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Photoredox/Cobalt-Catalyzed C(sp^3)–H Bond Functionalization toward Phenanthrene Skeletons with Hydrogen Evolution

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Cite This: https://dx.doi.org/10.1021/acs.orglett.0c03665 Read Online

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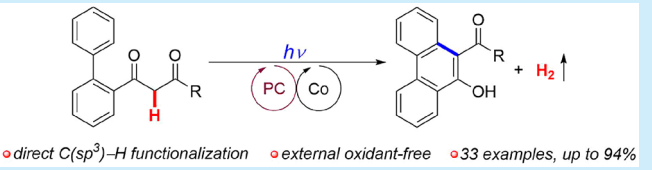
ABSTRACT: The first example of photoredox strategy for synthesis of phenanthrene skeletons through C(sp^3)–H functionalization under external oxidant-free conditions is achieved. This transformation relies on the keto–enol tautomerism of 1,3 dicarbonyl moiety, i.e., the enol form of 1,3-dicarbonyl derivatives with relatively lower oxidation potential can be activated by the excited acridinium photocatalyst. The electron and proton eliminated from the substrate are immediately captured by a cobaloxime catalyst to exclusively afford *a*-carbonyl radical for highly substituted 10-phenanthrenols in good to excellent yields.



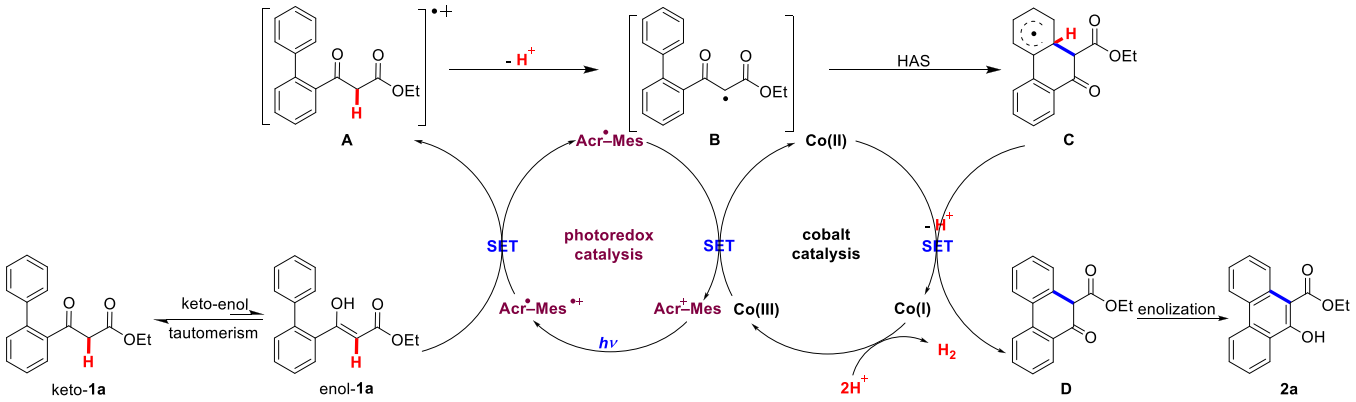
Photoredox catalysis, taking advantage of visible light as an energy input, has recently become general and efficient to construct complex molecular skeletons.[1] Because of the ability of photocatalysts to absorb visible light, a variety of organic substrates that are transparent to visible light have been activated to undergo either oxidative or reductive reactions with a photocatalyst, respectively, in the presence of an external oxidant and reductant.[2] As one of the significant structural elements of polycyclic aromatic compounds (PACs)[3] in organic synthesis,[4] medicinal chemistry,[5] and material sciences,[6] phenanthrene skeletons have been developed by photocatalytic protocols, such as photocyclization reactions of stilbene derivatives[7] and intermolecular[8] and intramolecular[9] benzannulation reactions of functionalized biphenyl derivatives. However, these approaches usually need functionalized substrates,[10] external oxidants,[11] and ultraviolet (UV) irradiation,[12] thereby leading to wasteful byproducts and side reactions. Direct C(sp^3)–H functionalization has recently attracted widespread interest to construct complex molecules for its high atom- and step-economy.[13] 1,3-Dicarbonyl derivatives were found as a significant synthon for phenanthrene skeletons formation.[14] Their high bond dissociation energy[15] and high oxidation potential require an excess oxidant[16] and substrate prefunctionalization[17] to produce *α*-carbonyl radicals for following transformation. For example, *N*-bromosuccinimide (NBS)-induced intramolecular cycloaromatization for the synthesis of 10-phenanthrenols from 1,3-dicarbonyl derivatives was accomplished by an excess of base and *tert*-butyl peroxide.[18] Very recently, a photocatalyst was directly used to generate a persistent ketyl radical and a transient *α*-carbonyl radical in situ from 1,3-dicarbonyl derivatives.[19] This finding stimulated us to get rid of substrate prefunctionalization and external oxidants. Instead, cobaloxime complexes[20] were used to coordinate with photoredox catalysis as proton-reduction catalyst[21] or hydrogen-transfer catalyst.[22]

Here, we present the direct *α*-C(sp^3)–H functionalization of 1,3-dicarbonyl derivatives by using a photocatalyst and a cobaloxime catalyst, an ideal catalytic system to exclusively access the *α*-carbonyl radical for phenanthrene skeletons formation under external oxidant-free conditions.

Our detailed working hypothesis is described, taking ethyl 3-([1,1′-biphenyl]-2-yl)-3-oxopropanoate (**1a**) as the model substrate. As shown in Scheme 1, the crucial step is chemoselective oxidation of the enol form of **1a** to the radical cation **A**. In light of the fact that the enol form of **1a** (E^{ox} = +1.79 V, vs SCE in CH_3CN) is less stable than its keto tautomer (E^{ox} = +2.18 V, vs SCE in CH_3CN), the enol form exists in very low concentration under equilibrium condition through keto–enol tautomerism[23] (keto:enol = 91:9 was detected by ^1H NMR in CD_3CN) (Figures S1, S3, S6, and S8). Herein, commercially available organophotoredox catalyst Acr^+–Mes ClO_4^- shows suitable reduction potential in its excited state ($^*E_{1/2}^{red}$ = +2.06 V vs SCE),[24] which is thermodynamically feasible for the oxidation of the enol form rather than the keto form of **1a**. The formed radical cation **A** immediately eliminates a proton to generate *α*-carbonyl radical **B**, which is able to occur an intramolecular homolytic aromatic substitution (HAS)[25] to produce intermediate **C**. Simultaneously, cobaloxime complexes immediately capture electron and proton eliminated from intermediates to generate 10-phenanthrenols and molecular hydrogen gas.

Received: November 4, 2020

Scheme 1. Working Hypothesis



We began our reaction by carrying out of **1a** (0.2 mmol), $Acr^+–Mes\ ClO_4^-$ (5 mol %) and $Co(dmgH)(dmgH_2)Cl_2$ (5 mol %) in dry and degassed CH_3CN (5 mL) with blue LEDs (λ = 445 nm) irradiation for 24 h at rt. As tabulated in Table 1,

Table 1. Reaction Optimization[a]

entry	photocatalyst	cobaloxime catalyst	yield[b] (%)
1[c]	$Acr^+–Mes\ ClO_4^-$	Co cat-I	71
2[c]	$Acr^+–Mes\ ClO_4^-$	Co cat-II	36
3[c]	$Acr^+–Mes\ ClO_4^-$	Co cat-III	63
4[d]	$Acr^+–Mes\ ClO_4^-$	Co cat-I	53
5[e,f]	$Acr^+–Mes\ ClO_4^-$	Co cat-I	90
6[e,g]	$Acr^+–Mes\ ClO_4^-$	Co cat-I	74
7[e,h]	$Acr^+–Mes\ ClO_4^-$	Co cat-I	71
8[e]	$Ru(bpy)_3Cl_2•6H_2O$	Co cat-I	0
9[e]	Eosin Y	Co cat-I	0

[a]Reaction conditions: **1a**, photocatalyst (5 mol %), cobaloxime catalyst (5 mol %) in dry CH_3CN (5 mL) under an Ar atmosphere and irradiation for 24 h by 3 W blue LEDs (λ = 445 nm) at rt. [b]Isolated yields. [c]**1a** (0.2 mmol). [d]**1a** (0.3 mmol). [e]**1a** (0.1 mmol). [f]83% hydrogen gas was detected by gas chromatography. [g]KH_2PO_4 (10 mol %) was used as the additive. [h]Benzoic acid (10 mol %) was used as the additive.

the desired benzannulation product ethyl 10-hydroxyphenanthrene-9-carboxylate (**2a**) was obtained in 71% isolated yield and the hydrogen gas was detected by GC–TCD (Table 1, entry 1). A screening of the cobaloxime catalysts showed a slight decrease in the reactivity of reaction (Table 1, entries 2–3). Due to the intramolecular reaction character, the yield of product **2a** was increased to 90%, even at a low concentration of **1a** (Table 1, entries 4–5 and Figure S2 in the Supporting Information). Air atmosphere resulted in a trace amount of product (Table S2, entry 6 in the Supporting Information). Other solvents such as DCM, THF and MeOH were inferior to this reaction (Table S2, entries 7–9 in the Supporting Information). Neither KH_2PO_4 nor benzoic acid was able to improve the conversion any more (Table1, entries 6–7). Limited by their low reduction potentials, commercially available photocatalysts, like $Ru(bpy)_3Cl_2•6H_2O$ ($E_{1/2}{}^{*II/I}$ = +0.77 V vs SCE)[26] and Eosin Y ($E_{1/2}{}^{*/•-}$ = +1.23 V vs SCE)[27] showed no catalytic activities at all (Table 1, entries 8–9).

Control experiments suggested the necessity of visible light, $Acr^+–Mes\ ClO_4^-$ and $Co(dmgH)(dmgH_2)Cl_2$ for this transformation (Table S2, entries 14–16). Figure 1a shows the

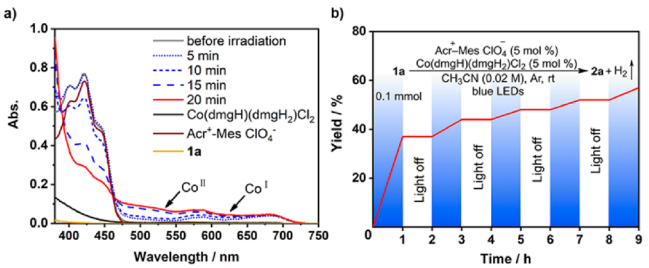
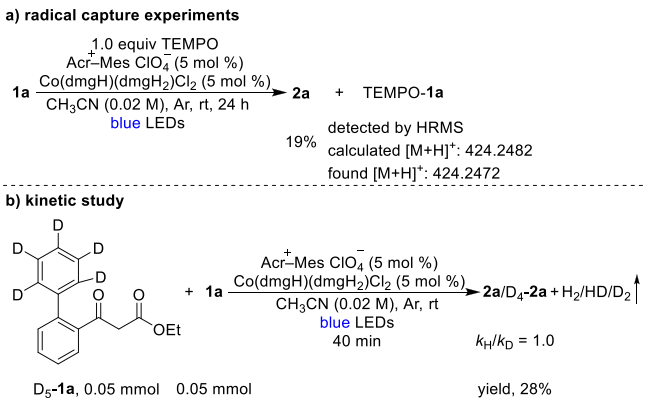


Figure 1. (a) UV–vis absorption spectra of an Ar-saturated CH_3CN solution of $Acr^+–Mes\ ClO_4^-$ (0.1 mM), $Co(dmgH)(dmgH_2)Cl_2$ (0.1 mM), and **1a** (2 mM) under irradiation (at t = 0–20 min). (b) Light off/on experiment.

UV–vis absorption spectrum of $Acr^+–Mes\ ClO_4^-$, $Co(dmgH)(dmgH_2)Cl_2$ and **1a** in degassed CH_3CN. Their mixture is the total of the respective components under the optimized reaction conditions. Upon irradiation, the system exhibited new absorption bands at 440–500 nm and 550–650 nm, which were in line with the production of Co(II) and Co(I) species.[28] Radical scavenger experiment showed that 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) greatly inhibited the transformation (Scheme 2a) and the formation of TEMPO-**1a** suggested that α-carbonyl radical generated from substrate **1a** in the reaction (Figure S13). The competitive

Scheme 2. Investigation of the Mechanism



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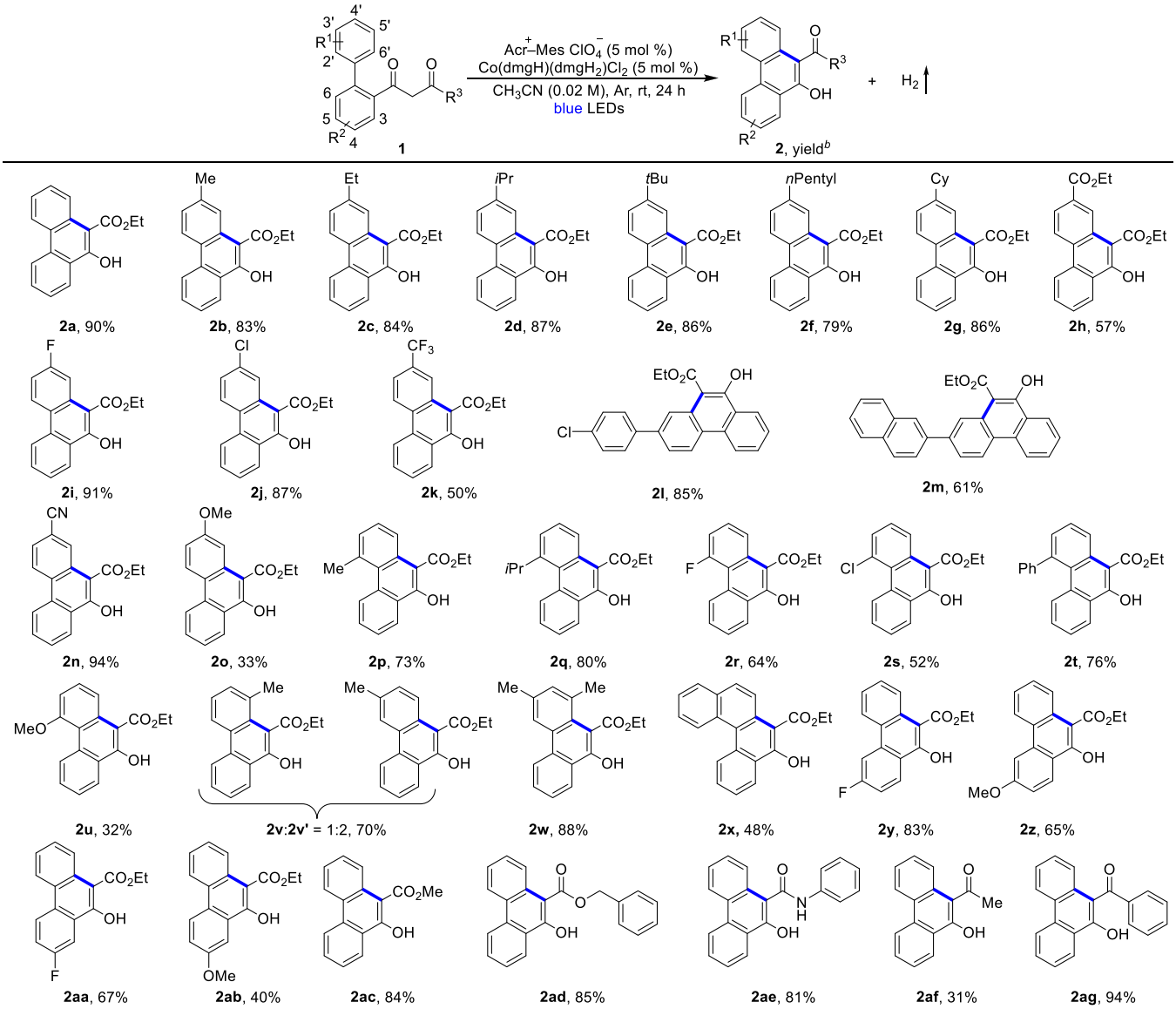
Scheme 3. Scope of the Substrates[a]



[a]Reaction conditions: **1** (0.1 mmol), Acr^+–Mes ClO_4^- (5 mol %), $Co(dmgH)(dmgH_2)Cl_2$ (5 mol %) in dry CH_3CN (5 mL) under an Ar atmosphere and irradiation for 24 h by 3 W blue LEDs (λ = 445 nm). [b]Isolated yields.

experiment with a 1:1 mixture of **1a** and D_5-**1a** under the optimal conditions afforded the kinetic isotope effect (k_H/k_D= 1.0), indicating that the deprotonation process is not the rate-determining step of this reaction (Scheme 2b and Figure S12). All of these experimental results supported the photoredox catalyst and cobaloxime catalyst cooperation of the reaction system.

The light off/on experiment under optimal conditions showed the reaction process was totally suppressed during the dark circumstances. Continuous irradiation of visible light is indispensable to the reaction. As shown in Figure 1b, the reaction decreased significantly during the photocatalytic process, possibly due to the photoinduced electron transfer from product **2a** to the excited Acr^+–Mes ClO_4^-. Indeed, the oxidation peak potential of **2a** (E^{ox} = +1.43 V, vs SCE in CH_3CN) is smaller than that of substrate **1a** (Figure S7), so that **2a** can quench the luminescence of Acr^+–Mes ClO_4^- to consume the photoredox ability of photocatalyst and decreased the reaction rate (Figures S10 and S11).[29] To eliminate the accumulation of product **2a** in the irradiated area, we executed the reaction by using a continuous-flow reactor (Figure S14).[30] As we expected, the flow processing afforded the transformation of **1a** from 90% in the batch reactor irradiation for 24 h to 82% in the flow reactor about 0.5 h reaction time. The scale up experiment (1 mmol) to synthesize **2a** in 74% isolated yield further demonstrated the scalability of the photocatalytic protocol.

The substrate scope of the photocatalytic reaction was examined. As shown in Scheme 3, the reaction tolerated 2-biphenyl substituted 1,3-dicarbonyl derivatives with various functional groups on the aromatic ring, including aryl, naphthyl, cyano, halogen (-F, -Cl), ester, aliphatic groups (methyl, ethyl, *i*-propyl, *t*-butyl, *n*-pentyl, cyclohexyl), which is particularly important for late-stage modification of complex molecules. *Para*-(**1b**–**1m**) and *ortho*-(**1p**–**1t**) substituted on the above aromatic ring substrate smoothly underwent the

https://dx.doi.org/10.1021/acs.orglett.0c03665
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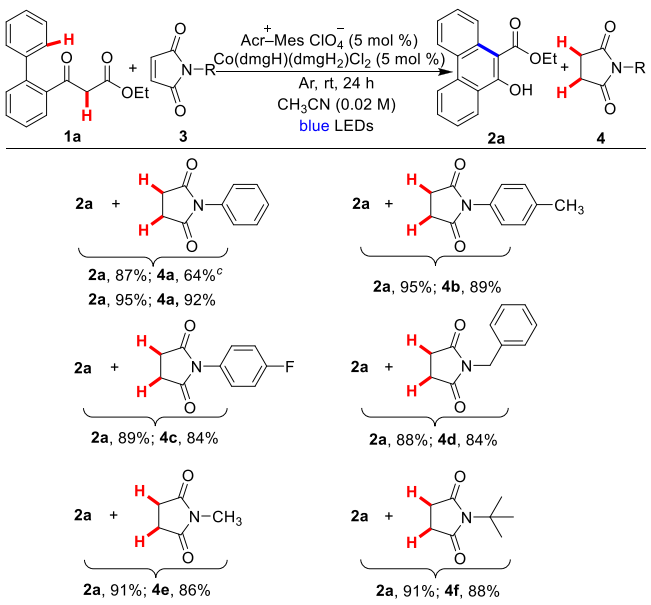
intramolecular benzannulation to generate corresponding 10-phenanthrenols in 50−91% yields. Compound **1n**, which bears a strong electron-withdrawing group with high oxidation potential (E^{ox} = +1.95 V, vs SCE in CH_3CN for enol form of **1n**, Figure S4) also afforded the corresponding product in 94% yield. However, **1o** gave the corresponding product with only 33% yield, because both keto (E^{ox} = +1.75 V, vs SCE in CH_3CN) and enol (E^{ox} = +1.50 V, vs SCE in CH_3CN) form of **1o** (Figure S5) were able to reductively quench the excited Acr^+−Mes ClO_4^- leading to the low chemoselectivity (*ortho*-OMe-, 32% yield). Considering that there are two possible benzannulation positions on the aromatic moiety of the meta-substituted **1a**, we conducted the reaction with *meta*-Me-substrate to understand the site selectivity. Here, the benzannulation provided a mixture of regioisomers **2v** and **2v′** in a 70% total yield with a ratio of 1:2. 3′,5′-Dimethyl group substituted on the above aromatic ring substrate produced the corresponding benzannulation product **2w** in a higher yield of 88%. The polycyclic aromatic compounds **2x** was also synthesized successfully in moderate yield. Furthermore, 2-biphenyl substituted 1,3-dicarbonyl derivatives with 5-F-, 5-OMe-, 4-F-, and 4-OMe- on the lower aromatic ring could be obtained in moderate to excellent yields of products **2y−2ab**. Having accomplished this reaction with various on the aromatic ring substituted substrate, we paid our attention to the scope with substituted substrates bearing −COOMe, −COOBn, -*N*-phenylamide, −COMe, and −COPh, which formed the corresponding 10-phenanthrenols **2ac−2ag** in 31−94% yields.

Considering that no external oxidant was present in the reaction and the electron and proton eliminated from substrate **1a**, we attempted to combine this oxidative benzannulation reaction with reductive hydrogenation of maleimides[31] in one pot (Scheme 4). We began the research by in situ hydrogen transfer from the substrate **1a** (0.1 mmol) to *N*-phenylmaleimide **3a** (0.1 mmol) under the external oxidant- and reductant-free conditions. To our delight, the benzannulation product **2a** and desired reductive hydrogenation product **4a** was observed. Altering the dosage of **3a** from 1 to 0.75 equivalence obtained corresponding benzannulation product **2a** and hydrogenation product **4a** in 95 and 92% yields, respectively. The reductive hydrogenation reaction was well established with *N*-aryl maleimides substituted with 4-Me- and 4-F- groups and *N*-alkyl maleimides substituted with benzyl, methyl, and *t*-butyl groups, giving rise to the corresponding hydrogenation product **4b−4f** in excellent yields.

Scheme 4. Generality of In Situ Hydrogenation of Maleimides[ab]



[a]Reaction conditions: **1a** (0.1 mmol), **3** (0.075 mmol), Acr^+−Mes ClO_4^- (5 mol %), Co(dmgH)$(dmgH_2)Cl_2$ (5 mol %) in dry CH_3CN (5 mL) under an Ar atmosphere and irradiation for 24 h by 3 W blue LEDs (λ = 445 nm) . [b]Isolated yields. [c]**3a** (0.1 mmol).

In summary, we have developed a unique photocatalytic C(sp^3)−H activation toward 10-phenanthrenols under external oxidant-free conditions. Our design relies on the α-carbonyl radical from 2-biphenyl substituted 1,3-dicarbonyl derivatives by synergistic merging of an organo acridinium photocatalyst and a cobaloxime catalyst. This reaction exhibits a wide range of functional groups tolerance and can be scaled up by the continuous-flow approach. The simple generation of α-carbonyl radical eliminates the need of prefunctionalization steps and avoids the usage of external oxidants and thereby providing an atom- and step-economic way to directly synthesize valuable 10-phenanthrenols under external oxidant-free conditions. Remarkably, the combination of the external oxidant-free benzannulation reaction and reductive hydrogenation of maleimides has been achieved in a one-pot reaction. It is anticipated that this research line would offer new solution to construct phenanthrene skeletons via C(sp^3)−H bond activation in external oxidant-free, scalable, atom- and step-economic manner.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03665.

Substrate preparation; reaction optimization; experimental procedures; mechanism study; characterization data; copies of ^1H, ^{13}C, and ^{19}F NMR (PDF)

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https://dx.doi.org/10.1021/acs.orglett.0c03665
Org. Lett. XXXX, XXX, XXX−XXX

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (22088102, 21933007, and 21861132004), the Ministry of Science and Technology of China (2017YFA0206903), the Strategic Priority Research Program of the Chinese Academy of Science (XDB17000000), the Key Research Program of Frontier Sciences of the Chinese Academy of Science (QYZDY-SSW-JSC029), and K. C. Wong Education Foundation.

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https://dx.doi.org/10.1021/acs.orglett.0c03665
Org. Lett. XXXX, XXX, XXX−XXX