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# Photocatalytic C−H Amination of Aromatics Overcoming Redox Potential Limitations

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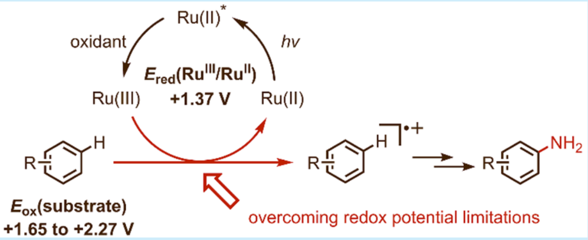
**ABSTRACT:** We report the photocatalytic C−H amination of aromatics overcoming redox potential limitations. Radical cations of aromatic compounds are generated photocatalytically using Ru(phen)$_3$(PF$_6$)$_2$, which has a reduction potential at a high oxidation state ($E_{red}$(Ru$^{III}$/Ru$^{II}$) = +1.37 V vs SCE) lower than the oxidation potentials of aromatic substrates ($E_{ox}$ = +1.65 to +2.27 V vs SCE). The radical cations are trapped with pyridine to give *N*-arylpyridinium ions, which were converted to aromatic amines.



In the past decade, significant attention has been paid to visible-light-induced photocatalytic methods because this approach enables sustainable organic transformations that have often been regarded as difficult without the use of stoichiometric amounts of metal-based or expensive organic redox reagents.[1] In general, the substrate scope of photoredox reactions can be limited by the redox potentials of the substrates and the photocatalysts.[2] Given that the redox potential is directly linked to the Gibbs free energy, chemists refer to a potential chart to determine if the electron transfer process required for the reaction to take place is thermodynamically favorable or not.[3] A typical example of the potential chart is shown in Figure 1.[3a] In the case of photocatalytic oxidation reactions, a photocatalyst can exergonically oxidize substrates having an oxidation potential lower than the reduction potential of the excited state (**PC***) or the high oxidation state of the photocatalyst [**PC(+1)**], which can be generated by the oxidative quenching of **PC*** (Figure 1, light blue region). As such, the thermodynamically favored single-electron oxidation process is common in photocatalytic oxidations. In contrast, photoredox reactions utilizing the thermodynamically disfavored single-electron oxidation process, which corresponds to electron transfer from substrates in the pink region of Figure 1 to **PC*** or **PC(+1)**, have rarely been reported.[4] In this context, overcoming such redox potential limitations provides opportunities to increase the design freedom of photoredox reactions.

A typical example of a photocatalytic reaction in which the substrate scope is limited by the redox potentials is the C−H functionalization of aromatic compounds via their radical cations.[5,6] The hydroxylation,[6a] bromination,[6b] fluorination,[6c] amination,[6d,e] cyanation,[6f] and phosphonylation[6g] of aromatics by photocatalysts have been reported (Figure 2a). Key to the success of these approaches is the highly positive excited-state reduction potential of the photocatalysts, such as 3-cyano-1-methylquinolinium (**PC1**), 9-mesitylacridinium (**PC2**), and Ru(bpz)$_3$(PF$_6$)$_2$ (**PC3**) [$E^*_{red}$(**PC1**) = +2.72 V,[6a] $E^*_{red}$(**PC2**) = +2.06 V,[6b] $E^*_{red}$(**PC3**) = +1.45 V[6g] vs the saturated calomel electrode (SCE)]. To the best of our knowledge, previously reported photocatalytic C−H functionalization reactions of aromatics via their radical cations have been applicable only to

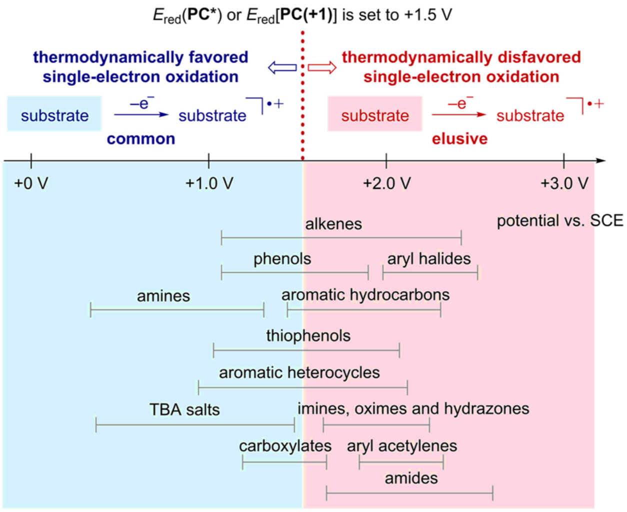


**Figure 1.** Oxidation potentials of common organic functional groups as described in ref 3a, and the thermodynamics of the electron transfer process it predicts. For the sake of brevity, the reduction potential of the oxidizing species of the photocatalyst [**PC*** or **PC(+1)**] is set to +1.5 V in this figure.

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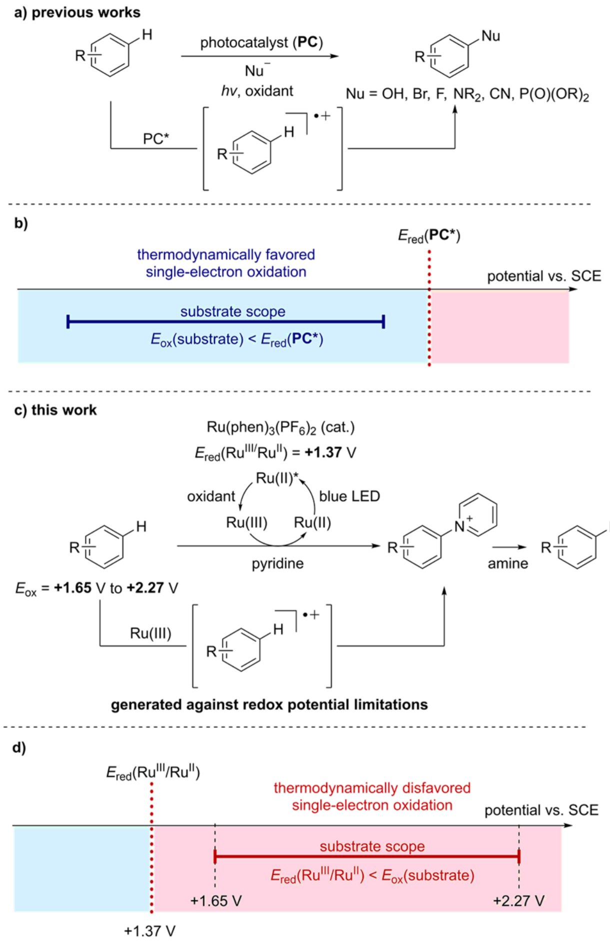


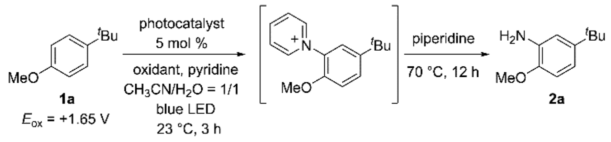
**Figure 2.** Generation of radical cations of aromatic compounds by photoredox catalysts. (a) Previous C−H functionalization of aromatics through their radical cations. (b) Redox potential range of applicable substrates in previous studies. (c) This work: the photocatalytic C−H amination of aromatics overcoming the redox potential limitations. (d) Redox potential range of applicable substrates in the present system.

aromatic compounds with oxidation potentials lower than the reduction potential of the photocatalyst excited state (Figure 2b). Although it is known that thermodynamic favorability is not a prerequisite for successful electron transfer,[7] it is a de facto requirement for the photocatalytic C−H functionalization of aromatics through their radical cations. For example, C−H phosphonylation using $\mathrm{Ru(bpz)_3(PF_6)_2}$ [$E^*_{\mathrm{red}}$(**PC3**) = +1.45 V] is only applicable to highly electron-rich aromatics such as di- or trimethoxy-substituted benzenes but not to anisole [$E_{\mathrm{ox}}$ = +1.76 V].[6g]

We herein report the photocatalytic C−H amination[8,9] of aromatics overcoming redox potential limitations. Radical cations of aromatic compounds were generated photocatalytically using $\mathrm{Ru(phen)_3(PF_6)_2}$, which has a reduction potential at a high oxidation state ($E_{\mathrm{red}}(\mathrm{Ru^{III}/Ru^{II}})$ = +1.37 V vs SCE) lower than the oxidation potentials of the aromatic substrates examined herein ($E_{\mathrm{ox}}$ = +1.65 to +2.27 V vs SCE) (Figure 2c). The generated radical cations are trapped with pyridine to give *N*-arylpyridinium ions, which are subsequently converted to aromatic amines. In this reaction, electron transfer from the aromatic substrate to photocatalytically generated Ru(III) is thermodynamically disfavored (Figure 2d); this disfavorability is up to +22.5 kcal/mol.

The irradiation of 4-*tert*-butylanisole (**1a**) with blue light in the presence of $\mathrm{K_2S_2O_8}$, pyridine, and $\mathrm{Ru(phen)_3(PF_6)_2}$ (cat.) in $\mathrm{CH_3CN/H_2O}$ (1:1) and subsequent treatment with piperidine gave the desired primary aromatic amine **2a** in an excellent yield (Table 1, entry 1). Indeed, irradiation was essential for the reaction to take place (entry 2). Interestingly, the choice of catalyst was important; $\mathrm{Ir[dF(CF_3)ppy]_2(dtbpy)}$,[10] $\mathrm{Ru(bpz)_3(PF_6)_2}$,[11] and $\mathrm{Ru(dfmb)_3(PF_6)_2}$,[12] which have reduction potentials at high oxidation states higher than those of $\mathrm{Ru(phen)_3(PF_6)_2}$ were not suitable (entries 3−5). Clearly, the oxidizing power of the photocatalyst was not correlated with the yield of product obtained. No product was obtained in the absence of the photocatalyst (entry 6). Furthermore, the choice of oxidant was also important, where persulfates were found to be suitable oxidants, irrespective of which countercation was employed (entries 7 and 8). In contrast, no desired amine was obtained when the common organic oxidant DDQ was utilized (entry 9). In addition, the use of $\mathrm{CBrCl_3}$, which is a typical oxidant for photocatalytic reactions,[13] failed to yield the desired product (entry 10).

**Table 1. Optimization of Photocatalytic C−H Amination***

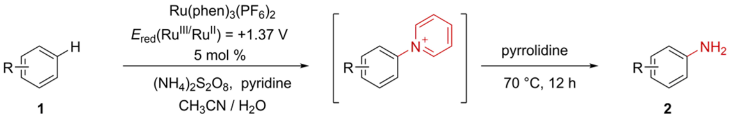


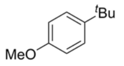
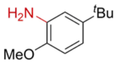
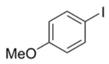
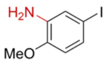
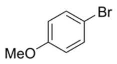
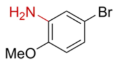
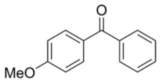
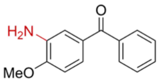
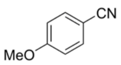
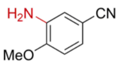
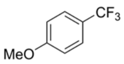
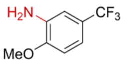
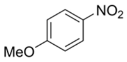
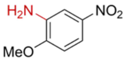
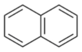
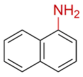
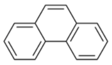
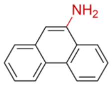
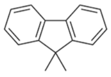
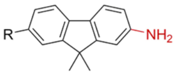
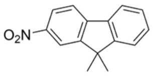
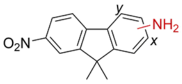
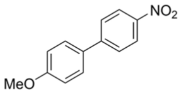
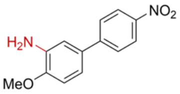
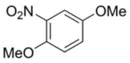
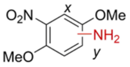
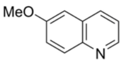
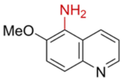
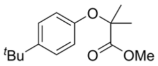
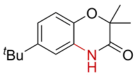
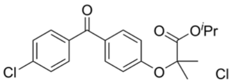
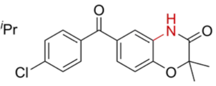
| entry | photocatalyst | oxidant | yield[a] (%) |
|---|---|---|---|
| 1 | $\mathrm{Ru(phen)_3(PF_6)_2}$ [$E_{\mathrm{red}}(\mathrm{Ru^{III}/Ru^{II}})$ = +1.37 V][b] | $\mathrm{K_2S_2O_8}$ | 96 |
| 2[c] | $\mathrm{Ru(phen)_3(PF_6)_2}$ | $\mathrm{K_2S_2O_8}$ | 0 |
| 3 | $\mathrm{Ir[dF(CF_3)ppy]_2(dtbpy)}$ [$E_{\mathrm{red}}(\mathrm{Ir^{IV}/Ir^{III}})$ = +1.80 V][b] | $\mathrm{K_2S_2O_8}$ | 0 |
| 4 | $\mathrm{Ru(bpz)_3(PF_6)_2}$ [$E_{\mathrm{red}}(\mathrm{Ru^{III}/Ru^{II}})$ = +1.79 V][b] | $\mathrm{K_2S_2O_8}$ | 40 |
| 5 | $\mathrm{Ru(dfmb)_3(PF_6)_2}$ [$E_{\mathrm{red}}(\mathrm{Ru^{III}/Ru^{II}})$ = +2.05 V][b] | $\mathrm{K_2S_2O_8}$ | 47 |
| 6 | none | $\mathrm{K_2S_2O_8}$ | 0 |
| 7 | $\mathrm{Ru(phen)_3(PF_6)_2}$ | $\mathrm{Na_2S_2O_8}$ | 98 |
| 8 | $\mathrm{Ru(phen)_3(PF_6)_2}$ | $\mathrm{(NH_4)_2S_2O_8}$ | 99 |
| 9 | $\mathrm{Ru(phen)_3(PF_6)_2}$ | DDQ | 0 |
| 10 | $\mathrm{Ru(phen)_3(PF_6)_2}$ | $\mathrm{CBrCl_3}$ | 0 |

[*] 4-*tert*-Butylanisole (**1a**) (0.2 mmol), pyridine (2 mmol), oxidant (0.4 mmol), and $\mathrm{Ru(phen)_3(PF_6)_2}$ (5 mol %) were stirred at 23 °C in $\mathrm{CH_3CN/H_2O}$ (1/1, 5 mL) for 3 h with blue light irradiation, and the resulting reaction mixture was treated with piperidine (10 mmol) at 70 °C for 12 h. [a] Determined by $^1$H NMR analysis [b] [$E_{\mathrm{red}}(\mathrm{M}^{n+1}/\mathrm{M}^{n})$] is a reduction potential of a high oxidation state of photocatalysts vs SCE. [c] Reaction was carried out in the dark.

The scope of the present photocatalytic amination was then examined (Table 2), and a remarkable functional group compatibility was revealed. More specifically, anisoles bearing iodo, bromo, benzoyl, cyano, trifluoromethyl, and nitro groups gave the corresponding primary aromatic amines in good to excellent yields (entries 2−7). Significantly, 4-nitroanisole (**1g**) gave the corresponding amine **2g** in 83% yield, despite electron transfer from **1g** ($E_{\mathrm{ox}}$ = +2.27 V) to Ru(III) [$E_{\mathrm{red}}(\mathrm{Ru^{III}/Ru^{II}})$ = +1.37 V] being disfavored by 22.5 kcal/mol, as calculated from the Δ*E* (+0.90 V; see the Supporting Information for derivation). In contrast, aniline was not obtained from benzene ($E_{\mathrm{ox}}$ = +2.54 V), presumably due to the fact that the electron transfer from benzene to Ru(III), which is disfavored by 28.7

**Table 2. Scope of the Photocatalytic C−H Amination Reaction via Thermodynamically Disfavored Electron Transfer***



| entry | substrate, $E_{ox}$ (V vs SCE) driving force for generating the radical cation $\Delta G^{a}$ | product yield (%)$^{b}$ |
|---|---|---|
| 1 | <br>**1a** (+1.65 V)<br>+8.2 kcal/mol | <br>**2a**: 89 (97)$^{c}$ |
| 2 | <br>**1b** (+1.75 V)<br>+10.5 kcal/mol | <br>**2b**: 73 |
| 3 | <br>**1c** (+1.80 V)<br>+11.6 kcal/mol | <br>**2c**: 46 |
| 4 | <br>**1d** (+2.01 V)<br>+16.5 kcal/mol | <br>**2d**: 91 |
| 5 | <br>**1e** (+2.17 V)<br>+20.1 kcal/mol | <br>**2e**: 99 |
| 6 | <br>**1f** (+2.20 V)<br>+20.8 kcal/mol | <br>**2f**: 71 |
| 7 | <br>**1g** (+2.27 V)<br>+22.5 kcal/mol | <br>**2g**: 83 |
| 8$^{d}$ | <br>benzene (+2.54 V)<br>+28.7 kcal/mol | no product |
| 9 | <br>**1h** (+1.79 V)<br>+11.4 kcal/mol | <br>**2h**: 42 |
| 10 | <br>**1i** (+1.77 V)<br>+10.9 kcal/mol | <br>**2i**: 31 |
| 11 | <br>**1j** (+1.77 V)<br>+10.9 kcal/mol | <br>**2j** : R=H<br>**2j'**: R=NH$_2$<br>71 (**2j**/**2j'** = 1.8/1) |
| 12$^{d}$ | <br>**1k** (+2.06 V)<br>+17.6 kcal/mol | <br>**2kx/2ky**<br>81 (**2kx/2ky** = 3.3/1) |
| 13$^{d}$ | <br>**1l** (+1.73 V)<br>+10.0 kcal/mol | <br>**2l**: 75 |
| 14 | <br>**1m** (+1.71 V)<br>+9.5 kcal/mol | <br>**2mx/2my**<br>54 (**2mx/2my** = 3.2/1) |
| 15 | <br>**1n** (+1.74 V)<br>+10.2 kcal/mol | <br>**2n**: 69 |
| 16 | <br>**1o** (+1.76 V)<br>+10.7 kcal/mol | <br>**2o**: 80 |
| 17 | <br>**1p** (+2.12 V)<br>+19.0 kcal/mol | <br>**2p**: 47 |

[*] Aromatic substrate (**1**) (0.5 mmol), pyridine (10 equiv), $(NH_4)_2S_2O_8$ (2−5 equiv), and $Ru(phen)_3(PF_6)_2$ (5 mol %) were stirred in $CH_3CN/H_2O$ for 24 h with blue light irradiation at 23 °C, and the resulting reaction mixture was treated with pyrrolidine (50 equiv) at 70 °C for 12 h. See the Supporting Information for details. [a] Calculated from $[E_{ox}(\mathbf{1}) - E_{red}(Ru^{III}/Ru^{II})]$. See the Supporting Information for derivation. [b] Isolated yield. [c] The yield in parentheses is $^1$H NMR yield. [d] Reaction run on a 0.2 mmol scale.

kcal/mol, as calculated from the $\Delta E$ (+1.17 V), was too slow (entry 8). Aromatic hydrocarbons, namely, naphthalene (**1h**) and phenanthrene (**1i**), gave the corresponding amines regioselectively in moderate yields (entries 9 and 10), whereas 9,9-dimethylfluorene (**1j**) gave the desired products **2j** and **2j′** in 46 and 25% yields, respectively (entry 11). The reaction of nitro-substituted arenes **1k**, **1l**, and **1m** gave the corresponding aromatic amines without affecting the nitro groups (entries 12−14), which is in sharp contrast to the conventional nitration/reduction process. In addition, heteroaromatic compound **1n** gave aromatic amine **2n** in a good yield (entry 15), whereas aryl ether bearing an ester group **1o** was efficiently converted to 2*H*-1,4-benzoxazin-3-one **2o** through photocatalytic C−H amination and subsequent intramolecular cyclization (entry 16).[5f] Furthermore, fenofibrate **1p** gave the corresponding 2*H*-1,4-benzoxazin-3-one **2p** (entry 17). We note here that the oxidation potentials of the applicable aromatic substrates range from +1.65 to +2.27 V, which are significantly higher than the reduction potential of Ru(III) $[E_{red}(Ru^{III}/Ru^{II}) = +1.37$ V]. Our results, therefore, confirm that, in the present reaction system, the redox potential limitations were clearly overcome.

A plausible mechanism for the present amination reaction is illustrated in Figure 3a. In this process, Ru(II) is excited by visible light to give Ru(II)*, which is converted to Ru(III) by oxidative quenching. Critically, although the reduction potential of Ru(III) $[E_{red}(Ru^{III}/Ru^{II}) = +1.37$ V] is significantly lower than the oxidation potential of the aromatic substrate [e.g., $E_{ox}(\mathbf{1a}) = +1.65$ V], the radical cation is still generated in an equilibrium system. This process was supported by Kochi's report that a stoichiometric amount of the isolable oxidant $Fe(phen)_3(PF_6)_3$ $[E_{red}(Fe^{III}/Fe^{II}) = +1.16$ V vs SCE] could oxidize 4-methoxytoluene ($E_{ox} = +1.60$ V vs SCE) in an equilibrium to generate the radical cations, which were trapped by nucleophiles.[14] In the present photocatalytic system, the resulting radical cation is then trapped by pyridine to give an *N*-arylpyridinium ion, which is converted to the aromatic primary amine upon treatment with pyrrolidine after photoirradiation.[15] The in situ trapping of the radical cations by pyridine was

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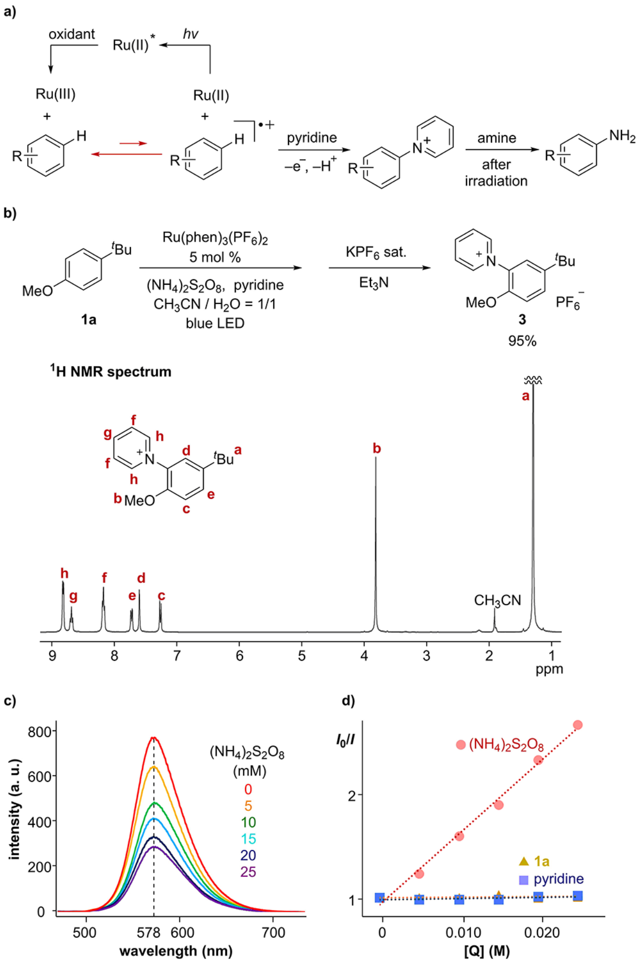


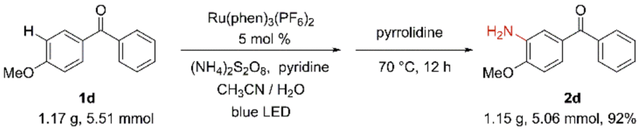
**Figure 3.** Plausible reaction mechanism and mechanistic study of the photocatalytic C−H amination. (a) Plausible reaction mechanism. (b) Isolation of *N*-arylpyridinium salt **3** and its $^1$H NMR spectrum. (c) Quenching of the fluorescence of Ru(phen)$_3$(PF$_6$)$_2$ by (NH$_4$)$_2$S$_2$O$_8$. (d) Stern−Volmer plots for the emission of Ru(phen)$_3$(PF$_6$)$_2$ in the presence of a quencher (Q = (NH$_4$)$_2$S$_2$O$_8$, **1a**, pyridine).

confirmed by the isolation of *N*-arylpyridinium salt **3** (determined by $^1$H NMR analysis, Figure 3b).

For the formation of *N*-arylpyridinium salt **3**, another reaction mechanism involving electron transfer from **1a** to Ru(II)*, energy transfer from Ru(II)* to **1a**, or electron transfer from **1a** to sulfate radical anion is conceivable. However, the first and second possibilities could be excluded because Stern−Volmer quenching experiments indicated that only (NH$_4$)$_2$S$_2$O$_8$ efficiently quenched the excited state of the Ru photocatalyst, whereas **1a** and pyridine did not (Figure 3c,d). The third possibility was also excluded because a thermal reaction of **1a**, pyridine, and (NH$_4$)$_2$S$_2$O$_8$ in CH$_3$CN/H$_2$O at 70 °C, which is a suitable condition for the thermal generation of a sulfate radical anion from persulfate,[16] followed by treatment with pyrrolidine did not give desired product **2a** (see the Supporting Information). Additionally, the generation of a pyridyl radical cation[15b,c] was excluded by considering the scope and regioselectivity of the amination, as shown in Table 2. The pyridyl radical cation can react with benzene; however, we could not obtain aniline from benzene (Table 2, entry 8). Additionally, the reaction of a pyridyl radical cation generally produces a mixture of regioisomers. However, the present amination system mostly gave a single regioisomer, which agrees with the regioselectivity of reactions that proceeded via electrochemically generated radical cations.[5d]

The present photocatalytic C−H amination is synthetically attractive because other photocatalytic methods for synthesizing aromatic primary amines, which are important synthetic intermediates, typically suffer from low product yields and poor regioselectivity.[6d,9c,15b,c] Furthermore, the scalability of this process was demonstrated by performing the reaction of **1d** on a gram scale. The reaction proceeded well to give desired amine **2d** in 92% yield (Scheme 1). It should be noted that, unlike the electrochemical amination via *N*-arylpyridinium ions,[5d,f] the present method does not require a large excess of Bu$_4$NBF$_4$, an expensive supporting electrolyte; instead, it involves the use of the low-cost persulfate oxidant.

**Scheme 1. Gram-Scale Experiment**



In conclusion, we developed the photocatalytic C−H amination of aromatic compounds that have an oxidation potential higher than the reduction potential of the high oxidation state of the Ru photocatalyst. The choice of the photocatalyst and oxidant was of particular importance. This protocol was successfully applied to the photocatalytic synthesis of aromatic primary amines bearing a variety of functional groups to give synthetic intermediates that are important in medicinal chemistry and materials science. The regioselectivity and scalability of the present amination is notable. Moreover, we synthesized aromatic amines in systems in which the electron transfer was disfavored by up to +22.5 kcal/mol. We believe that the proposed system overcomes the potential limitations and will facilitate the design of photocatalytic reactions. Further mechanistic studies are now in progress.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00822.

Experimental procedures, analytical data of synthesized compounds, and copies of NMR spectra (PDF)

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## Author Contributions

T.M. conceived the project and wrote the manuscript with G.I. and N.K. G.I. carried out the experiments. All authors discussed the experiments and have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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