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Direct Decarboxylative-Decarbonylative Alkylation of α-Oxo Acids with Electrophilic Olefins *via* Visible-Light Photoredox Catalysis

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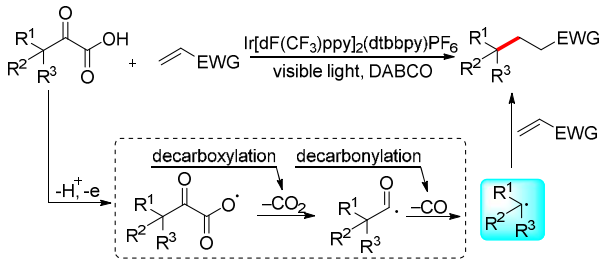


ABSTRACT

The decarbonylation of primary, secondary and tertiary alkyl-substituted acyl radicals has been investigated through photoredox catalysis. A series of quaternary carbons and γ-ketoesters have been directly constructed by the photoredox 1,4-conjugate addition of the corresponding alkyl ketoacids with electrophilic alkenes. And, the tertiary alkyl ketoacids have proved as good precursors of tertiary alkyl radicals.

KEYWORDS

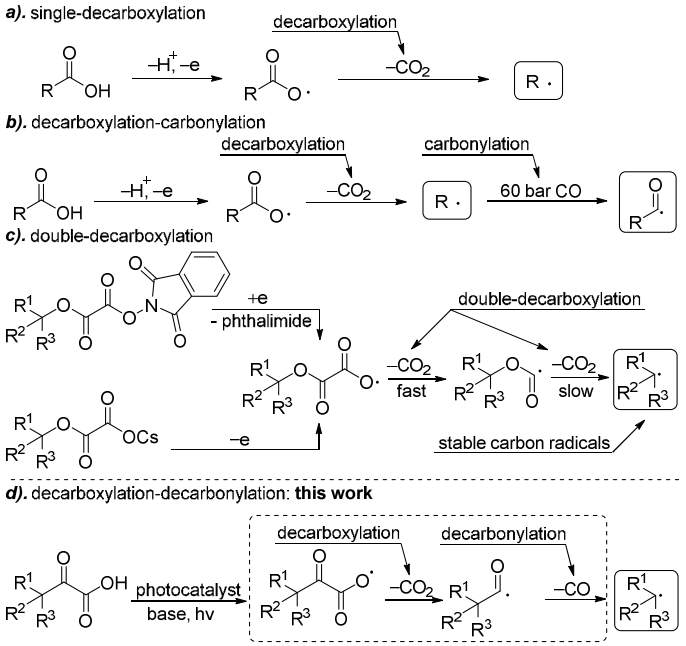
photocatalysis, decarboxylative, decarbonylative, quaternary carbons, γ-ketoesters

INTRODUCTION

Organic carboxylic acids and their derivatives have been widely found in natural products and commonly used in chemical synthesis.[1] Harnessing carboxylic acids as inexpensive and readily available starting materials to construct high-value organic molecules has been shown to be a promising method in modern organic chemistry. Especially, much effort has been devoted to the investigations of their radical decarboxylative functionalization through visible-light photoredox catalysis under mild conditions in recent years.[2-3] As shown in Scheme 1, only carbon dioxide is released in most of these conversions.[2] Compared with the decarboxylative coupling reactions, photoredox-catalyzed decarbonylative functionalization has not received much attention, and the considerable synthetic potential still remains largely unexploited.[2c] As such, the development of a common method for the direct decarbonylative coupling reaction induced by visible-light photoredox catalysis would make a significant complement to the field of the decarboxylative reaction. To this end, the photocatalytic radical carbonylative reactions have been achieved (Scheme 1b).[3] As the inverse process of the carbonylative reaction, we wanted to know whether or not this photocatalyzed

transformation would proceed. Inspired by Overman's introduction of oxalate derivatives for generating the alkyl radicals from alcohols after two consecutive decarboxylation steps (Scheme 1c),[4a-c] we envisioned that the decarbonylative functionalization could be realized through visible-light photoredox catalysis. The driving forces for the double-decarboxylative reaction are mainly the extrusion of stable carbon dioxide and the generation of stable tertiary carbon radicals which are useful intermediates for constructing the complex structures.[4] Therefore, we believed that when a tertiary carbon group was present at the α-position of the acyl radical, the decarbonylative reaction would be smoothly achieved,[5] as shown in Scheme 1d. The stable tertiary carbon radicals, generated from the acyl radical, would then be used for the construction of sterically encumbered *tetra*-substituted carbon centers. During the past several years, the transformations of the alkyl radicals have been widely investigated and precursors of alkyl radicals were mainly focused on the carboxylic acids and the alkyl halides.[2-4] In compared with the previous work, the transformation of the direct decarboxylation-decarbonylation under visible-light photocatalysis to provide the alkyl radicals has been less investigated.

Scheme 1. Photocatalyzed Decarboxylative Reactions of Acids

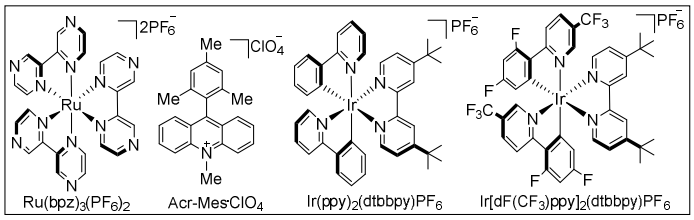


RESULTS AND DISCUSSION

As shown in Table 1, we began our investigation by screening conditions for the decarboxylative-decarbonylative reaction of 2-(*tert*-butyl)-2-oxoacetic acid (**1a**). To our delight, the only desired decarboxylative-decarbonylation product **3a**[4c, 6] (in a good yield of 71%) was observed at 25 °C by irradiation with blue LEDs when $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ was used as the photocatalyst, NaOAc as the base and benzyl acrylate (**2a**) as the alkyl radical acceptor (entry 1). When $Ir(ppy)_2(dtbbpy)PF_6$ was used instead of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, the yield of the product **3a** was drastically decreased to 24% (entry 2). Meanwhile, the reaction did not occur when other more

oxidizing photocatalysts at the excited states, yet less reducing at the reduced excited states, such as $Ru(bpz)_3(PF_6)_2$[7] and Acr-Mes•ClO_4 (entries 3-4), were used as the catalysts. The presence of the proton might have an effect on the redox potential of $Ru(bpz)_3(PF_6)_2$. And the reduced state catalyst ($Acr^{\bullet}$-Mes) could not reduce the enolate radical.[8] Other inorganic bases, which have been widely used in the decarboxylative functionalization by photoredox catalysis,[2] gave the slightly lower yields (entries 5-7). Unexpectedly, the screening of organic bases showed that 1,4-diazabicyclo[2.2.2]-octane (DABCO) was more effective in this decarboxylative-decarbonylative alkylation protocol, which can be readily oxidized by excited-state $*Ir^{III}$ complex ($E_{1/2}^{red}$ [$*Ir^{III}/Ir^{II}$] = + 1.21 V versus saturated calomel electrode (SCE))[2a] (entry 8). Next, the solvent screening was performed, and the optimal one was found to be acetone, gaving 91% yield (entry 15). Notably, when a protic solvent was used instead of acetone, the decarbonylation reaction did not occur (entry 13). This phenomenon helped us explore the single-electron-transfer (SET) process which could occur in the ketoacid oxidization step of the photocatalytic cycle. As expected, control experiments demonstrated that the base, the photocatalyst and the visible light were all essential components for this reaction (entries 16-18). When the catalytic amount of base was used, the yield of the product was decreased to 30% (entry 19) and the substrate (**2a**) was completely consumed.

Table 1. Screening of the Reaction Conditions for the Decarboxylative-Decarbonylative Alkylation of α-Oxo Acid[a]



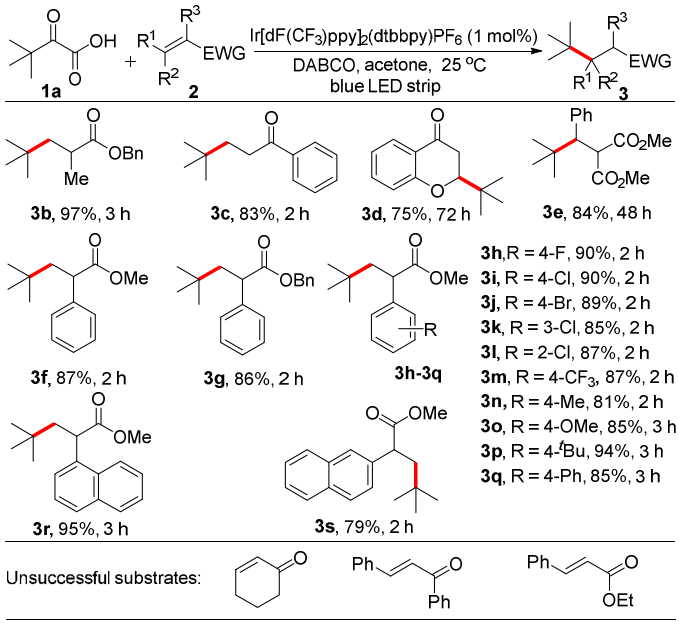
entry	photocatalyst	base	solvent	yield (%)[b]
1	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	NaOAc	DMF	71
2	$Ir(ppy)_2(dtbbpy)PF_6$	NaOAc	DMF	24
3	$Ru(bpz)_3(PF_6)_2$	NaOAc	DMF	0
4	Acr-Mes•ClO_4	NaOAc	DMF	0
5[c]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	Cs_2CO_3	DMF	67
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	K_2HPO_4	DMF	40
7	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	CsF	DMF	47
8	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DABCO	DMF	86
9[d]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	TMG	DMF	83
10	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	Et_3N	DMF	29
11	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DABCO	THF	82
12	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DABCO	CH_3CN	67
13	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DABCO	MeOH	0
14	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DABCO	CH_2Cl_2	77
15	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DABCO	acetone	91

16[e]	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	DABCO	acetone	0
17	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	—	acetone	5
18	—	DABCO	acetone	0
19[f]	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	DABCO	acetone	30

[a]Unless otherwise noted, the reaction conditions are as follows: **1a** (0.3 mmol), **2a** (0.2 mmol), photocatalyst (0.002 mmol), base (0.3 mmol), solvent (4 mL), 25 W blue LED strip, 25 °C, 2 h and under a N_2 atmosphere. [b]Isolated yield. [c]Reaction time: 5 h. [d]Reaction time: 3.5 h. [e]In the absence of a light source. [f]Base: 20 mol%. TMG = Tetramethylguanidine

Having optimized the conditions for this photoredox-catalyzed decarboxylative-decarbonylation reaction, the scope of Michael acceptors was then explored. As shown in Table 2, a broad range of electrophilic olefins could successfully participate in this CO-extrusion, conjugate addition protocol. Notably, methyl substitution at the α-position of acrylate olefins was tolerated very well to give the corresponding decarboxylative-decarbonylation product (**3b**) in excellent yield. Moreover, both of the acyclic and cyclic unsaturated ketones were well tolerated in this transformation (products **3c** and **3d**, with the yield of 83% and 75%, respectively). This protocol could also be extended to the alkylation of chromone, giving the corresponding 2-substituted chromanone scaffold (**3d**), which is a privileged structural motif found in a large number of natural products and pharmaceutical molecules, exhibiting many biological activities.[9] Sterically demanding olefins could also be readily converted into the target compounds, although the reaction times were longer (**3d-3e**). As expected, methyl 2-phenylacrylate and benzyl 2-phenylacrylate behaved similarly (**3f-3g**). Furthermore, both electron-deficient and electron-rich aryl substitution at the α-position of acrylate olefins were well accommodated in this conversion under the photoredox catalysis (**3h-3q**). It was also found that the substrates with a bulky naphthyl group were converted into the target compounds with good to excellent yields (**3r-3s**). However, the transformation of some other substrates was not success.

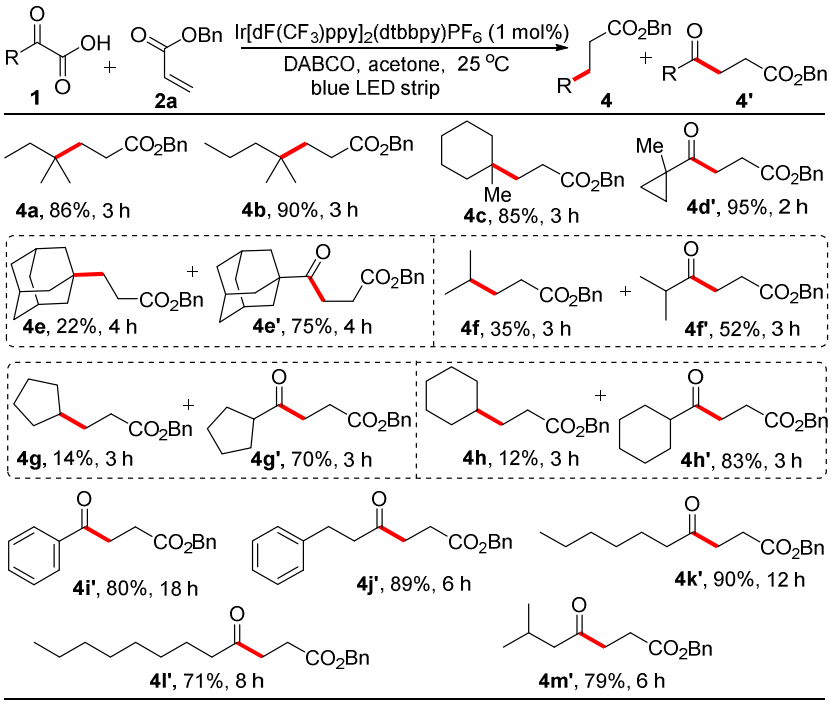
Table 2. Scope of Michael Acceptors in the Decarboxylative-Decarbonylation Reaction[a,b]



[a]Unless otherwise noted, reaction conditions are as follows: **1a** (0.3 mmol), **2** (0.2 mmol), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (0.002 mmol), DABCO (0.3 mmol), acetone (4 mL), 25 W blue LED strip, 25 °C and under a N_2 atmosphere. [b]Isolated yield.

Given the success of the decarboxylative and decarbonylative alkylation of 2-(*tert*-butyl)-2-oxoacetic acid (**1a**), we turned our attention to other α-keto acids to explore the potential of this transformation (Table 3). A range of the tertiary alkyl ketoacids could serve as viable tertiary carbon radicals under the optimal conditions (**4a-4c**). Notably, the substrate with a cyclopropyl group at the α-position of the keto acid was entirely converted into 1,4-dicarbonyl compound (**4d'**) without any decarbonylated or rearranged product. This significant result shows that the coupling rate of benzyl acrylate (**2a**) with the cyclopropyl formyl radical is faster than the ring opening.[13b] The reactions of adamantyl and secondary alkyl ketoacids led to the decarboxylative-decarbonylative coupling products (**4e-4h**)[10] in low yields with the major products of γ-ketoesters (**4e'-4h'**) derived from the coup-ling of the intermediate acyl radicals with benzyl acrylate. The aryl and primary alkyl ketoacids were entirely converted into the 1,4-dicarbonyl compounds (**4i'-4m'**).[11] In conclusion, the tertiary alkyl ketoacids are prone to rapid decarboxylation-decarbonylation, the aryl and primary alkyl substrates only undergo decarboxylation reaction, and the secondary acyl radicals will produce a small amount of decarbonylative alkylation products[12] with major decarboxylative alkylation products under the reaction conditions.

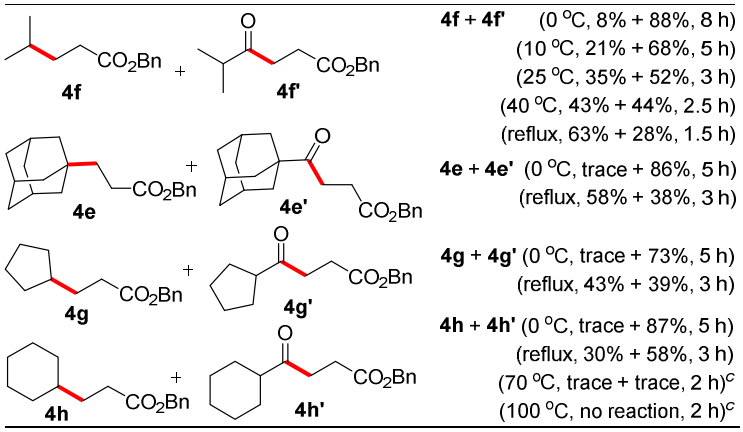
Table 3. Scope Evaluation of the α-Keto Acids[a,b]



[a]Unless otherwise noted, reaction conditions are as follows: **1** (0.3 mmol), **2a** (0.2 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.002 mmol), DABCO (0.3 mmol), acetone (4 mL), 25 W blue LED strip, 25 °C and under a N_2 atmosphere. [b]Isolated yield.

As another important parameter that can affect the decarboxylative-decarbonylative coupling reaction, temperature effect was also investigated.[13] With the temperature increased, the yield of the target product **4f** was improved. Especially at the boiling point of the solvent, the decarboxylation-decarbonylation yields of the adamantly and secondary ketoacids increased dramatically with the simultaneous decrease of the 1,4-dicarbonyl product yields. However, when further increased the temperature to 70 or 100 °C, the reaction did not success (Table 4, **4h**). The α-Oxo acids might be unstable at this high temperature. In contrast, the 1,4-dicarbonyl compounds were given at the highest yields with only trace of decarboxylation-decarbonylation products produced at low reaction temperature (0 °C).

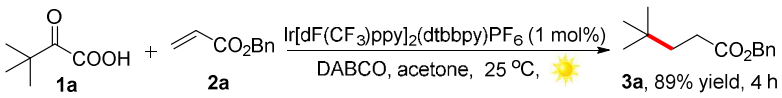
Table 4. Temperature-Dependent Decarboxylation-Decarbonylation of the Ketoacids[a,b]



[a]Unless otherwise noted, reaction conditions are as follows: ketoacids (0.3 mmol), **2a** (0.2 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.002 mmol), DABCO (0.3 mmol), acetone (4 mL), 25 W blue LED strip and under a N_2 atmosphere. [b]Isolated yield. [c]The reaction vessel was sealed with a teflon screw cap.

Demonstration of the synthetic utility of this decarboxylative-decarboxylative alkylation processes was also performed. As shown in Scheme 2, the decarbonylative alkylation reaction could also successfully proceed under natural sunlight irradiation, affording the desired product **3a** in a slightly longer reaction time

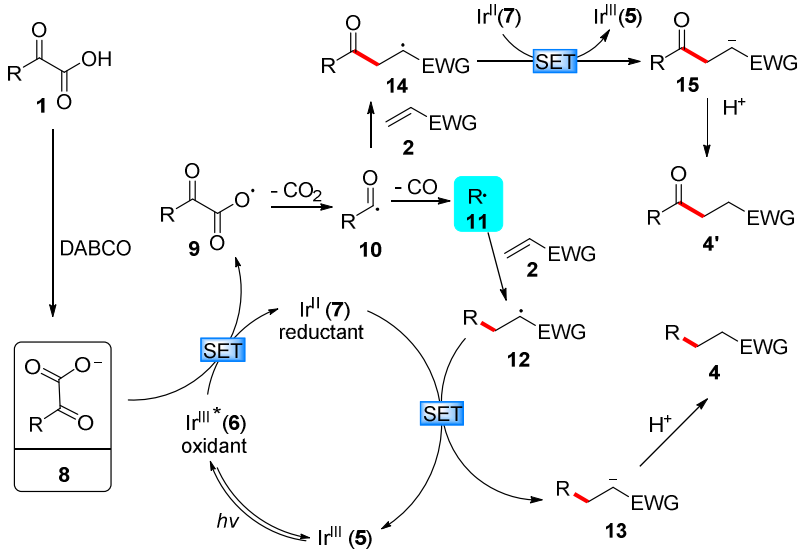
Scheme 2. Sunlight-Driven Reaction



Based on our previous work as well as other reports,[14] a plausible reaction mechanism was proposed, as illustrated in Scheme 3. Irradiation of the ground-state photocatalyst Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (**5**)

with visible light produces the excited-state photocatalyst (**6**). This photoexcited species is a strong electron acceptor ($E_{1/2}$ [$^{*}Ir^{III}/Ir^{II}$] = + 1.21 V vs. SCE in MeCN) and undergo a single electron transfer (SET) with the anion (**8**) formed by the proton translocation of ketoacid (**1**) in the presence of an organic base, which results in the generation of a α-oxo carboxyl radical (**9**). This radical can rapidly undergo CO_2-extrusion and produce an acyl radical (**10**) along with the reduced photocatalyst (**7**). Species **10** is then converted to the stabilized alkyl radical (**11**) through decarbonylation. The nucleophilic alkyl radical (**11**) readily undergoes the coupling reaction with an electrophilic olefin (**2**) to generate the new α-alkyl radical (**12**). The intermediate **12** ($E_{1/2}^{red}$ = - 0.60 V vs. SCE)[15] can be readily reduced by the strong reducing Ir^{II} species (**7**) ($E_{1/2}$ [Ir^{III}/Ir^{II}] = - 1.37 V vs. SCE)[2a] to generate the carbanion intermediate (**13**) and the ground-state photocatalyst **5**. The final product (**4**) is then afforded by the protonation of the species **13**. Likewise, in the case of the acylation reaction, acyl radical **10** readily undergoes conjugate addition with electron-deficient olefin **2** to give the 1,4-dicarbonyl compounds **4'**. To support the mechanism, a series of Stern–Volmer fluorescence quenching studies were performed which clearly showed that the anion (**8**) could efficiently quench the excited-state photocatalyst $^{*}Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (no quenching was observed by ketoacids in the absence of DABCO).

Scheme 3. A Plausible Reaction Mechanism



CONCLUSION

In summary, we have developed the visible-light photoredox catalysis to achieve the decarboxylative-decarbonylative alkylation of ketoacids with electron-deficient olefins. A series of quaternary carbons and γ-ketoesters have been directly constructed by the photoredox 1,4-conjugate addition of the corresponding alkyl ketoacids with electrophilic alkenes. The decarbonylation of primary, secondary and tertiary alkyl-substituted acyl radicals was investigated. And, the tertiary alkyl ketoacids have shown as good precursors of tertiary alkyl radicals. Mechanistic studies of the transformation were also performed and a plausible reaction mechanism was proposed.

EXPERIMENTAL SECTION

General Information. All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200−300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. The spectra were recorded in deuterochloroform ($CDCl_3$) as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.0 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet, br = broad), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. IR spectra were recorded on a FT-IR instrument and are reported in wave numbers (cm^{-1}). HRMS were performed on a Bruker Apex II mass instrument (ESI).

General procedure a for α-oxo acids.[16] To a solution of alkyl methyl ketone (5 mmol, 1.0 eq.) and NaOH (10.0 mmol, 2.0 eq.) in 15 mL H_2O cooled to 0 °C, $KMnO_4$ (10.0 mmol, 2.0 eq.) were added over a period of 30 minutes. The mixture was warmed to room temperature and stirred for additional 16 hours. The resulting suspension was filtered and washed several times with H_2O. Under cooling, the filtrate was treated with $HCl_{conc.}$ (2 mL) and extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The title compound was obtained as a white solid and was used in the following step without further purification.

General procedure b for α-oxo acids.[17] A solution of 1,3-diphenylimidazolidine-2,4,5-trione (**B**) (1.00 g, 3.76 mmol) in dry THF (5 mL) was added dropwise to a solution of Grignard reagent (1.1 equiv) in dry THF under a N_2 atmosphere at −78 °C and stirred for 1 h. The reaction mixture was poured into sat. aq. NH_4Cl and then extracted with AcOEt. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was chromatographed on silica gel with hexane−AcOEt (4:1) to further give product **C** as a yellow solid.

NaOH in H_2O (4 M, 3 mL) was added to a solution of compound **C** (2.94 mmol) in MeOH (10 mL) at room temperature and the mixture was heated at 50 °C for 1 h. The reaction mixture was then poured into H_2O and extracted with AcOEt to give an organic layer including *N,N'*-diphenylurea. The thus-obtained aqueous layer was acidified with 1N HCl, and then extracted with AcOEt. The AcOEt solution was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The title compound **D** was obtained as a white solid and was used in the following step without further purification.

General procedures for the photocatalytic reaction. α-Oxo acid **1** (0.3 mmol), benzyl acrylate **2a** (0.2 mmol) and DABCO (0.3 mmol) were added to a solution of photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1 mol%) in dry acetone (4 mL) at room temperature. The heterogenous mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus

equipped with a 25 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at 25 ^{o}C until the starting material was completely consumed as monitored by TLC. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by flash column chromatography on silica gel (hexanes / EA = 20:1 ~ 10:1), which furnished the title compounds as described.

Luminescence quenching experiments. Fluorescence quenching experiments were carried out with freshly prepared solutions of 1 mM $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ in acetone at room temperature. The solutions were excited at 385 nm and the fluorescence was measured from 430 nm to 600 nm. In a typical experiment, appropriate amount of quencher was added to the measured solution in a quartz cuvette and the emission spectrum of the sample was collected. A series of Stern–Volmer fluorescence quenching studies clearly showed that anion **8** (**1a** + DABCO) could efficiently quench the excited-state photocatalyst $^{*}Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (no quenching was observed by ketoacids in the absence of DABCO).

*benzyl 4,4-dimethylpentanoate (**3a**)*.[4c] Colorless oil; 40.2 mg, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.88 (s, 9H), 1.55−1.59 (m, 2H), 2.31−2.35 (m, 2H), 5.10 (s, 2H), 7.29−7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.0, 30.0, 30.1, 38.5, 66.1, 128.1, 128.2, 128.5, 136.0, 174.1; IR (KBr, cm^{-1}): 3452, 2956, 1738, 1467, 1366, 1297, 1213, 1146, 1021, 980, 698. HRMS (ESI) for $C_{14}H_{20}NaO_2$ $[M + Na]^+$ calcd 243.1356, found 243.1355.

*benzyl 2,4,4-trimethylpentanoate (**3b**)*.[18] Colorless oil; 45.4 mg, 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.86 (s, 9H), 1.16−1.20 (m, 4H), 1.88 (dd, *J* = 14.0, 9.2 Hz, 1H), 2.52−2.60 (m, 1H), 5.09 (s, 2 H), 7.30−7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 20.3, 29.4, 30.7, 36.2, 47.7, 66.1, 128.1, 128.1, 128.5, 136.1, 177.7; IR (KBr, cm^{-1}): 3375, 2956, 1737, 1595, 1458, 1252, 1186, 1148, 697. HRMS (ESI) for $C_{15}H_{22}NaO_2$ $[M + Na]^+$ calcd 257.1512, found 257.1514.

*4,4-dimethyl-1-phenylpentan-1-one (**3c**)*.[19] Colorless oil; 31.6 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.96 (s, 9H), 1.62−1.66 (m, 2H), 2.92−2.96 (m, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.97 (dd, *J* = 7.9, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.2, 30.2, 34.3, 38.1, 128.0, 128.5, 132.8, 137.0, 201.1; IR (KBr, cm^{-1}): 3357, 2956, 1687, 1449, 1366, 1288, 1221, 743, 691. HRMS (ESI) for $C_{13}H_{18}NaO$ $[M + Na]^+$ calcd 213.1250, found 213.1253.

*2-(tert-butyl)chroman-4-one (**3d**)*.[20] White solid; 30.6 mg, 75% yield; mp 57−59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.06 (s, 9H), 2.62−2.74 (m, 2H), 4.06 (dd, *J* = 12.3, 4.0 Hz, 1H), 6.97−7.01 (m, 2H), 7.45−7.49 (m, 1H), 7.87 (dd, *J* = 8.1, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 25.5, 34.1, 38.4, 85.2, 117.9, 120.7, 121.0, 126.8, 135.9, 162.2, 193.6; IR (KBr, cm^{-1}): 3354, 2960, 1693, 1604, 1465, 1307, 1234, 1115, 764,. HRMS (ESI) for $C_{13}H_{16}NaO_2$ $[M + Na]^+$ calcd 227.1043, found 227.1045.

*dimethyl 2-(2,2-dimethyl-1-phenylpropyl)malonate (**3e**)*.[21] White solid; 47.0 mg, 84% yield; mp 44−46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.88 (s, 9H), 3.25 (s, 3H), 3.47 (d, *J* = 11.0 Hz,1H), 3.77 (s, 3H), 4.03 (d, *J* = 11.0 Hz,1H), 7.13−7.27 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 28.1, 34.3, 52.1, 52.8, 54.7, 55.2, 126.5, 127.4, 139.9, 168.6, 169.9; IR (KBr, cm^{-1}): 3457, 2954, 1764, 1738, 1434, 1368, 1264, 1153, 1033, 707. HRMS (ESI) for $C_{16}H_{22}NaO_4$ $[M + Na]^+$ calcd 301.1410, found 301.1412.

*methyl 4,4-dimethyl-2-phenylpentanoate (**3f**)*. Colorless oil; 38.3 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.89 (s, 9H), 1.58 (dd, *J* = 14.0, 3.8 Hz, 1H), 2.31 (dd, *J* = 14.0, 9.3 Hz, 1H), 3.63−3.69 (m, 4H), 7.20−7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.3, 30.9, 47.4, 48.0, 52.0, 127.0, 127.7, 128.6, 140.9, 175.2; IR (KBr, cm^{-1}): 3372, 2953, 1739, 1435, 1366, 1208, 1153, 697. HRMS (ESI) for $C_{14}H_{20}NaO_2$ $[M + Na]^+$ calcd 243.1356, found 243.1355.

*benzyl 4,4-dimethyl-2-phenylpentanoate (**3g**)*.[22] White solid; 50.9 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.88 (s, 9H), 1.59 (dd, *J* = 14.0, 3.7 Hz, 1H), 2.33 (dd, *J* = 14.0, 9.3 Hz, 1H), 3.70 (dd, *J* = 9.3, 3.7 Hz, 1H), 5.01 (d, *J* = 12.4 Hz, 1H), 5.11 (d, *J* = 12.4 Hz, 1H), 7.20−7.34 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.4, 31.0, 47.2, 48.2, 66.6, 127.0, 127.8, 128.0, 128.0, 128.4, 128.6, 135.8, 140.8, 174.5; IR (KBr, cm^{-1}): 3437, 2952, 1726, 1455, 1368, 1207, 1170, 1153, 749, 697. HRMS (ESI) for $C_{20}H_{24}KO_2$ $[M + K]^+$ calcd 335.1408, found 335.1410.

*methyl 2-(4-fluorophenyl)-4,4-dimethylpentanoate (**3h**)*. Colorless oil; 43.0 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.89 (s, 9H), 1.55 (dd, *J* = 14.0, 4.0 Hz, 1H), 2.27 (dd, *J* = 14.0, 9.1 Hz, 1H), 3.59−3.68 (m, 4H), 6.98 (t, *J* = 8.7 Hz, 2H), 7.26−7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.4, 31.0, 47.3, 47.5, 52.1, 115.4 (d, *J* = 21.3 Hz), 129.3 (d, *J* = 7.9 Hz), 136.6 (d, *J* = 3.1 Hz), 161.9 (d, *J* = 243.7 Hz), 175.1; IR (KBr, cm^{-1}): 3451, 2954, 1739, 1509, 1367, 1225, 1152, 837, 517. HRMS (ESI) for $C_{14}H_{19}FKO_2$ $[M + K]^+$ calcd 277.1001, found 277.1004.

*methyl 2-(4-chlorophenyl)-4,4-dimethylpentanoate (**3i**)*. White solid; 45.7 mg, 90% yield; mp 43−45 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.89 (s, 9H), 1.55 (dd, *J* = 14.0, 4.0 Hz, 1H), 2.26 (dd, *J* = 14.0, 9.1 Hz, 1H), 3.62−3.65 (m, 4H), 7.24−7.29 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.3, 31.0, 47.3, 47.4, 52.1, 128.7, 129.1, 132.9, 139.3, 174.9; IR (KBr, cm^{-1}): 3449, 2957, 1736, 1491, 1367, 1208, 1153, 1093, 1016, 826, 740. HRMS (ESI) for $C_{14}H_{19}ClKO_2$ $[M + K]^+$ calcd 293.0705, found 293.0709.

*methyl 2-(4-bromophenyl)-4,4-dimethylpentanoate (**3j**)*. White solid; 52.9 mg, 89% yield; mp 41−43 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.88 (s, 9H), 1.54 (dd, *J* = 14.0, 4.0 Hz, 1H), 2.26 (dd, *J* = 14.0, 9.1 Hz, 1H), 3.60−3.63 (m, 4H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.3, 31.0, 47.2, 47.5, 52.1, 121.0, 129.5, 131.7, 139.8, 174.8; IR (KBr, cm^{-1}): 3456, 2954, 1738, 1488, 1366, 1208, 1153, 1074, 1012, 824. HRMS (ESI) for $C_{14}H_{19}BrKO_2$ $[M + K]^+$ calcd 337.0200, found 337.0206.

*methyl 2-(3-chlorophenyl)-4,4-dimethylpentanoate (**3k**)*. White solid; 43.2 mg, 85% yield; mp 38−40 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.89 (s, 9H), 1.55 (dd, *J* = 14.0, 3.8 Hz, 1H), 2.28 (dd, *J* = 14.0, 9.3 Hz, 1H), 3.61−3.70 (m, 4H), 7.18−7.22 (m, 3H), 7.32 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.3, 31.0, 47.3, 47.8, 52.1, 126.0, 127.2, 128.0, 129.8, 134.4, 142.8, 174.6; IR (KBr, cm^{-1}): 3456, 2954, 1739, 1595, 1477, 1432, 1367, 1208, 1154, 692. HRMS (ESI) for $C_{14}H_{19}ClKO_2$ $[M + K]^+$ calcd 293.0705, found 293.0709.

*methyl 2-(2-chlorophenyl)-4,4-dimethylpentanoate (**3l**)*. Colorless oil; 44.3 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.91 (s, 9H), 1.54 (dd, *J* = 14.0, 4.2 Hz, 1H), 2.25 (dd, *J* = 14.0, 8.6 Hz, 1H), 3.65 (s, 3H), 4.29 (dd, *J* = 8.6, 4.2 Hz, 1H), 7.13−7.18 (m, 1H), 7.19−7.24 (m, 1H), 7.36 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.44 (dd, *J* = 7.8, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.4, 31.1, 43.5, 47.1, 52.1, 127.1, 128.1, 128.7, 129.6, 133.3, 138.4, 174.7; IR (KBr, cm^{-1}): 3370, 2953, 1740,

1475, 1367, 1208, 1157, 1037, 749. HRMS (ESI) for $C_{14}H_{19}ClKO_2$ $[M + K]^+$ calcd 293.0705, found 293.0711.

*methyl 4,4-dimethyl-2-(4-(trifluoromethyl)phenyl)pentanoate (**3m**)*. Colorless oil; 50.1 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.90 (s, 9H), 1.57 (dd, *J* = 14.0, 3.9 Hz, 1H), 2.32 (dd, *J* = 14.0, 9.1 Hz, 1H), 3.65 (s, 3H), 3.73 (dd, *J* = 9.1, 3.9 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.3, 31.0, 47.4, 48.0, 52.2, 122.8, 125.6 (q, *J* = 3.7 Hz), 128.2, 129.4 (q, *J* = 32.2 Hz), 144.8, 174.5; IR (KBr, cm^{-1}): 3455, 2957, 1740, 1619, 1478, 1421, 1327, 1165, 1127, 1069, 1020. HRMS (ESI) for $C_{15}H_{19}F_3KO_2$ $[M + K]^+$ calcd 327.0969, found 327.0973.

*methyl 4,4-dimethyl-2-(p-tolyl)pentanoate (**3n**)*. Colorless oil; 37.9 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.89 (s, 9H), 1.55 (dd, *J* = 14.1, 3.7 Hz, 1H), 2.26−2.31 (m, 4H), 3.58−3.64 (m, 4H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 21.0, 29.3, 30.9, 47.4, 47.6, 51.9, 127.6, 129.3, 136.6, 137.9, 175.4; IR (KBr, cm^{-1}): 3456, 2954, 1738, 1513, 1435, 1366, 1206, 1152, 985, 820. HRMS (ESI) for $C_{15}H_{26}NO_2$ $[M + NH_4]^+$ calcd 252.1958, found 252.1957.

*methyl 2-(4-methoxyphenyl)-4,4-dimethylpentanoate (**3o**)*. Colorless oil; 42.6 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.89 (s, 9H), 1.56 (dd, *J* = 14.1, 6.2 Hz, 1H), 2.26 (dd, *J* = 14.0, 9.2 Hz, 1H), 3.59−3.63 (m, 4H), 3.77 (s, 3H), 6.83 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.4, 30.9, 47.1, 47.4, 51.9, 55.2, 114.0, 128.7, 133.0, 158.6, 175.5; IR (KBr, cm^{-1}): 3451, 2953, 1737, 1611, 1512, 1366, 1248, 1152, 1036, 832,. HRMS (ESI) for $C_{15}H_{22}KO_3$ $[M + K]^+$ calcd 289.1201, found 289.1200.

*methyl 2-(4-(tert-butyl)phenyl)-4,4-dimethylpentanoate (**3p**)*. Colorless oil; 51.8 mg, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.90 (s, 9H), 1.29 (s, 9H), 1.55 (dd, *J* = 14.1, 3.3 Hz, 1H), 2.32 (dd, *J* = 14.0, 9.8 Hz, 1H), 3.62−3.65 (m, 4H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.3, 31.0, 31.3, 34.4, 47.5, 47.5, 51.9, 125.5, 127.3, 137.8, 149.8, 175.4; IR (KBr, cm^{-1}): 3347, 2958, 1737, 1477, 1366, 1281, 1153, 1022, 834, 740. HRMS (ESI) for $C_{18}H_{28}KO_2$ $[M + K]^+$ calcd 315.1721, found 315.1720.

*methyl 2-([1,1'-biphenyl]-4-yl)-4,4-dimethylpentanoate (**3q**)*. White solid; 50.6 mg, 85% yield; mp 82−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.92 (s, 9H), 1.62 (dd, *J* = 14.0, 3.7 Hz, 1H), 2.34 (dd, *J* = 14.0, 9.3 Hz, 1H), 3.65 (s, 3H), 3.71 (dd, *J* = 9.3, 3.6 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.38−7.43 (m, 4H), 7.51−7.57 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.4, 31.0, 47.4, 47.7, 52.0, 127.0, 127.2, 127.3, 128.2, 128.7, 139.9, 140.0, 140.7, 175.2; IR (KBr, cm^{-1}): 3454, 2954, 1737, 1487, 1366, 1210, 1153, 839, 752, 698. HRMS (ESI) for $C_{20}H_{24}KO_2$ $[M + K]^+$ calcd 335.1408, found 335.1410.

*methyl 4,4-dimethyl-2-(naphthalen-1-yl)pentanoate (**3r**)*. Colorless oil; 51.4 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.00 (s, 9H), 1.69 (dd, *J* = 14.1, 3.2 Hz, 1H), 2.54 (dd, *J* = 14.0, 9.3 Hz, 1H), 3.65 (s, 3H), 4.53 (dd, *J* = 9.3, 3.1 Hz, 1H), 7.44−7.54 (m, 2H), 7.56−7.61 (m, 2H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 8.24 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.4, 31.2, 42.7, 47.3, 52.1, 123.1, 125.1, 125.5, 125.6, 126.3, 127.5, 129.0, 131.0, 134.0, 137.0, 172.3; IR (KBr, cm^{-1}): 3454, 2954, 1738, 1477, 1366, 1280, 1198, 1151, 779, 738. HRMS (ESI) for $C_{18}H_{22}NaO_2$ $[M + Na]^+$ calcd 293.1512, found 293.1511.

*methyl 4,4-dimethyl-2-(naphthalen-2-yl)pentanoate (**3s**)*. White solid; 42.5 mg, 79% yield; mp 63−64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.96 (s, 9H), 1.71 (dd, *J* = 14.0, 3.9 Hz, 1H), 2.43 (dd, *J* = 14.0, 9.1 Hz, 1H), 3.67 (s, 3H), 3.87 (dd, *J* = 9.1, 3.9 Hz, 1H), 7.43−7.52 (m, 3H), 7.79−7.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.4, 31.0, 47.3, 48.2, 52.0, 125.7, 126.0, 126.1, 126.4, 127.6, 127.7, 128.3, 132.5, 133.4, 138.3, 175.2; IR (KBr, cm^{-1}): 3449, 2953, 1734, 1431, 1197, 1147, 816, 739, 481. HRMS (ESI) for $C_{18}H_{22}KO_2$ $[M + K]^+$ calcd 309.1251, found 309.1256.

*benzyl 4,4-dimethylhexanoate (**4a**)*. Colorless oil; 40.2 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.81 (t, *J* = 7.6 Hz, 9H), 1.21 (q, *J* = 7.5 Hz, 2H), 1.53−1.58 (m, 2H), 2.28−2.32 (m, 2H), 5.11 (s, 2H), 7.29−7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 8.3, 26.2, 29.6, 32.4, 33.8, 35.9, 66.1, 128.1, 128.2, 128.5, 136.1, 174.3; IR (KBr, cm^{-1}): 3450, 2961, 1737, 1456, 1380, 1302, 1160, 996, 749, 698. HRMS (ESI) for $C_{15}H_{22}O_2Na$ $[M + Na]^+$ calcd 257.1512, found 257.1514.

*benzyl 4,4-dimethylheptanoate (**4b**)*. Colorless oil; 44.6 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.84 (s, 6H), 0.87 (t, *J* = 6.9 Hz, 3H), 1.11−1.17 (m, 2H), 1.19−1.28 (m, 2H), 1.54−1.58 (m, 2H), 2.28−2.32 (m, 2H), 5.10 (s, 2H), 7.30−7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.9, 17.1, 26.8, 29.6, 32.4, 36.4, 44.2, 66.1, 128.1, 128.2, 128.5, 136.1, 174.3; IR (KBr, cm^{-1}): 3450, 2926, 1738, 1455, 1380, 1301, 1161, 698. HRMS (ESI) for $C_{16}H_{24}O_2Na$ $[M + Na]^+$ calcd 271.1669, found 271.1670.

*benzyl 3-(1-methylcyclohexyl)propanoate (**4c**)*.[4c] Colorless oil; 44.1 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.84 (s, 3H), 1.19−1.32 (m, 5H), 1.37−1.47 (m, 5H), 1.58−1.62 (m, 2H), 2.29−2.33 (m, 2H), 5.11 (s, 2H), 7.30−7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 21.9, 24.4, 26.4, 28.9, 32.3, 36.6, 37.4, 66.1, 128.1, 128.2, 128.5, 136.1, 174.4; IR (KBr, cm^{-1}): 3449, 2926, 1738, 1455, 1300, 1161, 697. HRMS (ESI) for $C_{17}H_{24}O_2Na$ $[M + Na]^+$ calcd 283.1669, found 283.1668.

*benzyl 4-(1-methylcyclopropyl)-4-oxobutanoate (**4d'**)*. Colorless oil; 46.6 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.72 (q, *J* = 3.9 Hz, 2H), 1.25 (q, *J* = 4.0 Hz, 2H), 1.36 (s, 3H), 2.62 (t, *J* = 6.5 Hz, 2H), 2.73 (t, *J* = 6.6 Hz, 2H), 5.11 (s, 2H), 7.29−7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 18.3, 19.6, 26.4, 28.2, 32.7, 66.3, 128.1, 128.5, 135.8, 172.8, 209.6; IR (KBr, cm^{-1}): 3363, 2964, 1736, 1688, 1266, 1164, 1092, 737. HRMS (ESI) for $C_{15}H_{18}O_3Na$ $[M + Na]^+$ calcd 269.1148, found 269.1147.

*benzyl 3-((3r,5r,7r)-adamantan-1-yl)propanoate (**4e**)*. Colorless oil; 13.1 mg, 22% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.42−1.46 (m, 8H), 1.58−1.71 (m, 6H), 1.94 (br, 3H), 2.29−2.34 (m, 2H), 5.11 (s, 2H), 7.30−7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 28.2, 28.5, 31.9, 37.0, 38.9, 42.0, 66.1, 128.1, 128.2, 128.5, 136.1, 174.5; IR (KBr, cm^{-1}): 3450, 2957, 1738, 1456, 1299, 1257, 1160, 999, 748, 698. HRMS (ESI) for $C_{20}H_{26}O_2Na$ $[M + Na]^+$ calcd 321.1825, found 321.1828.

*benzyl 4-((3r,5r,7r)-adamantan-1-yl)-4-oxobutanoate (**4e'**)*. Yellow oil; 49.0 mg, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.71 (q, *J* = 14.1 Hz, 6H), 1.82 (d, *J* = 2.5 Hz ,6H), 2.03 (br, 3H), 2.61 (t, *J* = 6.6 Hz, 2H), 2.78 (t, *J* = 6.6 Hz, 2H), 5.10 (s, 2H), 7.29−7.37 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 27.8, 27.9, 30.9, 36.4, 38.2, 46.0, 66.3, 128.1,128.1, 128.4, 135.8, 172.8, 213.6; IR (KBr, cm^{-1}): 3450, 2906, 1738, 1701, 1453, 1347, 1205, 1154, 699. HRMS (ESI) for $C_{21}H_{26}O_3Na$ $[M + Na]^+$ calcd 349.1774, found 349.1774.

*benzyl 4-methylpentanoate (**4f**)*.[23] Colorless oil; 14.4 mg, 35% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.89 (d, *J* = 6.3 Hz, 6H), 1.52−1.60 (m, 3H), 2.36 (t, *J* = 7.7 Hz, 2H), 5.11 (s, 2H), 7.31−7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 22.2, 27.7, 32.4, 33.7, 66.1, 128.2, 128.5, 136.1, 173.8; IR (KBr, cm^{-1}): 3449, 2957, 1738, 1456, 1164, 993, 749, 697. HRMS (ESI) for $C_{13}H_{18}O_2Na$ [M + Na]$^+$ calcd 229.1199, found 229.1200.

*benzyl 5-methyl-4-oxohexanoate (**4f'**)*.[24] Colorless oil; 24.2 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.11 (d, *J* = 7.0 Hz, 6H), 2.60−2.67 (m, 3H), 2.79 (t, *J* = 6.4 Hz, 2H), 5.11 (s, 2H), 7.29−7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 18.2, 28.0, 34.7, 40.8, 66.4, 128.2, 128.5, 135.8, 172.7, 212.6; IR (KBr, cm^{-1}): 3407, 2970, 1737, 1713, 1384, 1164, 1093, 751, 699. HRMS (ESI) for $C_{14}H_{18}O_3Na$ [M + Na]$^+$ calcd 257.1148, found 257.1147.

*benzyl 3-cyclopentylpropanoate (**4g**)*. Colorless oil; 6.7 mg, 14% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.06−1.11 (m, 2H), 1.45−1.77 (m, 9H), 2.37 (t, *J* = 7.6 Hz, 2H), 5.11 (s, 2H), 7.30−7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 25.1, 31.1, 32.4, 33.7, 39.6, 66.1, 128.1, 128.2, 128.5, 136.1, 173.8; IR (KBr, cm^{-1}): 3392, 2950, 2863, 1738, 1454, 1261, 1169, 1135, 737, 697. HRMS (ESI) for $C_{15}H_{20}O_2Na$ [M + Na]$^+$ calcd 255.1356, found 255.1355.

*benzyl 4-cyclopentyl-4-oxobutanoate (**4g'**)*. Yellow oil; 36.3 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.52−1.68 (m, 4H), 1.71−1.86 (m, 4H), 2.64 (t, *J* = 6.7 Hz, 2H), 2.78 (t, *J* = 6.5 Hz, 2H), 2.85−2.93 (m, 1H), 5.11 (s, 2H), 7.29−7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 25.9, 28.0, 28.8, 36.0, 51.2, 66.3, 128.1, 128.5, 135.8, 172.7, 211.0; IR (KBr, cm^{-1}): 3452, 2955, 1737, 1711, 1454, 1353, 1166, 737, 699. HRMS (ESI) for $C_{16}H_{20}O_3Na$ [M + Na]$^+$ calcd 283.1305, found 283.1304.

*benzyl 3-cyclohexylpropanoate (**4h**)*.[25] Colorless oil; 6.0 mg, 12% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.84−0.92 (m, 2H), 1.11−1.25 (m, 4H), 1.52−1.57 (m, 2H), 1.62−1.70 (m, 5H), 2.37 (t, *J* = 7.7 Hz, 2H), 5.11 (s, 2H), 7.31−7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 26.2, 26.5, 31.9, 32.3, 32.9, 37.2, 66.1, 128.1, 128.2, 128.5, 136.1, 174.0; IR (KBr, cm^{-1}): 3451, 2923, 1737, 1451, 1292, 1161, 996, 736, 697. HRMS (ESI) for $C_{16}H_{22}O_2Na$ [M + Na]$^+$ calcd 269.1512, found 269.1513.

*benzyl 4-cyclohexyl-4-oxobutanoate (**4h'**)*. Yellow oil; 45.5 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.13−1.38 (m, 5H), 1.64−1.86 (m, 5H), 2.32−2.40 (m, 1H), 2.62 (t, *J* = 6.6 Hz, 2H), 2.76 (t, *J* = 6.4 Hz, 2H), 5.10 (s, 2H), 7.29−7.37 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 25.5, 25.7, 27.8, 28.3, 34.8, 50.6, 66.3, 128.1, 128.4, 135.8, 172.6, 211.8; IR (KBr, cm^{-1}): 3449, 2930, 1737, 1710, 1451, 1349, 1163, 999, 751, 699. HRMS (ESI) for $C_{17}H_{22}O_3Na$ [M + Na]$^+$ calcd 297.1461, found 297.1463.

*benzyl 4-oxo-4-phenylbutanoate (**4i'**)*.[26] Yellow oil; 42.9 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.82 (t, *J* = 6.6 Hz, 2H), 3.33 (t, *J* = 6.6 Hz, 2H), 5.15 (s, 2H), 7.28−7.36 (m, 5H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.54−7.58 (m, 1H), 7.96−7.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 28.2, 33.3, 66.4, 128.0, 128.1, 128.5, 128.6, 133.2, 135.8, 136.5, 172.7, 197.9; IR (KBr, cm^{-1}): 3454, 2918, 1736, 1687, 1450, 1216, 1160, 749, 693. HRMS (ESI) for $C_{17}H_{16}O_3Na$ [M + Na]$^+$ calcd 291.0992, found 291.0992.

*benzyl 4-oxo-6-phenylhexanoate (**4j'**)*. Yellow oil; 52.4 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.62−2.65 (m, 2H), 2.69−2.73 (m, 2H), 2.74−2.79 (m, 2H), 2.90 (t, *J* = 7.2 Hz, 2H), 5.11 (s,

2H), 7.15−7.20 (m, 3H), 7.24−7.38 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 27.9, 29.6, 37.1, 44.2, 66.4, 126.1, 128.1, 128.2, 128.2, 128.4, 128.5, 135.8, 140.9, 172.5, 207.8; IR (KBr, cm^{-1}): 3413, 2927, 1736, 1717, 1454, 1173, 1096, 699. HRMS (ESI) for $C_{19}H_{20}O_3Na$ $[M + Na]^+$ calcd 319.1305, found 319.1305.

*benzyl 4-oxodecanoate (**4k'**).* Yellow oil; 50.0 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.88 (t, *J* = 6.5 Hz, 3H), 1.26−1.32 (m, 6H), 1.53−1.59 (m, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 2.63 (t, *J* = 6.6 Hz, 2H), 2.73 (t, *J* = 6.5 Hz, 2H), 5.11 (s, 2H), 7.30−7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.0, 22.4, 23.7, 27.9, 28.8, 31.5, 36.9, 42.7, 66.4, 128.1, 128.1, 128.5, 135.8, 172.6, 209.0; IR (KBr, cm^{-1}): 3414, 2931, 1738, 1717, 1456, 1163, 1003, 738, 698. HRMS (ESI) for $C_{17}H_{24}O_3Na$ $[M + Na]^+$ calcd 299.1618, found 299.1618.

*benzyl 4-oxododecanoate (**4l'**).* Yellow oil; 43.2 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.88 (t, *J* = 6.6 Hz, 3H), 1.26 (br, 10H), 1.57 (t, *J* = 7.1 Hz, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 2.64 (t, *J* = 6.4 Hz, 2H), 2.73 (t, *J* = 6.5 Hz, 2H), 5.11 (s, 2H), 7.29−7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.1, 22.6, 23.7, 27.9, 29.1, 29.2, 29.3, 31.8, 36.9, 42.8, 66.4, 128.1, 128.2, 128.5, 135.8, 172.6, 209.1; IR (KBr, cm^{-1}): 3403, 2921, 1731, 1709, 1163, 749, 737, 698. HRMS (ESI) for $C_{19}H_{28}O_3Na$ $[M + Na]^+$ calcd 327.1931, found 327.1931.

*benzyl 6-methyl-4-oxoheptanoate (**4m'**).*[24] Colorless oil; 39.2 mg, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.91 (d, *J* = 6.6 Hz, 6H), 2.08−2.21 (m, 1H), 2.31 (d, *J* = 7.0 Hz, 2H), 2.61−2.64 (m, 2H), 2.69−2.73 (m, 2H), 5.11 (s, 2H), 7.29−7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 22.5, 24.6, 27.8, 37.5, 51.6, 66.4, 128.1, 128.1, 128.5, 135.8, 172.6, 208.5; IR (KBr, cm^{-1}): 3366, 2957, 1737, 1716, 1456, 1164, 993, 740, 699. HRMS (ESI) for $C_{15}H_{20}O_3Na$ $[M + Na]^+$ calcd 271.1305, found 271.1307.

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Notes

The authors declare no competing financial interest.

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Supporting Information

Devices for the photocatalytic reactions, ^{1}H and ^{13}C NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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