Advanced Synthesis & Catalysis

Accepted Article

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Authors: Tianju Shao, Yanli Yin, Richmond Lee, Xiaowei Zhao, Guobi Chai, and Zhiyong Jiang

To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201800135

Link to VoR: http://dx.doi.org/10.1002/adsc.201800135

10.1002/adsc.201800135

COMMUNICATION

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Sequential Photoredox Catalysis for Cascade Aerobic Decarboxylative Povarov and Oxidative Dehydrogenation Reactions of *N*-Aryl α-Amino Acids

Tianju Shao,[a] Yanli Yin,[a,b] Richmond Lee,[c] Xiaowei Zhao,[a] Guobi Chai,[d] and Zhiyong Jiang[a]*

[a] Key Laboratory of Natural Medicine and Immuno-Engineering, Henan University, Kaifeng, Henan, P. R. China 475004
E-mail: chmjzy@henu.edu.cn
[b] College of Bioengineering, Henan University of Technology, Zhengzhou 450001, China
[c] Singapore University of Technology and Design, 8 Somapah Road, Singapore 487372
[d] Key Laboratory of Tobacco Flavor Basic Research of CNTC, Zhengzhou Tobacco Research Institute of CNTC, Zhengzhou 450001, China

Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract. A visible-light-driven sequential photoredox catalysis to allow *N*-aryl α-amino acids to experience efficient cascade aerobic decarboxylative Povarov and oxidative dehydrogenation (ODH) reactions is described. With a dicyanopyrazine-derived chromophore (DPZ) as a photoredox catalyst in both transformations, two series of valuable azaarenes, i.e., 4-amino tetrahydroquinolines (THQs) and quinolines, were obtained in satisfactory yields featuring diverse 2- and 2,3-substituent patterns. To enable the ODH reaction of 4-amino THQs, a cooperative catalysis with *N*-hydroxyphthalimide was developed. Additionally, an unprecedented synthesis of chiral *N*-amino-2-methyl THQs with high enantioselectivities was realized.

Keywords: Photoredox catalysis; Sequential photoredox catalysis; Amino acids; Quinolines; Tetrahydroquinolines

Both 4-amino tetrahydroquinolines (THQs)[1] and quinolines[2] are extensively present in natural and synthetic compounds with interesting physical and pharmacological properties. The Povarov reaction is the commonly accepted strategy to furnish 4-amino THQs.[1,3-5] The direct use of enamines and imines as the feedstocks represents the most popular method, but the substrate scope using this method is limited, as enamines are usually restricted to those with terminal olefins, while imines, especially those bearing alkyl substituents, are typically difficult to isolate owing to their instability.[3,4] Although a few complementary methods have been developed, a general method to render 4-amino THQs with 2- and 2,3-substituents is still deficient.[1,5] On the other hand, the catalytic oxidative dehydrogenation (ODH) of THQs is an expedient approach to access quinolines, avoiding tedious multistep preparations of the starting materials and additional functionalization to introduce substituents at target locations.[6-7] Of note, sequential catalysis (or relay catalysis) as a biomimetic strategy offers a unique platform for organic synthesis.[8] The tandem use of catalytic reactions with minimum workup presents remarkable advantages, such as the use of simple and readily available materials to build complex molecules, reduced consumption of energy and time and lowered waste production and yield losses associated with the isolation and purification of intermediates through a multistep process. Accordingly, the development of a novel Povarov reaction with readily accessible, abundant and stable starting substrates and a relay catalysis platform to experience an efficient Povarov reaction and the sequential ODH transformation remains highly desirable, which would provide a robust approach to furnish these two series of important azaarenes concurrently with a wide variety of substituent patterns. Besides exploring competent feedstocks for the Povarov reaction, the underdeveloped catalytic ODH reaction of 4-amino THQs[7] and the potential incompatibility of the second catalytic system with residual materials from the preceding step in sequential catalysis constitute another two key challenges in this task.

α-Amino acids are a large category of environmentally benign and nonfossil carbon sources and have therefore been pursued by chemists as starting substrates.[9] In 2013, Tan and co-workers reported fluorescein-catalyzed aminoalkylation reactions of *N*-aryl glycine with nucleophiles under visible-light irradiation.[10] This elegant work demonstrates the feasibility of *N*-aryl glycines to generate imines via tandem SET oxidative decarboxylation and SET oxidation. We were

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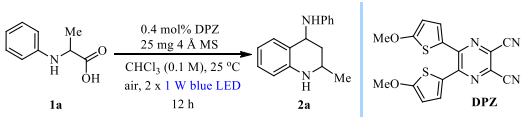
particularly intrigued by the lower yield in the Mannich-type chemistry using *N*-phenyl alanine as opposed to glycine. This anomalous result suggests that a possible side-reaction might be responsible for the decreased yield. As methyl substituted imines are prone to tautomerization, we surmised that [4+2] cycloaddition between an enamine and imine (i.e. the Povarov reaction) could be occurring. If a general phenomenon, this reaction would be an ideal method to approach 4-amino THQs with a broad substrate scope, as no purification of the unstable alkyl imines would be necessary, and a broad diversity of α-amino acids and *N*-aryls are available. As an extension of our research interest[11] in photoredox catalysis,[12] we were thus intrigued to verify this hypothesis, that is decarboxylative Povarov reaction, and develop an unprecedented photoredox ODH reaction of 4-amino THQs to quinolines. To provide a highly efficient and sustainable synthetic approach, we also anticipated to develop a visible-light-driven photocatalytic sequence[13] involving a cascade mechanism of these two transformations in a one-pot. Our preliminary results are described in this communication.

Table 1. Variation of the reaction parameters.[a]

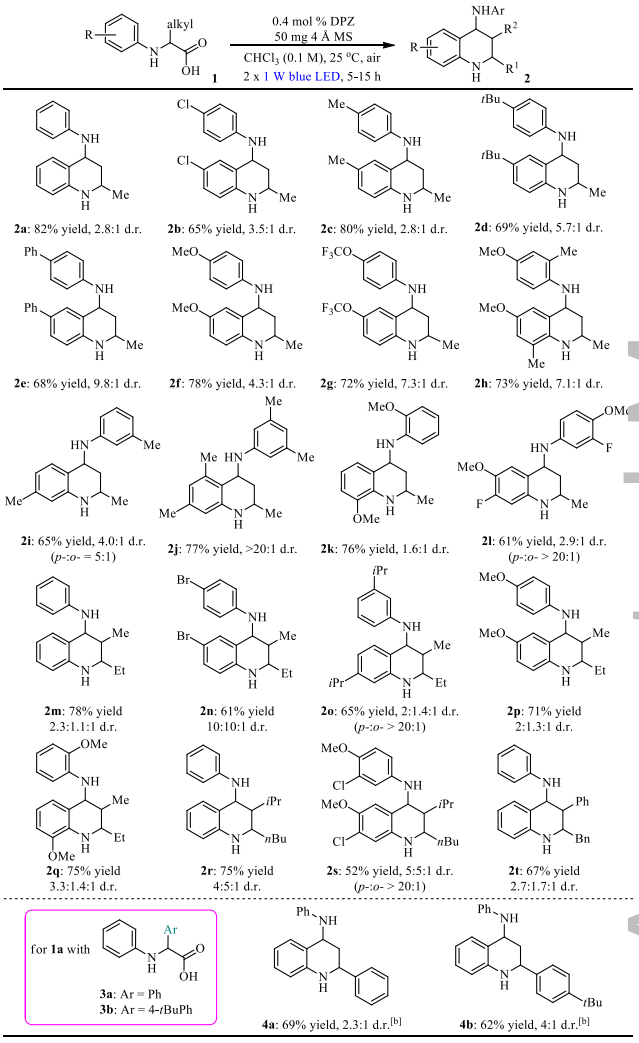


Entry	Deviation from standard conditions	Yield of **2a** [%][b]	*Trans*:*cis*[c]
1	None	84	3:1
2	$[Ru(bpy)_3]Cl_2$ instead of DPZ	52	1:1
3	Fluorescein instead of DPZ	34	1:2
4	23 W CFL instead of 2 x 1W blue LED	51	2.7:1
5	Sunlight instead of 2 x 1W blue LED	32	3:1
6	No DPZ	23	1:2.6
7	Argon instead of air	0	N.A.
8	No light	0	N.A.

[a] Reaction conditions: **1a** (0.1 mmol), DPZ (0.4 mol%), 5 Å MS (25 mg), $CHCl_3$ (1.0 mL), 25 °C. [b] Yield of isolated product. [c] The ratio was determined by ^1H NMR spectroscopy of the crude product. N.A. = not available.

We initiated our study by selecting *N*-phenyl alanine **1a** as the model substrate, and our developed dicyanopyrazine-derived chromophore (DPZ), instead of fluorescein, due to their comparable redox potentials[14] as a photoredox catalyst. The preliminary study furnished the desired product **2a** in 23% yield (see Table S1 in the Supporting Information [SI]), which prompted us to evaluate the reaction parameters further. The conditions involving 0.4 mol% of DPZ as a catalyst, 25 mg of 4 Å molecular sieves (MS) as an additive, $CHCl_3$ as a solvent (0.1 M), two 1 W blue light-emitting diodes (LEDs) as the energy source, at ambient temperature and under air were determined as optimal, affording **2a** in 84% yield with 3:1 d.r. (*trans*:*cis*) within 12 hours (entry 1, Table 1). Other photoredox catalysts, such as $[Ru(bpy)_3]Cl_2$ and fluorescein, were also examined (entries 2−3), but the yields were not improved. The use of a 23 W compact fluorescent light (CFL) or sunlight instead of the blue LED as the energy source gave decreased yield (entries 4−5). Without DPZ, **2a** was obtained in a much lower yield, affirming the indispensability of the photoredox catalyst to the reactivity (23% yield, entry 6). No reaction was observed in control experiments performed in the absence of air or visible light (entries 7−8, respectively), revealing the need for both air and visible light in the reaction.

Table 2. Synthesis of 4-amino THQs.[a]



[a] Reaction conditions: **1** (0.2 mmol), DPZ (0.4 mol%), 4 Å MS (50 mg), $CHCl_3$ (2.0 mL), 25 °C. Yield of isolated product. The ratio of *trans*:*cis* (d.r.) was determined by ^1H NMR spectroscopy of the crude products. The ratio of *p*-:*o*- (r.r.) was determined by the analysis of corresponding ODH products **5** as shown in Table 3. [b] **1a**:**3** = 1.5:1, LiH_2PO_4 (1.0 equiv), $CHCl_3$ (2.0 mL), 25 °C, 10 h.

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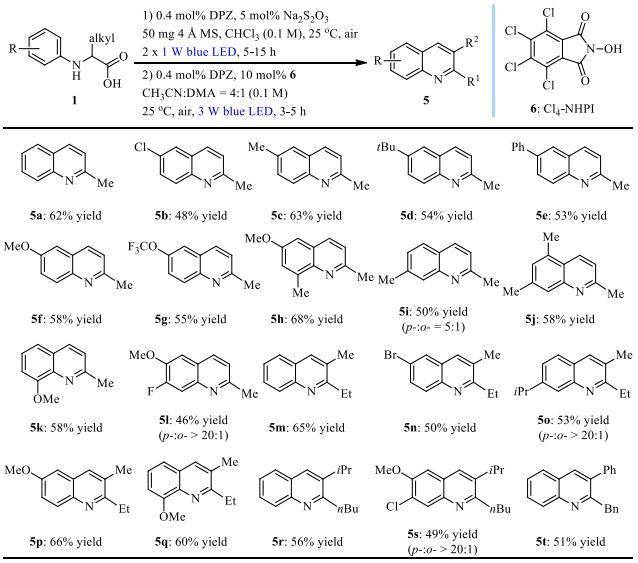
To identify the substrate scope, various *N*-aryl-α-alkyl α-amino acids **1** were subjected to the aerobic decarboxylative Povarov reaction under the established reaction conditions (Table 2). All the reactions were found complete within 5 to 15 hours, providing [4+2] annulation adducts **2a-t** in 52−82% yields. Both electron-deficient and electron-donating substituents located at different positions of the aromatic unit were well tolerated. Moreover, 2,3-disubstituted 4-amino THQs **2m-t** were successfully obtained by modulating the α-alkyl groups of the α-amino acids. Since the generated imines from *N*-aryl-α-aryl α-amino acids cannot tautomerize to form enamines, we anticipated that these species would react with enamines derived from α-alkyl α-amino acids. This reaction might feature competitive chemoselectivity for higher-reactivity alkyl imines, leading to the easier generation of adducts **2**. The desired products **4a** and **4b** were obtained in 69% and 62% yields, respectively, by evaluating two representative transformations of **1a** with *N*-aryl-α-aryl α-amino acids **3a-b** under slightly modified reaction conditions.

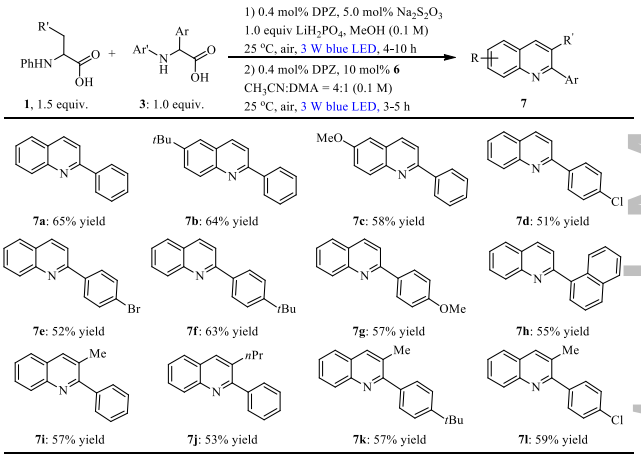
Table 3. Synthesis of 2-alkyl-substituted quinolines.[a]



[a] 0.2 mmol scale. Yield of isolated product. The ratio of *p*-:*o*- was determined by ^{1}H NMR spectroscopy of the crude product.

We next sought to develop an aerobic ODH of 4-amino THQs to quinolines via visible-light photoredox catalysis. The method reported by Balaraman for the transformation of THQs, but not the 4-amino variants, to quinolones[6i] was first attempted; the reaction of **2a** was performed with Rose Bengal as catalyst in *N*,*N*-dimethylacetamide (DMA) at 25 °C and under irradiation by a 1 or 3 W blue LED, but only trace product **5a** was obtained.[15] This performance suggests that the hydrogen-atom transfer (HAT) of *N*-α-C−H enabled by $O_2^{\bullet-}$ to form an iminium intermediate is likely not effective for 4-amino THQs under these conditions. Inspired by the report that a phthalimide-*N*-oxyl (PINO) radical is more active than a peroxyl radical in hydrogen abstraction,[16] we performed the cooperative photoredox catalysis with DPZ and *N*-hydroxyphthalimide (NHPI, $E_{1/2}^{red}$ = 0.78 vs saturated calomel electrode [SCE] in CH_3CN) as a catalyst.[16b] We were pleased to find that **5a** was obtained in 81% isolated yield after 3 hours using 0.4 mol% DPZ and 10 mol% Cl_4-NHPI **6** in CH_3CN and DMA mixed solvent (v/v = 4:1) under irradiation by a 3 W blue LED (see Table S2 in SI). The direct transformation of α-amino acids **1** to quinolines **5** through the sequential catalytic strategy was subsequently examined (see Table S3 in SI). A series of 2-alkyl and 2-alkyl-3-alkyl/aryl-substituted quinolines **5a-t** were furnished in 46−68% yields (Table 3). Notably, 0.4 mol% DPZ was still necessary in the second process likely due to the oxidation of DPZ by the generated H_2O_2 in the reaction system, leading to a loss of efficacy after the first step.

Table 4. Synthesis of 2-aryl-substituted quinolines.[a]



[a] 0.2 mmol scale. Yield of isolated product.

The synthesis of quinolines **7** featuring an aryl group at the 2-position was then carried out. Given the yield of THQs **4** was moderate (e.g., **4a-b**, Table 2), which should inevitably result in a poor yield of **7**, the reaction conditions for the first decarboxylative Povarov transformation had to be further improved. We found that the reactions between α-alkyl amino acids **1** and α-aryl amino acids **3** were complete within 4 to 10 hours using 0.4 mol% DPZ with 5.0 mol% $Na_2S_2O_3$ and 1.0 equiv. of LiH_2PO_4 as additives in methanol as a solvent; both 4-amino THQs and 4-methoxy THQs were observed as the mixed products (see Table S4 in SI). While the chemoselectivity was not satisfactory, both THQs could be smoothly transferred to the desired quinolines **7** in 52−65% yields over two steps when performing the subsequent cooperative catalysis

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without purification (Table 4). Notably, the substituent patterns of both **5** and **7** are extremely broad, as *N*-aryls and α-substituents of α-amino acids can be flexibly changed (Tables 3 and 4). The satisfactory yields of quinolines **5** and **7** also provide robust evidence that the second catalysis is compatible with the first catalytic system.

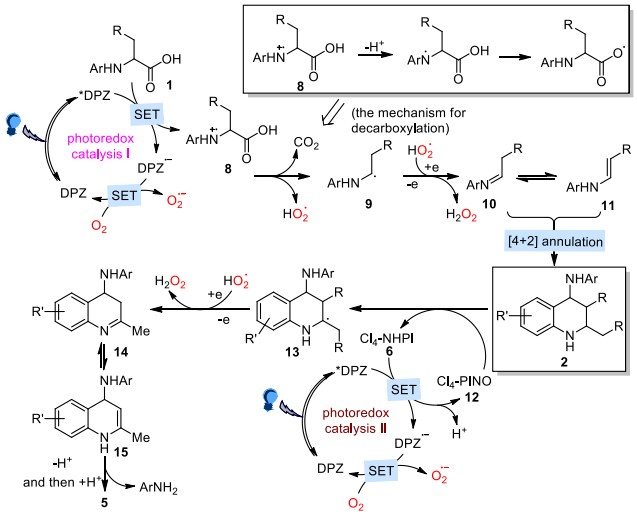
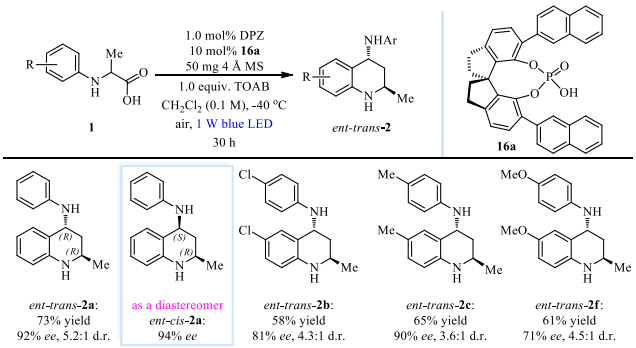


Figure 1. Plausible mechanism.

Figure 1 shows the proposed mechanism for the sequential catalysis platform involving aerobic decarboxylative Povarov and ODH reactions. A Stern-Volmer experiment showed that *N*-aryl-α-alkyl α-amino acid **1** as a reductive quencher can be oxidized by DPZ* (see Figure S1 in SI). The generated radical cation **8** will undergo decarboxylation to form radical species **9**, which is subsequently oxidized by $HO_2^{\bullet}$ to afford imine **10**.[10] The [4+2] annulation between imine **10** and its tautomer, i.e., enamine **11**, will furnish 4-amino THQ **2** as one of the desired products and the key intermediate for the next catalytic system. Since NHPI **6** is crucial to the ODH reaction and can be conveniently oxidized by DPZ* due to their matched redox potentials,[14,16] PINO **12** would be first generated from **6** in the second photoredox catalytic cycle. Hydrogen abstraction of **2** by PINO **12** can produce radical species **13**. After further oxidation by $HO_2^{\bullet}$,[6i] imine **14** is produced from **13** and tautomerizes to enamine **15**. The dissociation of arylamine, which can be detected by thin layer chromatography (TLC) and gas chromatography-mass spectrometry (GC-MS) analyses, furnishes quinoline **5**.



Scheme 1. Enantioselective synthesis of chiral 4-amino-2-methyl THQs.

The synthesis of *N*-amino THQs and quinolines with our catalysis system allowed abundant substituent diversity attributed to the use of α-amino acids as feedstocks. This feedstock greatly enriches the diversity of enamines and enables the generated imines, especially unstable alkyl imines, to participate directly in the transformations. Therefore, we anticipated the development of a dual-catalysis[17] enantioselective manifold for the aerobic decarboxylative Povarov reaction of *N*-aryl alanines, thus leading to valuable chiral *N*-amino-2-methyl substituted THQs.[1a-d] In recent years, many catalytic asymmetric Povarov reactions have been established to access chiral *N*-amino THQs featuring diverse 2-substituents,[18,19] but no examples of the synthesis of 2-methyl-substituted entities have been reported, likely due to the inconvenient manipulation of acetaldehyde[18] and the instability of acetaldehyde derived imines.[19] After examining the reaction conditions (see Table S5 in SI), the desired chiral *N*-amino-2-methyl-substituted THQs *ent-trans*-**2a–c** and *ent-trans*-**2f** were obtained after 30 hours in 58−73% yields with 71−92% *ee* and 3.6:1 to 5.2:1 d.r. by reacting *N*-aryl alanines **1** using 1.0 mol% DPZ and 10 mol% chiral SPINOL-phosphoric acid[20] **8a** as cooperative catalysts, 1.0 equiv. of *tetra-n*-octylammonium bromide (TOAB) as an additive in CH_2Cl_2 at −40 °C and irradiation with a 1 W blue LED (Scheme 1). Of note, the absolute configurations of both *ent-trans*-**2a** and *ent-cis*-**2a** were assigned based on the structures of the corresponding derivatives **17** and **18** determined as solved by single crystal X-ray diffraction.[21] It was found that the diastereoselectivity was formed at the 4-position. As shown in Table 1 (entries 3 and 5), the *cis*-isomer was the major product when the reaction was performed with fluorescein or without a catalyst. The results indicate that a distinct imine isomer is generated after the first Mannich reaction when with the DPZ catalyst.

In conclusion, we developed a sequential catalysis platform to achieve a one-pot cascade aerobic

reaction sequence including decarboxylative Povarov and ODH reactions. With DPZ as a photoredox organocatalyst and using *N*-aryl α-amino acids as the naturally abundant and inexpensive feedstocks, two series of valuable azaarenes, *N*-amino THQs and quinolines, were obtained in satisfactory yields featuring diverse 2- and 2,3-substituents, which indicates the good compatibility of the second catalysis with residual materials from the first catalysis and the versatility of this catalytic system. In addition to the advisable choice of α-amino acids as competent starting substrates, another crucial point in this method is the development of a cooperative DPZ and NHPI catalysis with the ODH transformation of 4-amino THQs to quinolines. The capability of *in situ* generating labile alkyl imines to experience the Povarov reaction also inspired an enantioselective manifold, facilitating the first asymmetric synthesis of important chiral *N*-amino-2-methyl THQs from *N*-aryl alanines.

Experimental Section

General experimental procedure for the synthesis of 4-amino THQs

General Procedure for preparing 2: 56 μL (0.0008 mmol, 0.4 mol%) of DPZ (1.0 mg of DPZ in 200 μL of toluene) was syringed into a 10 mL reaction bottle which equipped with a stir bar, and then solvent was removed in *vacuo*. Subsequently, **1** (0.2 mmol), 4 Å MS (50 mg), $CHCl_3$ (2 mL) were added successively, and then equipped with a rubber septum and an air balloon. The reaction mixture was stirred under irradiation by two 1 W blue LEDs (λ = 450−455 nm) at 25 °C (the temperature was maintained in an incubator) from a 1.5 cm distance. The reaction was monitored by TLC. Upon complete consumption of **1**, the solvent was removed in *vacuo* and the residue was purified by column chromatography on *silica gel* with hexane/ethyl acetate (80/1-40/1 ratio) to give the desired products **2**.

General Procedure for preparing 4a-4b: 56 μL (0.0008 mmol, 0.4 mol%) of DPZ (1.0 mg of DPZ in 200 μL of toluene) was syringed into a 10 mL reaction bottle which equipped with a stir bar, and then solvent was removed in *vacuo*. Subsequently, **3** (0.2 mmol), LiH_2PO_4 (0.2 mmol, 1.0 equiv.), $CHCl_3$ (2 mL) were added successively, and then equipped with a rubber septum and an air balloon. The reaction mixture was stirred and irradiated by two 1 W blue LEDs (λ = 450−455 nm) at 25 °C (the temperature was maintained in an incubator) from a 2.0 cm distance. TLC monitored until full consumption of **3**, **1a** (0.3 mmol) were added within 2 hours. After 10 hours, solvent was evaporated in *vacuo*, and the residue was purified by column chromatography on silica gel with hexane/ethyl acetate (80/1 to 40/1 ratio) to give **4**.

General experimental procedure for the synthesis of substituted quinolines.

Procedure for preparing 5: The step 1 was same as the above mentioned on the synthesis of **2**. After complete of the step 1, $CHCl_3$ was removed in *vacuo*, followed by the addition of DPZ (56 μL, 1.0 mg of DPZ in 200 μL of MeCN), Cl_4-NHPI (0.02 mmol, 0.1 equiv.), MeCN : DMA = 4:1 (2 mL), the reaction mixture was stirred and irradiated by a 3 W blue LED with a distance of 1.5 cm at 25 °C. With a full conversion of **2** under TLC analysis, the solvent was evaporated in *vacuo* and the product was purified from a short of *silica gel* (basified with Et_3N) with hexane/ethyl acetate (80/1-20/1) or hexane/DCM (5/1-2/1) to present the desired products **5**.

Procedure for preparing 7: 56 μL of DPZ (0.4 mol%, 1.0 mg of DPZ in 200 μL of toluene) were syringed into a 10 mL reaction bottle which was equipped with a stir bar, and then solvent was removed in *vacuo*. Subsequently, **3** (0.2 mmol), LiH_2PO_4 (0.2 mmol, 1.0 equiv.), $Na_2S_2O_3$ (0.01 mmol, 0.05 equiv.), MeOH (2 mL) were added successively, and then equipped with a rubber septum and an air balloon. The reaction mixture was stirred and irradiated by a 3 W blue LED (λ = 450−455 nm) at 25 °C (the temperature was maintained in an incubator) from a 2.0 cm distance. TLC monitored until full consumption of **3**, then **1a** (0.3 mmol) were added within 2 hours. After 5-10 h, solvent was evaporated in *vacuo*, followed by the addition of DPZ (56 μL, 1.0 mg of DPZ in 200 μL of MeCN), Cl_4-NHPI (0.02 mmol, 0.1 equiv.), MeCN : DMA = 4:1 (2 mL), the reaction mixture was stirred and irradiated by a 3W blue LED (λ = 450−455 nm) at 25 °C (the temperature was maintained in an incubator) from 2.0 cm distance. After 3-5 h, evaporated the solvent in *vacuo*, dissolved with DCM (0.5 mL) and purified from a short of *silica gel* (basified with Et_3N) with hexane/ethyl acetate (80/1-20/1) or hexane/DCM (5/1-2/1) to provide the desired product **7**.

Acknowledgements

Grants from NSFC (21402239, 21672052), Innovation Scientists and Technicians Troop Construction Projects of Henan Province and Henan Province (14IRTSTHN006, 162300410002) are gratefully acknowledged.

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[15] We also evaluated the reaction conditions for ODH with **2a** through a cooperative $Ru(bpy)_3Cl_2 \bullet 6H_2O$ and $TsOH \bullet H_2O$ catalysis, see W. Dong, Y. Yuan, B. Hu, X. Gao, H. Gao, X. Xie, Z. Zhang, *Org. Lett.* **2018**, *20*, 80. And **5a** was obtained in only 18% yield after 24 hours (30% conversion).

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10.1002/adsc.201800135

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