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

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ABSTRACT: We demonstrate 1) that halogen bonding is not critical for enabling light-driven radical generation from diaryliodonium salts and 2) radicals generated by this route can be captured by transition-metals for C–H arylation reactions. These results are the first step toward developing new metal-catalyzed aryl radical couplings 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 arylating 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] More recently, visible light induced PC-free radical generation reported by Chatani and coworkers demonstrated that N-methylpyrrole solutions of Ar_2I salts furnish N-methyl-2-phenylpyrrole products (Figure 1a).[9] Karchava et al.[12] and Lakhdar et al.[10] separately showed that neutral PR_3 Lewis bases (LBs) were more effective 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 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 that is either highly colored or features a detectable halogen bonding interaction.
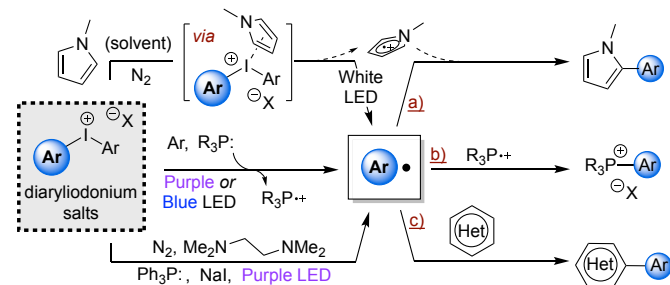

Figure 1. Known excited-state PC-free activations and reactions of Ar_2I salts (a-c).

Herein, we report single LB activator systems enabling PC-free aryl radical generation using Ar_2I salts as well as strong evidence suggesting against the need for highly colored EDA adducts or those bearing distinct halogen bonding interactions. This assertion is supported by UV-Vis, variable temperature (VT) ^1H NMR, kinetic rate measurements, stoichiometric reactions, and computational studies.

Beyond simple radical generation, PC-free methods focus on trapping aryl radicals with organic molecules like alkenes (e.g., Meerwein arylation)[13] or heteroarenes,[12] but not with transition-metals for site-selective arylation reactions. We interfaced our PC-free aryl radical generation strategy with Pd-catalyzed C–H activation processes to achieve regioselective arylation of C–H bonds. Altogether, our results show that activators for PC-free radical generation from Ar_2I salts can be a broad array of simple organic LBs and our approach is amenable to the creation of new organometallic arylation reactions without expensive PCs.

Lewis bases as Ar_2I activators. We first surveyed a range of Lewis basic molecules to ascertain their proclivity for aryl radical generation from diphenyliodonium salt **2a** ($[Ph_2I][OTf]$) under purple LED irradiation. To quantify Ph• generation, we leveraged B_2Pin_2 (BPin = 4,4,5,5-tetramethyl-1,3-dioxaborolane), which is a known aryl radical trap,[14] to furnish Ph-BPin **3**. *N.B.:* Higher concentrations of B_2Pin_2 do not impact obtained yields of **3** (SI Figure S22), so yield differences observed between tested activators arise from their radical generation ability. In the absence of any LB activator, **3** was detected in 13 ± 2% yield after 4 hours. Beneficial additives providing yields >25% are depicted in Figure 2. Of these, bulky **DG**$_{1,4,13,14}$ gave yields ≥60%. The results of this LB survey support the preliminary conclusion that halogen bonding interactions may not be a critical element enabling photoactivity in our system. For example, chelating 1,10-phenanthroline (**DG**$_5$) gave only 29% **3** whereas monodentate benzo[h]quinoline (**DG**$_4$) afforded 62%. Similarly, very bulky RuPhos (**DG**$_{15}$) afforded 44% **3** while PPh_3 (SI, Figure S20) gave only 30%. Lastly, reactions employing more hindered neocuproine (**DG**$_6$) versus less hindered **DG**$_5$ gave nearly identical yields. Taken together, in all cases where halogen bonding interactions should be stronger, lower yields were obtained when compared to similar reactions using bulkier LB activators.

Impact of activator electronic properties. **DG**$_{1-15}$ in Figure 2 consist of two components: a Lewis basic heteroatom and a proximal aryl ring. To determine which component plays a greater role in governing an activator's ability to generate radicals, we monitored the initial rate of aryl radical generation via borylation reactions in the presence of a range of electronically diverse 2-arylpyridines (**1a-j, 4b**) as activators (Figure 3). The background rate of **3** formation in the absence of any activator was 9.89×10^{-5} M min^{-1}.
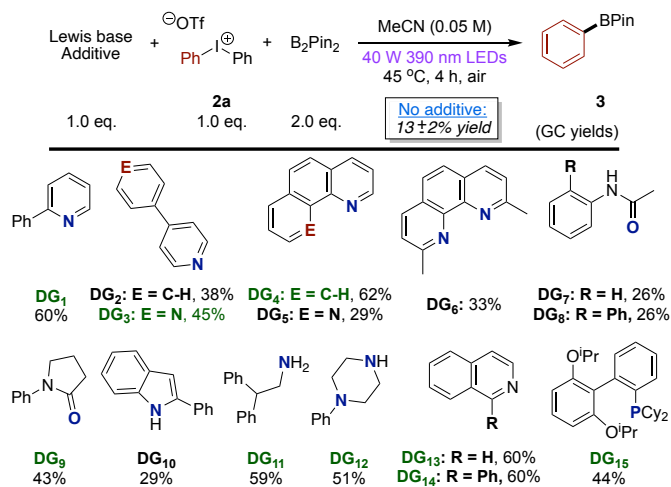
Figure 2. Select Lewis base additives demonstrate different abilities to furnish borylation products from **2a**. GC yields are calibrated vs. mesitylene as internal standard.
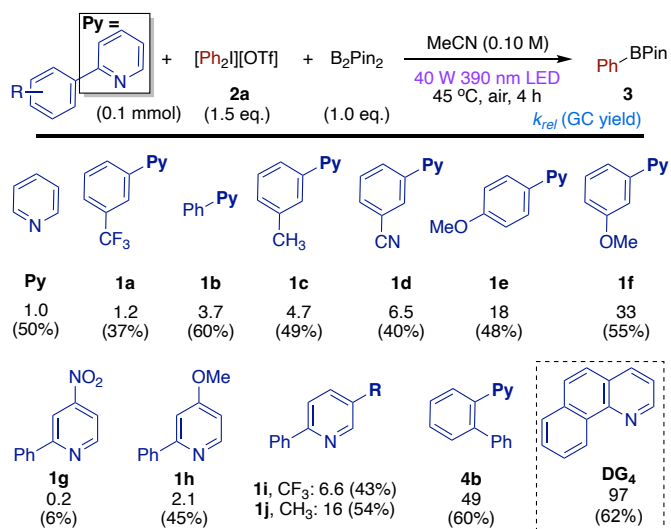

Figure 3. Relative rates and yields of aryl radical borylation using 2-arylpyridines. All k_{rel} are reported as relative to the rate of borylation with no additive.

Interrogating the impact of the C2-aryl ring on **3** formation elucidated clear trends. First, pyridine itself has no impact on the rate of radical generation.[9] Second, mesomeric FGs (**1d**-**f**) led to higher borylation rates than inductive FGs (**1a**-**c**). Third, extended conjugation (**4b**, **DG₄**) led to notably faster formation of **3** than other surveyed pyridine derivatives (k_{rel} = 49 and 97, respectively). Fourth, the most basic (i.e., coordinating) derivative (**1h**) gave slower reaction rates than less basic **1i-j**, which contrasts the expected trend for processes hinging upon halogen bonding interactions. From these data, a clear correlation between the energetics of the activator's π-system and aryl radical generation rate was observed rather than on the coordination ability of the activator.

Mechanistic insights. We began by gathering support that aryl radicals are formed under our conditions in two ways (SI, Figure S48-50). 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). We also 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.

In past works,[10a-d] halogen bonding interactions between the LB activator and the Ar₂I iodine atom was presented as a critical factor enabling photolytic radical release. In contrast, other groups noted the in-situ formation of strongly colored EDA adducts,[9,12] which enabled photoactivity. For us, combination of highly enabling **DG₄** and **2a** does not lead to colored solutions nor do new absorption bands appear by UV-Vis (SI, Figure S59-60 and S63). Since VT NMR was used by others to observe halogen bonding interactions between PR₃ activators and **2a**,[10e] we surveyed combinations of **DG₄** and **2a** at ±50 °C to determine whether resonance shifts could be observed using our best activator (Figure 4). Unfortunately, we did not observe any shifts in the C2–, C4–, nor C10–H resonances of **DG₄**.
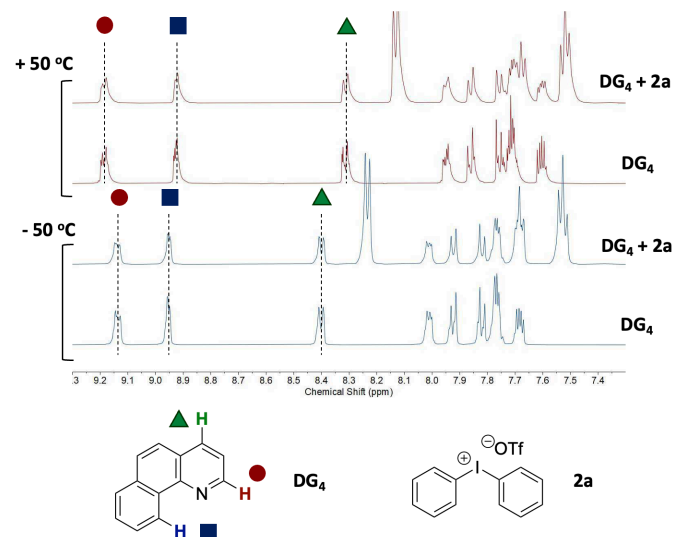

Figure 4. VT ¹H NMR spectra of a stoichiometric mixture of **DG₄** and **2a** at -50 and +50 °C depicting no shift in the C2-H (circle), C4-H (triangle), or C10-H (square) resonances of **DG₄**.

Based on these preliminary mechanistic insights, we conclude that detectable halogen bonding interactions between nor strongly colored EDA adducts are critical for PC-free, light-driven radical generation from Ar₂I salts.

Computational investigation. Next, we turned to computational chemistry to further investigate the importance of adduct formation and presence of halogen bonding in our system. Six LB derivatives from Figure 3 were selected as representative examples of activator prowess. For each, the free energy of association to the Ph₂I fragment was computed from optimized geometries (see SI for computational details) and plotted versus the experimentally determined k_{rel} values for each (Figure 5). Pyridine as additive resulted in no impact and most positive ΔG. Incorporation of an aryl group at C2 increased the radical generation rate, which correlates nearly linearly to the favorability of LB/Ph₂I formation up to **1i** at ΔG = -1.24 kcal/mol. Experimentally, **1i** constitutional isomer, 2-phenyl-3-methylpyridine, binds [Ph-I-Mes][BF₄] with K_{eq} = 154 at 80 °C,[5c] which validates the negative free energy of association we calculated using **1i**. In contrast, **4b** and **DG₄** do not adhere to this trend. For these LBs, energy of adduct formation increases up to 3.08 kcal/mol for **DG₄** while simultaneously exhibiting enhanced activation ability. From these calculations, the favorability of LB activator and iodonium salt association is not indicative of radical generation rate.
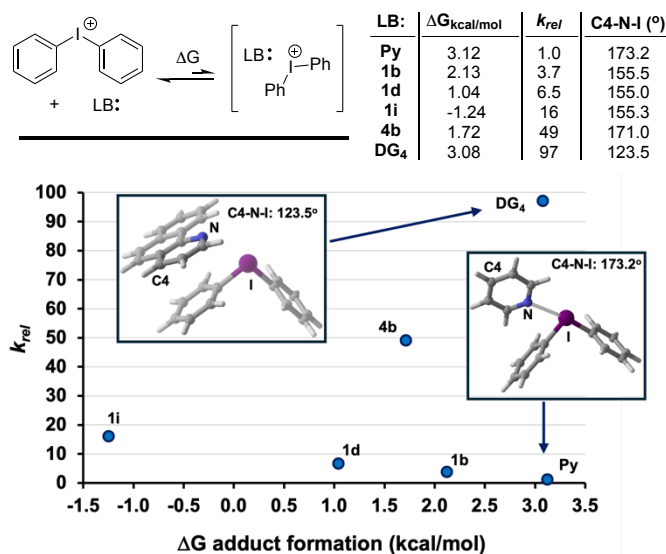
Figure 5. Plot of experimental k_{rel} versus calculated ΔG values for various pyridine-based activators. Left insert: Orientation of **DG₄** relative to **2a** supports experimental results that lack of a halogen bonding interaction does not obviate activation ability. Right insert: Discrete halogen bonding interaction does not guarantee light-driven radical generation.

To assess the potential of halogen bonding to act as an indicator of experimental activity, we examined the orientation of the nitrogen lone pair relative to the I–Ph bond since halogen bonds characteristically have ~180° bond angles (SI, Figure S106).[15] Nitrogen lone pair deviation from linearity relative to the I–Ph bond vector was measured using the C4-N-I angle. The lone pair of **Py** yielded a 173.2° angle (right inset), suggesting strong halogen bonding interactions. In contrast, the angles for **1b**, **1d**, and **1i** were all ~155°, suggesting minor distortion in halogen bonding ability, but not so much as to obviate a possible interaction. Interestingly, **4b** yielded a C4-N-I angle of 171°, like pyridine, but demonstrated notably increased activator ability, which supports our conclusion that halogen bonding is not the governing element for reactivity. Most conclusively, the optimized structure of the **DG₄**/Ph₂I adduct exhibits a C4-N-I angle of 123.5° (left inset) which is fully disengaged from interactions with the I-atom and likely only consists of π-π effects. The computed UV-vis spectrum of this adduct shows a shoulder potentially corresponding to an irradiation band;[10d] however, the tail of this absorption is slightly outside the range of the LEDs used in this study.

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 explosive[16] diazonium salts.[17] We set out to demonstrate that our protocol would enable analogous arylations of C(sp²)–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-arylpyridines 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. 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.
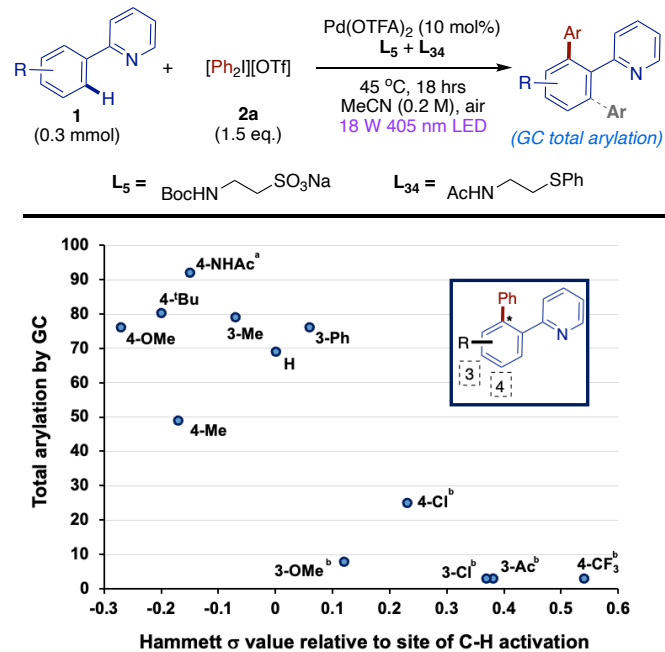

Figure 6. Visualization of approximate total arylation observed by GC-FID correlates to pyridine substrate electronic properties. *Presumed site of arylation shown only for Hammett value trend determination. Internal standard was mesitylene. [a]Multiple mono-arylation regioisomers observed. [b]Performed on a 0.1 mmol scale.

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 **DG₅₋₆**) and they have been previously used in C–H arylation reactions catalyzed by Pd,[17c,18] 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 and a proposed mechanism is presented in the SI (Figure S89 and S105, respectively).

Conclusions. In contrast to literature precedent, we discovered that combinations of simple LBs with diaryliodonium salts do not hinge upon the formation of discrete halogen bonding interactions for PC-free aryl radical generation. This conclusion was drawn from ocular spectroscopy of colorless reaction mixtures, VT NMR, UV-Vis spectroscopy, kinetic rate measurements, and computational studies. 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 inventing strategies to further enhance radical generation efficiency.

3

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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