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Palladium-Catalyzed Arylic/Allylic Aminations: Permutable Domino Sequences for the Synthesis of Dihydroquinolines from Morita–Baylis–Hillman Adducts

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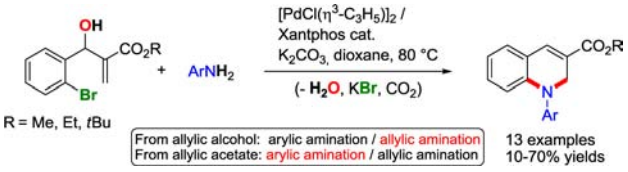
ABSTRACT



An efficient palladium-catalyzed synthesis of 1,2-dihydroquinolines has been developed via the reaction between anilines and Morita–Baylis–Hillman adducts derived from *o*-bromobenzaldehyde. This new Pd(0)-catalyzed pseudo-domino type I sequence involves a Buchwald–Hartwig arylic amination and an allylic amination. When starting from an *o*-bromo allylic alcohol, the chronology is arylic amination/allylic arylation. However, the sequence reverses when the reaction is performed on the corresponding *o*-bromo allylic acetate.

Transition-metal-mediated domino reactions[1] have reached an important place in the arsenal of the organic chemist, as they allow access to complex molecular structures in a single synthetic operation and often under mild conditions. Such transformations may involve either a single catalytic cycle entailing several elementary steps (pure domino)[2] or several sequential catalytic cycles (pseudo-domino),[3,4] driven by a single (type I)[5] or several catalysts (type II).[6] Following our ongoing interest in these domino transformations, as well as in the synthesis of

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nitrogen-based heterocycles,[7] we have initiated a study aimed at the development of a new palladium-catalyzed sequence for the rapid construction of dihydroquinoline frameworks, to be possibly adapted to pseudo-domino conditions.

Quinolines and their fully or partially hydrogenated derivatives are widely found in many biologically active natural or synthetic products.[8] In particular, 1,2-dihydroquinolines have received special attention because of their numerous applications as pharmaceuticals and agrochemicals, as well as their use as intermediates in the synthesis of other heterocycles of biological significance.[9]

Consequently, a number of strategies have been developed for the synthesis of these scaffolds including transition-metal-[10] or organo-catalyzed[11] reactions, as well as one-pot approaches from Morita–Baylis–Hillman (MBH) adducts. Indeed, the use of functionalized adducts derived from the MBH reaction[12] is a convenient synthetic approach for the construction of various quinoline derivatives.[13,14] However, to the best of our knowledge, there are no reports concerning their one-pot synthesis directly from MBH alcohol adducts.[15]

Herein, we describe a palladium-catalyzed synthesis of 1,2-dihydroquinolines through the formation of two C–N bonds via two mechanistically independent and chronologically switchable catalytic processes: an allylic amination[16] and a Buchwald–Hartwig arylic amination reaction.[17] The reaction, which starts from readily available MBH alcohol adducts, generates water and a halide salt as the byproducts and can be run under pseudo-domino conditions (Scheme 1).

Scheme 1. Domino Sequence to 1,2-Dihydroquinolines

We began our study by focusing our attention on the allylic amination of MBH adducts. In particular, we selected, for this step, a poorly nucleophilic amine such as aniline so as to avoid a competitive 1,4-addition on the α,β-unsaturated ester.[18]

Recent studies have shown that combinations of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ with a large bite-angle ligand allow the selective amination of allylic alcohols.[16] Accordingly, we decided to perform our first allylic amination tests on the MBH adduct **1a** lacking an *o*-halo substituent, using Xantphos as the ligand in the presence of 1.5 equivalents of aniline in 1,4-dioxane at 80 °C. While $Pd(OAc)_2$ or $Pd(dba)_2$ as Pd source gave no reaction (Table 1, entries 1 and 2), the dimer $[PdCl(\eta^3\text{-}C_3H_5)]_2$ afforded the desired allylic amine **2a** in 98% yield (entry 3). DPEPhos (entry 4) and dppf (entry 5) proved to be more efficient than monophosphine ligands (entry 6). When the reaction was carried out without either the precatalyst/ligand system (entry 7) or the precatalyst (entry 8), we recovered the unreacted starting material.[19] These two last experiments suggest that a transient η^3-allyl palladium complex is likely to be involved in this transformation and rule out an alternative S_N2' pathway.

Submission of the chloro-substituted MBH adduct **1b** to the reaction conditions as previously optimized with **1a** gave cleanly the corresponding allylic amination product **2b** (Table 1, entry 9). On the other hand, the corresponding bromoester **2c** could be obtained only when starting from the allylic acetate **1c′**[20] (Table 1, entry 11), while no reaction was obtained from the brominated MBH allylic alcohol **1c** (Table 1, entry 10).

These results strongly suggest that, under such conditions, the reactivity scale of oxidative addition to Pd(0) decreases in the order: allylic acetate > aryl bromide > allylic alcohol > aryl chloride (Scheme 2).

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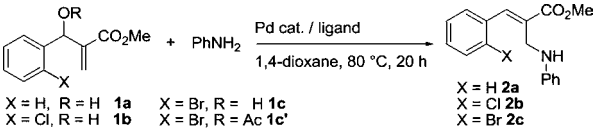
(19) Toluene as a solvent also gave full conversion. However, this solvent was highly detrimental for the domino process.

(20) This reaction was also described to occur without any catalyst. See ref 14.

Table 1. Optimization of the Palladium-Catalyzed Allylic Amination of MBH Adducts with Aniline[a]



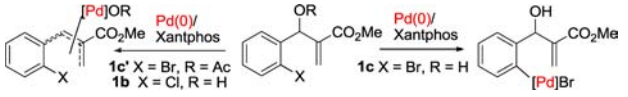
X = H, R = H **1a** X = Br, R = H **1c**
X = Cl, R = H **1b** X = Br, R = Ac **1c'**

X = H **2a**
X = Cl **2b**
X = Br **2c**

entry	R	X	catalyst	ligand	yield (%)
1	H	H	$Pd(OAc)_2$[b]	Xantphos	no reaction
2	H	H	$Pd(dba)_2$[b]	Xantphos	no reaction
3	H	H	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	Xantphos	**2a**, 98[c]
4	H	H	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	DPEPhos	**2a**, 81[d]
5	H	H	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	dppf	**2a**, 95[d]
6	H	H	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	XPhos[e]	**2a**, 50[d]
7	H	H			no reaction
8	H	H		Xantphos	no reaction
9	H	Cl	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	Xantphos	**2b**, 91[c,f]
10	H	Br	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	Xantphos	no reaction
11	Ac	Br	$[PdCl(\eta^3\text{-}C_3H_5)]_2$	Xantphos	**2c**, 56[c]

[a] Reaction conditions: **1** (1 equiv), $PhNH_2$ (1.5 equiv), Pd cat. (5 mol %), ligand (10 mol %), 1,4-dioxane (0.2 M). [b] 10 mol % of Pd cat. were used. [c] Isolated yield. [d] Spectroscopic (^{1}H NMR) yields using an internal standard (1,3,5-trimethoxybenzene). [e] 20 mol % of ligand were used. [f] Reaction time: 2 days.

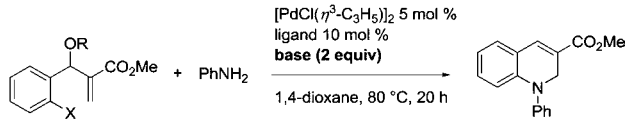
Scheme 2. Oxidative Addition Preferences of *o*-Halo-MBH Adducts



As in the Buchwald–Hartwig reaction, a base is needed to convert the amino complex $ArPdXNH_2R$ into the corresponding amido complex ArPdNHR, we surmised that the failure to react of **1c** was very likely due to a catalysis halt at the amino complex stage. We thus anticipated that generation of the desired dihydroquinoline in a domino fashion could be obtained via two different chronologies (allylation/arylation or vice versa) just by playing with the nature of the allylic and the arylic leaving groups. More precisely, we reasoned that in the case of the bromide **1c**, addition of a base to the previously optimized reaction conditions should trigger an initial Buchwald–Hartwig arylic amination, and the thus generated secondary amine may in turn undergo an intramolecular allylation, whereas a reversed chronological sequence might be achieved either from bromoacetate **1c′** or the chloroalcohol **1b**.

As expected, when the reaction between **1c** and aniline was repeated in the presence of K_2CO_3, a 65% yield of the desired 1,2-dihydroquinoline **3a** was obtained (Table 2, entry 1).[21] However, other biphosphine ligands which efficiently promoted the allylic amination gave lower yields in this domino sequence (entries 2 and 3). Similarly, the use of Cs_2CO_3 as the base led to a drop of yield (entry 4). Interestingly, the 1,2-dihydroquinoline **3a** could also be obtained (81% yield) submitting the bromoacetate **1c′** to the same reaction conditions as above (Table 2, entry 5).[22] Finally, **3a** could also be obtained (43% yield) starting from the chloroalcohol **1b** when working in the presence of both Xantphos[23] and Xphos[23,24] (Table 2, entry 6).[25] Indeed, while the former ligand turned out to be the optimal one for the allylation step, the latter one is known to be the ligand of choice to favor oxidative addition of aryl chlorides to Pd(0).

Table 2. Palladium-Catalyzed Arylic/Allylic Amination Domino Sequence of MBH Adducts with Aniline[a]



X = Cl, R = H **1b** X = Br, R = H **1c**
X = Br, R = Ac **1c'**

3a

entry	R	X	ligand	base	yield (%)
1	H	Br	Xantphos	K_2CO_3	65,[b] 58[c]
2	H	Br	DPEPhos	K_2CO_3	34[b]
3	H	Br	dppf	K_2CO_3	26[b]
4	H	Br	Xantphos	Cs_2CO_3	23[b]
5	Ac	Br	Xantphos	K_2CO_3	81[c]
6	H	Cl	Xantphos and Xphos	K_2CO_3	43[c,d]

[a] Reaction conditions: **1c** (1 equiv), $PhNH_2$ (1.5 equiv), $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (5 mol %), ligand (10 mol %), K_2CO_3 (2 equiv), 1,4-dioxane (0.2 M). [b] Spectroscopic (^{1}H NMR) yields using an internal standard (1,3,5-trimethoxybenzene). [c] Isolated yield. [d] Reaction time: 2 days.

With successful domino conditions in hands, we began to explore the sequence on a series of aromatic amines and various MBH adducts. In particular, we selected the variant starting from the bromo alcohols MBH adducts as it appears the most straightforward one (Scheme 3). In the event, electron-donating (**3b**,**3c**, **3f**) and electron-withdrawing (**3g**–**j**) groups on the aromatic ring of the amines were well tolerated and provided the target 1,2-dihydroquinolines in good yields,[26] except for the bulky 2,4,6-trimethylaniline (**3d**) and naphthalen-1-amine (**3e**).

(21) Under these conditions, the indanone derivative that could arise from an intramolecular Mizoroki–Heck coupling was not observed. (a) Park, J. B.; Ko, S. H.; Hong, W. P.; Lee, K-J. Bull *Korean Chem. Soc.* **2004**, *25*, 927. (b) Gaudin, J.-M. *Tetrahedron Lett.* **1991**, *32*, 6113.

(22) The yield of this domino process is better starting from acetate **1c′** than alcohol **1c**. However, as the synthesis of the former requires an unnecessary additional acylation step, the direct reaction from alcohol **1c** appears synthetically preferable.

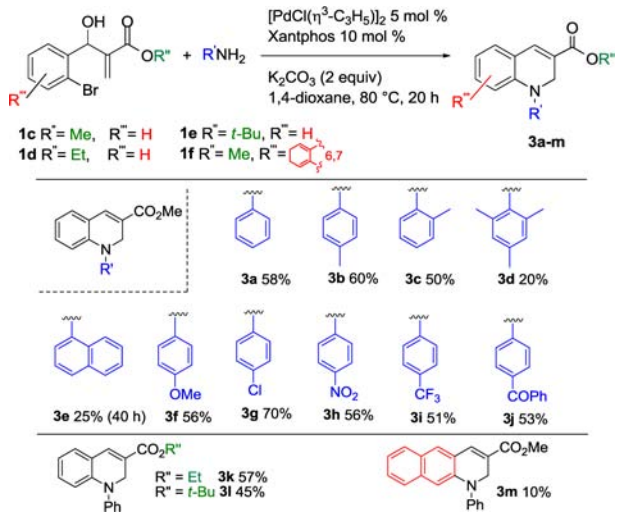
(23) For a review, see: Birkholz, M.-N.; Freixa, Z.; van Leeuwen, P. W. N. M. *Chem Soc Rev.* **2009**, *38*, 1099.

(24) For a review, see: Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 6338.

(25) Conversion of **1b** into **3a** could also be obtained in two separated (non domino) steps via isolation of **2b**.

(26) Dihydroquinolines are quite unstable in both pure form and in solution in $CDCl_3$, and isomerization and/or oxidation to form the corresponding quinolones can occur. For more details, see ref 13a.

Scheme 3. Scope of the Palladium-Catalyzed Arylic/Allylic Amination Domino Sequence from Bromo Alcohol MBH Adducts[a]

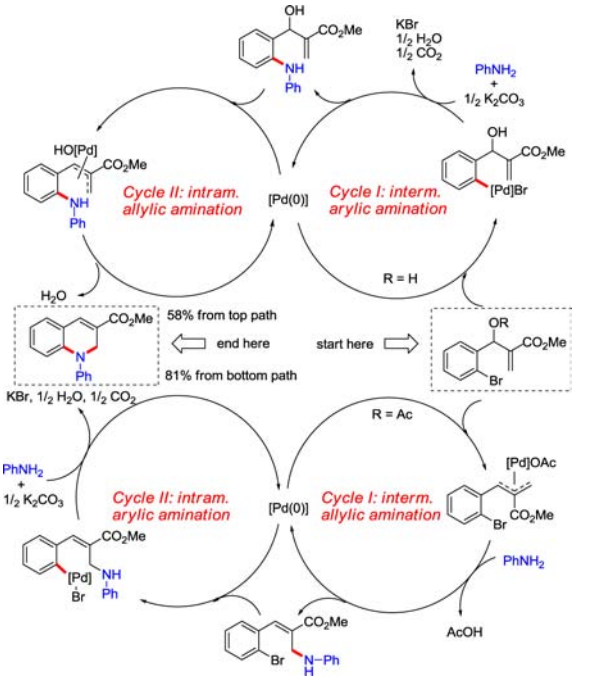


[a] Isolated yields. Reaction conditions: MBH (1 equiv), $ArNH_2$ (1.5 equiv), $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (5 mol %), Xantphos (10 mol %), K_2CO_3 (2 equiv), 1,4-dioxane (0.2 M).

The nature of the ester substituent had a minor effect on the yield (compare **3k** and **3l** vs **3a**).[27] Finally, the 6,7-benzo-1,2-dihydroquinoline (**3m**) could also be obtained, albeit with a low yield.

Coming back to the mechanistic details of this pseudo-domino transformation, the results of our previous experiments allow predicting the sequential chronology of the N−C bond forming reactions as a function of the nature of the leaving groups in the substrates. Indeed, starting from the bromo-substituted allylic acetate, the selected sequence will be allylic amination/arylic amination (Scheme 4, bottom from right to left, see also Table 1 entry 11, and Table 2 entry 5), while with bromo-substituted allylic alcohols the

Scheme 4. Possible Mechanism and Chronologies of the Palladium-Catalyzed Arylic/Allylic Amination Domino Sequence



sequence will reverse to arylic amination/allylic arylation (Scheme 4, top from right to left).[28−30]

In summary, we have developed a new pseudo-domino type I sequence that allows the expeditious synthesis of 1,2-dihydroquinolines from simple MBH alcohol adducts. Two distinct Pd(0) processes are at play in this transformation: a Buchwald−Hartwig coupling and an allylic amination. Interestingly, the chronology of the two N−C bond forming reactions can be selected as a function of the nature of the leaving groups. Extension of this methodology to other heterocycles and biologically relevant targets are currently underway in our laboratory.

Acknowledgment. This paper is dedicated to Prof. André Mortreux (UCCS, Université Lille) on the occasion of his 70th birthday. We thank Manuel Barday (IPCM) for his contribution in preliminary experiments and Omar Khaled (IPCM) for HRMS analyses. CNRS and UPMC are acknowledged for financial support.

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

The authors declare no competing financial interest.

(27) The reaction with the MBH adduct derived from acrylonitrile was unsuccessful, despite complete consumption of the starting material, probably due to the rapid degradation of the desired quinoline in the reaction conditions. The same issue was observed when aliphatic amines (cyclohexylamine, allylamine, and *tert*-butylamine) or tosylamine were employed.

(28) At the moment, no speculation on the step chronology can be advanced for the chloroalcohol MBH adduct **1b** when Xantphos and Xphos are both added the outset of the experiment in the presence of K_2CO_3.

(29) For precedents of generation of η^3-allyl complexes from the acetate esters of MBH adducts and their reaction with amines see: (a) Wang, Y.; Liu, L.; Wang, D.; Chen, Y.-J. *Org. Biomol. Chem.* **2012**, *10*, 6908. (b) Rajesh, S.; Banerji, B.; Iqbal, J. *J. Org. Chem.* **2002**, *67*, 7852. See also: (c) Cao, H.; Vieira, T. O.; Alper, H. *Org. Lett.* **2011**, *13*, 11.

(30) In the latter sequence type, the intramolecular allylic amination has, for geometric reasons, to take place on an *anti* configured η^3-allylpalladium complex.