

Exogenous Photocatalyst-Free Aryl Radical Generation from Diaryliodonium Salts and use in Metal-Catalyzed C–H Arylation

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ABSTRACT: Herein, we demonstrate 1) that Lewis base heteroatom coordination to diaryliodonium salts is not required for light-driven radical generation and 2) radicals generated by this route can be captured by transition-metals for coupling reactions. These results are the first step toward developing new aryl radical coupling reactions without exogenous photocatalysts.

Hypervalent iodine molecules have a rich history in organic synthesis as mild, non-toxic reagents, and oxidants.¹ Specifically, cationic diaryl-containing I(III) (Ar_2I) salts function as arylation reagents.² The attractiveness of these Ar_2I salts result from their robust preparatory methods,³ exceptional bench stability,⁴ and broad functional group (FG) tolerance. Aside from ground state arylation reactions,⁵ excited state photoredox reactions employing Ar_2I salts as aryl radical precursors have emerged as powerful tools for selective arylation under mild conditions.⁶

Alternatively, reactions induced by light, but without a photocatalyst (PC), are of particular interest for future sustainability.⁷ In general, PC-free photolysis of Ar_2I salts historically required UV light.⁸ However, visible light induced PC-free radical generation reported by Chatani and coworkers demonstrated that *N*-methylpyrrole solutions of Ar_2I salts furnish aryl radicals that arylate the pyrrole C2–H bond (Figure 1a).⁹ Karchava et al.¹² and Lakhdar et al.¹⁰ separately showed that neutral PR_3 Lewis bases (LBs) were more efficient activators of Ar_2I salts than pyrrole and underwent P-arylation by irradiation with purple or blue LEDs (b). In these approaches, aryl radical generation and recombination occurs rapidly within the solvent cage to yield arylation of the activator molecule.¹¹ Murarka et al. overcame this limitation by discovering a PC-free, light-driven 3-component system to activate Ar_2I salts (c).¹² Critical for photoactivity in most of these investigations is the formation of a ground state electron-donor-acceptor (EDA) complex between the activator(s) heteroatom and the Ar_2I salt, which is the intermediary species responsible for absorbing photons.

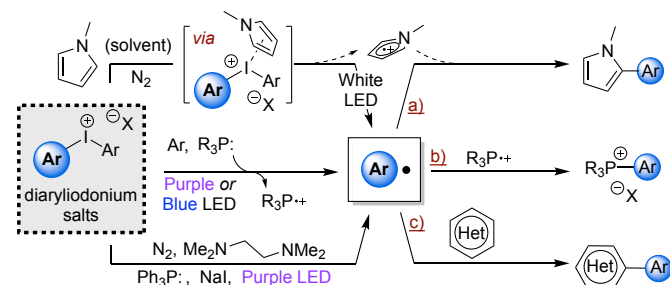


Figure 1. Known excited-state PC-free activations and reactions of Ar_2I salts (a-c).

Herein, we present strong evidence suggesting against a ground state heteroatom→I coordination-based EDA adduct to achieve PC-free aryl radical generation using Ar_2I salts. To support this assertion, a series of stoichiometric reactions, kinetic rate measurements, and NMR experiments demonstrate the importance of LB conjugation and electronics rather than the basicity of any Lewis basic

coordinating heteroatoms. Lastly, since literature precedents have focused on trapping aryl radicals using organic molecules like alkenes (e.g., Meerwein arylation)¹³ or heteroarenes,¹² we demonstrated that our PC-free aryl radical generation strategy can be interfaced with Pd-catalyzed C–H activation processes to achieve site-selective arylation of C–H bonds. Altogether, our results show that this PC-free, light-driven radical generation strategy is operationally simple and can be leveraged to create new organometallic arylation reactions using Ar_2I salts without expensive PCs.

Lewis bases as Ar_2I activators. We started by surveying a range of Lewis basic molecules to ascertain their ability for aryl radical generation from diphenyliodonium salt **2a** ($[\text{Ph}_2\text{I}][\text{OTf}]$) under purple LED irradiation. To quantify Ph^\bullet generation, we leveraged B_2Pin_2 ($\text{BPin} = 4,4,5,5\text{-tetramethyl-1,3-dioxaborolane}$), which is a commonly employed aryl radical trap,¹⁴ to furnish Ph-BPin **3**. In the absence of any LB activator, **3** was generated in $13 \pm 2\%$ yield after 4 hours. As such, additives providing yields $>20\%$ are considered beneficial and those giving yields $<20\%$ are classified as inactive (Figure 2).

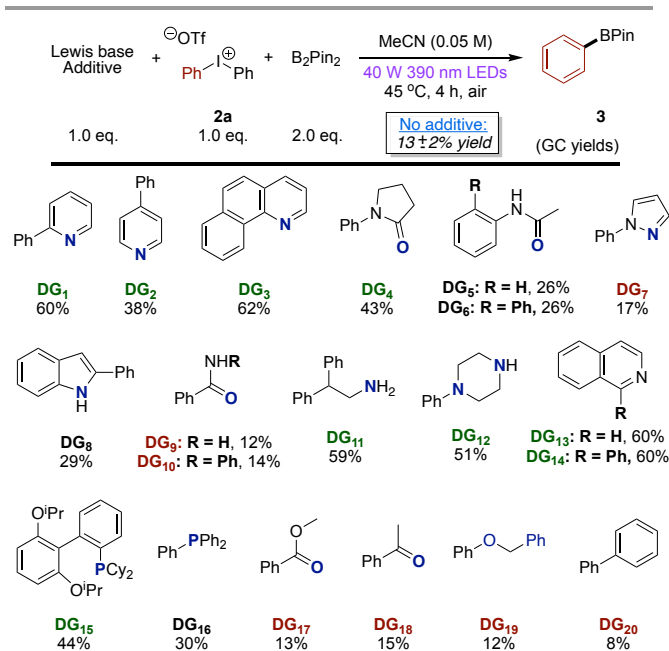


Figure 2. Different Lewis base additives demonstrate different abilities to furnish borylation products from **2a**. GC yields are calibrated vs. mesitylene as internal standard.

By these metrics, **DG**_{7,9-10,17-20} were ineffective. In contrast, we rated the best activators as those providing **3** in >40% yield (**DG**_{1-4,11-15}). Lastly, moderate activators gave **3** in 20-39% yield (**DG**_{5-6,8,16}), which is still sufficient to observe useful arylation reactivity. The classification of bulky **DG**₃ and **DG**₁₅ as good additives is unexpected since they are likely too sterically encumbered to coordinate the Ph₂I fragment. This result supports the conclusion that LB heteroatom→I coordination may not be a critical element enabling photoactivity in our system and non-covalent effects might be involved.

Impact of activator electronic properties. **DG**₁₋₁₉ in Figure 2 consist of two components: a Lewis basic heteroatom and a proximal aryl ring. We set out to determine which component plays a greater role in governing the activator's ability using borylation as a model reaction. We first confirmed that radical capture by B₂Pin₂ is not subject to concentration effects by showing a zero-order rate dependence of **3** formation on the [B₂Pin₂] (SI Figure S20). Thus, reaction rates are governed by the aryl radical generation step. Using a range of electronically diverse 2-arylpiperidines (**1a-j**) as activators, we monitored the initial rate of borylation by gas chromatography (Figure 3). The background rate of **3** formation in the absence of any activator was 9.89 × 10⁻⁵ Mmin⁻¹, which is identical to the reaction rate in the presence of ineffective pyridine.⁹

Interrogating the impact of the activator C2-aryl ring on Ph-BPin formation, mesomeric FG incorporations (**1d-f**) led to higher borylation rates than inductive FGs (**1a-c**). Surprisingly, a bulky phenyl group at the *ortho* position of the flanking ring (**4b**) led to notably faster formation of **3** than any other pyridine derivative surveyed here. Like mesomeric groups, extended conjugation impacts the energetics of the activator's aromatic π-system, which is a strategy to impact photophysical properties.¹⁵ In line with this phenomenon, using conjugated and bulky **DG**₃ as activator led to *k*_{rel} = 97 (Figure S34). Further supporting our hypothesis that LB coordination to Ar₂I may not be critical, the most coordinating derivative **1h** gave slower reaction rates than less basic **1i-j**, which is opposite the expected outcome if an association step is required.

Mechanistic insights. We began by gathering support that aryl radicals are formed under our conditions in two ways (Figure 4). First, borylation reactions in the presence of 2,2,6,6-tetramethyl-piperidine-*N*-oxide (TEMPO) show severely diminished yields relative to reactions without TEMPO (16% versus 60% yield, respectively).

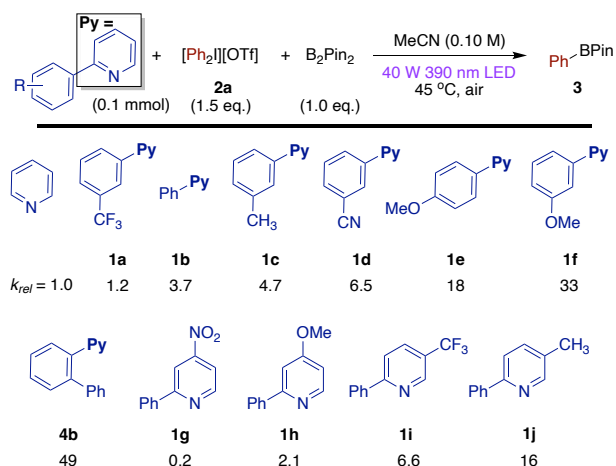


Figure 3. Relative rates of aryl radical borylation using 2-arylpiperidines depend on pyridine electronics. All *k*_{rel} are reported as relative to the rate of borylation with no additive.

Secondly, to address arguments regarding potential B₂Pin₂ non-innocence in promoting aryl radical generation,¹⁶ we tested our radical generation strategy using 1,1-diphenylethylene as the radical trap, which led to 30% 1,1,2-triphenylethylene (TPE) yield by GC. Like borylation reactions, alkene arylation in the presence of TEMPO was diminished (18% TPE yield), further supporting a radical mechanism.

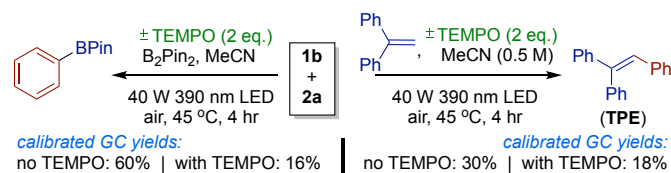


Figure 4. TEMPO inhibition and alternative radical trapping reagents using equimolar mixtures of **1b** and **2a** support a radical mechanism.

In the works of Chatani,⁹ Karchava,^{10a-c} and Lakhdar,^{10d,10e} association of the activator to the Ar₂I iodine atom was a critical factor enabling photoactivity. Sanford and coworkers previously demonstrated that 2-arylpiperidines bind to iodonium salts with *K*_{eq} > 100 in AcOH solvent.^{5c} In contrast, we do not observe evidence of any room temperature association between **DG**₃ or **1b** and **2a** as determined from lack of changes in i) solution colors (Figure 5a), ii) UV-Vis spectra (b), and iii) ¹H NMR spectra. To further probe whether a heteroatom-centered EDA complex forms and dissociates faster than the NMR time scale, we collected variable temperature (VT) ¹H NMR spectra for combinations of **DG**₃ and **2a** from -50 to +50 °C in CD₃OD (c). Importantly, MeOH as solvent in **2a** borylation reactions was comparable to reactions performed in MeCN (SI Figure S18). At each temperature surveyed, no notable changes were observed in the relevant **DG**₃ C-H chemical shifts.^{10e} Thus, on the basis of these data, we can conclude that LB heteroatom coordination to **2a** is not a critical intermediate preceding radical generation.

In further support of this assertion, our measured arene borylation rates using 2-phenylpyridine derivatives (**1b, 1g-j**) in Figure 3 display a non-linear correlation between p*K*_aH and borylation rate (d). This observed non-linearity can only be rationalized if any adducts formed within the mixture do not contain a heteroatom→I covalent interaction as part of the aryl radical generation event.

Radical capture by a Pd. While our ability to perform aryl radical borylation will set the stage for the development of other PC-free arylation processes of organic molecules, we were determined to interface our radical generation approach with Pd-catalyzed C–H arylation. Sanford et al. leveraged aryl radicals derived from Ar₂I salts and an Ir-based fluorophore to perform Pd-catalyzed C–H arylation at room temperature^{6g} without using explosive¹⁷ diazonium salts.¹⁸ We set out to demonstrate that our protocol would enable analogous arylations of C(*sp*²)-H bonds without a PC. Importantly, control reactions without Pd or light failed to provide detectable concentrations of arylated products. The full set of optimization and control experiments can be found in the supplementary information.

Using 2-arylpiperidines as both activator of **2a** and substrate for Pd, we sought to correlate pyridine structure to overall arylation capability. We used GC-FID to determine approximate total arylation for a range of pyridine derivatives under the conditions depicted in Figure 6. When total arylation percentage was plotted versus the Hammett σ value for each FG, a clear correlation was revealed. Electron-richness at the presumed site of C–H arylation led to high arylation percentages.

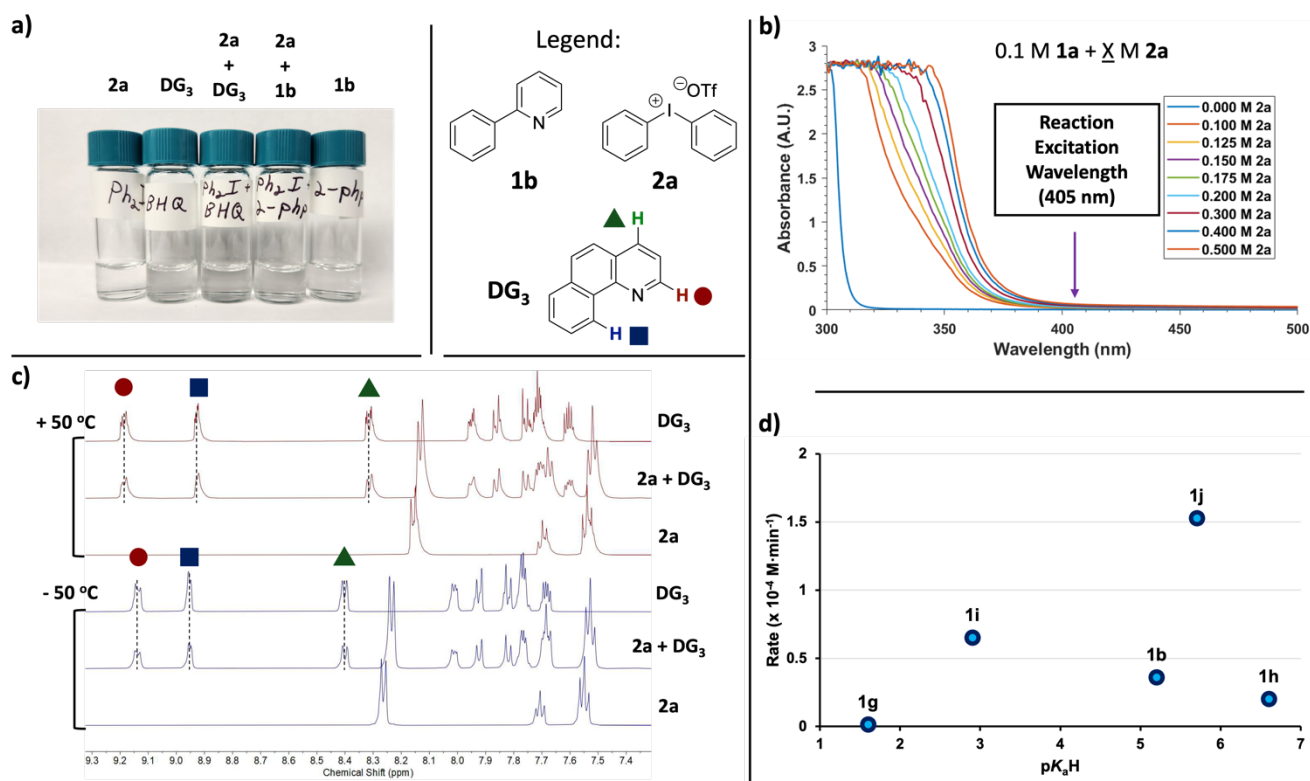


Figure 5. Mechanistic insights for the PC-free radical generation from Ar₂I salts with LBs. (a) Photographs of mixtures of **1b** or **DG₃** with **2a** demonstrating no color changes. (b) Stacked UV-Vis spectra of **1a** in the presence of increasing concentrations of **2a** showing no appearance of EDA absorbance bands. (c) 1D VT ¹H NMR spectra of a stoichiometric mixture of **DG₃** and **2a** at -50 and +50 °C depicting no shift in the C2-H (circle), C4-H (triangle), or C10-H (square) resonances of **DG₃**. (d) Plot of borylation rate vs. pK_aH of the activator showing non-linear behavior. Note: pK_aH values are of mono-substituted pyridines without the 2-phenyl group since the presence of this group is common to the depicted activators.

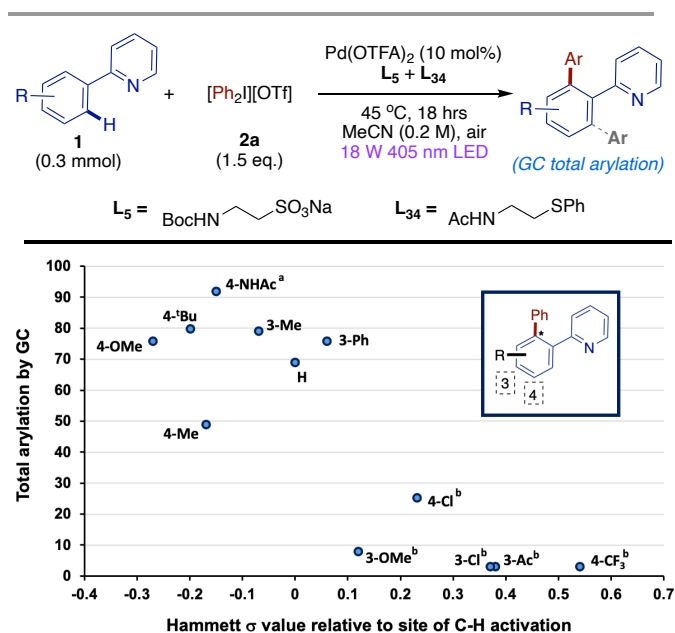


Figure 6. Visualization of approximate total arylation observed by GC-FID correlates to pyridine substrate electronic properties. ^aPresumed site of arylation shown only for Hammett value trend determination. Internal standard was mesitylene. ^bMultiple mono-arylation regioisomers observed. ^bPerformed on a 0.1 mmol scale.

In contrast, decreasing FG donor ability (i.e., as Hammett parameter increases) results in little to no arylation. In general, FGs with σ values greater than 0.1 gave minimal quantities of arylated products. Interestingly, substrate **1e** furnished 8% total Pd-catalyzed arylation despite demonstrating high rates of arene borylation in Figure 3. This example suggests observed limitations lie with the Pd-catalyzed process rather than aryl radical generation.

During our experiments, only acetamide as the FG on 2-phenylpyridine gave a second mono-arylation regioisomer, which we attributed to arylation via the directing capability of the amide function. Since acetanilides are capable of furnishing borylation products by our light-driven approach (see **DG_{5,6}**) and they have been previously used in C–H arylation reactions catalyzed by Pd,^{18c,19} we also showed that our light-driven strategy was applicable to Pd-catalyzed acetanilide arylation. After devising a new set of standard conditions, we found analogous trends for acetanilide directed C–H arylation as compared to pyridine substrates in Figure 6. A full accounting of these outcomes is presented in the SI.

Conclusions. In contrast to literature precedent, we discovered that combinations of simple LBs with diaryliodonium salts do not form heteroatom-involved EDA adducts prior to PC-free aryl radical generation when irradiated with purple LEDs. This conclusion was drawn from ocular spectroscopy of colorless reaction mixtures, VT NMR, UV-Vis spectroscopy, and kinetic rate measurements. After demonstrating that a wide variety of LBs enable PC-free aryl radical

generation, we interfaced our radical generation strategy with Pd-catalyzed C–H arylation to obtain biaryl products. Ongoing investigations in our laboratory are focused on elucidating the mechanism by which radical generation occurs in this study and strategies to further enhance reaction efficiency.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details; characterization data of novel compounds or isolated products; methods, and results (PDF). NMR spectra of prepared substrates or reagents and isolated products (PDF).

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Notes

The authors declare no competing financial interest.

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