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Photoredox-Mediated Direct Cross-Dehydrogenative Coupling of Heteroarenes and Amines

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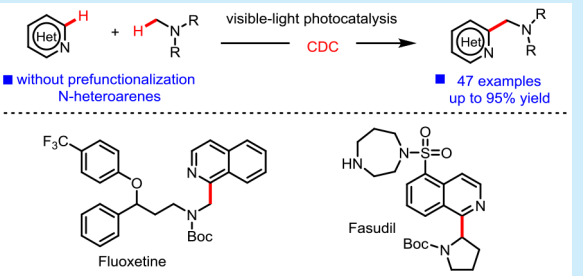
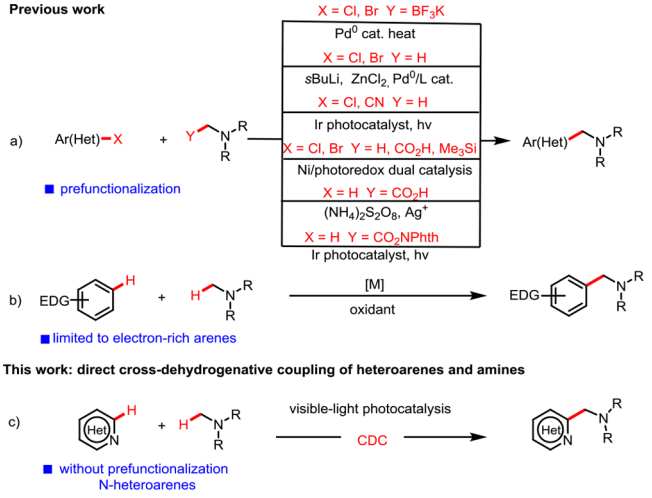
Supporting Information

ABSTRACT: A photoredox-mediated direct cross-dehydrogenative coupling reaction to accomplish α-aminoalkylation of *N*-heteroarenes is reported. This mild reaction has a broad substrate scope, offers the first general method for synthesis of aminoalkylated N-heteroarenes without the need for substrate prefunctionalization, and is scalable to the gram level. Furthermore, the reaction was found to be applicable to other hydrogen donors besides amines (i.e., ethers, an aldehyde, a formamide, *p*-xylene, and alkanes), thus enabling the preparation of *N*-heteroarenes bearing various types of substituents.



The benzylic amine group is present in a wide range of bioactive compounds, including pharmaceuticals, agrochemicals, and natural products.[1] In addition to the classical methods for benzylic amine synthesis,[2] palladium-catalyzed cross-coupling of α-metalated amines with aryl electrophiles, as developed by Molander, Dieter, Campos, Nakamura, and others, has emerged as an efficient alternative.[3−7] However, this method is limited to aryl halides and prefunctionalized amino reagents (Scheme 1a). Recently, visible-light-driven photoredox catalysis has been identified as a suitable method for generation of α-aminoalkyl radicals, and this method allows for coupling reactions between generated α-aminoalkyl radicals and aromatic compounds under mild conditions.[8] For example, MacMillan used photoredox-catalyzed C−H arylation to synthesize benzylic amines via the coupling of tertiary amines with cyanoarenes and chloroheteroarenes.[9] Subsequently, MacMillan and Molander reported a protocol for aminomethylation of aryl halides via Ni/photoredox dual catalysis. However, this approach involves the use of prefunctionalized heteroaromatic compounds or amino reagents (Scheme 1a).[10] Cowden and Fu reported a decarboxylative α-aminoalkylation of *N*-heteroarenes by means of a Minisci-type reaction, but the substrates are limited to α-amino acids (Scheme 1a).[11]

Scheme 1. α-Arylation of Amines for the Synthesis of Benzylic Amines



Considering the prevalence of amines and aromatic moieties in biological systems, the development of a method for direct cross-dehydrogenative coupling (CDC) of aromatic compounds and amines without prefunctionalization would be highly desirable.[12] Cross-dehydrogenative Friedel−Crafts-type aminomethylation of arenes in the presence of an oxidant was first reported in 2005 by Li et al. In the following years, proelectrophiles such as *N*,*N*-dialkylanilines and *N*-alkylamides were successfully coupled with a variety of electron-rich arenes, including indoles, indolizines, furans, and anisoles (Scheme 1b).[13] However, the reactions of electron-poor arenes remain unexplored due to the inherent problem of overoxidation of an α-aminoalkyl radical to the iminium cation, which cannot react with electron-deficient heteroaromatics.[14] Herein, we describe a photoredox CDC reaction for selective α-aminoalkylation of a wide variety of *N*-heteroarenes with diverse amines under mild conditions (Scheme 1c). This reaction, which is the first

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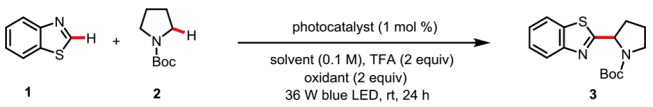
method for the synthesis of α-aminoalkylated *N*-heteroarenes without prefunctionalization, was also applicable to other hydrogen donors besides amines, such as ethers, a formamide, an aldehyde, *p*-xylene, and alkanes, and thus could be used to introduce various types of substituents onto *N*-heteroarenes.

The α-aminoalkylation of benzothiazole (**1**, 1.0 equiv) with *N*-Boc-pyrrolidine (**2**, 2.0 equiv) was used as a model reaction, and several solvents, photocatalysts, and oxidants were evaluated. We were delighted to find that in the presence of 1 mol % of $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ as a photocatalyst, trifluoroacetic acid (TFA) as a proton source, and *tert*-butyl peracetate (*t*-BPA) as an oxidant, reaction of **1** and **2** in acetone under irradiation with a 36 W blue LED afforded an excellent yield of desired product **3** (Table 1, entry 1; see the Supporting Information). Subsequent variation of the photocatalyst revealed that $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ was the most effective catalyst (entries 2 and 3). Other *tert*-alkyl peroxides (i.e., *tert*-butylhydroperoxide and *tert*-butyl peroxybenzoate) gave lower yields (entries 4 and 5). Persulfate is an inexpensive, environmentally benign oxidant that is often used in CDC reactions between ethers and heteroaromatics,[15] but we found that sodium persulfate and potassium persulfate had a deleterious effect on the reaction (entries 6 and 7). Control experiments showed that the reaction failed to proceed in the absence of light, photocatalyst, oxidant, or TFA (entries 8–11).

Table 1. Optimization of Conditions for α-Aminoalkylation of Benzothiazole with *N*-Boc-pyrrolidine[a]

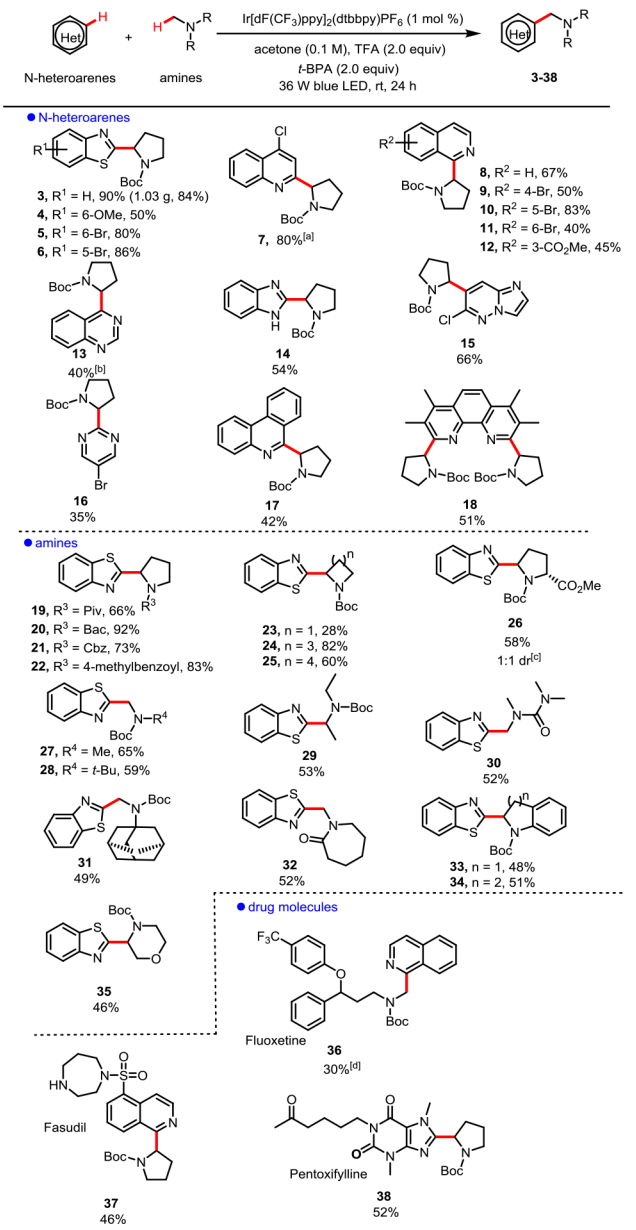


entry	photocatalyst	oxidant	yield[b] (%)
1	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	*t*-BPA	92 (90)[c]
2	$[Ir(dtbbpy)(ppy)_2][PF_6]$	*t*-BPA	55
3	$[Ru(bpy)_3](PF_6)_2$	*t*-BPA	<5
4	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	*t*-BHP	47
5	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	*t*-BPB	45
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$Na_2S_2O_8$	24
7	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$K_2S_2O_8$	20
8[d]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	*t*-BPA	<5
9		*t*-BPA	<5
10	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$		<5
11[e]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	*t*-BPA	<5

[a]General conditions: **1** (0.2 mmol), **2** (0.4 mmol), photocatalyst (0.002 mmol), oxidant (0.4 mmol), TFA (0.4 mmol), and acetone (2 mL) under an argon atmosphere. Abbreviations: *t*-BHP, *tert*-butylhydroperoxide; *t*-BPB, *tert*-butyl peroxybenzoate. [b]Determined by ^1H NMR spectroscopy using 1,3-benzodioxole as an internal standard. [c]Isolated yield. [d]Reaction performed in the absence of light. [e]No TFA.

With the optimized conditions in hand, we investigated the scope of the reaction with respect to the heteroarene (Scheme 2, upper panel). Various electron-deficient heteroarenes were readily α-aminoalkylated at the most electrophilic position with *N*-Boc-pyrrolidine (**2**) in good to excellent yields. Reactions of benzothiazole substrates with electron-withdrawing or electron-donating substituents proceeded smoothly with excellent selectivity for the C2 position to afford **3**–**6** in 50–90% isolated yields. The lower yield of **4** (50%) may have been the result of lower reactivity of the heteroarene substrate toward the nucleophilic α-aminoalkyl radical. Quinoline substrates with a chloro substituent at C4 were well tolerated, undergoing reaction selectively at C2 to afford **7** (80% yield). Reactions of **2** with 4-bromo-, 5-bromo-, 6-bromo-, and 3-methyl formate substituted isoquinolines afforded products of selective α-aminoalkylation at C2, along with isoquinoline (**8**–**12**, 40–83% yields). Quinazoline (**13**, 40%), 1*H*-benzo[*d*]-imidazole (**14**, 54%), 6-chloroimidazo[1,2-*b*]pyridazine (**15**, 66%), 5-bromopyrimidine (**16**, 35%), and phenanthridine (**17**, 42%) were also acceptable substrates. In addition, the reaction was applicable to the commercially available ligand 3,4,7,8-tetramethyl-1,10-phenanthroline, affording biaminoalkylated product **18** in good yield (51%). The reaction between **1**

Scheme 2. Substrate Scope of the CDC Reaction*



*Reactions were performed on a 0.2 mmol scale under the conditions listed in Table 1, unless otherwise noted; isolated yields are given. [a]Ten equivalents of *N*-Boc-pyrrolidine was used. [b]DMSO as solvent. [c]Diastereomeric ratio (dr) was determined by ^1H NMR spectroscopy. [d]*N*-Boc-fluoxetine (0.2 mmol) and benzothiazole (0.4 mmol) were used.

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and **2** is easy to upscale to gram scale, with **3** isolated in 84% yield on a 4 mmol scale.

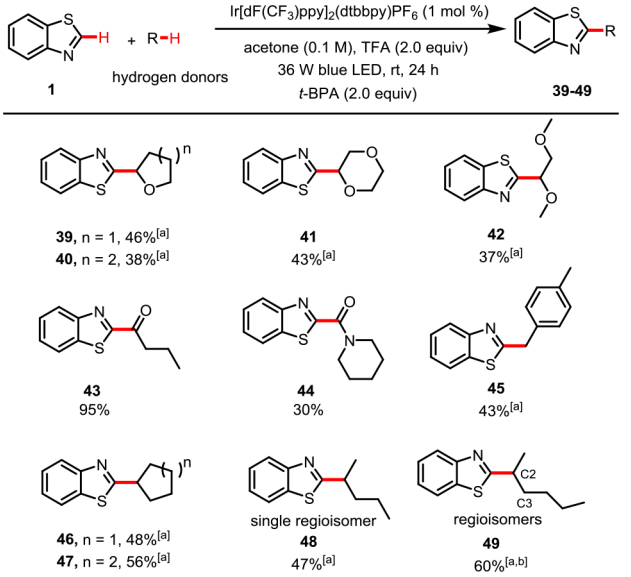
Next, we explored the scope of the CDC reaction with respect to the amine component by using **1** as the heteroarene (Scheme 2, lower panel). The reaction was amenable to amines with a wide range of substituents on the nitrogen atom, including carbamate, amide, and urea groups (giving **3**, **19**–**22**, and **30** in 52–92% yields). Furthermore, cyclic amines of various ring sizes (azetidine to azepane) afforded desired products **23**–**25** in 28–82% yields. An amine substituted with an *N*-Boc-proline methyl ester underwent selective arylation at the 5-methylene position to afford **26** in 58% yield. The CDC reaction was not restricted to cyclic substrates; reactions of acyclic amines afforded products **27**–**31** in 49–65% yields. When the reaction was carried out with a substrate bearing an exocyclic α-amino methyl group and an endocyclic methylene group, completely regioselective α-aminoalkylation at the former position was observed, affording **32** in 52% yield. Indoline and 1,2,3,4-tetrahydroquinoline, moieties that are present in various naturally occurring alkaloids, as well as in bioactive synthetic compounds (including pharmaceuticals),[16] reacted to give corresponding products **33** and **34** in good yields (48% and 51%, respectively). Interestingly, the use of *N*-Boc-morpholine resulted in selective alkylation at the α-nitrogen atom (**35**, 46% yield). Finally, we successfully used the CDC reaction for late-stage functionalization of some drug molecules. For instance, when *N*-Boc-fluoxetine was used as a representative drug molecule for diversification, α-amino-alkylation derivative was readily accessed (**36**). Fasudil carrying a free secondary NH group was selectively alkylated at C1 in good yield (**37**). Pentoxifylline with an amide group can be selectively alkylated at the C2 position (**38**). Considering the prevalence of amine and *N*-heteroarene moieties in bioactive molecules, this new coupling reaction may prove highly useful in drug discovery research.[17]

Having accomplished the α-arylation of amines, we suspected that other hydrogen donors might be suitable for the CDC reaction,[18] and in fact, we found that ethers were acceptable substrates (Scheme 3). Reactions of **1** with tetrahydrofuran, tetrahydropyran, 1,4-dioxane, and 1,2-dimethoxyethane afforded desired products **39**–**42**, respectively, in moderate yields (37–46%). In addition, butyraldehyde and piperidine-1-carbaldehyde afforded satisfactory yields of carbonylation products **43** and **44** (95% and 30%, respectively). Finally, we demonstrated that the reaction was applicable to alkanes, which afforded alkylation products in good yields (**45**–**49**, 43–60%).

To verify the utility of the CDC reaction for drug synthesis, we prepared compound **50**, a key intermediate in the synthesis of an antidiabetic agent, by deprotection of product **27** under acidic conditions (Scheme 4).[15f]

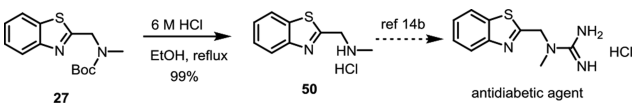
Having explored the substrate scope and utility of this photoredox-mediated CDC reaction of heteroarenes and amines, we turned our attention to the mechanism (Scheme 5). When the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was present in a reaction mixture containing **1** and **2**, compound **3** was obtained in less than 5% yield (see the SI). Byproduct **51** was observed by mass spectrometry, suggesting that a *tert*-butoxy radical had been generated. When vinyl sulfone **52** was used as a radical scavenger, a small amount of compound **53**, the product of α-vinylation of the *N*-Boc-pyrrolidine, was observed by mass spectrometry, which suggested that an α-aminoalkyl radical had been generated.[19] The reduction potential of *t*-BPA in CH_3CN was determined to be −1.56 V vs SCE (see the SI), indicating that direct reduction of *t*-BPA (E^0 = −1.56 V vs SCE) by Ir^{*3+} ($E_{1/2}^{IV/*III}$ = −0.89 V vs SCE) is thermodynamically disfavored; however, we surmised that proton-coupled electron transfer under acidic conditions significantly lowers the barrier to reduction and may be

Scheme 3. Reactions of Other Hydrogen Donors*

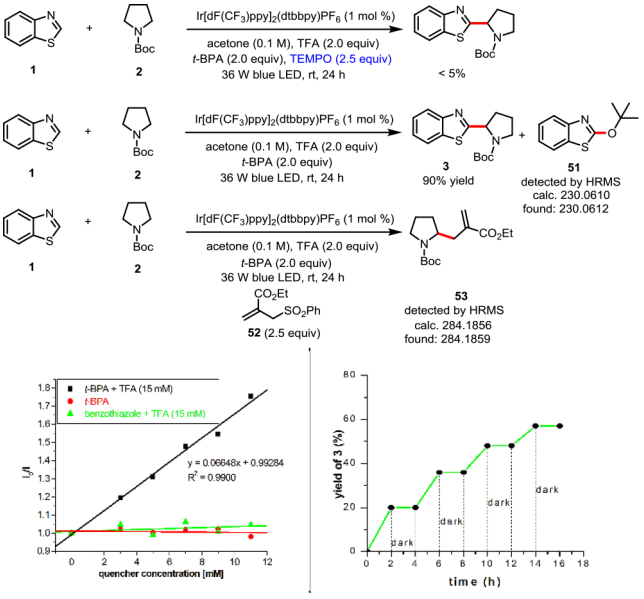


*Reactions were performed on a 0.2 mmol scale under the conditions listed in Table 1, unless otherwise noted; isolated yields are given. [a]Thirty equivalents of R-H, 48 h. [b]The ratio of regioisomers was determined by ^{1}H NMR spectroscopy; C2/C3 = 5:2.

Scheme 4. Use of the CDC Reaction to Prepared a Key Intermediate in the Synthesis of an Antidiabetic Agent



Scheme 5. Mechanistic Experiments



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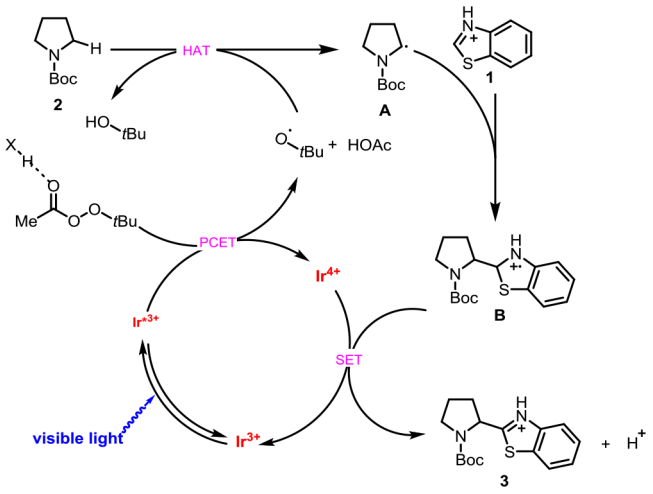
kinetically feasible.[20] Stern–Volmer fluorescence quenching experiments clearly demonstrated this hypothesis, and the excited state of the photocatalyst can be quenched by *t*-BPA in the presence of TFA (no quenching was observed by *t*-BPA in the absence of TFA). Moreover, we conducted a light/dark experiment, which showed that coupling product **3** formed only under continuous irradiation (Scheme 5). This result suggests that radical-chain propagation was not involved in the reaction.

On the basis of these observations and the literature reports, we propose the mechanism depicted in Scheme 6. Photo-

Scheme 6. Proposed Mechanism



excitation of the $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ photocatalyst with a blue LED produces a long-lived excited state Ir^{*3+}. The reduction of *t*-BPA (E^0 = −1.56 V vs SCE) by Ir^{*3+} ($E_{1/2}^{IV/*III}$ = −0.89 V vs SCE) via proton-coupled electron transfer under acidic conditions affords an oxidized iridium species (Ir^{4+}), acetic acid, and a *tert*-butoxy radical.[20] α-Aminoalkyl radical **A** is then generated by means of hydrogen-atom transfer (HAT) between the N-protected amine and the *tert*-butoxy radical. Radical **A** then adds to the protonated electron-deficient heteroarene (**1**) via a Minisci-type pathway to afford radical cation **B**. Single-electron oxidation of this intermediate by Ir^{4+} ($E_{1/2}^{IV/III}$ = +1.70 V vs SCE in $MeCN/H_2O$ = 2:1) and deprotonation gives the final α-aminoalkylated product **3** and closes the photoredox cycle.

In conclusion, we have described the first method for photoredox-mediated direct CDC to accomplish α-aminoalkylation of *N*-heteroarenes by a wide variety of amines. This mild and efficient reaction was applicable to *N*-heterocycles such as benzothiazoles, (iso)quinolones, phenanthridine, and other heterocyclic derivatives without the need for substrate prefunctionalization and is scalable to the gram level. Furthermore, the reaction was also suitable for other hydrogen donors, such as ethers, a formamide, an aldehyde, *p*-xylene, and alkanes. We expect that this reaction will be a useful complement to existing CDC technologies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02389.

Experimental procedures and spectroscopic data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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