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Palladium-Catalyzed Direct Arylation of Allylamines with Simple Arenes

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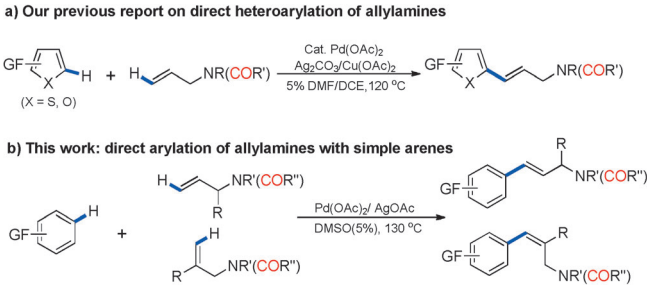
The $Pd(OAc)_2$-catalyzed direct C–H bond olefination of unreactive arenes with allylamines in the presence of AgOAc was developed. A variety of allylamines including β-substituted substrates underwent smooth coupling reactions with various arenes to give exclusively the terminal arylation products in high yields with excellent regioselectivities and stereoselectivities. The reaction is compatible with a range of functional groups in both coupling partners. The carbonyl group in the allylamine substrates is critical to catalysis, and the high regio- and stereocontrol observed is attributed to coordination between the carbonyl O and Pd atoms.

The efficient construction of allylamines has been the subject of extensive research over many years, because these amines are important structural units in many natural products and pharmaceuticals, and they also serve as important precursors for the synthesis of functionalized compounds.[1–3] Recent studies have revealed that biologically and synthetically important arylated allylamines can be readily accessed through Pd-catalyzed arylation of readily accessible allylamines with aryl triflates, aryl halides, arenediazonium salts, and arylboronic acids; furthermore, useful strategies have been developed to control the regioselectivity.[4] However, a preactivation step of the (hetero)arenes is required in these reactions, and it is clear that, from the viewpoint of atom economy and efficiency, the direct cross-coupling between simple (hetero)arenes and allylamines would be a straightforward and more efficient method. Transition-metal-catalyzed direct C–H functionalization reactions are currently emerging as powerful rivals to traditional organic transformations based on prefunctionalized substrates, owing to their improved atom economy and efficiency.[5] Therefore, it is not surprising that transition-metal-catalyzed direct dehydrogenative coupling reactions of arenes with olefins (also referred to as the Fujiwara–Moritani reaction) has attracted increasing research interest over the last decades.[6] Particularly, substantial progress has been made in the direct olefination of simple arenes not containing directing groups, and catalysts based on Pd,[7] Rh,[8] and Ru[9] complexes are notable for their high catalytic efficiency, functional group tolerance, and value of applications. Among these reported studies, electron-deficient olefins (e.g.,α, β-unsaturated esters and amides) and electron-neutral aliphatic olefins and styrenes have been broadly employed to yield promising results. Recent reports have demonstrated that other olefins, such as allyl esters,[10a–e,h] enamides,[10f] and trisubstituted cinnamates,[10g] can also undergo direct coupling reactions with simple arenes to give the target products with different reactivities and selectivities. In the course of exploring the regioselective arylation of olefins,[11] we recently disclosed that the combination of $Pd(OAc)_2$ and suitable oxidants could catalyze the highly regioselective direct heteroarylation of allylamines with thiophenes and furans to give the target products in high yields (Scheme 1 a), and it is noteworthy that the electronic



Scheme 1. Catalytic direct olefination of arenes with allylamines. FG = Functional group.

and steric properties of the allylamines have a significant impact on the catalytic activity and regiocontrol.[11c] Encouraged by this discovery, we became interested in the development of a direct coupling reaction of allylamines with simple arenes. Herein, we report that simple arenes can indeed react with allylamines in the presence of a $Pd(OAc)_2$ catalyst in combination with AgOAc as the oxidant (Scheme 1 b) to afford arylated allylamine products in a highly regioselective and stereoselective manner.[12]

We began our studies by investigating the arylation of *N*,*N*-$(Boc)_2$ allylamine (**2 a**, Boc = *tert*-butyloxycarbonyl) with $Pd(OAc)_2$ as the catalyst and Ag_2CO_3 as the oxidant; benzene (**1 a**) acted as both the coupling partner and the reaction medium. No reaction was observed in pure benzene (Table 1,

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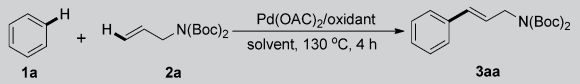
Table 1. Screening conditions for the Pd-catalyzed direct olefination of benzene (**1a**) with *N,N*-$(Boc)_2$-allylamine (**2a**).[a]



1a 2a 3aa

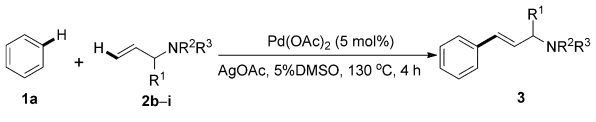
Entry	Oxidant	Solvent	Yield [%][b]
1	Ag_2CO_3	benzene	nd
2	Ag_2CO_3	benzene/DMF = 20:1	54
3	Ag_2CO_3	benzene/DMSO = 20:1	71
4	Ag_2CO_3	benzene/NMP = 20:1	nd
5	Ag_2CO_3	benzene/CH_3CN = 20:1	nd
6	Ag_2CO_3	benzene/THF = 20:1	nd
7	Ag_2CO_3	benzene/DMSO = 10:1	31
8	Ag_2CO_3	benzene/DMSO = 50:1	23
9[c]	Ag_2CO_3	DMSO	nd
10[c]	Ag_2CO_3	DCE/DMSO = 20:1	nd
11	BQ	benzene/DMSO = 20:1	nd
12	Ag_2O	benzene/DMSO = 20:1	nd
13	Ag_2SO4	benzene/DMSO = 20:1	nd
14	$AgNO_3$	benzene/DMSO = 20:1	34
15	AgOAc	benzene/DMSO = 20:1	91
16	Oxone	benzene/DMSO = 20:1	nd
17	$K_2S_2O_8$	benzene/DMSO = 20:1	nd
18	O_2	benzene/DMSO = 20:1	nd
19[d]	AgOAc	benzene/DMSO = 20:1	33
20[e]	AgOAc	benzene/DMSO = 20:1	45
21[f]	AgOAc	benzene/DMSO = 20:1	50
22[g]	AgOAc	benzene/DMSO = 20:1	44
23[h]	AgOAc	benzene/DMSO = 20:1	14
24[i]	AgOAc	benzene/DMSO = 20:1	82

[a] Reaction conditions: **1a** (2.0 mL), **2a** (0.4 mmol), $Pd(OAc)_2$ (5 mol%), oxidant (1.5 equiv.), co-solvent, 130 °C, 24 h. [b] Yield of isolated product. nd: not detected.[c] **1a**: 20 equiv. [d] $Pd(OAc)_2$ was replaced by $Pd(tfa)_2$. [e] $Pd(OAc)_2$ was replaced by $PdCl_2$. [f] $Pd(OAc)_2$ was replaced by $Pd(PPh_3)_4$. [g] $Pd(OAc)_2$ was replaced by $Pd_2(dba)_3$. [h] AcOH: 10 equiv. [i] Reaction temperature: 120 °C.

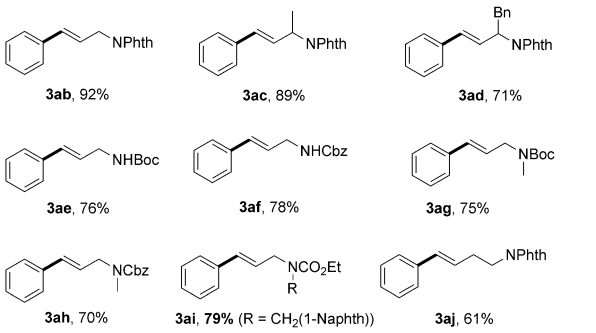
entry 1), but the addition of 5% DMF as a co-solvent led to the exclusive formation of target γ-arylated product **3aa** in 54% yield (Table 1, entry 2). Replacing DMF with DMSO gave rise to a higher yield of 71% (Table 1, entry 3), but the use of other solvents such as *N*-methyl-2-pyrrolidone (NMP), CH_3CN, and THF was not effective (Table 1, entries 4–6). Increasing or decreasing the amount of DMSO resulted in decreased yields (Table 1, entries 7 and 8), and if the reaction was performed with benzene (20 equiv.) in DMSO, no product was observed (Table 1, entry 9). Clearly, a specific amount of DMSO is capable of promoting this direct coupling reaction. On the basis of previous reports on Pd-catalyzed oxidative reactions, DMSO may function as a ligand in the present transformation.[13] The mixed solvent of DMSO/1,2-dichloroethane (DCE), which has been reported to facilitate the Pd-catalyzed direct heteroarylation of allylic amines with thiophenes and furans,[11c] proved to be inefficient in this case, as no reaction took place (Table 1, entry 10). To improve the reaction efficiency, the performance of other oxidants was examined (Table 1, entries 11–18), and AgOAc was found to be the best choice, as it provided **3aa** in 91% yield (Table 1, entry 15). For comparison, other palladium salts including $Pd(tfa)_2$ (tfa = trifluoroacetate), $PdCl_2$, $Pd(PPh_3)_4$, and $Pd_2(dba)_3$ (dba = dibenzylideneacetone) were screened (Table 1, entries 19–22), but none of them was superior to $Pd(OAc)_2$. Recent studies have demonstrated the promoting effect of carboxylic acids in Pd-catalyzed direct olefination reactions.[6] However, upon adding acetic acid to the current reaction, the yield of **3aa** dropped significantly (Table 1, entry 23). Further investigation indicated that lowering the reaction temperature decreased the reactivity as evidenced by the fact that a reduced yield of 82% was observed at 120 °C (Table 1, entry 24). It should be stressed that in all cases no internal arylation, allylic migration, or partial deprotection[4j] was detected, and only *E*-configured **3aa** was produced.

With the optimal reaction conditions in hand, we next investigated the direct olefination of **1a** with a range of other allylamines (Table 2). It was found that both *N,N*-diprotected (i.e., compounds **2b**, **2g–i**) and *N*-monoprotected (i.e., compounds **2e**, **2f**) allylamines underwent smooth arylation with **1a** under the optimized conditions to give the desired linear products (Table 2, see compounds **3ab**, **3af–ai**) in high yields regardless of the nature of the substituents on the allylic amine nitrogen atom, and excellent regioselectivities (terminal/internal > 99:1) and stereoselectivities (*E*/*Z* > 20:1) were observed in the reactions studied. It is noteworthy that the α-substituted allylic amines (i.e., compounds **2c** and **2d**) exhibited similar reactivity and selectivity and exclusively afforded the corresponding linear arylated allylamine products (Table 2, see compounds **3ac** and **3ad**) in good yields. Interestingly, under the current catalytic conditions, 2-(but-3-en-1-yl)isoindoline-1,3-dione (**2j**) also successfully participated in the direct coupling reaction to furnish terminal arylation product **3aj** in 61% yield. However, no reaction was detected in the arylation of very electron-rich *N,N*-diethylallylamine (**2k**), and strong coordination of the nitrogen atom to Pd is believed to cause catalyst poisoning, which thereby inhibits the arylation reaction.[11c,d]

Table 2. Pd-catalyzed direct olefination of **1a** with allylamines.[a]

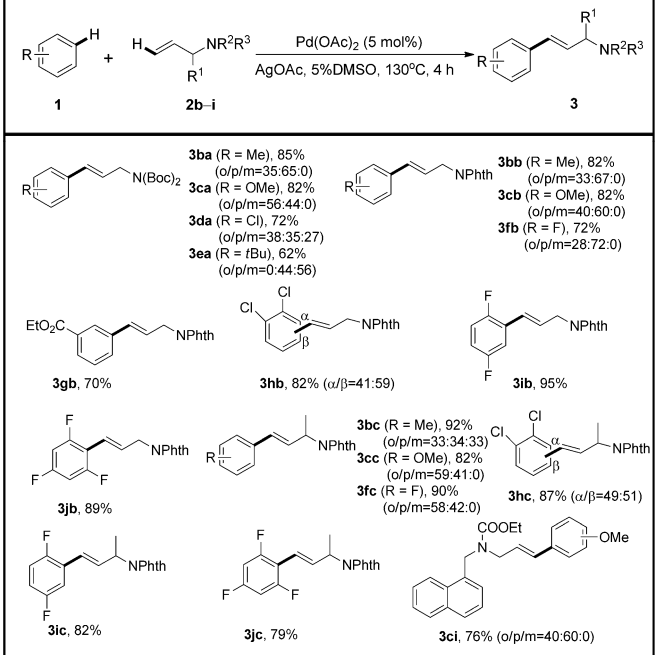


1a 2b–i 3



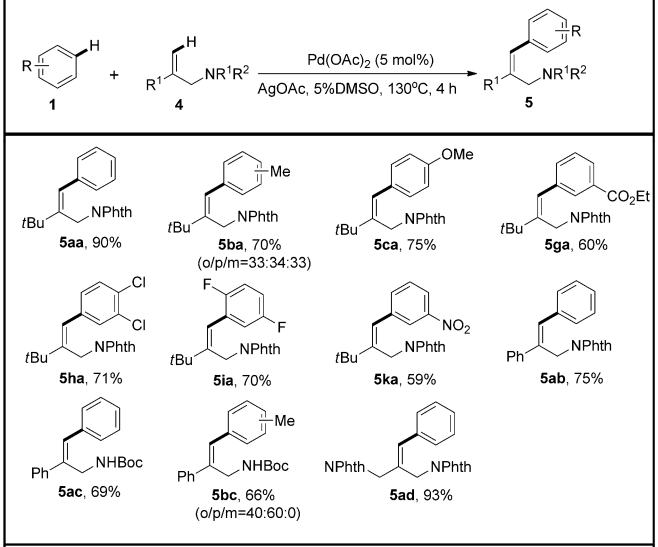
[a] Reaction conditions: **1a** (2.0 mL), **2** (0.4 mmol), $Pd(OAc)_2$ (5 mol%), AgOAc (0.6 mmol), DMSO (0.1 mL), 130 °C, 4 h. Yields of isolated products are given. Phth = phthaloyl, Bn = benzyl, Cbz = benzyloxycarbonyl.

Table 3. Pd-catalyzed direct olefination of substituted arenes with allylamines.[a]



[a] Reaction conditions: **1** (2.0 mL), **2** (0.4 mmol), $Pd(OAc)_2$ (5 mol%), AgOAc (0.6 mmol), DMSO (0.1 mL), 130 °C, 4 h. Yields of isolated products are given.

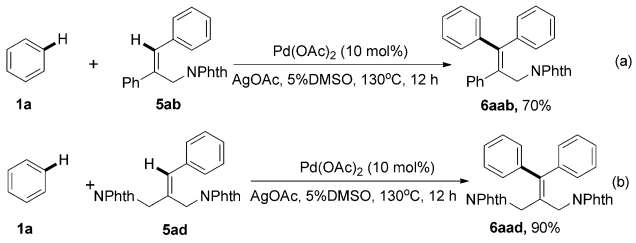
Table 4. Pd-catalyzed direct arylation of β-substituted allylamines with arenes.[a]



[a] Reaction conditions: **1** (2.0 mL), **2** (0.4 mmol), $Pd(OAc)_2$ (5 mol%), AgOAc (0.6 mmol), DMSO (0.1 mL), 130 °C, 4 h. Yields of isolated products are given.

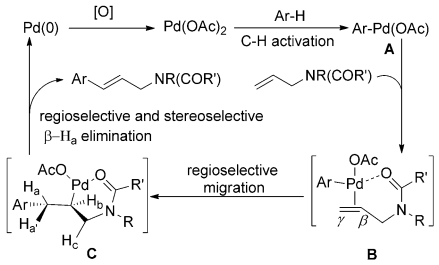
Next, we turned our attention to the direct coupling reactions of various substituted arenes with allylamine derivatives, and the results are summarized in Table 3. As can be seen, under the current catalysis various monosubstituted arenes were smoothly olefinated to provide the coupling products in high yields (Table 3, see compounds **3ba–ea**, **3bb**, **3cb**, **3fb**, **3gb**, and **3ci**), and regioisomeric mixtures were observed upon employing toluene (**1b**), anisole (**1c**), chlorobenzene (**1d**), *tert*-butylbenzene (**1e**), and fluorobenzene (**1f**) as the coupling partners, whereas electron-deficient ethyl benzoate (**1g**) only furnished *meta*-olefinated product **3gb** as a single regioisomer. Notably, electron-rich monosubstituted arenes **1b** and **1c**, chlorobenzene (**1d**), and fluorobenzene (**1f**) favored *ortho* and *para* olefination, but no *ortho* olefination was detected in the case of *tert*-butylbenzene (**1e**) owing to steric effects. Disubstituted arene **1h** was also reactive, and it provided a mixture of isomers in high yields (Table 3, see compounds **3hb** and **3hc**). Electron-deficient 1,4-difluorobenzene (**1i**) and 1,3,5-trifluorobenzene (**1j**) readily reacted with **2e** and **2c**, and corresponding products **3ib**, **3jb**, **3ic**, and **3jc** were isolated in excellent to good yields. Notably, frequently encountered partial deprotection in the arylation of *N*,*N*-diprotected allylamines did not occur in our hands.

The current catalytic system also worked well for the direct arylation of β-substituted allylamines. As shown in Table 4, electronically different arenes reacted well with β-substituted allylamine **4a** to generate the coupling products (Table 4, see compounds **5aa–ca**, **5ga–ia**, and **5ka**) in high yields. Notably, except for toluene (**1b**), substituted arenes **1c**, **1g–i**, and **1k** displayed complete site selectivity in that only one regioisomer was detected. 2-(2-Phenylallyl)isoindoline-1,3-dione (**4b**) and *tert*-butyl (2-phenylallyl)carbamate (**4c**) proved to be viable substrates, and olefinated arene products **5ab**, **5ac**, and **5bc** were isolated in satisfactory yields. β-Substituted allylamine **4d** was also observed to afford target product **5ad** in an excellent 93%yield. It is noteworthy that these obtained trisubstituted olefins were confirmed to be of the *Z* configuration by NMR spectroscopy. Moreover, these trisubstituted olefins underwent further arylation to provide tetrasubstituted olefin products. For example, under the catalysis of $Pd(OAc)_2$, **5ab** and **5ad** proceeded smoothly to afford products **6aab** and **6aad** in high yields (Scheme 2).



Scheme 2. Direct arylation of trisubstituted olefins.

On the basis of the observed experimental results and previous reports,[11b–e,14] a plausible mechanism is proposed in Scheme 3. The process is probably initiated by the reaction of $Pd(OAc)_2$ with ArH through C–H bond activation to afford intermediate **A**, which reacts with the allylamine to generate intermediate **B**. Coordination between the carbonyl O atom and the Pd atom in **B** promotes highly regioselective migration of



Scheme 3. Possible pathway for the direct olefination of arenes with allylamines.

the aryl moiety to the γ position rather than the β position of the olefin to give intermediate **C**; regio- and stereoselective β-H elimination then furnishes the expected product. The released Pd^0 is oxidized by AgOAc to Pd^{II} to finish the catalytic cycle. Similar chelation-assisted regio- and stereocontrol has also been reported in the Pd-catalyzed linear arylation of allyl derivatives and vinyl derivatives.[15]

In conclusion, we developed an efficient palladium catalytic system for the highly regioselective and stereoselective olefination of simple arenes with allylamine derivatives. By using $Pd(OAc)_2$ as the catalyst and AgOAc as the oxidant, both *N*,*N*-diprotected allylamines and *N*-monoprotected allylamines reacted well with differently substituted arenes to give exclusively the γ-arylated allylamine products in high yields, and a range of functionalities in both coupling partners was well tolerated. Our results reveal that the electronic nature of the allylamine substrates has an important impact on the catalytic activity and selectivity, and chelation between the carbonyl O and Pd atoms is believed to facilitate the highly regioselective and stereoselective β-H elimination reaction to give the target products. Further studies focusing on the synthetic application of this protocol and more mechanistic investigations are underway in our laboratory.

Experimental Section

General method

Unless otherwise noted, all experiments were performed in air. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Model Avance DMX 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 106 MHz). Chemical shifts are referenced to residual solvent peaks. The arenes, catalysts, and other common materials and solvents were commercially available and were used as received without further purification.

General procedure for the direct arylation of allylamines with simple arenes

An oven-dried pressure tube was sequentially charged with arene **1** (2.0 mL), allylamine **2** (0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), AgOAc (100 mg, 0.6 mmol), and DMSO (0.1 mL) (5%).The mixture was heated in the sealed tube and stirred vigorously at 130 °C for 4 h. The tube was then removed from the oil bath and cooled to room temperature. The mixture was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, ethyl acetate/hexane 10:90 to 15:85) to give the pure product.

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Keywords: allylamines · arenes · direct arylation · palladium · regioselectivity

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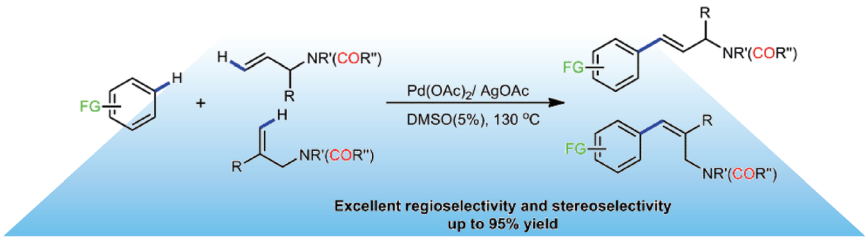
Palladium-Catalyzed Direct Arylation of Allylamines with Simple Arenes



CHa CHa CHa: The Pd^{II}-catalyzed direct arylation of allylamines with simple arenes is developed by using $Pd(OAc)_2$ as the catalyst and AgOAc as the oxidant. The reaction proceeds smoothly and provides the target products with high regioselectivities and stereoselectivities. A range of functional groups (FGs) in both coupling partners is well tolerated. The carbonyl group in the allylamine substrates is critical to catalysis.