

Room-Temperature Arylation of Arenes and Heteroarenes with Diaryliodonium Salts by Photoredox Catalysis

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Abstract: Aryl radicals produced by irradiation of diaryliodonium salts with visible light under the catalysis of $[\text{Ru}(\text{bpy})_3]^{2+}$ undergo coupling with a wide range of arenes and heteroarenes, affording various biaryls through direct C–H arylation at room temperature.

Key words: arenes, heteroarenes, visible light, aryl radicals, ruthenium

Photoredox catalysis promoted by visible light has arisen as a growing field in organic synthesis, which provides efficient synthetic methods and sustainable catalytic processes.¹ The group of MacMillan,² Yoon,³ Stephenson,⁴ Akita,⁵ and others⁶ have demonstrated the successful application of this concept in chemical synthesis. Despite these advances, the synthesis of biaryls under visible-light photoredox catalysis is still a challenge for chemists. Recently, Sanford^{7a} and König^{7b} reported the construction of aryl–aryl bonds by visible-light-driven catalysis. Using aryldiazonium salts as the source of the aryl moiety is of particular interest, as it provides good solutions for the preparation of compounds containing the biaryl motif.

Diaryliodonium salts⁸ are another source of aryl radicals,⁹ which have led to their widespread use as one of the most important photoinitiators for cationic polymerization.¹⁰ Although they have also been widely used as important arylating reagents in organic synthesis,^{11–13} their substantial applications catalyzed by visible light in organic synthesis are rare. In continuing our work in aryl–aryl coupling,¹⁴ herein we report the direct C–H bond arylation of arenes and heteroarenes with diaryliodonium salts, which requires visible light and $\text{Ru}(\text{bpy})_3\text{Cl}_2$ as a catalyst and which provides a valuable alternative method for the synthesis of biaryls.

Our initial investigation focused on the direct arylation of *N*-methylpyrrole (**2a**) with diphenyliodonium salt **1a**. Following the screening of a wide range of conditions (Supporting Information, Table S1), we were delighted to find that using a low-energy, 3W blue LED bulb (emitting at 460 ± 15 nm) as the source of visible light and

$[\text{Ru}(\text{bpy})_3][\text{Cl}]_2 \cdot 6\text{H}_2\text{O}$ (maximum absorption at $\lambda = 452$ nm) as photocatalyst, the expected product 2-phenyl-*N*-methylpyrrol (**3a**) was formed with 87% isolated yield after 12 hours reaction time in MeCN at room temperature (Table 1, entry 4). Notably, the Ru^{II} photocatalyst and visible light are all essential for the reaction. In the absence of any of these components, no reaction occurred (Table 1, entries 1–3). The amount of **2a** and the reaction temperature also play an important role; reducing the usage of **2a** led to lower yield and deviating from room temperature does not benefit the reaction either (Table 1, entries 5–8). The counteranion of diphenyliodonium appears to impact on the product yield as well, with the trifluoromethanesulfonate giving the most promising results (Table 1, entries 4, 9–12). This may not be surprising, as counteranions are known to affect the product distribution of diaryliodonium photolysis.^{9a} The Ru^{II} catalyst appears highly effective for the reaction. At 0.1 mol% or even 0.05 mol% loading, **3a** was still isolated in over 70% yield, showing the potential of such a photocatalyst in promoting visible-light-driven coupling reactions (Table 1, entries 13 and 14).

With the optimal conditions in hand, the substrate scope was subsequently investigated. First, the coupling of **2a** with a wide range of diaryliodonium salts **1** with the phenyl ring bearing various substituents, including OMe and NO_2 as well as CO_2Me and Br, was attempted at ambient temperature.¹⁶ As can be seen from Table 2, the desired products were isolated in better yields with electron-withdrawing substituents. This may stem from easier electron transfer from the excited $\text{Ru}^{\text{II}*}$ to such iodonium species (vide infra). In particular, the diaryliodonium salts containing halides afforded excellent yields regardless of the substitution position (**3c–i**). The C–X (X = F, Cl, and Br) bonds survived the mild reaction conditions, leaving space for further reactions.

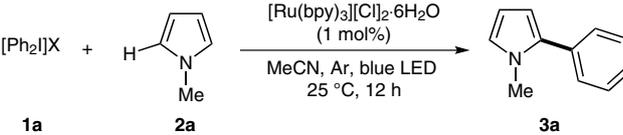
Unsymmetrical diaryliodonium salts are also viable, and it was found that it is the sterically less hindered aromatic moiety that is preferentially transferred. As can be seen from Table 3, a range of arylmesityliodonium salts underwent coupling with **2a** under the photocatalytic conditions above, affording arylated *N*-methylpyrrols **3** in good yield, albeit lower than those obtained with the symmetric iodonium salts in Table 2.¹⁶ Again, electron-withdrawing substituents in the transferring aryl group afforded the de-

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Table 1 Optimization of Conditions for the Photocatalytic Cross-Coupling of Diphenyliodonium Salt **1a** with *N*-Methyl Pyrrole (**2a**)^a


Entry	Reaction conditions	X	Time (h)	Yield (%) ^b
1	no catalyst, no light	OTf	24	0
2	catalyst, no light	OTf	24	0
3	no catalyst, light	OTf	24	0
4	catalyst, light	OTf	12	87
5	catalyst, light ^c	OTf	12	37
6	catalyst, light ^d	OTf	12	59
7	catalyst, light, 0 °C	OTf	12	54
8	catalyst, light, 40 °C	OTf	12	37
9	catalyst, light	PF ₆	12	84
10	catalyst, light	BF ₄	12	71
11	catalyst, light	OTFAc	12	70
12	catalyst, light ^e	Br	12	69
13	catalyst, light ^f	OTf	24	78
14	catalyst, light ^g	OTf	36	77

^a All the reactions were carried out at the scale of 0.4 mmol of **1** and 20 mmol of **2a** in 3 mL MeCN.

^b Isolated yields.

^c Conditions: 4 mmol of **2a**.

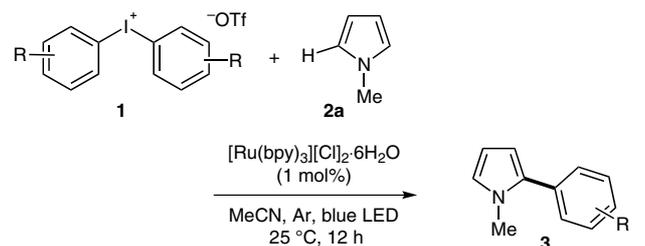
^d Conditions: 8 mmol of **2a**.

^e The solvent was DMSO.

^f Conditions: 0.1 mol% Ru^{II} catalyst were used.

^g Conditions: 0.05 mol% Ru^{II} catalyst were used.

sired products in better yields, and C–X bonds were tolerated. The flexibility of the arylating reagents enhances the applicability of this method in the preparation of biaryl compounds.

Table 2 Direct Arylation of *N*-Methyl Pyrrole (**2a**) with Symmetric Diaryliodonium Salts **1**^a

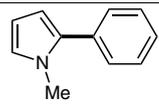
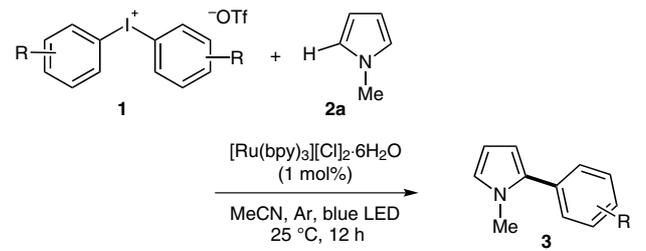
Entry	Product	Yield (%)
1		87
	3a	

Table 2 Direct Arylation of *N*-Methyl Pyrrole (**2a**) with Symmetric Diaryliodonium Salts **1**^a (continued)

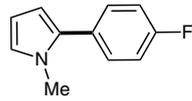
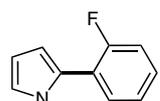
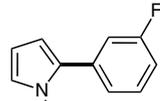
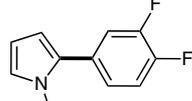
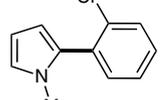
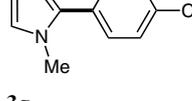
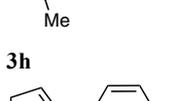
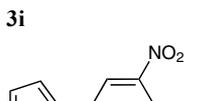
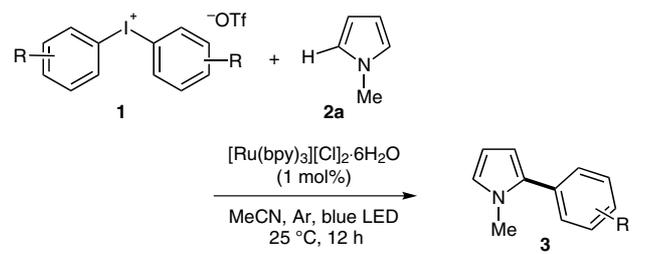
Entry	Product	Yield (%)
2		91
	3b	
3		91
	3c	
4		85
	3d	
5		92
	3e	
6		95
	3f	
7		94
	3g	
8		89
	3h	
9		89
	3i	
10		85
	3j	

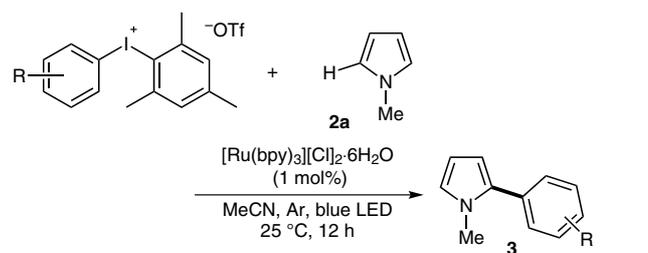
Table 2 Direct Arylation of *N*-Methyl Pyrrole (**2a**) with Symmetric Diaryliodonium Salts **1**^a (continued)

Entry	Product	Yield (%)
11		78
12		73
13		65
14		75
15		40
16		75

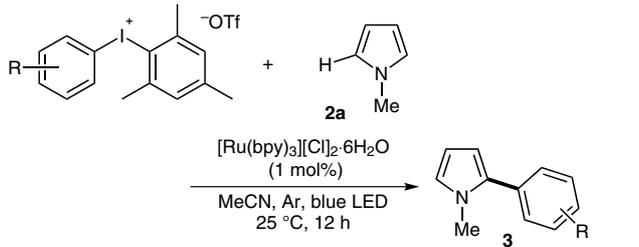
^a All the reactions were carried out at the scale of 0.4 mmol of **1** and 20 mmol of **2a** in 3 mL MeCN. Isolated yields.

Of particular interest is that the visible-light-promoted arylation can be extended into arenes and heteroarenes of diverse properties, including substituted benzenes, pyrroles, furans, and thiophenes. A broad range of aryl-heteroaryl and diaryl products **4a–p** were formed in good to excellent yield, as shown in Table 4. In many cases, the quantity of the arenes or heteroarenes can be reduced without adversely affecting the yield. Moreover, no protection was required for the arylation of pyrrole, where only monoarylation occurred. In general, electron-rich

arenes demonstrate higher reactivity than their electron-poor analogues. For instance, the yield of **4n** is significantly higher than that of **4j**, even though the former is sterically more demanding, and little reaction was observed when nitrobenzene was used. It is also worth noting that the reactions of pyrroles, furan, thiophenes, 2,3-benzothiophene, and 2,3-benzofuran with diaryliodonium salts all took place primarily at the 2-position of the heteroarenes. This regio-preference is probably a result of resonance stabilization of intermediate radical adduct generated during the photocatalysis (vide infra).

Table 3 Direct Arylation of *N*-Methyl Pyrrole (**2a**) with Unsymmetrical Diaryliodonium Salts^a

Entry	Product	Yield (%)
1		60
2		60
3		64
4		65
5		64
6		70

Table 3 Direct Arylation of *N*-Methyl Pyrrole (**2a**) with Unsymmetrical Diaryliodonium Salts^a (continued)


Entry	Product	Yield (%)
7		55
8		35
9		68
10		35
11		72

^a The conditions were the same as those given in Table 2.

Table 4 Direct Arylation of Arenes and Heteroarenes with Diaryliodonium Salt **1k**^a

Entry	Product	Yield (%)
1		81
2		85 ^b

Table 4 Direct Arylation of Arenes and Heteroarenes with Diaryliodonium Salt **1k**^a (continued)

Entry	Product	Yield (%)
3		90 ^b
4		63 ^b
5		60
6		82
7		66 ^b
8		56 ^b
9		45 ^b
10		50
11		55

Table 4 Direct Arylation of Arenes and Heteroarenes with Diaryliodonium Salt **1k**^a (continued)

Entry	Product	Yield (%)
12		70
13		51 ^b
14		79 ^b
15		65 ^b
16		52 ^b

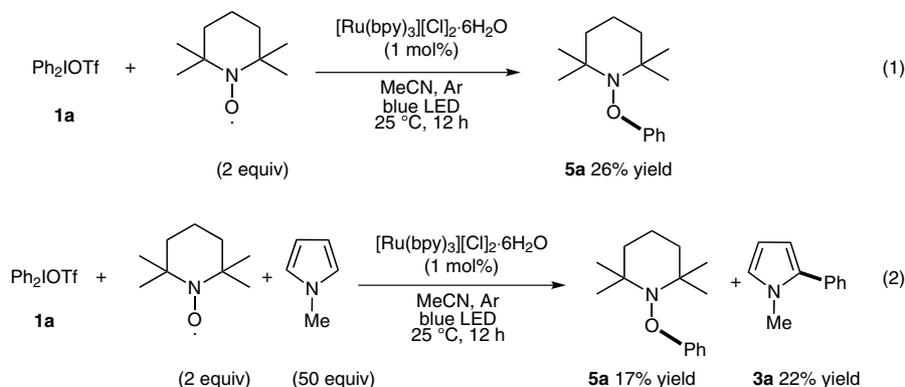
^a The reactions were carried out on a scale of 0.4 mmol of **1k** and 20 mmol of arene or heteroarene in 3 mL MeCN. Isolated yields are given.

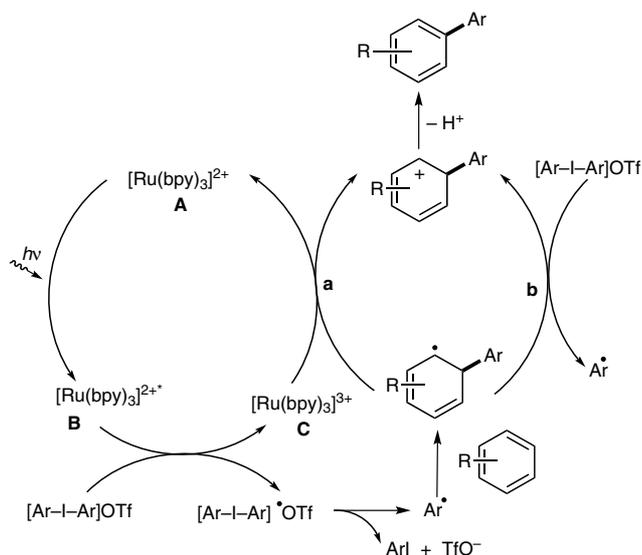
^b Conditions: 0.4 mmol of **1a** and 4 mmol of arene or heteroarene in 3 mL MeCN.

The C–H arylation described is likely to proceed through a radical mechanism, and this is supported by preliminary mechanistic investigations. Thus, when the diphenyliodonium salt **1a** was irradiated with the 3W blue LED bulb in the presence of a radical trap, 2,2,6,6-tetramethylpiperidinoxyl (TEMPO), while in the absence of *N*-methyl pyrrole (**2a**), compound **5a** was formed and isolated in 26% yield (Scheme 1). Furthermore, addition of TEMPO to the photocatalytic reaction of **1a** with **2a** suppressed the arylation process significantly, with **3a** obtained only in 22% yield (Scheme 1). The TEMPO-trapped intermediate **5a** was isolated in 17% yield. The formation of **5a** and the suppression of the arylation reaction in the presence of TEMPO lend support to radical being involved in the photocatalytic arylation.

A plausible mechanism is shown in Scheme 2 on the basis of the above experiments and literature reports.^{9,10} There are three key steps: (1) irradiation of the catalyst at the ground state **A**, generating excited $[\text{Ru}(\text{bpy})_3]^{II*}$ **B**; (2) single electron transfer from the excited catalyst **B** (–0.86 V vs. SCE)¹ to the diaryliodonium salt **1a** ($E_{1/2} = -0.2$ V vs. SCE, X = PF₆),¹⁵ releasing a phenyl radical while oxidizing the catalyst to $[\text{Ru}(\text{bpy})_3]^{III}$ **C**; (3) addition of the phenyl radical to the arene to give a new radical intermediate, which is subsequently transformed into a carbocation intermediate by two possible pathways: oxidation by the strongly oxidizing $[\text{Ru}(\text{bpy})_3]^{III}$ (pathway a) or by the diaryliodonium salt (pathway b). The latter would lead to a radical-chain transfer reaction and appears to be less likely, as judged by the reduction potentials of the two oxidants (1.3 against –0.2 V, vs. SCE)^{1,15} and by the observation that switching off the light stopped the arylation. Finally, deprotonation of the carbocation intermediate regenerates the aromatic system, furnishing the desired coupling adducts.

In summary, a highly effective visible-light-promoted coupling of arenes and heteroarenes with diaryliodonium salts has been developed. The reaction proceeds at room temperature and displays a broad substrate scope, thus providing a mild alternative method for the direct arylation of aromatic C–H bonds. The reaction mechanism and further application of diaryliodonium salts in other reactions are being actively explored in our group.

**Scheme 1** Mechanistic investigations



Scheme 2 A plausible mechanisms made possible by photocatalysis

Acknowledgment

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Supporting Information for this article is available online at <http://www.thieme-connect.com/ejournals/toc/synlett>.

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(16) **General Procedure for the Direct Arylation of Arenes and Heteroarenes with Diaryliodonium Salts**

Method A

A flame dried 10 mL Schlenk tube was equipped with a rubber septum and magnetic stir bar and was charged with tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate (3 mg, 0.004 mmol, 0.01 equiv), diaryliodonium salts (0.4 mmol, 1.0 equiv), arenes or heteroarenes (20 mmol, 50 equiv), and MeCN (3 mL). The mixture was degassed by the freeze-pump-thaw procedure with Ar, and then the Schlenk tube was placed at a distance of 10 cm from a 3w Blue LED bulb. After stirring at 25 °C for 12 h, the solvent was removed under reduced pressure, and the residue purified by flash chromatography to afford the product. The identity and purity of the product was confirmed by ¹H NMR and ¹³C NMR spectroscopy and MS or HRMS.

Method B

This method is the same as method A except that a smaller amount of arene or heteroarene (4 mmol, 10 equiv) was used. The method was used mainly for substrates that did not fully dissolve under the conditions in method A.

1-Methyl-2-Phenyl-1H-pyrrole (3a)

Compound **3a** was obtained following the method A. White

solid, mp 43–44 °C; *R_f* = 0.2 (PE–CH₂Cl₂ = 10:1); yield 87% (63 mg). ¹H NMR (400 MHz, CDCl₃): δ = 7.43–7.40 (m, 4 H), 7.34–7.31 (m, 1 H), 6.75 (s, 1 H), 6.27–6.24 (m, 2 H), 3.69 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 134.7, 133.5, 128.8, 128.4, 126.7, 123.7, 108.7, 107.8, 35.1. MS (EI): *m/z* = 158.1 [M + H]⁺.

1-Methyl-2-(4-Fluorophenyl)-1H-pyrrole (3b)

Compound **3b** was obtained following the method A. White solid, mp 64 °C; *R_f* = 0.2 (PE–CH₂Cl₂ = 20:1); yield 91% (64 mg). ¹H NMR (400 MHz, CDCl₃): δ = 7.39–7.36 (m, 2 H), 7.13–7.09 (m, 2 H), 6.73 (d, *J* = 2.0, 1 H), 6.23–6.22 (m, 2 H), 3.65 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 162.0 (d, *J_{C-F}* = 245.8 Hz), 133.6, 130.3 (d, *J_{C-F}* = 8.8 Hz), 129.5 (d, *J_{C-F}* = 3.3 Hz), 123.6, 115.3 (d, *J_{C-F}* = 21.3 Hz), 108.7, 107.8, 34.9. IR (KBr, plate): ν = 3429, 2950, 2923, 1719, 1609, 1494, 1437, 1279, 859, 779, 705 cm⁻¹. ESI-HRMS: *m/z* calcd for C₁₁H₁₁FN [M + H]⁺: 176.0876; found: 176.0866.

1-Methyl-2-(2-Fluorophenyl)-1H-pyrrole (3c)

Compound **3c** was obtained following the method A. Colorless oil; *R_f* = 0.2 (PE–CH₂Cl₂ = 20:1); yield 91% (64 mg). ¹H NMR (400 MHz, CDCl₃): δ = 7.38–7.32 (m, 2 H), 7.19–7.12 (m, 2 H), 6.78 (t, *J* = 2.0 Hz, 1 H), 6.25 (d, *J* = 2.0 Hz, 2 H), 3.58 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 160.0 (d, *J_{C-F}* = 245.0 Hz), 132.1 (d, *J_{C-F}* = 3.1 Hz), 129.2 (d, *J_{C-F}* = 8.1 Hz), 128.2, 124.1 (d, *J_{C-F}* = 3.4 Hz), 123.5, 121.2 (d, *J_{C-F}* = 15.3 Hz), 115.7 (d, *J_{C-F}* = 22.5 Hz), 109.9, 107.9, 34.7. ESI-HRMS: *m/z* calcd for C₁₁H₁₁FN [M + H]⁺: 176.0876; found: 176.0871.

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