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Exceptionally Mild Palladium(II)-Catalyzed Dehydrogenative C−H/C−H Arylation of Indolines at the C-7 Position under Air

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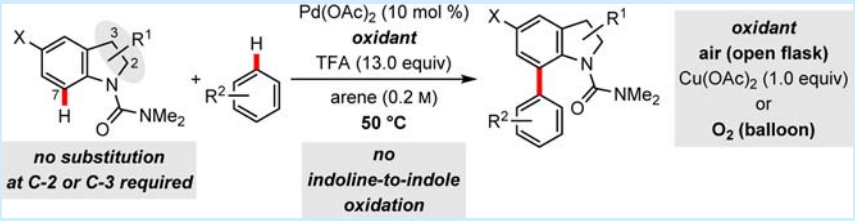
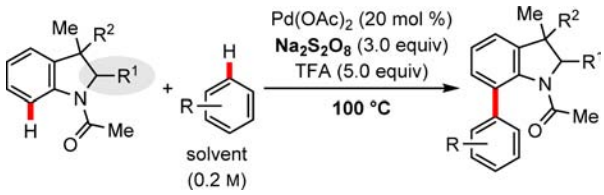
Supporting Information



ABSTRACT: An improved method for the dehydrogenative C−H/C−H cross-coupling at the C-7 position of indolines containing a urea as a directing group is reported. The new protocol is a rare example of an aerobic palladium(II)-catalyzed cross dehydrogenative coupling (CDC) reaction that proceeds at low temperature. The use of either $Cu(OAc)_2$ in an open flask or dioxygen (balloon) at 50 °C tolerates indolines not substituted at C-2 and C-3, thereby extending the scope of the previous method that suffers from indoline-to-indole oxidation.

Elaboration of the indole nucleus through site-selective C−H bond activation at the benzene core is currently being actively investigated. Major advances have recently been made in C-7-selective C−C bond formation[1−4] and heterofunctionalization[5] of indolines, but methods for addressing the C-6 position of indolines[6] and the C-4 position of indoles[7] have also been disclosed. We have been particularly focusing on oxidative palladium(II)-catalyzed C−C bond-forming reactions at the C-7 position[1d,2b] and accomplished the C−H arylation by cross-dehydrogenative coupling[8] (Scheme 1).[1d] As is typical for C−H/C−H cross-coupling reactions,[9−12] our protocol required high temperatures as well as the use of a strong oxidant. Indolines with no substitution at C-2 and C-3 were not compatible with these harsh oxidizing conditions, thereby limiting the substrate scope of the method significantly. Moreover, these substituents were needed not only to prevent indoline-to-indole oxidation but also to facilitate the C−H bond activation by steric repulsion with the amide directing group.

Scheme 1. C-7-Selective Oxidative C−H/C−H Cross-Coupling of 2,3-Substituted Indolines



The above results were obtained with an amide directing group. Lipshutz and co-workers achieved a urea-directed C−H activation[13] with 1,4-benzoquinone (BQ) as oxidant that includes examples of C-7-selective C−H arylation of indoline with boronic acids at room temperature.[1c] Stimulated by this work, we recently developed a broadly applicable procedure for the related C−H alkenylation of indolines that affords high yields at just 40 °C (not shown).[2b] With this precedence, we decided to systematically study that weakly binding donor in our cross-dehydrogenative coupling. We report here the identification of catalyst systems that enable low-temperature C−H/C−H cross-coupling of indolines using air (open flask) or dioxygen (balloon) as terminal oxidants.[9c,g,i,p,s] The exceptionally mild protocol is now applicable to indoline itself and, hence, superior to the existing methodology.

We began our catalyst screening using the strong oxidant $Na_2S_2O_8$[1d,14] at slightly elevated temperatures in the C−H arylation of urea-containing indoline with *o*-xylene (**1a** → **2aa**, Table 1, entries 1−4). Gratifyingly, the conversion and yield were promising at 30 °C, and these values improved substantially by raising the temperature to 50 °C (entries 1−3). The use of trifluoroacetic acid (TFA) as additive was crucial (entry 4).[15] However, what looked like a straightforward breakthrough was a disappointment when applied to coupling partners other than *o*-xylene (see Table S1, Supporting Information). Conversion was generally high, but isolated yields were low. We cannot explain these results as the same arenes have been compatible with $Na_2S_2O_8$ at 100 or even 120 °C in the C−H arylation of 2,3-substituted indolines.[1d] In any event, we had to abandon this catalyst system and continued to find a viable alternative.

We then turned toward $Cu(OAc)_2$ under dioxygen atmosphere and were delighted to again obtain promising conversion and yield (entry 5). This result already indicates that a strong

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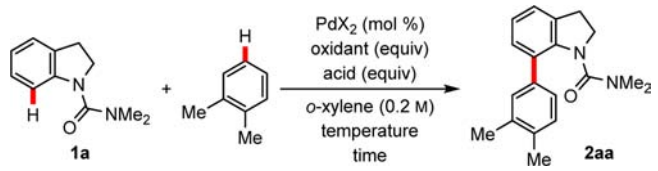
Table 1. Identification of the Catalyst System



entry	PdX_2/mol %	oxidant/equiv	atm	acid/equiv	temp (°C)	time (h)	conv[a] (%)	yield[b] (%)
1	$Pd(OAc)_2$/10	$Na_2S_2O_8$/3.0	N_2	TFA/5.0	30	16	40	34
2	$Pd(OAc)_2$/10	$Na_2S_2O_8$/3.0	N_2	TFA/5.0	40	16	86	62
3	**$Pd(OAc)_2$/10**	**$Na_2S_2O_8$/3.0**	**N_2**	**TFA/5.0**	**50**	**18**	**100**	**74**
4	$Pd(OAc)_2$/10	$Na_2S_2O_8$/3.0	N_2		50	16	no reaction	
5	$Pd(OAc)_2$/10	$Cu(OAc)_2$/2.5	O_2 (balloon)	TFA/5.0	50	18	41	30
6	**$Pd(OAc)_2$/10**	**$Cu(OAc)_2$/1.0**	**air (open flask)**	**TFA/13**	**50**	**22**	**100**	**81**
7	$Pd(TFA)_2$/10	$Cu(OAc)_2$/1.0	air (open flask)		50	18	no reaction	
8	**$Pd(OAc)_2$/10**		**O_2 (balloon)**	**TFA/13**	**50**	**22**	**100**	**85**
9	$Pd(OAc)_2$/10		air (open flask)	TFA/13	50	18	16	9
10	$Pd(OAc)_2$/10	$Cu(OAc)_2$/1.0	N_2	TFA/13	50	42	55	47
11	$Pd(OAc)_2$/5.0	$Cu(OAc)_2$/1.0	air (open flask)	TFA/13	50	42	24	*c*
12		$Cu(OAc)_2$/1.0	air (open flask)	TFA/13	50	16	no reaction	
13	$Pd(OAc)_2$/10	Ag_2CO_3/1.0	air (open flask)	TFA/13	50	18	10	traces
14	$Pd(OAc)_2$/10	BQ/1.0	air (open flask)	TFA/13	50	18	90	traces
15	$Pd(OAc)_2$/10	$Cu(OAc)_2$/1.0	air (open flask)	PivOH/10	50	18	no reaction	

[a]Determined by GLC analysis with tetracosane as internal standard. [b]Isolated yield after purification by flash column chromatography. [c]Not determined.

oxidant is not necessary to bring about this C−H/C−H cross-coupling. Much to our surprise, an increase in the amount of TFA[15] (13 vs 5.0 equiv) with a reduced loading of $Cu(OAc)_2$ (1.0 vs 2.5 equiv) in an open flask boosted the isolated yield from 30 to 81% at full conversion (entry 6). The use of $Pd(TFA)_2$ instead of $Pd(OAc)_2$/TFA was not effective in promoting this reaction (entry 7). Moreover, $Pd(OAc)_2$ as catalyst and dioxygen as the sole oxidant afforded the C-7-arylated indoline in even higher yield (entry 8). Conversely, little conversion was seen with air (open flask) in the absence of $Cu(OAc)_2$ (entry 9). The catalysis worked with $Cu(OAc)_2$ alone but was less efficient (entry 10). Lowering the catalyst loading from 10 to 5.0 mol % was detrimental (entry 11), and no reaction was seen in the absence of $Pd(OAc)_2$ (entry 12). It is worth noting that no byproduct was observed in all cases where $Cu(OAc)_2$ was employed as (co)oxidant (entries 5−7 and 10).

A few control experiments under air emphasized the crucial role of both $Cu(OAc)_2$ and TFA. Oxidants other than $Cu(OAc)_2$, e.g., Ag_2CO_3 and BQ, only gave trace amounts (entries 13 and 14), and no conversion was detected with PivOH as a replacement for TFA (entry 15). The decomposition of the indoline with BQ as oxidant was totally unexpected as it had served us well in the aforementioned C−H alkenylation (entry 14).[2b] The directing group was equally important, and none of those tested supported the C−H arylation using the optimized aerobic protocol (**1b−e**, Figure 1). No decomposition was seen in any of these reactions. The fact that indoline **1d** containing a urea with a free NH group did not react is remarkable but not understood.

The scope of the new aerobic cross-dehydrogenative coupling was then tested using the open-flask setup because of its ease of manipulation (cf. Table 1, entry 6). Selected reactions were repeated under dioxygen atmosphere (cf. Table 1, entry 8), but reaction times were generally longer and conversions lower (footnotes *b−e*, Scheme 2). We started with a systematic screening of other arene coupling partners, hoping not to

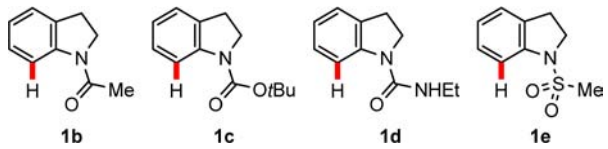


Figure 1. Directing groups that do *not* allow for C−H arylation at the C-7 position (see Table 1, entry 6, for the catalyst system).

experience the above-mentioned problems as with $Na_2S_2O_8$ (cf. Table 1, entry 3). Indeed, the mild procedure allowed for the installation of various electron-rich aryl groups at C-7 of the parent indoline (**1a** → **2aa−ak**, Scheme 2). Yields were generally good. With bulkier alkyl groups than in *o*-xylene, conversion and yield decreased (81% for **2aa** vs 62% for **2ab** vs 18% for **2ac**). Another *ortho*-disubstituted arene, electron-rich veratrol, participated with low conversion and yield after prolonged reaction time (18% for **2ad**). Electron-rich monosubstituted arenes such as toluene, anisol, and phenetol reacted in good yields (**2ae−ag**). It merits mentioning that the *para*:*meta* selectivity was excellent for anisol and phenetol. Similar to toluene, regiocontrol was poor with *m*-xylene (**2ae** and **2ah**), and *p*-xylene furnished only traces of cross-coupled **2ai**. Mesitylene did not convert into **2aj**. The dehydrogenative coupling of benzene proceeded with good yield at full conversion (71% for **2ak**). An *N*,*N*-dimethylaniline derivative underwent homocoupling exclusively, and only trace amounts along with consumption of **1a** were obtained with 1,2-dichlorobenzene (not shown).

To further expand the scope of the method, a range of indolines with substitution at C-2, C-3, and C-5 was subjected to the open-flask procedure (Scheme 3); one example using dioxygen (balloon) again required a longer reaction time (footnote *a*, Scheme 3). Previously problematic indolines with a methyl group at C-2 or C-3[1d] reacted in good to excellent yields (**3a** → **12aa** and **5a** → **14aa**). However, 2-phenylindoline was reluctant to undergo the coupling reaction (**4a** → **13aa**), and we ascribe this to a steric rather than electronic effect. As expected,

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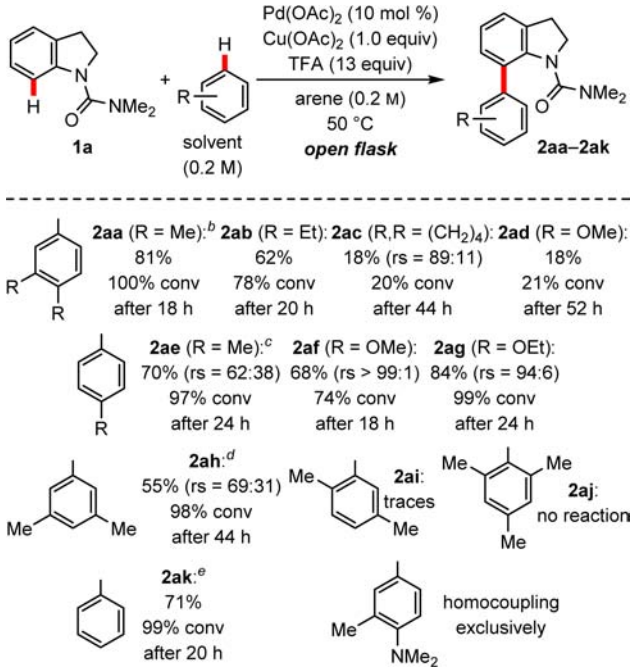
Scheme 2. Open-Flask C−H/C−H Cross-Coupling of Indoline and Various Arenes[a]

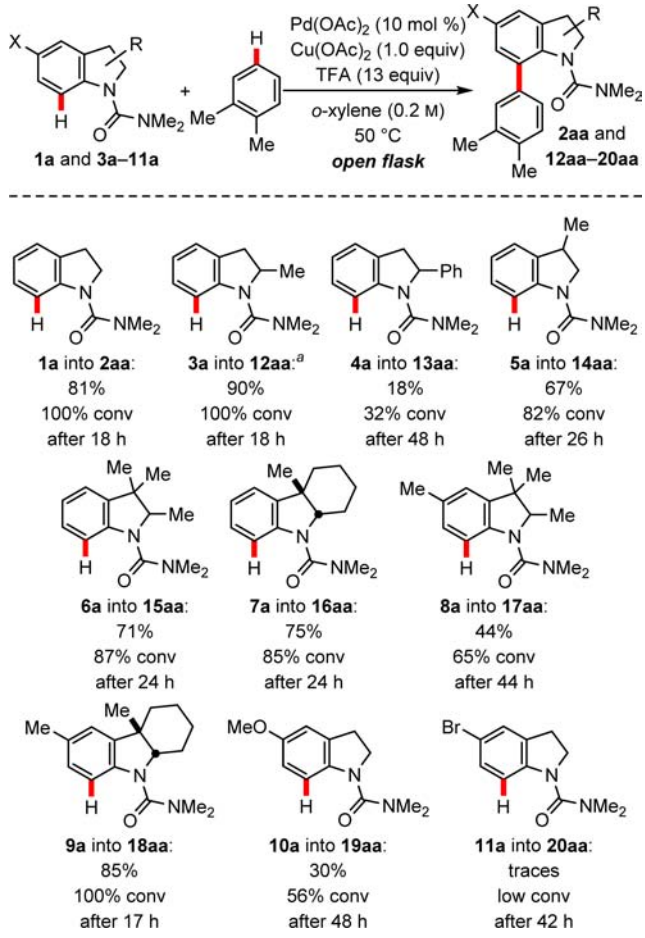


[a]rs = regioselectivity; major regioisomer shown. Results under copper-free conditions with dioxygen (balloon) as oxidant are as follows: [b]85%, 100% conv after 22 h. [c]26% (rs = 64:36), 60% conv after 48 h. [d]32% (rs = 74:26), 36% conv after 48 h. [e]76%, 100% conv after 48 h (70% conv after 24 h).

2,3,3-trisubstituted substrates converted cleanly into the corresponding C-7-arylated indolines (**6a** → **15aa** and **7a** → **16aa**). Interestingly, substitution in the C-5 position led to inconsistent results. For example, a methyl group at C-5 of those 2,3,3-trialkyl-substituted indolines had a significant effect in one case for no obvious reason (**8a** → **17aa** vs **9a** → **18aa**). That negative influence was even more pronounced with a methoxy group at C-5 (**10a** → **19aa**). These observations stand in stark contrast to our earlier work where electron-donating groups at C-5 were tolerated independent of the indoline motif.[1d] Bromination at C-5 disrupted the C−H bond activation at C-7 (**11a** → **20aa**). To demonstrate the practical value of the method, the model reaction was successfully repeated on a gram scale with slightly diminished conversion (96 vs 100%) and yield (72 vs 81%) (**1a** → **2aa**, Scheme 4).

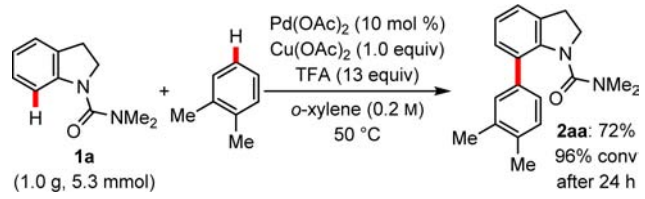
In summary, we present herein an operationally simply way for the direct installation of aryl groups at the C-7 position of indolines. A urea directing group secured an exceptionally mild protocol where either $Cu(OAc)_2$ in an open flask or dioxygen (balloon) serves as an oxidant at low temperature. As a result, indoline-to-indole oxidation did not occur, and hence, indolines without substitution in the C-2 and C-3 positions were also amenable to this C−H/C−H cross-coupling. This distinguishes the new method from the previous one.[1d] It is worth noting that other common directing groups, even a urea with a free NH group at the terminus, failed to facilitate the C−H bond activation.

Scheme 3. Open-Flask C−H/C−H Cross-Coupling of Various Indolines



[a]Using dioxygen (balloon) as oxidant: 70%, 86% conv after 48 h (35% conv after 18 h).

Scheme 4. Scale-up Experiment



■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General procedures, experimental details, and characterization data as well as ^1H and ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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