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Substituent-controlled regioselective arylation of carbazoles using dual catalysis†

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Regioselective arylation of carbazoles is reported using dual palladium–photoredox catalysis. Controlled monoarylation and diarylation of symmetrical and unsymmetrical carbazoles were achieved under mild reaction conditions with a broad substrate scope and functional group tolerance. Steric and electronic control the regioselectivity of the arylation of unsymmetrical carbazoles. Late-stage functionalization of a caprofen drug derivative and large-scale synthesis of mono- and di-arylated carbazoles were demonstrated to showcase the synthetic versatility of the method. Finally, we also showcased the synthesis of hyellazole analogues (a marine alkaloid) in a short route using our strategy.

1. Introduction

Carbazoles represent a class of heteroaromatic nitrogen-containing molecules that have great significance in organic chemistry. They are encountered in a wide range of natural products^{1,2} such as hyellazole,^{3–6} chlorohyellazole,³ and in many drug and bio-active molecules such as rimcazole,^{7,8} carvedilol,^{9–11} carprofen,^{12–14} carazalol,^{15–17} etc. Beyond their significance in natural products and pharmaceuticals, carbazole derivatives are also used as building blocks for LEDs,^{18,19} optoelectronic materials,^{20–22} and semiconductors.^{23–25} Similarly, biaryl moieties are vital molecular frameworks that are present in many drugs and bio-active compounds. Despite the importance of both carbazoles and biaryls, only a handful of reports are known for the direct arylation of carbazoles.^{26–31} Wu *et al.*³⁰ and Nageswar *et al.*³¹ independently reported pyridine- and pyrimidine-directed *ortho*-arylation of carbazoles. These methods suffer from disadvantages such as the use of oxidants, additives, higher reaction temperature, etc. Another major challenge is achieving site-selective functionalization of unsymmetrical carbazoles and controlling the site-selectivity. Given that the majority of carbazole-based drugs and natural products are unsymmetrical in nature, a new method for site-selective functionalization is highly desirable.

Recently, photo-mediated dual catalysis has emerged as an effective tool for functionalizing various sp^2 and sp^3 C–H bonds. In 2011, Sanford *et al.* reported the first dual Pd/Ru photoredox strategy³² for C–H arylation and in 2015, Toste and

coworkers presented mechanistic insights into dual metallo-photoredox catalysis.³³ Following this, several other groups reported photomediated organic transformations involving a dual metallophotoredox strategy.^{34,35} In this direction our group reported a dual palladium-photoredox strategy for C–H arylation of phenylureas.³⁶ Similarly, Itami and coworkers reported photo-induced arylation of carbazoles; however, it had limitations such as a higher reaction temperature (65 °C), lower yields, the use of near ultraviolet light and poor regioselectivity.³⁷

Recently, Jain *et al.* reported C–H arylation/acylation of carbazoles using a dual palladium–photoredox approach.³⁸ Unfortunately, this method suffers from limitations such as low to moderate yields, a narrow substrate scope (in terms of carbazoles) and the use of excess K_2CO_3 as an additive. More importantly, regioselective arylation of unsymmetrical carbazoles and diarylation of carbazoles were not well studied. In this context, we herein report a modular approach for site-selective and controllable *ortho*-arylation of carbazoles using a dual palladium–photoredox strategy under milder conditions without any additives. Furthermore, the regioselectivity of the reaction can be tuned by controlling the sterics and electronics of the substituents on the unsymmetrical carbazoles (Scheme 1).

2. Results and discussion

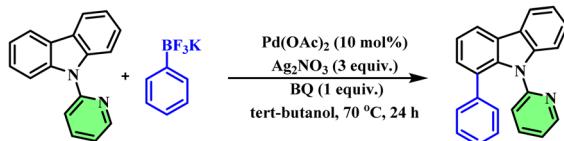
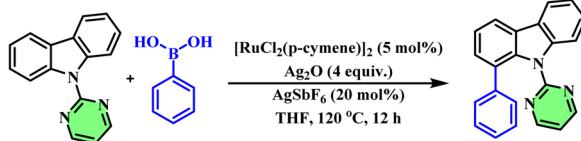
We began our investigation with 9-(pyrimidin-2-yl)-9*H*-carbazole (**1**) as a model substrate and an aryl diazonium salt as the arylating agent (Table 1). With Eosin Y (5 mol%) as a photocatalyst and $Pd(OAc)_2$ (10 mol%) as a transition metal catalyst in 0.1 M methanol, 54% yield of the desired product was obtained (entry 1). When we changed the photocatalyst to Ru

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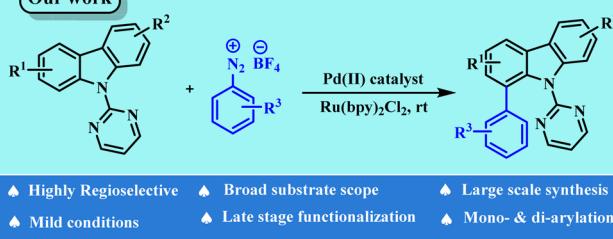
† Electronic supplementary information (ESI) available. CCDC 2267782–2267784 and 2292863. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3ob01827j>



Previous work

Wu *et al.*Nageshwar *et al.*

Our work



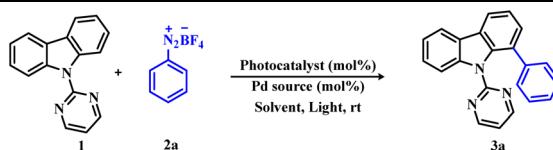
Scheme 1 Previous reports and our work.

(bpy)₃Cl₂ (5 mol%), 74% yield of the desired product was obtained (entry 2). Next, we investigated different palladium catalysts such as Pd(TFA)₂, Pd(MeCN)₂Cl₂, and Pd(PPh₃)₂Cl₂, but unfortunately the yield didn't improve in all these cases

(entries 3–5). Similarly, screening different solvents, such as toluene, DCE, dioxane, *etc.*, didn't improve the yield further (entries 6–9). Reducing the catalyst loading of palladium acetate to 1 mol% and 5 mol%, the yield dropped (entries 11 & 12). Interestingly, when Ru(bpy)₃Cl₂ catalyst loading was decreased from 5 mol% to 1 mol%, a slight increase in the yield was observed (entry 13). Finally, when 2.5 mol% Ru(bpy)₃Cl₂ was used, the yield increased to 82% (entry 14). Changing the solvent concentration further didn't improve the reaction yield (entries 10, 15 & 16).

With the optimized conditions in hand, we next investigated the scope of aryl diazonium salts (Scheme 2). Halo-substituted aryl diazoniums, such as *meta*-fluoro (80%), *meta*-bromo (78%), and *ortho*-bromo (69%) afforded good yields of the arylated products (3b–3d). Aryl diazonium salts bearing electron-withdrawing substituents such as *p*-nitro, *p*-cyano & *m*-trifluoromethyl were well tolerated and afforded the resultant biaryls (3e, 3f & 3g) in good yields. Similarly, electron-rich and disubstituted aryl diazonium salts also afforded good to excellent yields of the resultant arylated products (3h–3o). Surprisingly, the *para*-acetyl phenyl diazonium salt did not afford any arylated carbazole product (3p). Interestingly, the 2-amino dibenzofuran-based heteroaryl diazonium salt furnished the desired product 3q in 72% yield whereas the 8-aminoquinoline based diazonium salt did not furnish the expected product, 3r.

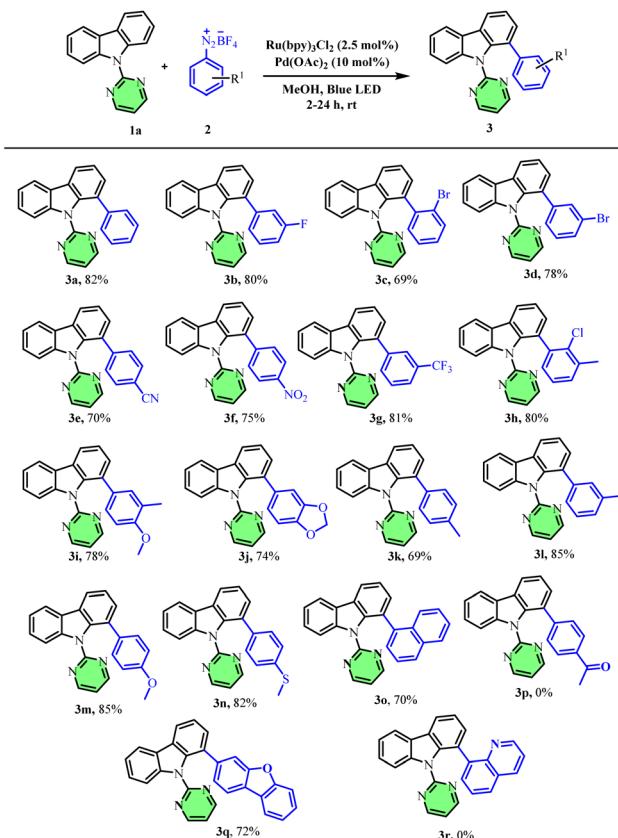
In general, most of the carbazole functionalizations are limited to simple and symmetrical carbazoles with very limited examples for unsymmetrical carbazoles as they generally give a mixture of regioisomers. Hence, we next focussed on the scope of less explored unsymmetrical carbazoles for

Table 1 Optimization of the reaction conditions^a

S. no.	Photocatalyst	TM	Solvent	Yield (%)
1	Eosin Y (5 mol%)	Pd(OAc) ₂ (10 mol%)	MeOH (0.1 M)	54%
2	Ru(bpy) ₃ Cl ₂ (5 mol%)	Pd(OAc) ₂ (10 mol%)	MeOH (0.1 M)	74%
3	Ru(bpy) ₃ Cl ₂ (5 mol%)	Pd(TFA) ₂ (10 mol%)	MeOH (0.1 M)	52%
4	Ru(bpy) ₃ Cl ₂ (5 mol%)	Pd(MeCN) ₂ (10 mol%)	MeOH (0.1 M)	30%
5	Ru(bpy) ₃ Cl ₂ (5 mol%)	Pd(pph ₃) ₂ Cl ₂ (10 mol%)	MeOH (0.1 M)	Traces
6	Ru(bpy) ₃ Cl ₂ (5 mol%)	Pd(OAc) ₂ (10 mol%)	Toluene (0.1 M)	—
7	Ru(bpy) ₃ Cl ₂ (5 mol%)	Pd(OAc) ₂ (10 mol%)	DCE (0.1 M)	28%
8	Ru(bpy) ₃ Cl ₂ (5 mol%)	Pd(OAc) ₂ (10 mol%)	Dioxane (0.1 M)	—
9	Ru(bpy) ₃ Cl ₂ (5 mol%)	Pd(OAc) ₂ (10 mol%)	MeCN (0.1 M)	41%
10	Ru(bpy) ₃ Cl ₂ (2.5 mol%)	Pd(OAc) ₂ (10 mol%)	MeOH (0.05 M)	60%
11	Ru(bpy) ₃ Cl ₂ (5 mol%)	Pd(OAc) ₂ (1 mol%)	MeOH (0.1 M)	62%
12	Ru(bpy) ₃ Cl ₂ (5 mol%)	Pd(OAc) ₂ (5 mol%)	MeOH (0.1 M)	68%
13	Ru(bpy) ₃ Cl ₂ (1 mol%)	Pd(OAc) ₂ (10 mol%)	MeOH (0.1 M)	76%
14	Ru(bpy)₃Cl₂ (2.5 mol%)	Pd(OAc)₂ (10 mol%)	MeOH (0.1 M)	82%
15	Ru(bpy) ₃ Cl ₂ (5 mol%)	Pd(OAc) ₂ (5 mol%)	MeOH (0.05 M)	68%
16	Ru(bpy) ₃ Cl ₂ (2.5 mol%)	Pd(OAc) ₂ (10 mol%)	MeOH (0.2 M)	75%

^a Conditions: carbazole 1 (1 equiv.), aryl diazonium salt 2a (4 equiv.), Pd(OAc)₂ (10 mol%), Ru(bpy)₃Cl₂ (2.5 mol%), in methanol under argon at room temperature for 24 hours, 44 W blue LED (Kessil).





Scheme 2 Scope of different aryl diazonium salts for carbazole arylation. Reaction conditions: carbazole 1 (1 equiv.), aryl diazonium salt 2 (4 equiv.), $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (2.5 mol%), $\text{Pd}(\text{OAc})_2$ (10 mol%), in methanol under argon at room temperature for 2–24 h, 44 W blue LED (Kessil).

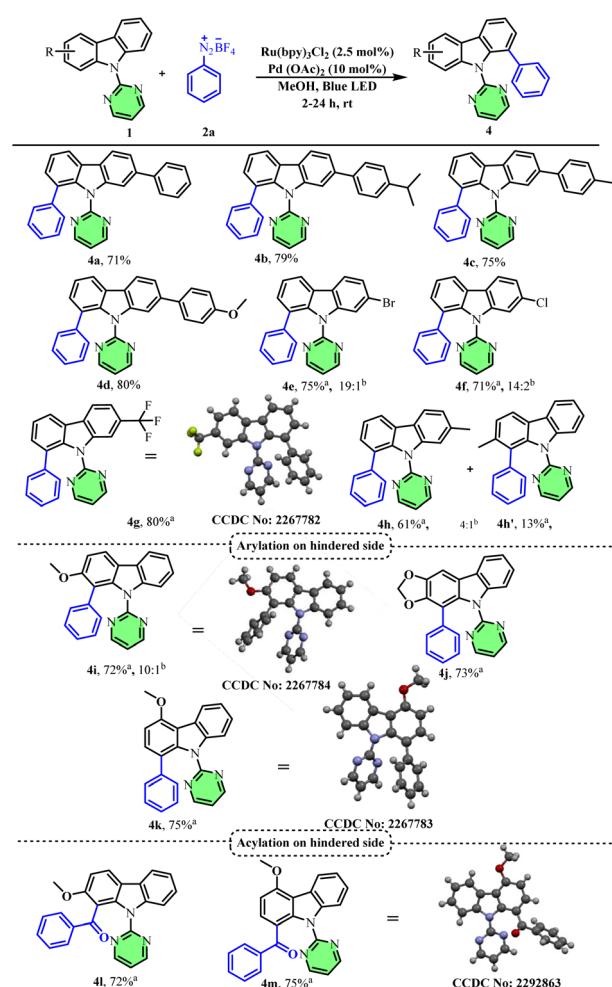
regioselective arylation. Accordingly, we attempted arylation of various 2-aryl substituted carbazoles under standard conditions but using a 1 : 1 mixture of methanol and acetonitrile as the solvent. Interestingly, all these substrates afforded the corresponding arylated products, **4a–4d**, (arylation on the less hindered side of carbazole aryl rings) with good yields and selectivity. Similarly, other C-2 substituted carbazoles such as 2-bromo, 2-chloro and 2-trifluoromethyl substituted carbazoles also afforded the corresponding C-8 arylated products (**4e–4g**) in good yields and high selectivity with a 12 W blue LED light. 2-Methyl substituted carbazole on the other hand furnished a mixture of regioisomers (**4h** & **4h'**) in a 4 : 1 ratio, although it still afforded the C-8 regioisomer as the major product.

Interestingly, electron-donating 2-methoxy and 2,3-methylenedioxy-substituted carbazoles afforded the corresponding C-1 arylated products (**4i** and **4j**) regioselectively (arylation on the more substituted side) in good yields. In order to understand the mechanism and to know if the change in selectivity is due to mere electronic effects or the directing group ability of methoxy substituents, we attempted arylation of 4-methoxy-substituted carbazole. Interestingly, we again obtained the corresponding C-1 arylated product (**4k**) regioselectively. This shows that the methoxy substituent does not function as a

directing group and an electrophilic palladation mechanism may be in operation.

We recently reported the regioselective acylation of carbazoles, wherein acylation selectively occurred on the less hindered carbazole aryl ring.³⁹ Inspired by the current findings, we further extended the scope of carbazole arylation to electron-rich systems. Accordingly, 2-methoxy and 4-methoxy substituted carbazoles afforded the corresponding C-1 acylated products (**4l** and **4m**) regioselectively in good yields. Single crystal XRD analysis of compounds **4g**, **4i**, **4k**, and **4m** further confirmed the structure of the correct regioisomer (Scheme 3).

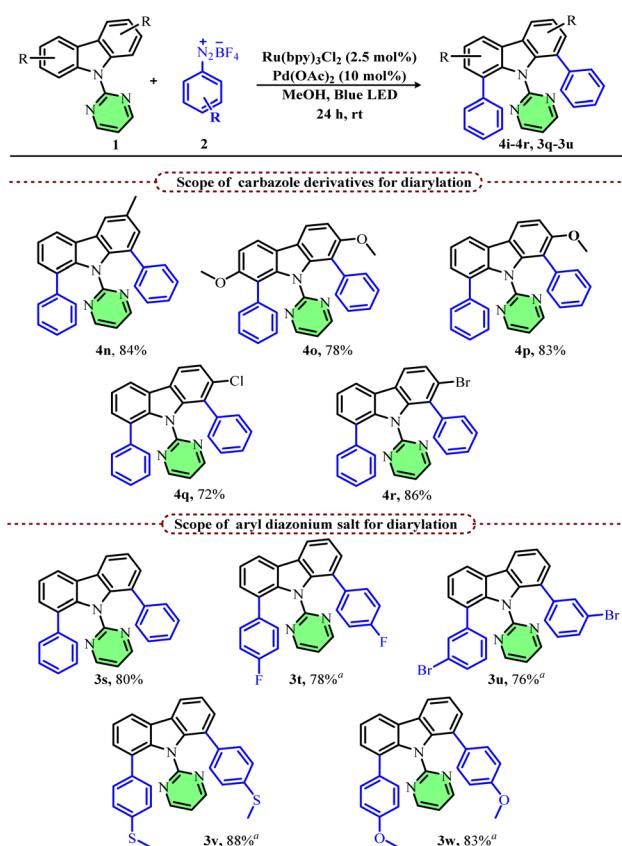
We next demonstrated the diarylation of various symmetrical and unsymmetrical carbazoles since most of the existing methods suffer from controlling the mono vs. diarylation products. After some initial screening, with higher diazonium salt equivalents (6 equiv.), we obtained diarylated carbazoles as the major product. Accordingly, 3-methyl carbazole and 2,7-dimethoxy carbazole afforded the desired diarylated products



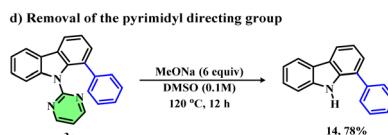
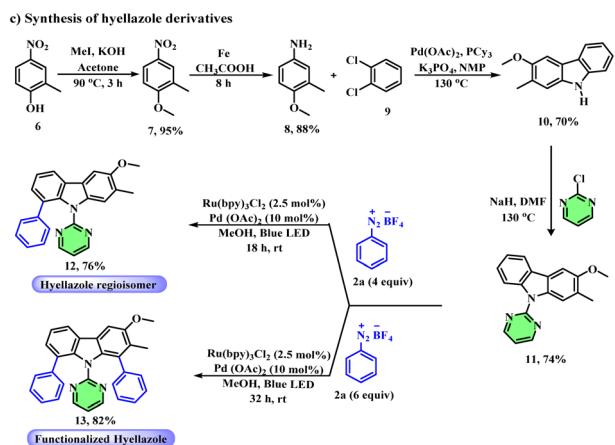
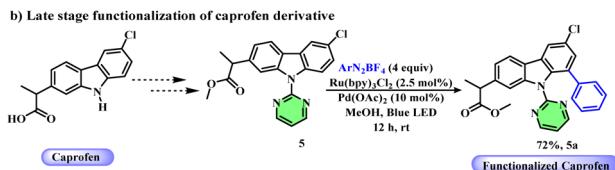
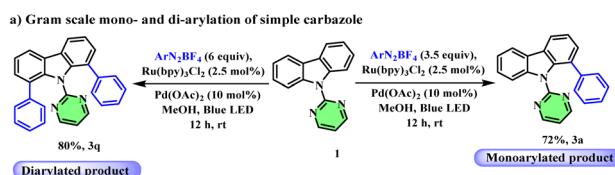
Scheme 3 Scope of aryl diazonium salts for regioselective arylation of carbazoles. Reaction conditions: carbazole 1 (1 equiv.), aryl diazonium salt 2 (4 equiv.), $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (2.5 mol%), $\text{Pd}(\text{OAc})_2$ (10 mol%), in methanol under argon at room temperature for 2–24 h, 44 W blue LED (Kessil). ^a 12 W blue LED, 2–6 h. ^b Regioisomeric ratio.

in good yields (**4n** & **4o**). Unsymmetrical carbazoles having substituents at the C-2 position also afforded the desired diarylated products in good yields (**4p**–**4r**). Furthermore, we investigated the scope of various aryl diazonium salts for the diarylation reaction using carbazole **1a** as the substrate (Scheme 4). A simple aryl diazonium salt afforded the corresponding diarylated product, **3s**, in 80% yield after 24 h, whereas other substituted aryl diazonium salts afforded the desired diarylated products with five equivalents only and in a shorter reaction time (12 h). Both *para*- and *meta*-substituted (**3t** & **3u**) aryl diazonium salts were suitable substrates and afforded the desired products in good yields (**3v** and **3w**).

In order to demonstrate the synthetic utility of our methodology, we focused on the gram-scale synthesis of mono- and di-arylated carbazoles. At first, monoarylation of a simple carbazole was achieved on a gram scale in 72% yield using 3.5 equivalents of aryl diazonium salts under the standard conditions. Similarly, diarylation of a simple carbazole was performed on a gram scale under the standard conditions to afford the desired product in 80% yield (Scheme 5a). Caprofen, a class of NSAID (nonsteroidal anti-inflammatory drugs) commonly used for the treatment of inflammation, con-



Scheme 4 Scope of diarylation reaction with different diazoniums and substituted carbazoles. Reaction conditions: carbazole **1** (1 equiv.), aryl diazonium salt **2** (6 equiv.), $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (2.5 mol%), $\text{Pd}(\text{OAc})_2$ (10 mol%), in methanol under argon at room temperature for 24 h, 44 W blue LED (Kessil). ^a Aryl diazonium salt **2** (5 equiv.).



Scheme 5 Application of the methodology.

tains a carbazole core. Hence, we next attempted the site-selective late-stage functionalization of the caprofen drug derivative, **5**, which afforded the desired product **5a** in 72% yield (Scheme 5b). Next, we demonstrated an efficient route for the synthesis of hyellazole (a marine alkaloid obtained from blue green algae *Hyella caespitosa*) derivatives. Accordingly, we started the synthesis from 4-nitro-*o*-cresol, **6**, which on simple methylation followed by reduction with iron and acetic acid gave 4-methoxy-3-methylaniline **8**. Compound **8** on coupling with 1,2-dibromo benzene **9** using palladium acetate afforded the corresponding carbazole **10**. Finally, the pyrimidine directing group was installed on compound **10** to form carbazole derivative **11**. Compound **11** was first subjected to monoarylation conditions to afford carbazole **12**, a regioisomer of hyellazole in 76% yield. Similarly, compound **11** under diarylation conditions afforded the corresponding aryl functionalized hyellazole derivative **13** in 82% yield (Scheme 5c). Finally, the removal of the pyrimidine directing group from 9-(pyrimidin-2-yl)-9H-carbazole was demonstrated by treating it with sodium methoxide (CH_3ONa) in DMSO at 120 °C for 12 hours to showcase the synthetic versatility of our method (Scheme 5d).



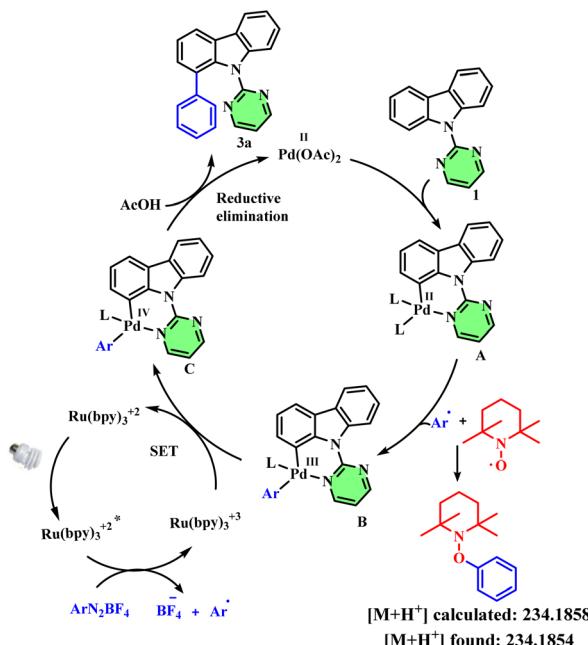


Fig. 1 Proposed reaction mechanism.

Finally, we carried out few mechanistic studies to understand the mechanism of this arylation reaction. Control experiments in the absence of blue LED irradiation led to no product formation. Similarly, in the absence of palladium acetate or the $\text{Ru}(\text{bpy})_3\text{Cl}_2$ photocatalyst, the reaction didn't furnish any desired product (Table S1,[†] entries 9–11). Next, we conducted a radical trapping experiment using TEMPO as the radical scavenger, which didn't afford any desired product, and gave the corresponding aryl-TEMPO adduct (observed in HRMS), thereby confirming the radical pathway. Based on these observations, we propose the following mechanism for the transformation: coordination of palladium(II) acetate with substrate 1 leads to the formation of complex A. Next, the aryl radical generated from the photoredox cycle reacts with complex A to form the corresponding Pd(III) intermediate B. In the photoredox cycle, the Ru^{2+} catalyst upon irradiation with blue light forms the excited-state photocatalyst, which then undergoes SET with the aryl diazonium salt to form the corresponding aryl radical and Ru^{3+} complex. This Ru^{3+} complex then undergoes reduction by accepting an electron from complex B to form Ru^{2+} and Pd(IV) intermediate C. Finally, reductive elimination of intermediate C affords the desired arylated product 3 and regenerates the Pd(II) catalyst (Fig. 1).

4. Conclusions

Herein, we have successfully developed a dual palladium-photoredox strategy for *ortho*-arylation of carbazoles and their derivatives using a pyrimidine directing group under mild conditions. We have achieved regioselective arylation of unsymmetrical carbazoles with good yields and selectivity. The regio-

selectivity of the carbazoles can be controlled by tuning the sterics and electronics of the substituents on the carbazole ring. Similarly, we also demonstrated controlled mono- vs. diarylation of carbazoles by a slight modification of the reaction conditions. In general, both mono- and di-arylation reactions show a broad substrate scope with good functional group tolerance. Next, we showcased the synthetic utility of our method *via* the late-stage functionalization of the caprofen drug derivative and by the synthesis of hyellazole derivatives.

Author contributions

The study was designed and conceptualized by PG and MS. MS and PM carried out all the experiments in consultation with PG. MS and PG wrote the manuscript. All authors agreed on the finalized version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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