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# A sustainable synthesis of 2-aryl-3-carboxylate indolines from *N*-aryl enamines under visible light irradiation

Received 00th January 20xx, Accepted 00th January 20xx

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With visible light irradiation of catalytic amount of  $Ir(ppy)_3$  at room temperature, a number of *N*-aryl enamines were transformed to their corresponding indoline products in good to excellent yields without requiring any extra additives. This is the first example to synthesize indolines via intramolecular cyclization of enamines under visible light irradiation.

Indolines and their derivatives are important scaffolds that are found in numerous naturally occurring alkaloids and synthetic drugs. Their importance has stimulated considerable interest in developing strategies for their synthesis.<sup>1-7</sup> Until now, direct reduction of indoles is still one of the most important approach toward this important class of compounds (Scheme 1a).<sup>1-2</sup> However, reduction of the highly resonance-stabilized aromatic nucleus was not an easy task. Usually, superstoichiometric amounts of hydride reagents<sup>1</sup> or high hydrogen pressure and elevated reaction temperature<sup>2</sup> were required. Transition-metal mediated cyclization<sup>3</sup> was another important strategy to synthesize indolines, which included aryl amination, olefinic amination and so on to construct C-C or C-N bonds. For example, Buchwald and co-workers reported the Pd-catalyzed aryl amination and amidation reactions, which allow efficient access to a variety of indolines (Scheme 1b).<sup>3a</sup> In addition, other methods such as anionic cyclization (Scheme 1c),<sup>4</sup> and radical cyclization (Scheme 1d)<sup>5</sup> were also found to work. Despite the progress achieved in the synthesis of indolines, most of the existing methods require harsh reaction conditions, and extra additives such as ligand, acid or base. Development of mild and convenient procedures for the synthesis of indolines is highly desirable.

Owing to its mild, green and selective properties, visible light is recently being explored as the energy source in

we report below a new route to indolines under visible light irradiation. By utilizing catalytic amounts of Ir(ppy)<sub>3</sub> as the photosensitizer and visible light as the energy source, we have achieved the synthesis of indolines via intramolecular cyclization of enamines at room temperature (Scheme 1e). The system contained only photosensitizer as the catalyst and easily synthesizable enamine as the reactant making the reaction condition very much affordable. Moreover, no other additives were required to achieve the transformation. By employing the above strategy, we have transformed a large number of enamines to their corresponding indolines. To the best of our knowledge, such a methodology has not been achieved earlier.

numerous organic synthetic transformations.<sup>8</sup> In this context,



Scheme 1. Representative synthesis of indolines.

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We initially established the feasibility of the proposed methodology and optimized the conditions with N-aryl enamine 1a as the starting material, and Ir(ppy)<sub>3</sub> as the photosensitizer. A degassed solution containing 0.2 mmol of 1a and 2 mol% of  $Ir(ppy)_3$  in 3 mL DMF was irradiated with blue LEDs at room temperature. Following 12 h irradiation, 50% of indoline product 2a was obtained with a diastereoisomeric ratio of 2:1 (Table 1, entry 1). Among the solvents screened,  $\rm CH_3CN$  was found to be the best which gave indoline 2a in 76% yield and 4:1 diastereoselectivity (Table 1, entries 2-4). We also investigated the optimum volume of solvent, which suggested that 4.0 mL CH<sub>3</sub>CN was the best to yield indoline product in a yield of 86%, with the diastereoisomeric ratio of 4:1 (Table 1, entries 4-7). Variation of the photosensitizer concentration revealed that 2 mol% of  $Ir(ppy)_3$  gave the best yield (Table 1, entries 8-10). Further, of the four common photosensitizers attempted in this reaction, only Ir(ppy)<sub>3</sub> gave the best result (Table S1, entries 1-3, ESI<sup>+</sup>). Control experiments established that both visible light and  $Ir(ppy)_3$  were required for the reaction (Table 1, entries 11-12), and direct excitation of enamine **1a** with UV light ( $\lambda$  > 300 nm) did not yield **2a** in the absence of  $Ir(ppy)_3$  (Table S1, entry 4, ESI<sup>+</sup>). To summarize, the visible light catalyzed conversion of enamines to indolines proceeded well under the optimized condition which included irradiation (450 nm LED; 12 h) of 4.0 mL degassed CH<sub>3</sub>CN solution of 0.2 mmol 1a and 2 mol% Ir(ppy)<sub>3</sub>. The structure of the major product 2a was confirmed to be trans-indoline by converting 2a to 3a (Scheme S1, ESI<sup>+</sup>) and determining its crystal structure (Fig. 1).<sup>9</sup>

We have established the generality of the reaction with a number of N-aryl enamines substituted with electronwithdrawing, electron-donating and bulky alkyl groups, which

<b>Table 1.</b> Optimization of reaction conditions <sup>a</sup>				
		Iso nm LEDs r.t. 12 h	CO <sub>2</sub> Et H rans 2a	CO <sub>2</sub> Et
Entry	lr(ppy)₃	Solvent	Yield <sup>b</sup>	dr (trans/cis) <sup>c</sup>
1	2%	3 mL DMF	50%	2.0:1
2	2%	3 mL CH <sub>3</sub> OH	45%	2.9:1
3	2%	3 mL THF	68%	5.1:1
4	2%	3 mL CH <sub>3</sub> CN	76%	4.0:1
5	2%	2 mL CH <sub>3</sub> CN	70%	4.0:1
6	2%	4 mL CH <sub>3</sub> CN	86%	4.0:1
7	2%	5 mL CH <sub>3</sub> CN	85%	4.0:1
8	1%	4 mL CH <sub>3</sub> CN	65%	4.0:1
9	3%	4 mL CH <sub>3</sub> CN	84%	4.0:1
10	4%	4 mL CH <sub>3</sub> CN	80%	4.0:1
11 <sup><i>d</i></sup>	2%	4 mL CH <sub>3</sub> CN	None	
12	0%	$4 \text{ mL CH}_3\text{CN}$	None	

<sup>a</sup> Reaction conditions: 0.2 mmol **1a**, corresponding Ir(ppy)<sub>3</sub> were added in solvent, and the solution was strictly deaerated with N2 and irradiated under blue LEDs ( $\lambda$  = 450 nm) for 12 hours at room temperature. <sup>b</sup> Yield was determined by <sup>1</sup>H NMR analysis of the unpurified reaction mixture using diphenylacetonitrile as an internal standard. <sup>c</sup> Diastereomer ratios were determined by <sup>1</sup>H NMR analysis of the unpurified reaction mixture. <sup>*a*</sup> In dark.



<sup>a</sup> Reaction conditions: 0.2 mmol 1a, 2 mol% Ir(ppy)<sub>3</sub> were added in 4 mL CH<sub>3</sub>CN, and the solution was strictly deaerated and irradiated under blue LEDs ( $\lambda$  = 450 nm) for 12 hours at room temperature. <sup>b</sup> Yield was determined <sup>1</sup>H NMR analysis of the unpurified reaction mixture using bv diphenylacetonitrile as an internal standard; isolated total yields of two diastereomers are given in parentheses. <sup>c</sup> Diastereomer ratios (trans/cis) were determined by <sup>1</sup>H NMR analysis of the unpurified reaction mixture.

are presented in Table 2. Analysis of these results lead to the following conclusions: (a) N-aryl enamines substituted with electron-withdrawing and electron-donating groups gave the indoline products in modest diastereoselectivity. (b) Substitution with electron-withdrawing fluorine substituent resulted in poorer yield (2b, 2k, 2n) than the ones substituted with electron-donating groups (2c-2j, 2l-2m). (c) Of the various substituents, 3,5-dimethyl and 3,4,5-trimethoxy group substituted enamines produced indolines in highest yields of 91% (2f) and 94% (2g). The later gave the product in high diastereoselectivity (>19:1) as well. (d) The ethyl ester of the enamine could be replaced by *n*-hexyl, *i*-propyl, cyclopentyl, and cyclohexyl esters, which could also proceed smoothly to afford corresponding indolines (20-2r). The large gram-scale reaction was performed to give indolines in 68% yield (Scheme S2, ESI+).

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Fig. 1. X-ray crystal structure of compound 3a.

To probe the mechanism of the reaction, we monitored the quenching of photosensitizer  $Ir(ppy)_3$  by **1a** through steady state and time resolved emission techniques (Fig. 2a-b). Similar quenching constants obtained by monitoring the emission intensity  $(2.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})$  and the lifetime  $(1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})$ confirmed that the quenching occurs by a dynamic process and there is no static component (i.e., there is no aggregation of the photosensitizer and the enamine substrate 1a in the ground state). According to our previous study,<sup>10</sup> the oxidation potential of 1a was 0.71 V vs. SCE and the reduction potential of excited Ir(ppy)<sub>3</sub>\* was 0.26 V vs. SCE, the electron transfer from **1a** to the excited Ir(ppy)<sub>3</sub>\* was excluded to be the cause for the above emission quenching. Therefore, we speculated that the quenching of the excited photosensitizer  $Ir(ppy)_3^*$  by 1a is the result of singlet-singlet or triplet-triplet energy transfer. Because of the non-overlapping absorption spectra of enamine 1a and emission spectra of photosensitizer Ir(ppy)<sub>3</sub>\* at room temperature (Fig. 2c), we concluded that singletsinglet energy transfer is unlikely. Thus, the emission spectra of  $Ir(ppy)_3^{11}$  and **1a** at 77 K were recorded to investigate the feasibility of triplet-triplet energy transfer. The occurence of overlap between the emission of Ir(ppy)<sub>3</sub> and phosphorescence of 1a at 77 K (Fig. 2d) suggested that the



**Fig. 2.** (a) Emission spectra of  $Ir(ppy)_3^*$  (1×10<sup>-4</sup> M) as a function of concentration of **1a** in degassed CH<sub>3</sub>CN. The inset shows the plot of  $I_0/I$  versus [**1a**] for the reaction of  $Ir(ppy)_3^*$  with **1a**. (b) Lifetime of  $Ir(ppy)_3^*$  (1×10<sup>-4</sup> M) as a function of concentration of **1a** in degassed CH<sub>3</sub>CN. The inset shows the plot of  $\tau_0/\tau$  versus [**1a**] for the reaction of  $Ir(ppy)_3^*$  with **1a**. (c) UV-vis absorption of **1a** (5×10<sup>-5</sup> M) and normalized emission spectra of  $Ir(ppy)_3$  (1×10<sup>-4</sup> M) in degassed CH<sub>3</sub>CN at room temperature with excitation at 350 nm. (d) Normalized emission intensity of  $Ir(ppy)_3$  (1×10<sup>-4</sup> M) and enamine **1a** (1×10<sup>-2</sup> M) in degassed DMF at 77K with excitation at 350 nm.



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**Scheme 2.** (a) Photoinduced geometric isomerization. (b) Proposed reaction mechanism.

triplet-triplet energy transfer from  $Ir(ppy)_3^*$  to **1a** is possible. The fact that rate constant (~10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>) for energy transfer is two orders of magnitude lower than diffusion constant (~10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>) in CH<sub>3</sub>CN is in line with the slightly higher triplet energy of enamine **1a** (Fig. 2d, 58 kcal/mol) than that of  $Ir(ppy)_3^*$  (Fig. 2d, 57 kcal/mol).

Occurence of triplet-triplet energy transfer was supported by geometric isomerziation of enamines (Scheme 2a), a process well known to take place in the excited state.<sup>10,12</sup> Prior to visible light irradiation, the structure of **1a** was confirmed by <sup>1</sup>H NMR to be in the Z-form. Intramolecular hydrogen bonding, most likely, favored this isomer in CH<sub>3</sub>CN (Fig. S2a, ESI<sup>+</sup>).<sup>13</sup> However, <sup>1</sup>H NMR signal of the E-isomer of **1a** was detected when the system containing Ir(ppy)<sub>3</sub> and **1a** in degassed CD<sub>3</sub>CN was irradiated by blue LEDs for 1 minute (Fig. S2b, ESI<sup>+</sup>). Clearly, geometric isomerization competes with the cyclization in the excited state. Thus the final indolines most likely derive from both E and Z isomers of *N*-aryl enamines.

Based on the above experimental observations, we proposed a plausible mechanism outlined in Scheme 2b for the conversion of N-aryl enamine to indolines. We believe that the excited photosensitizer  $Ir(ppy)_3^*$  transfers energy to both E and Z isomers of 1a to generate the excited triplet state of 1a via triplet-triplet energy transfer process, and the latter undergoes geometric isomerziation and electrocyclization yielding the diradical intermediate **b**.<sup>14-15</sup> The diradical intermediate **b** relaxes to a zwitterionic intermediate **c**, which affords a mixture of cis and trans diastereoisomeric indoline product via multiple 1,2-hydrogen shifts. Feasibility of cyclization of enamine type of molecules from triplet state has been established earlier.<sup>16</sup> We believe that geometric isomerization of Z to E competes with the cyclization process but eventually both isomers are converted to indolines as the final isolated product.

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In summary, we developed a green methodology to synthesize indolines under visible light irradiation. By using catalytic amount of Ir(ppy)<sub>3</sub> as the photosensitizer, a number of N-aryl enamines were transformed to their corresponding indoline products in good to excellent yields without requiring any extra additives. This is, to the best of our knowledge, the first example to synthesize indolines via intramolecular cyclization of enamines by visible light catalysis. Mechanistic studies revealed that the reaction was initiated at the triplet state of the enamines produced by energy transfer from the excited  $Ir(ppy)_3$  sensitizer. The generated triplet enamines then underwent intramolecular  $6\pi$ -cyclization to afford diastereoisomeric indoline products under extremely mild condition. We believe that such a mild methdology could find wide applications in organic synthetic transformations.

Financial support for this research from the Ministry of Science and Technology of China (2013CB834804, 2014CB239402 and 2013CB834505), the National Natural Science Foundation of China (21390404 and 91027041), the Strategic Priority Research Program of the Chinese Academy of Science (XDB17030400), and the Chinese Academy of Sciences is gratefully acknowledged. V. Ramamurthy acknowledges the Chinese Academy of Sciences for a fellowship and the US National Science Foundation (CHE-1411458) for its support.

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