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Full Paper

C–H Activation

Copper(II)-Catalyzed Synthesis of Indoloquinoxalin-6-ones through Oxidative Mannich Reaction

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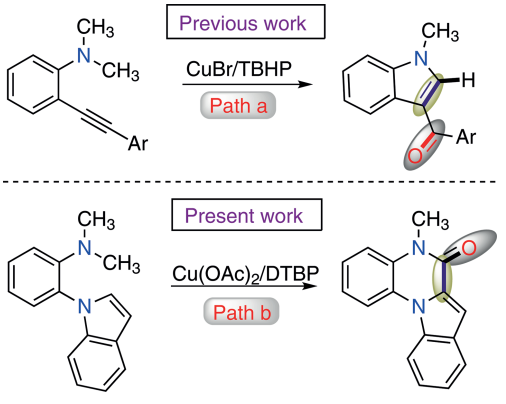
Abstract: A Cu-catalyzed synthesis of indoloquinoxalin-6-one has been developed that starts from *o*-indolyl-*N*,*N*-dialkylamines through sp^3 C–H bond oxidation α to the nitrogen atom with di-*tert*-butyl peroxide as oxidant. Other heterocycles, such as pyrrole, imidazole and benzimidazole derivatives also reacted successfully to give their respective fused quinoxalin-6-one derivatives. In this process, one of the methyl groups is transformed into a carbonyl group.

Introduction

The classic Mannich reaction, which leads to the synthesis of substituted β-amino carbonyl compounds, involves three components: an enolizable aldehyde (or a ketone); an amine (1° or 2°); and formaldehyde. This important C–C bond-forming process comprises two steps: formation of an imine or iminium ion, which is obtained by the condensation of an amine with formaldehyde; and nucleophilic attack of an enolizable aldehyde or a ketone at the reactive carbon end of the imine or iminium ion.[1] In general, an imine or iminium ion generated through an alternative route will react with a suitable nucleophile and likely provide similar results.

An appropriate redox-active transition metal in conjunction with a suitable oxidant can oxidize *N*,*N*-dialkylanilines to the corresponding iminium ion, which, if trapped with a nucleophile, will install the desired functionality at the carbon atom adjacent to nitrogen.[2] This oxidative Mannich concept forms the basis of transition metal catalyzed inert sp^3 C–H functionalization reactions α to nitrogen atoms in *N*,*N*-dialkylanilines.[2] The in-situ generated iminium carbon can be attacked either intermolecularly or intramolecularly with a suitable nucleophile. The intermolecular cross-coupling reaction with tertiary amines has undergone significant advances to encompass a wide range of nucleophiles,[2,3] although the intramolecular version of this reaction has been little studied.[1f,4] The motivation to explore the intramolecular oxidative Mannich reaction led to our recent report on Cu-catalyzed synthesis of 3-aroylindoles from 2-alkynyl-*N*,*N*-dialkylamines, in which the alkynyl group serves as an internal nucleophile (Scheme 1, Path A).[4a] However, other such internal nucleophiles may behave similarly to the alkynyl group. The indolyl moiety is known to act as the coupling partner in intermolecular CDC reactions, in which it forms a $C(sp^2)$–$C(sp^3)$ bond by C3 attack at the iminium ion generated from *N*,*N*-dialkylamines.[5] If the same indolyl moiety is anchored at the *ortho* position of *N*,*N*-dialkylanilines, the stereochemical orientation will inhibit C3 attack and a *6-endo-dig* cyclization reaction takes place by C2 attack. To examine the feasibility of this envisaged intramolecular CDC reaction, 2-indolyl-*N*,*N*-dimethylamine (**1a**) was treated with CuBr (10 mol-%) and aqueous *tert*-butyl hydroperoxide (TBHP; 70 %; 3 equiv.) in dimethyl sulfoxide (DMSO) at 80 °C. Interestingly, the reaction resulted in the formation of indolo[1,2-*a*]quinoxalin-6-one (**1′a**) in 19 % yield (Table 1, Entry 1) through the expected intramolecular $C(sp^2)$–$C(sp^3)$ bond-forming reaction and numerous other products. This process is accompanied by concomitant installation of a carbonyl functionality at the expense of the remaining two sp^3 C–H bonds (Scheme 1, Path B).



Scheme 1. Intramolecular oxidative cyclization reaction of tertiary amines.

The indolo- or pyrrole-fused quinoxalinone moiety is found in compounds that display a variety of pharmacological properties, such as anticancer, anxiolytic, antimicrobial, analgesic, and antiallergic activities.[6] Some of the biologically active molecules that contain quinoxalin-6-one as the core unit are shown in Figure 1. Although an important scaffold, only a few reports are available in the literature for their synthesis that include: (i) two-step reaction of indole-2-carboxylates with 2-fluoronitrobenzenes;[7] (ii) intramolecular Cu-catalyzed *N*-arylation reaction of pyrrole and indole carboxamides and carboxylates

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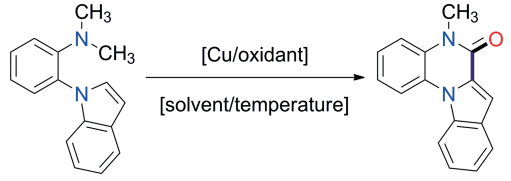
Table 1. Screening of the reaction conditions.[a]



Entry	Catalyst [mol-%]	Oxidant [equiv.]	Temp. [°C]	Solvent	Yield[b] [%]
1	CuBr (10)	TBHP[c] (3)	80	DMSO	19
2	CuCl (10)	TBHP[c] (3)	80	DMSO	16
3	Cu_2O	TBHP[c] (3)	80	DMSO	21
4	$CuBr_2$ (10)	TBHP[c] (3)	80	DMSO	12
5	$CuCl_2$ (10)	TBHP[c] (3)	80	DMSO	10
6	$Cu(OAc)_2$ (10)	TBHP[c] (3)	80	DMSO	24
7	$Cu(OTf)_2$ (10)	TBHP[c] (3)	80	DMSO	18
8	$Cu(OAc)_2$ (10)	TBHP[d] (3)	80	DMSO	15
9	$Cu(OAc)_2$ (10)	DTBP (3)	80	DMSO	29
10	$Cu(OAc)_2$ (10)	H_2O_2[e] (3)	80	DMSO	8
11	$Cu(OAc)_2$ (10)	DTBP (3)	100	DMSO	33
12	$Cu(OAc)_2$ (10)	DTBP (3)	120	DMSO	36
13	$Cu(OAc)_2$ (10)	DTBP (5)	120	DMSO	46
14	**$Cu(OAc)_2$ (10)**	**DTBP (6)**	**120**	**DMSO**	**52**
15	$Cu(OAc)_2$ (10)	DTBP (6)	120	DMF	21
16	$Cu(OAc)_2$ (10)	DTBP (6)	120	MeCN	16
17	$Cu(OAc)_2$ (10)	DTBP (6)	120	toluene	47
18	$Cu(OAc)_2$ (10)	DTBP (6)	120	dioxane	12
19	–	DTBP (6)	120	DMSO	<5

[a] Reaction conditions: *N*,*N*-dimethyl-2-(indolyl)aniline (**1a**; 0.25 mmol) for 13 h. [b] Isolated yield. [c] 70 % aqueous solution. [d] Decane solution (5–6 M). [e] 50 % aqueous solution.

linked with a pendant haloarene;[8] (iii) Pd-catalyzed intramolecular cyclization reaction of indole carboxamides that bear a suitable *o*-halosubstituted aryl group at the amide nitrogen;[9] and (iv) Stevens rearrangement of a spiro-quinoxaline-derived ammonium ylide.[10] However, no method has been reported based on a C–H functionalization strategy. Herein, we have developed an elegant method for the synthesis of indolo[1,2-*a*]quinoxalin-6-one that follows a C–H functionalization protocol.

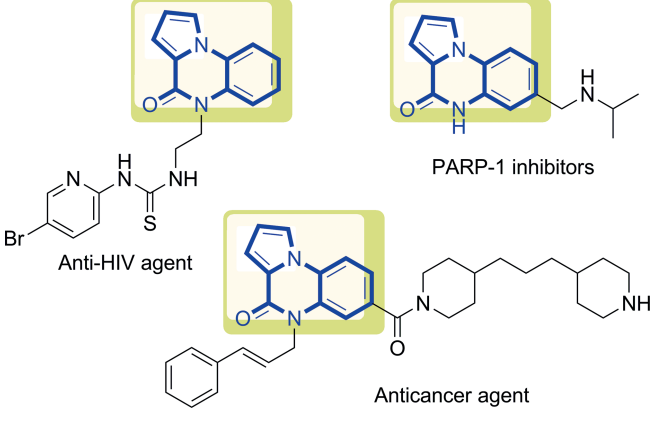


Figure 1. Some biologically active quinoxalin-6-ones.

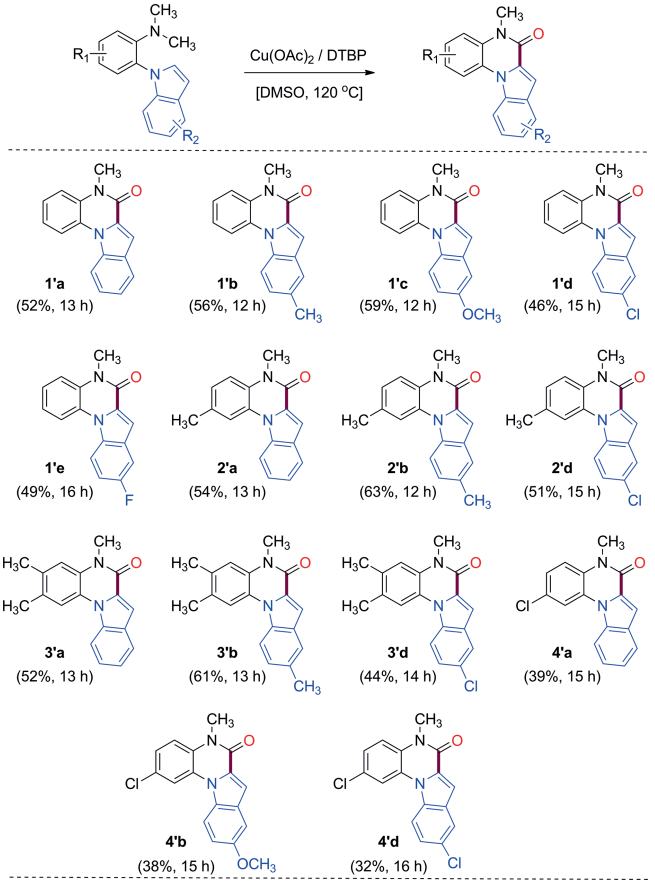
Results and Discussion

To determine the most suitable reaction conditions for this transformation, various reaction parameters, such as catalysts, oxidants, solvents, and temperatures were screened and the results are summarized in Table 1. Various Cu^{I} [CuBr, CuCl, Cu_2O] and Cu^{II} salts [$Cu(OAc)_2$, $CuBr_2$, $CuCl_2$, $Cu(OTf)_2$] tested (Table 1, Entries 1–7) revealed $Cu(OAc)_2$ to be the most effective catalyst (Table 1, Entry 6).

By changing the oxidant from aqueous TBHP to decane TBHP (3 equiv.) an inferior yield (15 %) of the product was obtained (Table 1, Entry 8). No doubt the use of TBHP at 80 °C gave expected product **1′a** with disappearance of starting material **1a**, but it is also associated with mono-demethylation of the starting material and a demethylated cyclized product, which led to difficulties in separating the individual components. The use of di-*tert*-butyl-peroxide (DTBP) as the oxidant slightly increased the product yield, whereas H_2O_2 was almost inactive towards the desired transformation (Table 1, Entries 9 and 10). No doubt, the reaction was slower and the starting material remain unreacted at 80 °C even after 20 h, although formation of demethylated side products was not observed when DTBP was used as oxidant. An increase in the reaction temperature to 100 °C and 120 °C resulted in an increased yield of product, 33 and 36 % respectively (Table 1, Entries 11 and 12). The reaction produced better yields, 46 and 52 % upon increasing the oxidant quantity to 5 and 6 equiv., respectively (Table 1, Entries 13 and 14). Overall, DTBP was found to be advantageous relative to commonly used oxidant TBHP for this transformation. Finally, various other polar [dimethylformamide (DMF), acetonitrile) and non-polar solvents (toluene, dioxane) were screened (Table 1, Entries 15–18). Apart from toluene, which produced a comparable yield to DMSO, other solvents show no positive effects on the reaction. In the absence of copper salt the reaction produces only a trace of the desired product (<5 %), which suggests it is essential (Table 1, Entry 19). The addition of copper salt increases the rate of formation of the iminium ion thereby increasing the product yield. Thus, the optimal reaction conditions were found to be $Cu(OAc)_2$ (10 mol-%) and DTBP (6 equiv.) in DMSO at 120 °C, which were adopted for all following reactions.

After determining the optimized conditions for the reaction, the substrate scope of the methodology was explored. The effects of various substituents on the indolyl ring (R^2) were examined by keeping the aniline part fixed. Substitution on the aryl ring R^2 with electron-donating groups, such as 5-Me (**1b**) and 5-OMe (**1c**), and electron-withdrawing groups, such as 5-Cl (**1d**) and 5-F (**1e**), all afforded corresponding indoloquinoxalin-6-ones (**1′b**–**1′e**) in 46–59 % yields (Scheme 2). However, the yields were better and the times taken were shorter for substrates that possessed electron-donating groups **1′b** (56 %) and **1′c** (59 %) than for substrates that possessed electron-withdrawing groups **1′d** (46 %) and **1′e** (49 %). The structure of **1′b** was confirmed by X-ray crystallography (Figure 2).[11] If the amine-bearing aryl ring R^1 of 2-indolyl-*N*,*N*-dimethyl aniline is substituted with an electron-donating group, such as 4-Me, and aryl moiety R^2 is either without a substituent (**2a**) or substituted, such as 5-Me (**2b**) and 5-Cl (**2d**), then the reactions all

yielded corresponding indoloquinoxalin-6-ones in moderate yields (Scheme 2). The yield improved more if both of the rings contained electron-donating groups, such as 4-Me as for **2′b** (63 %) than for substrates that contained electron-neutral groups, such as **2′a** (54 %), or electron-withdrawing groups, such as **2′d** (51 %), in aryl ring R^2. Similar reactivity trends were observed when aryl ring R^1 was substituted with an electron-donating group, such as 3,4-diMe, and the substituents on aryl ring R^2 were varied from electron-neutral (**3a**), electron-donating (**3b**), and electron-withdrawing (**3d**). Substitution of aryl ring R^1 with a moderately electron-withdrawing group, such as 4-Cl, resulted in relatively lower yields of expected products irrespective of the nature of the substituents on the other ring, as demonstrated with substrates **4a**, **4c**, and **4d** (Scheme 2).



Scheme 2. Substrate scope for indoloquinoxalin-6-ones.[a,b] [a] Reaction conditions: *o*-indolyl-*N*,*N*-dimethylamine (0.25 mmol), $Cu(OAc)_2$ (0.025 mmol), and DTBP (1.5 mmol) in DMSO (1 mL) at 120 °C. [b] Yield of isolated pure product.

Electrophilic aromatic substitution in indoles takes place at C-3 on the five-membered ring. But as seen above, with a favorable intramolecular process electrophilic substitution takes place at the C-2 position on the nitrogen-bearing heterocycle (Scheme 2). Pyrrole, which is a reactive heterocycle, undergoes substitution at the C-2 position. Thus, an analogous fused pyrrole system should react to give pyrroloquinoxalin-6-ones. Fused pyrroles **1f**, **2f**, and **4f** reacted under optimized conditions to give pyrroloquinoxalin-6-ones **1′f**, **2′f**, and **4′f**, respectively, in modest yields (Scheme 3). Other starting materials **1g**, **2g**, and **4g** contained an imidazole moiety, a five membered di-nitrogen heterocycle, for which electrophilic substitution is favored at the C-2 position were specifically designed. Compounds **1g**, **2g**, and **4g** underwent intramolecular oxidative heterocyclization under the present reaction conditions to give corresponding imidazoloquinoxalin-6-ones **1′g**, **2′g**, and **4′g**, respectively, in moderate yields (Scheme 3). The success of this oxidative Mannich reaction was finally applied to benzimidazole-based precursors **1h**, **2h**, and **4h**, all of which afforded respective oxidative cyclized products **1′h**, **2′h**, and **4′h**, respectively, in modest yields (Scheme 3).

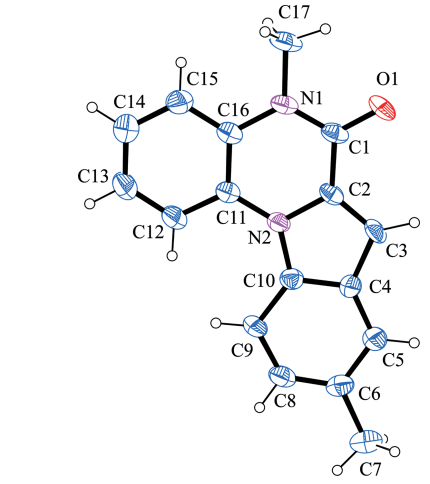
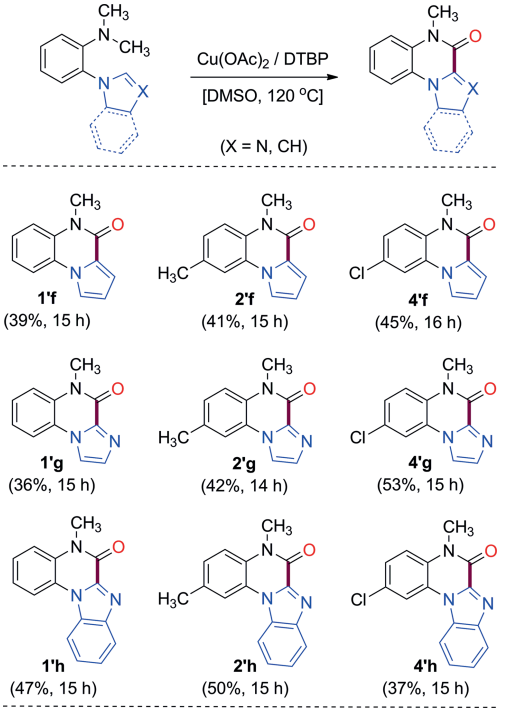
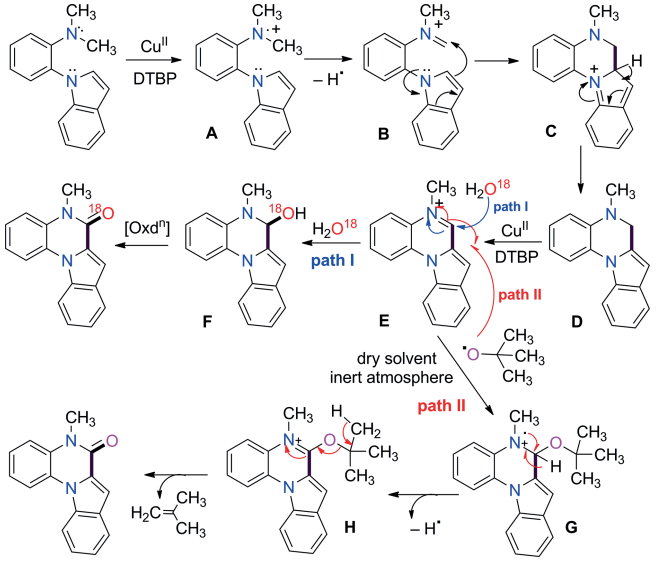


Figure 2. ORTEP view of **1′b**.[11]



Scheme 3. Substrate scope for quinoxalin-6-ones.[a,b] [a] Reaction conditions: Substrate (0.25 mmol), $Cu(OAc)_2$ (0.025 mmol), and DTBP (1.5 mmol) in DMSO (1 mL) at 120 °C. [b] Isolated yield of pure product.

To gain insight into the reaction mechanism, an experiment was carried out in the presence of radical scavenger TEMPO (6 equiv.) under otherwise identical conditions. Retardation in the expected product formation was observed along with formation of numerous side products, which indicates that the mechanism involves radicals. Based on literature reports[2e–2h,3a–3c,4a,4f,12] and the yields pattern obtained for substituted indoloquinoxalin-6-one derivatives (Scheme 2), a plausible mechanism is proposed for this transformation (Scheme 4). Aminyl radical cation **A** is generated by a single electron transfer that is facilitated by Cu^{II} in combination with peroxide. Subsequent abstraction of the hydrogen radical alpha to nitrogen on aminyl radical cation **A** produces iminium ion intermediate **B**. Intermediate **B** undergoes intramolecular cyclization reaction by nucleophilic attack from the C2 position of the indolyl ring to produce intermediate **C**. Rearomatization of intermediate **C** generates 5-methyl-5,6-dihydroindolo[1,2-*a*]quinoxaline (**D**). Similar iminium intermediate **E** is also generated by a single electron transfer/proton abstraction process. This process is then followed by nucleophilic attack of water at the iminium carbon to produce intermediate **F**, which finally oxidizes to product **1′a** (Scheme 4, Path I). The reaction of substrate **1a** under an atmosphere of nitrogen afforded 5-methylindolo[1,2-*a*]quinoxalin-6(5*H*)-one (**1′a**) without affecting the yield. This result suggests that atmospheric oxygen is not the source of carbonyl oxygen. In another experiment, substrate **1a** was treated $H_2{}^{18}O$ (20 equiv.) under otherwise identical conditions. ^{18}O-incorporated 5-methylindolo[1,2-*a*]quinoxalin-6(5*H*)-one (**1′′a**) was obtained as confirmed by HRMS analysis of the reaction mixture (see the Supporting Information). This result confirms that water is the source of carbonyl oxygen, which is often present in commercial-grade DMSO. However, in anhydrous DMSO and under a nitrogen atmosphere the reaction was found to be equally effective. This result suggests that, in addition to water as the nucleophile, perhaps a tertiary-butyl radical obtained from DTBP through homolytic cleavage attacks iminium intermediate **E** to furnish intermediate **G** (Scheme 4, Path II). Loss of a hydrogen radical gives iminium ion intermediate **H**, which loses a molecule of isopropylene to give the expected product.



Scheme 4. Plausible mechanism for the formation of indoloquinoxalin-6-one.

Thus, both Path I and Path II mechanisms operate in tandem. Further, addition of external water (1, 2, and 3 equiv.) to the reaction medium under otherwise identical conditions did not improve the product yield. This indirectly supports the dual mechanism proposal because there are sufficient nucleophiles (water and tertiary butyl radicals) present in the medium. The mechanism with other heterocycles, such as pyrrole, imidazole and benzimidazole, is expected to follow the same pathways.

Conclusions

In conclusion, we have developed a Cu-catalyzed method for the synthesis of indoloquinoxaline-6-ones that starts from *o*-indolyl-*N*,*N*-dimethylarylamines through an intramolecular oxidative coupling reaction with DTBP as the oxidant. The process involves formally the cleavage of three sp^3 C–H bonds and one sp^2 C–H bond with concomitant installation of C–C and C–O bonds to form indoloquinoxalin-6-ones. The use of a cheap catalytic system and extension of the methodology to other heterocyclic systems establishes the practical applicability of the present protocol.

Experimental Section

General Procedure for the Synthesis of 2-(1*H*-Indol-1-yl)-*N*,*N*-dimethylaniline (1a): A mixture of 1*H*-Indole (2 mmol), cuprous oxide (0.15 mol), and potassium hydroxide (3 mmol) was placed into a 25 mL round-bottomed flask and charged with N_2 gas (balloon). To this, DMSO (2 mL) and then 2-iodo-*N*,*N*-dimethylaniline (1 mmol) was added. The resultant mixture was then put into a preheated oil bath at 120 °C and stirred for 24 h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate (20 mL) and then filtered through a pad of Celite. Water (5 mL) was added to the filtrate and the organic layer was collected. The aqueous layer was extracted with ethyl acetate (10 mL). The organic phase was dried with anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography with silica gel (hexane/ethyl acetate, 50:1) to give 2-(1*H*-indol-1-yl)-*N*,*N*-dimethylaniline (**1a**; 58 %, 137 mg).

However, the aforementioned method provides inferior yields for chloro derivatives **4a**–**4g** and they were synthesized by means of an alternative method.[13]

General Procedure for the Synthesis of 5-Methylindolo[1,2-*a*]quinoxalin-6(5*H*)-one (1′a): To a solution of *N*,*N*-dimethyl-2-(indolyl) aniline (**1a**; 59.08 mg, 0.25 mmol) in DMSO (1 mL) was added $Cu(OAc)_2$ (4.54 mg, 0.025 mmol), followed by DTBP (219 mg, 1.5 mmol) and the resultant mixture was heated (oil bath; 120 °C) for 13 h. The resultant reaction mixture was admixed with water (5 mL) and the product was extracted with ethyl acetate (2 × 20 mL). The organic phase was dried with anhydrous sodium sulfate, decanted, and concentrated in vacuo. The crude product was purified with silica gel (hexane/ethyl acetate, 9:1) to give 5-methylindolo[1,2-*a*]quinoxalin-6(5*H*)-one (**1′a**; 52 %, 32.27 mg).

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Keywords: Synthetic methods · Homogeneous catalysis · Cross-coupling · Nitrogen heterocycles · C–H activation · Copper

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[11] CCDC 1429999 (for **1′b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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