Synthesis of 2-Aryloxy Butenoates by Copper-Catalysed Allylic C−H Carboxylation of Allyl Aryl Ethers with Carbon Dioxide

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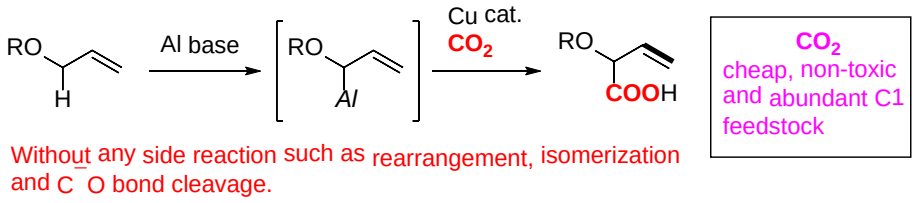
α-Aryloxy carboxylic acids are an important structural unit in the area of medicinal and bioorganic chemistry. 2-Aryloxy-3-butenoic acids and their derivatives bearing a skeleton of the α-aryloxy carboxylic acid and an additional olefin moiety are considered to be potentially useful compounds as the building block for the synthesis of α-aryloxy carboxylic acid derivatives. The straightforward way to obtain such 3-butenoic acids is sequential deprotonation by base and carboxylation using carbon dioxide (CO_2). However, such method has still been challenging; for instance, deprotonation of allylic C−H on allyl phenyl ethers using strong base such as BuLi and amide-Li causes some undesirable side reactions.[1]

Recently, we reported a formal C−H bond carboxylation of aromatic compounds, which consists of deprotonative alumination of aromatic C−H bond by using weak base *i*Bu_3Al(TMP)Li and the subsequent nucleophillic carboxylation of the generated arylaluminum species catalyzed by (IPr)CuCl and KO*t*Bu.[2] Herein, we would like to report an efficient synthesis of α-aryloxy-3-butenoic acids by the combination of deprotonative alumination of allyl aryl ethers with the subsequent copper catalyzed carboxylation with CO_2



[1] C. Su, P. G. Williard, *Org. Lett.* **2010**, *12*, 5378.
[2] A. Ueno, M. Takimoto, W. N. O. Wylie, M. Nishiura, T. Ikariya, Z. Hou, *Chem. Asian J.* **2015**, *10*, 1010.