

Cu-Catalyzed Direct C6-Arylation of Indoles

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S Supporting Information

ABSTRACT: The first example of direct and site-selective arylation of indoles at the C6 position has been reported. The key to this high regioselectivity is the appropriate choice of the N–P(O)^tBu₂ directing group and the use of diaryliodonium triflate salts as the coupling partners in the presence of catalytic CuO. The protocol is distinguished by mild reaction system that avoids ligand and additives, exhibiting wide scope of indole and arene coupling components without compromising its efficiency and scalability, thus representing a significant advancement in the implementation of regioselective direct arylation of indoles.

The ubiquity and relatively low cost of hydrocarbons makes C–H functionalization an attractive alternative to traditional coupling protocols.¹ Due to the presence of multiple C–H bonds with subtle difference in activation barrier, controlling the positional selectivity represents the key challenge.² As an important structural motif, considerable attention has been turned to the selective functionalization of indole C–H bonds over the years.³ There are six C–H bonds in the indole core on C2 to C3 (pyrrole core) and C4 to C7 (benzene core) positions that can be functionalized. The usual reactivity of indoles suggested that metalation occurs preferentially at the C3 position.⁴ To override this intrinsic selectivity, introducing a directing group on N atom can exhibit C2-selectivity.⁵ In contrast to these much more accessible positions, methods for selective C–H functionalization on the benzene core of indole have received much less attention.⁶ Directing groups like silyl and pivalyl on N atom have been developed to control the regioselectivity at C7 positions to achieve successful C–H borylation,⁷ olefination,⁸ and amidation.⁹ Yu and Baran group has reported C–H olefination (four examples)^{10a} and borylation^{10b} of indoles at C6 position, respectively. However, indoles with blocking groups at the pyrrole core are needed in these two reactions to shield this part from reacting. Undoubtedly, the implicit challenge of a strategy accessing the only C6 selectivity of indoles is evident. A particularly challenging transformation is the intermolecular direct arylation at the C6 position, for which no protocol has been reported so far.

The development of effective and regioselective methods for aryl-indolyl bond formation has been long attracted interest of synthetic chemists. After several years of effort, direct and site-selective arylation of indoles at C2 and C3 position has been

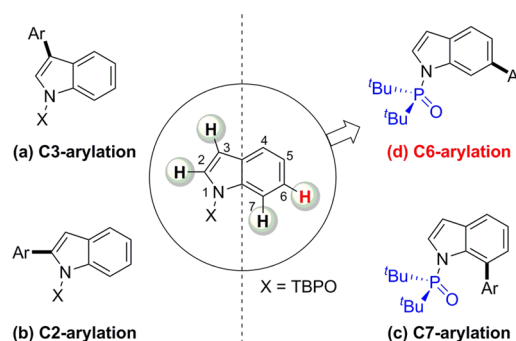


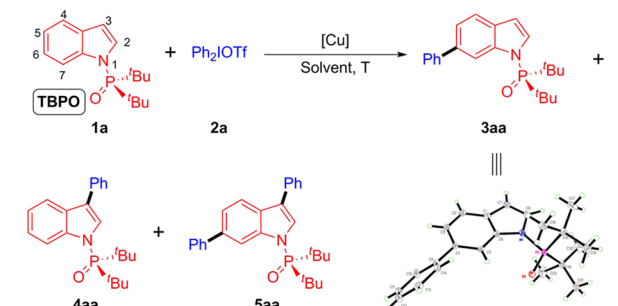
Figure 1. Regioselective direct arylation of indoles.

solved by adopting different strategies (Figure 1a,b).¹¹ As a versatile aryating reagent, diaryliodonium salts¹² are received tremendous attention in this field. For instance, Sanford and co-workers reported Pd-catalyzed direct arylation of indoles with diaryliodonium salts affording 2-arylindoles in high yields under mild reaction conditions;¹³ Gaunt et al. disclosed a Cu(II)-catalyzed C–H functionalization process that can arylate indoles selectively either at C2 or C3 position with diaryliodonium salts;¹⁴ Greaney group also uncovered a Cu-catalyzed tandem C–H/N–H arylation, producing various 1,3-diarylindoles that incorporate both aryl groups from diaryliodonium salts.¹⁵ Until recently, the first direct C7-arylation of indoles has been developed by our group (Figure 1c).¹⁶ The key to the success of this C7-selectivity is the appropriate choice of a N–P(O)^tBu₂ (TBPO) directing group¹⁷ in the presence of Pd(OAc)₂ catalyst using arylboronic acids as the coupling partner. Due to steric hindrance from the di-*tert*-butyl group, the formation of metallacycle through C–H bond activation at C7 position is completely preferable over C2 position. As part of our studies toward regioselective direct arylation processes, herein, we have reported a highly efficient method for direct C6-arylation of indoles (Figure 1d). This regioselective transformation still rests on the former developed TBPO directing group at indole N atom and in combination with diaryliodonium triflate salts as the aryating agents and Cu catalyst.

We began our investigations by monitoring the reactivity of N–P(O)^tBu₂ indole **1a** with diphenyliodonium triflate (**2a**) in the presence of copper catalysts (Table 1). By employing 10.0 mol % of Cu(OTf)₂ in dioxane at 80 °C, we indeed observed a C6–

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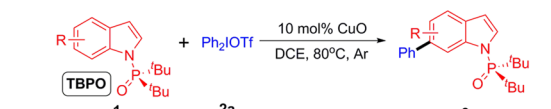
Table 1. Optimization of the Reaction Conditions^a


entry	[Cu] (mol %)	solvent	3aa/4aa/5aa ^b	yield of 3aa (%) ^c
1	Cu(OTf) ₂ (10)	dioxane (1 mL)	77:20:3	12
2	Cu(OTf) ₂ (10)	toluene (1 mL)	36:49:15	18
3	Cu(OTf) ₂ (10)	DCM (1 mL)	81:4:15	53
4	Cu(OTf) ₂ (10)	DCE (1 mL)	85:3:12	70
5	CuCl (10)	DCE (1 mL)	86:4:10	68
6	Cu(OAc) ₂ (10)	DCE (1 mL)	89:3:8	76
7	CuO (10)	DCE (1 mL)	86:2:12	79
8	CuO (10)	DCE (2 mL)	91:1:8	88
9	CuO (10)	DCE (3 mL)	96:1:3	91 (88%)^d
10	CuO (10)	DCE (4 mL)	95:1:4	83
11	CuO (2.5)	DCE (3 mL)	95:1:4	62
12 ^e	CuO (10)	DCE (3 mL)	96:4:0	15
13 ^f	CuO (10)	DCE (3 mL)		0
14 ^g	CuO (10)	DCE (3 mL)		0
15	Pd(OAc) ₂ (10)	DCE (3 mL)		0
16		DCE (3 mL)		0

^aReaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv) in solvent for 12 h under argon. ^bRatios were determined by GC. ^cGC yields. ^dIsolated yield after chromatography. ^eAt 60 °C. ^fAt 50 °C. ^gUsing PhB(OH)₂ instead of Ph₂IOTf.

arylation product **3aa** in 12% yield along with the byproducts **4aa** and **5aa** (**3aa/4aa/5aa** = 77:20:3, entry 1). Remarkably, the TBPO directing group totally overrides the site selectivity for the arylation of indole at the C2- and C7-positions in this catalytic system. Then we have extensively screened the solvent and found DCE to be very effective providing 70% yield of the desired product with encouraging levels of C6-selectivity (**3aa/4aa/5aa** = 85:3:12, entries 2–4). Further screening of Cu-catalysts also had shown noticeable influence (entries 5–7). Among them, utilizing one of the cheapest copper sources CuO, 79% yield of **3aa** was observed with slightly changed regioselectivity (entry 7). Interestingly, the byproducts could be diminished greatly by lowering the concentration of the solution (entries 8–10), and 0.033 M solution of **1a** led to the best result (**3aa/4aa/5aa** = 96:1:3, entry 9). Under these conditions, reducing the amount of CuO led to lower yield (entry 11). Temperature effect was also examined, and 80 °C was found to be optimal (entries 12–13). It is noted that other aryl sources such as PhB(OH)₂ (entry 14), and other metals such as Pd(OAc)₂ were completely ineffective for this transformation (entry 15). Finally, the control experiment confirmed the transformation did not occur in the absence of Cu catalyst after carefully cleaned apparatus (entry 16).

With the set of optimized reaction conditions in hand, we first examined the scope of various indole motifs in this direct C6-arylation process (Table 2). Cross-coupling reactions of Ph₂IOTf (**2a**) with a broad range of *N*-P(O)^tBu₂ indoles were first examined. Indoles bearing electron-neutral and donating substituents including methyl (**3ba–3da**) and methoxy (**3ea**)

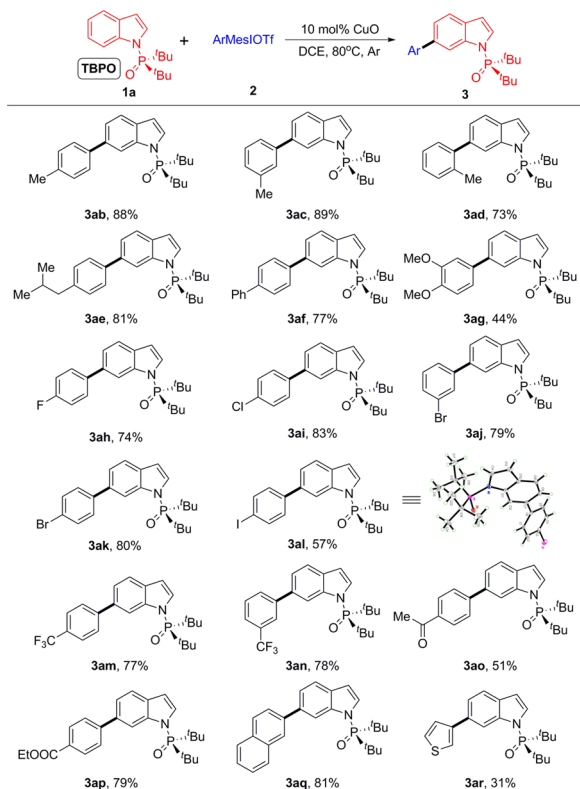
Table 2. Scope of the Indole Coupling Component^a


3ba , 80%	3ca , 87% ^b	3da , 95%
3ea , 72%	3fa , 85%	3ga , 82%
3ha , 74%	3ia , 89%	3ja , 77%
3ka , 34%	3la , 79%	3ma , 68%
3na , 93%	3oa , 82% ^c	

^aReaction conditions: 10 mol % CuO, **1** (0.20 mmol, 1.0 equiv), **2a** (0.30 mmol, 1.5 equiv) in 6 mL of DCE at 80 °C for 12 h under argon. Isolated yields after chromatography. ^bUsing PhMesIOTf (**2a'**) instead of **2a**. ^c20 mol % CuO, **1** (0.10 mmol, 1.0 equiv), **2a** (0.30 mmol, 3.0 equiv) in 6 mL of DCE at 80 °C for 12 h under argon.

groups at the C3–C5 positions underwent facile arylation affording the corresponding products in 72–95% yields. C5-Substitution on indole that exerts steric effect to C6 position also delivered the coupled product **3da** and **3ea** in very high yields. The halogen-containing motifs (F, Cl, Br, and I) work well under the reaction conditions (**3fa–3ka**), highlighting the potential of this process in combination with further conventional cross-coupling transformations. Indole substrates bearing ester (**1l**) and alkenyl (**1m**) group were also compatible affording the desired products **3la** and **3ma**, respectively, in good yields. Remarkably, the direct arylation of 3-indolepropionic acid¹⁸ and 3,3'-dindolylmethane (DIM)¹⁹ derivatives **1n–1o** particularly underlined the power of the present direct arylation reaction, as conventional methods would not allow their synthesis with such great ease.

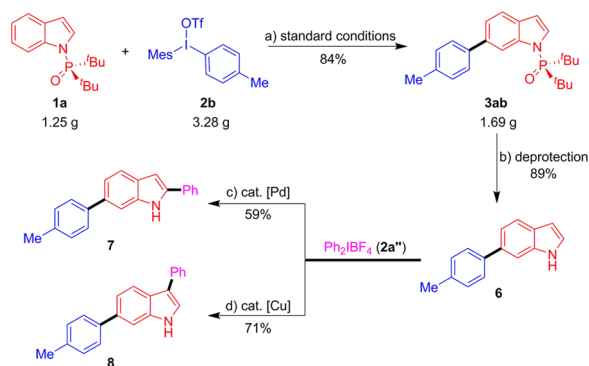
Next, we sought to expand the scope of diaryliodonium salts to achieve transfer of diverse aryl groups to the indole core, and we were very pleased to find that a range of nonsymmetrical arylmesityl reagents **2** worked well with indole **1a** (Table 3). Aromatic groups with various substitution patterns can be transferred effectively from the corresponding iodonium salts irrespective of the position and electronic profile (**3ab–3ag**, 44–89%). *ortho*-Methyl substituted aryl derivative lead to a good yield (**3ad**), suggesting that the increased steric congestion does not affect the reactivity. Useful halogenated arenes including F, Cl, Br, and I were successful (**3ah–3al**), again providing

Table 3. Scope of the (Hetero)arene Coupling Component^a

^aReaction conditions: 10 mol % CuO, **1a** (0.20 mmol, 1.0 equiv), **2** (0.30 mmol, 1.5 equiv) in 6 mL of DCE at 80 °C for 12 h under argon. Isolated yields after chromatography.

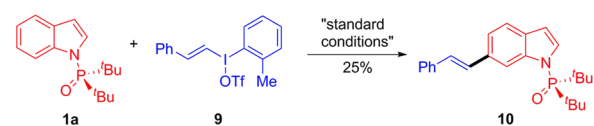
possibilities for subsequent chemical transformations of the products. Aryl group with electron-withdrawing substitutions such as trifluoromethyl (**3am**–**3an**), acyl (**3ao**), and ethyl ester (**3ap**) could be installed on the indole core without any compromise. A naphthalene-containing substrate was also found tolerable under the mild reaction conditions affording the C6-selective product **3aq** in 81% yield. In addition, we were pleased to report that coupling of the heterocyclic aromatic motif such as thiophenyl group (**3ar**) was possible, albeit with a lower yield.

A major benefit of the present protocol is its amenability to gram-scale applications (Scheme 1). Under the standard

Scheme 1. Further Investigations^a

^aReaction conditions: (a) 10 mol % CuO, DCE, 80 °C; (b) 6.0 equiv of LiAlH₄, dioxane, rt; (c) 5.0 mol % IMesPd(OAc)₂, AcOH; (d) 10 mol % Cu(OTf)₂, 1.5 equiv of 2,6-di-*tert*-butylpyridine, DCE.

conditions, gram-scale synthesis of **3ab** without notable erosion of yield proved the practicality of this new method. Moreover, the *N*-P(O)^tBu₂ directing group can be easily removed by treatment of **3ab** with LiAlH₄ to provide unprotected indole **4** in 89% yield. With the desired compound in hand, we have investigated their synthetic utility with diphenyliodonium salt **2a''**. By the action of IMesPd(OAc)₂ catalyst, 6-(*p*-tolyl)-1*H*-indole (**6**) reacted with **2a''** in a C2-selective coupling manner to afford 2,6-diarylindole **7** in moderated yield.¹³ Alternatively, the C–H bond at C3 position of **6** can also be arylated directly with **2a''** in the presence of catalytic Cu(OTf)₂ to generate 3,6-diarylindole **8** in 71% yield.¹⁴

Scheme 2. C–H Olefination of Indole **1a** at C6 Position

To further demonstrate the value of this new strategy, we showed that C–H olefination of indole can also be accommodated as part of the C6 selective functionalization process (Scheme 2). Our preliminary experiments revealed that the reaction between indole **1a** and vinyl(aryl)iodonium **9** is also possible, forming the desired vinyl-substituted indole **10** in 25% yield with excellent regioselectivity.

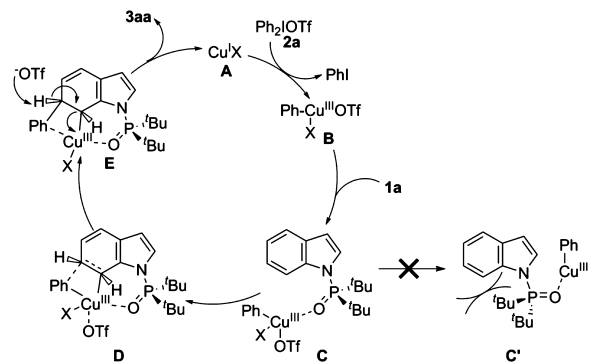


Figure 2. Proposed catalytic cycle.

Precedent DFT calculations of copper-catalyzed *meta*-selective direct arylation of anilide using diaryliodonium salts²⁰ revealed that the selectivity may proceed via a Heck-type four-membered-ring transition state involving an aryl-Cu^{III} species.²¹ On the basis of these studies, we proposed a mechanism of our reaction as shown in Figure 2. Oxidative addition of diaryliodonium triflate **2a** to an Cu^I species **A** resulted from CuO disproportionation²² appears to trigger the reaction to afford the Cu^{III} intermediate **B**. Cu species coordinates to the oxygen atom of the TBPO group on indole leading to the formation of complex **C**. Based on our previous investigation,¹⁶ the steric hindrance of substituents on phosphinoyl groups is crucial to the relative stabilities of **C** and **C'**, which affect the selectivity of reaction. Afterward, the phenyl group bonded to copper is transferred to the C6 position of indole via the Heck-type four-membered-ring transition state **D**, leading to the formation of intermediate **E** with Cu^{III} and phenyl added at the C6 positions. Finally, a base-assisted E2-type elimination delivers the arylated product **3aa** and regenerates the active Cu catalyst.

In summary, we have reported the first CuO-catalyzed C6-selective C–H arylation of indoles with the aid of a sterically hindered and removable $N\text{-P}(\text{O})^t\text{Bu}_2$ directing group. This developed catalytic system can override *ortho*-directing effects as well as electronic biases at the indole C2, C3, and C7 positions. Further development of new cross-coupling reactions as well as mechanistic investigations is going in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.6b05777](https://doi.org/10.1021/jacs.6b05777).

Experimental procedures, characterization data, and spectra of new compounds (PDF)

X-ray crystal structures of **3aa** (CIF)

X-ray crystal structures of **3ja** (CIF)

X-ray crystal structures of **3al** (CIF)

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Notes

The authors declare no competing financial interest.

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