Helical Carbenium Ion: A Versatile Organic Photoredox Catalyst in Red-Light-Mediated Reactions

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Supporting Information

ABSTRACT: Red light has the advantages of low energy, less health risk and high penetration depth through various media. Herein, a helical carbenium ion (*N,N'*-di-*n*-propyl-1,13-dimethoxyquinacridinium (*n*Pr-DMQA⁺) tetrafluoroborate) has been used as an organic photoredox catalyst for photoreductions and photooxidations in the presence of red light ($\lambda_{\text{max}} = 640$ nm). It has catalyzed red-light-mediated dual transition-metal/photoredox-catalyzed C-H arylation and intermolecular atom transfer radical addition through oxidative quenching, affording products in 57-93% yields. Moreover, its potential in photooxidation catalysis has also been demonstrated by successful applications in red-light-induced aerobic oxidative hydroxylation of arylboronic acids and benzylic C(sp³)-H oxygenation through reductive quenching, delivering products in up to 92% yield. Thus, a versatile organic photoredox catalyst (helical carbenium ion) for red-light-mediated photoredox reactions has been developed.

Over the past decade, photoredox catalysis has taken the world of synthetic chemistry by a storm.¹ Iridium and ruthenium polypyridyl complexes such as **1a** and **1b** are among the most powerful photoredox catalysts (PCs) due to their unique properties such as stable and long-lived excited states, large redox windows, and as effective excited state oxidants and reductants (Figure 1). However, given the intrinsic disadvantages of transition-metal catalysts such as high cost, low sustainability and potential toxicity, researchers have been looking for inexpensive and environmental-friendly alternatives. In recent years, organic molecules such as acridiniums (e.g. 9-mesityl-10-methylacridinium **1c**) or xanthene dyes (e.g. Eosin Y **1d**) have proven to be efficient alternatives (Figure 1).⁴ Despite the general merits of organic PCs, there are disadvantages to overcome. For example, the most widely used catalyst in this category **1c**, first introduced by Fukuzumi⁵ and expanded by Nicewicz,^{4,6} is mainly used for reductive quenching. Similarly, the narrow redox window, pH dependence, and susceptibility to bleaching have also rendered **1d** less effective.⁷ Therefore, developing more versatile organic PCs is still highly desirable.

Figure 1. Commonly Used Photoredox Catalysts

Despite the impressive progress in photoredox catalysis to date, most light-induced reactions are accomplished under high-energy blue, green or white light.^{1,4} Besides the health hazards (photo-oxidative damage to retina),⁸ blue and green light are also more prone to induce undesired mixtures due to the possible photon absorptions by reactants or products.⁹ In contrast, red light (600-700 nm) has advantages such as low energy, fewer side reactions,

less health risk and is naturally abundant from sunlight. More importantly, it penetrates turbid media, and great success have been made in its biology-related applications.¹⁰ Yet reports on red-light-mediated synthetic methodologies still remain scarce, and only handful examples can be found (Scheme 1a). Ferroud and coworkers introduced a red-light-induced methylene blue (**2a**)-catalyzed aerobic photooxidation and photocyanation of hydrazines (Scheme 1a, I).¹¹ Though more applications of **2a** in photocatalysis have been reported, they all employ blue, green or white light.^{4,12} Similarly, PCs **2b-2d** have also achieved some successes in red-light-mediated methodologies, while no further applications was conducted (Scheme 1a, II-IV).¹³ Notably, Rovis and Campos have recently introduced an elegant work on near-infrared light-induced transformations in the absence of a PC, or in the presence of **1b**, **1d**, or Rose Bengal via triplet fusion upconversion,¹⁴ followed by the development of a series of Os(II)-based PCs for infrared photoredox catalysis.¹⁵ These important examples all suggest that applying red light in photoredox catalysis is of great significance.

The helical carbenium ion – dimethoxyquinacridinium (DMQA⁺), has been well-studied regarding its photophysical,¹⁶ electrochemical properties,^{16b,17} and post-functionalization^{16b,18} since its discovery by Laursen and coworkers.^{16a} Applications of DMQA⁺ have been primarily reserved to the biological arena.¹⁹ In 2005, the Lacour group revealed the first and only example of photocatalysis using DMQA⁺, which demonstrated the aerobic photooxidation of benzylamine in the presence of *N,N'*-di-*n*-propyl-1,13-dimethoxyquinacridinium (*n*Pr-DMQA⁺) tetrafluoroborate (**3**) under photoirradiation (600 W lamp) to afford benzylimine in 15% NMR yield at 70 °C.²⁰ Based on the reported extraordinary photophysical and electrochemical properties of **3**, as well as Lacour's results on photocatalysis, we speculated that **3** could serve as a versatile organic PC. Herein, we report the photoredox properties of [*n*Pr-DMQA⁺][BF₄⁻] (**3**), and its reactivity in a wide range of red-light-mediated reactions including reductive and oxidative quenching (Scheme 1b).

Scheme 1. (a) Previous Work on Red-Light-Mediated Methodologies and (b) a Versatile Organic PC in This Work

(a) Previous Work on Red-Light-Mediated Methodologies

I. Ferroud, 2000, ref. 11

II. Derksen, 2016, ref. 13a

III. Shibata, 2017, ref. 13b

IV. Postigo, 2019, ref. 13c

(b) This work

Absorption $\lambda_{\text{max}} = 616 \text{ nm}$

- ✓ A versatile organic photoredox catalyst
- ✓ Taking advantage of low-energy red light
- ✓ Catalyzing 5 diverse reactions (reductive and oxidative quenching)
- ✓ High substrate generality (23 examples, up to 93% yield)

Before testing the photocatalytic reactivity of **3**, we first calculated the excitation energy ($E_{0,0}$), excited state oxidation ($E_{1/2}(C^{++}/C^+)$) and reduction potentials ($E_{1/2}(C^+/C\cdot)$) based on the reported absorption and emission spectra^{16b} and cyclic voltammetry data¹⁷ (Table S1, see details in Supporting Information).^{4a} To our delight, **3** possesses moderate ground state oxidation and reduction potentials $E_{1/2}(C^{++}/C^+) = +1.32 \text{ V}$ and $E_{1/2}(C^+/C\cdot) = -0.78 \text{ V}$ vs. the saturated calomel electrode (SCE), as well as moderate excited state oxidation and reduction potentials $E_{1/2}(C^{++}/C^+) = -0.61 \text{ V}$ and $E_{1/2}(C^+/C\cdot) = +1.15 \text{ V}$ (Table S1 and Scheme 3). These features render **3** a mild reductant and oxidant whether a reductive or oxidative quenching is involved during photocatalysis. Moreover, the excited state lifetime ($\tau = 5.5 \text{ ns}$)^{16b} is comparable to those of other commonly used organic PCs (2 – 20 ns in general).⁴ In particular, the peak absorption (λ_{max}) is 616 nm,^{16b} which makes our goal of taking advantage of low-energy red light feasible.

Initial reactivity studies began with a red-light-mediated dual Pd/Pr-DMQA⁺⁺-catalyzed C(sp²)-H arylation, which was first reported by the Sanford group using Ru(bpy)₃²⁺ in the presence of 26 W compact fluorescent light (CFL).²¹ In the reported reaction, Ru(bpy)₃²⁺ ($E_{1/2}(\text{Ru(III)}/\text{Ru(II)}) = -0.81 \text{ V}$ vs. SCE) acted as a photoreductant by reducing ArN₂⁺ to aryl radical (PhN₂[•]/Ph[•] = -0.10 V vs. SCE)²² through oxidative quenching, followed by oxidation of Pd(III) to Pd(IV) to regenerate Ru(bpy)₃²⁺ ($E_{1/2}(\text{Ru(III)}/\text{Ru(II)}) = +1.29 \text{ V}$ vs. SCE). Given $E_{1/2}(C^{++}/C^+) = -0.61 \text{ V}$ and $E_{1/2}(C^+/C\cdot) = +1.32 \text{ V}$ for **3**, this reaction was deemed suitable to display its photoreduction ability. To our delight, the reaction between 1-([1,1'-biphenyl]-2-yl)pyrrolidin-2-one **4a** and benzenediazonium tetrafluoroborate **5a** proceeded smoothly in the presence of Pd(OAc)₂ and **3** under red LED ($\lambda_{\text{max}} = 640 \text{ nm}$), affording the desired product **6a** in 95% NMR yield after 4 hours (Table S2). Consistent with Sanford's work,²¹ in the absence of **3**, red light, or Pd(OAc)₂, significantly lower yields ($\leq 25\%$) of **6a** was observed (Table S2).

With satisfying results in hand, we sought to expand the substrate scope of this red-light-mediated dual Pd/Pr-DMQA⁺⁺-catalyzed C(sp²)-H arylation (Table 1). Using **4a** as model substrate, electron-neutral, electron-deficient and electron-rich aryl diazonium salts **5a-5c** were tested. Reactions proceeded

smoothly, delivering the desired products **6a-6c** in 86-93% yields (Table 1, entry 1). Substrate **4b** containing pyridine as the directing group (DG) was well-tolerated as well, furnishing the corresponding products **6d-6f** in 60-73% yields by reacting with **5a-5c** (entry 2). In addition, the desired C-H arylated product **6g** could also be obtained in 57% yield when **4c** with pyrimidine as the directing group reacted with **5a** (entry 3). Lastly, oxime **6h** was isolated in 64% yield when **4d** was reacted with **5a** (entry 4). Notably, all the products **6** were obtained in relatively higher yields compared to the previous work except for **6d**.²¹ Furthermore, control experiments in the absence of **3**, red light or Pd(OAc)₂ resulted in much lower yields for all substrates (Table S3). The successful application of **3** in this red-light-mediated C-H arylation demonstrates that it is capable of engaging in oxidative quenching during photocatalysis.

Table 1. Red-Light-Mediated Dual Pd/Pr-DMQA⁺⁺-Catalyzed C(sp²)-H Arylation^a

Entry	Substrate 4	Substrate 5	Product 6: yield
1			 6a : R = H, 93% ^b 6b : R = Cl, 92% ^b 6c : R = OMe, 86%
2			 6d : R = H, 73% 6e : R = Cl, 68% 6f : R = OMe, 60%
3			 6g : 57%
4			 6h : 64%

^aReactions conducted on 0.2 mmol scale. Isolated yields shown.

^bThe reaction was ran for 4 h.

Next, we turned our attention to photo-induced aerobic oxidative hydroxylation of arylboronic acids, which is a well-documented reaction via reductive quenching under white or blue light.²³ The reaction mainly involves the oxidation of *i*Pr₂NEt (DIPEA) by an excited state PC* to form the radical cation *i*Pr₂NEt^{•+} (*i*Pr₂NEt/*i*Pr₂NEt^{•+} = +0.72 V vs. SCE)²⁴ and the reduction of O₂ by the PC⁻ to generate the superoxide radical anion O₂^{•-} (O₂/O₂^{•-} = -0.57 V vs SCE).^{24a,25} With $E_{1/2}(C^+/C\cdot)$ at +1.15 V and $E_{1/2}(C^+/C\cdot)$ at -0.78 V, **3** should be competent to serve as an efficient PC for this reaction. Gratifyingly, phenol **8a** was obtained in 87% NMR and 83% isolated yield when phenylboronic acid **7a** was treated with DIPEA and **3** in the presence of air and red light for 24 hours in DMF (Table S4). In

accordance with reported results,²³ in the absence of PC or red light, little or no conversion was observed (Table S4).

Substrate scope results for oxidative hydroxylation of arylboronic acids are presented in Table 2. A wide range of arylboronic acids **7** with diverse useful functional groups such as halide (**7c**), nitrile (**7d**), aldehyde (**7e**), ester (**7f**), carboxylic acid (**7g**) and nitro (**7k**) were well-tolerated, giving rise to the desired phenols **8a-8i** in moderate to high yields. Additionally, the substitution pattern on the phenyl ring or electronic properties of **7** did not have much influence over the reaction outcome. For example, **8b-8g** were isolated in 41-87% yields when **7b-7g** with different electron-donating groups (EDG) or electron-withdrawing groups (EWG) at *para* position were examined. Substrates **7h-7k** with diverse substituents at *ortho* or *meta* position also provided the corresponding phenols **8h-8k** in 55-73% yields. 2-Naphthylboronic acid **7l** was also suitable for this oxidative hydroxylation, providing naphthalen-2-ol **8l** in 65% yield. This red-light-induced *n*Pr-DMQA+-catalyzed aerobic oxidative hydroxylation shows that **3** is an efficient PC for photocatalysis involving reductive quenching.

Table 2. *n*Pr-DMQA+-Catalyzed Aerobic Oxidative Hydroxylation of Arylboronic Acids under Red Light^a

$\text{ArB(OH)}_2 \xrightarrow[\text{Red LED } (\lambda_{\text{max}} = 640 \text{ nm})]{\text{DIPEA, PC 3 (2 mol\%)}, \text{DMF, air, rt, 24 h}} \text{ArOH}$			
8a , 83%	8b , 71%	8c , 81%	8d , 87%
8e , 66%	8f , 80%	8g , 41%	8h , 72%
8i , 55%	8j , 67%	8k , 73%	8l , 65%

^aReactions conducted on 0.5 mmol scale. Isolated yields shown.

To further illustrate the generality of **3** as a PC, additional red-light-induced transformations were investigated (Scheme 2). As another classic example of photocatalysis involving in reductive quenching and O₂·, visible-light-mediated aerobic benzylic C(sp³)-H oxygenation using oxygen as the oxidant was extensively studied.²⁶ When a tertiary amine **9** was treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and **3** in the presence of air and red light, amide **10** was isolated in 92% yield (Scheme 2a). Atom transfer radical addition (ATRA) of organic halides to olefins serves as an atom-economical approach of simultaneously forming C-C and C-X bonds.²⁷ As presented in Scheme 2b, in the presence of LiBr and **3**, a red-light-induced reaction between 4-nitrobenzyl bromide **11** and styrene **12** was realized, affording the desired adduct **13** in 59% yield (see Table S5 and S6 for more optimization and Scheme S1 for mechanism). At last, **3** could also act as a viable alternative for Glorius's dual gold/photoredox-catalyzed C(sp)-H arylation of terminal alkyne **14** with **5a**,²⁸ providing the desired product **15** in 62% yield (Scheme 2c, see more optimization in Table S7). Control experiments in the absence of **3**, red light, or other reagents such as DBU, LiBr or Au(PPh₃)Cl were also performed (Scheme S2). The reduced

yields of **10**, **13**, and **15** further supports the essential roles of **3** and red light for these reactions.

Scheme 2. Additional Examples of Red-Light-Induced *n*Pr-DMQA+-Catalyzed Reactions^a

^aReactions conducted on 0.2 mmol scale. Isolated yields shown.

Based on previous work,^{21,23} two plausible catalytic cycles involving in oxidative or reductive quenching are proposed (Scheme 3). Scheme 3-I shows proposed mechanism for dual Pd/*n*Pr-DMQA+-catalyzed C(sp²)-H arylation.²¹ Firstly, photoexcitation of **3** generates *n*Pr-DMQA⁺, which reduces **5** to form an aryl radical and *n*Pr-DMQA⁺⁺ through oxidative quenching. Then, addition of the aryl radical to the Pd(II) intermediate **A** (generated by C-H activation of substrate **4**) affords the Pd(III) species **B**, followed by an one-electron oxidation with *n*Pr-DMQA⁺⁺ to regenerate *n*Pr-DMQA⁺ and form the Pd(IV) intermediate **C**. Lastly, reductive elimination of the intermediate **C** furnishes the arylated product **6**. Mechanism for *n*Pr-DMQA+-catalyzed aerobic oxidative hydroxylation is presented in Scheme 3-II.²³ *n*Pr₂NEt is first oxidized to an ammonium radical cation by the excited state of **3**, along with formation of a helicene radical *n*Pr-DMQA· through reductive quenching. Then, the helicene radical, which has been previously observed and characterized *in situ* by Laursen,¹⁷ further reacts with oxygen to regenerate **3** and form an O₂·. Finally, follow-up oxidative attack onto substrates **7** and hydrolysis afford phenols **8**.

Scheme 3. Plausible Catalytic Cycles For (I) C(sp²)-H Arylation, and (II) Aerobic Oxidative Hydroxylation

In summary, we have disclosed a helical carbenium ion – [*n*Pr-DMQA⁺][BF₄⁻] (**3**), which catalyzes photoreductions and photooxidations in the presence of low-energy red light. The role of **3** as an efficient PC in oxidative and reductive quenching were evaluated by transition-metal/*n*Pr-DMQA⁺-catalyzed C-H arylations and intermolecular ATRA (oxidative quenching), as well as aerobic oxidative hydroxylation of arylboronic acids and benzylic C(sp³)-H oxygenation (reductive quenching). Eight diverse substrates were well-tolerated for red-light-mediated dual Pd/*n*Pr-DMQA⁺-catalyzed C(sp²)-H arylation. Moreover, with twelve different arylboronic acids as the substrates, red-light-induced *n*Pr-DMQA⁺-catalyzed aerobic oxidative hydroxylation proceeded smoothly as well. The successful applications of **3** in these red-light-mediated reactions have established its role as a versatile organic PC, which can serve as a complementary option for current white, blue or green-light-mediated photocatalysis. Further investigations on the applications of **3** towards more challenging photoredox catalysis are in progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information contains experimental procedures, characterization, and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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Table of Content

Supporting Information

Helical Carbenium Ion: A Versatile Organic Photoredox Catalyst in Red-Light-Mediated Reactions

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1. General remarks

Unless otherwise specified, all reactions were carried out in oven-dried (overnight) vials or Schlenk tubes with magnetic stirring in a glove box. ^1H , ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance III-400 MHz or DRX-500 MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards. The chemical shifts are shown in δ scales. Multiplicities of ^1H NMR signals are designated as s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), quin (quintet), m (multiplet), etc.. Compounds were named using ChemDraw and assignments of NMR spectra were done using MestReNova. All chemicals and solvents were purchased from Sigma Aldrich, Fisher Scientific, or VWR. Organic solvents used were dried by a standard solvent purification system (J. C. Meyer or Vigor Solvent Systems). Commercially obtained reagents were used without further purification. All reactions were monitored by TLC silica gel 60 F₂₅₄ (EMD Millipore). Flash column chromatography was carried out using SiliaFlash silica gels F60, 40-63 μm , 60 Å (SiliCycle) at increased pressure. All reactions were performed under N_2 using standard Schlenk techniques or in a glove box (Mbraun glove box).

Substrates **4b**,¹ **4c**,² and **4d**³ were prepared according to the previously reported procedures. Aryl diazonium tetrafluoroborates **5a-5c** were prepared according to the previously reported procedures.⁴ 2-Phenyl-3,4-dihydroisoquinolin-1(2H)-one **9** was prepared according to the previously reported procedure.⁵ $\text{Au}(\text{PPh}_3)\text{Cl}$ was prepared from PPh_3 and $\text{AuCl}(\text{SMe}_2)$ according to the previously reported procedure.⁶

2. Synthesis and characterization of dimethoxyquinacridinium (DMQA⁺) tetrafluoroborate **3**

3 was synthesized according to a modified procedure from previous paper.⁷

A solution of **S1** (1.02 g, 2 mmol, 1.0 equiv.) and **S2** (2.95 g, 50 mmol, 25.0 equiv.) in MeCN (20 mL) was stirred at 85 °C for 18 hours. A dark green solution was formed. The mixture was cooled to room temperature, transferred to a 250 mL round bottom flask and a large excess of Et₂O (200 mL) was added to crash out the crude product **3** as a dark green solid (924 mg). After layering in DCM/MeCN/MeOH/Et₂O for 2 days, 811 mg of pure product **3** was obtained as a dark green solid after filtration.

3: Yield: (811 mg, 81%). A dark green solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.24 (dd, *J* = 8.4, 8.4 Hz, 1H, ArH), 7.95 (dd, *J* = 8.4, 8.4 Hz, 2H, ArH), 7.68 (d, *J* = 8.4 Hz, 2H, ArH), 7.60 (d, *J* = 8.4 Hz, 2H, ArH), 7.01 (d, *J* = 8.4 Hz, 2H, ArH), 4.77-4.68 (m, 2H, CH₂), 4.51-4.42 (m, 2H, CH₂), 3.71 (s, 6H, OMe), 2.04-1.92 (m, 4H, CH₂), 1.15 (t, *J* = 7.2 Hz, 6H, CH₃). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 159.12, 141.78, 141.59, 138.22, 137.16, 136.71, 118.58, 112.27, 107.69, 105.09, 103.01, 55.67, 50.56, 19.38, 10.82. ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -148.25, -148.30.

3. Photophysical and electrochemical properties of **3**

The photophysical properties of **3** have been well-documented in the previous literature,^{7,8} which is featured with peak absorption at 616 nm and peak emission at 667 nm. The electrochemical behavior of **3** has been well-studied by cyclic voltammetry (CV) in previously reports,^{8,9} which was featured

with a quasi-reversible oxidation of C^+ to C^{++} ($E_{1/2}(C^{++}/C^+)$) at 1.32 V *versus* the saturated calomel electrode (SCE) and a fully reversible reduction of C^+ to $C^\bullet$ ($E_{1/2}(C^+/C^\bullet)$) at -0.78 V *versus* SCE in acetonitrile.

Based on the reported literature,¹⁰ excitation energy ($E_{0,0}$) is estimated by calculating the energy of the wavelength at which the compound's UV-Vis absorption and emission spectra overlap or of the wavelength at the midpoint between absorption and emission maxima. Then, excited state reduction potential $E_{1/2}(C^{+*}/C^\bullet)$ is calculated by $E_{1/2}(C^{+*}/C^\bullet) = E_{1/2}(C^+/C^\bullet) + E_{0,0}$; while excited state oxidation potential $E_{1/2}(C^{++}/C^{+*})$ is calculated by $E_{1/2}(C^{++}/C^{+*}) = E_{1/2}(C^{++}/C^+) - E_{0,0}$. Thus, we can obtain the corresponding photophysical and electrochemical properties of **3** (Table S1).

Absorption $\lambda_{\max} = 616$ nm

Emission $\lambda_{\max} = 667$ nm

Midpoint of absorption and emission maxima $\lambda = 642$ nm

$E_{0,0} = 1240/642 \text{ eV} = 1.93 \text{ eV}$

$E_{1/2}(C^{+*}/C^\bullet) = -0.78 + 1.93 \text{ V} = 1.15 \text{ V}$

$E_{1/2}(C^{++}/C^{+*}) = 1.32 - 1.93 \text{ V} = -0.61 \text{ V}$

PC	$E_{0,0}$ (eV) ^a	$E_{1/2}(C^{++}/C^+)$ (V) ^b	$E_{1/2}(C^+/C^\bullet)$ (V) ^b	$E_{1/2}(C^{++}/C^{+*})$ (V) ^c	$E_{1/2}(C^{+*}/C^\bullet)$ (V) ^c	excited state lifetime τ (ns) ^d	absorption $\lambda_{\max}$ (nm)	emission $\lambda_{\max}$ (nm)
3	1.93	+1.32	-0.78	-0.61	+1.15	5.5	616	667

^a Measured in MeCN (10^{-5} M). ^b Determined by cyclic voltammetry in MeCN versus SCE. See ref 9.

^c Excited state potentials were estimated from ground state redox potentials and the midpoint of the absorption and emission maxima. ^d Excitation at 470 nm. See ref 8.

Table S1. Photophysical and electrochemical properties of **3**

4. Reaction setup for photocatalysis

The reaction was set up by referring to MacMillan group.¹¹

Two 25 mL Schlenk tubes are placed in a water bath (Pyrex crystallizing dish, 125 x 65mm, No. 3140) at the center of a stir plate. Two parallel Red LED lamps (KSPR160L-640-C Red LED 640nm Photoredox Light customized wavelength, Kessil LED Lights) are placed perpendicular to the sidewall of Schlenk tubes, so that the two tubes can be equally exposed to the LEDs. The stir plate/water bath/LEDs are surrounded by an open-top cardboard box covered with aluminum foil to increase the light reflections. A fan (Honeywell, TurboForce Power HT900) over the water bath is always turned on when the reaction is running.

Note: The combination of an overhead fan and a water bath is to offset the heat generated from the LED lights and stabilize reaction temperature for reproducible results. The water bath needs to be refilled with room temperature deionized water every 12-18 hours. With the above setup, the reaction temperature can be maintained at 21-23 °C during the reaction for us.

Figure S1. Reaction setup for photocatalysis.

5. Typical procedure for red-light-mediated dual Pd/*n*Pr-DMQA+-catalyzed C-H arylation

In a N₂ glove box, Pd(OAc)₂ (4.5 mg, 0.02 mmol, 10 mol%), **3** (2.5 mg, 0.005 mmol, 2.5 mol%), the substrate **4** (0.2 mmol, 1.0 equiv.) and the aryldiazonium salt **5** (0.8 mmol, 4.0 equiv.) were added to an oven-dried (overnight) Schlenk tube containing a stirring bar, followed by adding degassed anhydrous MeOH (2.0 mL, 0.1 M). The Schlenk tube was then sealed, removed from the glove box

and stirred at room temperature under red LED ($\lambda_{\text{max}} = 640 \text{ nm}$) irradiation. After 16 hours, the mixture was quenched with a saturated solution of NaHCO_3 (2 mL), followed by adding deionized water (2 mL). The crude reaction mixture was then extracted with ethyl acetate ($3 \times 10 \text{ mL}$), and the combined organic layers were washed with brine (20 mL) and dried over anhydrous Na_2SO_4 . After filtration, the solvent was removed under reduced pressure on RotaVap. The crude product was purified by flash chromatography (FC) on silica gel (eluent: Hexanes/EtOAc = 20/1 $\sim$ 1/1) to yield the desired product **6**.

1-([1,1'-biphenyl]-2-yl)pyrrolidin-2-one (**6a**): Yield (44 mg, 93%). A clear viscous oil. $R_f = 0.2$ (Hexanes/EtOAc = 1/2). FC (Hexanes/EtOAc = 1/1). ^1H NMR (400 MHz, C_6D_6) δ 7.39-7.35 (m, 2H, ArH), 7.33 (dd, $J = 8.0, 1.6 \text{ Hz}$, 1H, ArH), 7.21 (dd, $J = 7.6, 1.6 \text{ Hz}$, 1H, ArH), 7.17-7.04 (m, 5H, ArH), 2.78 (t, $J = 6.8 \text{ Hz}$, 2H, CH_2), 2.04 (t, $J = 8.0 \text{ Hz}$, 2H, CH_2), 1.19 (tt, $J = 6.8, 8.0 \text{ Hz}$, 2H, CH_2). ^{13}C NMR (101 MHz, C_6D_6) δ 174.18, 140.13, 140.08, 137.67, 130.98, 129.18, 128.82, 128.63, 128.48, 127.74, 127.64, 49.70, 31.11, 19.06. ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.31 (m, 9H, ArH), 3.21 (t, $J = 6.8 \text{ Hz}$, 2H, CH_2), 2.42 (t, $J = 8.0 \text{ Hz}$, 2H, CH_2), 1.87 (tt, $J = 6.8, 8.0 \text{ Hz}$, 2H, CH_2). ^{13}C NMR (101 MHz, CDCl_3) δ 175.70, 139.73, 139.22, 136.43, 130.92, 128.65, 128.51, 128.49, 128.45, 128.12, 127.67, 50.26, 31.30, 19.08.

1-(4'-chloro-[1,1'-biphenyl]-2-yl)pyrrolidin-2-one (**6b**): Yield (50 mg, 92%). A light yellow solid. $R_f = 0.2$ (Hexanes/EtOAc = 1/2). FC (Hexanes/EtOAc = 1/1). ^1H NMR (400 MHz, C_6D_6) δ 7.24 (dd, $J = 8.0, 1.2 \text{ Hz}$, 1H, ArH), 7.15-7.04 (m, 7H, ArH), 2.73 (t, $J = 6.8 \text{ Hz}$, 2H, CH_2), 2.00 (t, $J = 8.0 \text{ Hz}$, 2H, CH_2), 1.18 (tt, $J = 6.8, 8.0 \text{ Hz}$, 2H, CH_2). ^{13}C NMR (101 MHz, C_6D_6) δ 174.18, 138.86, 138.46, 137.53, 133.78, 130.79, 130.21, 129.01, 128.82, 128.81, 49.77, 31.03, 19.01. ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.30 (m, 8H, ArH), 3.26 (t, $J = 6.8 \text{ Hz}$, 2H, CH_2), 2.43 (t, $J = 8.0 \text{ Hz}$, 2H, CH_2), 1.92 (tt, $J = 6.8, 8.0 \text{ Hz}$, 2H, CH_2). ^{13}C NMR (126 MHz, CDCl_3) δ 175.83, 138.71, 137.78, 136.49, 133.87, 130.85, 129.88, 129.10, 128.79, 128.58, 128.34, 128.33, 50.33, 31.13, 18.95.

1-(4'-methoxy-[1,1'-biphenyl]-2-yl)pyrrolidin-2-one (**6c**): Yield (46 mg, 86%). An orange viscous oil. $R_f = 0.2$ (Hexanes/EtOAc = 1/2). FC (Hexanes/EtOAc = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.34 (m, 3H, ArH), 7.32-7.28 (m, 3H, ArH), 6.94-6.92 (m, 2H, ArH), 3.84 (s, 3H), 3.22 (t, $J = 6.8$ Hz, 2H, CH_2), 2.44 (t, $J = 8.0$ Hz, 2H, CH_2), 1.89 (tt, $J = 6.8, 8.0$ Hz, 2H, CH_2). ^{13}C NMR (101 MHz, CDCl_3) δ 175.76, 159.25, 139.37, 136.42, 131.58, 130.94, 129.59, 128.49, 128.30, 128.12, 113.96, 55.37, 50.18, 31.35, 19.11.

2-(3-methyl-[1,1'-biphenyl]-2-yl)pyridine (**6d**): Yield (36 mg, 73%). A clear viscous oil. $R_f = 0.4$ (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 20/1). ^1H NMR (500 MHz, CDCl_3) δ 8.63 (ddd, $J = 5.0, 2.0, 1.0$ Hz, 1H, ArH), 7.44 (ddd, $J = 7.5, 7.5, 1.5$ Hz, 1H, ArH), 7.36 (dd, $J = 7.5, 7.5$ Hz, 1H, ArH), 7.31-7.26 (m, 2H, ArH), 7.16-7.11 (m, 3H, ArH), 7.10-7.06 (m, 3H, ArH), 6.88 (ddd, $J = 7.5, 7.5, 1.5$ Hz, 1H, ArH), 2.19 (s, 3H, Me). ^{13}C NMR (101 MHz, CDCl_3) δ 159.69, 148.92, 141.77, 141.36, 139.41, 136.80, 135.81, 129.75, 129.71, 129.52, 128.15, 127.70, 127.69, 126.32, 125.74, 121.40, 20.59.

2-(4'-chloro-3-methyl-[1,1'-biphenyl]-2-yl)pyridine (**6e**): Yield (38 mg, 68%). A pale yellow viscous oil. $R_f = 0.4$ (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 20/1). ^1H NMR (400 MHz, CDCl_3) δ 8.62 (ddd, $J = 4.8, 4.8, 1.2$ Hz, 1H, ArH), 7.48 (ddd, $J = 7.6, 7.6, 2.0$ Hz, 1H, ArH), 7.38-7.28 (m, 2H, ArH), 7.23 (dd, $J = 7.6, 1.2$ Hz, 1H, ArH), 7.13-7.09 (m, 3H, ArH), 7.03-6.99 (m, 2H, ArH), 6.89 (ddd, $J = 7.6, 7.6, 1.2$ Hz, 1H, ArH), 2.18 (s, 3H, Me). ^{13}C NMR (101 MHz, CDCl_3) δ 159.40, 149.11, 140.26, 140.07, 139.42, 136.97, 136.00, 132.46, 130.99, 129.83, 128.24, 127.91, 127.53, 125.64, 121.58, 20.55.

2-(4'-methoxy-3-methyl-[1,1'-biphenyl]-2-yl)pyridine (**6f**): Yield (33 mg, 60%). A clear viscous oil. $R_f = 0.4$ (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 20/1). ^1H NMR (400 MHz, CDCl_3) δ 8.63 (ddd, $J = 4.8, 4.8, 1.2$ Hz, 1H, ArH), 7.46 (ddd, $J = 7.6, 7.6, 2.0$ Hz, 1H, ArH), 7.34 (dd, $J = 7.6, 7.6$ Hz, 1H, ArH), 7.28-7.23 (m, 2H, ArH), 7.09 (ddd, $J = 7.6, 4.8, 1.2$ Hz, 1H, ArH), 7.02-6.97 (m, 2H, ArH), 6.88 (d, $J = 8.0$ Hz, 1H, ArH), 6.70-6.66 (m, 2H, ArH), 3.73 (s, 3H, OMe), 2.18 (s, 3H, Me). ^{13}C NMR (101 MHz, CDCl_3) δ 159.93, 158.17, 148.98, 140.90, 139.45, 136.78, 135.86, 134.22, 130.78, 129.18, 128.11, 127.69, 125.71, 121.33, 113.18, 55.20, 20.60.

2-(4-methyl-[1,1'-biphenyl]-2-yl)pyrimidine (**6g**): Yield (28 mg, 57%). A clear viscous oil. $R_f = 0.3$ (Hexanes/EtOAc = 3/1). FC (Hexanes/EtOAc = 15/1). ^1H NMR (400 MHz, CDCl_3) δ 8.63 (d, $J = 4.8$ Hz, 2H, ArH), 7.61 (d, $J = 1.6$ Hz, 1H, ArH), 7.37 (d, $J = 7.6$ Hz, 1H, ArH), 7.32 (dd, $J = 7.6, 1.6$ Hz, 1H, ArH), 7.24-7.18 (m, 3H, ArH), 7.14-7.10 (m, 2H, ArH), 7.08 (dd, $J = 4.8, 4.8$ Hz, 1H, ArH), 2.46 (s, 3H, Me). ^{13}C NMR (101 MHz, CDCl_3) δ 168.37, 156.83, 141.67, 138.76, 138.12, 137.28, 131.19, 130.79, 130.29, 129.28, 128.05, 126.39, 118.50, 21.18.

1-(4-methyl-[1,1'-biphenyl]-2-yl)ethan-1-one oxime (**6h**): Yield (29 mg, 64%). A white solid. $R_f = 0.4$ (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 20/1). ^1H NMR (400 MHz, C_6D_6) δ 8.69 (s, 1H, OH), 7.40-7.37 (m, 2H, ArH), 7.32 (d, $J = 2.0$ Hz, 1H, ArH), 7.13-7.03 (m, 3H, ArH), 6.96 (dd, $J = 7.6, 2.0$ Hz, 1H, ArH), 2.09 (s, 3H, Me), 1.78 (s, 3H, Me). ^{13}C NMR (101 MHz, C_6D_6) δ 159.07, 141.64, 138.32, 137.39, 137.27, 130.55, 130.44, 129.86, 129.37, 128.69, 127.31, 20.85, 16.30. ^1H NMR (500 MHz, CDCl_3) δ 8.15 (s, 1H, OH), 7.42-7.37 (m, 4H, ArH), 7.35-7.31 (m, 1H, ArH), 7.30-7.28 (m, 1H, ArH), 7.27-7.24 (m, 2H, ArH), 2.41 (s, 3H, Me), 1.69 (s, 3H, Me). ^{13}C NMR (101 MHz, CDCl_3) δ 159.50, 141.10, 137.89, 137.31, 136.73, 130.38, 129.90, 129.84, 129.09, 128.54, 127.25, 21.12, 16.12.

6. Optimization of red-light-mediated dual Pd/ π Pr-DMQA+-catalyzed C-H arylation

Using 1-([1,1'-biphenyl]-2-yl)pyrrolidin-2-one **4a** and benzenediazonium tetrafluoroborate **5a** as

model substrates, Pd(OAc)₂ as catalyst, **3** as PC, MeOH as solvent, the reaction time was screened and the results are outlined in Table S2. Under red LED ($\lambda_{\text{max}} = 640$ nm), the reaction proceeded smoothly to afford the desired product **6a** in 95% NMR yield after 8 hours (Table S2, entry 1). By decreasing the reaction time to 6 h, 4 h and 2 h, the desired product **6a** was obtained in 95%, 95% and 85% NMR yield, respectively (Table S2, entries 2-4). To test the background reactions, several control experiments have also been performed. In the absence of PC **3**, red light or Pd(OAc)₂, significantly lower yields ($\leq 25\%$) of **6a** was observed for all the conditions (Table S2, entries 5-9), which is in accordance with the reported photocatalytic mechanism for this reaction.¹²

Entry ^a	PC	Light source	Time [h]	Yield [%] ^b	SM-4a [%] ^b
1	3	Red LED (640 nm)	8	95	trace
2	3	Red LED (640 nm)	6	95	trace
3	3	Red LED (640 nm)	4	95	trace
4	3	Red LED (640 nm)	2	85	10
5	-	Red LED (640 nm)	4	22	73
6	-	Red LED (640 nm)	8	25	70
7	3	-	4	12	83
8	3	-	8	16	79
9 ^c	3	Red LED (640 nm)	4	trace	95

^a The reaction was conducted with **4a** (0.1 mmol), **5a** (0.4 mmol), Pd(OAc)₂ (10 mol%), and PC (2.5 mol%) in MeOH (1.0 mL).

^b NMR yield by using 1,3,5-trimethoxybenzene as internal standard.

^c Without Pd(OAc)₂

Table S2. Optimization and control experiments of red-light-mediated dual Pd/*n*Pr-DMQA+-catalyzed C(sp²)-H arylation

7. NMR results for control reactions for Table 1

To further demonstrate the essential roles of red light, PC **3** and Pd catalyst, control experiments to determine the background reaction yields for all substrates have been conducted and the NMR results are presented in Table S3. In general, in the absence of red light, $\leq 15\%$ NMR yield was observed for all the substrates, except for 36% NMR yield for the reaction of **4a** and 4-chlorobenzenediazonium tetrafluoroborate **5b**. In the absence of **3**, $\leq 40\%$ NMR yield was observed

for all the substrates, except for 45% NMR yield for the reaction of **4a** and **5b**. However, in Sanford's work, the reaction of **4a** and **5b** was reported with 97% GC yield under 26 W CFL in the absence of Ru(bpy)₃²⁺ for 4 hours.¹² This major difference in reaction yield presumably results from the fact that diazonium salts show blue light absorption.¹³ The lower background observed in the present system highlights the great potential of low-energy red light towards reaction selectivity. At last, in the absence of Pd catalyst, trace amount of products **6** was observed for all the substrates, which supports the essential role of palladium for activating the substrate **4** during the catalytic cycle.¹²

$ \begin{array}{c} \text{DG} \text{---} \text{C}_6\text{H}_4\text{---} \text{H} + \text{Ar---N}_2^+ \text{BF}_4^- \xrightarrow[\text{MeOH, N}_2, \text{rt, 16 h}]{\text{Pd(OAc)}_2 (10 \text{ mol\%}), \text{PC } \mathbf{3} (2.5 \text{ mol\%})} \text{DG} \text{---} \text{C}_6\text{H}_4\text{---} \text{Ar} \\ \text{Red LED } (\lambda_{\text{max}} = 640 \text{ nm}) \\ \mathbf{4} \qquad \qquad \mathbf{5} \qquad \qquad \qquad \qquad \mathbf{6} \end{array} $						
Entry	Substrate 4	Substrate 5	Product 6 : yield ^a	Without light [%] ^b	Without 3 [%] ^b	Without Pd [%] ^b
1			 6a : R = H, 93% ^c 6b : R = Cl, 92% ^c 6c : R = OMe, 86%	6a : 13% 6b : 36% 6c : 3	6a : 24% 6b : 45% 6c : 14	6a : trace ^c 6b : trace ^c 6c : trace
2			 6d : R = H, 73% 6e : R = Cl, 68% 6f : R = OMe, 60%	6d : 3 6e : 9 6f : 1	6d : 16 6e : 40 6f : 5	6d : trace 6e : trace 6f : trace
3			 6g : 57%	4	28	trace
4			 6h : 64%	4	5	trace

^a The reaction was conducted with **4** (0.2 mmol), **5** (0.8 mmol), Pd(OAc)₂ (10 mol%), and **3** (2.5 mol%) in MeOH (2.0 mL). Isolated yields were shown. ^b The reaction was conducted with **4** (0.1 mmol), **5** (0.4 mmol), Pd(OAc)₂ (10 mol%), and **3** (2.5 mol%) in MeOH (1.0 mL). NMR yield by using 1,3,5-trimethoxybenzene as internal standard were shown. ^c The reaction was ran for 4 h.

Table S3. NMR results for control reactions for Table 1

8. Typical procedure for *n*Pr-DMQA+-catalyzed aerobic oxidative hydroxylation of arylboronic acids under red light

To a mixture of arylboronic acid **7** (0.50 mmol, 1.0 equiv.) and PC **3** (5.0 mg, 0.01 mmol, 2 mol%) in DMF (5.0 mL, 0.1 M) was added DIPEA (129 mg, 1.0 mmol, 2.0 equiv.) in a Schlenk tube. The solution was stirred at room temperature under red LED ($\lambda_{\text{max}} = 640 \text{ nm}$) irradiation in open to air (without bubbling air). After 24 hours, the reaction mixture was cooled to 0 °C and quenched by adding aqueous solution of HCl (10%, 5 mL) slowly, followed by extracting with Et₂O (3 x 10 mL). The combined organic layers were washed with brine (10 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under reduced pressure on RotaVap. The crude product was purified by flash chromatography (FC) on silica gel (eluent: Hexanes/EtOAc = 20/1 ~ 1/2) to furnish the desired product **8**.

Phenol (**8a**): Yield (39 mg, 83%). A colorless solid. $R_f = 0.4$ (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 15/1). ¹H NMR (500 MHz, CDCl₃) δ 7.27-7.23 (m, 2H, ArH), 6.96-6.92 (m, 1H, ArH), 6.87-6.83 (m, 2H, ArH), 5.10 (s, 1H, OH). ¹³C NMR (126 MHz, CDCl₃) δ 155.75, 129.89, 120.97, 115.50.

4-Methoxyphenol (**8b**): Yield (44 mg, 71%). A colorless solid. $R_f = 0.2$ (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 10/1). ¹H NMR (400 MHz, CDCl₃) δ 6.84-6.77 (m, 4H, ArH), 4.76 (s, 1H, OH), 3.80 (s, 3H, OMe). ¹³C NMR (101 MHz, CDCl₃) δ 153.89, 149.59, 116.19, 115.02, 55.96.

4-Chlorophenol (**8c**): Yield (52 mg, 81%). A colorless oil. $R_f = 0.4$ (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.18 (m, 2H, ArH), 6.78-6.75 (m, 2H, ArH), 4.86 (s, 1H, OH). ^{13}C NMR (101 MHz, CDCl_3) δ 154.22, 129.67, 125.83, 116.80.

4-Cyanophenol (**8d**): Yield (52 mg, 87%). A light yellow solid. $R_f = 0.1$ (Hexanes/EtOAc = 3/1). FC (Hexanes/EtOAc = 5/1). ^1H NMR (400 MHz, CDCl_3) δ 7.57-7.54 (m, 2H, ArH), 6.96-6.93 (m, 2H, ArH), 6.69 (s, 1H, OH). ^{13}C NMR (101 MHz, CDCl_3) δ 160.34, 134.47, 119.37, 116.61, 103.16.

4-Hydroxybenzaldehyde (**8e**): Yield (40 mg, 66%). A white solid. $R_f = 0.3$ (Hexanes/EtOAc = 3/1). FC (Hexanes/EtOAc = 5/1). ^1H NMR (400 MHz, Methanol- d_4) δ 9.76 (s, 1H, CHO), 7.78-7.75 (m, 2H, ArH), 6.93-6.90 (m, 2H, ArH). ^{13}C NMR (101 MHz, Methanol- d_4) δ 192.81, 165.15, 133.42, 130.30, 116.85.

Methyl 4-hydroxybenzoate (**8f**): Yield (61 mg, 80%). A white solid. $R_f = 0.3$ (Hexanes/EtOAc = 3/1). FC (Hexanes/EtOAc = 5/1). ^1H NMR (400 MHz, CDCl_3) δ 7.97-7.93 (m, 2H, ArH), 6.91-6.87 (m, 2H, ArH), 6.46 (s, 1H, OH), 3.90 (s, 3H, OMe). ^{13}C NMR (101 MHz, CDCl_3) δ 167.65, 160.44, 132.11, 122.39, 115.45, 52.26.

4-Hydroxybenzoic acid (**8g**): Yield (28 mg, 41%). A white solid. $R_f = 0.2$ (Hexanes/EtOAc = 1/1). FC (Hexanes/EtOAc = 1/1). ^1H NMR (400 MHz, Methanol- d_4) δ 7.89-7.86 (m, 2H, ArH), 6.83-6.80 (m, 2H, ArH). ^{13}C NMR (126 MHz, Methanol- d_4) δ 170.26, 163.54, 133.13, 122.81, 116.13.

o-Cresol (**8h**): Yield (39 mg, 72%). A light yellow oil. $R_f = 0.5$ (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 20/1). ^1H NMR (500 MHz, CDCl_3) δ 7.14-7.11 (m, 1H, ArH), 7.11-7.06 (m, 1H, ArH), 7.14-7.11 (m, 1H, ArH), 6.77 (dd, $J = 8.0, 1.5$ Hz, 1H, ArH), 4.65 (s, 1H, OH), 2.26 (s, 3H, Me). ^{13}C NMR (101 MHz, CDCl_3) δ 153.89, 131.16, 127.27, 123.80, 120.89, 115.01, 15.84.

2-Methoxyphenol (**8i**): Yield (34 mg, 55%). A white solid. $R_f = 0.5$ (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 20/1). ^1H NMR (500 MHz, CDCl_3) δ 6.94-6.91 (m, 1H, ArH), 6.90-6.84 (m, 3H, ArH), 5.60 (s, 1H, OH), 3.89 (s, 3H, OMe). ^{13}C NMR (126 MHz, CDCl_3) δ 146.82, 145.92, 121.66, 120.34, 114.72, 110.90, 55.97.

m-Cresol (**8j**): Yield (36 mg, 67%). A colorless oil. $R_f = 0.5$ (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 20/1). ^1H NMR (400 MHz, CDCl_3) δ 7.13 (dd, $J = 7.6, 8.0$ Hz, 1H, ArH), 6.76 (d, $J = 7.6$ Hz, 1H, ArH), 6.68-6.62 (m, 2H, ArH), 4.76 (s, 1H, OH), 2.32 (s, 3H, Me). ^{13}C NMR (101 MHz, CDCl_3) δ 155.53, 139.97, 129.56, 121.77, 116.15, 112.40, 21.48.

3-Nitrophenol (**8k**): Yield (51 mg, 73%). A white solid. $R_f = 0.4$ (Hexanes/EtOAc = 3/1). FC (Hexanes/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (dd, $J = 8.4, 2.0$ Hz, 1H, ArH), 7.71 (dd, $J = 2.4, 2.0$ Hz, 1H, ArH), 7.41 (dd, $J = 8.4, 8.4$ Hz, 1H, ArH), 7.19 (dd, $J = 8.4, 2.4$ Hz, 1H, ArH), 5.63 (s, 1H, OH). ^{13}C NMR (101 MHz, CDCl_3) δ 156.39, 149.25, 130.46, 122.16, 116.08, 110.70.

Naphthalen-2-ol (**8l**): Yield (47 mg, 65%). A light yellow solid. $R_f = 0.3$ (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 15/1). ^1H NMR (400 MHz, CDCl_3) δ 7.78 (dd, $J = 8.4, 8.4$ Hz, 2H, ArH), 7.69 (d, $J = 8.4$ Hz, 1H, ArH), 7.48-7.43 (m, 1H, ArH), 7.38-7.33 (m, 1H, ArH), 7.16 (d, $J = 2.4$ Hz,

1H, ArH), 7.12 (dd, $J = 8.8, 2.4$ Hz, 1H, ArH), 5.16 (s, 1H, OH). ^{13}C NMR (101 MHz, CDCl_3) δ 153.36, 134.70, 130.01, 129.09, 127.90, 126.68, 126.51, 123.79, 117.84, 109.67.

9. Optimization of *n*Pr-DMQA+-catalyzed aerobic oxidative hydroxylation

Using phenylboronic acid **7a** as model substrate, DIPEA as base, **3** as PC, air as oxidant, DMF as solvent, the reaction time was screened and the results are shown in Table S4. Under red LED ($\lambda_{\text{max}} = 640$ nm), the reaction proceeded smoothly to afford phenol **8a** in 77% NMR yield after 18 hours (Table S4, entry 1). By increasing the reaction time to 24 hours, **8a** was obtained in 87% NMR yield, along with 83% isolated yield (Table S4, entry 2). Running the reaction for 28 h did not improve the result (Table S4, entry 3). Several control experiments have also been performed. In the absence of **3** or red light, little or no conversion was observed (Table S4, entries 4-5), which is consistent with the photocatalytic model for this reaction in the reported literature.^{14–17}

$\text{PhB(OH)}_2 \xrightarrow[\text{DMF, air, rt, Time, Light source}]{\text{DIPEA, PC (2 mol\%)}} \text{PhOH}$				
	7a		8a	
Entry ^a	PC	Light source	Time [h]	Yield [%] ^b
1	3	Red LED (640 nm)	18	77
2	3	Red LED (640 nm)	24	87 (83) ^c
3	3	Red LED (640 nm)	28	88
4	-	Red LED (640 nm)	28	9
5	3	-	28	n. d.

^a The reaction was conducted with **7a** (0.5 mmol), DIPEA (1.0 mmol), and **3** (2 mol%) in DMF (5.0 mL) under air at rt.

^b NMR yield by using 1,3,5-trimethoxybenzene as internal standard.

^c Isolated yield.

Table S4. Optimization and control experiments of *n*Pr-DMQA+-catalyzed aerobic oxidative hydroxylation of arylboronic acids

10. Experimental procedure for red-light-induced *n*Pr-DMQA+-catalyzed oxygenation

To a mixture of tertiary amine **9** (42 mg, 0.20 mmol, 1.0 equiv.) and PC **3** (2.5 mg, 0.005 mmol, 2.5

mol%) in DMF (2.0 mL, 0.1 M) was added DBU (46 mg, 0.3 mmol, 1.5 equiv.) in a Schlenk tube. The solution was stirred at room temperature under red LED ($\lambda_{\text{max}} = 640 \text{ nm}$) irradiation in open to air (without bubbling air) for 20 hours. The mixture was concentrated in vacuo to yield the crude product, which was purified by flash chromatography (FC) on silica gel (eluent: Hexanes/EtOAc = 10/1 ~ 5/1) to yield the desired amide **10** as a white solid.

2-phenyl-3,4-dihydroisoquinolin-1(2H)-one (**10**): Yield (41 mg, 92%). A white solid. $R_f = 0.3$ (Hexanes/EtOAc = 3/1). FC (Hexanes/EtOAc = 10/1 ~ 5/1). ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 7.6 \text{ Hz}$, 1H, ArH), 7.55-7.36 (m, 6H, ArH), 7.29-7.24 (m, 2H, ArH), 4.01 (t, $J = 6.4 \text{ Hz}$, 2H, CH_2), 3.16 (t, $J = 6.4 \text{ Hz}$, 2H, CH_2). ^{13}C NMR (101 MHz, CDCl_3) δ 164.29, 143.24, 138.42, 132.13, 129.85, 129.02, 128.86, 127.30, 127.05, 126.34, 125.43, 49.53, 28.75.

11. Experimental procedure for red-light-induced *n*Pr-DMQA+-catalyzed ATRA

In a N_2 glove box, **3** (1.0 mg, 0.002 mmol, 1 mol%), 4-nitrobenzyl bromide **11** (43 mg, 0.2 mmol, 1.0 equiv.) and LiBr (35 mg, 0.4 mmol, 2.0 equiv.) were added to an oven-dried (overnight) Schlenk tube containing a stirring bar, followed by adding dry MeCN (1.0 mL, 0.2 M) and styrene **12** (208 mg, 2.0 mmol, 10.0 equiv.). The Schlenk tube was then sealed, removed from the glove box and stirred at room temperature under red LED ($\lambda_{\text{max}} = 640 \text{ nm}$) irradiation for 17 hours. The mixture was concentrated in vacuo to yield the crude product, which was purified by flash chromatography (FC) on silica gel (eluent: Hexanes/EtOAc = 200/1) to yield the desired product **13** as a colorless oil.

1-(3-bromo-3-phenylpropyl)-4-nitrobenzene (**13**): Yield (38 mg, 59%). A colorless oil. R_f = 0.4 (Hexanes/EtOAc = 10/1). FC (Hexanes/EtOAc = 200/1). ^1H NMR (400 MHz, CDCl_3) δ 8.18-8.14 (m, 2H, ArH), 7.40-7.28 (m, 7H, ArH), 4.88 (dd, J = 8.4, 6.0 Hz, 1H, CH), 2.95 (ddd, J = 14.4, 9.2, 5.6 Hz, 1H, CH_2), 2.82 (ddd, J = 14.4, 8.8, 6.4 Hz, 1H, CH_2), 2.69-2.59 (m, 1H, CH_2), 2.50-2.41 (m, 1H, CH_2). ^{13}C NMR (101 MHz, CDCl_3) δ 148.37, 146.77, 141.53, 129.47, 128.99, 128.78, 127.34, 123.94, 54.09, 40.90, 34.30.

12. Optimization of red-light-induced *n*Pr-DMQA+-catalyzed intermolecular ATRA

Initial examination of ATRA reaction was tested by reacting 4-nitrobenzyl bromide **11** (1.0 equiv.) with styrene **12** (5.0 equiv.) in the presence of LiBr (2.0 equiv.) and PC **3** in MeCN under red LED (λ_{max} = 640 nm) (Table S5). Running the reaction with 1 mol% of **3** at rt for 20 hours delivered the desired adduct **13** in 40% NMR yield, along with 50% starting material **11** (**SM-11**) (Table S5, entry 1). Increasing the PC loading of **3** to 2.5 mol% gave lower yield of **13**, along with more byproducts, which could be the dimer, polymers or other side-products from the radical intermediates (Table S5, entry 2). Thus, 1 mol% the PC loading was chosen for all the follow-up screenings. When the reaction was run at 50 °C for 24 hours, only 25% of desired product **13** was observed, along with a lot of byproducts and no **SM-11** (Table S5, entry 3). Two control experiments have also been performed, and no reaction occurred at 50 °C in the absence of red light or PC **3** (Table S5, entries 4-5). Performing the reaction at 35 °C didn't improve any reaction result (Table S5, entry 6). When the reaction was conducted in a higher concentration (0.2 M), the reaction yield was improved from 40% to 54% (Table S5, entry 1 vs entry 7). Moreover, when the reaction was performed with 10.0 equiv. of styrene **12** in a higher concentration (0.2 M), **13** was achieved in 65% yield, along with 12% **SM-11** (Table S5, entry 8). Further increasing the reaction concentration (0.4 M) did not increase the reaction yield (Table S5, entry 9). Thus, the current optimal reaction condition is reacting **11** (1.0 equiv.) with styrene **12** (10.0 equiv.) in the presence of LiBr (2.0 equiv.) and PC **3** (1 mol%) in MeCN (0.2 M) at rt for 17 hours under red LED (λ_{max} = 640 nm) (Table S5, entry 8).

Entry ^a	PC	PC loading/x	Light source	Temp. [°C]	Time [h]	Yield [%] ^b	SM-11 [%] ^b
1	3	1	Red LED (640 nm)	rt	20	40	50
2	3	2.5	Red LED (640 nm)	rt	20	30	50
3	3	1	Red LED (640 nm)	50	24	25	0
4	3	1	-	50	24	0	95
5	-	1	Red LED (640 nm)	50	24	0	95
6	3	1	Red LED (640 nm)	35	18	42	20
7 ^c	3	1	Red LED (640 nm)	rt	20	54	30
8 ^d	3	1	Red LED (640 nm)	rt	17	65	12
9 ^e	3	1	Red LED (640 nm)	rt	17	47	13

^a The reaction was ran with **11** (0.2 mmol), **12** (1.0 mmol), PC (x mol%) and LiBr (0.4 mmol) in MeCN (2 mL).

^b NMR yield by using 1,3,5-trimethoxybenzene as internal standard.

^c 1 mL of MeCN was used.

^d 2.0 mmol of **12** and 1 mL of MeCN were used.

^e 2.0 mmol of **12** and 0.5 mL of MeCN were used.

Table S5. Initial examination of red-light-induced *n*Pr-DMQA⁺-catalyzed intermolecular ATRA

Based on the above preliminary results, further optimization by screening the solvents and reaction times were carried out and the results are summarized in Table S6. The examination of solvent effects revealed that the reaction in MeCN provided a higher yield than those in DMF/H₂O (1/4),^{18,19} MeOH and DMSO (Table S6, entry 1 vs 2-4). Increasing the reaction time from 17 to 24 hours in MeCN gave the product **13** in 59% yield along with trace amount of **SM-11** (Table S6, entry 5). Next, several control experiments have also been conducted. No reaction occurred in the absence of **3** or red light, which is consistent with the results at 50 °C (Table S6, entries 6-7 vs Table S5, entries 4-5). In addition, in the absence of LiBr, **13** was obtained in 14% yield along with 75% of **SM-11** (Table S6, entry 8). On the basis of these experiments, we chose reacting **11** (1.0 equiv.) with styrene **12** (10.0 equiv.) in the presence of LiBr (2.0 equiv.) and PC **3** (1 mol%) in MeCN (0.2 M) at rt for 17 hours under red LED ($\lambda_{\text{max}} = 640 \text{ nm}$) as the optimal reaction condition (Table S6, entry 1).

	11	12			13	
Entry ^a	PC	Light source	Solvent	Time [h]	Yield [%] ^b	SM-11 [%] ^b
1	3	Red LED (640 nm)	MeCN	17	65 (59) ^c	12
2	3	Red LED (640 nm)	DMF/H ₂ O (1/4)	17	messy	0
3	3	Red LED (640 nm)	MeOH	17	0	95
4	3	Red LED (640 nm)	DMSO	17	30	trace
5	3	Red LED (640 nm)	MeCN	24	59	trace
6	-	Red LED (640 nm)	MeCN	17	0	95
7	3	-	MeCN	17	0	95
8 ^d	3	Red LED (640 nm)	MeCN	17	14	75

^a The reaction was ran with **11** (0.2 mmol), **12** (2.0 mmol), PC (1 mol%) and LiBr (0.4 mmol) in MeCN (1 mL). ^b NMR yield by using 1,3,5-trimethoxybenzene as internal standard. ^c isolated yield.

^d Without LiBr.

Table S6. Further optimization of red-light-induced *n*Pr-DMQA+-catalyzed intermolecular ATRA

13. Proposed mechanism for red-light-induced *n*Pr-DMQA+-catalyzed intermolecular ATRA

Based on previous work,^{18–22} plausible reaction mechanism was proposed for red-light-induced *n*Pr-DMQA+-catalyzed intermolecular ATRA (Scheme S1). Firstly, oxidative quenching of the red light-induced excited state of *n*Pr-DMQA+* by 4-nitrobenzyl bromide **11** generates a 4-nitrobenzyl radical (4-NO₂-PhCH₂Br/4-NO₂-PhCH₂• = -0.65 V vs. SCE),^{23,24} along with bromide anion. Then, addition of the 4-nitrobenzyl radical to styrene **12** forms another benzyl radical intermediate **S3**, which undergoes a single electron transfer (SET) process with *n*Pr-DMQA++ to regenerate the PC *n*Pr-DMQA+ and form the carbocation species **S4** (PhCH⁺CH₃/PhCH•CH₃ = +0.37 V vs. SCE).^{22,25} Final product **13** is formed by the nucleophilic attack of bromide anion to the carbocation species **S4**. Alternatively, **13** could be also obtained through a radical chain transfer mechanism.

Scheme S1. Proposed mechanism for red-light-induced *n*Pr-DMQA⁺-catalyzed ATRA

14. Experimental procedure for red-light-mediated dual Au/*n*Pr-DMQA⁺-catalyzed C(sp)-H arylation

In a N₂ glove box, Au(PPh₃)Cl (9.9 mg, 0.02 mmol, 10 mol%), **3** (2.5 mg, 0.005 mmol, 2.5 mol%), 1-ethynyl-4-methylbenzene **14** (23 mg, 0.2 mmol, 1.0 equiv.) and benzenediazonium tetrafluoroborate **5a** (154 mg, 0.8 mmol, 4.0 equiv.) were added to an oven-dried (overnight) Schlenk tube containing a stirring bar, followed by adding dry DMF (2.0 mL, 0.1 M). The Schlenk tube was then sealed, removed from the glove box and stirred at room temperature under red LED (λ_{max} = 640 nm) irradiation. After 1 hour, the mixture was quenched with a saturated solution of NaHCO₃ (2 mL), followed by adding deionized water (2 mL). The crude reaction mixture was then extracted with ethyl acetate (3 × 10 mL), and the combined organic layers were washed with brine (20 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under reduced pressure on RotaVap. The crude product was purified by flash chromatography (FC) on silica gel

(eluent: Hexanes/EtOAc = Hexanes ~ 200/1) to yield the desired product **15** as a white solid.

1-methyl-4-(phenylethynyl)benzene (**15**): Yield (24 mg, 62%). A white solid. R_f = 0.45 (Hexanes). FC (Hexanes/EtOAc = Hexanes ~ 200/1). ^1H NMR (400 MHz, CDCl_3) δ 7.56-7.53 (m, 2H, ArH), 7.45 (d, J = 7.6 Hz, 2H, ArH), 7.38-7.31 (m, 3H, ArH), 7.17 (d, J = 7.6 Hz, 2H, ArH), 2.39 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.51, 131.68, 131.63, 129.25, 128.45, 128.20, 123.63, 120.33, 89.70, 88.86, 21.65.

15. Optimization of red-light-mediated dual Au/*n*Pr-DMQA+-catalyzed C(sp)-H arylation

Optimization of C(sp)-H arylation by screening the solvents were performed and the results are presented in Table S7. The examination of solvent effects showed that the reaction in DMF gave a higher yield than those in DMSO and MeOH (Table S7, entry 1 vs 2-3). Control experiments have also been conducted. In the absence of **3** or red light, the desired product **15** was obtained in 24% and 5% yield, respectively, while the reaction was messy in the absence of $\text{Au}(\text{PPh}_3)\text{Cl}$ (Table S7, entries 4-6). Thus, we chose reacting **14** (1.0 equiv.) with benzenediazonium tetrafluoroborate **5a** (4.0 equiv.) in the presence of $\text{Au}(\text{PPh}_3)\text{Cl}$ (10 mol%) and PC **3** (2.5 mol%) in DMF at rt for 1 hour under red LED (λ_{max} = 640 nm) as the optimal reaction condition (Table S7, entry 1).

Entry ^a	PC	Light source	Solvent	Yield [%] ^b
1	3	Red LED (640 nm)	DMF	64
2	3	Red LED (640 nm)	DMSO	47
3	3	Red LED (640 nm)	MeOH	19
4	-	Red LED (640 nm)	DMF	24
5	3	-	DMF	5
6 ^c	3	Red LED (640 nm)	DMF	messy

^a The reaction was conducted with **14** (0.1 mmol), **5a** (0.4 mmol), $\text{Au}(\text{PPh}_3)\text{Cl}$ (10 mol%) and PC (2.5 mol%) in solvent (1.0 mL) under N_2 .

^b NMR yield by using 1,3,5-trimethoxybenzene as internal standard.

^c Without $\text{Au}(\text{PPh}_3)\text{Cl}$.

Table S7. Optimization and control experiments of red-light-mediated dual Au/*n*Pr-DMQA+-catalyzed C(sp)-H arylation

16. NMR results for control reactions for Scheme 2

Several control experiments have also been performed for the red-light-induced aerobic benzylic C(sp³)-H oxygenation, intermolecular ATRA and dual Au/ⁿPr-DMQA⁺-catalyzed C(sp)-H arylation (Scheme S2). For aerobic benzylic C(sp³)-H oxygenation, no conversion was observed in the absence of PC **3** or red light, while the reaction was messy in the absence of DBU (Scheme S2a). For intermolecular ATRA, no reaction occurred in the absence of PC **3** or red light, while the desired adduct **13** was obtained in 14% yield along with 75% of **SM-11** in the absence of LiBr (Scheme S2b). For dual Au/ⁿPr-DMQA⁺-catalyzed C(sp)-H arylation, in the absence of PC **3** or red light, the desired product **15** was formed in 24% and 5% yield, respectively, while the reaction was messy in the absence of Au(PPh₃)Cl (Scheme S2c).

^a Reactions were conducted on 0.1 mmol scale. NMR yields by using 1,3,5-trimethoxybenzene as internal standard were shown.

Scheme S2. NMR results for control reactions for Scheme 2

17. NMR spectra charts for compounds **3**, **6**, **8**, **10**, **13**, and **15**

18. References

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