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Synthesis of *N*-(2-Pyridyl)indoles via Pd(II)-Catalyzed Oxidative Coupling

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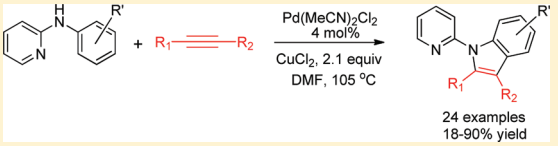
Supporting Information

ABSTRACT: Readily available Pd(II) chloride catalysts can catalyze selective and efficient oxidative coupling between *N*-aryl-2-aminopyridines and internal alkynes to yield *N*-(2-pyridyl)indoles. This process involves the ortho C−H activation of *N*-aryl-2-aminopyridines, and $CuCl_2$ was used as an oxidant. Compared to our previously reported Rh(III)-catalyzed synthesis of this class of product, this method is advantageous with a wider scope of alkynes and cost-effective Pd(II) catalysts. Molecular oxygen can be used as a terminal oxidant.



Transition metal-catalyzed direct functionalization of C−H bonds via C−H activation pathway represents an important and atom-economic strategy to construct complex structures.[1] Activation of a C−H bond, particularly under chelation assistance, followed by oxidative coupling of unsaturated molecules has attracted considerable attention because condensed (hetero)cycles are generated and these structural motifs are widely present in natural products and pharmaceuticals.[2] Recently, Cp*Rh(III) complexes have stood out to catalyze the oxidative coupling of arenes with alkynes with high efficiency, and groups of Satoh and Miura, Fagnou, Jones, Glorius, Rovis, and Li have successfully achieved selective ortho C−H activation of various arenes for the synthesis of condensed heterocycles such as isoquinolones,[3] indoles,[4] isoquinolines,[5] pyrroles,[6] isocoumarins,[7] and pyridones.[8] Despite the success, convenient and cost-effective synthetic methods are still necessary.

Palladium catalysts are well-known for their outstanding capacity to mediate oxidative C−H activation via a C−H activation pathway with high functional group compatibility and low cost, and this area has been extensively reviewed.[2e,9] However, palladium(II)-catalyzed C−H activation followed by oxidative coupling with alkynes is less well-studied, and only limited examples have been reported.[10] The compatibility of the reaction conditions for C−H activation and for alkyne functionalization sometimes might pose problems. We recently reported the oxidative coupling between *N*-aryl-2-aminopyridines and internal alkynes for the synthesis of substituted indoles using $[RhCp^*Cl_2]_2$ as a catalyst.[11] In this reaction, the pyridyl ring proved to be an effective directing group to facilitate the C−H activation of the *N*-aryl ring. Despite the high selectivity, the alkyne substrates are limited to symmetrically substituted ones. For example, an unsymmetrically substituted alkyne such as PhC≡CMe failed. In addition, the high cost of the rhodium catalyst makes it less competitive. Ideally, it is desirable to use oxygen or even air as a terminal oxidant. Therefore, our objective is to achieve this reaction with high efficiency using low-cost catalysts such as palladium(II) complexes that can cover a broader substrate scope (Chart 1). In fact stoichiometric reactions between *N*-aryl-2-aminopyridines and Pd(II) complexes have been reported to give a cyclometalation product,[12] although no catalytic reaction has been developed. These results make our objective plausible.

We initiated our studies with the coupling between *N*-phenyl-2-aminopyridine (**1a**), and PhC≡CPh using $Pd(OAc)_2$ (4 mol %) as a catalyst in the presence of an oxidant. The desired product **3aa** was isolated in 36% yield when $Cu(OAc)_2$ (2.1 equiv) was selected as an oxidant (entry 1, Table 1). Switching to silver oxidants such as Ag_2CO_3 and AgOAc gave essentially no desired product, although no starting material remained (entry 2). Other solvents such as acetone (105 °C, sealed tube) turned out to be less efficient, where the coupled product was obtained in 25% yield. Compared to $Pd(OAc)_2$ catalysts, a higher isolated yield of **3aa** was obtained when several Pd(II) chloride catalysts were used (entries 4 and 6−9). Further screening of catalysts and oxidants revealed that a combination of inexpensive $Pd(MeCN)_2Cl_2$ (4 mol %) and $CuCl_2$ (2.1 equiv) provides optimal conditions, under which product **3aa** was isolated in 89% yield (Conditions A, entry 8). Importantly, O_2 (1 atm) can be used as a terminal oxidant when 20 mol % of $CuCl_2$ was used as a co-oxidant (conditions B), although the couple was isolated in slightly lower yield (entry 10). It is noteworthy that neither O_2 nor air can be applied as a terminal oxidant when $[RhCp^*Cl_2]_2$ was used as a catalyst and decomposition of the starting material was observed.

With the optimized conditions (A and B) in hand, we further explored the scope of this coupling reaction. As given in Table 2, coupling of **1a** with various symmetrically substituted alkynes

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Chart 1

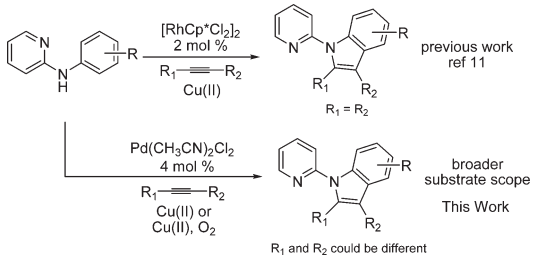
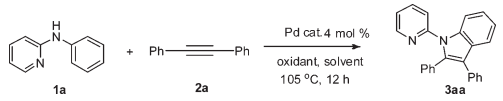


Table 1. Screening of Reaction Conditions[a]

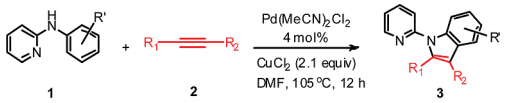


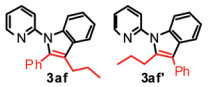
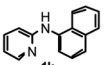
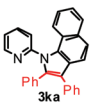
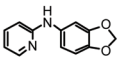
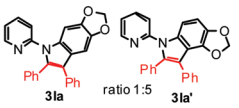
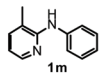
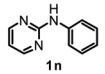
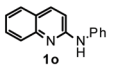
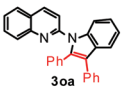
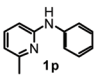
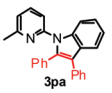
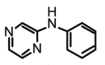
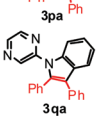
entry	catalyst	oxidant	solvent	yield (%)[b]
1	$Pd(OAc)_2$	$Cu(OAc)_2$	DMF	36
2	$Pd(OAc)_2$	Ag_2CO_3	DMF	0
3	$Pd(OAc)_2$	$Cu(OAc)_2$	acetone	25
4	$Pd(PPh_3)_2Cl_2$	$Cu(OAc)_2$	DMF	57
5	$Pd(PPh_3)_4$	$Cu(OAc)_2$	DMF	32
6	$Pd(COD)Cl_2$	$Cu(OAc)_2$	DMF	55
7	$Pd(CH_3CN)_2Cl_2$	$Cu(OAc)_2$	DMF	72
8	$Pd(CH_3CN)_2Cl_2$	$CuCl_2$	DMF	89
9	$Pd(PPh_3)_2Cl_2$	$CuCl_2$	DMF	71
10	$Pd(CH_3CN)_2Cl_2$	$CuCl_2$ (20 mol %), O_2	DMF	75

[a] Reaction conditions: **1a** (0.6 mmol), **2a** (0.9 mmol), 1.5 equiv of Ag_2CO_3 or 2.1 equiv of CuX_2, catalyst (4 mol %), solvent (3.0 mL). [b] Isolated yield.

offered indole products in 82−89% yield under Conditions A (entries 1−4 and 7). In addition, heteroaryl-substituted alkyne (**2g**) readily undergoes coupling with **1a** to give **3ag** in high yield (entry 7). In contrast to the failure of coupling of unsymmetrically substituted alkynes such as PhC≡CMe with **1a** using our previously reported Rh(III) catalysts,[11] here a clean reaction was observed and product **3ae** was isolated as a single regioisomer in 71% yield, where the phenyl group in the alkyne unit is disposed adjacent to the nitrogen atom. When PhC≡CPr was applied to couple with **1a**, a mixture of two regioisomers were isolated in 8:1 ratio (entry 6), with the major product (**3af**) being analogous to product **3ae**. The decreased selectivity is likely ascribed to the increased steric bulk of the alkyne. Analogously, unsymmetrically heteroaryl- and alkyl-substituted alkyne **2h** undergoes ready coupling with **1a** to give **3ah** in 75% yield as a single isomeric product (entry 8). Here the isolation of **3ah** as a single product highlights the electronic differences between a 2-thiophenyl group and a phenyl group in terms of the selectivity of alkyne insertion. Product **3ah** is also inaccessible under rhodium(III)-catalyzed oxidative coupling conditions. The observed regioselectivity agrees with that in other Rh(III)-catalyzed oxidative coupling reactions involving alkynes.[13] Other *N*-aryl-2-aminopyridines also successfully coupled with PhC≡CPh. As given in Table 2, both electron-donating (entries 9−11, 13, and 17) and withdrawing groups (entries 14−16) at the ortho or para position of the *N*-aryl can be tolerated and the coupling products,

Table 2. Palladium-Catalyzed Oxidative Coupling[a]



entry	1	alkyne	product	yield (%)[b]
1	R' = H (**1a**)	$R_1 = R_2$ = Ph (**2a**)	**3aa**	89 (A), 75 (B)
2		$R_1 = R_2 = {}^n$Pr (**2b**)	**3ab**	83 (A)
3		$R_1 = R_2$ = 4-(OMe)C_6H_4 (**2c**)	**3ac**	82 (A)
4		$R_1 = R_2$ = 4-ClC_6H_4 (**2d**)	**3ad**	84 (A)
5		R_1 = Ph, R_2 = Me (**2e**)	**3ae**	71 (A)
6		R_1 = Ph, $R_2 = {}^n$Pr (**2f**)	 **3af** **3af'** ratio 8:1	75 (A)
7		$R_1 = R_2$ = 2-thiophenyl (**2g**)	**3ag**	87 (A)
8		R_1 = 2-thiopehnyl, $R_2 = {}^n$Pr (**2h**)	**3ah**	75 (A)
9	R' = 4-Me (**1b**)	**2a**	**3ba**	80 (A)
10	R' = 2-Me (**1c**)	**2a**	**3ca**	35 (A), 62(A)[c]
11	R' = 2-OMe (**1d**)	**2a**	**3da**	58 (A)
12	R' = 3-OMe (**1e**)	**2a**	**3ea**	74 (A), 66 (B)
13	R' = 4-OMe (**1f**)	**2a**	**3fa**	55 (A), 72 (A)[c]
14	R' = 4-F (**1g**)	**2a**	**3ga**	85 (A)
15	R' = 2-Ph (**1h**)	**2a**	**3ha**	56 (A)
16	R' = 4-Cl (**1i**)	**2a**	**3ia**	87 (A), 70 (B)
17	R' = 4-^{t}Bu (**1j**)	**2a**	**3ja**	77 (A)
18	 **1k**	**2a**	 **3ka**	32 (A), 58 (A)[c]
19	 **1l**	**2a**	 **3la** ratio 1:5 **3la'**	44 (A)
20	 **1m**	**2a**	 **3ma**	90 (A), 75 (B)
21	 **1n**	**2a**	 **3na**	75 (A)
22	 **1o**	**2a**	 **3oa**	25 (A), 40 (A)[c]
23	 **1p**	**2a**	 **3pa**	18 (A), 32 (A)[c]
24	 **1q**	**2a**	 **3qa**	66 (A)

[a] Reaction conditions A: **1** (0.60 mmol), **2** (0.90 mmol), $Pd(MeCH_3)_2Cl_2$ (4 mol %), $CuCl_2$ (2.1 equiv), DMF (3 mL), 105 °C, 12 h. Reaction conditions B: **1** (0.60 mmol), **2** (0.90 mmol), $Pd(MeCH_3)_2Cl_2$ (4 mol %), $CuCl_2$ (0.12 mmol), O_2 (1 atm), DMF (3 mL), 105 °C, 14 h. [b] Isolated yield, set of conditions after parentheses. [c] 8 mol % of $Pd(MeCH_3)_2Cl_2$ was used.

including **3ja**, were isolated in high yield. C−H activation of **1e** bearing a 3-OMe group (entry 12) occurs exclusively at the less hindered position as a result of steric effect. It is noteworthy that for reasons that are unclear **3ja** cannot be obtained by using our reported Rh(III)-catalyzed conditions.[11] When ortho

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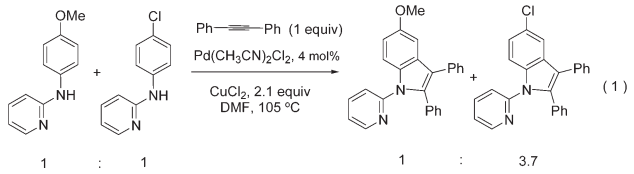
substituents such as Me, OMe, and Ph were introduced into the *N*-aryl ring, somewhat lower yields (entries 10, 11, 15, and 18) were obtained, indicating limited steric tolerance of this reaction. For these substrates, using 8 mol % loading of the catalyst slightly increased the yield. Importantly, O_2 can be consistently used as a terminal oxidant and $CuCl_2$ (20 mol %) as a co-oxidant (conditions B, entries 1, 12, 16, and 20), although the yield is slightly lower than that obtained by using only $CuCl_2$ as an oxidant. These results indicate that this reaction can be made eco-friendly and cost-effective. In contrast, under rhodium(III)-catalyzed conditions decomposition occurred when O_2 was used as a terminal oxidant and Cu(II) as a co-oxidant. In addition, when **1*l*** was allowed to react with PhC≡CPh (entry 19), two regioisomers were isolated as a mixture in 5:1 ratio, and the major product corresponds to C−H activation at the more hindered position. This selectivity has been observed and is most plausibly ascribed to the directing effect of the oxygen atom.[14] With the tethering effect, the $-OCH_2O-$ group is less sterically bulky compared to a OMe group (entry 12) and can accommodate C−H activation at a more hindered position.[14] Besides pyridine rings, the pyrimidine (entry 21) and pyrazine ring (entry 24) can also act as an effective directing group to give **3na** and **3qa**. In contrast, a lower yield (52%) of **3na** was isolated when rhodium(III)-catalyzed conditions were used.

Steric bulk at the 3-position in the pyridine ring can be tolerated when a 3-methyl group is introduced into the pyridine ring, as evidenced by the isolation of **3ma** in 90% yield (entry 20). However, introduction of a methyl group into the 6-position significantly retarded this reaction, and the coupled product **3pa** was isolated in only 18% yield. Similarly, using a quinoline analogue of **1a** afforded the coupled product (**3oa**) in 25% yield (entry 22). These yields can be somewhat improved when higher loading (8 mol %) of $Pd(MeCN)_2Cl_2$ was applied. These results suggest that this reaction is sensitive to the steric bulk around the pyridine nitrogen and in the *N*-aryl ring. Coordination of this nitrogen seems to play an important role in this reaction by assisting the cleavage of the C−H bond in the *N*-aryl group.

A competitive reaction was carried out to probe the electronic effect of the *N*-aryl ring. An equimolar mixture of **1f**, **1i**, and **2a** was allowed to react under Conditions A (eq 1). ^{1}H NMR analysis of the crude products revealed that products **3fa** and **3ia** were generated in a 1:3.7 ratio. This result indicates that coupling is favored for electron-withdrawing groups in this *N*-aryl ring, which stands in sharp contrast to the Rh(III)-catalyzed version,[11] indicating that they may follow different mechanisms or proceed with different rate-determining steps.



Our previous studies revealed that *N*-aryl-2-aminopyridines can readily couple with various acrylates to give pyridyl-substituted 2-quinolones under Rh(III) catalysis conditions,[11] and these conditions are essentially the same as those for the rhodium-(III)-catalyzed coupling with alkynes. However, under the current Pd(II) catalysis conditions, no such coupling was achieved when acrylates were used, and only decomposition products were observed. These results revealed that when properly designed, Rh(III) and Pd(II) catalysis can be complementary.

In conclusion, we have demonstrated a palladium-catalyzed oxidative coupling between *N*-aryl-2-pyridines and alkynes for the synthesis of substituted indoles. This coupling reaction readily occurred by using simple $Pd(MeCN)_2Cl_2$ catalyst and no additional ligand is necessary. The C−H bond activation is regioselective, and a broad scope of substrate has been defined. This synthetic method proved superior to our previously reported Rh(III)-catalyzed version in terms of both substrate scope and the cost of catalyst. This method has potential applications in the synthesis of complex structures.

EXPERIMENTAL SECTION

A Typical Procedure for the Synthesis of 2,3-Diphenyl-1-(pyridin-2-yl)-1*H*-indole (3aa). Compound **1a** (102.2 mg, 0.60 mmol), diphenylacetylene (160.5 mg, 0.90 mmol), anhydrous $CuCl_2$ (169.5 mg, 1.26 mmol), and $Pd(CH_3CN)_2Cl_2$ (6.2 mg, 4 mol %) were charged into a 10 mL Schlenk tube. After the tube was filled with nitrogen, anhydrous DMF (3 mL) was added via a syringe and the mixture was stirred at 105 °C for 12 h. The mixture was diluted with deionized water then extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over Na_2SO_4. The solvent was removed under vacuum. Purification of the product was performed by flash column chromatography on silica gel, using EtOAc and petroleum ether (1:20). Yield: 184.5 mg (0.53 mmol, 89%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, J = 4.4 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.69 (d, J = 8.0 Hz), 7.55 (td, J = 7.6, 1.2 Hz, 1H), 7.30−7.36 (m, 4H), 7.22−7.27 (m, 3H), 7.11−7.20 (m, 6H), 6.82 (d, J = 4.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 151.8, 149.1, 137.5, 137.4, 135.9, 134.6, 131.7, 130.9, 130.3, 128.3, 128.2, 128.0, 127.4, 126.1, 123.4, 122.2, 121.6, 121.5, 119.6, 118.2, 111.5. HRMS (ESI) Calcd for $[C_{25}H_{18}N_2 + H]^+$ 347.1548, found 347.1546.

ASSOCIATED CONTENT

Supporting Information. Experimental procedure and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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