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Photocatalysis

Merging Visible-Light Photocatalysis and Palladium Catalysis for C–H Acylation of Azo- and Azoxybenzenes with α-Keto Acids

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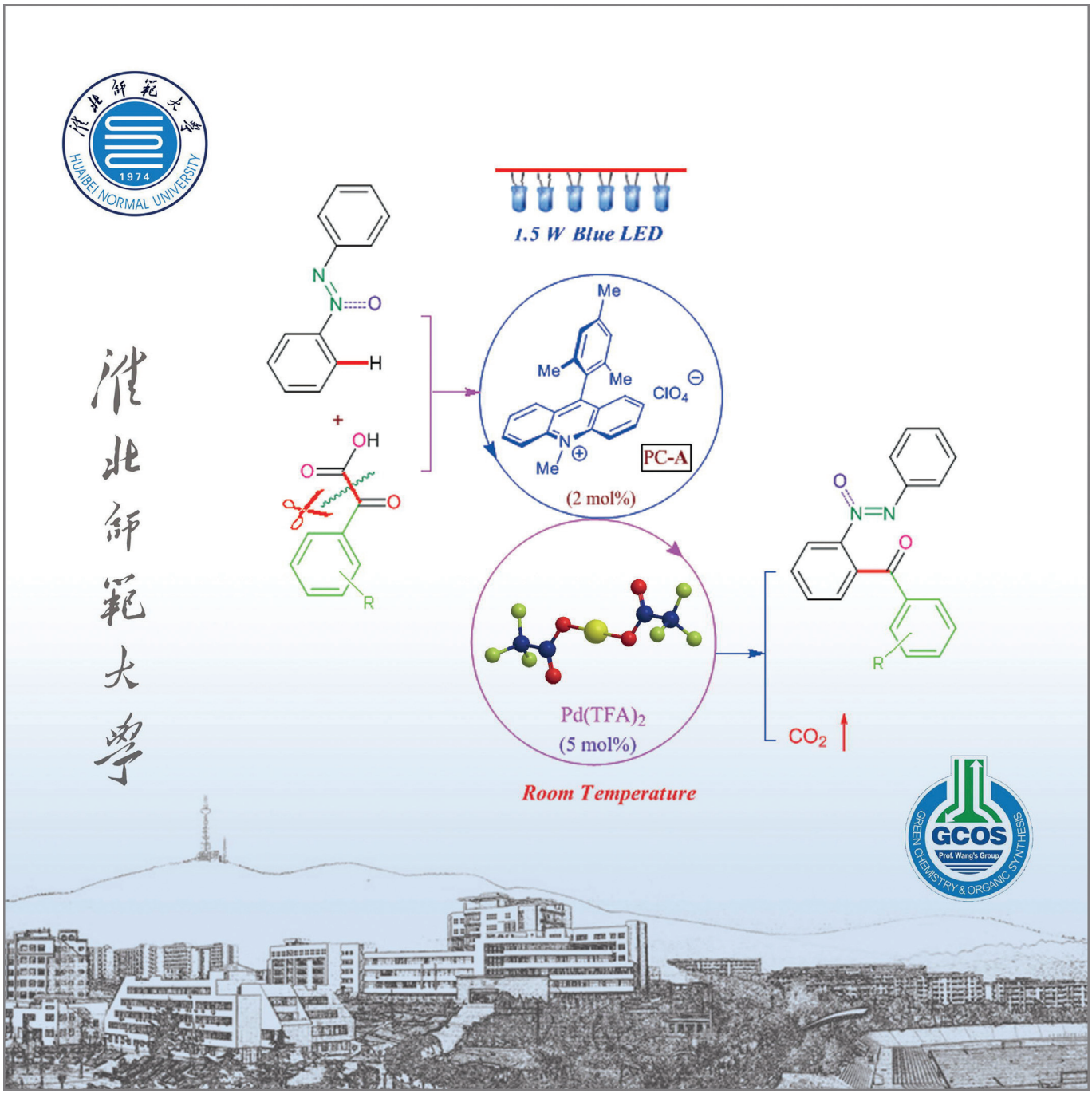
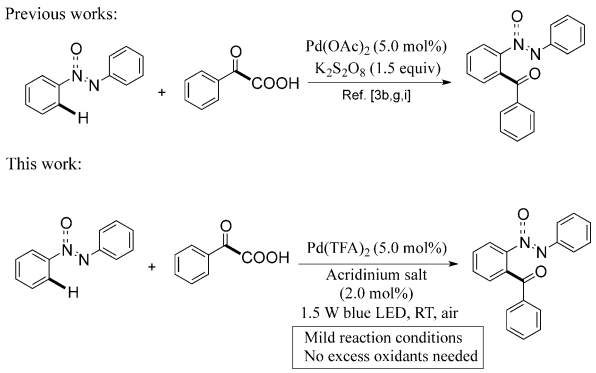


Abstract: An efficient C–H acylation of azo- and azoxybenzenes with α-keto acids has been developed by a combination of palladium catalysis and visible-light photoredox catalysis at room temperature under 1.5 W blue LED irradiation. This method tolerates a variety of disubstituted azo- and azoxybenzenes, as well as α-keto acids regardless of the nature of the substituents. A number of aryl ketones were obtained in good yields under mild reaction conditions.

Azo-substituted aryl ketones are very important in the chemical and pharmaceutical industries, and they have been widely used in the fields of photochemical dyes, drug intermediates, biosensors, and food additives. In addition, these compounds can be easily converted into the corresponding amino or hydrazine products in organic synthesis.[1] As a result, a variety of strategies has been established to realize them. Classic methods are the coupling of diazonium salts with arenes and the oxidation of the corresponding azo-containing secondary alcohols.[2] However, these methodologies suffer from the harsh reaction conditions and relatively limited substrate scope. In recently years, much attention has been focused on the transition-metal-catalyzed oxidative sp^2 C–H acylation of azo- and azoxybenzenes with aldehydes, aryl methanes, alcohols, and α-oxocarboxylic acids.[3] Despite these important advances, most of the current methods have some limitations. Drawbacks of the C–H acylation, in most cases, are stoichiometric amounts of an external oxidant and higher reaction temperature.[3a–h] Therefore, development of a mild, atom-efficient, and eco-friendly method for the synthesis of azo-substituted aryl ketones is highly desirable.

Most recently, visible-light-induced photoredox catalysis has emerged as an important platform for the development of unique single electron-transfer pathway under remarkably mild reaction conditions.[4] Particularly, dual catalysis realized by merging photocatalysis with transition-metal catalysis can accomplish the novel organic transformations, which are unfeasible or not accessible by a single catalytic system.[5] In 2011, Sanford and co-workers achieved a Pd-catalyzed C–H arylation by merging palladium catalysis with visible-light photoredox catalysis.[5a] Subsequently, many efforts have been devoted towards the construction of C–C and C–heteroatom bonds by combining visible-light-induced photoredox and transition-metal catalysis.[5b–j] However, recent studies in the dual catalytic system have focused on the use of Ru and Ir complexes as photoredox catalysts, whereas combining organic dyes as photoredox catalysts with transition-metal catalysts in synthetic chemistry has not yet been explored.

In recent years, α-keto acids, as acylating reagents, have shown high reactivity in the synthesis of ketones by a decarboxylative process to acyl-free radicals along with the extrusion of CO_2.[3b,g,6] Meanwhile, a few examples of acridinium salts, used as photoredox catalysts, have been reported in a single catalyst system.[7] Herein, we have developed a combination of palladium and acridinium salt as a photoredox catalyst under visible-light irradiation for the C–H acylation of azo- and azoxybenzenes with α-keto acids that provides a mild and green methodology for the synthesis of azo-substituted aryl ketones in good yields (Scheme 1).



Scheme 1. Synthetic strategies for azo-substituted aryl ketones from azo- and azoxybenzenes with α-oxocarboxylic acids.

Our initial studies focused on a Pd-catalyzed model reaction of C–H acylation of azobenzene (**1a**) with 2-oxo-2-phenylacetic acid (**2a**). Inspired by the reported literature,[4,5,8] Ru complex was employed as a photocatalyst firstly, and blue LED was utilized as the source of visible light. To our delight, the model reaction underwent smoothly to generate the desired C–H acylation product **3aa** in 72% yield at room temperature in the presence of $Pd(TFA)_2$ (5.0 mol%) and $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ (2.0 mol%) in toluene under an oxygen atmosphere and 1.5 W blue LED irradiation for 16 h at room temperature (Table 1, entry 1). Subsequently, various Ru and Ir complexes, such as $[Ru(bpy)_3][PF_6]_2{\cdot}6H_2O$, $[Ru(phen)_3]Cl_2{\cdot}6H_2O$, $[Ru(phen)_3][PF_6]_2{\cdot}6H_2O$, and *fac*-$[Ir(ppy)_3]$, were screened (entries 2–5), and a slightly improved yield of **3aa** was observed in the presence of $[Ru(bpy)_3][PF_6]_2{\cdot}6H_2O$ (entry 2). In an attempt to improve the yield of the desired product, a series of organic dyes, such as Na_2-eosinY, eosin Y, rose bengal, and 9-mesityl-10-methylacridinium perchlorate (PC-**A**) were examined as photoredox catalysts[4i,7,9] instead of Ru-complex.

Gratifyingly, the use of PC-**A** enhanced the acylation of **1a** with **2a**, leading to the formation of **3aa** in 78% yield under either oxygen or air atmosphere (Table 1, entries 6–10). It is evident that organic dyes, such as eosin Y and PC-**A**, are cheaper and easier to be modified, and can be degraded compared with transition-metal photoredox catalysts (Ru and Ir com-

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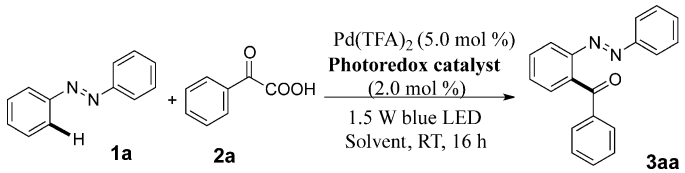
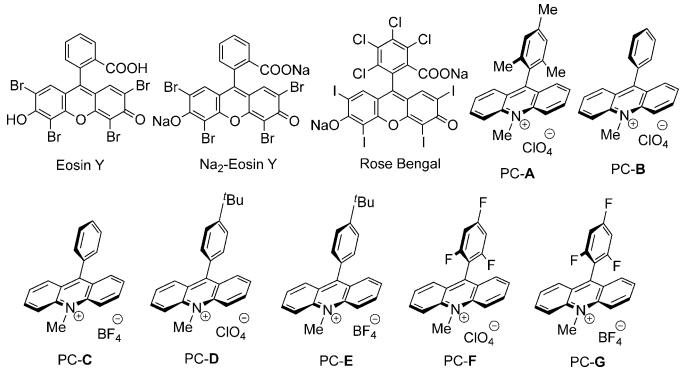
Table 1. Optimization of photoredox catalyst and solvent[a]



Entry	Photoredox Catalyst	Solvent	Yield [%][b]
1	$[Ru(bpy)_3]Cl_2·6H_2O$	toluene	72
2	$[Ru(bpy)_3][PF_6]_2·6H_2O$	toluene	76
3	$[Ru(phen)_3]Cl_2·6H_2O$	toluene	73
4	$[Ru(phen)_3][PF_6]_2·6H_2O$	toluene	trace
5	*fac*-$[Ir(ppy)_3]$	toluene	trace
6	Na_2-eosinY	toluene	trace
7	eosin Y	toluene	trace
8	rose bengal	toluene	trace
9	PC-**A**	toluene	78
10[c]	**PC-A**	**toluene**	**78**
11	–	toluene	N.R.
12[d]	PC-**A**	toluene	N.R.
13[e]	PC-**A**	toluene	N.R.
14[f]	PC-**A**	toluene	N.R.
15	PC-**B**	toluene	73
16	PC-**C**	toluene	76
17	PC-**D**	toluene	76
18	PC-**E**	toluene	75
19	PC-**F**	toluene	48
20	PC-**G**	toluene	63
21	PC-**A**	CH_3CN	trace
22	PC-**A**	MeOH	trace
23	PC-**A**	DCM	58
24	PC-**A**	DCE	60
25	PC-**A**	DME	65
26	PC-**A**	THF	37
27	PC-**A**	acetone	71
28	PC-**A**	$CHCl_3$	67
29	PC-**A**	PhCl	57
30	PC-**A**	$PhCF_3$	trace
31	PC-**A**	DMSO	N. R.



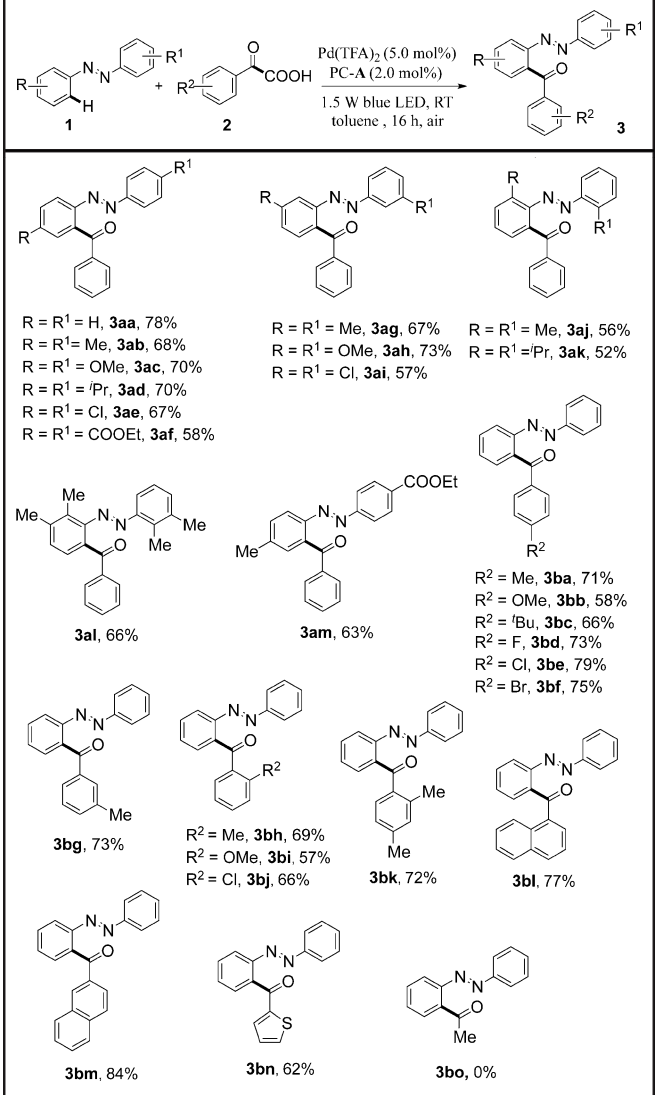
[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.24 mmol), $Pd(TFA)_2$ (5.0 mol%), photoredox catalyst (2.0 mol%), 1.5 W blue LED, and solvent (2.0 mL) at room temperature under oxygen for 16 h. [b] Isolated yield. [c] Under air. [d] In the absence of $Pd(TFA)_2$. [e] In the absence of light. [f] Under nitrogen. DME = 1,2-dimethoxyethane; DMSO = dimethyl sulfoxide; N.R. = no reaction.

plexes). Further experiments indicated that the photoredox catalyst, palladium catalyst, visible-light irradiation, and molecular oxygen were all essential for the reaction, and no reaction occurred in their absence (entries 11–14). Further optimization of acridinium salts showed that 9-mesityl-10-methylacridinium perchlorate (PC-**A**) was the best of choice among the examined acridinium salts, including 9-phenyl-10-methylacridinium perchlorate (PC-**B**), 9-phenyl-10-methylacridinium tetrafluoroborate (PC-**C**), 9-(*tert*-butylphenyl)-10-methylacridinium perchlorate (PC-**D**), 9-(*tert*-butylphenyl)-10-methylacridinium tetrafluoroborate (PC-**E**), 9-(2,4,6-trifluorophenyl)-10-methylacridinium perchlorate (PC-**F**), and 9-(2,4,6-trifluorophenyl)-10-methylacridinium tetrafluoroborate (PC-**G**; entries 15–20). In addition, solvent screening indicated that toluene was the best reaction medium for the model reaction (entries 21–31). Further investigations on the light source, palladium catalyst, molar ratio of substrates, and catalyst loading are also presented in Tables S1, S2, and S3 in the Supporting Information.

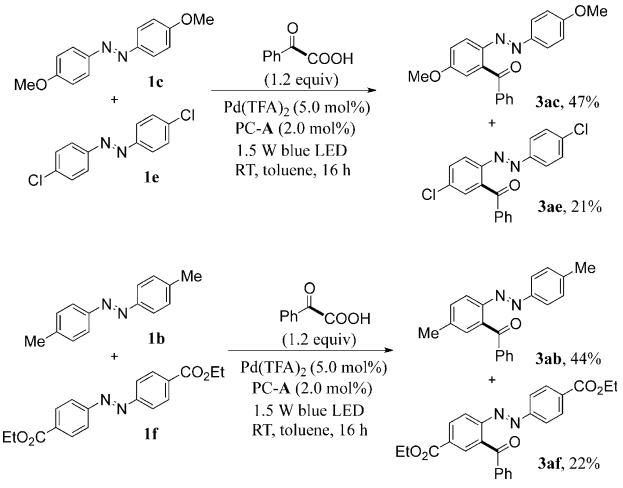
With the optimized reaction conditions (**1** (0.20 mmol), **2** (0.24 mmol), $Pd(TFA)_2$ (5.0 mol%), and PC-**A** (2.0 mol%) in toluene (2.0 mL) under air atmosphere and 1.5 W blue LED irradiation at room temperature for 16 h) in hand, we next explored the functional group compatibility of this transformation using a series of typical disubstituted azobenzenes. As shown in Table 2, the reaction of various azobenzenes with 2-oxo-2-phenylacetic acid (**2a**) proceeded well and generated the desired acylated products in good yields. Substituents on the aromatic moiety of the azo compounds showed an electronic effect of the coupling reaction. In general, aromatic azo compounds with electron-donating groups were more reactive than that with electron-withdrawing groups, providing higher yields of the desired products. These results were also supported by the intermolecular competing experiments shown in Scheme 2. For example, azobenzenes substituted with electron-donating groups, such as Me, OMe, and *i*Pr, at the *para* positions generated the desired products (**3ab**–**ad**) in 68-70% yields. Meanwhile, azobenzenes with electron-withdrawing groups, including Cl and COOEt, at the *para* positions delivered the corresponding products **3ae** and **3af** in 67 and 58% yields, respectively. It should be noted that *meta*-substituted azobenzenes also worked well in the reaction to afford the anticipated products **3ag**–**ai** in 57–73% yields. Notably, *ortho*-substituted azobenzenes gave relatively lower product yields (**3aj** and **3ak**) than *para*- or *meta*-substituted azobenzenes due to their steric hindrance. To our delight, when tetra-substituted azobenzene **1l** reacted with **2a**, the desired product **3al** was obtained in 66% yield. The reaction of unsymmetrical azobenzene **1m** also proceeded well and the acylation occurred on the electron-rich aromatic ring selectively, providing the product **3am** in 63% yield.

Next, the representative α-oxocarboxylic acids were synthesized and their performance was examined for the C–H acylation of azobenzenes under the optimized reaction conditions. As can be seen in Table 2, 2-oxo-2-arylacetic acids with electron-rich and -poor substituents, such as Me, MeO, *t*Bu, F, Cl, and Br on *para* positions of aromatic rings gave the desired products (**3ba**–**bf**) in good yields. Generally, 2-oxo-2-arylacetic acids with electron-withdrawing groups on the benzene rings were more suitable substrates and gave

Table 2. The scope of acylation of azobenzenes with α-oxocarboxylic acids.[a,b]



[a] Reaction conditions: **1** (0.20 mmol), **2** (0.24 mmol), $Pd(TFA)_2$ (5.0 mol%), PC-**A** (2.0 mol%), 1.5 W blue LED, and toluene (2.0 mL) at room temperature in air for 16 h. [b] Isolated yield.



Scheme 2. Intermolecular competing experiments.

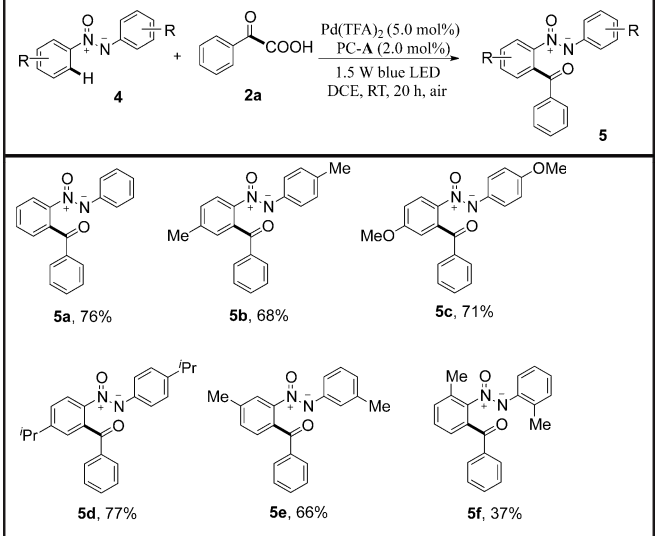
higher yields than 2-oxo-2-arylacetic acids with electron-donating groups on the benzene rings (**3ba**–**bc** versus **3bd**–**bf**). 2-Oxo-2-(*meta*-methylphenyl)acetic acid (**2g**) worked well in the reaction, and the desired product **3bg** was obtained in 73% yield. Evidently, the steric hindrance effect was observed in the reaction of 2-oxo-2-arylacetic acids with azobenzenes, generating the products (**3bh**–**bj**) in 57–69% yields under the present reaction conditions. Furthermore, 2-oxo-2-(2,4-dimethylphenyl)-acetic acid (**2k**) showed good reactivity in the reaction and provided product **3bk** in 72% yield. It should be noted that reactions of 2-(naphthalen-1-yl)-2-oxoacetic acid (**2l**) and 2-(naphthalen-2-yl)-2-oxoacetic acid (**2m**) with **1a** afforded the corresponding products **3bl** and **3bm** in 77 and 84% yields, respectively. Encouraged by these results, the heterocyclic-substituted α-oxocarboxylic acid **2n** was evaluated, and a moderate yield of the product **3bn** was obtained under the optimized reaction conditions. However, an aliphatic α-oxocarboxylic acid, such as 2-oxopropanoic acid (**2o**), did not react with **1a**, and the desired product **3bo** was not obtained.

Next, the optimization of the reaction conditions for the C–H acylation of azoxybenzene **4a** with 2-oxo-2-phenylacetic acid (**2a**) showed that the reaction did indeed occur with 76% yield of the desired product (**5a**) in the presence of $Pd(TFA)_2$ (5.0 mol%), PC-**A** (2.0 mol%), 1.5 W blue LED, and DCE (2.0 mL) at room temperature in air for 20 h (for details of the optimization, see Table S4–7 in the Supporting Information). To explore the applicability of this protocol, some typical disubstituted azoxybenzenes were examined and the results are listed in Table 3. The reaction of azoxybenzenes with 2-oxo-2-phenylacetic acid (**2a**) provided the corresponding products **5a**–**e** in 66–77% yields, and tolerated a variety of functional groups, including Me, MeO, and *i*Pr groups, in the substrates of azoxybenzenes. However, *ortho*-substituted azoxybenzene **4f** generated **5f** in lower yield due to the steric hindrance.

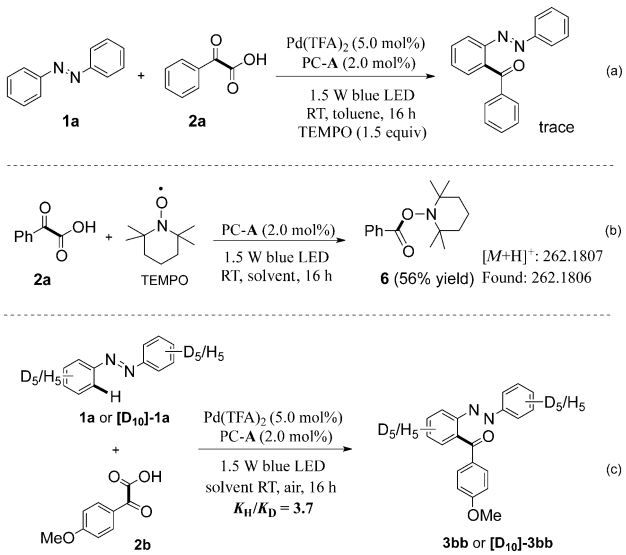
To gain insight into the mechanism of this transformation, some control experiments and an intermolecular competing kinetic isotope effect (KIE) were carried out. The addition of 1.5 equivalent of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) to the mixture of azobenzene **1a** and 2-oxo-2-phenylacetic acid (**2a**) suppressed the reaction completely (Scheme 3a). Moreover, TEMPO trapped the benzoyl radical to generate **6** (Scheme 3b). The intermolecular kinetic isotopic effect was observed with $k_H/k_D = 3.7$ (Scheme 3c), indicating the sp^2 C–H bond cleavage involved in the rate-determining step of the reaction.

On the basis of our preliminary mechanistic study and previous related literature,[4,5,7,10] a possible mechanism of this transformation is proposed in Scheme 4. The reaction begins with the photoexcitation of mesityl acridinium catalyst (PC-**A**) by visible light to generate its excited state (PC-**A***), which is subsequently oxidized by the molecular oxygen (single-electron process) to afford PC-**A**·, along with the generation of superox-

Table 3. The scope of acylation of azoxybenzenes with 2-oxo-2-phenylacetic acid.[a,b]



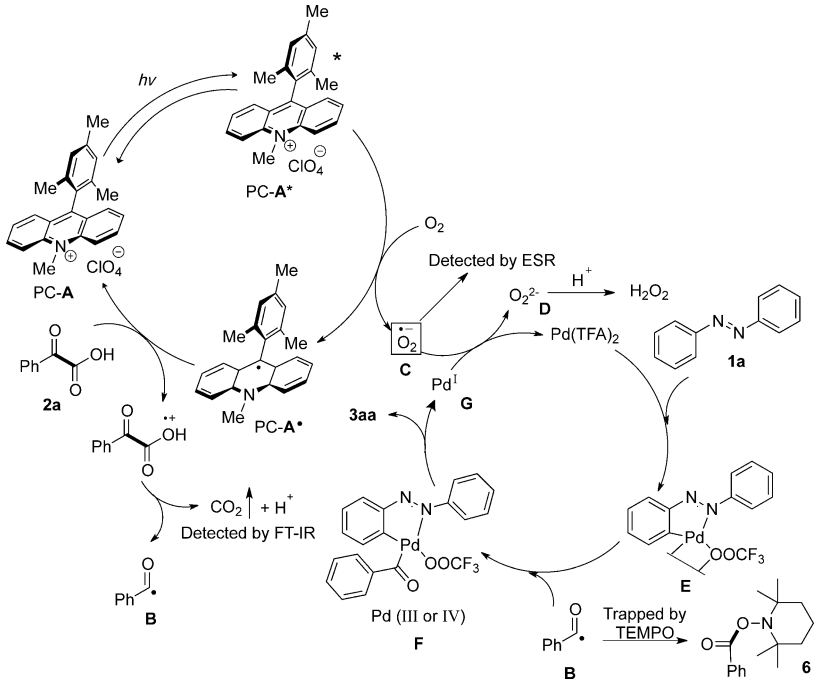
[a] Reaction conditions: **4** (0.20 mmol), **2a** (0.24 mmol), $Pd(TFA)_2$ (5.0 mol%), PC-**A** (2.0 mol%), 1.5 W blue LED, and DCE (2.0 mL) at room temperature in air for 20 h. [b] Isolated yield.



Scheme 3. Preliminary mechanistic study.

ide anion **C**. Meanwhile, a single-electron oxidation of **2a** by the formed PC-**A**• regenerates ground-state photocatalyst PC-**A** for the next run, and generates the corresponding carboxyl radical species, which undergoes the decomposition to from the critical benzoyl radical species **B**, along with extrusion of CO_2 (for FTIR analysis of the resulting CO_2 gas, see the Supporting Information). On the other hand, Pd catalytic cycle can be initiated by a C–H activation of the azobenzene to form the palladacyclic intermediate **E**. Palladacycle **E** then reacts with acyl radical **B**, generated from the decomposition of **2a** in situ, to afford Pd^{IV} or Pd^{III} species **F**.[3a,11] The reductive elimination of **F** leads to the desired acylated product **3a** and generates the Pd^{I} intermediate **G**, which is reoxidized by superoxide anion **C** to regenerate Pd^{II} catalyst to complete the catalytic cycle along with the formation of O_2^{2-} (**D**) and H_2O_2.

To support the generation of superoxide radical anion **C** ($O_2^{-}\cdot$) in proposed mechanism, 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) was used as a probe to capture the active species.[12a,c] As shown in Figure 1, when a toluene solution of



Scheme 4. Plausible reaction mechanism.

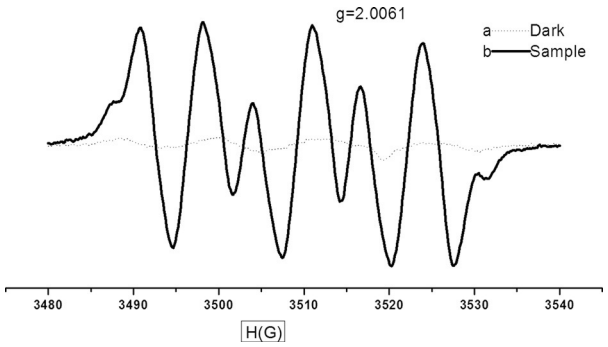


Figure 1. ESR spectra of air-saturated toluene solution of **2a** (1.0×10^{-3} M), PC-**A** (2.0×10^{-5} M), and DMPO (2.0×10^{-2} M): a) Without blue LED irradiation; b) under blue LED irradiation for 60 s.

DMPO, **2a**, and PC-**A** was without the blue LED irradiation, no signal was detected (Figure 1 a). In contrast, when the same solution was under the blue LED irradiation, a signal of trapped radical $O_2^{-}\cdot$ was clearly observed (Figure 1 b). It revealed that the superoxide radical anion ($O_2^{-}\cdot$) is generated from the molecular oxygen by single-electron transfer (SET)[5d,e,h,12] under the present reaction conditions.

In summary, this communication describes a mild and general approach combined with palladium catalysis and visible-light photocatalysis for the C–H acylation of azo- and azoxybenzenes with α-keto acids. The use of a catalytic amount of the photoredox catalyst under the irridation of 1.5 W blue LED avoids a typical high loading of external oxidant. This transformation, performed at room temperature, made the acylation of azo- and azoxybenzenes with a wide spectrum of substrates and reagents. Further investigations on the combination of organic dyes as photocatalyst with transition-metal catalysts in organic transformations are currently underway in our laboratory.

Experimental Section

Typical procedure for the acylation of azoxybenzenes

A mixture of azobenzene (**1a**, 36.4 mg, 0.20 mmol), 2-oxo-2-phenylacetic acid (**2a**, 36 mg, 0.24 mmol), $Pd(TFA)_2$ (3.3 mg, 0.01 mmol), and 9-mesityl-10-methylacridinium perchlorate (PC-**A**; 1.6 mg, 0.004 mmol) was dissolved in toluene (2.0 mL) in a 10 mL oven-dried reaction vessel equipped with a magnetic stirring bar. The reaction vessel was irradiated using 1.5 W blue LED for 16 h at room temperature under air. After the reaction was completed, the resulting mixture was extracted with EtOAc (2×5.0 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, ethyl acetate/petroleum ether 1:50, v/v) affording the desired product **3aa** as a yellow liquid (44.6 mg, 78% yield).

Acknowledgements

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Keywords: acylation · azo compounds · blue LED · palladium · visible-light photocatalysis

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