ChemistrySelect

Research Article
doi.org/10.1002/slct.202304786

Chemistry Europe
European Chemical Societies Publishing

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Direct Amide Formation *via* Carbamoylation of Aromatic Bromides using Heteropoly Acid and UV-Light

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We performed direct carbamoylation using heteropoly acid (HPA) photocatalysts with a Keggin structure under UV-light. Carbamoyl radicals were generated *via* the decarboxylation of *N*,*N*-disubstituted dimethyloxamic acid under these conditions. The HPA catalyst functioned as a photocatalyst when the dicarbonyl bond was broken, generating carbon dioxide. We found that disubstituted carbamoyl radicals readily coupled with aromatic bromides to generate diverse benzoic amides. In particular, using a homogeneous HPA photocatalyst improved the reaction's transmittance, which had been a problem of the existing heterogeneous photocatalyst. This reaction condition can be easily handled, mild, and safer than the traditional benzoic amide synthesis. This method can be scaled up efficiently, is eco-friendly, and can be applied to producing active pharmaceutical ingredients.

Introduction

Amides are stable, functional groups that play a crucial role in various fields, such as natural products, polymers, ecosystems, material engineering, peptides, DNA, pharmaceuticals, and RNA.[1] They are also present in various small-molecule drugs which have biological activities. In 2021, 80% of the top 200 selling small-molecule drugs included amide bonds,[2] and among them, approximately 3% of drug structures contain aromatic tertiary amide moieties.

The classical method for benzoic amide formation involves the condensation of benzoic acid with an amine. Benzoic acid is easily synthesised. However, in the case of highly substituted benzoic acid, it is costly and difficult to synthesise the amide at the end of synthetic steps because of harsh condensation conditions. If starting from simple benzoic acid, more steps will be needed to obtain the substituted benzoic amide. Therefore, substituted benzoic amides usually have problems during the development of synthetic procedures.

As reported in the literature, several efforts have been made to synthesise substituted benzoic amides. In some cases, the nitrile introduced in the aromatic ring undergoes a photoreaction and catalytic synthesis. Blue LEDs,[1a,c,d,3] visible light,[4] and solar simulators[5] have been used to synthesise amides using photoreactions. Photoreactions have recently attracted attention because of their applications in green chemistry, resulting in many studies investigating their use. The photocatalyst mainly uses, iridium,[3–4] iron,[1d,5] and ruthenium-based[4c] metal catalysts and other non-metal[1a] catalysts. The classical catalyst mainly uses copper,[6] nickel[1f,7] and palladium (Pd)[3b,8] catalysts. Examples include $[(Ph)_3P]_4Ni(0)$, a nickel-based catalyst, which was used at 75 °C for 20 hours or more.[1f] In another example, $Pd(OAc)_2$, a palladium-based catalyst, was tested at 80 °C for more than 24 hours.[8a] Another palladium catalyst, $Pd(TFA)_2$, was used to react at 150 °C for up to 24 hours.[8f] These catalysts were used in reactions conducted at relatively high temperatures. Conditions for decarboxylative coupling using palladium catalyst ($Pd(PhCN)_2Cl_2$) and iridium catalyst ($[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$) in blue LED at room temperature are highly reactive but difficult to use industry because the catalyst is too expensive.[3b]

Here, we focus on the development of efficient methods that are economical and eco-friendly for the synthesis of benzoic amides (Figure 1). We found that using a heteropoly

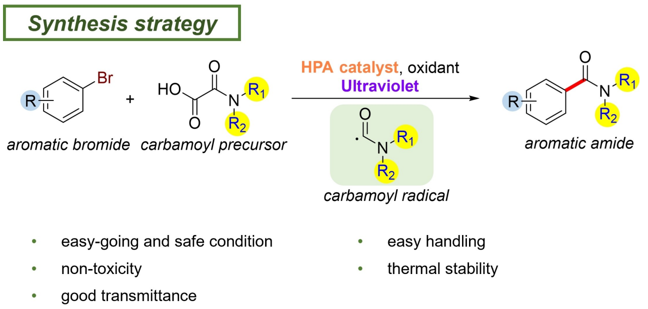

Figure 1. Synthesis strategy of this study.

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.202304786

acid (HPA) with a Keggin structure (Figure 2) as a homogeneous photocatalyst[9] and a metal-oxygen cluster[10] has many advantages.[9b,11] It is acidic, oxidative, and is important as a catalyst that enables effective oxidation through photoinduced photoredox reactions in the wavelength range of 200 to 500 nm.[12] We confirmed the oxidizing potentials of HPA at 253.7 nm wavelength. HPAs are highly regarded for their stability, fast proton mobility, electron transfer capability,[13] and excellent physicochemical structure.[14] Besides, they are readily soluble in polar solvents,[9b,15] and their transmittance to light can be increased. In particular, the Keggin structure shows a stronger Brønsted acid than other conventional acids.[9b,14] HPAs act as excellent electron acceptors and increase their binding capabilities with active sites.[14] HPAs exhibit strong UV absorption and efficiently receives intramolecular charge transfer in response to photoirradiation.[14] Recently, many research results on HPAs have been reported,[16] and active research is also being conducted in the pharmaceutical field.[15]

We selected phosphomolybdic acid (PMA, $H_3[PMo_{12}O_{40}]$) as the HPA photocatalyst. PMA is mainly used as a stain in organic synthesis and is often used in acid-catalysed reactions.[17] It is attractive as a catalyst for green chemistry reactions because of its environmentally friendly characteristics and is considered safe for humans.[11] An organic synthesis method using PMA has been developed and commercialised.[11b] PMA is a classic catalyst used in the past, and has recently been used as an acid catalyst for the synthesis of challenging structures.[18] However, we applied it to our study, confirming that it was also used as a catalyst in a simple structure such as cresol, fluorophenol, and methoxyphenol.[9d]

UV was selected because the high energy gap between HPA's lowest unoccupied molecular orbital (LUMO) and its highest occupied molecular orbital (HOMO) is activated only under UV irradiation. After UV absorption, PMA was activated to generate O→M (metal) ligand-to-metal charge transfer (LMCT).[19] Based on the existing photo-HPA,[20] the PMA electrons from O^{2-} to Mo^{6+} are expected to form a photoexcited state from the HOMO to the LUMO.

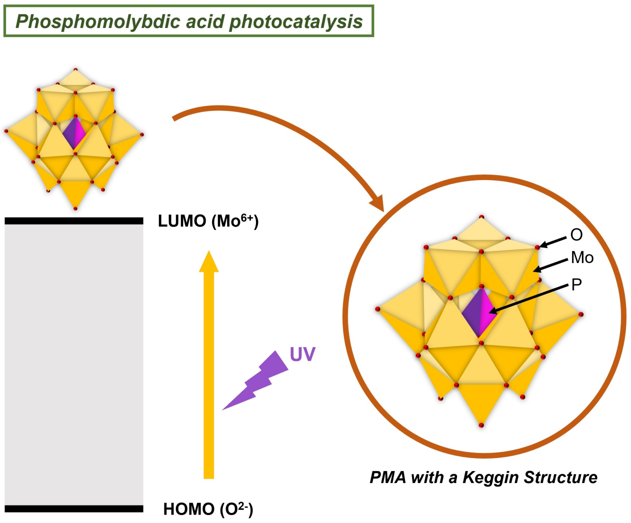


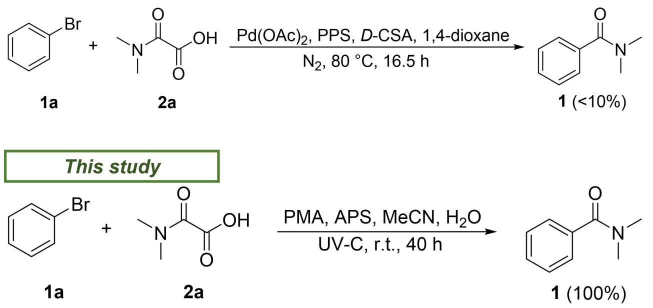
Figure 2. PMA structure and the expected molecular orbital system of PMA.

To develop a direct and environment friend amide formation method, we tried to connect a carbamoyl radical and aromatic radical under photoinduced condition. Here, we introduced a *N*,*N*-dimethyloxamic acid which can play single-electron transfer (SET) role companied by losing one molecular of CO_2 under UV-C and PMA conditions finally formed a carbamoyl radical.[1c,3a,4a,b,21] As a count partner of this reaction, aromatic radical is formed *via* photoinduced electron transfer (PET) under UV-C conditions from aromatic bromide.[22] After lots of attempt, we achieved desired result to direct form an amide bond under UV-C conditions. Herein, we describe the synthesis of aromatic amides using UV irradiation, PMA, and oxidants at room temperature to couple a carbamoyl precursor with an aromatic bromide. We developed a method for generating carbamoyl radicals through SET of PMA for carbamoylation. The reaction proceeded under straightforward and safe conditions and was easy to handle during experiments. The synthesis process is non-toxic and thermally stable. Because a homogeneous catalyst was used, the UV transmittance and efficiency of the reactant are well-established, and the catalyst can be easily removed from the reaction mixture during the work up process. These properties are desirable for large-scale pharmaceutical manufacturing.

Results and Discussion

Our study started with procuring an α-keto amide, a carbamoyl moiety, and an easy-to-obtain aromatic bromide moiety. We expected that the α-keto amide would provide carbamoyl radicals through SET-based decarboxylation and directly lead to carbamoylation. Based on this concept, we developed a synthetic method.

To get a mild and homogeneous carbamoylation method as a final goal, we attempted a Pd-catalysed cross-coupling method, as shown in previous study of Scheme 1, and less than 10% carbamoyl product **1** was obtained after purification. This approach, which involved $Pd(OAc)_2$, *D*-CSA, and 1,4-dioxane under N_2,[8a] required a high temperature and a long reaction time. Therefore, we envisioned that a photoreaction capable of



Scheme 1. Reaction applied to the previous study and this study; APS: ammonium persulfate; *D*-CSA: camphorsulfonic acid; MeCN: acetonitrile; N_2: nitrogen gas; $Pd(OAc)_2$: palladium(II) acetate; PMA: phosphomolybdic acid hydrate; PPS: potassium persulfate; UV: ultraviolet.

activating radical generation energy would be more suitable than previous study of Scheme 1 to obtain a radical coupling product.

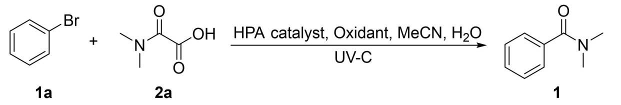
As we found from reports, carbamoyl radicals[1c,3a,4a,b,21] and aromatic bromide radicals[22] can be generated by UV-C irradiation which can be directly used for carbamoylation. We developed a carbamoylation method in which the PMA catalyst enters an excited state under UV irradiation and undergoes a radical coupling decarboxylation reaction through SET (this study of Scheme 1). Few studies have investigated PMA as an HPA catalyst. To confirm PMA as a suitable photocatalyst, an experiment was conducted in a quartz test tube in the presence and absence of UV. We tested PMA, tungstosilicic acid (TSA, $H_4[SiW_{12}O_{40}]$), and phosphotungstic acid (PTA, $H_3[PW_{12}O_{40}]$), which are well-known and easy to obtain among homogeneous HPA catalysts. In addition, ammonium persulfate and potassium persulfate were selected because they are known oxidants that help decarboxylation to produce radicals (Table S1).[23] A study by Mai *et al.* showed that adding potassium persulfate attacks the α-position of the quinoline derivative.[24]

The reactions reported in Tables S1, 1 and 2 were performed in a black box with a 40 W UV-C lamp emitting energy at 253.7 nm. A solvent mixture of acetonitrile (MeCN) and water, with a ratio of 1:1, was selected due to its high UV-C transmittance and oxidant dissolution capability, respectively. In the oxidation process wherein α-keto amide was inserted, it was observed that without UV-C and HPA catalysts, there was no electronically excited state of electrons. At higher reaction temperatures, SET oxidation still did not occur, radicals were deactivated, and the reaction did not proceed (Table S1, entries 1, 5, and 7). Additionally, it did not react without the HPA catalyst at room temperature (Table S1, entry 6). The reaction did not proceed even in the absence of UV-C, HPA catalysts, and oxidants (Table S1, entries 7, and 8). Although it proceeded in visible light by changing the wavelength band of light, it was confirmed that SET oxidation and radicals were inactivated (Table S1, entry 9).

For the HPA catalyst to act as a photocatalyst, electrons are excited with light energy to become HPA* and then $HPA^{\bullet -}$ through a SET process. Simultaneously, *N*,*N*-dimethyloxamic acid releases CO_2 during the SET process to form carbamoyl radicals.[1c] However, when experiments were conducted with the HPA catalyst and oxidant without UV-C, the reaction did not proceed (Table S1, entries 1 and 9). HPA was not activated because SET did not proceed. Since, there was no light energy, *N*,*N*-dimethyloxamic acid did not release CO_2. Consequently, no carbamoyl radicals were generated. Furthermore, little reactivity was observed when the reaction was carried out with an oxidant and without an HPA catalyst (Table S1, entries 5 and 6). In consequence, the oxidant was discovered to play an auxiliary role in carbamoylation.

When reacted solely with an HPA catalyst, the TSA yield was 31 %, which was relatively good compared with other HPAs (Table S1, entry 3). However, when reacted with potassium persulfate, the yield of PMA was significantly better at 81 % (Table 1, entry 1). Because molybdenum has a larger binding energy (227.95 eV) than tungsten (31.37 eV),[25] the yield would have been better if PMA had been used. When an equal amount of potassium persulfate (3 equiv.) was used, the yield increased as the amount of HPA increased. However, the low solubility of potassium persulfate's in water (4.49 g/100 mL at 20 °C) caused synthesis problems owing to slow radical production. Accordingly, the experiment was conducted under similar conditions (PMA 0.1 equiv., ammonium persulfate 3 equiv.) to that of potassium persulfate by changing to ammonium persulfate with better solubility in water (80 g/100 mL at 25 °C). Since a large amount of ammonium persulfate could be dissolved without heating due to an increase in the solubility, the attack of carbamoyl radical on aromatic bromide increased. Consequently, we obtained **1** with a 100 % yield (Table 1, entry 7). We measured the spectra in UV-Vis of PMA and *N*,*N*-dimethyloxamic acid, which are important catalyst and substrate in our study (Figure 3). We used a 1:1 ratio of MeCN and water solution for PMA and *N*,*N*-dimethyloxamic acid. These two compounds have meaningful observances within the wavelength range of UV-C (200–280 nm), which can be activated under UV-C.

Table 1. Optimisation of reaction conditions.[a]



Entry	Catalyst	equiv.	Oxidant	*T* [°C]	Yield[b] [%]
1	PMA	0.1	PPS	50	81
2	PMA	0.05	PPS	50	64
3	TSA	0.1	PPS	50	77
4	TSA	0.05	PPS	50	67
5	PTA	0.1	PPS	50	58
6	PTA	0.05	PPS	50	50
7	PMA	0.1	APS	r.t.	100

[a] Reactions were performed on a 100 μmol scale for 40 h under a 40 W UV-C lamp ($\lambda_{max} = 253.7$ nm) using **1 a** (1 equiv.), **2 a** (1 equiv.), HPA catalyst (0.1 equiv.), oxidant (3 equiv.), MeCN, and water. [b] Yields of products refer to isolated material after purification. APS: ammonium persulfate; MeCN: acetonitrile; PMA: phosphomolybdic acid hydrate; TSA: tungstosilicic acid hydrate; PPS: potassium persulfate; PTA: phosphotungstic acid hydrate; UV: ultraviolet.

The generality of the HPA-catalysed carbamoylation was tested using the optimised values in Tables S1 and 1 (Table 2).

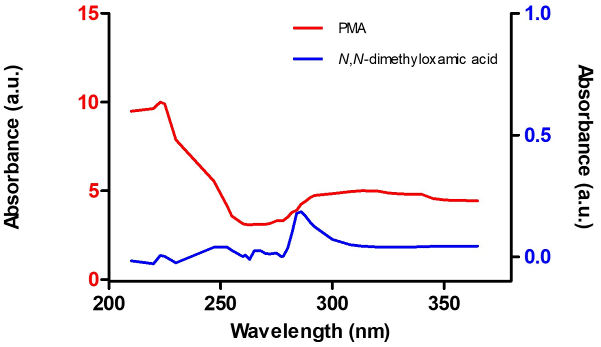
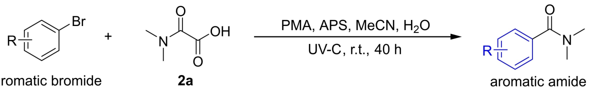
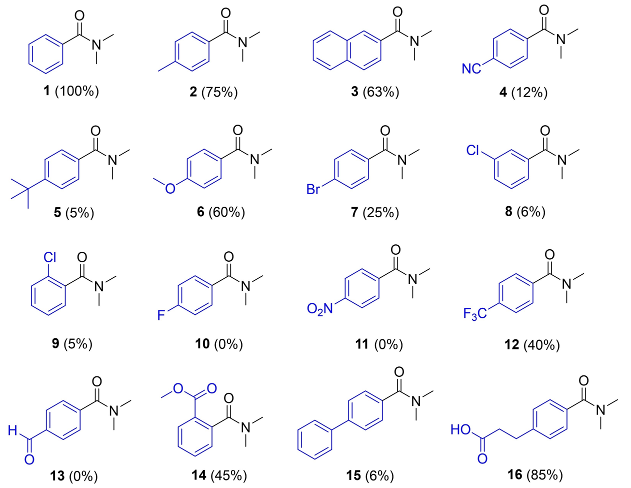


Figure 3. UV-Vis spectra of PMA and *N*,*N*-dimethyloxamic acid.

Table 2. Scope of aromatic bromides.[a]





Reactions were performed on a 1 mmol scale at room temperature for 40 h under a 40 W UV-C lamp ($\lambda_{max}=253.7$ nm) using aromatic bromide (1 equiv.), **2a** (3 equiv.), PMA (0.1 equiv.), APS (3 equiv.), MeCN, and water. [a] Yields of products refer to isolated material after purification. APS: ammonium persulfate; MeCN: acetonitrile; PMA: phosphomolybdic acid hydrate; UV: ultraviolet.

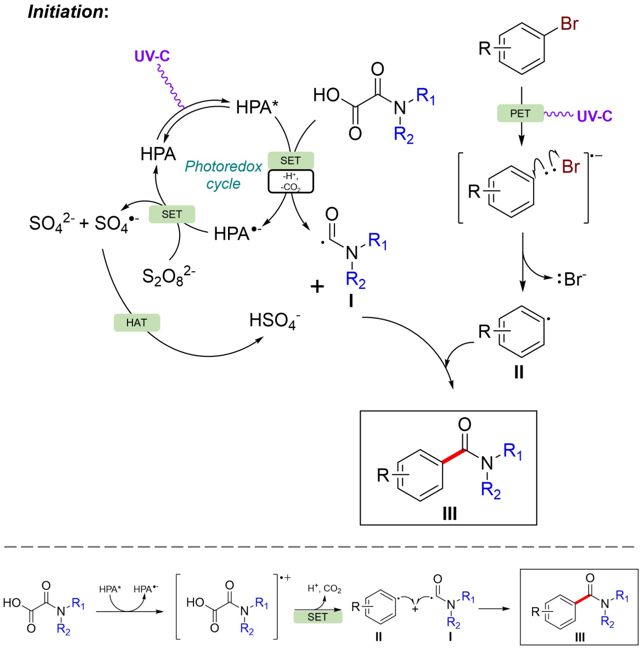


Figure 4. The mechanism for carbamoylation using HPA of aromatic bromide.

We evaluated different types of aromatic bromides with various substituents. Electron-donating groups such as benzene (**1**), toluene (**2**), naphthalene (**3**), a methoxy group (**6**), and phenylpropanoic acid (**16**) were obtained in high yields. The electron-rich C–C σ-bonds were advanced, and the carbamoylation reactivity was excellent. The aromatic halides Br (**7**), *meta*-Cl (**8**), *ortho*-Cl (**9**), fluorine (**10**) are moderately electron-withdrawing substituents, but only the slight possibility of carbamoylation could be confirmed due to the intervention of the second –Br, –Cl, and –F of each structure. Among the electron-withdrawing groups, only some groups such as cyanide (**4**), trifluoromethyl group (**12**), and methyl benzoate (**14**) can be synthesized, and nitrogen dioxide (**11**) and aldehyde (**13**) did not react. *tert*-Butyl (**5**) and biphenyl (**15**) were also able to confirm the possibility of carbamoylation. Our study conditions confirmed that carbamoylation synthesis in the aromatic bromide of the electron-withdrawing group is well performed. In the industry, our photoreaction conditions can be applied when scale-up synthesis of electron-withdrawing substituents.

The proposed mechanism is shown in Figure 4. The HPA catalyst (PMA) was activated by UV at a wavelength of 253.7 nm, causing *N*,*N*-dimethyloxamic acid to reach an excited state,[21d] and decarboxylation through SET was performed to escape CO_2.[3a,26] As in the study of Bai *et al.* and Jouffroy *et al.* UV-C activation of the HPA photocatalyst permits it to reach an excited state HPA* that is sufficiently oxidising to generate SET from *N*,*N*-dimethyloxamic acid *via* reductive quenching.[1c,3a] This process produced a nucleophilic carbamoyl radical (**I**). The process of transferring the aromatic bromide to the aromatic radical begins with the conversion of UV-C to the aromatic bromide radical anion through PET.[22] Aromatic bromide radical anion causes negative ion-mediated cleavage of carbon-bromide bonds, resulting in Br^- escaping and generating highly reactive aromatic bromide radical intermediate (**II**) used in various aromatic bromide synthesis.[22] Simultaneously, as in the report of Jouffroy *et al.* the $HPA^{\bullet-}$ was oxidised by persulfate ($S_2O_8^{2-}$) to obtain sulphate dianions (SO_4^{2-}) and highly oxidisable sulphate radical anions ($SO_4^{\bullet-}$) to activate the HPA catalyst.[1c] As in the report of Westwood *et al.* the sulphate radical anion escapes to form hydrogen sulphate ions (HSO_4^-) *via* hydrogen atom transfer (HAT).[27] **II** participates in the reaction between carbamoyl radical (**I**) and HSO_4^- *via* termination of radical addition to produce the expected carbamoyl product (**III**). This carbamoyl radical mechanism suggests that carbamoyl products were produced.

Conclusions

We report a photoreaction method that enables carbamoylation at room temperature using UV and HPA catalysts. This carbamoyl radical generation developed an HPA coupling process by synthesising α-keto amides with readily available aromatic bromides. This uncomplicated method can be applied to various aromatic bromides and α-keto amides to generate disubstituted benzoic amides. This can contribute to a faster, safer, and more environmentally friendly synthesis method for the pharmaceutical industry, organic synthesis, and biochemistry. We have confirmed that the yield at scale-up of this study in gram-scale in pharmaceutically meaningful derivatives is more than 50 %, and it will be reported in due course.

Experimental Section

A general procedure for HPA-catalysed carbamoylation of aromatic bromide under UV-C is outlined hereafter: Ammonium persulfate (3 equiv.) was added to a 20 mL vial and dissolved in water (6 mL). Aromatic bromide (300 mg, 1 equiv.), *N*,*N*-dimethyloxamic acid (3 equiv.), PMA hydrate (0.1 equiv.) and MeCN (6 mL) were added to a quartz test tube. Transfer the dissolved mixtures in the vial to the quartz test tube. The quartz test tube was placed in a black box with a 40 W UV-C lamp and stirred at room temperature. The quartz test tube was stirred under UV-C (253.7 nm) for 40 h. After completion of the reaction, reactant, and dichloromethane (20 mL) was added to the separatory funnel, and the reaction was quenched saturated sodium bicarbonate solution (20 mL). Then, the product was washed with water (20 mL). The organic layer was dried using magnesium sulphate and filtered. The organic layer was then concentrated using a rotary evaporator.

* When using an UV lamp, experimental suits and UV safety goggles are worn to avoid injury due to direct exposure of UV to the human eye and skin.

* Safety devices should be installed to avoid injuries caused by UV exposure when manufacturing scaled-up UV photoreactor equipment.

Supporting Information Summary

The supporting Information includes general information, synthesis of the substrates, optimisation of the study, experimental procedure, spectral data (^{1}H NMR, ^{13}C NMR, and HRMS).

Acknowledgements

We acknowledge financial support from the National Research Foundation of Korea (NRF-2018R1A6A1A03023718), funded by the Ministry of Education, Republic of Korea.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: amides · cross-coupling · photocatalyst · photochemistry · radical reactions

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Manuscript received: November 27, 2023