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Photoredox-Catalyzed Redox-Neutral Minisci C–H Formylation of *N*-Heteroarenes

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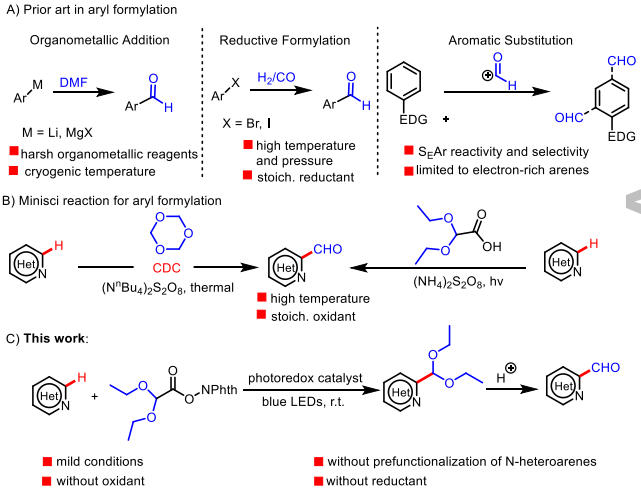
Abstract: We report a protocol for redox-neutral Minisci C–H formylation of *N*-heteroarenes using 1,3-dioxoisoindolin-2-yl 2,2-diethoxyacetate as a formyl equivalent at room temperature. This scalable benchtop protocol offers a distinct advantage over traditional reductive carbonylation and Minisci C–H formylation methods in not requiring the use of carbon monoxide, pressurized gas, a stoichiometric reductant, or a stoichiometric oxidant.

Keywords: Formylation; Minisci reaction; *N*-heteroarenes; Photoredox catalysis; Redox-neutral conditions

Aromatic aldehydes are among the most versatile intermediates for the synthesis of natural products and fine chemicals such as fragrances and pharmaceuticals,[1] in part because other functional groups can be rapidly generated from aldehydes by means of C–C ad C–X bond forming reactions. Despite the widespread use of aromatic aldehydes, the number of methods for their preparation is limited (Scheme 1A). They are traditionally synthesized through the addition of organometallic reagents to DMF under cryogenic conditions, but the functional group tolerance of this method is poor.[2] The most general method reported to date for the synthesis of aryl aldehydes is palladium-catalyzed reductive carbonylation of aryl halides under 100 atm of syngas (1:1 H_2/CO) at 150 °C,[3] a procedure that was first reported by Heck and co-workers in 1974.[4] However, reductive formylation reactions are limited to simple arenes, owing to the high reaction temperature and the use of stoichiometric reducing agents. Recently, the groups of Doyle[5a] and Wang[5b] reported visible-light-promoted formylation reactions between aryl halides and formyl radical equivalents with combined nickel and photoredox catalysis. Direct formylation of C–H bonds is perhaps the most atom-economical way of constructing aromatic aldehydes,[6] but existing approaches such as the Vilsmeier–Haack and Duff reactions suffer from relatively poor regioselectivity (due to the nature of aromatic electrophilic substitution reactions) and are limited to electron-rich arenes.[7]

Formylated heterocycles such as *N*-heteroarenes are also of interest because *N*-Heteroarenes are present in a wide variety of natural products, organic materials, small-molecule drugs, and ligands.[8] The development of methods for rapid and reliable access to formylated heterocycles via direct C–H bond conversion would therefore greatly expedite progress in the synthesis of such compounds. The well-established Minisci reaction is a useful tool for this purpose,[9] and the groups of Yeung[10a] and Xia[10b] recently reported Minisci C–H formylation of heteroarenes using trioxane and glyoxylic acid diethyl acetal, respectively, as the formyl equivalent with persulfate as an excess oxidant (Scheme 1B). The excess amount of strong oxidant is responsible for the generation of formyl radical equivalents and rearomatization to deliver the formylated *N*-heteroaromatic products. However, the need for a strong oxidant makes the reaction incompatible with functionalities that are readily oxidized, and a variety of radical-addition by-products are formed.[11] To our knowledge, a satisfactory method for direct C–H formylation of *N*-heteroarenes under mild redox-neutral conditions has not previously been reported.



Scheme 1. Methods for aryl formylation.

Our group is interested in Minisci reactions,[12] and we recently developed a protocol for copper-

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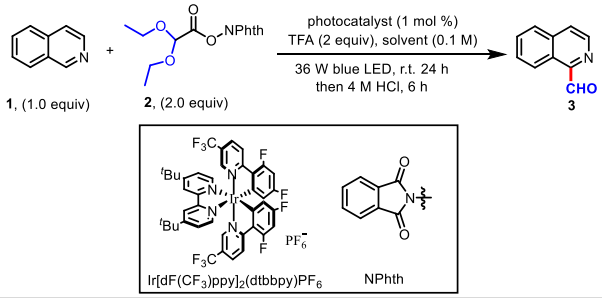
catalyzed Minisci C–H alkylation reactions of heteroarenes with *N*-(acyloxy)phthalimide under redox-neutral conditions;[12d] a similar approach involving visible-light irradiation had previously been reported by the groups of Fu,[13] Sherwood,[14] Opatz and Phipps.[15] Inspired by recent reports on photoredox-catalyzed formylation reactions using inexpensive glyoxylic acid diethyl acetal as a formyl radical equivalent,[16,5b,10b] we envisioned that 1,3-dioxoisoindolin-2-yl 2,2-diethoxyacetate, which is easily prepared from glyoxylic acid diethyl acetal and *N*-(hydroxyl) phthalimide, might serve as a formyl radical equivalent for the formylation of *N*-heteroarenes without the need for an external oxidant. Indeed, we are now able to report a protocol for photoredox-catalyzed redox-neutral Minisci C–H formylation reactions of *N*-heteroarenes (Scheme 1C). The high efficiency, broad substrate scope, excellent functional group tolerance, and mild conditions make this protocol particularly suitable for installing an aldehyde handle on medicinally relevant heterocycles.

Table 1. Optimization of reaction conditions.[a]



entry	photocatalyst	solvent	yield (%)[b]
1	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMA	88 (85[c])
2	$[Ir(dtbbpy)(ppy)_2][PF_6]$	DMA	58
3	$[Ru(bpy)_3](PF_6)_2$	DMA	<5
4	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMSO	7
5	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DCM	45
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	CH_3CN	43
7[d]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMA	70
8[e]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMA	30
9	–	DMA	NR
10[f]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMA	NR
11[g]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMA	<5

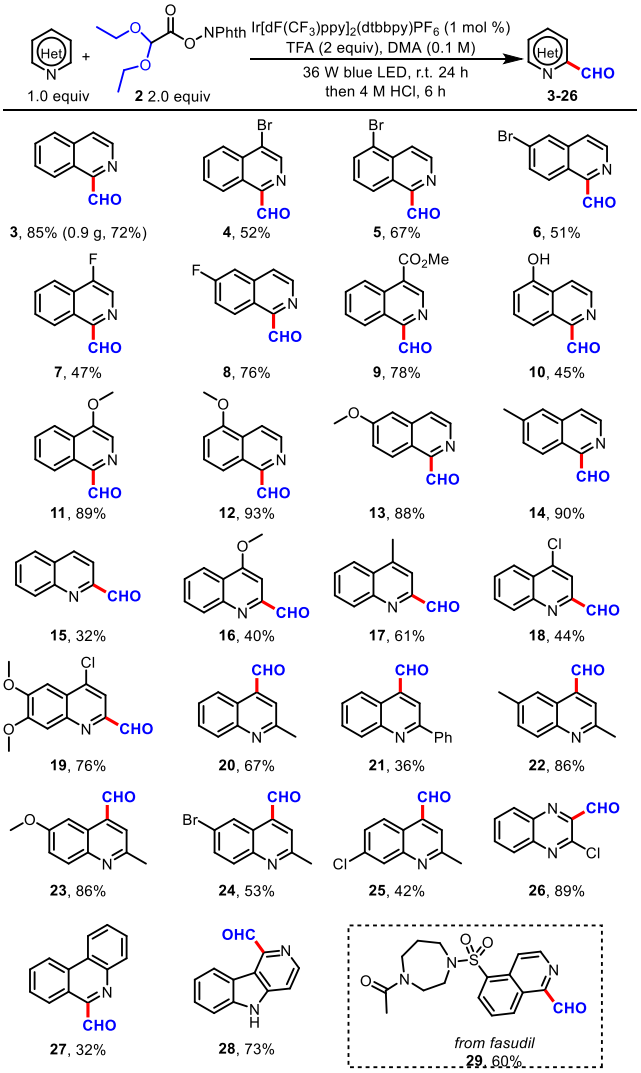
[a]General conditions, unless otherwise noted: **1** (0.3 mmol), **2** (0.6 mmol), photocatalyst (0.003 mmol), TFA (0.6 mmol), and DMA (3.0 mL) under an argon atmosphere at rt for 24 h. DCM = dichloromethane. [b]Yields were determined by ^1H NMR spectroscopy with dibromomethane as an internal standard. NR = no reaction. [c]Isolated yield. [d]$In(OTf)_3$ (20 mol %) was used instead of TFA. [e]$B(C_6F_5)_3$ (20 mol %) was used instead of TFA. [f]The reaction was performed in the absence of light. [g]The reaction was performed in the absence of TFA.

As a model reaction, we investigated the formylation of isoquinoline (**1**, 1.0 equiv) with 1,3-dioxoisoindolin-2-yl 2,2-diethoxyacetate (**2**, 2.0 equiv) under various conditions (Table 1). First, a number of photocatalysts were screened, with 2.0 equiv trifluoroacetic acid (TFA) as the proton source and *N*,*N*-dimethylacetamide (DMA) as the solvent under irradiation with a 36 W blue LED (see the Supporting Information). To our delight, desired aldehyde **3** was obtained in excellent yield when 1 mol % of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ was used as the photocatalyst (entry 1); in contrast, other photocatalysts gave lower yields (entries 2 and 3). Screening of several other solvents (entries 4–6) revealed that DMA was the most effective. We then tried replacing TFA with a Lewis acid ($In(OTf)_3$ or $B(C_6F_5)_3$) as a co-catalyst and found that the yields decreased substantially (entries 7 and 8). Control experiments showed that the reaction failed to proceed in the absence of photocatalyst, light, or TFA (entries 9–11).

With the optimized conditions in hand, we examined the scope of the formylation with respect to the *N*-heteroarene (Table 2). We found that electron-deficient heteroarenes could readily be formylated at the most electrophilic position to afford the corresponding aldehydes in fair to excellent yields. More importantly, in contrast to strategies involving organometallic catalysts, our approach left aryl bromides and chlorides intact.[2] Halogenated molecules account for approximately 50% of the market-leading drugs because they are less susceptible to oxidation by cytochrome P450.[17] Furthermore, they offer a valuable platform for generating molecular complexity through cross-coupling reactions.[18] Specifically, isoquinoline substrates with electron-withdrawing (bromide, fluorine and ester) or electron-donating substituents (hydroxyl, methoxy and methyl) underwent selective formylation at C1, regardless of the location of the substituent, giving **3**–**14** in 45–93% yields. Notably, quinoline was selectively formylated at C2 to afford **15**, albeit in only 32% yield. Quinolines bearing electron-donating substituents (methoxy and methyl), electron-withdrawing substituents (halides and bromide), or both also gave the products of formylation at C2 or C4 (**16**–**25**) in moderate to good yields (36–86%). Although radical-type S_NAr reactions have been reported,[19] we did not observe any products of substitution reactions involving the C–Cl bonds of the substrates that gave aldehydes **18**, **19** and **25**. Compounds with fluoro substituent, which are often linked to the drug-like activity of pharmaceutical leads, were compatible with our protocol (giving **7** and **8**). We were pleased to find that the reaction could be extended to 2-chloroquinazoline (to afford **26**, 89%), phenanthridine (**27**, 32%), and 5*H*-pyrido[4,3-*b*]indole (**28**, 73%). Incomplete conversion of the starting heterocycles accounted for the modest yields. Unfortunately, pyridine substrates showed no reactivity. Notably, the reaction of **1** and **2** could be

carried out on a gram scale (8 mmol) to afford **3** in an isolated yield of 72%.

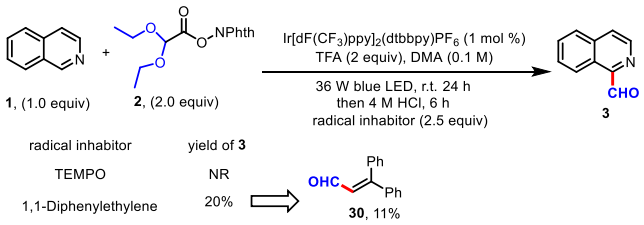
Table 2. Scope of the formylation reaction with respect to the *N*-heteroarene.[a]



[a]Reactions were performed on a 0.3 mmol scale, unless otherwise noted. Isolated yields are given.

Additionally, we evaluated the applicability of this method in a medicinal compound, fasudil, a potent vasodilator. Fortunately, N-acetylated fasudil underwent selective formylation at C1 to give a 60% yield of **29** (no reaction when NH group is not protected). The direct formylation of a drug molecule such as fasudil displays the utility of this reaction in the functionalization and diversification of sensitive late-stage intermediates.

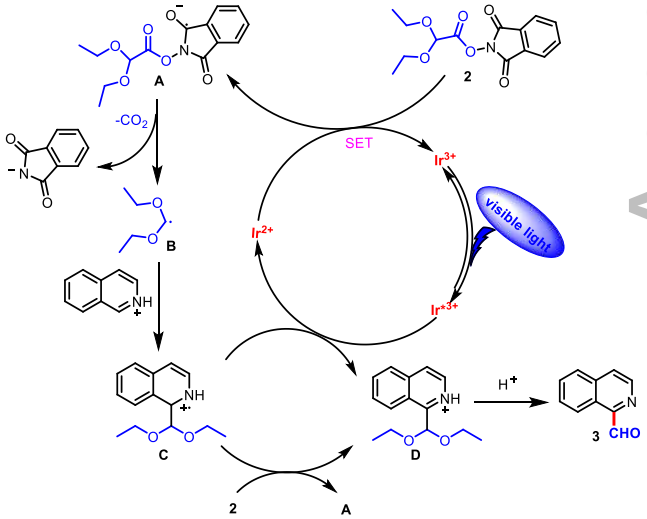
Having explored the substrate scope and some applications of the reaction, we turned our attention to the mechanism (Scheme 2). When the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was present in a reaction mixture containing **1** and **2**, the formation of **3** was completely inhibited. In addition, when 1,1-diphenylethylene was used as a radical scavenger, the yield of **3** decreased markedly (to 20%), and radical trapping product 3,3-diphenylacrylaldehyde (**30**) was isolated in 11% yield. These experiments clearly point to a radical pathway. Moreover, we conducted a



Scheme 2. Mechanistic experiments.

light/dark experiment, which showed that coupling product **3** also formed during the dark periods (see SI). And the measurement of quantum yield revealed a value of $\phi = 5.2$ (see SI). These results suggest that the reaction involved radical chain propagation, probably initiated by the photoredox catalyst.

On the basis of our experimental observations and literature reports,[12–15] we propose the mechanism depicted in Scheme 3. Analysis of the redox potentials of the photoredox catalysts and 1,3-dioxoisoindolin-2-yl 2,2-diethoxyacetate **2** revealed that oxidation of Ir^{III} to Ir^{IV} by **2** is thermodynamically unfavorable, whereas oxidation of Ir^{II} to Ir^{III} is feasible: the redox potential of **2** is −1.10 V vs. SCE, and the $E_{1/2}^{*III/II}$, $E_{1/2}^{III/II}$, $E_{1/2}^{IV/*III}$, and $E_{1/2}^{IV/III}$ values for $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ are +1.21, −1.37, −0.89, and +1.69 V (all vs. SCE), respectively. Therefore, we propose an Ir^{III}/Ir^{II} redox cycle, in which Ir^{II} is the active catalyst that initiates the photoredox catalytic cycle and Ir^{III} acts as a precatalyst. The initial transformation of $*Ir^{III}$ to Ir^{II} may involve oxidation of the solvent (DMA) or oxidation of the carboxylate anion generated via decomposition of **2**. This process was explained by Fu and co-workers in the context of their alkylation of *N*-heteroarenes.[13] Once generated, Ir^{II} reduces **2** to generate Ir^{III} and alkyl radical **B**, after extrusion of 1 equiv of CO_2. Radical **B** then adds to the protonated electron-deficient heteroarene via a Minisci-type pathway to afford radical cation **C**. $*Ir^{III}$ oxidizes **C** to cation **D**, and acid-catalyzed hydrolysis of **D** produces formylated product **3**. Alternatively, 1,3-dioxoisoindolin-2-yl 2,2-diethoxyacetate (**2**) can act as a chain carrier, oxidizing **C** to provide cation **D**.



Scheme 3. Proposed mechanism for direct C–H formylation of *N*-heteroarenes.

In conclusion, we have developed a protocol for visible-light-mediated Minisci C–H formylation of heteroarenes by using readily prepared 1,3-dioxoisoindolin-2-yl 2,2-diethoxyacetate as a formyl equivalent under mild redox-neutral conditions. This protocol avoids the need for an oxidant and for heteroarene prefunctionalization. Its high efficiency, broad substrate scope, excellent functional group tolerance, and mild conditions make it suitable for formylation of nitrogen-containing natural products and drugs.

Experimental Section

To a 15 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36 mg, 0.003 mmol, 1 mol %), 1,3-dioxoisoindolin-2-yl 2,2-diethoxyacetate **2** (176 mg, 0.6 mmol, 2.0 equiv), heteroarene (0.3 mmol, 1.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of DMA. The reaction mixture was degassed by bubbling with argon for 30 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. After completion of the reaction, the reaction was quenched by 6 mL of 4.0 M HCl in 1,4-dioxane, stirred for 6 h, then saturated $NaHCO_3$ solution was added to adjust pH to basic. Then the solution was extracted with DCM (three times). The combined organic layer was washed with brine and then dried over anhydrous Na_2SO_4 and evaporated in vacuum. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

Acknowledgements

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