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Combining Transition Metal Catalysis with Radical Chemistry: Dramatic Acceleration of Palladium-Catalyzed C–H Arylation with Diaryliodonium Salts

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Abstract

This paper describes a photoredox palladium/iridium-catalyzed C–H arylation with diaryliodonium reagents. Details of the reaction optimization, substrate scope, and mechanism are presented along with a comparison to a related method in which aryldiazonium salts are used in place of diaryliodonium reagents. The unprecedentedly mild reaction conditions (25 °C in methanol), the requirement for light and a photocatalyst, the inhibitory effect of radical scavengers, and the observed chemoselectivity trends are all consistent with a radical-thermal reaction with diaryliodonium reagents that is believed to proceed *via* an ‘ionic’ $2e^-$ pathway and requires a much higher reaction temperature (100 °C).

Keywords

C–H activation; diaryliodonium salts; palladium; photochemistry; radicals

Introduction

The merger of transition metal catalysis with radical chemistry has emerged as a powerful strategy for achieving high-yielding transformations under mild conditions.^[1] The ability to reroute textbook metal-catalyzed reactions *via* alternative metal/radical-mediated pathways can lead to improvements in rate, functional group tolerance, and/or substrate scope. Manolikakes and Knochel recently reported a striking example of this strategy in the context of the Pd-catalyzed Kumada coupling.^[2] They showed that the addition of *i*-PrI led to a remarkable rate acceleration in the coupling of aryl bromides with aryl Grignard reagents.^[2a] This rate enhancement was rationalized based on a new ‘radical-catalyzed’ mechanistic manifold involving *in situ* generated alkyl and aryl radicals as key intermediates.

We hypothesized that a similar strategy could be used to accelerate Pd-catalyzed C–H arylation reactions with diaryliodonium reagents. As shown in Scheme 1a, Pd(OAc)₂ is known to catalyze ligand-directed C–H arylation *via* an ‘ionic’ mechanism involving $2e^-$ oxidation of a palladacycle intermediate by Ar₂I⁺.^[3–5] However, these transformations are extremely sluggish, typically requiring high temperatures (80–110 °C) over extended periods of time (8–24 h) in acetic acid.^[6] We reasoned that the rates of these reactions could

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potentially be enhanced by rerouting them through radical pathways in which Ar_2I^+ is converted into $\text{Ar}\cdot$ *in situ* (Scheme 1b).

Tentative support for the feasibility of this approach is provided by recent reports showing Pd-catalyzed C–H arylation using $\text{Ar}\cdot$ generated from aroyl peroxides^[7a] or aryl diazonium salts.^[7b] We report herein that this strategy enables C–H arylation with Ar_2I^+ under extremely mild conditions (room temperature in MeOH). We also present evidence supporting the proposal that two fundamentally different mechanisms are operating in the ionic (Scheme 1a) versus radical (Scheme 1b) systems. Finally, we compare this new transformation to a related method that uses aryl- N_2^+ as the arylating reagent.^[7b]

Results and Discussion

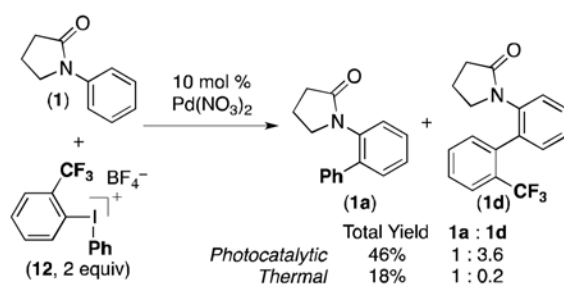
Ph_2I^+ can be converted to $\text{Ph}\cdot$ under mild conditions using visible light and a photocatalyst [$\text{Ru}(\text{bpy})_3\text{Cl}_2$ or $\text{Ir}(\text{ppy})_3$; bpy = 2,2'-bipyridine, ppy = cyclometalated 2-phenylpyridine].^[8,9] Thus, we initiated investigations of Pd-catalyzed C–H phenylation of **1** with $[\text{Ph}_2\text{I}]\text{BF}_4$ in combination with a photocatalyst. Visible light irradiation was provided by a 26 W household fluorescent light bulb, and the reactions were set up on the bench top with no precautions to exclude moisture or air. Remarkably, the use of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ resulted in a modest yield (18%) of the desired arylated product **1a** after 15 h in MeOH at room temperature (Table 1, entry 1). Evaluation of several different Pd^{II} catalysts revealed that $\text{Pd}(\text{NO}_3)_2$ provides the best results, generating **1a** in 23% yield (entry 2). $\text{Ru}(\text{bpy})_3\text{Cl}_2$ and $\text{Ir}(\text{ppy})_3$ afforded comparable results (entries 2 and 3), but the cationic photocatalyst $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (dtbbpy = 4,4'-ditertbutyl-2,2'-bipyridine)^[10] provided a significant improvement (57% yield, entry 4). Replacing $[\text{Ph}_2\text{I}]\text{BF}_4$ with the corresponding triflate salt led to a further enhancement (66% yield, entry 5). Finally, briefly sparging the mixture with N_2 prior to the start of the reaction resulted in 94% yield of **1a** (entry 6).^[11] Importantly, both of the metal catalysts, as well as visible light, are critical for efficient room temperature C–H phenylation.^[12] Without any one of these three components, only traces of product **1a** were formed (0–2%, entries 7–9).

A variety of aromatic substrates underwent room temperature C–H phenylation under these conditions (Table 2). In addition to pyrrolidinones **1** and **2**, other *N*-aryl amides were effective directing groups (entries 3 and 4). *C*-Aryl amides, such as benzamides **5** and **6**, also underwent room temperature C–H phenylation, albeit in moderate yields (40% and 54%). The *N,N*-disubstituted analog **7** provided phenylated product **7a** in poor yield (9%), suggesting that C–H arylation is facilitated by the presence at least one N–H bond in this substrate class. 2-Arylpyridines **8** and **9** as well as ketoxime and aldoxime ethers **10** and **11** were also good substrates. The ability to use oxime ethers as directing groups is particularly notable, as these do not undergo C–H arylation with diaryliodonium reagents under the previously reported thermal reaction conditions.^[3]

Diaryliodonium salts containing diverse arene substituents were evaluated in this photocatalytic C–H arylation. As shown in Table 3, the highest yields were obtained with those bearing relatively electron neutral substituents (*e.g.*, *p*-Cl, *p*-Br, *p*-CH₃, *o*-CH₃, entries 4–7). Nonetheless, oxidants possessing more strongly electron-donating and electron-withdrawing substituents were also effective. For example, C–H arylation with *p*-methoxyphenyl (entry 9) as well as *p*-, *m*-, and *o*-trifluoromethylphenyl (entries 1–3) reagents proceeded in moderate to good yields. Remarkably, even the highly sterically hindered mesityl group could be transferred, albeit in low yield (11%, entry 8). Notably, the analogous thermal reaction of $[\text{Mes}_2\text{I}]\text{OTf}$ with **1** did not provide detectable quantities of **1i** (as determined by GC).

We propose that the Ir/Pd-catalyzed photocatalytic C–H arylation proceeds via a fundamentally different mechanism than the analogous thermal reaction, despite the fact that the reagents and products are the same in both processes. A first piece of evidence to support this proposal is the reaction outcome in the presence of free radical scavengers. As shown in Table 4, the thermal C–H arylation reaction is not inhibited by the addition of 25 mol % galvinoxyl or 100 mol % of TEMPO. With both radical scavengers, the reactions proceed to complete conversion and afford comparable yield (entries 1–3). In contrast, the % conversion and the % yield of the photocatalytic reaction are suppressed in a dose-dependent manner by galvinoxyl and TEMPO (entries 4–8). These results are consistent with the intermediacy of radicals in the latter but not the former reaction.

In addition, the chemoselectivity of the reaction between **1** and unsymmetrical iodonium reagent **12** is highly dependent on the reaction conditions (eq 1). Under the thermal conditions, the less hindered phenyl group is transferred selectively, providing a 1 : 0.2 ratio of **1a** : **1d**. In contrast, selective transfer of the *o*-CF₃C₆H₄ group occurs under the photocatalytic conditions, affording a 1 : 3.6 ratio of **1a** : **1d**. These differences in chemoselectivity provide further support for divergent mechanistic pathways.



(1)

We preliminarily propose a reaction pathway that merges Pd^{II/IV} and Ir^{III/IV} catalytic cycles. As shown in Scheme 2, ground state Ir³⁺ undergoes photoexcitation by visible light (step *i*), and the resultant Ir^{3+*} complex can reduce Ar₂I⁺ to generate Ar•, ArI, and Ir⁴⁺ (step *ii*).^[8,9] Ar• could then enter the Pd catalytic cycle by oxidizing cyclopalladated complex **13** (step *iii*). Complex **14** could then be further oxidized to **15** by Ir⁴⁺ (step *iv*), regenerating Ir³⁺. Finally, C–Ar bond-forming reductive elimination from **15** would afford product **16** and regenerate Pd²⁺ (step *v*). Importantly, a number of other pathways are also possible (for example, Pd^{I/III} catalysis) and cannot be distinguished based on the current data.

We have recently reported a related room temperature photocatalytic C–H arylation reaction that was proposed to proceed via a mechanism similar to that shown in Scheme 1.^[7b] However, this previously reported transformation used a different Ar• precursor (aryl diazonium salts), a different photocatalyst (Ru(bpy)Cl₂), a different Pd catalyst (Pd(OAc)₂) and slightly different optimized reaction conditions. Thus, a final set of studies was conducted to compare these two processes.

As illustrated in Table 5, the performance of the two systems is often comparable (*e.g.*, for substrates **1** and **11**). However, for benzamide substrates **5–7** and ketoxime ether **10**, the Pd/Ir/Ph₂I⁺ system provided better yields of C–H phenylation. Conversely, the Pd/Ru/PhN₂⁺ system performed better for acetanilide **3**, and it is effective for hydroxyl oxime **17**, a substrate class that undergoes decomposition in the Pd/Ir/Ph₂I⁺ system. Overall, the room-

temperature Pd/photocatalyzed C–H arylation methods using Ar_2I^+ and ArN_2^+ reagents are often complementary in terms of substrate scope.^[13]

Conclusion

In summary, this paper describes a photoredox Pd/Ir-catalyzed C–H arylation with diaryliodonium reagents. The unusually low reaction temperature, the requirement for light and a photocatalyst, the inhibitory effect of radical scavengers, and the observed chemoselectivity trends are all consistent with a radical mechanism for this transformation. This stands in contrast to the analogous thermal reaction that requires dramatically higher temperature (100 °C) and is believed to proceed via an ‘ionic’ $2e^-$ pathway. This example adds to a growing body of work suggesting that re-routing traditional metal-catalyzed transformations *via* radical pathways can offer major advantages in terms of reaction rates, substrate scope and functional group tolerance.^[1,2,14]

Experimental Section

Representative procedure for C–H phenylation of substrate 1

N-Phenylpyrrolidinone **1** (80.6 mg, 0.50 mmol, 1.0 equiv), $[\text{Ph}_2\text{I}]\text{OTf}$ (430 mg, 1.00 mmol, 2.0 equiv), $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (22.8 mg, 0.025 mmol, 0.05 equiv), and $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (13.3 mg, 0.05 mmol, 0.10 equiv) were combined in MeOH (2.5 mL) in a 4 mL scintillation vial. The reaction mixture was cooled in an ice bath (to prevent solvent evaporation) and sparged with N_2 using a submerged needle for 10 min, and the vial was then immediately sealed with a Teflon-lined cap. The vial was placed on a stir plate with two 26 W compact fluorescent light bulbs (one on either side of the vial about 5–8 cm away), and the reaction mixture was allowed to stir at room temperature for 15 h. The reaction mixture was diluted with EtOAc (50 mL) and washed with 10% aqueous Na_2SO_3 (2×25 mL) and brine (1×25 mL). The combined aqueous layers were extracted with EtOAc (3×10 mL), and the organic layers were then combined, dried over MgSO_4 , filtered, concentrated, and purified by column chromatography on silica gel ($R_f = 0.17$ in 20% hexanes/80% Et_2O). Product **1a** was obtained as a pale yellow oil (96.3 mg, 81% yield). ^1H and ^{13}C NMR data matched those reported in the literature.^[6b]

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

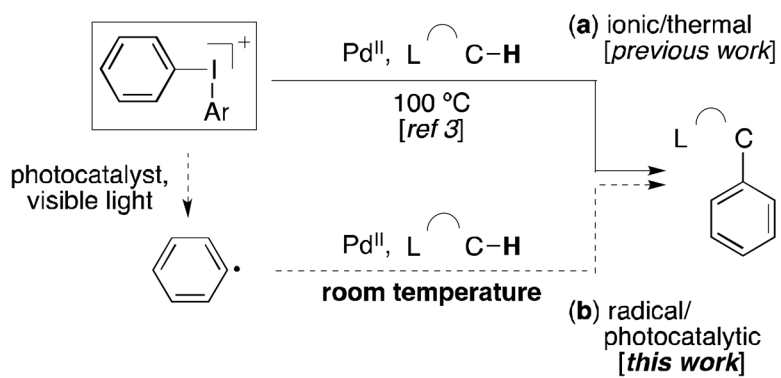
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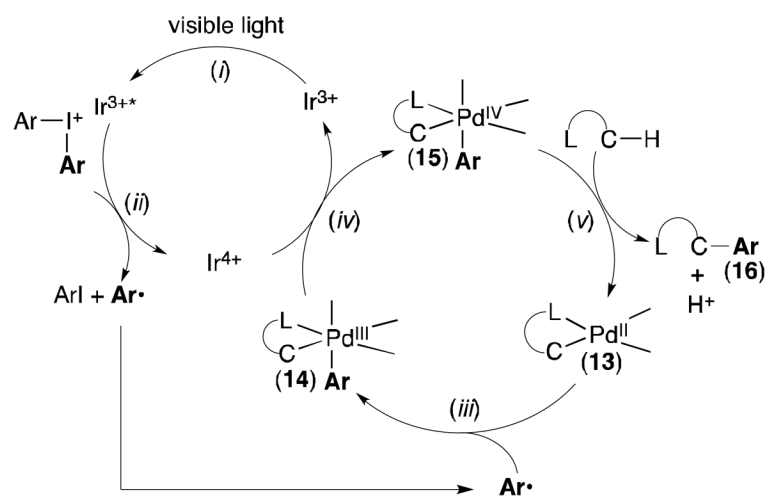
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6. Arylation of substrates containing activated C–H bonds, such as the electron rich C–H bonds in indole, do not necessarily require forcing conditions (see ref 4b for an example). For one rare instance of room temperature ligand-directed arylation of unactivated aromatic C–H bonds with Ar_2I^+ , see ref 4d. However, the latter transformation requires added TfOH and has not been demonstrated to be general for any directing groups beyond phenol esters.
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12. Although one equivalent of H^+ is generated over the course of the reaction, the growing acid concentration does not appear to influence the reaction rate. For example, when 20 mol % TfOH is added to the reaction of substrate 1, the GC calibrated yield of 1a after 2 h is 33%, compared to 32% in the absence of added TfOH.
13. The comparative advantages/drawbacks of diaryliodonium salts versus aryldiazonium salts is somewhat subjective and has been the topic of a recent review: Bonin H, Fouquet E, Felpin FX. *Adv Synth Catal.* 2011; 353:3063–3084.
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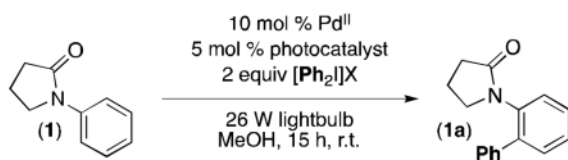
**Scheme 1.**

Two different pathways for Pd-catalyzed C-H arylation with Ph_2I^+ .

**Scheme 2.**

Possible mechanism for the Pd/Ir-catalyzed C-H arylation with Ar₂I⁺.

Table 1

Optimization of the room-temperature C–H phenylation reaction of **1** with Ph_2I^{+a} 

Entry	Pd ^{II}	Photocatalyst	X	Yield (%) ^[b]
1	Pd(OAc) ₂	Ru(bpy) ₃ Cl ₂	BF ₄ ⁻	18
2	Pd(NO ₃) ₂	Ru(bpy) ₃ Cl ₂	BF ₄ ⁻	23
3	Pd(NO ₃) ₂	Ir(ppy) ₃	BF ₄ ⁻	17
4	Pd(NO ₃) ₂	Ir(ppy) ₂ (dtbbpy)PF ₆	BF ₄ ⁻	57
5	Pd(NO ₃) ₂	Ir(ppy) ₂ (dtbbpy)PF ₆	OTf ⁻	66
6 ^[c]	Pd(NO ₃) ₂	Ir(ppy) ₂ (dtbbpy)PF ₆	OTf ⁻	94
7 ^[c]	none	Ir(ppy) ₂ (dtbbpy)PF ₆	OTf ⁻	2
8 ^[c]	Pd(NO ₃) ₂	none	OTf ⁻	2
9 ^[c,d]	Pd(NO ₃) ₂	Ir(ppy) ₂ (dtbbpy)PF ₆	OTf ⁻	0

^[a]General conditions: **1** (1 equiv), Pd^{II} (0.10 equiv), photocatalyst (0.05 equiv), [Ph₂I]X (2 equiv), MeOH (0.2 M in **1**), 26 W lightbulb, 15 h, rt.

^[b]Yields determined by GC.

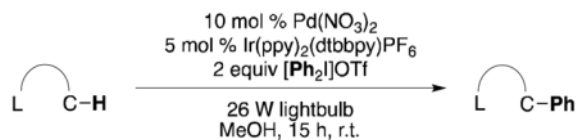
^[c]Reaction was degassed by sparging with N₂ for 1 min.

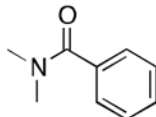
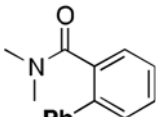
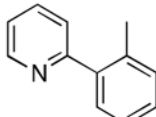
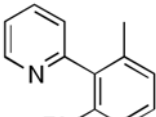
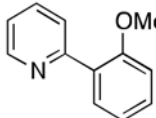
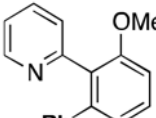
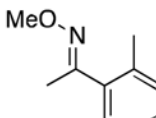
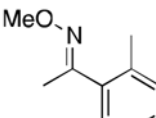
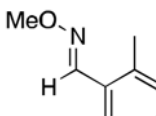
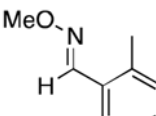
^[d]General conditions, but with no light.

Table 2

Substrate scope for the Pd/Ir-catalyzed C–H phenylation reaction with Ph_2I^{+} .^[a]

Entry	Substrate	Product	Isolated yield (%)
1			81
2			94
3 ^[b]			72
4 ^[b,c,d]			44
5			40
6			54



Entry	Substrate	Product	Isolated yield (%)
7			9
	(7)	(7a)	
8			62
	(8)	(8a)	
9			67
	(9)	(9a)	
10			60
	(10)	(10a)	
11			57
	(11)	(11a)	

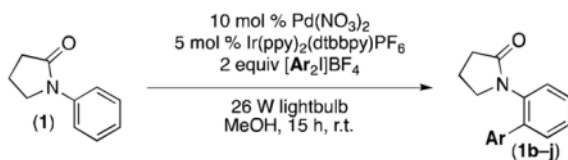
[a] General conditions: substrate (1 equiv), [Ph₂I]OTf (2 equiv), Pd(NO₃)₂ (0.10 equiv), Ir(ppy)₂(dtbbpy)PF₆ (0.05 equiv), MeOH (0.2 M in substrate), 26 W lightbulb, 15 h, r.t., degassed by sparging with N₂.

[b] [Ph₂I]BF₄ was the oxidant.

[c] With 1 equiv MgO.

[d] 0.20 equiv Pd(NO₃)₂.

Table 3

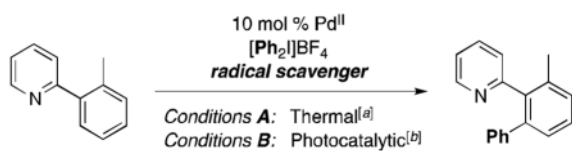
Scope of Ar₂I⁺ salts for Pd/Ir-catalyzed C–H arylation of **1**.^[a]

Entry	Ar	Product	Isolated yield (%)
1	<i>p</i> -CF ₃ C ₆ H ₄	1b	69
2	<i>m</i> -CF ₃ C ₆ H ₄	1c	56
3	<i>o</i> -CF ₃ C ₆ H ₄	1d	46
4	<i>p</i> -ClC ₆ H ₄	1e	77
5	<i>p</i> -BrC ₆ H ₄	1f	79
6	<i>p</i> -CH ₃ C ₆ H ₄	1g	87
7	<i>o</i> -CH ₃ C ₆ H ₄	1h	85
8 ^[b]	Mes	1i	11
9	<i>p</i> -CH ₃ OC ₆ H ₄	1j	41

^[a]General conditions: **1** (1 equiv), [Ar₂I]BF₄ (2 equiv), Pd(NO₃)₂ (0.10 equiv), Ir(ppy)₂(dtbbpy)PF₆ (0.05 equiv), MeOH (0.2 M in **1**), 26 W lightbulb, 15 h, r.t., degassed by

^[b]OTf salt of oxidant. sparging with N₂.

Table 4

Effect of radical scavengers on the Pd/Ir-catalyzed C–H arylation of **8**.

Entry	Scavenger	Mol %	Conditions	Yield (%) ^[c]
1	none	--	A	79 ± 7
2	galvinoxyl	25	A	81 ± 1
3	galvinoxyl	100	A	74 ± 8
4	none	--	B	52 ± 4
5	galvinoxyl	10	B	42 ± 2
6	galvinoxyl	25	B	20 ± 9
7	TEMPO	50	B	34 ± 14
8	TEMPO	100	B	6 ± 2

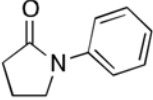
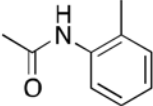
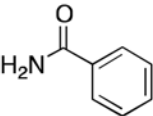
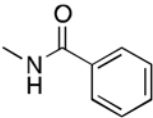
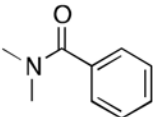
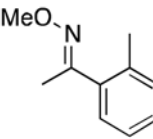
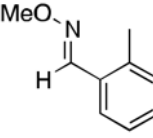
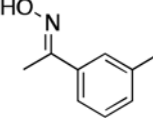
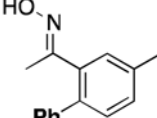
^[a]Thermal conditions **A**: **8** (1 equiv), [Ph₂I]BF₄ (1.1 equiv), Pd(OAc)₂ (0.10 equiv), AcOH (0.12 M in **8**), 15 h, 100 °C.

^[b]Photocatalytic conditions **B**: **8** (1 equiv), [Ph₂I]BF₄ (2 equiv), Pd(NO₃)₂ (0.10 equiv), Ir(ppy)₂(dtbbpy)PF₆ (0.05 equiv), MeOH (0.2 M in **8**), 26 W lightbulb, 15 h, r.t., degassed by sparging with N₂.

^[c]GC calibrated yield reported as % yield ± standard deviation.

Table 5

Comparison of Pd/Ir-catalyzed C–H phenylation with Ph_2I^+ vs Pd/Rucatalyzed C–H phenylation with PhN_2^+ .

Substrate	Product	Yield (%) with $\text{Ph}_2\text{I}^+[a,b]$	Yield (%) with $\text{PhN}_2^+[a,c]$
	1a	89	91
(1)			
	3a	69 ^[d]	89
(3)			
	5a	54	25
(5)			
	6a	52	38
(6)			
	7a	11	8
(7)			
	10a	52	23
(10)			
	11a	63	68
(11)			
		<1 ^[e]	66
(17)			

[a] GC calibrated yield.

[b] General conditions: substrate (1 equiv), [Ph₂I]OTf (2 equiv), Pd(NO₃)₂ (0.10 equiv), Ir(ppy)₂(dtbbpy)PF₆ (0.05 equiv), MeOH (0.2 M in substrate), 26 W lightbulb, 15 h, r.t., degassed by sparging with N₂.

[c] General conditions: substrate (1 equiv), [PhN₂]BF₄ (4 equiv), Pd(OAc)₂ (0.10 equiv), Ru(bpy)₃Cl₂•6H₂O (0.025 equiv), MeOH (0.1 M in substrate), 26 W lightbulb, r.t., 15 h, degassed by sparging with N₂.

[d] [Ph₂I]BF₄ was the oxidant.

[e] Product **17a** was not detected by GC, and only traces amounts of **17** and 3'-methylacetophenone were formed.