CARBENE INSERTION TO C_{SP²}-H BONDS CATALYZED BY A NON-HEME IRON COMPLEX

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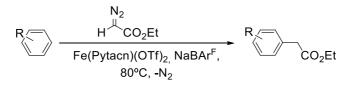
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The functionalization of non-activated C-H bonds is a reaction of high interest since it becomes a starting point for the synthesis of value-added compounds. Among all transformations, metal-catalyzed carbene transfer reaction from diazocompounds to inert C-H bonds is a promising methodology to generate new C-C bonds. [1] Until now, copper and rhodium complexes have been found to be the most efficient metals to perform this transformation. However, the iron-catalyzed carbene transfer reactions have been less explored and they are mainly based on porphyrinic ligands. [2]

Although benzene is an important structure present in most of the pharmaceuticals, its use in carbene insertion reaction using commercially available diazoesters has not been extensively explored due to the existence of a competing reaction, called Buchner reaction, which generates a cycloheptatriene as side product, yielding a mixture of products at the end of the reaction. [3]

Herein, we present the functionalization of different arenes catalyzed by an Fell complex bearing tetradentate aminopyridine-based ligand, through the insertion of ethyl diazoacetate into C-H bonds. The high selectivity towards Csp2-H bonds and the absence of neither cycloheptatriene product nor carbene dimers provides an efficient transformation catalyzed by a non-precious metal complex. In addition, experimental and theoretical studies have been carried out to disclose the mechanism of the reaction. [4]



[1] (a) M. P. Doyle, R. Duffy, M. Ratnikov, *Chem. Rev.* **2010**, 110, 704. (b) M. M. Díaz-Requejo, P. J. *Pérez, Chem. Rev.* **2008**, 108, 3379.

[2] Y. Li, J. Huang, Z. Zhou, C. Che, J. Am. Chem. Soc. 2002, 124, 13185.

[3] (a) E. Büchner, T. Curtius, *Ber. Dtsch. Chem. Ges.* 1885, 18, 2371. (b) M. R. Fructos, T. R. Belderrain, P. de Fremont, N. M. Scott, S. P. Nolan, M.M. Díaz-Raquejo, P. J. Pérez, *Angew. Chem. Int. Ed.* 2005, 44, 5284.
[4] A. Conde, G. Sabenya, M. Rodríguez, V. Postils, J. M. Luis, M. M. Díaz-Requejo, M. Costas, P. J. Pérez, *Angew. Chem. Int. Ed.* 2016, 22, 6530.