

New Pd-catalyzed C-O and C-H activation reactions

Sara L. S. Gomes¹ (PG), Victor Snieckus² (PQ), Alcides J. M. da Silva¹ (PQ)*

¹Laboratório de Catálise Orgânica, Instituto de Pesquisa de Produtos Naturais, Centro de Ciências da Saúde, Bl. H, Cidade Universitária, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, 21941-902, Brasil. ²Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6, Canada.

Email: alcides@nppn.ufrj.br

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Introduction

Transition metal catalyzed reactions constitute an important synthetic tool for the construction of new C-C bonds. The combination of C-O activation with cross-coupling reactions to achieve more complex molecules is a widespread methodology in organic synthesis. In this work we would like to highlight the use of *O*-carbamates for these transformations¹ since they are known to be inert to Pd-catalysis.

Results e Discussion

Herein we report the reaction between 2-*N,N*-diethyl *O*-carbamate of lawsone (**1**) and ethyl acrylate (**2**) under Heck conditions, which, surprisingly, provided the anthraquinone (**4**) as the major product.

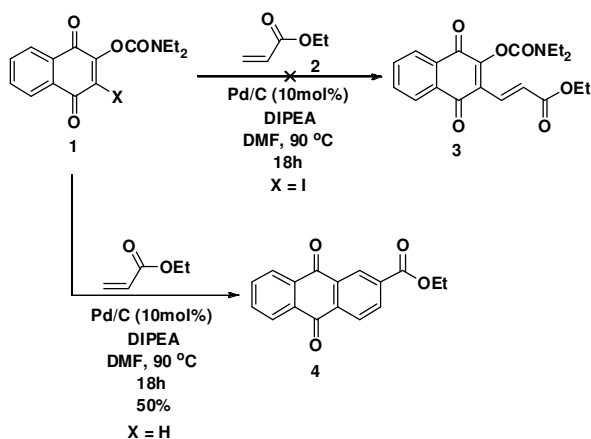


Figura 1. Obtenção de anthraquinone (**4**).

The optimization of the reaction conditions was extensively studied and the best result is described below (50% yield). An experiment without palladium was conducted proving that the presence of the catalyst is essential for the reaction to occur.

Tabela 1. Palladium source optimization.

Entry	[Pd]	Yield
1	Pd(OAc) ₂	35%
2	Pd/C	50%
3	PdCl ₂	19%
4	Pd ₂ (dba) ₃	35%
5	-	-

Different types of olefins were tested and less bulky electron withdrawing alkenes were found to give better results.

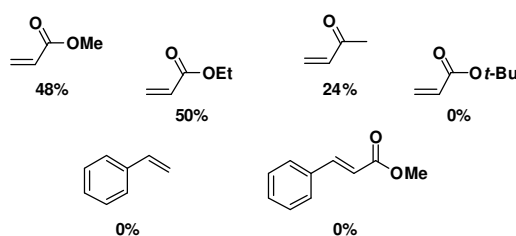


Figura 2. Olefins tested on the study.

Experiments are being done to clarify whether the reaction mechanism passes through a two-fold Heck reaction followed by 6 π -electrocyclization and dehydrogenation² or a C-H activation reaction followed by a Heck-type reaction.³

Conclusions

Despite the low yields, the current reaction represents the first Pd-catalyzed C-O activation involving the *O*-carbamate moiety as a leaving group. Studies about the reaction mechanism are ongoing in our lab.

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