Pd(II)-Catalyzed Nondirected C(sp^2)–H Alkoxycarbonylation of Simple Arenes

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Aromatic esters and carboxylic acids are ubiquitous motives throughout organic chemistry, making their efficient synthesis an attractive goal for method development. State of the art Pd-catalyzed reactions enable their synthesis through the reaction of aryl halides with CO and an alcohol[1] or -in a more atom-economical way- through directed C–H-functionalization[2]. However, complementary nondirected methods for C–H functionalization, which can be applied to a large variety of substrates, remained underdeveloped.[3] In this study we describe the use of our dual-ligand enabled Pd-catalysts[4] for the development of a nondirected C(sp^2)–H alkoxycarbonylation method. Using a CO-source and HFIP as the solvent, the respective HFIP-esters or carboxylic acids can be obtained from a large variety of simple arenes and heteroarenes under steric control of regioselectivity.[5]

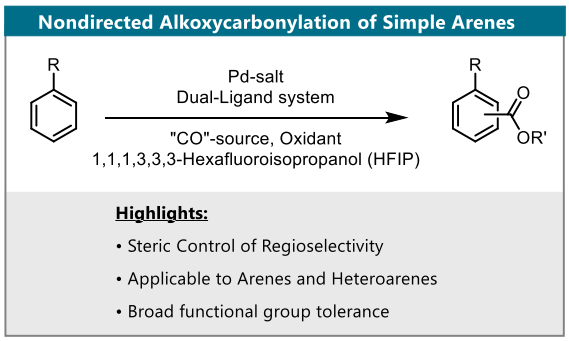

Figure 1. Pd(II)-Catalyzed Nondirected C(sp^2)–H Alkoxycarbonylation of Simple Arenes.

1 A. Brennführer, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.* **2009**, *48*, 4114.
2 See for example: S. Liu, S. Prévost, *Org. Lett.* **2023**, *25*, 1380.
3 For a few specific examples, see: P. Wang, P. Verma, G. Xia, J. Shi, J. X. Qiao, S. Tao, P. T. W. Cheng, M. A. Poss, M. E. Farmer, K.-S. Yeung, J.-Q. Yu, *Nature* **2017**, *551*, 489.
4 S. Kaltenberger, M. van Gemmeren, *Acc. Chem. Res.* **2023**, *56*, 2459.
5 S. Kaltenberger, J. Meinshausen, J. Dey, M. van Gemmeren, *manuscript in preparation*.