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Pd/C-Catalyzed Carbonylative C-H Activation with DMF as the CO Source

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ABSTRACT

An interesting Pd/C-catalyzed carbonylative cyclization of *N*-arylpyridin-2-amine derivatives via C-H activation has been developed. With DMF as the CO source, the desired quinazolinones were formed in moderate to good yields with good functional group tolerance.

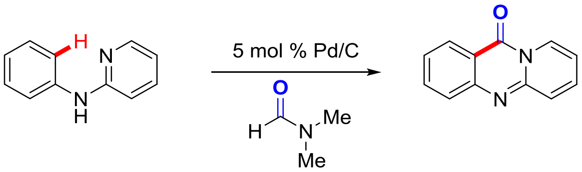
Introduction

Palladium-catalyzed carbonylation reactions are considered as a powerful toolbox in modern organic synthesis. Various carboxylic acid derivatives can be prepared readily by these procedures.[1] However, by going through the literatures on this topic, the combination of aryl halides and carbon monoxide gas are the most frequently explored system. In order to overcome the necessity of pre-activation of starting materials, directly functionalization of the C-H bond provides an ideal alternative pathway.[2] To our delight, many CO gas based carbonylative C-H activation procedures have been established during the last few years.[3] On the other hand, concerning the high toxicity of CO gas, the exploration of alternative CO sources is also interesting.[4] DMF as a cheap and easily accessible solvent has been applied as CO source as well.[5] In 2002, Alterman, Hallberg and their co-workers developed the first palladium-catalyzed aminocarbonylation of aryl bromides with DMF as the CO source.[6] Good yields of the desired amides can be achieved at 180-190 °C in the presence of KOtBu under microwaves. Hiyama and Nozaki described an aminocarbonylation of aryl and alkenyl iodides by using DMF as the amide source with $POCl_3$ (phosphoryl chloride) as the promoter.[7] Later on, Bhanage *et al* studied this transformation with Pd/C as well as $Pd(OAc)_2$/Xantphos as the catalytic systems and provided broader substrates scope.[8] More recently, Ge and co-workers demonstrated that the methyl group from DMF can service as a carbonyl source on nickel-catalyzed carbonylative C-H activation.[9] Based on our continual interests on carbonylation transformations,[10] here we wish to report our new finding on using the carbonyl part of DMF as the CO source for Pd/C-carbonylative C-H activation.

Results and Discussion

We started our optimization with *N*-phenylpyridin-2-amine as the model substrate in the presence of Pd/C and $Cu(acac)_2$ in DMF and AcOH. Different oxidants were tested at the first stage, 11*H*-pyrido[2,1-*b*]quinazolin-11-one as the desired product can be obtained in all the cases (Table 1, entries 1-5). Surprisingly, 75% of the product was formed by using oxygen as the only oxidant (Table 1, entry 6). Then various additives were tested and no better results were achieved (Table 1, entries 8-13). Finally, we found that by using TFA as the co-solvent and with oxygen as the sole oxidant, 80% of the desired quinazolinone was produced at 140 °C (Table 1, entry 20). Further decreasing the temperature resulted lower conversion and yield.

Table 1. Optimizations.[a]



Entry	Cu (mol %)	Oxidant (equiv.)	Additive (equiv.)	Solvent (mL)	Yield (%)
1	$Cu(acac)_2$	$K_2S_2O_8$ (3)	THAB	DMF-HOAc	4%,0[b]
2	$Cu(acac)_2$	$Na_2S_2O_8$ (3)	THAB	DMF-HOAc	6%
3	$Cu(acac)_2$	$Ce(SO_4)_2$ (3)	THAB	DMF-HOAc	3%