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Synthesis of Carbazoles by a Merged Visible Light Photoredox and Palladium-Catalyzed Process

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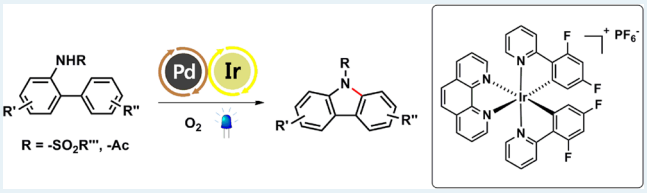
Supporting Information

ABSTRACT: Carbazoles have attracted great interest in recent years for a variety of applications in organic and medicinal chemistry as well as in materials science. In this work, an efficient method for the synthesis of carbazoles through the intramolecular C−H bond amination of *N*-substituted 2-amidobiaryls has been developed. Under visible light and an aerobic atmosphere, the transformation requires only catalytic amounts of $Pd(OAc)_2$ and $[Ir(dFppy)_2phen]PF_6$ (dFppy = 2-(2,4-difluorophenyl)pyridine; phen = 1,10-phenanthroline), the latter of which is utilized in synthetic chemistry for the first time. Spectroscopic and electrochemical studies revealed that the reaction is initiated by photoinduced electron transfer from a palladacyclic intermediate, formed from the 2-amidobiaryl and Pd^{II} species, to the photoexcited Ir catalyst. This step triggers reductive elimination in a Pd^{III}-containing palladacycle to produce the carbazole and a Pd^{I} species. The one-electron-reduced photocatalyst is reoxidized by O_2 to generate the original form of the photocatalyst, and the Pd^{I} species can be oxidized to the resting state through oxidative electron transfer to O_2 or the excited-state photocatalyst.



KEYWORDS: *carbazole, amination, C−H activation, visible light, photocatalysis*

INTRODUCTION

Owing to their occurrence in a large number of bioactive natural products and pharmaceutical agents, carbazoles have garnered significant interest among synthetic organic and medicinal chemists (Figure 1).[1] The carbazole motif is also found in a variety of electronic materials, including photoconducting polymers and organic optoelectronic materials.[2]

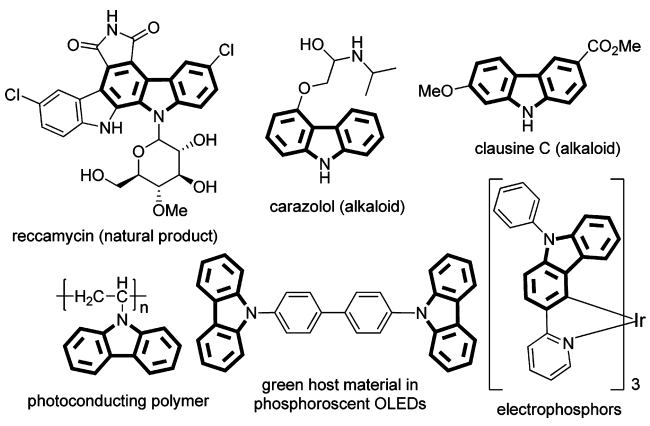


Figure 1. Molecules containing the carbazole structural motif.

Consequently, intense efforts have been devoted toward the development of methods that can be used to prepare substances containing carbazole moieties.[1f,3−13] Among the various routes devised thus far to synthesize these target compounds, transition-metal-catalyzed intramolecular C−H bond amination of *N*-substituted 2-amidobiaryls is perhaps the most atom-economical route (Scheme 1).[12,13]

In 2005, Buchwald and co-workers disclosed that the Pd-catalyzed intramolecular C−H bond amination of 2-acetamidobiaryls resulted in the production of carbazole derivatives by using $Cu(OAc)_2$ as the oxidant.[12a] Later, Gaunt and co-workers showed that *N*-alkyl-substituted (Me, ^{t}Bu, allyl, and benzyl) 2-aminobiaryls could be transformed to *N*-substituted carbazoles upon treatment with stoichiometric quantities of a hypervalent iodine complex in the presence of a Pd catalyst.[12b] Hypervalent iodine complexes were also utilized as oxidants by Chang and co-workers to promote Cu-catalyzed or metal-free carbazole formation from *N*-substituted 2-amidobiaryls.[12c] Youn also reported that carbazoles could be produced by a Pd-catalyzed intramolecular C−H bond amination using oxone as the oxidant in the presence of *p*-TsOH.[12d] Miura and his co-

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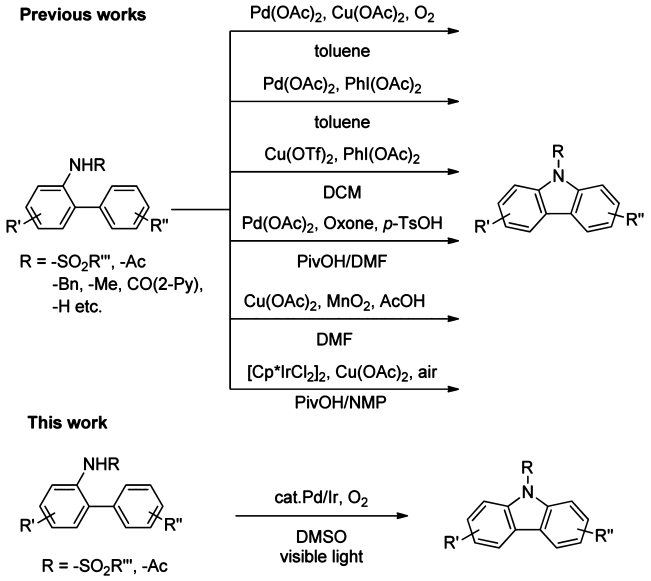
Scheme 1. Intramolecular C−H Bond Amination Reactions of *N*-Substituted Amidobiaryls



workers developed a Cu-catalyzed synthesis using a picolinamide-based bidentate directing group and MnO_2 as terminal oxidant in the presence of AcOH in DMF.[12e] Recently, the same group reported an Ir-catalyzed process of 2-aminobiaryls to 9*H*-carbazoles using $Cu(OAc)_2$ and molecular oxygen as oxidants (Scheme 1).[12g] In addition, organocatalytic intramolecular C−H bond amination of 2-acetamidobiaryls was done by the Antonchick group using 2,2′-diiodo-4,4′,6,6′-tetramethylbiphenyl and AcOOH as an organocatalyst and an oxidant, respectively.[13]

Despite these advances, the processes described above have limitations associated with the requirements of high reaction temperatures and stoichiometric use of strong ground-state oxidants. This raises concerns regarding atom economy and environmental issues. Therefore, a new approach for the highly efficient preparation of carbazoles, with minimal reagent use, is highly desirable.

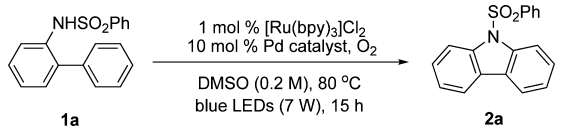
In another arena, visible light photoredox catalysis has attracted substantial attention, owing to its environmental compatibility and versatility in a large number of synthetically important reactions.[14] Recently, visible-light-promoted, single-electron-transfer (SET) processes have been devised for the oxidation or reduction of transition-metal complex intermediates in Ni-,[15] Cu-,[16] Rh-,[17] Au-,[18] and Pd-catalyzed[19] reactions.[14f,g] We envisioned that the combined use of photoredox and transition-metal catalysis would be both environmentally friendly and applicable to the synthesis of industrially important substances. In such processes, the use of photon energy would obviate the need to use strong chemical additives.

Experience gained in earlier studies of photoredox catalysis[20] and C−H bond amination reactions[12] enabled us to design a protocol for the synthesis of *N*-substituted carbazoles where an intramolecular C−H bond amination would take place by visible light irradiation of a solution of a *N*-substituted 2-amidobiaryl in the presence of catalytic amounts of Pd^{II} and a visible-light-absorbing, electron-accepting photocatalyst under an O_2 atmosphere (Scheme 1).

RESULTS AND DISCUSSION

To explore this proposal, a study was conducted using *N*-benzenesulfonyl amidobiphenyl **1a** as the model substrate (Table 1). Visible light irradiation of a solution of **1a** in air-saturated DMSO, containing 10 mol % of $Pd(OAc)_2$ and 1 mol % of $[Ru(bpy)_3]Cl_2$, at 80 °C led to the production of the desired carbazole **2a** in 52% yield (Table 1, entry 1). Notably, strong ground-state oxidants were not required for this Pd-catalyzed reaction. A variety of Pd catalysts were employed in the reaction; $Pd(OAc)_2$, the most widely used catalyst in C−H bond functionalization reactions, was found to be optimal (Table 1, entries 1−6). Control experiments revealed that visible light, the Pd catalyst, the photocatalyst, and molecular oxygen were essential for transformation of **1a** to **2a** (Table 1, entry 1 vs entries 7−10). When the reaction was performed at room temperature, a lower yield of **2a** was obtained (Table 1, entry 11).

Table 1. Palladium Catalyst Screening[a]



1a **2a**

entry	catalyst	yield (%)[b]
1	$Pd(OAc)_2$	52
2	$[Pd(PPh_3)_2]Cl_2$	9
3	$[Pd(CH_3CN)_4](BF_4)_2$	16
4	$Pd(dba)_2$	4
5	$Pd(PPh_3)_4$	27
6	K_2PdCl_4	trace
7	no Pd catalyst	
8[c]	$Pd(OAc)_2$ and no O_2	
9	$Pd(OAc)_2$ and no $[Ru(bpy)_2]Cl_2$	17
10	$Pd(OAc)_2$ and no blue LEDs	18
11	$Pd(OAc)_2$ at room temp	25

[a]Reaction scale: **1a** (0.1 mmol). [b]The yield was determined using gas chromatography. [c]The reaction mixture was deoxygenated by repeating vacuum−freeze−thaw cycles.

The new, merged catalytic, carbazole-forming process was optimized in an exploration examining a variety of Ru-, Pt-, and Ir-based photocatalysts (1 mol %) in the presence of 10 mol % of $Pd(OAc)_2$ in oxygenated DMSO (Table 2). The investigated photoredox catalysts included Pt(ppy)acac (**4**),[20i] $[Ir(ppy)_2(dtbbpy)]PF_6$ (**5**),[21] *fac*-$Ir(ppy)_3$ (**6**), and *fac*-$Ir(dFppy)_3$ (**7**) (Table 2; ppy = 2-phenylpyridinato, acac = 2-acetylacetonate, and dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine). Interestingly, Ir^{III} complexes containing electron-withdrawing ligands, such as *fac*-$Ir(dFppy)_3$ (**7**), $[Ir(dFppy)_2phen]PF_6$ (**8**), and $[Ir(dCF_3ppy)_2phen]PF_6$ (**9**; dCF_3ppy = 2-(2,4-bis(trifluoromethyl)phenyl)pyridinato), promoted the highest yielding reactions (**7**, 83%; **8**, 95%; **9**, 95%). On the basis of these observations, $[Ir(dFppy)_2phen]PF_6$ (**8**) was selected for use in further studies because it is more readily available than $[Ir(dCF_3ppy)_2phen]PF_6$ (**9**). It is noted that the synthetic utility of the complexes **8** and **9**[22] has yet to be fully evaluated to date.

The effects of several parameters, including solvent, temperature, and concentration, on the efficiency of the reaction were also examined. Among various solvents, including DCM, DMSO, DMF, and MeOH, DMSO showed the best reactivity

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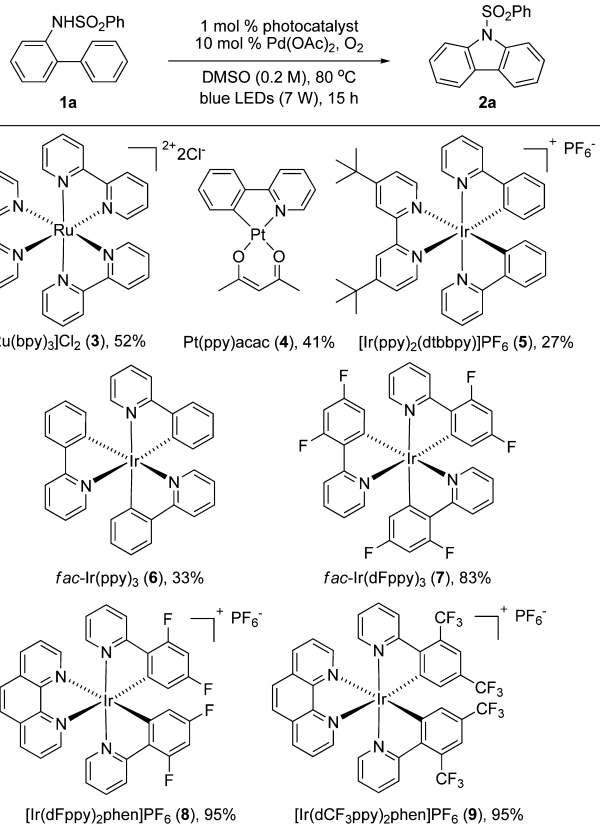
Table 2. Photocatalyst Screening[a,b]

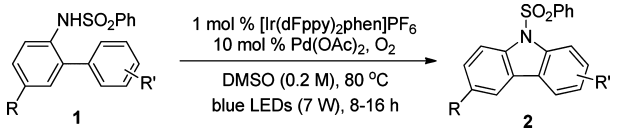


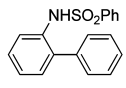
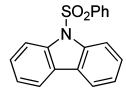
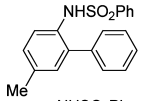
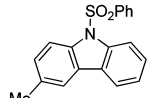
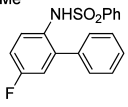
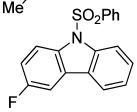
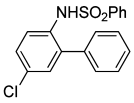
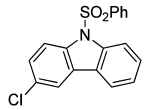
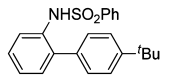
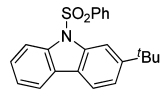
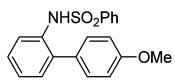
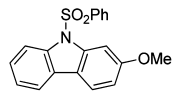
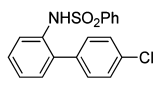
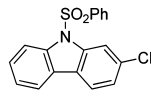
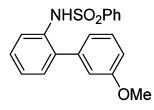
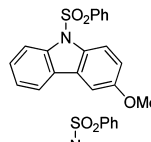
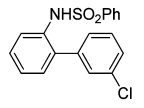
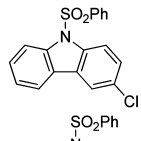
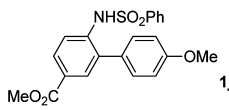
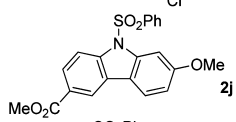
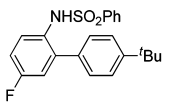
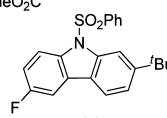
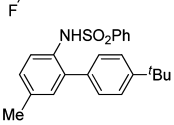
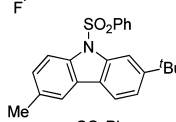
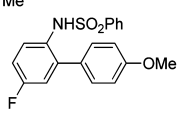
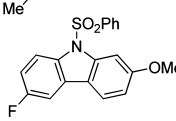
[a]Reaction scale: **1a** (0.1 mmol). [b]The yield was determined using gas chromatography.

for the transformation. Although the reaction proceeded at lower temperatures (25, 40, and 60 °C), 80 °C was chosen for the higher efficiency and reproducibility of the process. The highest yielding process occurred when 10 mol % of $Pd(OAc)_2$ and 1 mol % of $[Ir(dFppy)_2(phen)]PF_6$ (**8**) were utilized in 0.20 M DMSO under an oxygen atmosphere and visible-light irradiation at 80 °C. Using these conditions, the substrate scope of the carbazole-forming process was investigated. A variety of *N*-benzenesulfonyl amidobiaryls were converted to the corresponding *N*-benzenesulfonyl carbazoles in good to excellent yields (Table 3). Importantly, while the efficiencies of previous reactions employed in other methods depended on the substitution pattern of the amidobiaryls,[12c] the yields obtained using this approach were not significantly altered by the electronic properties or positions of aryl ring substituents. Substrates **1d,i**, which contain Cl groups at different positions but both generate 3-chloro-9-(phenylsulfonyl)-9*H*-carbazole (**2d**), reacted with nearly equal efficiencies (Table 3, entries 4 and 9). Notably, the reactions of **1h,i**, which have the potential of producing two regioisomeric carbazoles, generated the single carbazoles **2h,i**, respectively, as a consequence of steric effects (Table 3, entries 8 and 9).

Not only *N*-benzenesulfonyl amidobiaryls but also heteroatom-containing substrates worked for this process. Although the reactivity was not as good as those of simple biaryl systems, *N*-(2-(thiophen-3-yl)phenyl)benzenesulfonamide (**10**) smoothly underwent C−H amination to produce the tricyclic system **11** (Scheme 2). Notably, the process was highly regioselective, producing only the isomer **11**, where heteroatoms N and S have a syn orientation.

Table 3. Substrate Scope of the Intramolecular C−H Bond Amination Reaction of *N*-Benzenesulfonyl Amidobiaryls[a]



entry	substrate		product		isolated yield[b]
1		**1a**		**2a**	94
2		**1b**		**2b**	83
3		**1c**		**2c**	80
4[c]		**1d**		**2d**	85
5		**1e**		**2e**	92
6		**1f**		**2f**	85
7[c]		**1g**		**2g**	81
8		**1h**		**2h**	80
9[c]		**1i**		**2i (2d)**	81
10		**1j**		**2j**	86
11[c]		**1k**		**2k**	80
12		**1l**		**2l**	83
13		**1m**		**2m**	84

[a]Reaction scale: **1** (0.3 mmol). [b]Isolated yield based on an average of two runs. [c]15 mol % of $Pd(OAc)_2$ was used.

The effects of N substituents on the efficiencies of the reaction were also explored (Table 4). *N*-sulfonyl-containing (*p*-toluenesulfonyl (**12**) and methylsulfonyl (**14**)) and *N*-acetyl-containing (**16a**) substrates reacted to produce the corresponding *N*-substituted carbazoles (Table 4, entries 1−3).

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Scheme 2. Intramolecular C−H Amination of *N*-(2-(thiophen-3-yl)phenyl)benzenesulfonamide

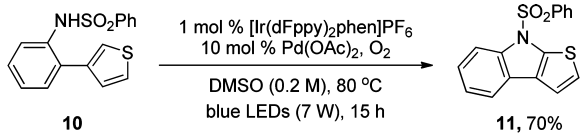
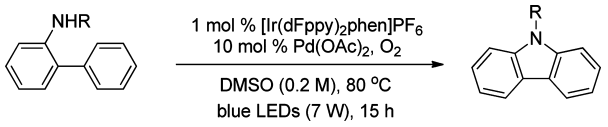
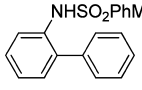
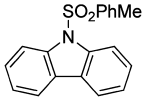
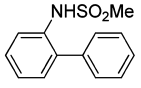
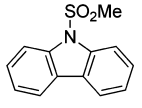
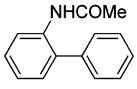
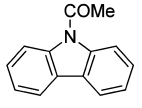
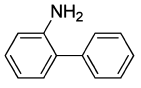
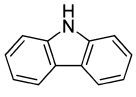
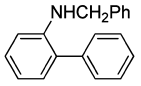
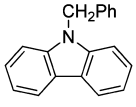
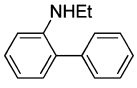
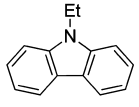


Table 4. *N*-Substituent Effects[a]



entry	substrate		product		isolated yield[b]
1		**12**		**13**	93
2[c]		**14**		**15**	89
3[c]		**16a**		**17a**	81
4		**18**		**19**	trace
5		**20**		**21**	trace
6		**22**		**23**	trace

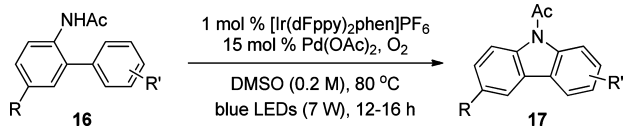
[a]Reaction scale: substrate (0.3 mmol). [b]Isolated yield based on an average of two runs. [c]15 mol % of $Pd(OAc)_2$ was used.

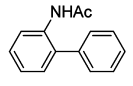
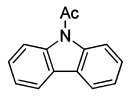
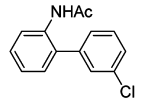
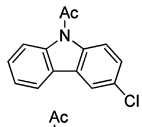
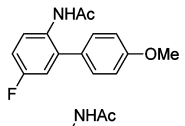
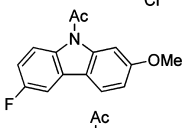
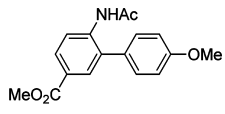
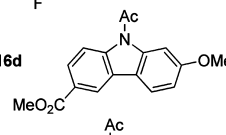
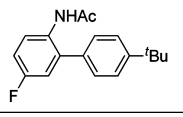
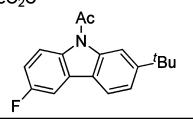
However, 2-aminobiphenyl (**18**) and *N*-alkyl-substituted aminobiphenyls, such as benzyl (**20**) and ethyl (**22**), did not undergo the intramolecular C−H amination (Table 4, entries 4−6).[23]

Specifically, 2-acetamidobiaryls containing both electron-donating and electron-withdrawing aryl substituents reacted smoothly to form the corresponding *N*-acetylcarbazoles (Table 5). The reactivities of the *N*-acetyl substrates were lower than those of their *N*-benzenesulfonyl analogues, as 15 mol % of $Pd(OAc)_2$ was required to drive these reactions to completion. However, the relatively facile removal of *N*-acetyl as compared to *N*-sulfonyl groups makes the use of 2-acetamidobiaryls (**16**) more practical.

The results described above clearly demonstrate the feasibility and scope of the merger of $Pd(OAc)_2$ and Ir^{III} photoredox catalysts for transformation of amidobiaryls to the corresponding carbazoles. To further explore the utility of our method, we attempted the preparation of clausine C (an alkaloid; Figure 1) using the merged catalysis. The intermediate, the acetylated carbazole **17d** (Table 5, entry 4),

Table 5. Substrate Scope of the Intramolecular C−H Bond Amination Reaction of 2-Acetamidobiaryls[a]

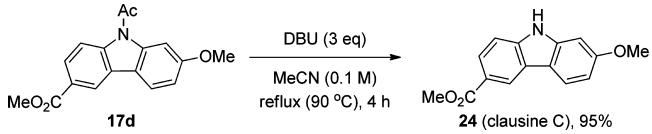


entry	substrate		product		isolated yield[b]
1		**16a**		**17a**	81
2		**16b**		**17b**	75
3		**16c**		**17c**	83
4		**16d**		**17d**	82
5		**16e**		**17e**	76

[a]Reaction scale: **1** (0.3 mmol). [b]Isolated yield based on an average of two runs.

was prepared according to our protocol. **17d** was then converted to clausine C by deacetylation under basic conditions (Scheme 3). This demonstration illustrates that the merged catalysis is applicable to production of pharmaceutically and industrially relevant compounds.

Scheme 3. Synthesis of an Alkaloid, Clausine C, through Deacetylation of 17d



As the final phase of our study, spectroscopic and electrochemical investigations were performed in order to gain insight into the reaction mechanism. The UV−vis absorption spectrum of a DMSO solution containing $Pd(OAc)_2$ and **1a** preincubated at 80 °C for 12 h under an anaerobic atmosphere differed significantly from that of DMSO solutions of **1a** or $Pd(OAc)_2$ (Figure S1, Supporting Information). This observation may be indicative of generation of a palladacycle. We obtained ESI-MS (positive) spectra, which revealed the presence of $[KPd^{II}(\mathbf{1a}\text{-H})(DMSO)_3]^+$, supporting this notion (Figure S2, Supporting Information). The formation of a trinuclear carbopalladacycle of amidobiaryls under similar conditions was reported by Gaunt and co-workers.[12b] We hypothesized that the palladacycle might be the key species responsible for SET with the photoexcited Ir catalyst. Comparisons of the oxidation potentials (E_{ox}) of **1a** (1.86 V vs SCE), **2a** (1.83 V vs SCE), and the palladacycle of **1a** (1.21 V vs SCE) with the excited-state reduction potential of **8** (E^*_{red}

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= 1.49 V vs SCE) revealed that exoergic SET to the excited state of **8** (**8***) is allowed only from the palladacycle with a positive driving force of 0.28 eV (Figure S3, Supporting Information). Actually, the phosphorescence lifetime of **8*** decreased in a concentration-dependent manner from 1.48 to 0.986 μs upon the addition of the palladacycle (0–0.800 mM; Figure 2a). A pseudolinear fit of the data yielded an electron-

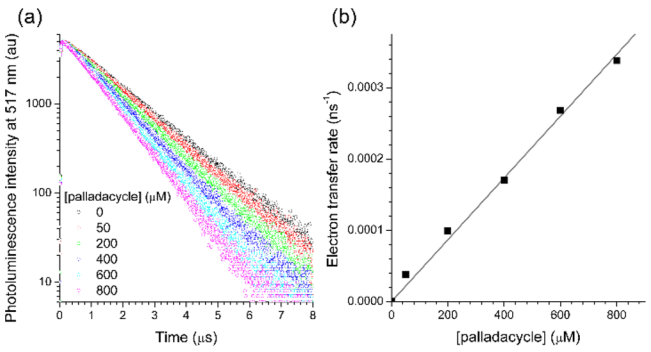

Figure 2. (a) Phosphorescence decay traces of 1.00 mM [Ir(dFppy)$_2$(phen)]PF$_6$ (**8**) (deaerated DMSO) with increasing concentrations of the palladacycle (0–0.800 mM) (λ_{ex} = 377 nm, λ_{obs} = 571 nm, temporal resolution = 8 ns). (b) Pseudolinear fit of the electron transfer rates, which were obtained from the electron transfer rate = $1/\tau - 1/\tau_0$, to the concentration of the palladacycle. τ and τ_0 correspond to the observed phosphorescence lifetimes in the presence and absence of palladacycle, respectively.

transfer rate constant of (4.33 ± 0.09) × 10^8 M^{-1} s^{-1}, which corresponded to a SET rate that was ca. 15 and 2 times faster than those for the radiative (k_r = 5.73 × 10^4 s^{-1}) and nonradiative (k_{nr} = 4.64 × 10^5 s^{-1}) decay of 2.0 mM **8** (Figure 2b).[22] The SET involved oxidation of Pd^{II} in the palladacycle, as similar photoinduced reductive quenching of **8*** by Pd(OAc)$_2$ occurred with a relatively smaller rate constant ((3.98 ± 0.12) × 10^8 M^{-1} s^{-1}; Figure S4, Supporting Information). As expected, phosphorescence quenching of **8*** did not take place in the presence of **1a** and **2a** (Figure S5, Supporting Information).

In the ensuing steps in the mechanistic pathway, the one-electron-reduced photocatalyst is oxidized to re-form **8** upon donation of the extra electron to O$_2$. The Pd^{III} palladacycle undergoes reductive elimination to produce a C–N bond as part of the carbazole ring system, as well as a Pd^{I} species. Since the redox potential of Pd$^{II/I}$ should be more cathodic than that of Pd$^{III/II}$, the Pd^{I} species should be capable of reducing the photoexcited catalyst. However, direct monitoring of this process was presumably hampered by the short lifetime of this transient species.

These results enabled us to postulate a plausible mechanism for the carbazole-forming reaction (Figure 3). In the initial step of the route, coordination of the amido group of **1a** to Pd(OAc)$_2$ facilitates cyclopalladation, leading to the six-membered palladacycle **1A**.[12a] The palladacycle, having a Pd^{II} oxidation state, is oxidized to a Pd^{III} complex by SET to the photoexcited Ir catalyst (i.e., *[Ir^{IV}(dFppy)$_2$phen$^{\bullet-}$]$^+$), with generation of the one-electron-reduced catalyst [Ir^{III}(dFppy)$_2$phen$^{\bullet-}$]^0. Reductive elimination of the Pd^{III} palladacycle leads to the formation of carbazole **2a** and a Pd^{I} species (path A). The Pd^{I} species is subsequently oxidized to generate the original Pd^{II} complex through SET to the photoexcited Ir catalyst or molecular oxygen. However, it is

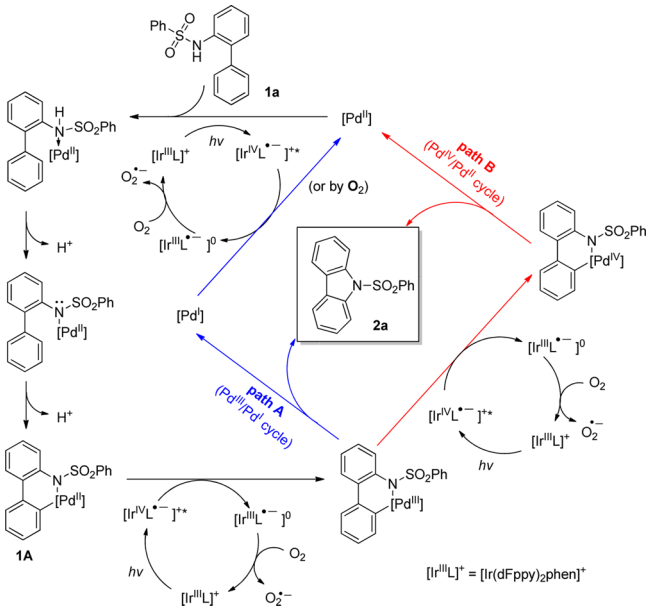

Figure 3. Proposed mechanism for C–H bond amination reactions of *N*-substituted amidobiaryls.

not possible to rule out a mechanism that follows path B, in which one-electron transfer to the photoexcited catalyst from a Pd^{III} intermediate occurs prior to reductive elimination (i.e., *[Ir^{IV}(dFppy)$_2$phen$^{\bullet-}$]$^+$ + Pd^{III} → [Ir^{III}(dFppy)$_2$phen$^{\bullet-}$]^0 + Pd^{IV}).[24] In either case, the one-electron-reduced Ir catalyst donates one electron to dioxygen with a positive driving force of 0.65 eV (e[E_{red}([Ir(dFppy)$_2$phen]$^+$) − E_{red}(O$_2$)]; E_{red}([Ir(dFppy)$_2$phen]$^+$) = −1.30 V vs SCE and E_{red}(O$_2$) = −0.75 V vs SCE), being restored to its original state. Alternatively, *[Ir^{IV}(dFppy)$_2$phen$^{\bullet-}$]$^+$ can be oxidatively quenched to [Ir^{IV}(dFppy)$_2$phen]$^{2+}$ by O$_2$, followed by SET from the palladacycle (i.e., [Ir^{IV}(dFppy)$_2$phen]$^{2+}$ + Pd^{II} → [Ir^{III}(dFppy)$_2$phen]$^+$ + Pd^{III}). Since one-electron oxidation of **8** occurs at 1.58 V vs SCE, the driving force for the generation of the Pd^{III} species is greater than the case for **8*** by 0.09 eV. This may be indicative of a preference for the oxidative quenching pathway, but it is likely that both reductive and oxidative quenching of **8*** would be operative.

CONCLUSION

In conclusion, in the investigation described above we have developed an efficient method for the synthesis of *N*-substituted carbazoles, which involves intramolecular C–H bond amination of *N*-substituted 2-amidobiaryls. The process utilizes the merged visible light photoredox and Pd catalysis and, as such, does not require strong oxidants for regeneration of the Pd catalyst. In addition, observations made in electrochemical and transient photoluminescence spectroscopy studies showed that the catalysis is initiated by SET from a palladacyclic intermediate to the photoexcited Ir complex. Moreover, the photocatalyst is regenerated by molecular oxygen promoted oxidation of its reduced form, and the catalytic Pd^{II} species is regenerated by SET from a Pd^{I} species to molecular oxygen or the excited photocatalyst. The strategy employed in this study, which combines transition-metal catalysis and photocatalysis and negates the use of stoichiometric amounts of harsh or potentially toxic chemical additives,

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might be applicable to the development of other environmentally benign reactions.

EXPERIMENTAL SECTION

Synthesis of *N*-Benzenesulfonyl Carbazole (2). An oven-dried resealable tube equipped with a magnetic stir bar was charged with the *N*-benzenesulfonyl amidobiaryl compound **1** (0.3 mmol), $Pd(OAc)_2$ (10 mol %, 0.03 mmol), and $[Ir(dFppy)_2(phen)]PF_6$ (**8**; 1 mol %, 0.003 mmol) in DMSO (1.5 mL, 0.2 M). Then oxygen gas was bubbled through the reaction mixture for 3 min and the tube was sealed with a silicone septum screw cap. The tube was then placed under blue LEDs (7 W) at 80 °C. The progress of the reaction was checked by TLC or gas chromatography. The reaction mixture was then diluted with dichloromethane (DCM) and washed with brine. The organic layer was dried over $MgSO_4$, concentrated under vacuum, and purified by flash column chromatography to furnish the pure *N*-benzenesulfonyl carbazole **2**.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00817.

Experimental procedures, additional experimental data, analytical data, and ^1H and ^{13}C NMR spectra of compounds (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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