Visible-light-driven arylcarboxylation of styrenes with carbon dioxide and aryl halides

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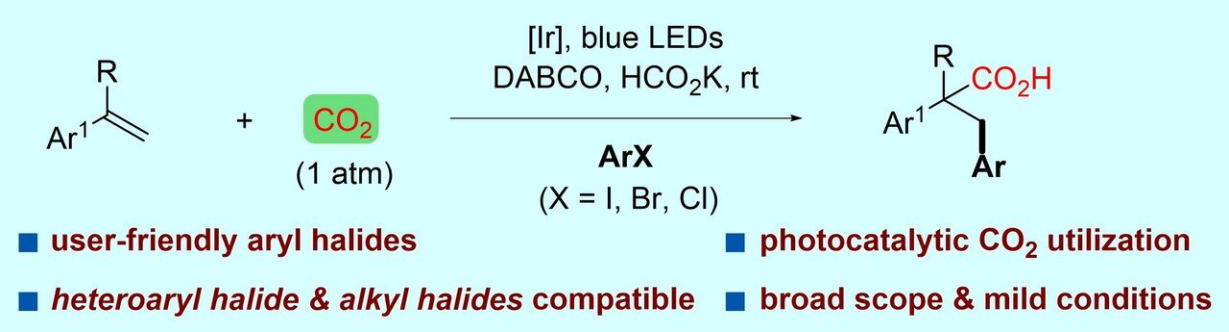

Figure: Visible-light-driven arylcarboxylation of styrenes with CO2 and aryl halides. Credit: Prof. LI's group

The use of carbon dioxide (CO_2), which is an ideal one-carbon (C1) building block and is sustainable, abundant, low-cost and nontoxic, has attracted great attention in fine chemical synthesis. However, traditional CO_2 fixation usually suffers from high temperature, high pressure of CO_2 and the use of strong base.

Visible-light-driven photoredox catalysis (PRC) for CO_2 use is an environmentally friendly process in organic synthesis of complex molecules.

In a study published in the *Journal of the American Chemical Society*, a group led by Prof. LI Gang at Fujian Institute of Research on the

Structure of Matter of the Chinese Academy of Sciences reported an interesting protocol of visible-light-driven reductive arylcarboxylation of styrene derivatives with CO_2 (1 atm) and aryl halides.

This is the first example of the visible-light-driven Meerwein-arylation-type difunctionalization of alkenes using aryl halides, which are often bench-stable, inexpensive and widely available.

The researchers found that a wide range of aryl iodides and bromides were viable with this reaction to produce arylcarboxylation products of various styrene derivatives. Besides, pyridyl halides, alkyl halides and electron-deficient aryl chlorides that are challenging to reduce were also compatible with this reaction.

In the preliminary mechanistic study, the control experiments without using aryl halides could afforded a decarboxylation product, suggesting that a highly reductive CO_2 radical anion might be involved in this reaction to reduce aryl halides to generate aryl radicals. When a "radical clock" substrate was used, ring-opening product was produced, indicating a benzyl radical might be involved. Besides, the reaction could be scalable without significant decrease in the yield of desired products.

This study may provide a new opportunity for exploring novel visible-light-driven Meerwein-type arylation-addition reactions employing user-friendly aryl halides as the radical sources, as well as developing new photocatalytic use reactions of CO_2.

More information: Hao Wang et al. Visible-Light-Driven Reductive Carboarylation of Styrenes with CO2 and Aryl Halides, *Journal of the American Chemical Society* (2020). DOI: 10.1021/jacs.0c03144