C–H Activation

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Palladium-Catalyzed Carbonylative C–H Activation of Heteroarenes**

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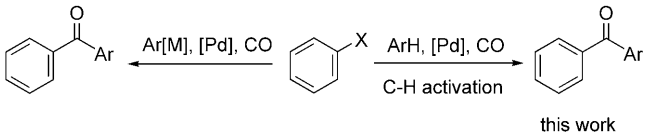
Transition metal catalyzed C–H functionalization reactions of arenes and heteroarenes are finding increasing application in the preparation of organic building blocks and therapeutically important scaffolds.[1] Notably, these methods can avoid the use of stoichiometric amounts of organometallic reagents along with any problems associated with their synthesis, stability, and/or functional group compatibility. Recent prominent examples include: transition metal (Rh, Pd, Ru, Ni, Cu) catalyzed arylation,[2a–e,i] alkylation,[2f,j] alkynylation,[2g,h] alkenylation,[2i,j] and benzylation[2i–k] of (hetero)arenes. In this context, the related carbonylative coupling reactions of (hetero)arenes using C–H functionalization to afford carboxylic acid derivatives have been scarcely studied, and previous systems have been limited to chelation-assisted intramolecular reactions.[3] In particular, the apparently simply synthesis of (hetero)aryl ketones from nonchelating substrates through an intermolecular carbonylative coupling reaction has not yet been reported.

Among the various ways for the synthesis of (hetero)aryl ketones that have been developed,[4] the palladium-catalyzed carbonylative coupling reactions of aryl halides with organometallic reagents has gained recent interest in modern organic synthesis (Scheme 1).[5,6] Typical organometallic



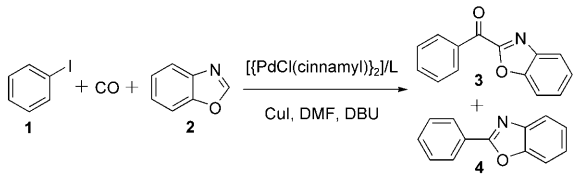
Scheme 1. Strategies for palladium-catalyzed diarylketone syntheses. M = $B(OH)_2$[11], $SnBu_3$[10], SiR_3[9], AlR_2[8].

reagents employed in such reactions are organoaluminium,[7] organosilane,[8] and organotin compounds,[9] as well as aryl boronic acids.[10] Clearly, the direct carbonylative coupling of aryl halides with easily available heteroarenes would offer a new and improved route to the desired di(hetero)aryl ketones by C–H functionalization (Scheme 1).

Owing to the synthetic importance of di-(hetero)aryl ketones,[4] and based on our continuing interest in carbonylative coupling reactions,[6d–i,11] herein we disclose the first carbonylative cross-coupling of aryl iodides with non-preactivated heteroarenes to give a variety of di-(hetero)aryl ketones.

Initially, we investigated the carbonylative cross-coupling of iodobenzene **1** and benzoxazole **2** as a benchmark reaction to give 2-(benzoyl)benzoxazole **3** (Table 1). In a preliminary variation of palladium precursors and ligands, a simple catalytic system consisting of [{(cinnamyl)$PdCl}_2$]/PPh_3 in the presence of CuI[12] under 10 bar of CO pressure at 120 °C yielded the desired ketone **3** in 12% yield. This result demonstrated that the target reaction was indeed possible, however 43% of the noncarbonylative couple product **4** was formed as the major product (Table 1, entry 1).

Table 1: Palladium-catalyzed carbonylative C–H functionalization of benzoxazole.[a]



Entry	[{Pd}$_2$] [mol%]	Ligand (mol%)	Yield of **3** [%][b]	Yield of **4** [%][b]
1	2.5	PPh_3 (10)	12	43
2	2.5	$BuPAd_2$ (10)	22	33
3	2.5	dppp (5)	27	39
4	2.5	dppe (5)	12	20
5	2.5	dppb (5)	21	5
6	2.5	dpppe (5)	23	12
7[c]	2.5	dppp (5)	31	11
8[c]	5	dppp (10)	51	3
9[c,d]	5	dppp (10)	58	0
10[d,e]	5	dppp (10)	73	0
11[d,e,f]	5	dppp (10)	54	5

[a] [{(cinnamyl)$PdCl}_2$], ligand, DMF (2 mL), DBU (1 mmol), CuI (1.2 equiv), iodobenzene (1 mmol), benzoxazole (1.2 equiv), CO (10 bar), 120 °C, 20 h. [b] Yields were determined by GC, using hexadecane as internal standard. [c] CO (30 bar). [d] 1.5 equiv of benzoxazole. [e] CO (40 bar), 30 h. [f] CO (50 bar). DMF = *N*,*N*-dimethylformamide, Ad = adamantyl, dppp = 1,3-bis(diphenylphosphanyl)-propane, dppe = 1,2-bis(diphenylphophanyl)ethane, dppb = 1,4-bis(diphenylphosphanyl)butane, dpppe = 1,5-bis(diphenylphosphanyl)pentane.

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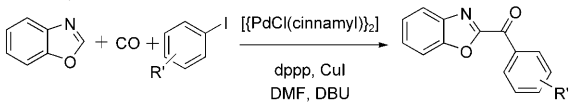
By testing different ligands, it turned out that chelating bidentate phosphines gave better results compared to monodendate ligands (Table 1, entries 2–6). Changing the bite angle of the bidentate ligand showed a significant influence on the outcome of the reaction. In the presence of 1,3-bisdiphenylphosphinopropane (dppp) ketone **3** was obtained in 27% yield (Table 1, entry 3). When increasing the CO pressure to 30 bar, the yield of **3** increased slightly (Table 1, entry 7). Addition of an excess (1.5 equiv) of benzoxazole further improved the yield of **3** to 58%. Notably, the chemoselectivity also improved considerably (Table 1, entry 9). Finally, the best result was obtained at 40 bar CO pressure to give the target compound in 73% yield with excellent selectivity (Table 1, entry 10). Notably, at higher pressure, the yield and chemoselectivity decreased (Table 1, entry 11).

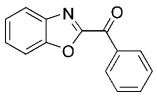
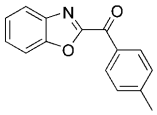
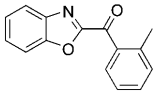
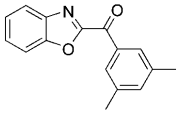
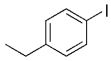
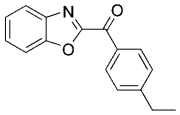
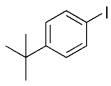
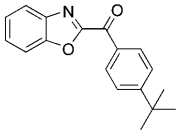
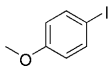
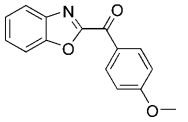
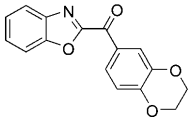
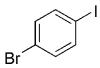
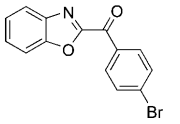
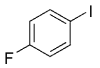
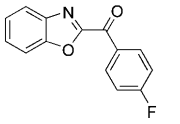
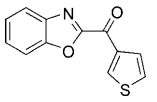
With acceptable conditions in hand (Table 1, entry 10), we tested the scope of this methodology for different aryl iodides (Table 2) and heteroarenes (Table 3). As shown in Table 2, *ortho*-, *meta*-, and *para*-substituted aryl iodides worked well in the present system to give moderate to good yields of 2-aroylbenzoxazoles (40–67%; Table 2, entries 2–4). Similarly, ethyl- and *tert*-butyl-substituted iodobenzenes led to their corresponding ketones in 63% and 54% yield, respectively (Table 2, entries 5 and 6). In addition, both electron-donating and electron-withdrawing substituents on the arene ring were well-tolerated in the carbonylative C–H functionalization reaction and their corresponding ketones were isolated in good yield (Table 2, entries 7–10). Heterocyclic iodide 3-iodothiophene also underwent a smooth reaction to furnish the corresponding di-(heteroaryl) ketone in 62% yield (Table 2, entry 11).

After demonstrating the general applicability of this procedure for aryl iodides, we explored the scope of the C–H-activation substrates. We chose 4-iodoanisole as the coupling partner for the carbonylative coupling with various other heteroarenes (Table 3). First, oxazoles and benzoxazoles with different substitution patterns were tested. Encouragingly, yields of 60–70% were obtained in these carbonylative C–H functionalizations (Table 3, entries 1–3). Similarly, commercially available thiazole and substituted thiazoles as well as benzothiazole were effectively converted into their corresponding ketones in 65-71% yield (Table 3, entries 4–6). Notably, even imidazole, an important family of heteroarenes, was also activated under these conditions (Table 3, entry 7). On the other hand, the reaction of bromobenzene with benzoxazole under the optimized conditions for aryl iodides gave only 5% of the desired product together with starting material and iodobenzene.

Taking previous reports on noncarbonylative C–H-functionalization into account, we proposed the following reaction mechanism for this novel reaction (Scheme 2). It is well known that oxidative addition of iodobenzene onto a ligated palladium(0) species generates the arylpalladium(II) complex **I**, which produces the key arylpalladium(II) complex **II** following CO insertion.[5] Next, complex **III** can be formed by transmetalation with the preformed copper/arene species resulting from the heteroarene.[13] Reductive elimination of the ketone from complex **III** completes the catalytic cycle and regenerates the active palladium species. In some cases the noncarbonylative coupling product was observed as a side-product, thereby demonstrating that even at 40 bar of CO,

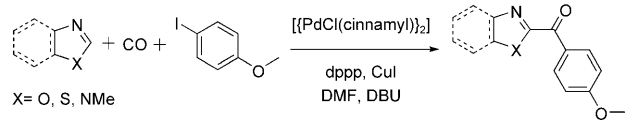
Table 2: Palladium-catalyzed carbonylative coupling of benzoxazole with different aryl iodides.[a]

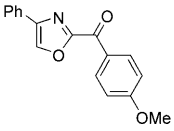
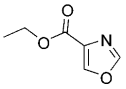
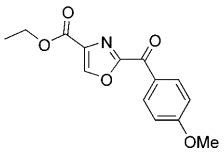
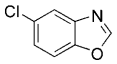
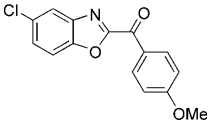
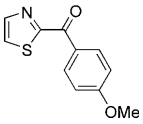
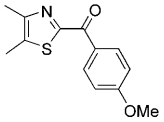
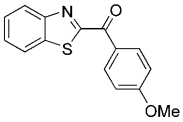
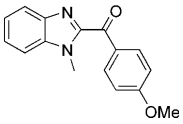


Entry	Aryl iodide	Ketone	Yield [%][b]
1			70
2			67[c]
3			40[d]
4			55[c]
5			63[c]
6			54[c]
7			75[c]
8			72[c]
9[e]			45
10			62
11[e]			62[d]

[a] [{(cinnamyl)PdCl}$_2$] (5 mol%), dppp (10 mol%), DMF (2 mL), DBU (1 mmol), CuI (1.5 equiv), aryl iodide (1 mmol), benzoxazole (1.5 equiv), CO (40 bar), 120°C, 30 h. [b] Yield of isolated product. [c] 130°C. [d] 100°C, 40 h. [e] 5–10% of the noncarbonylative coupling product was obtained.

Table 3: Palladium-catalyzed carbonylative coupling of heteroarenes.[a]

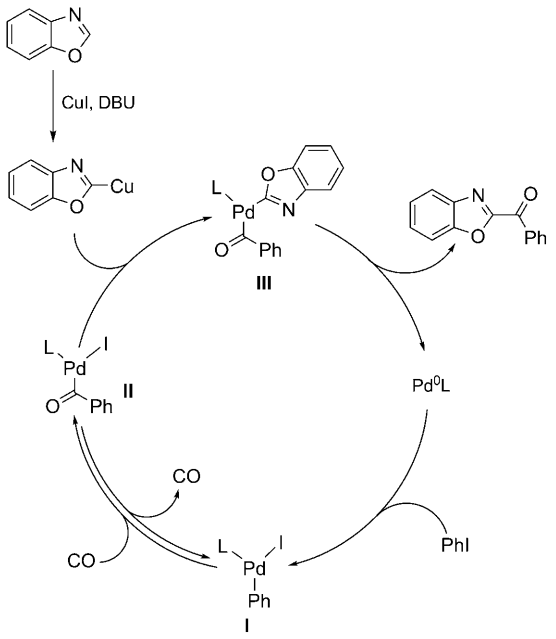


Entry	Heteroarene	Ketone	Yield [%][b]
1			65
2[c]			70
3[c]			60
4			66
5[c]			65
6[c]			71
7[c]			56

[a] [{(cinnamyl)PdCl}$_2$] (5 mol%), dppp (10 mol%), DMF (2 mL), DBU (1 mmol), CuI (1.5 equiv), 4-iodoanisole (1 mmol), heteroarene (1.5 equiv), CO (40 bar), 130°C, 30 h. [b] Yield of isolated product. [c] 5–10% of the noncarbonylative coupling product was obtained.

transmetalation of the heteroaryl copper intermediate is competitive with the carbonylation of the aryl palladium species.[14] Notably, the palladium-catalyzed reaction of benzoxazole with benzoyl chloride in the absence of CO exclusively gave 2-phenylbenzoxazole as the decarbonylative coupling product. This result also shows the reversibility of the carbonylation step.

In conclusion, the first carbonylative C–H activation reactions of heteroarenes to form diaryl ketones have been developed. Applying various aryl iodides and different heteroarenes, such as oxazoles, thiazoles, and imidazole in the presence of a palladium/copper system affords the corresponding coupling products in a straightforward manner. Compared with the established carbonylative cross-coupling reactions for the synthesis of ketones, no additional organometallic reagents are needed, thus making this methodology a useful extension of palladium-catalyzed coupling reactions. Further extension of this chemistry towards other aryl halides and heteroarenes is currently underway.



Scheme 2. Proposed reaction mechanism. DBU = 1,8-diazabicyclo-[5.4.0]undec-7-ene.

Experimental Section

3: The reaction was carried out in a Parr Instruments 4560 series 300 mL autoclave containing an alloy plate with wells for four 12 mL Wheaton vials. [{(cinnamyl)PdCl}$_2$] (5 mol%), dppp (10 mol%), CuI (1.5 equiv), benzoxazole (1.5 equiv) and a magnetic stirrer bar were placed in each of the vials, which were then capped with a septum equipped with an inlet needle and flushed with argon. Then, iodobenzene (1 mmol), DBU (1 mmol), and DMF (2 mL) were added to a vial with a syringe. The vials were placed in an alloy plate, which was then placed in the autoclave. Once sealed, the autoclave was purged several times with CO, then pressurized to 40 bar at room temperature and heated at 120°C for 30 h. It was then cooled to room temperature and vented to discharge the excess CO. Water (2 mL) was added, and the product was extracted with ethyl acetate (3 × 3 mL). The organic layers were washed with brine, dried over Na_2SO_4, and evaporated to yield the crude product. Purification by column chromatography on silica gel (eluent: heptane/EtOAc = 100:0–40:1) gave the title compound (156 mg, 70%) as a white solid.

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Keywords: carbonylation · C–H activation · heterocycles · ketones · palladium

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