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Volume 40 | Number 1 | January 2016 | Pages 1–846

NJC

New Journal of Chemistry
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ISSN 1144-0546

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Journal Name

COMMUNICATION

Palladium/Copper-Catalyzed Arylation of Alkenes with *N′*-Acyl Arylhydrazines

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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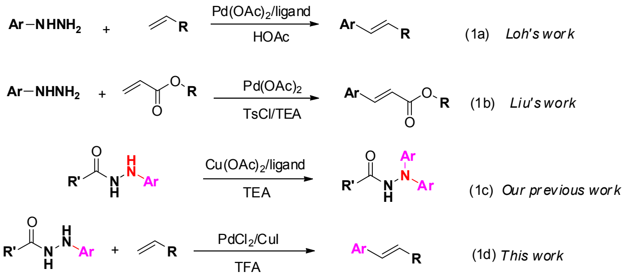
A novel ligand-free palladium/copper-catalyzed Heck-type coupling reaction of alkenes and *N′*-acyl arylhydrazines has been developed by using air as terminal oxidant. This protocol featured wide functional group tolerance and highly chemoselective and regioselective products with good to excellent yields.

Transition metal-catalyzed C-C bond forming reactions represent powerful synthetic methods in organic synthesis,[1] which have been broadly applied in organometallic chemistry, medicinal chemistry and materials science.[2] Among them, the palladium-catalyzed Mizoroki–Heck reaction is one of the most important methods used for the preparation of aryl olefins.[3] Although several types of aryl sources including aryl halides, aryl sulfonates,[4] arene carboxylic acids and their derivatives[5] have proved efficient coupling partners for this Nobel-named reaction, further broadening the scope of electrophiles will be of great significance in organic synthesis.

Recently, C-C bond formation *via* C-N bond cleavage has attracted considerable attention and versatile activated C-N bond containing partners, such as diazonium salts,[6] triazoles[7] and azaheterocycles[8] have been explored in cross-coupling reactions under transition metal catalysis. However, existing methods still suffer from the harsh reaction conditions, limited substrate scope and the poor stability of the substrates. On this basis, there is still a great demand for developing new methods to cleave C-N bonds. Due to the stability and high dissociation energy of the C-N bond, arylhydrazines have recently become a hot topic as potential coupling partners.[9] In 2011, Loh and co-workers presented the first Heck coupling reaction using arylhydrazines as partners under palladium-catalysis (Scheme 1a).[10] Various arylhydrazines can be coupled with olefins to smoothly generate their corresponding styrene derivatives with high efficiency and good functional group tolerance. In this process, both Pd(0) and Pd(II) species are involved in the catalytic cycle and a bidentate ligand (bathocuproine) was essential for the transformation. Later, Liu and co-workers developed another coupling reaction involving arylhydrazines with acrylates.[11] Unlike the previous report, this procedure proceeded under alkaline conditions and underwent *via* active *N*′-Ts arylhydrazine intermediates (Scheme 1b). Though good results were revealed, this transformation showed poor regioselectivity and the *p*-tol group of the *N*′-Ts arylhydrazine intermediate was also involved as a coupling partner when reacted with aryl olefins; this finding may limit its application as a general methodology in organic synthesis. Our previous work demonstrated that *N′*-acyl arylhydrazine is an efficient coupling partner that could undergo meaningful coupling reactions in the presence of $Cu(OAc)_2 \cdot H_2O$ (Scheme 1c)[12] and can also undergo coupling reactions with dialkyl phosphites *via* a CDC (cross-dehydrogenative coupling) reaction under mild conditions.[13] Inspired by these pioneering studies, we envisioned that *N′*-acyl arylhydrazine may also be utilized as an aryl donor in the Heck-type coupling reaction to form aryl olefins. Herein, we reported our recent findings on the preparation of aryl alkenes *via* the Heck-type coupling of *N′*-acyl arylhydrazines with aryl olefins as well as acrylates under ligand-free conditions (Scheme 1d).



Scheme 1 (a) Heck-type coupling of arylhydrazines under ligand assisted conditions; (b) Coupling of arylhydrazines with acrylates using TsCl as activating agent; (c) Copper(II)-catalyzed coupling reaction of *N′*-acyl arylhydrazines; (d) Heck-type coupling of *N′*-acyl arylhydrazines with olefins.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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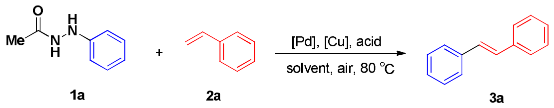
To begin this study, *N'*-acetyl phenylhydrazine (**1a**) and styrene (**2a**) were chosen as model substrates. Various conditions were screened and the results summarized in Table 1. In the presence of 5 mol% $PdCl_2$ and 1.2 equiv. of TsOH, the desired Heck-type coupling product **3a** was obtained in an isolated yield of 45% at 80 °C using DMSO as the reaction solvent (Table 1, entry 1). The yield was markedly improved by the introduction of 10 mol% CuI as a co-catalyst (67%, entry 2). Encouraged by this result, several other conventional copper salts, such as CuBr, CuCl and $Cu(OAc)_2$, were also assessed (entries 3–5). Though a slight decrease in yield was noticed using CuBr as the co-catalyst, neither CuCl nor $Cu(OAc)_2$ was compatible with this coupling process. To improve the reaction efficiency, various organic acids were taken into consideration (entries 6–8) and the use of TFA led to a higher yield being obtained for this catalytic reaction (from 67% to 75%, entry 6). Other palladium complexes such as $Pd(OAc)_2$, $Pd[P(Ph)_3]_4$ and $Pd_2(dba)_3$ were also evaluated, but only inferior results were obtained (entries 9–11). A detailed investigation on the molar ratio of TFA revealed that 2.0 equiv. was optimal for the Heck-type reaction (86%, entry 13). Increasing the amount of $PdCl_2$ to 8 mol% led to a lower yield (entry 15). Two types of ligands, PPh_3 and 1,10-Phen were introduced into the catalytic system to test whether the presence of a ligand could promote the reaction. Unfortunately, both of them showed negative effects on the catalytic process (entries 16 and 17). Different solvents were also evaluated and all of them displayed disappointing results (entries 18–20). An external oxidant NMO led to a dramatic decrease in yield. For comparison, the reaction was also performed under a pure O_2 atmosphere to give product **3a** in a yield of 88% (entry 22), which indicated that oxygen was essential for this catalytic system, the higher concentration of molecular oxygen led to a higher yield (entries 13 and 22). To our surprise, the reaction also worked under an argon atmosphere albeit with a much lower yield (entry 23); a similar result was found in our previous work and the reaction may occur *via* a different mechanism in the absence of oxygen.[12,14]

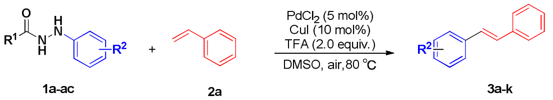
Table 1 Optimization of the reaction conditions.[a]

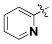


Entry	[Pd]	[Cu]	Acid	Solvent	Yield[b] (%)
1	$PdCl_2$	None	TsOH	DMSO	45
2	$PdCl_2$	CuI	TsOH	DMSO	67
3	$PdCl_2$	CuBr	TsOH	DMSO	59
4	$PdCl_2$	CuCl	TsOH	DMSO	trace
5	$PdCl_2$	$Cu(OAc)_2$	TsOH	DMSO	trace
6	$PdCl_2$	CuI	TFA	DMSO	75
7	$PdCl_2$	CuI	AcOH	DMSO	53
8	$PdCl_2$	CuI	pivalic acid	DMSO	57
9	$Pd(OAc)_2$	CuI	TFA	DMSO	32
10	$Pd[P(Ph)_3]_4$	CuI	TFA	DMSO	Trace
11	$Pd_2(dba)_3$	CuI	TFA	DMSO	59
12	$PdCl_2$	CuI	TFA (1.0 eq)	DMSO	62
13	**$PdCl_2$**	**CuI**	**TFA (2.0 eq)**	**DMSO**	**86**
14	$PdCl_2$	CuI	TFA (2.5 eq)	DMSO	63
15	$PdCl_2$ (8 mol%)	CuI	TFA (2.0 eq)	DMSO	76
16	$PdCl_2$	CuI	TFA (2.0 eq)	DMSO	65[c]
17	$PdCl_2$	CuI	TFA (2.0 eq)	DMSO	63[d]
18	$PdCl_2$	CuI	TFA (2.0 eq)	CH_3OH	65
19	$PdCl_2$	CuI	TFA (2.0 eq)	dioxane	trace
20	$PdCl_2$	CuI	TFA (2.0 eq)	DMF	trace
21	$PdCl_2$	CuI	TFA (2.0 eq)	DMSO	57[e]
22	$PdCl_2$	CuI	TFA (2.0 eq)	DMSO	89[f]
23	$PdCl_2$	CuI	TFA (2.0 eq)	DMSO	30[g]

[a] **1a** (0.3 mmol), **2a** (0.45 mmol), acid (1.2 equiv.), [Pd] (5 mol%), [Cu] (10 mol%), DMSO (2.0 mL, dried over 4Å MS), 80 °C,12-24 h. [b] Isolated yields. [c] 20 mol% PPh_3 was added; [d] 20 mol% 1,10-Phen was added; [e] 20 mol% NMO was added; [f] Proceed under O_2; [g] Proceed under Ar.

Table 2 Coupling reactions of various *N'*-acyl arylhydrazines with styrene.[a]



Entry	R^1	R^2	Product	Yield[b]
1	Me	H (**1a**)	**3a**	86
2	Me	4-F (**1b**)	**3b**	83
3	Me	4-Cl (**1c**)	**3c**	86
4	Me	4-Br (**1d**)	**3d**	82
5	Me	3-Cl (**1e**)	**3e**	83
6	Me	2-Cl (**1f**)	**3f**	65
7	Me	4-OMe (**1g**)	**3g**	92
8	Me	4-CF_3 (**1h**)	**3h**	74
9	Me	4-NO_2 (**1i**)	**3i**	67
10	Me	3,5-*di*-Me (**1j**)	**3j**	89
11	Me	3-Me (**1k**)	**3k**	89
12	OBu-*t*	H (**1l**)	**3a**	76
13	OBu-*t*	4-OMe (**1m**)	**3g**	87
14	OBu-*t*	3-Me (**1n**)	**3k**	87
15	OBu-*t*	3,5-*di*-Me (**1o**)	**3j**	84
16	OBu-*t*	4-NO_2 (**1p**)	**3i**	70
17	OBu-*t*	4-F (**1q**)	**3b**	78
18	OBu-*t*	4-Cl (**1r**)	**3c**	90
19	OBu-*t*	4-Br (**1s**)	**3d**	94
20	OBu-*t*	3-Cl (**1t**)	**3e**	86
21	Ph	H (**1u**)	**3a**	70
22	4-NO_2-Ph	H (**1v**)	**3a**	72
23	2-Br-Ph	H (**1w**)	**3a**	86
24	TsNHNHPh (**1x**)		**3a**	78
25	4-NH_2-Ph	H (**1y**)	**3a**	90
26	4-OMe-Ph	H (**1z**)	**3a**	77
27	2-I-Ph	H (**1aa**)	**3a**	76
28	 (**1ab**)		**3a**	41

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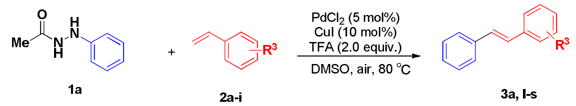
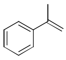
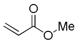
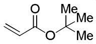
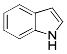
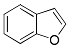
[a] 1 (0.3 mmol), 2a (0.45 mmol), TFA (2.0 equiv.), $PdCl_2$ (5 mol%), CuI (10 mol%), DMSO (2.0 mL, dried over 4Å MS), 80 °C, 12-24 h. [b] Isolated yields.

Having established the optimal reaction conditions, the scope of the Pd/Cu-catalyzed Heck-type coupling reaction was investigated. Various *N*′-acyl arylhydrazines with both electron-donating and electron-withdrawing groups attached to the aromatic ring were all good partners in this transformation, affording their corresponding products in good to excellent yields (Table 2). In general, various halide substituents on the aryl ring of the *N*′-acyl arylhydrazine were well tolerated (entries 2–5) and electron- donating groups such as Me and OMe on the aromatic ring showed higher reaction efficiencies than those with electron-withdrawing substituents (entries 7, 8, 9, 10, 11, 13, 14 and 16). The reaction was sensitive to the steric hindrance of the substrate, for example, *ortho*-chloro substituted *N*′-acyl arylhydrazine **1f** only afforded a moderate yield (entry 6), which was consistent with our previous findings.[12] The reaction scope was further expanded to *N*′-Boc and *N*′-aroyl substituted arylhydrazines (entries 12–20 and 21–28) and both types of substrates were well compatible under the optimal reaction conditions and a wide variety of functional groups were well tolerated. Intriguingly, highly regioselective products were obtained using *N*′-aroyl substituted arylhydrazines as the coupling partners and only the aryl ring directly attached to the hydrazine was involved in the transformation, which was distinguished from the previous report (entries 21–28).[15] An excellent chemoselectivity was also displayed when substrates bearing halide substituents such as chloro, bromo and iodo substituted on both aryl (entries 3–6) and aroyl (entries 23 and 27) moieties underwent the standard reaction conditions. Notably, only a moderate yield was obtained when *N*'-phenyl picolinohydrazide (**1ac**) was involved (entry 28); this may be due to the co-ordinating effect of the pyridyl ring with the catalysts, which may reduce their catalytic efficiency.

Table 3 Coupling reactions of *N*′-acetyl phenyl hydrazine with various olefins.[a]

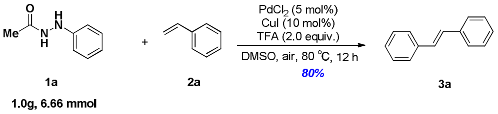


Entry	R^3	Product	Yield[b]
1	H (**2a**)	**3a**	86
2	4-Cl (**2b**)	**3c**	82
3	4-Br (**2c**)	**3d**	90
4	4-OMe (**2d**)	**3g**	84
5	 (**2e**)	**3l**	71
6	 (**2f**)	**3m**	65
7	 (**2g**)	**3n**	55
8	 (**2h**)	**3o**	49
9	 (**2i**)	**3p**	57

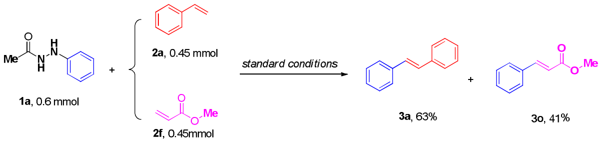
[a] **1a** (0.3 mmol), **2** (0.45 mmol), TFA (2.0 equiv.), $PdCl_2$ (5 mol%), CuI (10 mol%), DMSO (2.0 mL, dried over 4Å MS), 80 °C, 12-24 h. [b] Isolated yields.

The reaction scope was further expanded to various olefins (Table 3). Diverse functional groups on the aromatic ring of the olefin were well tolerated, giving the desired coupling products in high yield (entries 2-4). Prop-1-en-2-ylbenzene (**3l**) will also react smoothly with *N*′-acetyl phenyl hydrazine to give the desired product in moderate yields (entry 5). The scope of the acrylate was also evaluated, and both methyl and *tert*-butyl acrylate showed good compatibilities and afforded the corresponding products in acceptable yields (entries 6 and 7). Excitingly, heteroaromatic partners such as indole and benzofuran also revealed moderate reactivity with *N*′-acetyl phenyl hydrazine (entries 8 and 9) and have great potential for applications in the formation of heterocyclic molecules with high biological activities.[16]

Moreover, an additional scale-up experiment showed that this palladium/copper-catalyzed Heck-type coupling reaction can be performed on a gram scale with only a slight drop in yield (Scheme 2). Besides, we also performed competition experiments of **1a** coupling with **2a** and **2f** in one-pot under the standard conditions (Scheme 3); we found that both **3a** and **3o** were generated in lower yields when compared with their independent experiments (Table 3, entries 1 and 6). We conclude that a higher concentration of catalysts and TFA in the system may cause an inhibitory effect instead of promotion for this Heck-type coupling reaction.

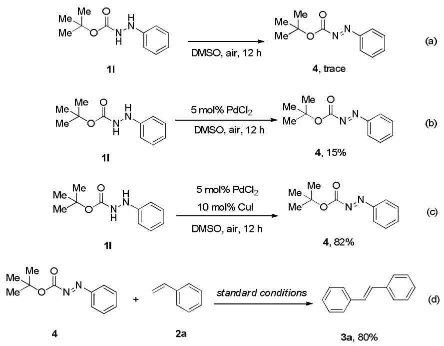


Scheme 2. Gram scale preparation of **3a**.



Scheme 3. Competition experiments of **1a** coupling with **2a** and **2f**.

To further explore the mechanism of this palladium/copper-catalyzed reaction, we carried out some control experiments (Scheme 4). Firstly, we used **1l** as the substrate and subjected it to the standard conditions without adding the catalyst or TFA (Scheme 4a) and no diazene intermediate **4** was detected in the system. When 5 mol% $PdCl_2$ was introduced, we obtained **4** in an isolated yield of 15% (Scheme 4b). Surprisingly, a sharp increase in yield of **4** was revealed when 10 mol% CuI was further added as a co-catalyst (Scheme 4c). We concluded that CuI may promote the regeneration of [Pd(0)] in this process. Taking **4** and **2a** as coupling partners, the desired product **3a** was obtained in 80% yield under the optimal reaction conditions (Scheme 4d).



Scheme 4. Control experiments.

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Based on these experiments and the literature,[10,12,15,17] we have proposed the possible mechanism for this palladium/copper-catalyzed Heck-type coupling reaction (Fig. 1). *N*′-acyl arylhydrazine (**A**) was oxidized by PdXY (X, Y = Cl, I, CF_3COO) to give the diazene intermediate **B**. The reductive Pd(0) coordinates with **B** to form the azo-palladium complex (**C**), which undergoes a regioselective alkene insertion under the acidic conditions with the release of R^1Y, CO and N_2. Degeneration of the organopalladium intermediate **D** afforded a coupling product **E** and regenerated the Pd(0) species, which may be reoxidized to PdXY in the presence of air (Table 1, entry 1) or under the mediation of the copper salt.

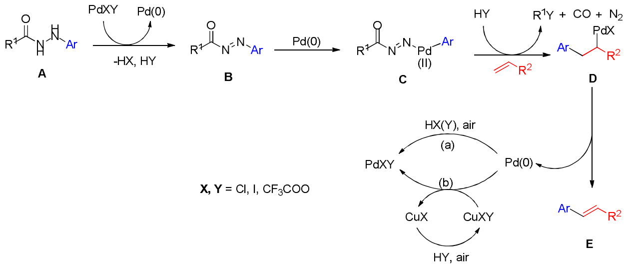

Fig. 1 Proposed mechanism.

Conclusions

In summary, with *N*′-acyl arylhydrazines as aryl donors, we have developed a novel, ligand-free and regioselective palladium/copper catalyzed arylation of alkenes. This protocol, using air as terminal oxidant, is simple, readily operated and tolerates a broad substrate scope, which makes it quite applicable in practical organic synthesis.

Experimental Section

A mixture of *N*′-acyl arylhydrazine **1** (0.3 mmol), alkene **2** (0.45 mmol), $PdCl_2$ (0.015 mmol), CuI (0.03 mmol) and TFA (0.6 mmol) in DMSO (2.0 mL) was stirred at 80 °C for 12-24 h. After completion of the reaction (indicated by TLC), the mixture was quenched with saturated NaCl solution and extracted with EtOAc, followed by washing with H_2O and saturated NaCl solution, and finally dried over Na_2SO_4. The crude product was purified by flash column chromatography to provide the corresponding product **3**.

Acknowledgements

This work was financially supported by National Science Fundation of P. R. China (No. 81660573), National Science Grand Fundation of Guizhou Province (No. JZ[2016]2001), Social Development of Technical Supporting Fundation of Guizhou Province (No. [2016]2819) and the Ph.D. Research Foundation of Guizhou Medical University (No. J[2015]006).

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View Article Online
DOI: 10.1039/C6NJ03718F

Palladium/Copper-Catalyzed Arylation of Alkenes with *N*'-Acyl Arylhydrazines

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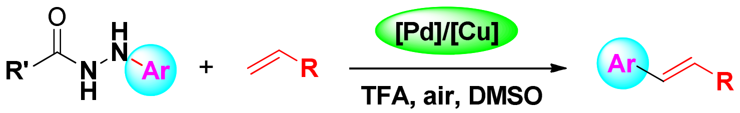
Abstract

A novel ligand-free palladium/copper-catalyzed Heck-type coupling reaction of alkenes and *N*'-acyl arylhydrazines has been developed by using air as terminal oxidant. This protocol featured wide functional group tolerance and highly chemoselective and regioselective products with good to excellent yields.

Text

An efficient andl ligand-free palladium/copper-catalyzed Heck-type coupling reaction of N'-acyl arylhydrazines with olefins for the practical synthesis of arylalkenes.

Colour graphic



ligand-free
36 examples, good to excellent yields
highly chemoselectivity and regioselectivity
both aryl olefines and acrylates are good coupling partners