7.6\) Hz, 1H), 7.46 (t, \(J = 7.6\) Hz, 1H), 7.40-7.30 (m, 4H), 7.23-7.12 (m, 5H), 6.99 (d, \(J = 7.6\) Hz, 1H), 4.33 (t, \(J = 7.6\) Hz, 1H), 2.98-2.81 (m, 2H), 2.61-2.52 (m, 1H), 2.30-2.21 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 203.4, 199.7, 139.6 (q, \(J = 1.8\) Hz), 137.1, 136.8, 133.0, 131.4, 129.9, 129.0, 128.8, 128.5, 128.2, 127.9, 127.7, 126.6 (q, \(J = 5.0\) Hz), 125.0, 122.3, 57.5, 35.6, 26.8; \(^{19}\)F NMR (375 MHz, CDCl\textsubscript{3}) \(\delta\): -57.7; IR (KBr, cm\(^{-1}\)): 1688, 1674; LRMS (EI, 70 eV) \(m/z\) (%): 397 (M\(^++\)1, 21), 396 (M\(^+\), 14), 223 (49), 105 (100); HRMS \(m/z\) (ESI) calcd for C\textsubscript{24}H\textsubscript{20}F\textsubscript{3}O\textsubscript{4} ([M+H]\(^+\)) 397.1415, found 397.1432.

1-(2,5-Difluorophenyl)-2,5-diphenylpentane-1,5-dione (3pa): The \(^1\)H NMR spectrum of the crude product showed a 3:2 mixture of 3pa and a compound tentatively assigned as 3pa’ based on the methine peak at \(\delta\) 5.13 for 3pa and at \(\delta\) 4.63 for 3pa’. 58.2 mg, 80%; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 7.99 (d, \(J = 7.6\) Hz, 1.2H), 7.92-7.88 (m, 2.0H), 7.56-7.50 (m, 1.6H), 7.44-7.42 (m, 3.6H), 7.30-7.20 (m, 2.0H), 7.12-7.07 (m, 0.4H), 7.04-6.96 (m, 1.6H), 6.90-6.84 (m, 1.6H), 5.13 (t, \(J = 7.2\) Hz, 0.6H), 4.63 (t, \(J = 7.6\) Hz, 0.4H), 3.10-2.88 (m, 2.0H), 2.64-2.56 (m, 1.0H), 2.29-2.19 (m, 1.0H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 199.6, 199.2, 198.5 (2C), 137.6, 136.7 (2C), 135.9, 133.4, 133.1, 133.0, 128.9, 128.7, 128.6 (2C), 128.5, 128.0 (2C), 127.5, 121.0, 120.9, 120.8, 120.7, 118.2, 118.1, 117.9 (2C), 117.1, 117.0, 116.9, 116.8, 116.7, 116.6, 115.7 (2C), 115.6 (2C), 115.4 (4C), 56.5, 56.4, 43.7, 36.0, 35.7, 27.7, 27.2.; \(^{19}\)F NMR (375 MHz, CDCl\textsubscript{3}) \(\delta\): -115.3 (d, \(J = 18.4\) Hz, 1F), -117.3 (d, \(J = 17.6\) Hz, 1F), -117.6 (d, \(J = 18.8\) Hz, 1F), -124.1 (d, \(J = 28.9\) Hz, 1F); IR (KBr, cm\(^{-1}\)): 1710, 1674; LRMS (EI, 70 eV) \(m/z\) (%): 365 (M\(^++\)1, 16), 364 (M\(^+\), 9), 224 (11), 105 (100); HRMS \(m/z\) (ESI) calcd for C\textsubscript{23}H\textsubscript{19}F\textsubscript{2}O\textsubscript{2} ([M+H]\(^+\)) 365.1353, found 365.1369.
1-(2-Chlorophenyl)-2-(4-chlorophenyl)-5-phenylpentane-1,5-dione (3qa): 57.0 mg, 72%; White solid; mp 85.5-86.4 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.90 (d, $J = 7.2$ Hz, 2H), 7.55 (t, $J = 7.6$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.34-7.28 (m, 2H), 7.27-7.23 (m, 2H), 7.20-7.11 (m, 4H), 4.61 (t, $J = 7.6$ Hz, 1H), 3.07-2.95 (m, 2H), 2.68-2.59 (m, 1H), 2.32-2.23 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 202.6, 199.5, 139.2, 136.7, 135.9, 133.4, 133.1, 131.4, 130.4, 130.3, 130.0, 129.1, 128.9, 128.6, 127.9, 126.7, 56.0, 35.7, 26.9; IR (KBr, cm$^{-1}$): 1782, 1674; LRMS (EI, 70 eV) m/z (%): 398 (M$^+$+2, 7), 396 (M$^+$, 10), 257 (30), 139 (100); HRMS m/z (ESI) calcd for C$_{23}$H$_{19}$Cl$_2$O$_2$ ([M$^+$+H]$^+$) 397.0762, found 397.0777.

2-(Naphthalen-1-yl)-1,5-diphenylpentane-1,5-dione (3ra): 43.8 mg, 58%; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.01 (d, $J = 8.0$ Hz, 2H), 7.88 (d, $J = 7.2$ Hz, 2H), 7.80-7.74 (m, 4H), 7.53-7.33 (m, 9H), 4.95 (t, $J = 7.2$ Hz, 1H), 3.08-2.92 (m, 2H), 2.72-2.63 (m, 1H), 2.43-2.34 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 199.9, 199.6, 136.7, 136.6 (2C), 133.6, 133.0, 132.9, 132.5, 128.9, 128.8, 128.5 (2C), 128.0, 127.7, 127.6, 127.2, 126.2, 125.9, 52.5, 35.9, 28.2; IR (KBr, cm$^{-1}$): 1710, 1674; LRMS (EI, 70 eV) m/z (%): 379 (M$^+$+1, 22), 378 (M$^+$, 12), 258 (11), 105 (100); HRMS m/z (ESI) calcd for C$_{27}$H$_{23}$O$_3$ ([M$^+$+H]$^+$) 379.1711, found 379.1693.

1,5-Diphenyl-2-(thiophen-2-yl)pentane-1,5-dione (3sa): 56.8 mg, 85%; Red solid; mp 75.4-76.2 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.06 (d, $J = 7.2$ Hz, 2H), 7.90 (d, $J = 7.2$ Hz, 2H), 7.56-7.51 (m, 2H), 7.45-7.41 (m, 4H), 7.19-7.18 (m, 1H), 6.90-6.89 (m, 2H), 5.15 (t, $J = 7.6$ Hz, 1H), 3.09-2.94 (m, 2H), 2.65-2.56 (m, 1H), 2.36-2.28 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 199.7, 198.7, 141.1, 136.7, 136.0, 133.2, 133.1, 128.8, 128.6, 128.5, 128.0, 126.9, 126.0, 125.2, 46.7, 35.5, 29.0; IR (KBr, cm$^{-1}$): 1678, 1674; LRMS (EI, 70 eV) m/z (%): 335 (M$^+$+1, 32), 334 (M$^+$, 12), 229 (32), 105 (100); HRMS m/z (ESI) calcd for C$_{21}$H$_{19}$O$_2$S ([M$^+$+H]$^+$) 335.1113, found 335.1100.

1,4-Diphenylhexane-1,5-dione (3ta): 39.9 mg, 75%; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.89-7.87 (m, 2H), 7.56-7.52 (m, 1H), 7.45-7.41 (m, 2H), 7.36-7.32 (m, 2H), 7.30-7.28 (m, 1H), 7.21 (d, $J = 6.8$ Hz, 2H), 3.81 (t, $J = 7.6$ Hz, 1H), 2.96-2.81 (m, 2H), 2.50-2.41 (m, 1H), 2.16-2.11 (m, 1H), 2.07
(s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 208.1, 199.8, 138.4, 136.7, 133.1, 129.1, 128.6, 128.3, 128.0, 127.5, 58.4, 35.8, 29.1, 26.3; IR (KBr, cm$^{-1}$): 1674, 1652; LRMS (EI, 70 eV) m/z (%): 267 (M$^+$+1, 17), 266 (M$^+$, 8), 206 (11), 105 (100); HRMS m/z (ESI) calcd for C$_{18}$H$_{19}$O$_2$ ([M$^+$+H]$^+$) 267.1385, found 267.1393.

**Methyl 5-(2-chlorophenyl)-2-methyl-5-oxo-4-phenylpentanoate (3nh):** d.r. = 1:1; 49.5 mg, 75%; Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.32 (d, $J$ = 7.6 Hz, 1.0H), 7.28-7.21 (m, 4.0H), 7.19-7.10 (m, 3.0H), 7.10-7.06 (m, 1.0H), 4.52-4.48 (m, 1.0H), 3.67 (s, 1.5H), 3.60 (s, 1.5H), 2.57-2.46 (m, 1.0H), 2.38-2.20 (m, 1.6H), 2.07-2.00 (m, 0.6H), 1.22 (d, $J$ = 6.8 Hz, 1.5H); 13C NMR (100 MHz, CDCl$_3$) $\delta$: 202.6 (2C), 176.7, 176.5, 139.4, 139.3, 137.0, 136.9, 131.2, 131.1, 130.4 (2C), 130.2, 130.1, 128.9, 128.8 (2C), 128.6, 127.5 (2C), 126.5 (2C), 55.7, 55.6, 51.6, 51.5, 37.4, 36.8, 36.0, 35.9, 18.0, 17.4; IR (KBr, cm$^{-1}$): 1711, 1704; LRMS (EI, 70 eV) m/z (%): 332 (M$^+$+2, 6), 332 (M$^+$, 16), 236 (10), 139 (100); HRMS m/z (ESI) calcd for C$_{19}$H$_{20}$ClO$_3$ ([M$^+$+H]$^+$) 331.1101, found 331.1109.

**Diethyl 2-(3-(2-chlorophenyl)-3-oxo-2-phenylpropyl)-2-methylmalonate (3nl):** 70.7 mg, 85%; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.30-7.25 (m, 3H), 7.22 (t, $J$ = 6.4 Hz, 1H), 4.66 (t, $J$ = 6.0 Hz, 1H), 4.14-4.09 (m, 2H), 4.06-3.98 (m, 1H), 3.87-3.79 (m, 1H), 3.05-2.99 (m, 1H), 2.45-2.40 (m, 1H), 1.43 (s, 3H), 1.22 (t, $J$ = 7.2 Hz, 3H), 1.14 (t, $J$ = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl$_3$) $\delta$: 200.8, 172.2, 171.7, 138.7, 137.6, 131.3, 130.9, 130.3, 129.1, 128.9, 128.7, 127.4, 126.4, 61.3, 61.2, 53.7, 53.0, 37.1, 21.1, 13.9, 13.8; IR (KBr, cm$^{-1}$): 1726, 1704; LRMS (EI, 70 eV) m/z (%): 418 (M$^+$+2, 5), 416 (M$^+$, 13), 177 (14), 139 (100); HRMS m/z (ESI) calcd for C$_{23}$H$_{26}$ClO$_5$([M+H]$^+$) 417.1469, found 417.1684.

**Ethyl 5-(2-chlorophenyl)-2,2-difluoro-5-oxo-4-phenylpentanoate (3nm):** 60.0 mg, 82%; Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.32-7.27 (m, 2H), 7.25-7.21 (m, 4H), 7.19-7.15 (m, 3H), 4.80 (t, $J$ = 6.4 Hz, 1H), 4.16-4.07 (m, 2H), 3.33-3.19 (m, 1H), 2.69-2.55 (m, 1H), 1.25 (t, $J$ = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl$_3$) $\delta$: 199.7, 163.7 (t, $J$ = 32.4 Hz), 138.2, 135.8, 131.6, 130.9, 130.4, 129.1, 129.0, 128.7, 127.9, 126.5, 115.3 (t, $J$ = 249.2 Hz), 62.9, 51.0 (t, $J$ = 3.8 Hz), 36.6 (t, $J$ = 23.5 Hz), 13.7; $^{19}$F
NMR (375 MHz, CDCl₃) δ: -103.4 (d, J = 258.8 Hz), -104.0 (d, J = 258.8 Hz); IR (KBr, cm⁻¹): 1770, 1704; LRMS (EI, 70 eV) m/z (%): 368 (M⁺+2, 7), 366 (M⁺, 21), 165 (15), 139 (100); HRMS m/z (ESI) calcd for C₁₉H₁₈ClF₂O₃ ([M⁺+H]⁺) 367.0913, found 367.0927.

Acknowledgments. We thank the Natural Science Foundation of China (No. 21172060), Specialized Research Fund for the Doctoral Program of Higher Education (No. 20120161110041), and Hunan Provincial Natural Science Foundation of China (No. 13JJ2018) for financial support.

Supporting Information Available: Copies of ¹H and ¹³C spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References and notes


reported a mild photocatalytic process for selective arylalkylation of allylic alcohols with α-bromo
diethyl malonate via unique 1,2-arylmigration using fac-Ir(ppy)₃ (0.005 mmol) with a 1W blue
LEDs; however, the reaction required a longer reaction time (143 h) and was limited to only
α-bromo diethyl malonates: (p) H.-L. Huang, H. Yan, C. Yang and W. Xia, Chem. Commun., 2015,
51, 4910.