JOC The Journal of Organic Chemistry

Note

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b02310 • Publication Date (Web): 05 Nov 2019

Just Accepted

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Visible-light-mediated oxidative coupling of vinylarenes with bromocarboxylates leading to γ-ketoesters

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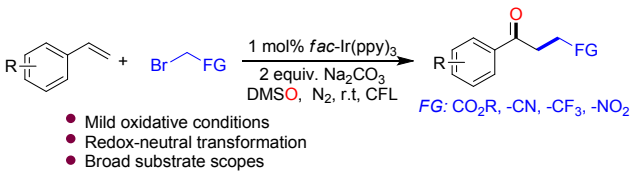
Abstract Graphics



Abstract

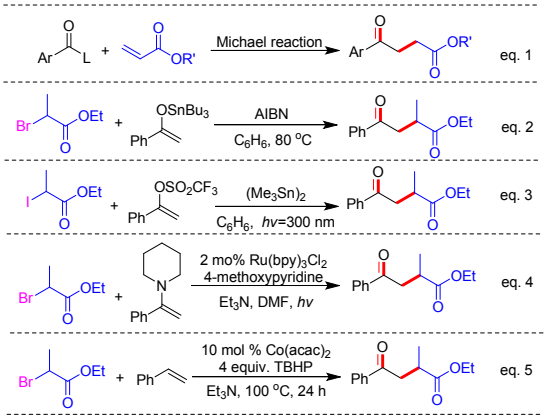
A photocatalytic strategy for the synthesis of γ-ketoesters was reported. Using dimethyl sulfoxide (DMSO) as both the solvent and the terminal oxidant, oxidative coupling of vinylarenes with bromocarboxylates proceeded readily, giving a variety of γ-ketoesters in good isolated yields and with a broad functional-group tolerance.

γ-Ketoesters are versatile building blocks in organic synthesis since ketone and ester groups are reactive centers in many well-established transformations.[1] Moreover, carbonyl moiety is a ubiquitous structural feature of many natural products and lists among the most significant structural elements of pharmaceuticals.[2] Thus, the development of diverse synthetic approaches to prepare these compounds has been the subject of intense research. Typically, these compounds can be prepared through the conjugate addition of an acyl group to a Michael acceptor (Scheme 1, eq. 1).[3]

Another attractive approach toward γ-ketoesters involves intermolecular addition of carbonyl alkyl radicals to olefins. Since inefficiency of intermolecular radical reactions, highly efficient radical acceptors were usually employed to solve this problem, and such preformed compounds include: enolates[4] and enamines.[5] In this regard, Hosomi et al. reported the AIBN-initiated reaction of ethyl 2-bromopropanoate with tributylstannyl enolate to produce γ-ketoester (Scheme 1, eq. 2).[4b] Kim et al. reported photoinduced radical alkylations of activated alkyl iodides using vinyl triflates in the presence of hexadimethyltin in benzene under irradiation at 300 nm, which gave γ-ketoesters after homolytic scission of the *O*-sulfone bond (Scheme 1, eq. 3).[4e] However, these methodologies require organotin compounds either as a starting material or as a radical initiator, which negatively impact the environment. Zhang and coworkers recently reported the visible-light-mediated radical addition of α-brominated carboxylates to

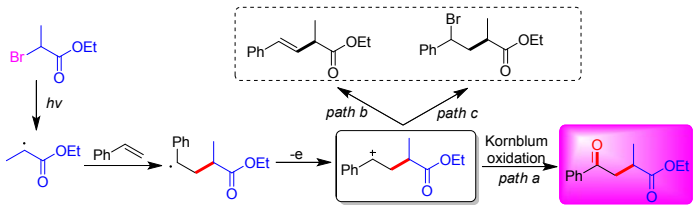
enamines to give the corresponding γ-ketoesters (Scheme 1, eq. 4).[5c] Overall, these above-mentioned methodologies require preformed radical acceptors as a substrate, which are sometimes difficult to make and thus detract from the practicality of these methods. Therefore, the oxidative coupling involving the direct C–H functionalization of alkenes would be an attractive alternative to the preparation of γ-ketoesters due to its step economy by the avoidance of the pre-functionalization process.[6] For example, the Wan group recently reported an elegant cobalt-catalyzed oxidative coupling between vinylarenes and α-bromoesters to construct γ-ketoesters involving a cascade organocobalt addition/trapping/Kornblum−DeLaMare rearrangement (Scheme 1, eq. 5).[7] However, this protocol suffers from high reaction temperatures as well as needs to be carried out under strong oxidative conditions and the use of triethylamine as solvent.

Scheme 1 Synthesis of γ-ketoesters



It is well known that α-bromocarboxylate can generate electrophilic alkyl radicals under visible-light irradiation.[8] Accordingly, we envisioned that these electron-deficient radicals generated by the photocatalyzed reduction of the C-Br bond in α-bromocarboxylates can be applied in the oxyalkylation of alkenes, leading to the formation of γ-ketoesters, which may overcome the aforementioned limitations.[9] In this process, the photogenerated carbonyl alkyl radicals are trapped by styrene, followed by single electron transfer (SET) and Kornblum-type oxidation,[10] finally furnishing γ-ketoesters (Scheme 2, path a). From a synthetic point of view, this methodology is intriguing due to its mild conditions and the use of readily available styrenes and α-bromocarboxylates as starting materials. However, we need to overcome several obstacles in this transformation. One obstacle is determining how to avoid the undesired deprotonation reaction, which gives the alkenylation product (path b).[8d] Another noticeable side reaction is the well-documented atom transfer radical addition (ATRA) of α-bromocarboxylates to styrenes (path c).[8b, 8c]

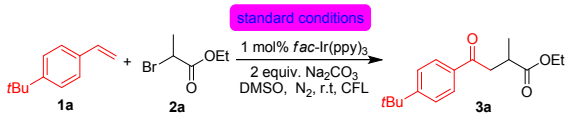
Scheme 2. Our strategy for the synthesis of γ-ketoesters



With these considerations in mind, we commenced our investigation with the optimization of the reaction conditions by irradiating a degassed DMSO

solution of 4-tertbutylstyrene (**1a**) and ethyl 2-bromopropanoate (**2a**) in the presence of 1 mol% *fac*-Ir(ppy)$_3$ and 2 equiv. of Na_2CO_3 under a 24 W household fluorescent lamp. To our delight, the desired γ-ketoester **3a** was obtained in 83% isolated yield after 20 h of irradiation (entry 1). Based on this encouraging preliminary result, the reaction parameters such as the photocatalyst or base used were examined to obtain the optimal reaction conditions, and the results are summarized in Table 1. As shown in Table 1, [Ir(ppy)$_2$(dtbbpy)](PF$_6$) was also able to promote the reaction but to a lesser extent than *fac*-Ir(ppy)$_3$ (entry 2). Other common photocatalysts such as Ru(bpy)$_3$Cl$_2$·6H$_2$O and the organic photocatalyst Rose Bengal, showed comparatively less catalytic activity since these photocatalysts provided trace amounts of **3a** (entries 3 to 4). The base could influence the reaction efficiency as it could potentially neutralize the byproduct HBr (entries 5 to 10). Replacing Na_2CO_3 with other inorganic bases such as K_2CO_3, K_3PO_4 or $NaHCO_3$ led to a drop in isolated yield (entries 5 to 7). No improvement of the yield was observed when organic bases were employed (entries 8 to 10). The effect of bases on reaction outcomes was further confirmed by the observation of a significant drop of yield when reaction was performed in the absence of base (entry 11 vs entry 1). Control experiments showed that light and photoredox catalysts were essential for the successful transformation because the reactions did not proceed in the absence of light irradiation or a photocatalyst (entries 12 and 13).

Table 1 Optimization of the reaction conditions [a]



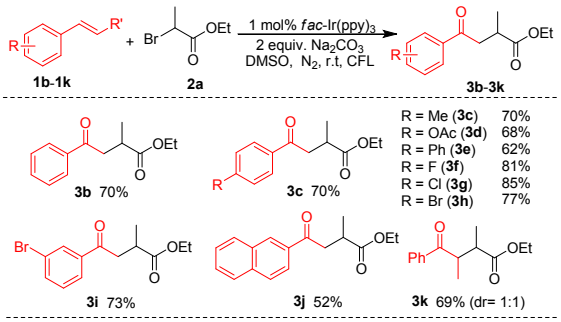
entry	change from the "standard conditions"	yield (%)[b]
1	standard conditions	83
2	$[Ir(ppy)_2(dtbbpy)](PF_6)$ instead of *fac*-$Ir(ppy)_3$	71
3	$Ru(bpy)_3Cl_2 \cdot 6H_2O$ instead of *fac*-$Ir(ppy)_3$	<2
4	Rose Bengal instead of *fac*-$Ir(ppy)_3$	<2
5	K_2CO_3 instead of Na_2CO_3	70
6	K_3PO_4 instead of Na_2CO_3	49
7	$NaHCO_3$ instead of Na_2CO_3	53
8	Et_3N instead of Na_2CO_3	40
9	DBU instead of Na_2CO_3	51
10	Pyridine instead of Na_2CO_3	33
11	No base	37
12	No photocatalyst	NR[c]
13	No light	NR[c]

[a] Reaction conditions: **1a** (0.50 mmol, 1.00 equiv.), **2a** (1.00 mmol, 2.00 equiv.), photocatalyst (5 μmol, 0.010 equiv.), base (1.00 mmol, 2.00 equiv.), DMSO (2 mL), 24 W CFL, N_2, r.t., 20 h. [b] isolated yield, [C] NR = No reaction.

With the optimized reaction conditions established, we then examined the substrate scope of this transformation with an array of styrenes using ethyl 2-bromopropanoate **2a** as the alkyl radical source. As shown in Scheme 3, a variety of substituted vinylarenes was compatible with the optimal conditions and afforded the corresponding γ-ketoesters in moderate to good yields. The electronic effect of the arenes had little impact on the course of the reaction, and terminal vinylarenes bearing electron-donating substituents such as methyl (**3c**) and acetoxy (**3d**) groups and electron-withdrawing substituents such as phenyl (**3e**) and halogen (**3f-3i**) groups at the *para*-position all delivered the corresponding products in good yields. Additionally, 3-substituted styrene (**1i**) and naphthalene-derived substrate **1j** worked well in this reaction, and the

corresponding ketoesters was obtained in acceptable yields. Furthermore, the internal alkene **1k** can react smoothly to give the desired product **3k** in 69% yield. Unfortunately, aliphatic alkenes failed to give desired products in this transformation.

Scheme 3. Scope of styrenes [a]

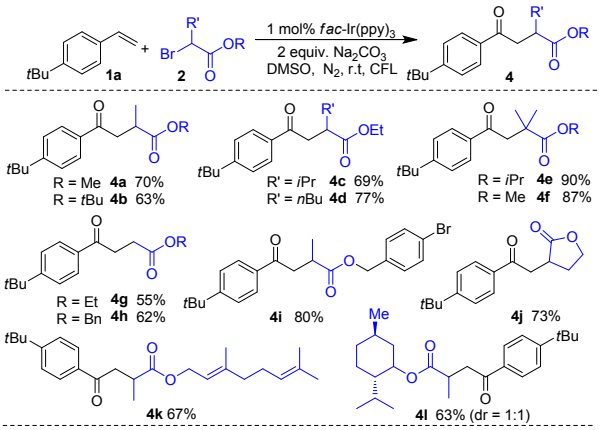


[a] Reaction conditions: **1** (0.50 mmol, 1.00 equiv.), **2a** (1.00 mmol, 2.00 equiv.), *fac*-Ir(ppy)$_3$ (5 μmol, 0.010 equiv.), Na_2CO_3 (1.00 mmol, 2.00 equiv.), DMSO (2 mL), 24 W CFL, N_2, r.t., 20 h.

Next, we examined the generality of this transformation with respect to different α-bromoesters, and the results are summarized in Scheme 4. As depicted in Scheme 4, this photoinduced oxidative coupling is effective for a variety of α-brominated carboxylates. For example, methyl and *tert*-butyl 2-bromopropanoate as well as isopropyl and *n*-butyl ethyl bromoacetate engage in the coupling in good yield (**4a**-**4d**). In addition, tertiary α-carbonyl alkyl bromides worked well in the current reaction system, and the corresponding γ-ketoesters were obtained in good yield (**4e** and **4f**). It is known that primary α-carbonyl alkyl bromides are less likely to undergo single-electron reduction of C-Br bonds than are their secondary and tertiary counterparts due to the relatively instability of the primary alkyl radicals generated.[11]

To our delight, primary alkyl bromides **2g** and **2h** proved to be a compatible reaction partner in the current transformation and afforded the desired products **4g** and **4h**, respectively, in moderate isolated yield. Furthermore, γ-butyrolactone also exhibited robust reactivity in the reaction, with the desired product obtained in good yield (**4j**). Notably, this methodology can also be applied to more complex α-bromoesters derived from geraniol and L-menthol, giving the desired product in good yields (**4k** and **4l**).

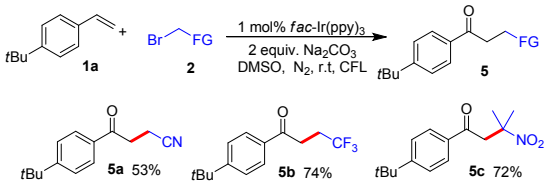
Scheme 4. Scope of α-bromoesters [a]



[a] Reaction conditions: **1a** (0.50 mmol, 1.00 equiv.), **2** (1.00 mmol, 2.00 equiv.), *fac*-Ir(ppy)$_3$ (5 μmol, 0.010 equiv.), Na_2CO_3 (1.00 mmol, 2.00 equiv.), DMSO (2 mL), 24 W CFL, N_2, r.t., 20 h.

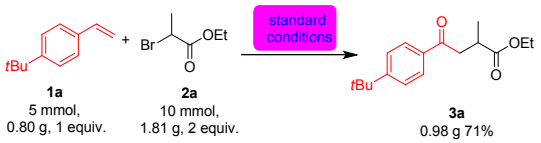
To further evaluate the synthetic utility and generality of the current reaction, we extend the application scope of this procedure to the preparation of other functionalized ketones. As depicted in Scheme 5, γ‑ketonitrile (**5a**),[12] β-CF_3 ketone (**5b**)[13] and β-nitro ketone (**5c**)[14] could be readily synthesized from the corresponding alkyl bromides through the oxidative alkylation of styrenes under light-mediated conditions.[15]

Scheme 5. Scope of alkyl bromides **2** [a]



[a] Reaction conditions: **1a** (0.50 mmol, 1.00 equiv.), **2** (1.00 mmol, 2.00 equiv.), *fac*-Ir(ppy)$_3$ (5 μmol, 0.010 equiv.), Na_2CO_3 (1.00 mmol, 2.00 equiv.), DMSO (2 mL), 24 W CFL, N_2, r.t., 20 h.

Scheme 6. Gram-scale reaction

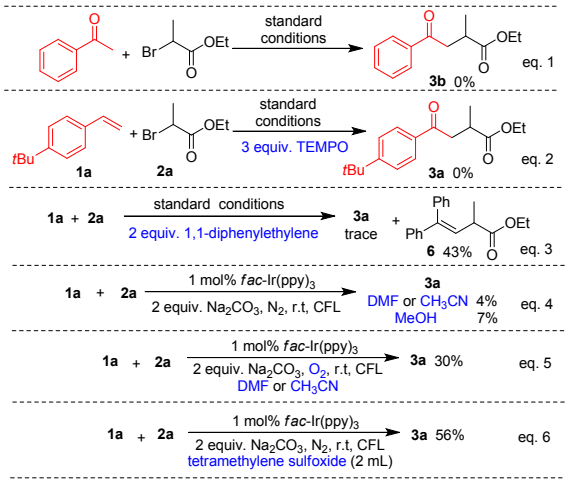


To evaluate the scalability of the current protocol, a 5 mmol scale for the synthesis of **3a** was carried out (Scheme 6). The reaction of 5 mmol **1a** with 10 mmol **2a** could proceed smoothly under standard conditions and afforded the γ-ketoester **3a** in 71% isolated yield.

To gain further insight into the reaction mechanism, several control experiments were carried out. First, no desired γ-ketoester **3b** could be detected when using acetophenone as the substrate instead of styrene, suggesting a late-stage oxidation of the alkene double bond in this transformation (Scheme 7, eq. 1). Second, the reaction was totally shut down in the presence of the radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (Scheme 7, eq. 2). Additionally, alkyl radical **A** (Scheme 8) could be trapped with

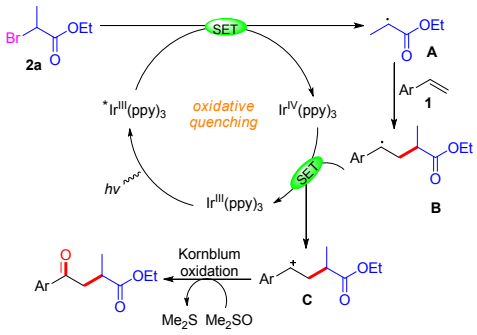
1,1-diphenylethylene to give the product **6** in 43% yield (Scheme 7, eq. 3). These results, along with the control experiments shown in Table 1, suggested both the visible-light- driven nature and the intermediacy of an alkyl radical in the reaction. Third, trace amounts of **3a** was detected when the reaction was carried out in DMF, CH_3CN or MeOH under otherwise identical conditions (Scheme 7, eq. 4). It is possible that the residual O_2 in the N_2 gas reacted with radical intermediate **B** (Scheme 8) to form compound **3a**.[16] Furthermore, product **3a** was obtained in 30% yield when reaction was performed under an atmosphere of oxygen (Scheme 7, eq. 5). These results reveal that O_2 was also able to promote the reaction but not a major pathway. Finally, to classify the oxidation of DMSO, the use of tetramethylene sulfoxide in place of DMSO also led to **3a** in moderate yield (Scheme 7, eq. 6). This result indicates that DMSO plays a key role in this photoinduced oxidative coupling.

Scheme 7. Mechanistic studies



According to the aforementioned information and previous reports,[8d, 17] a possible reaction pathway for this transformation is outlined in Scheme 8. First, photocatalyst *fac*-$Ir^{III}(ppy)_3$ is irradiated with visible light to provide a photoexcited state, **fac*-$Ir^{III}(ppy)_3$ ($E_{1/2}^{IV/*III}$ = −1.73 V vs SCE in MeCN),[18] which readily reduces α-bromoester **2a** (E^{red} = −0.8 V vs SCE in MeCN)[19] via single electron transfer to generate the reactive alkyl radical **A**, along with the oxidized photocatalyst *fac*-$Ir^{IV}(ppy)_3$. Radical **A** then undergoes the rapid addition reaction with styrene **1** to afford the new radical **B**. Subsequently, intermediate **B**[20] is oxidized by *fac*-$Ir^{IV}(ppy)_3$ ($E_{1/2}^{IV/III}$ = +0.77 V vs SCE in MeCN)[18] to produce carbocation **C** and close the photoredox catalytic cycle. Finally, the Kornblum-type oxidation of intermediate **C** with DMSO affords the corresponding γ-ketoesters.

Scheme 8. Tentative reaction pathway



In summary, we have successfully developed a visible-light-induced reaction of a wide variety of α-brominated carboxylates with styrenes to prepare various synthetically important γ-ketoesters. A distinct advantage of this protocol over

all previous methods is the use of inexpensive and readily available substrates as well as the use of DMSO as both the solvent and the terminal oxidant. We envisage that these features render the present protocol to be attractive in the syntheses of an array of medicinally and agrochemically relevant carbonyl compounds.

Experimental Section

General experimental information: Reagents were used as received without further purification unless otherwise indicated. Solvents were dried and distilled prior to use. Reactions were monitored with thin layer chromatography using silica gel GF_{254} plates. Organic solutions were concentrated in vacuo with a rotavapor. Flash column chromatography was performed using silica gel (200−300 meshes). Petroleum ether used had a boiling point range of 60−90°C. Melting points were measured on a digital melting point apparatus without correction of the thermometer. Nuclear magnetic resonance spectra were recorded at ambient temperature (unless otherwise stated) at 400 MHz (100 MHz for ^{13}C) in $CDCl_3$. Chemical shifts were reported in ppm (δ) using TMS as internal standard, and spin−spin coupling constants (*J*) were given in Hz. High resolution mass spectrometry (HRMS) analyses were carried out on an FTICR HR-ESI-MS.

General procedure for the synthesis of γ-ketoesters: *fac*-$Ir(ppy)_3$ (5.00 μmol, 0.010 equiv.) and Na_2CO_3 (1.00 mmol, 2.00 equiv.) were added to a flame-dried Schlenk

flask containing a stirring bar and purged by evacuating the flask and backfilling with argon three times. Then anhydrous DMSO (2 mL), vinylarene (0.50 mmol, 1.00 equiv.) and bromocarboxylate (1.00 mmol, 2.00 equiv.) were added. The reaction mixture was degassed by the freeze-pumpthaw method and then irradiated with a 24W household fluorescent lamp from a distance of 2 cm for 20 h. After completion of the reaction, the mixture was added with 10 mL of H_2O and extracted with ethyl acetate (10 mL) for three times. The combined organic layer was dried (Na_2SO_4) and concentrated to give crude residue which was purified by flash column chromatography to give the corresponding product.

Ethyl 4-(4-(*tert*-butyl)phenyl)-2-methyl-4-oxobutanoate (**3a**, known compound, cas: 1522361-86-9). Compound **3a** was obtained as an oil in 83% yield (115 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm= 7.84 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.38 (dd, *J* = 17.4, 7.7 Hz, 1H), 3.11 – 2.98 (m, 1H), 2.93 (dd, *J* = 17.4, 5.7 Hz, 1H), 1.27 (s, 9H), 1.22 – 1.15 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm= 197.8, 176.0, 156.9, 134.2, 128.0, 125.5, 60.6, 41.8, 35.1, 35.1, 31.1, 17.3, 14.2. Spectral data are in good agreement with literature values.[7]

Ethyl 2-methyl-4-oxo-4-phenylbutanoate (**3b**, known compound, cas: 6938-44-9). Compound **3b** was obtained as an oil in 70% yield (77 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm= 7.94 – 7.81 (m, 2H), 7.56 – 7.44 (m, 1H), 7.43 – 7.32 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.41 (dd, *J* = 17.5, 7.8 Hz, 1H), 3.21 – 2.99 (m, 1H), 2.94

(dd, J = 17.5, 5.5 Hz, 1H), 1.28 – 1.15 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm= 198.1, 176.0, 136.7, 133.2, 128.6, 128.0, 60.6, 41.9, 35.1, 17.3, 14.2. Spectral data are in good agreement with literature values.[7]

Ethyl 2-methyl-4-oxo-4-phenylbutanoate (**3c**, known compound, cas: 1522361-90-5). Compound **3c** was obtained as an oil in 70% yield (82 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 60:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm= 7.80 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 4.08 (q, J = 7.1 Hz, 2H), 3.38 (dd, J = 17.4, 7.8 Hz, 1H), 3.08 – 3.01 (m, 1H), 2.92 (dd, J = 17.5, 5.6 Hz, 1H), 2.34 (s, 3H), 1.23 – 1.14 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm= 197.8, 176.1, 144.0, 134.3, 129.3, 128.2, 60.6, 41.8, 35.1, 21.7, 17.5, 14.2. Spectral data are in good agreement with literature values.[7]

Ethyl 4-(4-acetoxyphenyl)-2-methyl-4-oxobutanoate (**3d**, new compound). Compound **3d** was obtained as an oil in 68% yield (95 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm=7.94 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 4.08 (q, J = 7.1 Hz, 2H), 3.39 (dd, J = 17.6, 8.0 Hz, 1H), 3.10 – 2.97 (m, 1H), 2.91 (dd, J = 17.6, 5.5 Hz, 1H), 2.25 (s, 3H), 1.23 – 1.15 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=195.9, 174.9, 167.9, 153.3, 133.3, 128.6, 120.8, 59.6, 40.9, 34.0, 20.1, 16.3, 13.1. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}O_5$ 279.1232; Found 279.1228.

Ethyl 4-([1,1'-biphenyl]-4-yl)-2-methyl-4-oxobutanoate (**3e**, new compound). Compound **3e** was obtained as white solid in 62% yield (92 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 60:1). mp= 80-82 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm=8.05 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.57 (m, 2H), 7.54 – 7.45 (m, 2H), 7.44 – 7.38 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.52 (dd, *J* = 17.5, 7.8 Hz, 1H), 3.21 – 3.09 (m, 1H), 3.04 (dd, *J* = 17.4, 5.5 Hz, 1H), 1.33 – 1.23 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=196.7, 175.0, 144.8, 138.8, 134.4, 127.9, 127.6, 127.2, 126.2, 126.2, 59.6, 40.9, 34.1, 16.3, 13.2. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}O_3$ 297.1491; Found 297.1487

Ethyl 4-(4-fluorophenyl)-2-methyl-4-oxobutanoate (**3f**, known compound, cas: 1522361-88-1). Compound **3f** was obtained as an oil in 81% yield (96 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 60:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm= 8.04 – 7.84 (m, 2H), 7.13 – 6.99 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.39 (dd, *J* = 17.6, 8.1 Hz, 1H), 3.12 – 2.96 (m, 1H), 2.90 (dd, *J* = 17.6, 5.4 Hz, 1H), 1.24 – 1.14 (m, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ= -105.1. ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=195.5, 174.9, 164.7 (d, *J* = 254.7 Hz), 132.1 (d, *J* = 3.0 Hz), 129.6 (d, *J* = 9.4 Hz), 114.7 (d, *J* = 21.8 Hz), 59.6, 40.8, 34.0, 16.3, 13.1. Spectral data are in good agreement with literature values.[7]

Ethyl 4-(4-chlorophenyl)-2-methyl-4-oxobutanoate (**3g**, known compound, cas: 54029-07-1). Compound **3g** was obtained as an oil in 85% yield (108 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 60:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm= 7.83 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 4.07 (q, *J* =

7.1 Hz, 2H), 3.38 (dd, *J* = 17.6, 8.1 Hz, 1H), 3.13 – 2.97 (m, 1H), 2.89 (dd, *J* = 17.6, 5.4 Hz, 1H), 1.25 – 1.14 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm= 196.9, 175.8, 139.6, 135.0, 129.5, 128.9, 60.7, 41.9, 35.0, 17.3, 14.2. Spectral data are in good agreement with literature values.[7]

Ethyl 4-(4-bromophenyl)-2-methyl-4-oxobutanoate (**3h**, known compound, cas: 1522361-87-0). Compound **3h** was obtained as an oil in 77% yield (115 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 60:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm= 7.76 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.38 (dd, *J* = 17.6, 8.1 Hz,1H), 3.18 – 2.96 (m, 1H), 2.88 (dd, *J* = 17.6, 5.3 Hz, 1H), 1.25 – 1.13 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=196.1, 174.8, 134.4, 130.9, 128.5, 127.3, 59.7, 40.8, 34.0, 16.3, 13.1. Spectral data are in good agreement with literature values.[7]

Ethyl 4-(3-bromophenyl)-2-methyl-4-oxobutanoate (**3i**, known compound, cas: 1522361-89-2). Compound **3i** was obtained as an oil in 73% yield (109 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm= 8.03 (t, *J* = 1.8 Hz, 1H), 7.82 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.62 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.28 (t, *J* = 7.9 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.39 (dd, *J* = 17.7, 8.2 Hz, 1H), 3.13 – 2.97 (m, 1H), 2.89 (dd, *J* = 17.7, 5.3 Hz, 1H), 1.25 – 1.16 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=195.8, 174.7, 137.4, 135.0, 130.1, 129.2, 125.5, 121.9, 59.7, 40.9, 34.0, 16.3, 13.1. Spectral data are in good agreement with literature values.[7]

Ethyl 2-methyl-4-(naphthalen-2-yl)-4-oxobutanoate (**3j**, known compound, cas: 856810-67-8). Compound **3j** was obtained as a white solid in 52% yield (70 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 40:1). mp= 56-58 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm= 8.50 (d, *J* = 1.7 Hz, 1H), 8.03 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.97 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.94 – 7.82 (m, 2H), 7.63 – 7.54 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.85 – 3.50 (m, 1H), 3.33 – 2.99 (m, 2H), 1.37 – 1.24 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=197.0, 175.0, 134.6, 133.0, 131.4, 128.7, 128.5, 127.5, 127.4, 126.7, 125.8, 122.7, 59.6, 41.0, 34.1, 16.4, 13.2. Spectral data are in good agreement with literature values.[21]

Ethyl 2,3-dimethyl-4-oxo-4-phenylbutanoate (**3k**, known compound). Compound **3k** was obtained as an oil in 69% yield (81 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm=7.95 – 7.89 (m, 2H), 7.59 – 7.45 (m, 1H), 7.46 – 7.39 (m, 2H), 4.12 – 4.05 (m, 1H), 4.03 – 3.97 (m, 1H), 3.75 – 3.64 (m, 1H), 3.03 – 2.78 (m, 1H), 1.25 – 1.14 (m, 4H), 1.14 – 1.05 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=202.5, 201.6, 174.8, 174.6, 135.6, 135.0, 132.2, 131.9, 127.7, 127.6, 127.34, 127.30, 59.6, 59.5, 42.5, 42.0, 41.73, 40.7, 15.5, 15.2, 13.5, 13.2, 13.1, 13.0. Spectral data are in good agreement with literature values.[5c]

Methyl 4-(4-(*tert*-butyl)phenyl)-2-methyl-4-oxobutanoate (**4a**, new compound). Compound **4a** was obtained as an oil in 70% yield (92 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm=7.84 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 3.63 (s, 3H),

3.39 (dd, *J* = 17.5, 7.8 Hz, 1H), 3.13 – 3.01 (m, 1H), 2.94 (dd, *J* = 17.5, 5.6 Hz, 1H), 1.27 (s, 9H), 1.20 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=196.6, 175.5, 155.9, 133.0, 127.0, 124.5, 50.9, 40.8, 34.1, 33.9, 30.0, 16.3. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{23}O_3$ 263.1647; Found 263.1643.

***tert*-Butyl 4-(4-(*tert*-butyl)phenyl)-2-methyl-4-oxobutanoate** (**4b**, new compound). Compound **4b** was obtained as an oil in 63% yield (96 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm= 7.84 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 3.33 (dd, *J* = 17.1, 7.5 Hz, 1H), 3.01 – 2.89 (m, 1H), 2.86 (dd, *J* = 17.1, 5.8 Hz, 1H), 1.36 (s, 9H), 1.27 (s, 9H), 1.16 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=196.9, 174.3, 155.7, 133.3, 127.0, 124.5, 79.2, 40.8, 35.0, 34.1, 30.1, 27.0, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{28}O_3Na$ 327.1936; Found 327.1934.

Ethyl 4-(4-(*tert*-butyl)phenyl)-2-isopropyl-4-oxobutanoate (**4c**, known compound, cas:1522362-04-4). Compound **4c** was obtained as an oil in 69% yield (105 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm=7.85 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 4.15 – 4.00 (m, 2H), 3.47 – 3.37 (m, 1H), 3.00 – 2.78 (m, 2H), 2.17 – 1.91 (m, 1H), 1.26 (s, 9H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.92 (dd, *J* = 6.9, 1.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=197.4, 173.8, 155.7, 133.2, 127.0, 124.4, 59.3, 45.5, 36.3, 34.06, 30.1, 29.2, 19.3, 18.9, 13.2. Spectral data are in good agreement with literature values.[7]

Ethyl 2-(2-(4-(*tert*-butyl)phenyl)-2-oxoethyl)hexanoate (**4d**, new compound). Compound **4d** was obtained as an oil in 77% yield (123 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 70:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm=7.84 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 4.08 (qd, *J* = 7.1, 2.4 Hz, 2H), 3.36 (dd, *J* = 18.6, 10.0 Hz, 1H), 3.06 – 2.86 (m, 2H), 1.69 – 1.51 (m, 2H), 1.30 – 1.21 (m, 13H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.83 (t, *J* = 12.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=197.0, 174.7, 155.8, 133.1, 127.0, 124.5, 59.4, 39.4, 39.3, 34.1, 30.9, 30.1, 28.3, 21.5, 13.2, 12.9. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{31}O_3$ 319.2273; Found 319.2269.

Isopropyl 4-(4-(*tert*-butyl)phenyl)-2,2-dimethyl-4-oxobutanoate (**4e**, new compound). Compound **4e** was obtained as an oil in 90% yield (137 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 60:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm=7.81 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 4.94 (p, *J* = 6.2 Hz, 1H), 3.18 (s, 2H), 1.27 (s, 9H), 1.23 (s, 6H), 1.11 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=196.2, 175.8, 155.6, 133.6, 126.8, 124.4, 66.4, 47.3, 39.0, 34.1, 30.1, 24.7, 20.6. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{29}O_3$ 305.2117; Found 305.2113.

Methyl 4-(4-(*tert*-butyl)phenyl)-2,2-dimethyl-4-oxobutanoate (**4f**, new compound). Compound **4f** was obtained as an oil in 87% yield (120 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 60:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm=7.81 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 3.59 (s, 3H), 3.21 (s, 2H), 1.26 (s, 9H), 1.24 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=196.2,

176.9, 155.8, 133.4, 126.9, 124.5, 50.9, 47.5, 39.0, 34.1, 30.0, 24.7. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{25}O_3$ 277.1804; Found 277.1802.

Ethyl 4-(4-(*tert*-butyl)phenyl)-4-oxobutanoate (**4g**, known compound, cas: 75237-09-1). Compound **4g** was obtained as an oil in 55% yield (72 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 70:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm= 7.93 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.30 (t, *J* = 6.7 Hz, 2H), 2.75 (t, *J* = 6.7 Hz, 2H), 1.39 – 1.26 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm= 196.8, 172.0, 155.9, 133.0, 127.0, 124.5, 59.6, 34.1, 32.3, 30.1, 27.3, 13.2. Spectral data are in good agreement with literature values.[22]

Benzyl 4-(4-(*tert*-butyl)phenyl)-4-oxobutanoate (**4h**, new compound). Compound **4h** was obtained as an oil in 61% yield (101 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm= 7.85 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.35 – 7.22 (m, 5H), 5.08 (s, 2H), 3.25 (t, *J* = 6.7 Hz, 2H), 2.75 (t, *J* = 6.7 Hz, 2H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=196.7, 171.8, 155.9, 134.9, 132.9, 127.5, 127.2, 127.0, 124.5, 65.5, 34.1, 32.2, 30.1, 27.3. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{25}O_3$ 325.1804; Found 325.1796.

4-Bromobenzyl 4-(4-(*tert*-butyl)phenyl)-2-methyl-4-oxobutanoate (**4i**, new compound). Compound **4i** was obtained as an oil in 80% yield (167 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 40:1). ^{1}H NMR (400

MHz, $CDCl_3$) δ/ppm=7.82 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 6.0 Hz, 2H), 7.38 (d, *J* = 6.0 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 5.05 – 4.96 (m, 2H), 3.39 (dd, *J* = 17.6, 8.0 Hz, 1H), 3.17 – 3.04 (m, 1H), 2.95 (dd, *J* = 17.6, 5.4 Hz, 1H), 1.30 – 1.17 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=196.5, 174.7, 156.0, 134.1, 133.0, 130.6, 128.7, 127.0, 124.5, 121.0, 64.5, 40.7, 34.1, 34.0, 30.1, 16.2. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{25}BrO_3Na$ 439.0885; Found 439.0877.

3-(2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl)dihydrofuran-2(3H)-one (**4j**, known compound, cas: 1522362-11-3). Compound **4j** was obtained as a white solid in 73% yield (95 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 30:1). mp= 112-114 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ/ppm=7.85 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 4.38 (td, *J* = 8.9, 2.0 Hz, 1H), 4.22 (ddd, *J* = 10.4, 9.1, 6.6 Hz, 1H), 3.66 – 3.52 (m, 1H), 3.20 – 3.03 (m, 2H), 2.63 – 2.55 (m, 1H), 1.89 (dtd, *J* = 12.8, 10.4, 8.7 Hz, 1H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=195.6, 178.3, 156.4, 132.5, 127.0, 124.7, 65.9, 38.3, 34.3, 34.2, 30.0, 28.2. Spectral data are in good agreement with literature values.[7]

(*E*)-3,7-Dimethylocta-2,6-dien-1-yl

4-(4-(*tert*-butyl)phenyl)-2-methyl-4-oxobutanoate (**4k**, new compound). Compound **4k** was obtained as an oil in 67% yield (129 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ/ppm= 7.84 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 5.25 (tt, *J* = 5.7, 1.3 Hz, 1H), 5.00 (ddt, *J* = 6.9, 5.4, 1.7 Hz, 1H), 4.68 – 4.43 (m, 2H), 3.38 (dd, *J* = 17.4, 7.6 Hz, 1H), 3.13 – 2.98 (m, 1H), 2.92 (dd, *J* = 17.4, 5.9 Hz, 1H), 2.06 – 1.92 (m, 4H), 1.63 – 1.59 (m,

6H), 1.52 (s, 3H), 1.26 (s, 9H), 1.19 (d, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=196.7, 175.0, 155.8, 141.0, 133.2, 130.7, 127.0, 124.5, 122.8, 117.3, 60.5, 40.8, 38.5, 34.1, 30.0, 25.3, 24.7, 16.7, 16.3, 15.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{36}O_3Na$ 407.2562; Found 407.2554.

(*2S*,*5R*)-2-Isopropyl-5-methylcyclohexyl 4-(4-(tert-butyl)phenyl)-2-methyl-4-oxobutanoate (**4l**, new compound). Compound **4l** was obtained as an oil in 63% yield (122 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 50:1).^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm= 7.84 (dd, J = 8.5, 1.8 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 4.59 (tt, J = 10.9, 4.4 Hz, 1H), 3.38 (ddd, J = 17.4, 9.7, 7.8 Hz, 1H), 3.16 – 2.97 (m, 1H), 2.96 – 2.75 (m, 1H), 2.00 – 1.84 (m, 1H), 1.80– 1.74 (m, 1H), 1.61 – 1.55 (m, 2H), 1.45 – 1.34 (m, 1H), 1.26 (s, 9H), 1.19 (dd, J = 7.1, 3.9 Hz, 4H), 1.03 – 0.88 (m, 2H), 0.86 – 0.79 (m, 6H), 0.77 (d, J = 7.1 Hz, 2H), 0.67 (dd, J = 9.9, 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=196.7, 196.6, 174.5, 174.5, 155.6, 155.7, 133.3, 133.2, 127.0, 126.9, 124.4, 73.2, 73.2, 45.94, 40.8, 40.6, 39.7, 39.6, 34.4, 34.3, 34.1, 33.3, 30.4, 30.3, 30.1, 25.1, 25.0, 22.3, 22.2, 21.0, 21.0, 19.8, 19.7, 16.74, 15.2, 15.0. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{39}O_3$ 387.2899; Found 387.2889.

4-(4-(*tert*-Butyl)phenyl)-4-oxobutanenitrile (**5a**, known compound, cas:1154885-60-5). Compound **5a** was obtained as a white solid in 53% yield (57 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 30:1). mp= 66-68 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm=7.83 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 3.30 (t, J = 14.6 Hz, 2H), 2.71 (t, J = 14.6 Hz, 2H), 1.28 (s, 9H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ/ppm=193.9, 156.78, 132.0, 127.0, 124.8, 118.3, 34.2, 33.1, 30.0, 10.8. Spectral data are in good agreement with literature values.[12a]

1-(4-(*tert*-Butyl)phenyl)-4,4,4-trifluorobutan-1-one (**5b**, known compound, cas: 1468771-50-7). Compound **5b** was obtained as a white solid in 74% yield (96 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 40:1). mp= 53-55 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm=7.84 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 3.16 (t, *J* = 7.8 Hz, 2 H), 2.60 – 2.42 (m, 2H), 1.28 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ/ppm=-66.4. ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=195.0, 156.4, 132.5, 127.0, 124.7, 34.1, 30.0, 27.3 (q, *J* = 29.7 Hz). Spectral data are in good agreement with literature values.[13d]

1-(4-(*tert*-Butyl)phenyl)-3-methyl-3-nitrobutan-1-one (**5c**, new compound). Compound **5c** was obtained as a white solid in 72% yield (95 mg) after flash chromatography (Silica gel, petroleum ether: ethyl acetate = 30:1). mp= 113-135 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm= 7.80 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 3.59 (s, 2H), 1.68 (s, 6H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=194.7, 157.5, 133.8, 128.0, 125.7, 84.9, 47.0, 35.2, 31.1, 26.7. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{22}NO_3$ 264.1600; Found 264.1596.

Gram-scale reaction for the synthesis of γ-ketoester 3a: *fac*-Ir(ppy)$_3$ (32.75 mg, 0.050 mmol, 0.010 equiv.) and Na_2CO_3 (1.01g, 10.00 mmol, 2.00 equiv.) were added to a flame-dried Schlenk flask containing a stirring bar and purged by evacuating the flask and backfilling with argon three times. Then anhydrous DMSO (25 mL),

4-*tert*-butylstyrene **1a** (0.80 g, 5.00 mmol, 1.00 equiv.) and ethyl 2-bromopropanoate **2a** (1.81 g, 10.00 mmol, 2.00 equiv.) were added. The reaction mixture was degassed by the freeze-pumpthaw method and then irradiated with a 24W household fluorescent lamp from a distance of 2 cm for 20 h. After completion of the reaction, the mixture was added with 20 mL of H_2O and extracted with ethyl acetate (30 mL) for three times. The combined organic layer was dried (Na_2SO_4) and concentrated to give crude residue which was purified by flash column chromatography (Silica gel, petroleum ether: ethyl acetate = 50:1) to give **3a** in 71% yield (0.98 g).

Control experiments (Scheme 7. eq. 3). *fac*-Ir(ppy)$_3$ (3 mg, 5.00 μmol, 0.010 equiv.) and Na_2CO_3 (106 mg, 1.00 mmol, 2.00 equiv.) were added to a flame-dried Schlenk flask containing a stirring bar and purged by evacuating the flask and backfilling with argon three times. Then anhydrous DMSO (2 mL), 4-*tert*-butylstyrene **1a** (80 mg, 0.50 mmol, 1.00 equiv.), ethyl 2-bromopropanoate **2a** (181 mg, 1.00 mmol, 2.00 equiv.) and 1,1-diphenylethylene (180 mg, 1.00 mmol, 2.00 equiv.) were added. The reaction mixture was degassed by the freeze-pumpthaw method and then irradiated with a 24W household fluorescent lamp from a distance of 2 cm for 20 h. After completion of the reaction, the mixture was added with 10 mL of H_2O and extracted with ethyl acetate (10 mL) for three times. The combined organic layer was dried (Na_2SO_4) and concentrated to give crude residue which was purified by flash column chromatography (Silica gel, petroleum ether: dichloromethane = 4:1) to give **6** as an oil in 83% yield (60 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm= 7.39 – 7.24 (m, 3H), 7.24 – 7.10 (m, 7H), 6.05 (d, J = 10.3 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 3.19 (dq, J =

10.3, 7.0 Hz, 1H), 1.24 – 1.14 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm=173.9, 141.9, 140.8, 138.3, 128.7, 127.3, 127.1, 126.8, 126.3, 126.2, 59.6, 39.4, 17.5, 13.2. Spectral data are in good agreement with literature values.[8d]

Associated content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Copies of NMR spectra for the obtained compounds (PDF).

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Notes

The authors declare no competing financial interest.

Acknowledgements

This study was supported by the Natural Science Foundation of Jiangsu Province in China (BK20170439), and Large Instruments Open Foundation of Nantong University (KBJN1952). We thank Prof. Yanan Zhang (Nantong) for his support of chemical reagents. We also thank Prof. Till Opatz (University of Mainz) for helpful discussions.

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