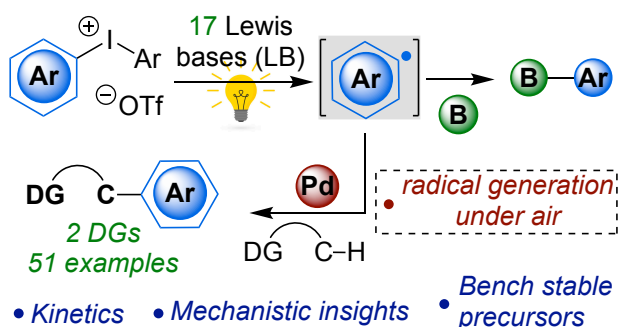


Exogenous Photocatalyst-Free Aryl Radical Generation from Diaryliodonium Salts and use in Pd-Catalyzed C–H Arylation

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Supporting Information Placeholder



ABSTRACT: Diaryliodonium salts are bench stable aryl radical precursors. While photocatalysts are generally responsible for radical generation, 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-containing molecules like Dess-Martin periodinane, 2-iodoxybenzoic acid (IBX), (diacetoxyiodo)benzene (PIDA), and others have a rich history in organic synthesis as mild, non-toxic reagents and oxidants.¹ Additionally, PIDA serves as a common non-metallic oxidant in organic chemistry, which is beneficial from cost and sustainability standpoints.² In contrast, cationic diaryl-containing I(III) salts function as arylation reagents³ and are experiencing a resurgence in popularity.⁴ The attractiveness of diaryliodonium (Ar_2I) salts are a result from facile preparatory methods incorporating wide ranging functional group (FG) patterns, exceptional bench stability, and broad FG tolerance in many different arylation reactions.⁵

On one hand, Ar_2I salts can be activated by TM complexes⁶ or attacked by nucleophiles⁷ to furnish arylated products in ground state processes (Figure 1a and b). On the other hand, excited state transformations employing Ar_2I salts as aryl radical precursors have emerged as powerful tools for selective arylation. By various photoredox approaches, (hetero)arenes,⁸ heteroatoms,⁹ alkenes,¹⁰ and $\text{C}(sp^2)\text{-H}$ bonds¹¹ can be arylated at room temperature (Figure 1c).

Reactions of Ar_2I salts induced by light, but in the absence of a photocatalyst (PC), are of particular interest for a sustainable future (Figure 1d).¹² Chatani and coworkers demonstrated that *N*-methylpyrrole solutions of Ar_2I salts generate aryl radicals when irradiated by white LEDs.¹³ While limited to *N*-methylpyrrole in solvent quantities, the resulting radicals selectively arylate the pyrrole C2–H bond showing that PC-free, light-driven arylation can be achieved.

Years later, Karchava et al. discovered that phosphines¹⁴ and phosphinamines¹⁵ were more efficient activators of Ar_2I salts than pyrrole and underwent P-arylation to furnish phosphonium salts in excellent yields under purple LED irradiation. In these cases, aryl radical generation and recombination dominates due to radical cage effects,¹⁶ which explains how solvent molecules encapsulating pairs of generated radicals hinder diffusion of radicals away from each other. Most recently, Murarka et al. overcame this limitation for a PC-free, light-driven activation of Ar_2I salts using a triad activator system consisting of NaI, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), and PPh_3 .¹⁷ While this report serves as an exciting development, alternative bases besides TMEDA would provide additional opportunities when creating new reactions of aryl radicals, especially those using transition-metal-based catalysts.

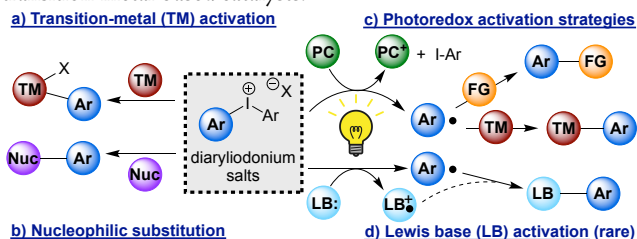


Figure 1. Previous uses of Ar_2I salts for ground and excited state transformations (a–d). This work investigates Lewis base generated aryl radicals for direct and organometallic arylation reactions.

Herein, we report that numerous Lewis bases (LBs) are competent to serve as sole activators of Ar₂I salts permitting they contain an aryl group proximal to the coordinating heteroatom. 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. In addition to aryl radical borylation, we demonstrate that this PC-free aryl radical generation strategy can be interfaced with a Pd-catalyzed C–H activation manifold to perform selective arylation reactions. Altogether, our results demonstrate that this simple PC-free, light-driven radical generation strategy can be leveraged to create new arylation reactions using bench stable Ar₂I salt precursors without the need for expensive photocatalysts or stoichiometric additives.

Lewis bases as Ar₂I activators. We began our investigation 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 settled on trapping the generated radicals by B₂Pin₂ (BPin = 4,4,5,5-tetramethyl-1,3-dioxaborolane), which is a commonly employed aryl radical trap,¹⁸ 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 between ≤15% are classified as inactive (Figure 2). We chose 30 mol% LB loading so we could determine whether any LBs catalytically generate radicals.

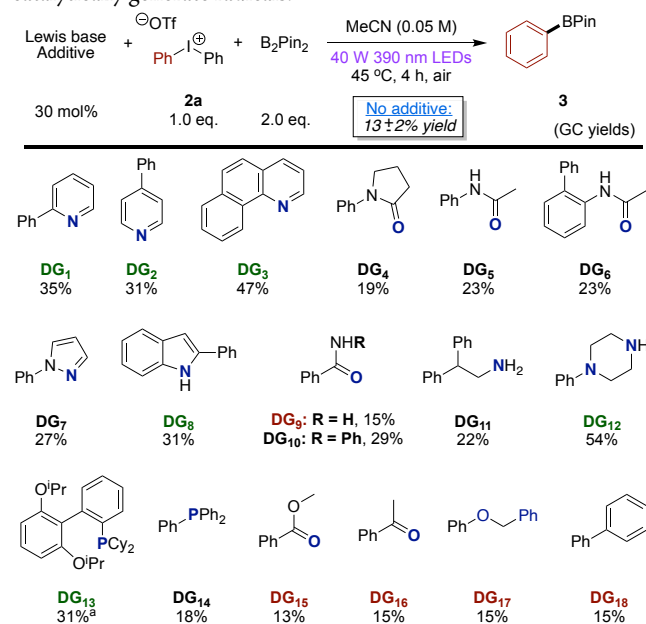


Figure 2. Different Lewis base additives and their ability to furnish borylation products from **2a**. All reported GC yields are determined relative to mesitylene as internal standard using the calibration curves for independently prepared **3**. ^aPerformed under N₂.

By these metrics, oxygen-only activators (DG₁₅₋₁₇) were ineffective. We attribute this outcome to the weak coordinative capabilities of esters, ethers, and carbonyls. In contrast, we rated the best activators as those providing **3** in >30% yield (DG_{1-3,7-8,12-14}). Importantly, 30% was the chosen threshold because it equates to the additive loading amount. Thus, yields greater than 30% suggest catalytic turnover is occurring. The commonality linking the best additives is the presence of a strongly coordinating functional group. Instead, weak to moderate activators give **3** in 17-29% yield. Importantly, these data support the conclusion that stronger

coordinating functional groups¹⁹ lead to better activation of Ar₂I salts while weaker groups lead to marginal, if any, activation beyond that observed in the absence of an activator. See the SI for a deeper discussion regarding the importance of additive loading for those featuring weakly coordinating groups.

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 the rate of borylation. Here, we assume that radical capture by B₂Pin₂ is fast, and that the borylation reaction rates are governed by the aryl radical generation step. Using a range of readily prepared, electronically diverse 2-arylpiperidine derivatives **1a-j** as activators, we used gas chromatography to monitor the initial rate of borylation to determine the impact of FG modifications on **1** (Figure 3). As a baseline for this study, the rate of formation of **3** in the absence of any activator was 9.89 × 10⁻⁵ M·min⁻¹, which is identical to the reaction rate in the presence of simple pyridine. This result supports the importance of the C2 aryl group.

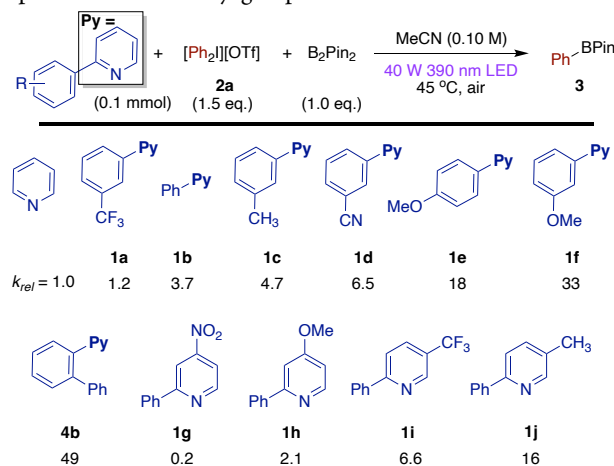


Figure 3. Relative rates of aryl borylation using 2-arylpiperidines. All k_{rel} are reported as relative to the rate of borylation with no additive.

Interrogating the impact of the flanking aryl ring on Ph-BPin formation, we determined that mesomeric donor/acceptor groups (**1d-f**) gave higher rates than inductive donors/acceptors (**1a-c**). Surprisingly, a phenyl group at the 2-position on the flanking ring (**4b**) lead to notably faster generation of **3** than any other derivative surveyed here. Like mesomeric groups, arenes can impact the aromatic π-system of the activator by extending conjugation, which is a well-known strategy to impact photophysical properties.²⁰ Looking at the basicity of the pyridine moiety, mesomeric groups gave slower borylation rates than inductive groups, indicating a narrow basicity range exists for optimal reactivity. Like on the flanking ring, donor groups were better than the corresponding withdrawing groups.

Mechanistic insights. We began by gathering additional support of radical generation by our LB/Ar₂I system by exchanging B₂Pin₂ as our trapping reagent for the equally common 1,1-diphenylethylene.²¹ Irradiation of a mixture of diphenylethylene, **2a**, and 30 mol% **1b** led to the formation and detection of 1,1,2-triphenylethylene by GC-MS (SI Figure S26 and S27). In the works of Chatani¹³ and Karchava,¹⁴⁻¹⁵ association of the activator to the iodine atom was postulated, leading to a photoactive intermediate.²² Supporting potential EDA adduct formation in our system, Sanford and coworkers previously demonstrated that 2-arylpiperidines of type **1** bind to iodonium salts with K_{eq} > 100 at 110 °C.^{6d} In contrast to these precedents, we do not observe evidence of any association between

1b and **2a** by UV-Vis nor ¹H NMR (see SI for more information and stacked plots). Additionally, no color changes were observed in any reactions once assembled. Thus, if an association occurs between these species under our reaction conditions, the *K_{eq}* must be very small to preclude detection. However, the importance of heteroatom basicity in our LB screen strongly supports adduct formation.

Previous investigations propose electron transfer (ET) from the Lewis base to the iodonium as the dominant radical formation mechanism.¹³⁻¹⁵ However, we argue that ET from the pyridine N-atom to iodine is not supported based upon the kinetic data we obtained. In a mechanism where such an ET event occurs, mesomeric groups bound to the pyridine ring would exhibit a beneficial rate impact since the added electron density would support the generated pyridinium radical cation. In contrast, **1h** was among the worst activators surveyed. While it could be possible that ET from the C2-aryl ring to the iodonium group occurs, our rate data do not support this conclusion. Specifically, electron-donating substituents (**1c,e-f**) would be expected to give higher reaction rates than electron-withdrawing groups (**1a,d**) giving lower *k_{rel}*. This trend was not observed. In fact, our results suggest that energetic and orbital manipulation of the aromatic π-system on the C2-aryl ring is key. This conclusion is supported by the high yield of **3** when using benzo[*h*]quinoline (DG₃) in Figure 2 and exceptional *k_{rel}* with **4b**. As such, our data suggests that energy transfer (EnT) from the proximal aryl ring to the iodonium moiety, rather than ET, may be the radical generation pathway under our conditions. Detailed experiments are ongoing to gather conclusive data in this regard.

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 challenge our system by interfacing 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^{11b} without using explosive diazonium^{21b,23} salts.²⁴ We set out to demonstrate that our protocol would enable analogous arylations of C(*sp*²)-H bonds without a PC. In support of metal-mediated C–H activation occurring under our conditions, control reactions without Pd failed to provide detectable concentrations of arylated pyridine 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 4). 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** in 9% yield was only obtained by addition of K₂CO₃ to the reaction, indicating the rate of cyclopalladation might play an important 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 4. When total arylation percentage was plotted versus the Hammett σ value for each functional group, a clear correlation was revealed (Figure 5).²⁵

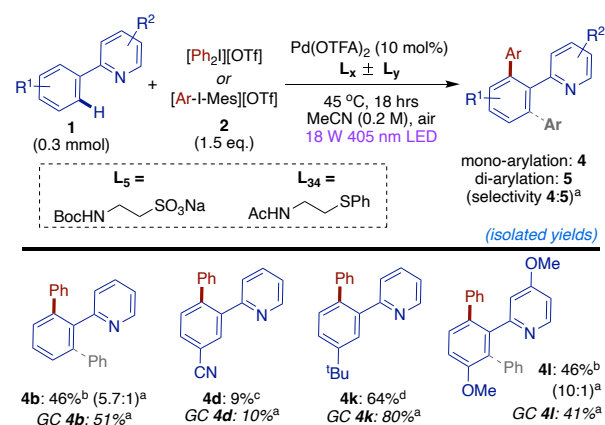


Figure 4. Proof of concept Pd-catalyzed arylation of **1**. Yields are of isolated products. ^aSelectivities for **4** versus **5** and GC yields were determined by GC-FID analysis of crude reaction mixtures relative to an internal standard using the calibration curves generated for **4b** and **5b**. ^b20 mol% L₅ + 40 mol% L₃₄. ^c30 mol% L₅ + 1.5 eq. K₂CO₃. ^d30 mol% L₅.

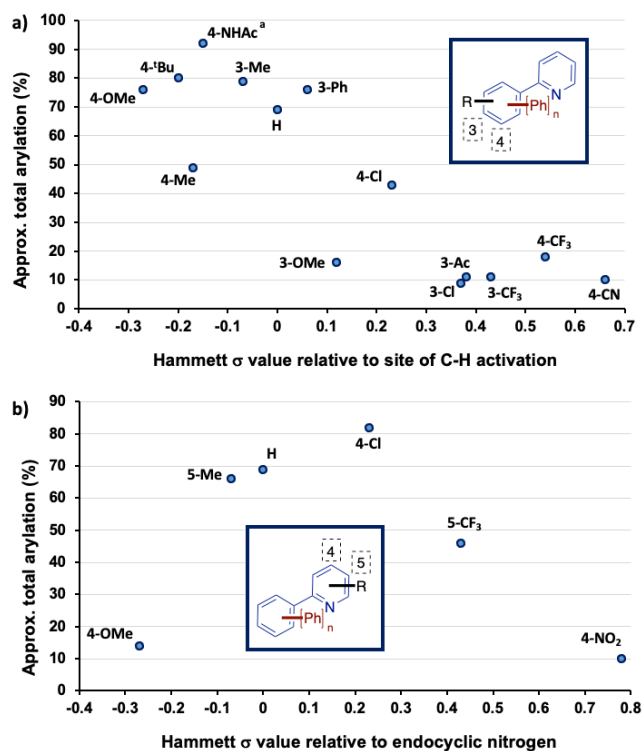


Figure 5. Visualization of approximate total arylation observed by GC-FID for a range of **1** functionalized on the flanking ring (a) and on the pyridine ring (b). ^aPresumed site of arylation for (a) shown only for Hammett value comparisons. Internal standard was mesitylene. ^aMultiple mono-arylation regioisomers observed.

Figure 5a demonstrates the importance of electron-richness at the presumed site of C–H arylation. In general, total arylation percentage 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 additive K₂CO₃ for any arylation products to form. From a mechanistic standpoint, this trend and the kinetic experiments presented in Figure 3 suggest the possibility that an electrophilic C–H palladation step is hindering reactivity of the most electron deficient substrates. In contrast, the total arylation trend observed in Figure 5b aligns well with the substituent trend

observed in Figure 3 for substitution of the pyridine ring. Specifically, strong mesomeric donor/acceptor FGs gave poor arylation counts while inductive donors/acceptors gave moderate to good total arylation percentages. At this point, we cannot rule out the possibility that this trend does not have origins in reactivity of the Pd catalyst.

The impact of functional groups on the iodonium salt reagent using 2-phenylpyridine **1b** as activator demonstrate the positive effect of electron-withdrawing groups on total arylation (Figure 6a). Interestingly, incorporation of ethyl or methoxy groups at the *meta* position of the Ar₂I salt led to depressed yields as compared to a methyl group at the same position. We expect that this decline in arylation efficiency results from the slightly increased steric hindrance associated with those groups, indicating an extreme sensitivity of radical generation to FG size. Plotting total arylation for *para* functionalized iodonium salts versus Hammett-Brown σ^+ values gave a linear correlation (Figure 6b). The positive slope is consistent with Lewis acid/base reactivity, which supports the importance of pyridine coordination to diaryliodonium salts for photoactivity, despite our inability to spectroscopically observe such interactions.

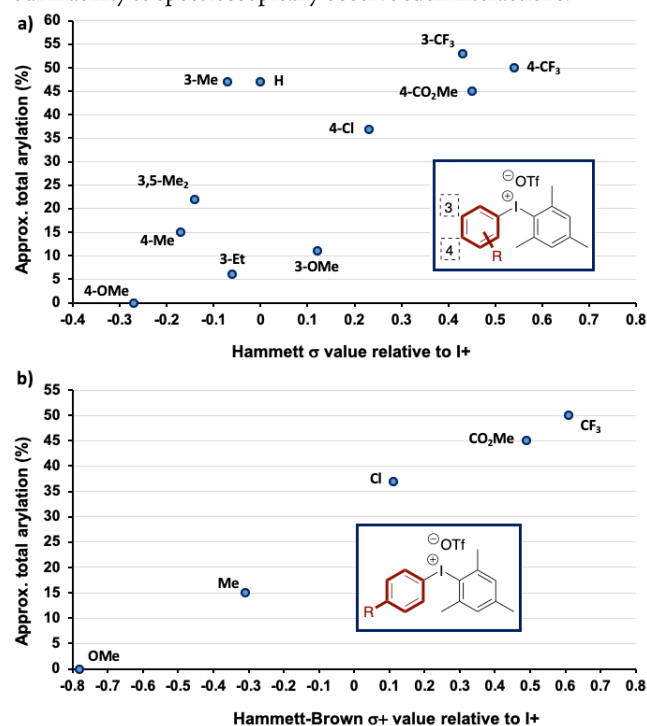


Figure 6. Impact of the FG electronics on iodonium salt function as an aryl radical precursor. Approximate total arylation was determined via GC-FID using ⁿdodecane as an internal standard.

In Figure 5a, 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,^{21b,26} 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 parameter increases. Here too, the most electron-withdrawing groups like CN or NO₂ 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 Ar₂I activation approach can be applied broadly to transition-metal-catalyzed C–H arylation reactions even if the substrate doubles as the iodonium salt activator.

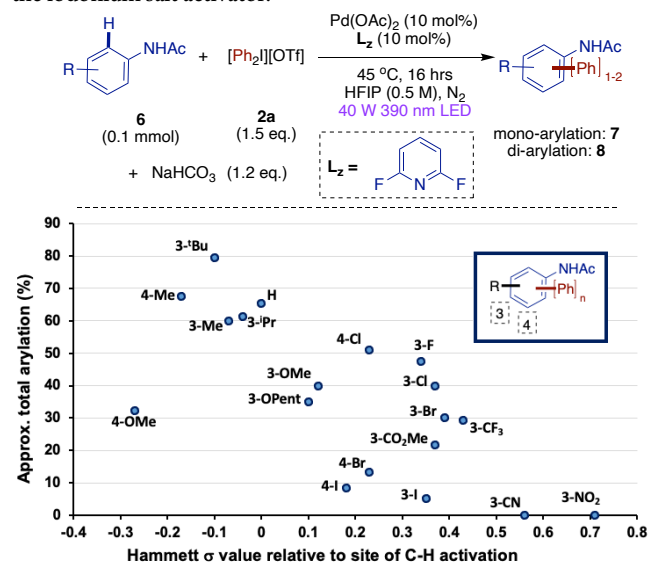


Figure 7. Pd-catalyzed arylation of **6**. Visualization of approximate total arylation observed by GC-FID for a range of **6**. *Presumed site of arylation shown only for Hammett value comparisons. Internal standard was ⁿdodecane.

In summary, we have disclosed a strategy to generate aryl radicals from bench-stable diaryliodonium salt precursors using organic Lewis base activators and visible light. Our results indicate a broad array of Lewis bases can serve as activators even if a Lewis acid/base adduct is not spectroscopically observable. In contrast to literature precedent, kinetic studies suggest an EnT mechanism of radical generation rather than ET is occurring. Following homolysis, we demonstrated that the aryl radicals can escape the solvent cage and be captured by diboron reagents. Alternatively, generated aryl radicals can be captured by a TM for use in organometallic C–H arylation reactions. In either case, our results serve as conclusive evidence that aryl radicals generated from Ar₂I salts using only visible light and Lewis basic molecules can arylate molecules/complexes not involved in the radical generation step. Investigations are ongoing in our laboratory to interrogate the mechanisms of the radical generation step (EnT versus ET) 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 reactions leveraging aryl radicals generated without a PC.

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. 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.

ACKNOWLEDGMENTS

This work was supported by start-up funds provided by the University of California San Diego. Dr. Delphine Pichon-Barre is thanked for assistance with preliminary experiments. Dr. Rodolphe Jazzar and Mr. Patrick Yorkgitis are thanked for helpful discussions.

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