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

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Supporting Information Placeholder
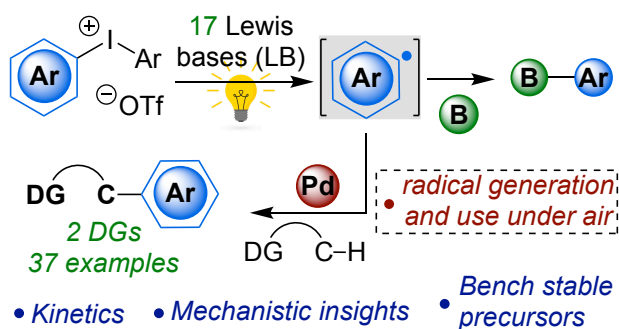
ABSTRACT: While photocatalysts are generally responsible for radical generation from bench stable diaryliodonium salts, recent reports have emerged exhibiting photocatalyst-free radical generation using select Lewis bases as activators. Herein, we demonstrate 1) the ability of numerous Lewis bases to enable light-driven radical generation and 2) these radicals can be captured by transition-metals for coupling reactions. These results are the first step toward developing new organometallic aryl radical coupling reactions without photocatalysts.

Hypervalent iodine molecules have a rich history in organic synthesis as mild, non-toxic reagents, and oxidants.[1] Within this class of compounds, cationic diaryl-containing I(III) salts function exclusively as arylation reagents.[2] The attractiveness of these diaryliodonium (Ar₂I) salts are the result of robust preparatory methods, exceptional bench stability, and broad functional group (FG) tolerance.[3] While Ar₂I salts can be activated in ground state processes by transition-metal (TM) complexes[4] or attacked by nucleophiles[5] to furnish arylated products, excited state photoredox reactions employing Ar₂I 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 a seminal contribution, Chatani and coworkers demonstrated that N-methylpyrrole solutions of Ar₂I salts generate aryl radicals when irradiated by white LEDs, which selectively arylate the pyrrole C2–H bond (Figure 1a).[8] Years later, Karchava et al. discovered that phosphines[9] and phosphinamines[10] were more efficient activators of Ar₂I salts than pyrrole and underwent P-arylation under purple LED irradiation, furnishing phosphonium salts (b). In these cases, aryl radical generation and recombination occurs rapidly to yield arylation of the activator molecule.[11] Murarka et al. overcame this limitation by creating a PC-free, light-driven 3-component activator system to activate Ar₂I salts (c).[12] While this report serves as an exciting development, a broader array of Lewis bases and single component catalyst systems would provide additional opportunities when creating new

radical reactions, especially those using TM-based catalysts, which are unknown in PC-free approaches.
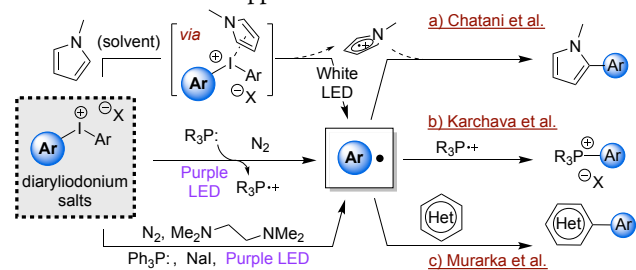

Figure 1. Critical excited-state PC-free activations and reactions of Ar₂I salts (**a-c**).

Herein, we report that numerous Lewis bases (LBs) under purple LED irradiation can function as activators of Ar₂I salts. Through a series of kinetic rate measurements, we conclude that the electronic parameters of the adjacent aryl ring are more important than the basicity of the coordinating atom. Additionally, we demonstrate that this PC-free aryl radical generation strategy can be interfaced with Pd-catalyzed C–H activation. Altogether, our results demonstrate that this simple PC-free, light-driven radical generation strategy can be leveraged to create new organometallic arylation reactions using Ar₂I salts without expensive photocatalysts.

Lewis bases as Ar₂I activators. We began by surveying a range of Lewis basic molecules ascertain their ability to generate aryl radicals from diphenyliodonium salts ([Ph₂I][OTf], **2a**) under purple LED irradiation. To quantify Ph• generation, we leveraged B₂Pin₂ (BPin = 4,4,5,5-tetramethyl-1,3-dioxaborolane), which is a commonly employed aryl radical trap,[13] to furnish Ph-BPin **3**. In the absence of any LB activator, **3** was generated in 13 ± 2% yield after 4 hours. As such, additives providing yields >15% are considered beneficial and those giving yields ≤15% are classified as inactive (Figure 2). Lastly, 30 mol% LB loading was chosen so we could determine whether LB radical generation is catalytic.
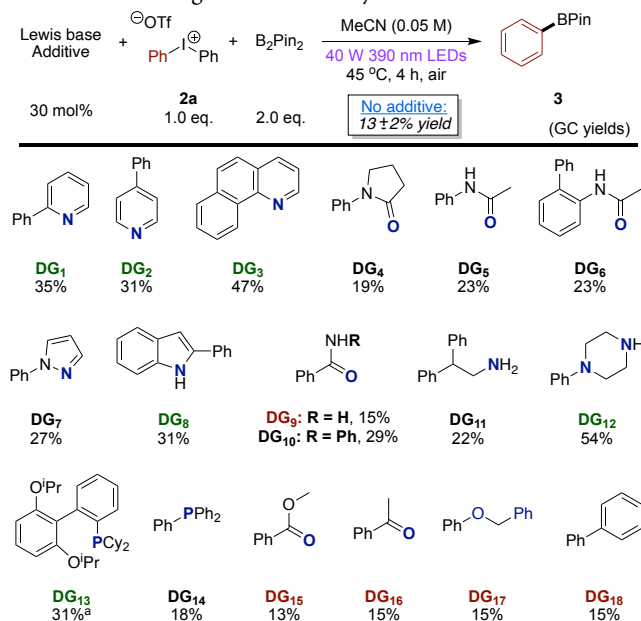

Figure 2. Different Lewis base additives and their ability to furnish borylation products from **2a**. All reported GC yields are determined relative to mesitylene as internal standard. [a]Performed under N₂.

By these metrics, **DG₉,₁₅-₁₇** were ineffective. We attribute this outcome to the non-basic properties of esters, ethers, and carbonyls. In contrast, we rated the best activators as those providing **3** in >30% yield (**DG₁-₃,₈,₁₂-₁₃**), which was chosen because yields greater than 30% suggest catalytic turnover is likely occurring. The common property linking the best additives is the presence of a strongly coordinating/basic N- or P-based group. Weak to moderate activators gave **3** in 18-29% yield and are likely only useful as stoichiometric activators (see SI for more details). Importantly, these data support the conclusion that more basic/coordinating functional groups[14] lead to better Ar₂I activation while weakly basic groups led to marginal, if any, activation beyond that observed without an activator. Interestingly, planar **DG₃** and bulky **DG₁₃** were both good additives despite potentially being too sterically encumbered to coordinate the Ph₂I fragment. This suggests that strong coordination may not be the most critical element enabling photoactivity in our system.

Impact of activator electronic properties. DG₁-₁₇ in Figure 2 consist of two components: a Lewis basic group and a proximal aryl ring. We set out to determine which component played a greater role in activation ability using borylation as a model reaction. We assume that radical capture by B₂Pin₂ is fast, and that reaction rates are governed by the aryl radical generation step. Using a range of readily prepared, electronically diverse 2-arylpyridines (**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 x 10⁻⁵ M·min⁻¹, which is identical to the reaction rate in the presence of simple pyridine.
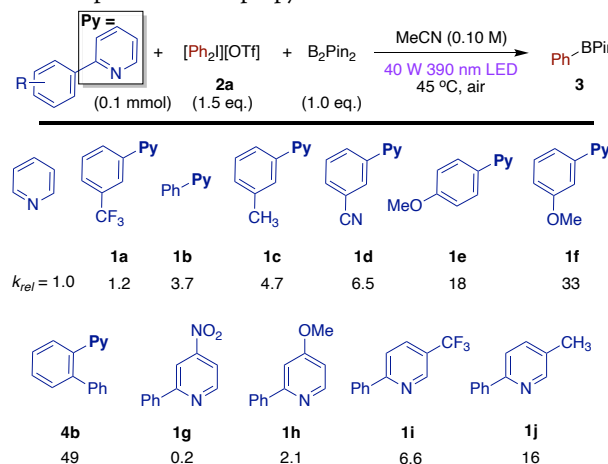

Figure 3. Relative rates of aryl borylation using 2-arylpyridines. All k_{rel} are reported as relative to the rate of borylation with no additive.

Interrogating the impact of the flanking aryl ring on Ph-BPin formation, mesomeric groups (**1d-f**) gave higher reaction rates than inductive FGs (**1a-c**). Surprisingly, a phenyl group at the *ortho* position of the flanking ring (**4b**) lead to notably faster generation of **3** than any other pyridine derivative surveyed here. Like mesomeric groups, extending conjugation impacts the aromatic π-system of the activator, which is a well-known strategy to impact photophysical properties.[15] In line with this phenomenon, **DG₃** as activator doubled the rate observed with **4b** to k_{rel} = 97 (Figure S28). Further supporting our hypothesis that LB coordination to Ar₂I may not be critical, more basic **1h** gave slower reaction rates than less basic **1i** and rates with **1g-j** exhibited a narrower range as compared to **1a-f,4b**.

Mechanistic insights. We began by gathering conclusive evidence in support of radical generation by our LB/Ar₂I system. Using 30 mol% **DG₁** and **2a**, aryl radical trapping experiments by B₂Pin₂ or 1,1-diphenylethylene (furnishing 1,1,2-triphenylethylene)[16] gave lower yields in the presence of 2,2,6,6-tetramethylpiperidinyl N-oxide (TEMPO) (10% and 15%, respectively) than in reactions without TEMPO (35% and 57%, respectively) (Figure 4). These experiments strongly support the formation of radical intermediates under our conditions.
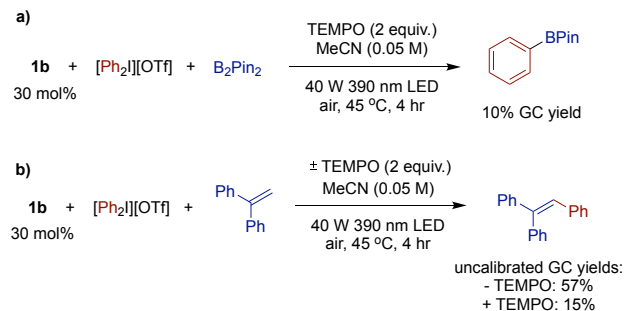

Figure 4. TEMPO inhibition and alternative radical trapping reagents.

In the works of Chatani[8] and Karchava,[9-10] association of the activator to the Ar₂I iodine atom was postulated, which led to a photoactive intermediate.[17] Although, Sanford and coworkers previously demonstrated that 2-arylpyridines of type **1** bind to iodonium salts with K_{eq} > 100 at 110 °C,[4d] we do not observe evidence of any association between **1b** and **2a** by UV-Vis, ¹H NMR, nor by changes in solution color (see Figure S33-S37). Moreover, since electronic

effect modifications of the pyridine ring in our radical borylation reactions also do not support an association complex, we predict that any EDA complexes preceding aryl radical formation may not be occurring via the LB heteroatom.

Radical capture by a transition-metal. While our ability to perform aryl radical borylation will set the stage for the development of other PC-free aryl 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 Ar$_2$I salts and an Ir-based fluorophore to perform Pd-catalyzed C–H arylation at room temperature[6h] without using explosive diazonium[16b, 18] salts.[19] 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 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-arylpyridines as both activator of **2a** and substrate for Pd, we obtained **4b** from **1b** in 46% isolated yield (Figure 5). Curious whether faster aryl radical generation would furnish higher conversions to arylated products, we tested CN derivative **1d**, which promoted the model borylation reaction *ca.* 50% faster than **1b**. Surprisingly, arylated product **4d** was only obtained in 9% yield after addition of K$_2$CO$_3$, indicating the rate of cyclopalladation might play a limiting role for electron-poor derivatives. Derivative **1k** with a *tert*-butyl group underwent arylation to give **4k** in 64% yield with no traces of **5k**. Lastly, difunctionalized **1l** was prepared and subjected to these arylation conditions, giving 46% yield of mono-arylated **4l**.

Next, we sought to correlate pyridine structure to arylation capability. So, we used GC-FID to determine approximate total arylation (sum of mono- and di-arylation) for a range of pyridine derivatives under the conditions depicted in Figure 5. When total arylation percentage was plotted versus the Hammett σ value for each functional group, a clear correlation was revealed (Figure 6).[20]
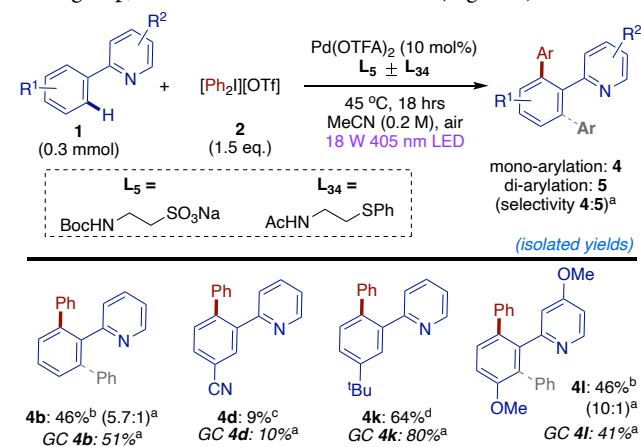

Figure 5. Proof of concept Pd-catalyzed arylation of **1**. Yields are of isolated products. [a]Selectivities for **4** versus **5** and GC yields were determined by GC-FID analysis of crude reaction mixtures relative to an internal standard using the calibration curves generated for **4b** and **5b**. [b]20 mol% L$_5$ + 40 mol% L$_{34}$. [c]30 mol% L$_5$ + 1.5 eq. K$_2$CO$_3$. [d]30 mol% L$_5$.

Figure 6a demonstrates the importance of electron-richness at the presumed site of C–H arylation. In general, total arylation decreases as FG donor ability decreases (i.e., as Hammett parameter increases). As a result, FGs with σ values greater than 0.3 were inactive and required K$_2$CO$_3$ for any arylation products to form. From a mechanistic standpoint, this trend suggests the possibility that C–H palladation proceeds by an electrophilic mechanism and is hindering

reactivity of the most electron deficient substrates. In contrast, the total arylation trend observed in Figure 6b for substitution of the pyridine ring aligns well with the analogous trend observed in Figure 3. Specifically, strong mesomeric donor/acceptor FGs gave poor arylation while inductive donors/acceptors gave moderate to good total arylation. At this point, we cannot completely rule out the possibility that these trends actually result from the aryl radical generation step.
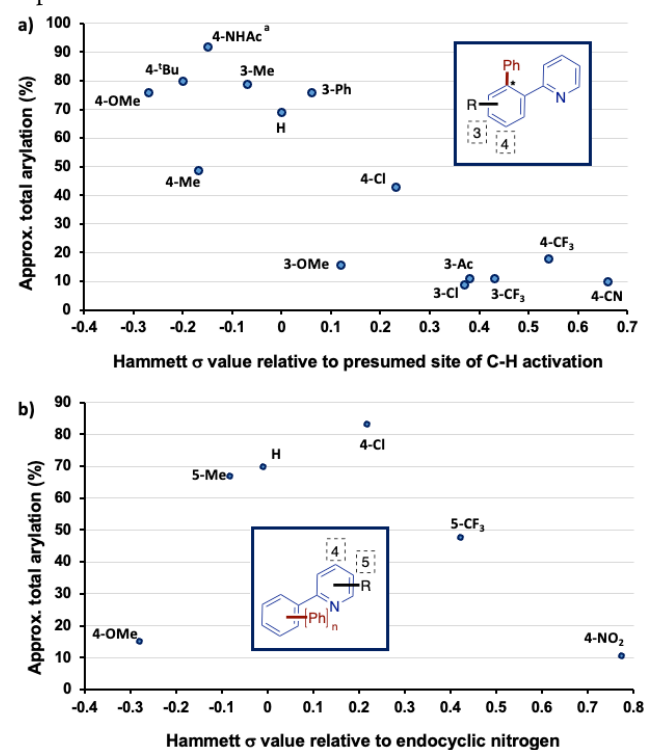

Figure 6. Visualization of approximate total arylation observed by GC-FID for a range of **1** functionalized on the flanking ring (a) and on the pyridine ring (b). *Presumed site of arylation for (a) shown only for Hammett value trend determination. Internal standard was mesitylene. [a]Multiple mono-arylation regioisomers observed.

The impact of FG modifications on the iodonium salt reagent using 2-phenylpyridine **1b** as activator demonstrated the positive effect of electron-withdrawing groups on total arylation (Figure S73a). Interestingly, incorporation of ethyl or methoxy groups at the *meta* position of the Ar$_2$I salt led to depressed yields as compared to a methyl group at the same position. We suspect that this decline in arylation efficiency results from the slightly increased steric hindrance associated with those groups, indicating sensitivity of radical generation to sterics. Plotting total arylation for *para* functionalized iodonium salts versus Hammett-Brown σ$^+$ values gave a linear correlation with a positive slope (Figure S73b).

In Figure 6a, 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,[16b, 21] we sought to show that our light-driven strategy was also applicable to Pd-catalyzed acetanilide arylation. As with **1** as substrates, control reactions using **6b** without Pd fail to provide detectable concentrations of arylated products. Using our optimized conditions, we observed a negative correlation for arylation of acetanilide substrates **6** as Hammett

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parameter increases. Here too, the most electron-withdrawing groups like CN or NO$_2$ afford no detectable arylation products (Figure 7). As with 2-arylpyridine derivatives, the factor limiting application of this methodology to electron-poor acetanilides is most likely cyclopalladation and not aryl radical generation; however, thorough mechanistic investigations are needed before firm conclusions can be drawn. Nevertheless, these results suggest that our light-driven Ar$_2$I activation approach can be applied broadly to transition-metal-catalyzed C–H arylation reactions even if the substrate doubles as the iodonium salt activator.
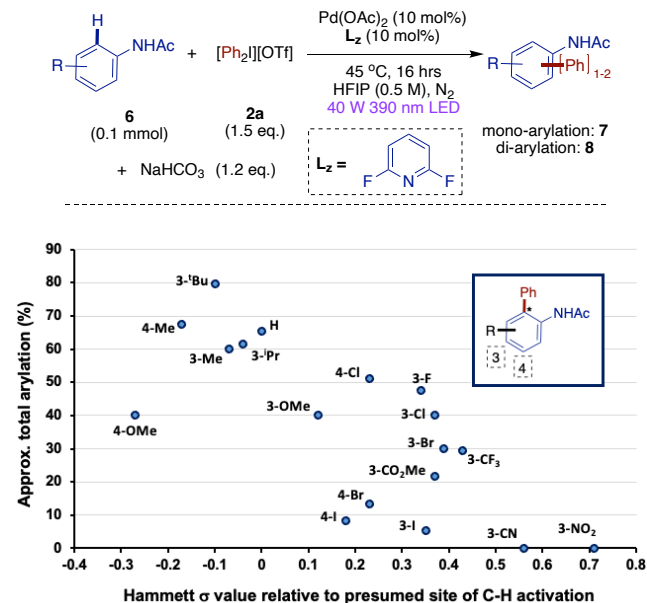

Figure 7. Pd-catalyzed arylation of **6**. Visualization of approximate total arylation observed by GC-FID for a range of **6**. *Presumed site of arylation shown only for Hammett value trend determination. Internal standard was ^{n}dodecane.

In summary, we have disclosed a strategy to generate aryl radicals from bench-stable diaryliodonium salt precursors using only an organic Lewis base and visible light. Following radical generation, we demonstrated that the aryl radicals can be captured by diboron, alkene reagents, or by Pd^{II} for use in organometallic C–H arylation reactions. Our results serve as conclusive evidence that aryl radicals generated by our method can arylate molecules/transition-metals not involved in the radical generation step. Investigations are ongoing in our laboratory to interrogate the mechanisms of the radical generation step and of the Pd-catalyzed C–H arylation reaction to understand why electron-poor substrates are incompatible. We expect that these results will spur the development of new organometallic reactions leveraging aryl radicals generated without PCs.

ASSOCIATED CONTENT

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

Experimental details; characterization data including NMR spectra of novel compounds and reactions; methods, and results (PDF).

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Author Contributions
J.G. performed the kinetic investigation of pyridine the substrates in borylation reactions and radical trapping studies. J.H. and J.G. elucidated the LB scope of aryl radical generation from iodonium salts. M.D.G. identified preliminary conditions enabling a Pd-catalyzed photocatalyst-free arylation reactions on aryl pyridine substrates. N.R.M. performed the full optimization, and substrate scopes for the aryl pyridine and iodonium salts. C.W.B. optimized and elucidated the substrate scope for acetanilide-directed arylation reactions. E.A.R. devised and managed the project and wrote the manuscript. All authors read, commented, and approved the final version of the manuscript.

†J.G. and N.R.M. contributed equally and reserve the right to list their names first on their respective CVs.

Notes
The authors declare no competing financial interest.

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