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Photocatalytic Hydrogen-Evolving Cross-Coupling of Arenes with Primary Amines

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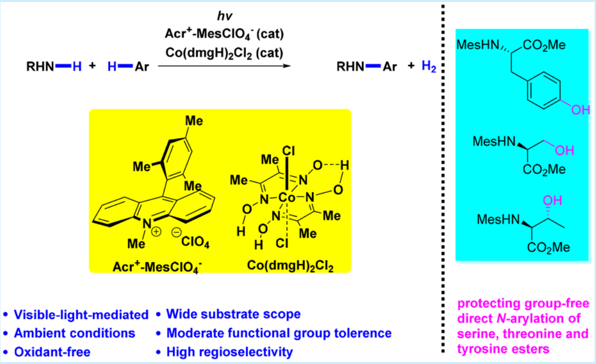
Supporting Information

ABSTRACT: Herein, we described a cooperative catalyst system consisting of an acridinium photoredox catalyst and a cobalt-based proton-reduction catalyst that is effective for the C−H amination of arenes with concomitant generation of hydrogen. This oxidant-free method allows a variety of amines with diverse functional groups to be converted to aromatic amines. Additionally, this protocol can also be extended to hydrolytically unstable benzophenone imines.



Aromatic amines are common in nature and play an important role in chemical industry.[1] Therefore, over the past few decades, diverse synthetic routes to aromatic amines, including transition-metal-catalyzed Ullmann−Goldberg, Buchwald−Hartwig, and Chan−Lam aminations, have been well described in the literature and have found broad applications in industry.[2] However, prefunctionalization of the starting materials is usually required for these transformations, which results in the generation of a large amount of undesired waste from the raw materials.

Recently, the direct, intermolecular dehydrogenative cross-coupling of aryl C−H bonds with simple amines has attracted tremendous attention since this method circumvents the need for prefunctionalization of either coupling partner.[3] A transition-metal-catalyzed, chelation-directed aryl C−H activation method has been developed for this transformation (Figure 1a).[4] While this protocol proceeds with high regioselectivity, the requirements of elaborate directing groups and expensive sacrificial oxidants hamper the widespread application of this method. Hence, a more general, environmentally friendly and sustainable protocol with a broad substrate scope would be therefore of great interest. Recently, based on their previous work on direct C−H amination reactions of arenes and heteroarenes with nitrogen-containing heterocycles,[5] Nicewicz and co-workers disclosed a visible-light-mediated aryl C−H amination using primary amines as the nitrogen source and O_2 as the terminal oxidant (Figure 1b).[6] The application of this method is mainly restricted to electron-rich heteroarenes or arenes with electron-donating groups, such as alkyloxy and aryloxy groups. Only a few examples were described with methyl-substituted arenes, as they are known to be easily oxidized under oxidative conditions. Given the “magic methyl effect”[7] in bioactive compounds as well as the limited number of examples of the direct C−H amination of methylarenes, the development of a more general catalyst system for the direct C−H amination of methylarenes is urgently needed. In this context, Lei and co-workers recently developed a selective C−H amination of methylarenes using heterocyclic azoles as the nitrogen source by employing a photocatalytic cross-coupling hydrogen-evolution (CCHE) strategy,[8] as pioneered by Wu, Tung, Lei

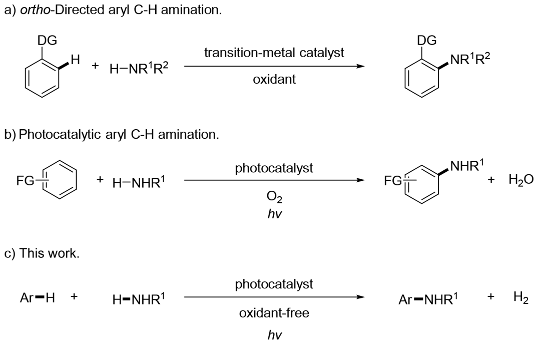


Figure 1. Strategies for dehydrogenative cross-coupling of arenes with nonactivated amines.

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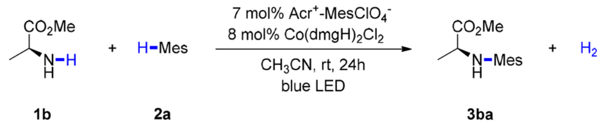
and co-workers.[9−12] This reaction does not require any sacrificial oxidants, and hydrogen is generated as the only side product.

Intrigued by these recent developments in visible-light photoredox-mediated aryl C−H aminations, we explored the possibility of dehydrogenative cross-couplings of arenes with amines. To the best of our knowledge, visible-light photoredox-catalyzed acceptorless dehydrogenative cross-couplings of arenes with amines with the extrusion of hydrogen have not been reported previously (Figure 1c).

We commenced our study by evaluating the visible-light photoredox-mediated dehydrogenative cross-coupling of mesitylene (**2a**) with L-alanine methyl ester (**1b**) under blue LED irradiation (Table 1). A variety of photocatalysts, proton-reduction catalysts, and their respective loadings were investigated in acetonitrile. To our delight, the use of 7 mol % of Acr$^+$−MesClO$_4^-$ and 8 mol % of Co(dmgH)$_2$Cl$_2$ resulted in the formation of hydrogen and the desired coupling product **3ba** with no erosion enantiopurity (entry 1). Replacing Acr$^+$−MesClO$_4^-$ with other photocatalysts, such as Eosin Y, Ru(bpy)$_3$Cl$_2$, and Ir(ppy)$_2$(dtb-bpy)PF$_6$, led to no detectable product (entries 2−4). A slightly decreased yield was observed when Co(dmgH)$_2$PyCl was used as a proton-reduction catalyst (entry 5). Other solvents, such as CH$_2$Cl$_2$ and THF, resulted in inferior results (entries 6 and 7). Finally, no product was detected in the absence of the photocatalyst Acr$^+$−MesClO$_4^-$, the proton-reduction catalyst Co(dmgH)$_2$Cl$_2$, or light (entries 8−10). These results indicated that the photocatalyst, the proton-reduction catalyst, and light were essential for this transformation.

Table 1. Optimization of the Reaction Conditions[a]

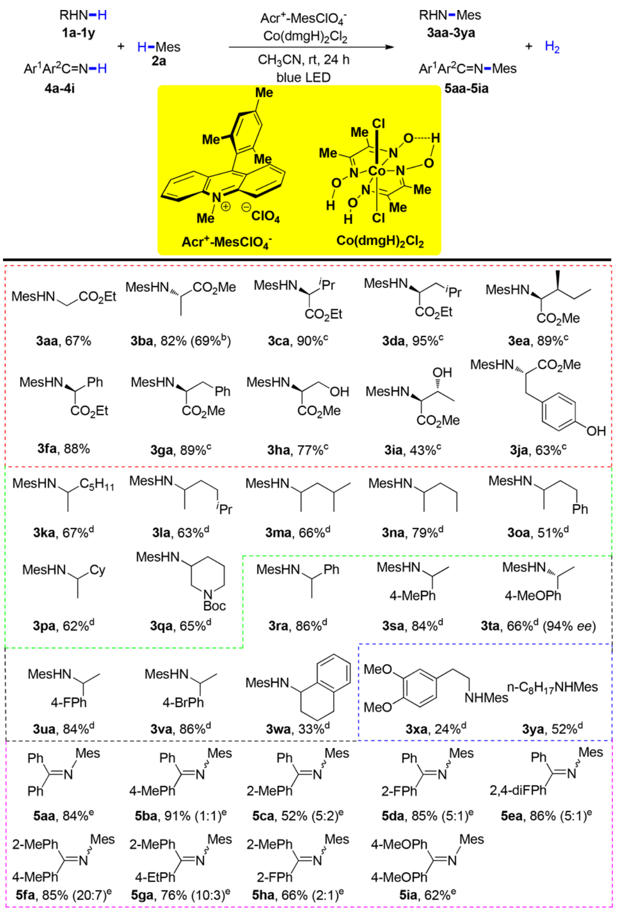


entry	variation from the standard conditions	yield[b] (%)
1[c]	none	86
2	Eosin Y instead of Acr$^+$−MesClO$_4^-$	0
3	Ru(bpy)$_3$Cl$_2$ instead of Acr$^+$−MesClO$_4^-$	0
4	Ir(ppy)$_2$(dtb-bpy)PF$_6$ instead of Acr$^+$−MesClO$_4^-$	0
5	Co(dmgH)$_2$PyCl instead of Co(dmgH)$_2$Cl$_2$	64
6	CH$_2$Cl$_2$ instead of CH$_3$CN	77
7	THF instead of CH$_3$CN	16
8	without Acr$^+$−MesClO$_4^-$	0
9	without Co(dmgH)$_2$Cl$_2$	0
10	without light	0

[a] L-Alanine methyl ester **1b** (0.2 mmol), mesitylene **2a** (10 equiv), Acr$^+$−MesClO$_4^-$ (7 mol %), Co(dmgH)$_2$Cl$_2$ (8 mol %), and MeCN (3.5 mL) were stirred in a Schlenk tube irradiated by a blue LED lamp (6 W) at rt under Ar atmosphere for 24 h. [b] Yield was determined by ^{1}H NMR with CH$_2$Br$_2$ as an internal standard. [c] Hydrogen was detected by ^{1}H NMR.

Under the optimized conditions, the generality of this cross-coupling reaction was investigated, and the results are described in Scheme 1. Using mesitylene as the arene coupling partner, the nature of the amine and the reaction's compatibility with various substituents and functional groups were studied in more detail. Amino acid esters bearing nonpolar aliphatic or aromatic side chains led to excellent yields of products **3aa**−**3ga**. Notably, serine and threonine esters bearing branched hydroxyalkyl side chains reacted smoothly and afforded C−N coupling products **3ha** and **3ia**, respectively, while the formation of the C−O coupling side products was not observed. L-Tyrosine methyl ester, which bears a free phenol group in the side chain, afforded a good yield of product **3ja** (63%). A series of α-branched aliphatic amines also smoothly underwent the desired cross-coupling reactions (**3ka**−**3pa**). Importantly, the presence of a nitrogen-containing heterocycle or an *N*-Boc functional group have no influence on the reaction, and the corresponding product was delivered in good yield (**3qa**, 65%). Benzyl amines bearing electron-withdrawing and electron-donating moieties in the para position reacted smoothly to give the corresponding products in moderate to good yields (**3ra**−**3va**). Notably, the

Scheme 1. Scope of Amines and Imines[a]



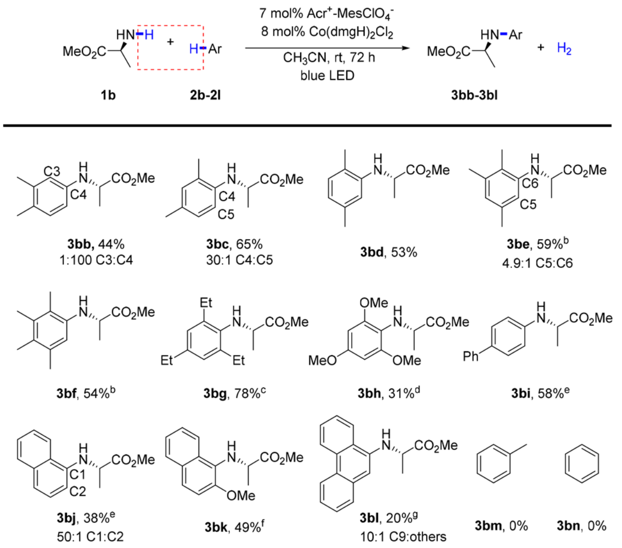
[a] Unless otherwise stated, amine **1** (0.2 mmol), **2a** (10 equiv), Acr$^+$−MesClO$_4^-$ (7 mol %), Co(dmgH)$_2$Cl$_2$ (8 mol %), and MeCN (3.5 mL) were stirred in a Schlenk tube irradiated by a blue LED lamp (6 W) at rt under an Ar atmosphere for 24 h. All are isolated yields. [b] 5 mmol scale. [c] **2a** (50 equiv) and MeCN (2.0 mL) were used. [d] **2a** (100 equiv), Acr$^+$−MesClO$_4^-$ (7 mol %), Co(dmgH)$_2$Cl$_2$ (9 mol %), 4 Å MS (200 mg), and CH$_3$CN (1.2 mL) were stirred in a Schlenk tube and irradiated by a blue LED lamp (6 W) at rt under an Ar atmosphere for 24 h, and then Acr$^+$−MesClO$_4^-$(3.5 mol %) and Co(dmgH)$_2$Cl$_2$ (4.5 mol %) were added and stirred for another 24 h. [e] **2a** (20 equiv), Acr$^+$−MesClO$_4^-$ (9 mol %), Co(dmgH)$_2$Cl$_2$ (9 mol %), and CH$_3$CN (3.0 mL) were stirred in a Schlenk tube and irradiated by a blue LED lamp (6 W) at rt under an Ar atmosphere for 24 h, and then Acr$^+$-MesClO$_4^-$ (4.5 mol %) and Co(dmgH)$_2$Cl$_2$ (4.5 mol %) were added and stirred for another 48 h. The ratio of *E*/*Z* isomer was determined by ^{1}H NMR.

coupling of (*R*)-1-(4-methoxyphenyl)ethylamine afforded the enantiopure desired cross-coupling product in good yield with retention of stereochemistry (**3ta**, 66% yield, 94% *ee*). Although nonbranched linear amines reacted efficiently to produce desired products **3xa** and **3ya**, the *N*-dealkylation side product was also observed in these two reactions. Furthermore, the scalability of this method is illustrated by a 5 mmol reaction of **1b** to generate 773 mg of product **3ba** (69% yield).

In view of the versatility and impact of triarylmethanimines in medicine chemistry and organic synthesis,[13] we further extended the substrate scope to benzophenone imines. Gratifyingly, a series of hydrolytically unstable benzophenone imines bearing methyl, ethyl, methoxyl, or fluoride groups on the aromatic ring gave rise to the corresponding triarylmethanimine products in good to excellent yields (52%−91%).

Next, the scope of arenes was explored by utilizing L-alanine methyl ester (**1b**) as the amine coupling partner (Scheme 2).

Scheme 2. Scope of Arenes[a]



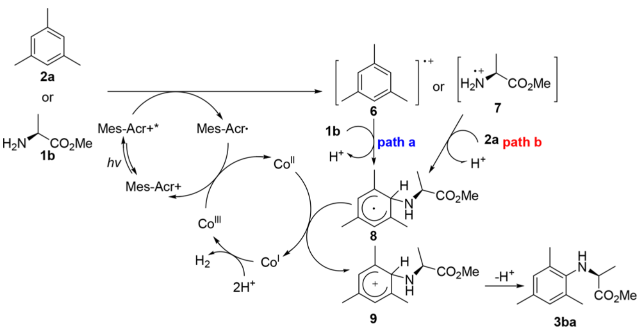
[a]Unless otherwise stated, **1b** (0.2 mmol), arene **2** (50 equiv), Acr$^+$−MesClO$_4^-$ (7 mol %), Co(dmgH)$_2$Cl$_2$ (8 mol %), and MeCN (2.0 mL) were stirred in a Schlenk tube irradiated by a blue LED lamp (6 W) at rt under Ar atmosphere for 72 h. All are isolated yields. The ratio of regioisomers was determined by NMR spectroscopy. [b]The reaction time was 96 h. [c]The reaction time was 24 h. [d]**2** (60 equiv) and MeCN (4 mL) were used, and the reaction time was 48 h. [e]**2** (40 equiv) and MeCN (4 mL) were used. [f]**2** (60 equiv) and MeCN (4 mL) were used. [g]**2** (20 equiv) and MeCN (4 mL) were used.

The reactions of *o*- and *m*-xylene proceeded well and afforded products **3bb** and **3bc** in moderate to good yields and with excellent regioselectivities. *p*-Xylene also reacted smoothly to give product **3bd** in 53% yield. Other multimethyl-substituted benzenes, such as 1,2,4-trimethylbenzene and 1,2,3,4-tetramethylbenzene, participated in this transformation and afforded desired products **3be** and **3bf** in moderate yields. Not only a methyl substituent but also an ethyl substituent were tolerated in these oxidant-free conditions. For example, 1,3,5-triethylbenzene smoothly underwent amination to afford product **3bg** in 54% yield. In addition, a multimethoxy-substituted benzene was also converted into the corresponding amine product **3bh** in modest yield. This protocol could also be expanded to other aromatic compounds. Once again, excellent regioselectivities were observed for biphenyl and naphthalene and its *β*-methoxy-substituted derivative. High regioselectivity was also observed for the amination of anthracene, and product **3bl** was obtained, albeit in low yield (20%). Disappointingly, attempts to use insufficiently electron-rich arenes, such as benzene and toluene, failed.

To probe the possible pathway of this reaction, a series of Stern−Volmer quenching experiments were conducted to identify the active species during this amination process. The results show that L-alanine methyl ester (**1b**), mesitylene (**2a**), and *p*-xylene (**2d**) can effectively quench the excited state of photocatalyst Acr-Mes-Me^{+*} ($E_{1/2\ \mathrm{red}}$ = 2.06 V vs SCE[14]); however, toluene cannot quench this catalyst (see Supporting Information (SI), Figure S2). These results suggest that an arene radical cation is most likely involved in the reaction pathway, and an amine radical cation pathway cannot be ruled out at this stage. In addition, we also observed that the reaction of **1b** with **2a** took place smoothly upon irradiation with visible light, while no product formed in the absence of light (SI, Figure S3). The result indicates that a photoredox catalytic pathway rather than a radical-chain pathway may be involved. Furthermore, the UV−vis spectra were employed to characterize the cobalt species involved in the reaction. Upon irradiation, characteristic absorptions at 450 nm, 585 and 677 nm appear (SI, Figure S6), which are assigned to Co(II) and Co(I) species, respectively.[10b,c,15]

Taken together with our findings and previous literature, a plausible mechanism is proposed by using the reaction of **1b** and **2a** as an example (Scheme 3). Initially, photoexcitation of Acr-Mes-Me$^+$ would generate an excited state photocatalyst (Acr-Mes-Me^{+*}, $E_{1/2\ \mathrm{red}}$ = 2.06 V vs SCE), which could oxidize mesitylene ($E_{1/2\ \mathrm{red}}$ = 2.05 ± 0.01 V vs SCE[16]) or L-alanine methyl ester (**1b**) to produce an Acr-Mes-Me radical as well as mesitylene radical cation **6** or a *N*-central radical cationic intermediate **7**. The Acr-Mes-Me radical ($E_{1/2\ \mathrm{red}}$ = −0.49 V vs SCE[14]) could be oxidized by a Co(III) ($E_{1/2\ \mathrm{red}}$ [Co$^{\mathrm{III}}$/Co$^{\mathrm{II}}$] = −0.77 V vs SCE[17]) catalyst to turn over the photoredox catalytic cycle and generate the Co(II) catalyst. Nucleophilic addition of **1b** to mesitylene radical cation **6** (path a) or the addition of *N*-central radical cationic intermediate **7** to mesitylene (path b) would generate a cyclohexadienyl radical intermediate **8**. The intermediate **8** could further undergo a single-electron transfer with the Co(II) catalyst to form intermediate **9**, which could be aromatized to amine product **3ba** by losing a proton. Finally, the generated proton can be reduced by the Co(I) catalyst to release a molecule of hydrogen and regenerate the Co(III) catalyst at the same time, turning over the cobalt catalytic cycle.

Scheme 3. Proposed Mechanism



In summary, we have developed a method for the direct C−H amination of arenes by combining an acridinium photoredox catalyst with a cobalt-based proton-reduction catalyst. Notable features of this protocol are its wide substrate scope, moderate functional group tolerance, high regioselectivity, and mild reaction conditions. Further extending this cooperative catalyst system to other synthetically interesting substrates is ongoing in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03089.

Experimental procedures, isolated products' characterization data, detailed mechanistic investigations (PDF)

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Notes

The authors declare no competing financial interest.

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