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Palladium-catalyzed Cascade Cyclization-Coupling Reaction of Benzyl Halides with N, N-Diallylbenzoylamide

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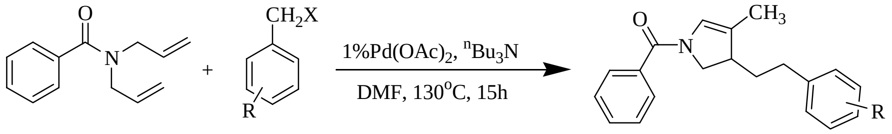
Abstract: A novel type of palladium-catalyzed cascade cyclization-coupling reaction has been found. Reaction of N, N-diallylbenzoylamide **1** with benzyl halides **2** afforded the corresponding dihydropyrroles **3** in moderate to excellent yields.

Keywords: Palladium, Heck reaction, benzyl halides, cyclization, cascade reaction.

Palladium catalyzed vinylation of benzyl halides is an important part of the Heck reaction[1-3]. We have conducted some studies on the reactions. Several interesting results have been obtained including discovery of the reaction of benzylic quanternary ammonium salts[4] and an unusual rearrangement of α-chloromethylnaphthalene[5]. In the course of our continuing efforts in the study of palladium catalyzed reactions of benzylic compounds, we found that benzylic halides can react with 1, 6-dienes, in the presence of palladium catalyst, to form cyclic compounds *via* cascade coupling pathway. Reported herein is the reaction of N, N-diallylbenzoylamide **1** with benzyl halides (**2a-k**). Dihydropyrroles (**3a-k)** were obtained in moderate to excellent yields (**Scheme 1**).

Scheme 1 The typical experimental procedure



1 **2a-k** **3a-k**

A mixture of N, N-diallylbenzoylamine (1 equiv), benzyl halide (1.1 equiv), tributylamine (1.2 equiv) and Pd(OAc)$_2$(1-2 mol%) were heated in DMF under nitrogen atmosphere. The reaction was completed in 15 hours at about 130°C as indicated by TLC monitor. The results are summarized in **Table 1.** All the products obtained are yellowish oil, which were isolated by flash column chromatography on silica gel. As indicated in **Table 1**, yields of the reactions were dependent on the

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substituents on the phenyl ring. The benzylic chlorides with eletrondonating substituents, such as methyl group in entries 2-4, led to smooth reaction and afforded higher yields. Strong electron-withdrawing group such as carboxylate (entry 9) and nitro group (entry 11) suppressed the reaction substantially.

Table 1 Reactions of N, N-diallylbenzoylamine with benzyl halides

Entry	X	R	Product[a]	Yield(％)[b]
1	Cl	H	3a	88
2	Cl	p-CH_3	3b	82
3	Cl	o-CH_3	3c	79
4	Cl	m-CH_3	3d	74
5	Cl	o-Cl	3e	67
6	Cl	p-Cl	3f	69
7	Cl	o-CN	3g	56
8	Cl	p-Br	3h	61
9	Cl	m-$COOCH_3$	3i	52
10	Br	H	3j	70
11	Br	p-NO_2	3k	21

a. The structures of all compounds were confirmed by ^{1}HNMR, MS, IR and elemental analysis.

b. b. Isolated yields.

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References

1. J. Tsuji, *Palladium Reagents and Catalysis,Innovations in Organic Synthesis*, Wiley, New York, **1995**.
2. E. Negish, C. Coperet, S. Ma, S. Y. Liou, F. Liu, *Chem. Rev.,* **1996**, *96*, 365.
3. A. D. Meijere, F. E. Meyer, *Angew. Chem. Int. Ed. Engl.*, **1994**, *33*, 2379.
4. Y. Pan, Z. Y. Zhang, H. W. Hu, *Synthesis*, **1995**, 245.
5. L. S. Wang, Y. Pan, X. Jiang, H. W. Hu, *Tetrahedron Lett*., **2001**, *41*, 725.

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