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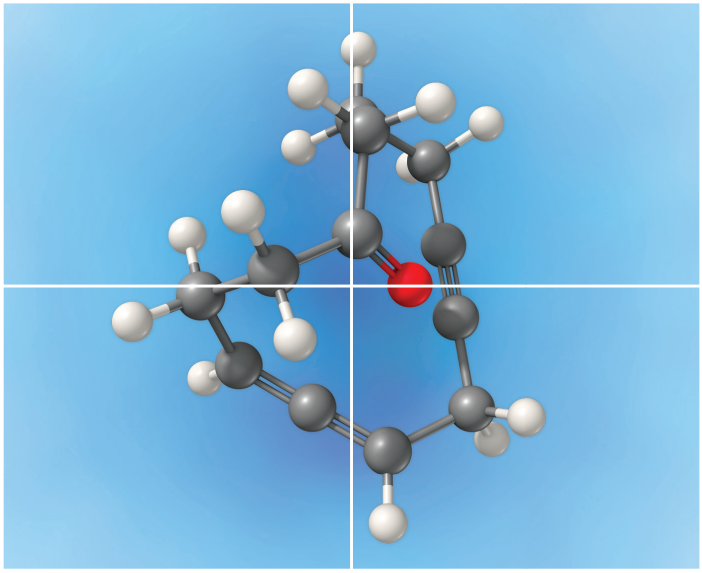

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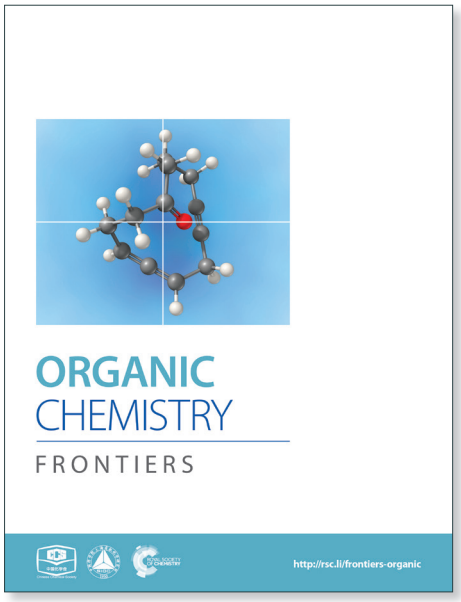

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Alkylation/1,2-Aryl Migration of α-Aryl Allylic Alcohols with α-Carbonyl Alkyl Bromides Using Visible-Light Photoredox Catalysis

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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.

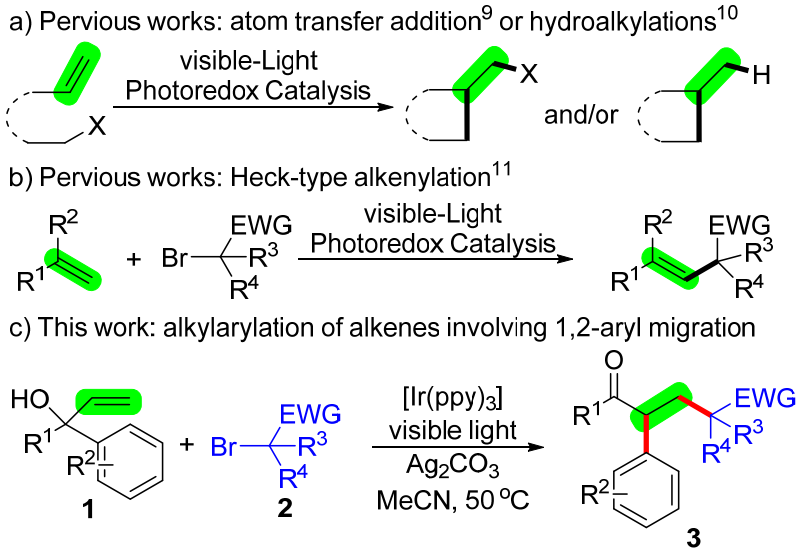
Introduction

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.[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[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.[3-5,7] Liu group has first reported the alkylarylation of activated alkenes with aryl C(sp^2)-H bonds and alkyl C(sp^3)-H bonds adjacent to a CN group in the presence of Pd(II) catalysts and hypervalent iodine reagents to assemble CN-containing oxindoles.[3] Later, our group illustrated an oxidative alkylarylation of activated alkenes with aryl C(sp^2)-H bonds and alkyl C(sp^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.[4] The group of Liu[5a], the group of Cheng[5b] and our groups[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 (α,α-diaryl allylic alcohols) with alkyl C(sp^3)-H bonds adjacent to an oxygen atom through intramolecular 1,2-aryl migration.[6] A Pd-catalyzed oxidative Heck-type insertion strategy for the alkylarylation of activated alkenes with aryl C(sp^2)-H bonds and α-C(sp^3)-Br bonds in α-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^2)-H functionalization to access oxindoles and related heterocycles.[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.[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),[9] hydroalkylation (Scheme 1a)[10] and alkenylation (Scheme 1b)[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).[12] 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.



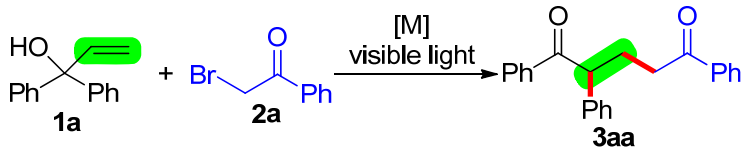
Scheme 1. Functionalization of Alkenes with Alkyl Halides Using Visible-Light Photocatalysis.

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)$_3$Cl$_2$] and Eosin (entries 1-3). In the presence of 2 mol % [Ir(ppy)$_3$], 1.2 equiv Ag_2CO_3 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 Ag_2CO_3, Ag_2O, AgOAc, Na_2CO_3 and NaOH, improved the reaction, and using 1.2 equiv Ag_2CO_3 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 ^oC 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[a]



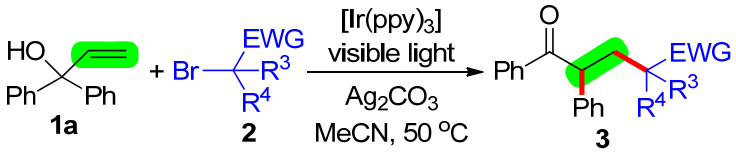
Entry	[M] (mol %)	Base (equiv)	Solvent	T (^oC)	Yield (%)
1	$[Ir(ppy)_3]$ (2)	Ag_2CO_3 (1.2)	MeCN	50	90
2	$[Ru(bpy)_3Cl_2]$ (2)	Ag_2CO_3 (1.2)	MeCN	50	8
3	Eosin Y (2)	Ag_2CO_3 (1.2)	MeCN	50	5
4	—	Ag_2CO_3 (1.2)	MeCN	50	0
5	$[Ir(ppy)_3]$ (5)	Ag_2CO_3 (1.2)	MeCN	50	91
6[b]	$[Ir(ppy)_3]$ (2)	Ag_2CO_3 (1.2)	MeCN	50	55
7[c]	$[Ir(ppy)_3]$ (2)	Ag_2CO_3 (1.2)	MeCN	50	0
8	$[Ir(ppy)_3]$ (2)	—	MeCN	50	23
9	$[Ir(ppy)_3]$ (2)	Ag_2CO_3 (2)	MeCN	50	90
10	$[Ir(ppy)_3]$ (2)	Ag_2CO_3 (1)	MeCN	50	85
11	$[Ir(ppy)_3]$ (2)	Ag_2O (1.2)	MeCN	50	52
12	$[Ir(ppy)_3]$ (2)	AgOAc (1.2)	MeCN	50	62
13	$[Ir(ppy)_3]$ (2)	Na_2CO_3 (1.2)	MeCN	50	75
14	$[Ir(ppy)_3]$ (2)	NaOH (1.2)	MeCN	50	35
15	$[Ir(ppy)_3]$ (2)	Ag_2CO_3 (1.2)	MeCN	rt	60
16	$[Ir(ppy)_3]$ (2)	Ag_2CO_3 (1.2)	MeCN	80	45
17	$[Ir(ppy)_3]$ (2)	Ag_2CO_3 (1.2)	toluene	50	50
18	$[Ir(ppy)_3]$ (2)	Ag_2CO_3 (1.2)	DMF	50	13
19[d]	$[Ir(ppy)_3]$ (2)	Ag_2CO_3 (1.2)	MeCN	50	92

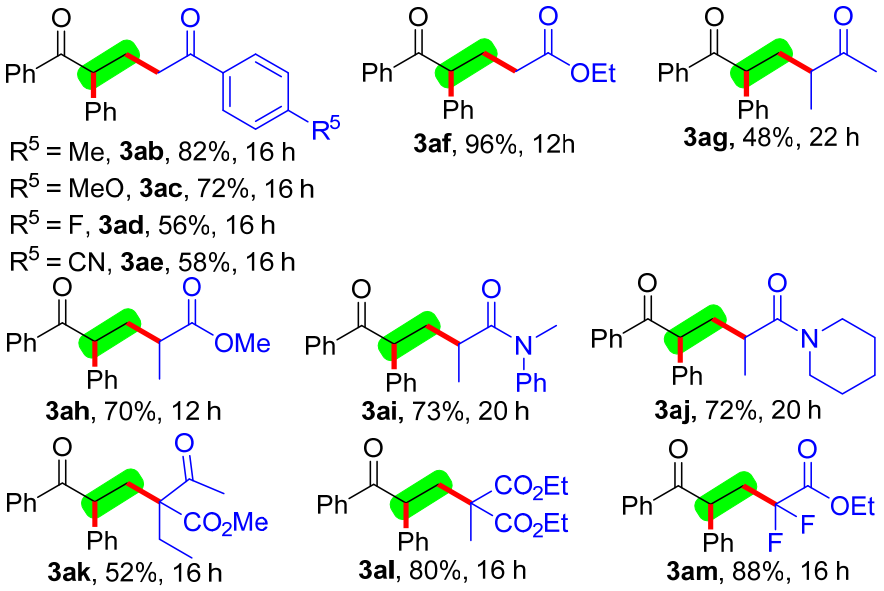
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [M], base and solvent (2 mL) with 36 W compact fluorescent light under argon atmosphere for 16 h. [b] 5 W blue LED light instead of 36 W compact

fluorescent light. [c] Without additional light. [d] **1a** (1 g, 4.76 mmol) for 72 h.

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)$_3$], Ag_2CO_3 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**)[a]





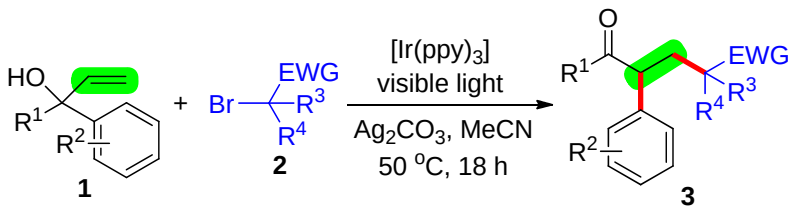
[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), [Ir(ppy)$_3$] (2 mol %), Ag_2CO_3 (1.2 equiv) and MeCN (2 mL) with 36 W compact fluorescent light at 50 ^oC under argon atmosphere.

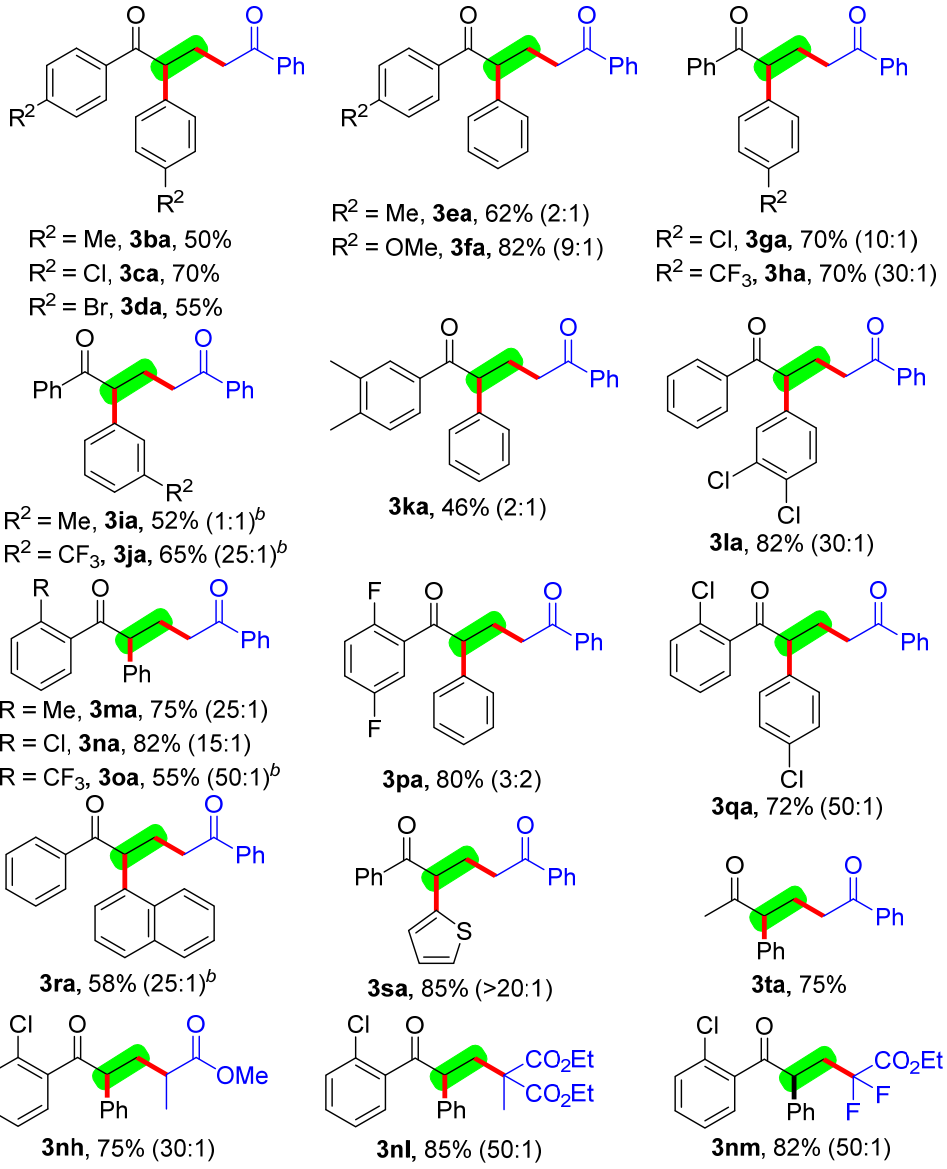
We next set out to apply the optimal conditions to the alkylation/1,2-aryl migration of various α-aryl allylic alcohols **1** with 2-bromoacetophenone (**2a**), methyl 2-bromopropanoate (**2h**), diethyl 2-bromo-2-methylmalonate (**2l**) or 2-bromo-2,2-difluoroacetate (**2m**) (Table 3). In the presence of 2-bromoacetophenone (**2a**), [Ir(ppy)$_3$], Ag_2CO_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-CF_3Ph 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**)[a]

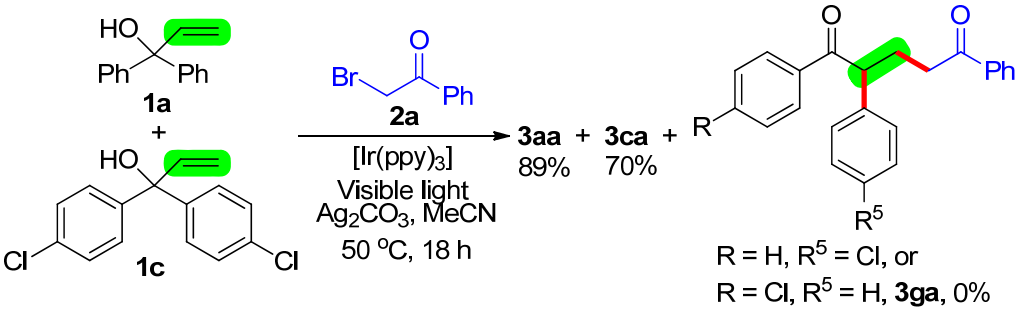




[a] Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), $[Ir(ppy)_3]$ (2 mol %), Ag_2CO_3 (1.2 equiv) and MeCN (2 mL) with 36 W compact fluorescent light at 50 °C under argon atmosphere for 18 h. The ratio of product **3**/its isomer is given in parenthesis determined by GC-MS or ^{1}H NMR analysis of the crude product. [b] For 24 h.

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

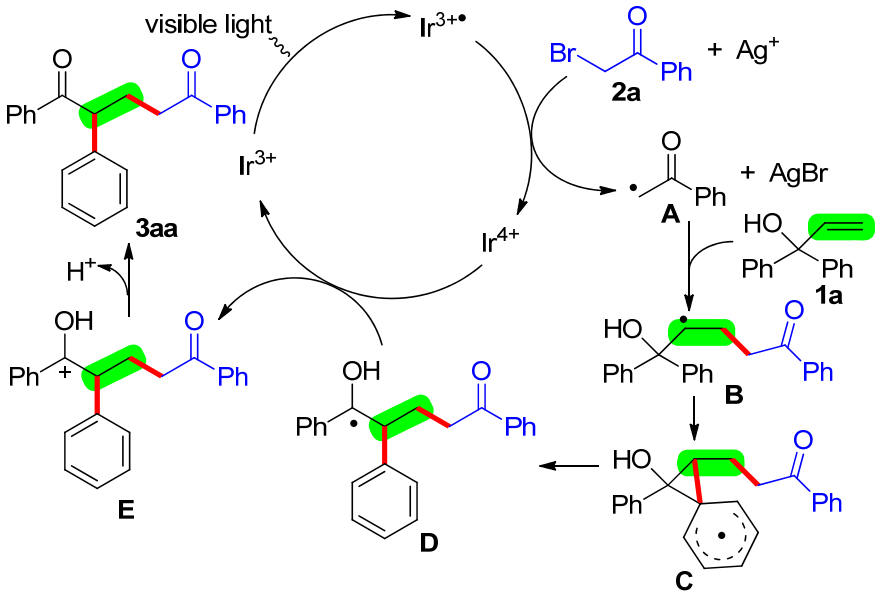
BHT, were added to the reaction of alcohol **1a** with 2-bromoacetophenone (**2a**) and resulted in no detectable product **3aa**, implying that this current reaction includes a radical process.



Scheme 2. 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 α-aryl allylic alcohols with α-carbonyl alkyl bromides through the visible-light photoredox catalysis. This new method successfully works with primary, secondary and tertiary α-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 %), Ag_2CO_3 (1.2 equiv), and MeCN (2 mL). Then the tube was charged with argon, and was stirred at 50 ^oC (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 Na_2SO_4 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 ^oC (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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, 35.9, 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 $C_{23}H_{21}O_2$ ($[M+H]^+$) 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 ^oC (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100

MHz, $CDCl_3$) δ: 199.7, 199.6, 143.8, 139.1, 136.6, 134.3, 132.9, 129.2, 129.0, 128.7, 128.5, 128.3, 128.1, 127.2, 52.4, 35.8, 28.3, 21.6; IR (KBr, cm^{-1}): 1686, 1665; LRMS (EI, 70 eV) *m/z* (%): 343 (M^++1, 8), 342 (M^+, 13), 238 (26), 105 (100); HRMS *m/z* (ESI) calcd for $C_{24}H_{23}O_2$ ($[M+H]^+$) 343.1693, found 343.1699.

5-(4-Methoxyphenyl)-1,2-diphenylpentane-1,5-dione (3ac): 51.6 mg, 72%; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 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, 4H), 7.20 (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, $CDCl_3$) δ: 199.7, 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), 207 (10), 150 (31), 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; ^1H NMR (400 MHz, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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, $CDCl_3$) δ: -105.3 (m); IR (KBr, cm^{-1}): 1686, 1660; 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); ^1H NMR (400 MHz, $CDCl_3$) δ: 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, 4H), 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, $CDCl_3$) δ: 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^{-1}): 1686, 1653; LRMS (EI, 70 eV) *m/z* (%): 354 (M^++1, 20), 353 (M^+, 11), 246 (16), 105 (100); HRMS *m/z* (ESI) calcd for $C_{24}H_{20}NO_2$ ($[M+H]^+$) 354.1488, found 354.1489.

Ethyl 5-oxo-4,5-diphenylpentanoate (3af): 56.8 mg, 96%; Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 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^{-1}): 1708, 1686; LRMS (EI, 70 eV) *m/z* (%): 297 (M^++1, 19), 296 (M^+, 13), 117 (21), 105 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{21}O_3$ ($[M+H]^+$) 297.1497, found 297.1485.

4-Methyl-1,2-diphenylhexane-1,5-dione (3ag): d.r. = 3:2; 26.9 mg, 48%; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 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, 128.7, 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^{-1}): 1686, 1660; LRMS (EI, 70 eV) *m/z* (%): 381 (M^++1, 8), 380 (M^+, 3), 176 (21), 105 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{21}O_2$ ($[M+H]^+$) 281.1549, found 281.1536.

Methyl 2-methyl-5-oxo-4,5-diphenylpentanoate (3ah): d.r. = 3:2; 41.4 mg, 70%; Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 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^{-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 $C_{19}H_{21}O_3$ ([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, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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 $C_{23}H_{28}NO_2$ ([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, $CDCl_3$) δ: 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), 7.21-71.5 (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, $CDCl_3$) δ: 206.0, 205.2, 198.9, 198.7, 172.8, 172.7, 140.0, 139.7, 136.6, 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, $CDCl_3$) δ: 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), 7.19-71.5 (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, $CDCl_3$) δ: 198.5, 172.3, 171.6, 139.9, 136.3, 132.8, 129.0, 128.7, 128.5, 128.1, 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, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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 (J = 23.3 Hz, 1C), 13.7; ^{19}F NMR (375 MHz, $CDCl_3$) δ: -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 $C_{19}H_{19}F_2O_2$ ($[M+H]^+$) 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 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91-7.86 (m, 4H), 7.53 (d, J = 7.6 Hz, 1H), 7.42 (t, J =

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, $CDCl_3$) δ: 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^+, 21), 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 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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^+, 18), 207 (6), 105 (100); HRMS *m/z* (ESI) calcd for $C_{23}H_{19}Cl_2O_2$ ($[M+H]^+$) 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, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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^+, 19), 303 (12), 207 (24), 105 (100); HRMS *m/z* (ESI) calcd for $C_{23}H_{19}Br_2O_2$ ($[M+H]^+$) 486.9731, found 486.9745.

2,5-Diphenyl-1-(*p*-tolyl)pentane-1,5-dione (3ea): d.r. = 2:1; 42.4 mg, 62%; White solid; mp 88.3-89.6 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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 ^oC (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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^++1, 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; ^1H NMR (400 MHz, $CDCl_3$) δ: 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, $CDCl_3$) δ: 199.7, 199.3, 137.6, 136.7, 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; ^1H NMR (400 MHz, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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, $CDCl_3$) δ: -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 $C_{24}H_{20}F_3O_4$ ($[M+H]^+$) 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 acompound tentatively assigned as **3ia'** based on the methyl peak at δ 2.34 for **3ia** and at δ 2.28 for **3ia'**. 35.6 mg, 52%; White solid; mp 92.7-94.1 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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, $CDCl_3$) δ: -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 $C_{24}H_{20}F_3O_4$ ($[M+H]^+$) 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 acompound tentatively assigned as **3ka'** based on the methyl peak at δ 2.16 for **3ka** and at δ 2.10 for **3ka'**. 32.8 mg, 46%; White solid; mp 98.4-99.3 ^{o}C (uncorrected);^{1}H NMR (400 MHz, $CDCl_3$) δ: 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{25}H_{25}O_2$ ($[M+H]^+$) 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); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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, 128.7, 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 $C_{23}H_{19}Cl_2O_2$ ($[M+H]^+$) 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); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, J = 7.2 Hz, 2H), 7.58-7.51 (m, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.28-7.22 (m, 5H), 7.21-7.12 (m, 3H), 4.61 (t, J = 7.6 Hz, 1H), 3.05-2.89 (m, 2H), 2.66-2.57 (m, 1H), 2.33-2.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{24}H_{23}O_2$ ($[M+H]^+$) 343.1689, found 343.1695.

1-(2-Chlorophenyl)-2,5-diphenylpentane-1,5-dione (3na): 59.4 mg, 82%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) 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, $CDCl_3$) δ: 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 $C_{23}H_{20}ClO_2$ ($[M+H]^+$) 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, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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, $CDCl_3$) δ: -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 $C_{24}H_{20}F_3O_4$ ($[M+H]^+$) 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 acompound tentatively assigned as **3pa'** based on the methine peak at δ 5.13 for **3pa** and at δ 4.63 for **3pa'**. 58.2 mg, 80%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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, $CDCl_3$) δ: -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 $C_{23}H_{19}F_2O_2$ ($[M+H]^+$) 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, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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 $C_{23}H_{19}Cl_2O_2$ ($[M+H]^+$) 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, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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 $C_{21}H_{19}O_2S$ ($[M+H]^+$) 335.1113, found 335.1100.

1,4-Diphenylhexane-1,5-dione (3ta): 39.9 mg, 75%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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* = 7.2 Hz, 1.5H), 1.17 (d, *J* = 6.8 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 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, $CDCl_3$) δ: 7.30-7.25 (m, 3H), 7.22 (t, *J* = 6.4 Hz, 2H), 7.17 (t, *J* = 6.0 Hz, 4H), 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 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, $CDCl_3$) δ: 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 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, $CDCl_3$) 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 $C_{19}H_{18}ClF_2O_3$ ($[M+H]^+$) 367.0913, found 367.0927.

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

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