Cross-Couplings of Acyl Halides with Potassium Perfluorobenzoates via Decarboxylation and Decarbonylation

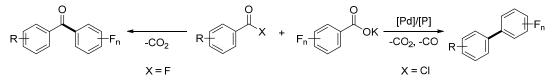
(¹Graduate School of Natural Science and Technology, Okayama University, ²Research Institute of Interdisciplinary Science, Okayama University)

OLiyan Fu,¹ Qiang Chen,¹ Jingwen You,¹ Yasushi Nishihara²

Keywords: Decarboxylation; Decarbonylation; Potassium Perfluorobenzoate; Acyl Fluoride; Acyl Chloride

Over the past few decades, carboxylic acids and their derivatives have attracted great interest in the field of organic synthesis due to their ready availability, abundance, and environmental friendliness. For this reason, benzoic acids and their derivatives have been developed as convenient surrogates for conventional coupling partners by decarbonylative¹ and decarboxylative² couplings via loss of CO or CO₂. These methods avoid the use of either toxic organic halides or expensive organometallic reagents, but the employment of either is still necessary. As a result, the development of synthesized from benzoic acid is of great interest.

Acyl halides are among the simplest carboxylic acid derivatives and can be readily prepared from related carboxylic acids and other carboxylic acid derivatives.³ On the other hand, synthetic approaches to perfluorinated arenes have attracted much attention in the field of material and pharmaceutical sciences due to their attractive properties. Previously, we developed a transition-metal-free decarboxylative cross-coupling reaction of acyl fluorides with potassium perfluorobenzoates.⁴ Along this line, we herein report the palladium-catalyzed decarbonylative and decarboxylative cross-coupling reactions of acyl chlorides with potassium perfluorobenzoates affording unsymmetrical biaryls. This transformation is a unique reaction in which the decarbonylation and decarboxylation proceeded simultaneously under redox-neutral conditions. In comparison to conventional cross-coupling protocols for the synthesis of unsymmetrical ketones and biaryls, in these synthetic strategies, all reactants can be readily prepared from abundant and inexpensive aromatic carboxylic acids. These methods also allowed for two efficient and highly selective approaches for the installation of perfluorobenzol groups.



1) H. Lu, T.-Y. Yu, P.-F. Xu, H. Wei, *Chem. Rev.* **2020**, doi: 10.1021/acs.chemrev.0c00153. 2) J. Cornella, I. Larrosa, *Synthesis* **2012**, *44*, 653. 3) Y. Ogiwara, N. Sakai, *Angew. Chem., Int. Ed.* **2020**, *59*, 574. 4) L. Fu, Q. Chen, Y. Nishihara, *Org. Lett.* **2020**, *22*, 6388.