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Visible-light induced 1,2-dicarbofunctionalization of alkenes with quinoxalin-2(1*H*)-ones and malonic esters†

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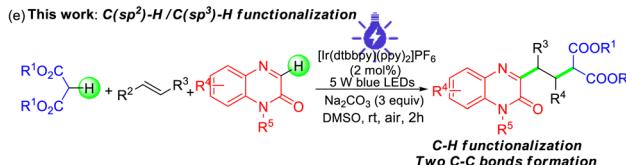
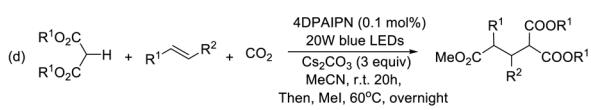
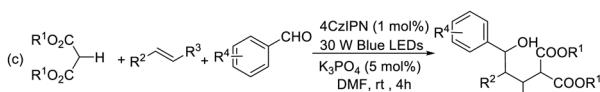
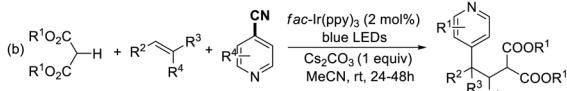
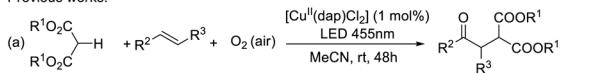
Visible-light photoredox catalyzed 1,2-arylation of alkenes with quinoxalin-2(1*H*)-ones and malonic esters has been developed through direct C(sp²)-H/C(sp³)-H functionalization under mild conditions. A number of quinoxalin-2(1*H*)-one containing esters could be obtained in moderate to good yields in a step and atom-economic manner. This transformation proceeded through a radical process, which features the advantages of mild conditions, a clean energy source, a wide substrate scope, and favorable functional group compatibility.

Difunctionalization of alkenes is a practical and powerful protocol for rapidly synthesizing complex molecular structures through the introduction of two functional groups into one molecular skeleton.^{1,2} During the past decade, visible-light photoredox catalyzed difunctionalization of alkenes has been increasingly utilized in modern organic synthesis due to its advantages such as mild conditions, a clean energy source and sustainability.^{3–6} In this context, photocatalytic difunctionalization of alkenes with malonates has been elegantly developed for constructing substituted esters *via* direct cleavage of the C–H bond of malonates.^{7–10} For example, in 2022, Reiser reported visible-light-induced Cu(II)-catalyzed oxoalkylation of alkenes with malonates and dioxygen leading to an oxoalkylated product (Scheme 1a).⁷ In 2022, Deng described photoinduced *fac*-Ir(ppy)₃ three-component

carboarylation of alkenes with cyano-substituted pyridines and malonic esters (Scheme 1b).⁸ In 2024, Yi's group presented photoredox-catalyzed 1,2-dicarbofunctionalization of alkenes with aldehydes and malonates to access δ -hydroxy esters and δ -keto esters in the presence of K₃PO₄ (Scheme 1c).⁹ Very recently, Abel and Beletskaya reported photoredox-catalyzed bi-functionalization of alkenes with malonic esters and CO₂ to prepare 3-arylpropane-1,1,3-tricarboxylic acid esters (Scheme 1d).¹⁰ Although significant advances have been achieved in these reactions, the development of new difunctionalization of alkenes with malonic esters and aromatic C–H feedstocks to construct more diverse functionalized esters in an atom-economic manner is still highly desirable.

Quinoxalin-2(1*H*)-ones are highly valuable heteroaromatic structural motifs present in many natural products, biologically

Previous works:



Scheme 1 Photoinduced difunctionalization of alkenes with malonic esters.

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active compounds and pharmaceuticals.¹¹ The direct C3(sp^2)-H functionalization of quinoxalin-2(1*H*)-ones has attracted great interest from chemists owing to the special chemical and biological activities of C3-substituted quinoxalin-2(1*H*)-one derivatives.^{12–15} With our continued interest in photoredox catalyzed reactions,¹⁶ herein, we wish to report visible-light photoredox catalyzed 1,2-arylation of alkenes with quinoxalin-2(1*H*)-ones and malonic esters *via* direct C(sp^2)-H/C(sp^3)-H functionalization at room temperature. The present transformations could be conducted in a step and atom-economic manner to access a series of quinoxalin-2(1*H*)-one containing esters in moderate to good yields (Scheme 1e).

At the outset of our investigations, the model reaction of styrene (**1a**), quinoxalin-2(1*H*)-one (**2a**), and diethyl malonate (**3a**) was employed to screen the reaction conditions (Table 1). As shown in entry 1, the desired product **4aa** could be obtained in 33% yield when Rose Bengal (2 mol%) was used as a photocatalyst with the addition of Na_2CO_3 in DMSO. The screening of other photocatalysts such as Rhodamine 6G, Eosin Y, Rhodamine B, $[Ir(dtbbpy)(ppy)_2]PF_6$, $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$, 4CzIPN, Mes-Acr-ClO₄, Ru(bpy)₃Cl₂·H₂O, and $[Ir(dtbbpy)(ppy)_2]PF_6$ found that $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ was the best one to provide product **4aa** in 81% yield (entry 5). Then, the reactions performed in a number of solvents including DCE, DCM, CH₃CN, 1,4-dioxane, DME, THF, and toluene were examined. No product or only a

trace amount of product was observed in the above solvents (entries 11–17). Further investigations of various bases demonstrated that Na_2CO_3 was still the best base to promote this transformation (ESI[†]). Changing the loading of the photocatalyst did not improve the reaction efficiency (entries 18 and 19). No transformation was observed in the absence of photocatalysts (entry 20). Testing of other light sources showed that green light LEDs, white light LEDs and purple light LEDs would lead to low reaction efficiency (entries 21–23). In addition, the desired product was obtained in 76% yield when the model reaction was conducted in the presence of dioxygen (entry 24).

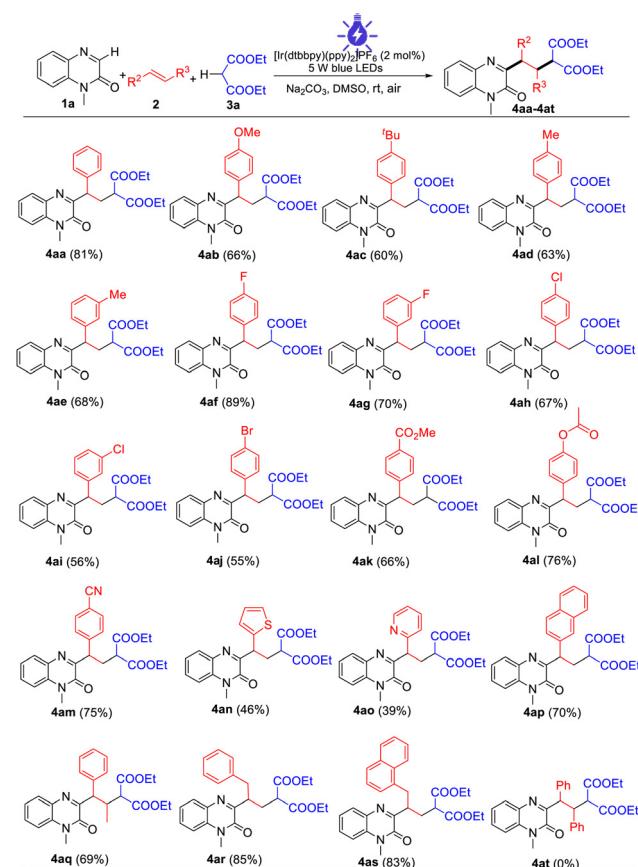
With the established reaction conditions in hand, we then investigated the scope of this 1,2-dicarbofunctionalization of alkenes with quinoxalin-2(1*H*)-ones and malonic esters (Table 2). A wide range of aromatic alkenes bearing both electron-donating groups and electron-withdrawing groups proved to be suitable for the reaction, and the corresponding products **4ab**–**4am** were isolated in moderate to good yields. It is worth noting that sensitive functionalities such as halogen, ester, acetoxy, and cyano groups were also tolerated in this procedure, highlighting the potential synthetic transformations of this protocol. Aromatic heterocyclic olefins such as 2-vinylthiophene and 2-vinylpyridine

Table 1 Optimization of the reaction conditions^a

Entry	Photocatalysts (x mol%)	Solvent	Yield ^b (%)
1	Rose Bengal (2)	DMSO	33
2	Rhodamine 6G (2)	DMSO	0
3	Eosin Y (2)	DMSO	26
4	Rhodamine B (2)	DMSO	40
5	$[Ir(dtbbpy)(ppy)_2]PF_6$ (2)	DMSO	81
6	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (2)	DMSO	65
7	4CzIPN (2)	DMSO	56
8	Mes-Acr-ClO ₄ (2)	DMSO	59
9	Ru(bpy) ₃ Cl ₂ ·3H ₂ O (2)	DMSO	48
10	$[Ir(dtbbpy)(ppy)_2]PF_6$ (2)	DMF	15
11	$[Ir(dtbbpy)(ppy)_2]PF_6$ (2)	DCE	0
12	$[Ir(dtbbpy)(ppy)_2]PF_6$ (2)	DCM	0
13	$[Ir(dtbbpy)(ppy)_2]PF_6$ (2)	DME	0
14	$[Ir(dtbbpy)(ppy)_2]PF_6$ (2)	1,4-Dioxane	0
15	$[Ir(dtbbpy)(ppy)_2]PF_6$ (2)	CH ₃ CN	Trace
16	$[Ir(dtbbpy)(ppy)_2]PF_6$ (2)	THF	Trace
17	$[Ir(dtbbpy)(ppy)_2]PF_6$ (2)	Toluene	0
18	$[Ir(dtbbpy)(ppy)_2]PF_6$ (1)	DMSO	75
19	$[Ir(dtbbpy)(ppy)_2]PF_6$ (5)	DMSO	76
20	—	DMSO	0
21	$[Ir(dtbbpy)(ppy)_2]PF_6$ (2)	DMSO	26 ^c
22	$[Ir(dtbbpy)(ppy)_2]PF_6$ (2)	DMSO	30 ^d
23	$[Ir(dtbbpy)(ppy)_2]PF_6$ (2)	DMSO	5 ^e
24	$[Ir(dtbbpy)(ppy)_2]PF_6$ (2)	DMSO	76 ^f

^a Conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), **3a** (0.25 mmol), photocatalyst (1–5 mol%), Na_2CO_3 (2 equiv.), solvent (2 mL), 5 W blue LEDs, air, r.t., 2 h. ^b Isolated yields based on **1a**. ^c Green light LEDs. ^d White light LEDs. ^e Purple light LEDs. ^f Under dioxygen.

Table 2 The scope of alkenes^{a,b}

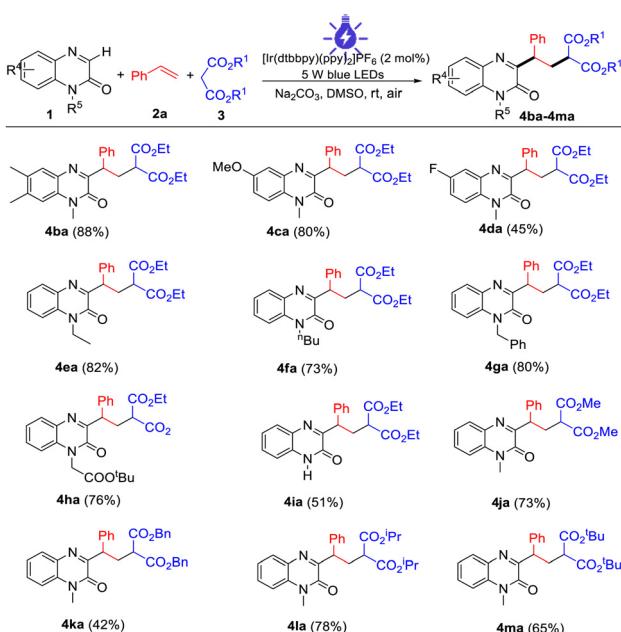


^a Reaction Conditions: **1a** (0.1 mmol), **2** (0.2 mmol), **3a** (0.25 mmol), $[Ir(dtbbpy)(ppy)_2]PF_6$ (2 mol%), Na_2CO_3 (0.3 mmol), DMSO (2 mL), 5 W blue LEDs, air, r.t., 2 h. ^b Isolated yields.

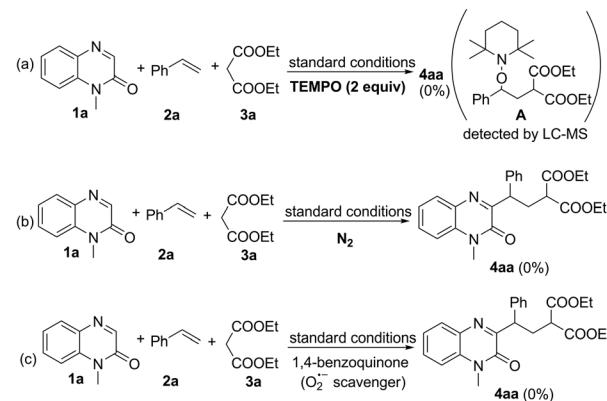
were suitable substrates to provide the corresponding products **4an** and **4ao**, albeit in relatively lower yields. 2-Naphthalene and internal olefin were also compatible with this procedure, and the corresponding products **4ap** and **4aq** were obtained in 70% and 69% yields, respectively. In addition, this protocol was also shown to be applicable to aliphatic olefins. When allylbenzene and 1-allylnaphthalene were employed as substrates, the desired products **4ar** and **4as** were obtained in good yields. Nevertheless, when 1,2-diaryl-substituted alkenes such as (*E*)-1,2-diphenylethene were employed in this reaction system, none of the desired products was observed.

The capacity of the present multi-component reaction was also illustrated by the scope of quinoxalin-2(*H*)-ones with malonic esters (Table 3). Quinoxalin-2(*H*)-ones with substituents such as Me, MeO, and F on the benzene ring were compatible with this procedure, providing the desired products (**4ba**–**4da**) in moderate to high yields. Other *N*-substituted substrates such as *N*-ethyl, *N*-butyl, *N*-benzyl, and *N*-esteryl quinoxalin-2(*H*)-ones also displayed good reactivity and provided the products **4ea**–**4ha** in 73–82% yields. Notably, *N*-free protected quinoxalin-2(*H*)-one also proceeded smoothly to afford the product **4ia** in 51% yield. With respect to other malonic esters, in addition to diethyl malonate, dimethyl malonate, dibenzyl malonate, diisopropyl malonate, and di-*tert*-butylmalonate malonate were also suitable for the photocatalytic reactions, providing the corresponding **4ja**–**4ma** in moderate to good yields. Unfortunately, the desired products were not detected when keto esters such as ethyl 3-oxo-3-phenylpropanoate and ethylacetacetate were investigated in this reaction procedure.

Table 3 The scope of quinoxalin-2(*H*)-ones and malonic esters^{a,b}



^a Reaction conditions: **1** (0.1 mmol), **2a** (0.2 mmol), **3** (0.25 mmol), $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ (2 mol%), Na_2CO_3 (0.3 mmol), DMSO (2 mL), 5 W blue LEDs, air, r.t., 2 h. ^b Isolated yields.



Scheme 2 Control experiments.

Next, several control experiments were performed to obtain some insight into the possible reaction mechanism (Scheme 2). First, when TEMPO (a radical scavenger) was added to the model reaction system, this photocatalytic multi-component reaction was completely suppressed and TEMPO-trapped complex **A** was observed by LC-MS. This result indicated that this reaction might involve the radical mechanism (Scheme 2a). Second, none of the desired products was observed when the model reaction was carried out under N_2 , suggesting that O_2 in air is essential for promoting this transformation (Scheme 2b). Third, this transformation was also completely inhibited by the addition of 1,4-benzoquinone (a superoxide radical anion scavenger), indicating that $\text{O}_2^{\bullet-}$ played a significant role in this reaction (Scheme 2c). Finally, the behavior of the visible light-excited step was further revealed by Stern–Volmer fluorescence quenching experiments. As a result, the emission intensity of the excited photocatalyst was obviously quenched with increasing concentration of the deprotonated enolate anion of malonate. Such a phenomenon was not observed between the excited photocatalyst and alkene **2a** or malonate **3a** under visible-light irradiation (Fig. 1). This result suggested that the interaction between the excited photocatalyst and the deprotonated enolate anion of malonate should exist in this reaction system (see the ESI†).

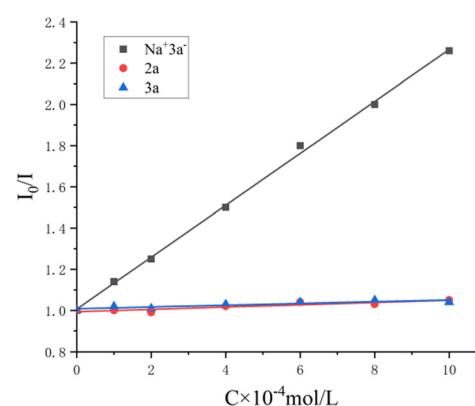
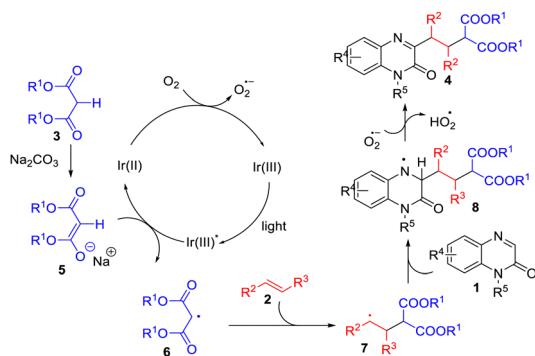


Fig. 1 Stern–Volmer plots. I_0 is the inherent fluorescence intensity of $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$. I is the fluorescence intensity of $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ in the presence of Na^+3a^- , **2a** or **3a**.



Scheme 3 Proposed mechanism.

On the basis of the abovementioned results and literature,^{7–10,17} a possible mechanism was proposed as shown in Scheme 3. Under light irradiation, the photocatalyst Ir^{III} complex was firstly excited to give the excited-state *Ir^{III}, which can be readily reduced by the deprotonated enolate anion 5 affording the reduced Ir^{II} and malonate radical 6. Then, the Ir^{II} complex was oxidized by dioxygen (O₂) to generate a superoxide radical anion (O₂^{•-}), along with regeneration of the ground-state Ir^{III} complex. Subsequently, the selective addition of malonate radical 6 to alkene 2 produced alkyl radical 7, which reacted with quinoxalin-2(1H)-one 1 to provide nitrogen radical intermediate 8. Finally, the deprotonation of the nitrogen radical 8 by the superoxide radical anion (O₂^{•-}) afforded the desired product 4.

In conclusion, we have developed visible-light photoredox catalyzed 1,2-dicarbofunctionalization of alkenes with quinoxalin-2(1H)-ones and malonic esters at room temperature. Through this methodology, a series of quinoxalin-2(1H)-one containing esters were efficiently obtained in a step and atom-economic manner through direct C(sp²)-H/C(sp³)-H functionalization. This three-component reaction proceeded through a radical process, in which two carbon–carbon bonds were consecutively formed in a one pot procedure. The advantages of high atom economy, a clean energy source, mild conditions, and good functional group tolerance make this method attractive in synthetic chemistry.

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Conflicts of interest

The authors declare no competing financial interest.

Data availability

The data supporting this article have been included as part of the ESI,† which include general synthetic experimental details, characterization data, and NMR spectra, respectively.

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