

## Review

Transition metal-catalyzed carboxylation of unsaturated substrates with CO<sub>2</sub>

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## ABSTRACT

The utilization of CO<sub>2</sub> as a C1 building block for the synthesis of valuable chemicals is of great importance. The transition metal-catalyzed carboxylation of unsaturated substrates with CO<sub>2</sub> has proved to be an effective and versatile strategy for the incorporation of CO<sub>2</sub> in organic substrates with unsaturated bonds. Different kinds of carboxylation reactions with CO<sub>2</sub> have provided a direct access to a myriad of functionalized carboxylic acids and derivatives. This review focuses on carboxylation of unsaturated substrates with CO<sub>2</sub> via transition metal catalysis. Various kinds of carboxylations with different catalytic systems are discussed.

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## 1. Introduction

As an ideal C1 source, carbon dioxide (CO<sub>2</sub>) has attracted significant attention in organic synthesis due to its high abundance, low cost, nontoxicity and renewability [1]. The research on transformation of CO<sub>2</sub> into highly value-added chemicals has become one of the most active and promising field in green chemistry. In recent years, numerous chemical transformations involving CO<sub>2</sub> have been well developed [2]. Among these transformations, synthesis of carboxylic acids with CO<sub>2</sub> through C–C bond formation is highly attractive [3], because carboxylic acids widely exist in myriad natural products, agrochemicals and pharmaceuticals (Fig. 1) [4]. Furthermore, carboxylic acids can serve as useful building blocks in chemical industry to manufacture cosmetics, detergents, rubbers, dyes, plastics and so on [5]. On account of the significance of carboxylic acids and the advantages of CO<sub>2</sub> in the construction of carboxylic acid compounds, great effort has been devoted to synthesis of this motif following various strategies [3]. Notably, the transition metal-catalyzed carboxylation of unsaturated substrates with CO<sub>2</sub> has been well documented in the last decades and it provides a direct access to various functionalized carboxylic acids and derivatives [6]. Generally, the formation of a carboxylic acid is facilitated by the insertion of CO<sub>2</sub> into a carbon–metal bond which is generated through insertion of the unsaturated bond into a metal–Nu species [6b]. Moreover, the carboxylation process can also be achieved via oxidative cyclometallation of CO<sub>2</sub> and unsaturated substrates with a low-valent transition metal [6b]. Until now, the catalytic carboxylation reactions with CO<sub>2</sub> have been accomplished by several kinds of transition metals, such as Ni, Cu, Pd, Au, Rh, and so on [6d]. For catalytic carboxylation of unsaturated substrates, Ni and Cu are most widely investigated. This review focuses on the transition metal-catalyzed

carboxylation of unsaturated substrates with CO<sub>2</sub> through various strategies. Specifically, we will introduce the significant progresses in this field according to the different types of carboxylation reactions.

## 2. Hydrocarboxylation of unsaturated substrates with CO<sub>2</sub>

### 2.1. Hydrocarboxylation of alkenes

In 1978, Lapidus and co-workers reported the first catalytic procedure by using Rh and Pd complexes for accessing propionic acid from ethylene and CO<sub>2</sub> [7]. After that, Höberg found that five-membered nickelalactone could be generated by treating olefins and CO<sub>2</sub> with electron-rich Ni(0) complexes [8–10] (Scheme 1). Besides, studies showed that Ti [11], Zr [12] and Fe [13] could also react with ethylene and CO<sub>2</sub> to form metalalactones. While the metallalactone intermediates have been demonstrated very early, a catalytic procedure remains a challenge for a long time. Much effort has been devoted to the stoichiometric transformation of the intermediates of nickelalactone, such as homologation with styrenes, 1,3-diene, or allenes, among others to access high-ordered carboxylic acid [14] and β-hydride elimination to prepare acrylic acids (Scheme 1) [15]. However, it was not until 2012 that Limbach and co-workers reported first catalytic synthesis of acrylic acids by carboxylation of ethylene using bis-dentate phosphine ligands and sodium *tert*-butoxide [16]. The following investigation by the same group found that metal phenoxides efficiently promoted the formation of the acrylate Ni(0) complex in the presence of CO<sub>2</sub>, achieving the targeted product from ethylene and CO<sub>2</sub> [17]. Although some advances have been realized in this field, more research should be conducted for a more efficiently catalytic

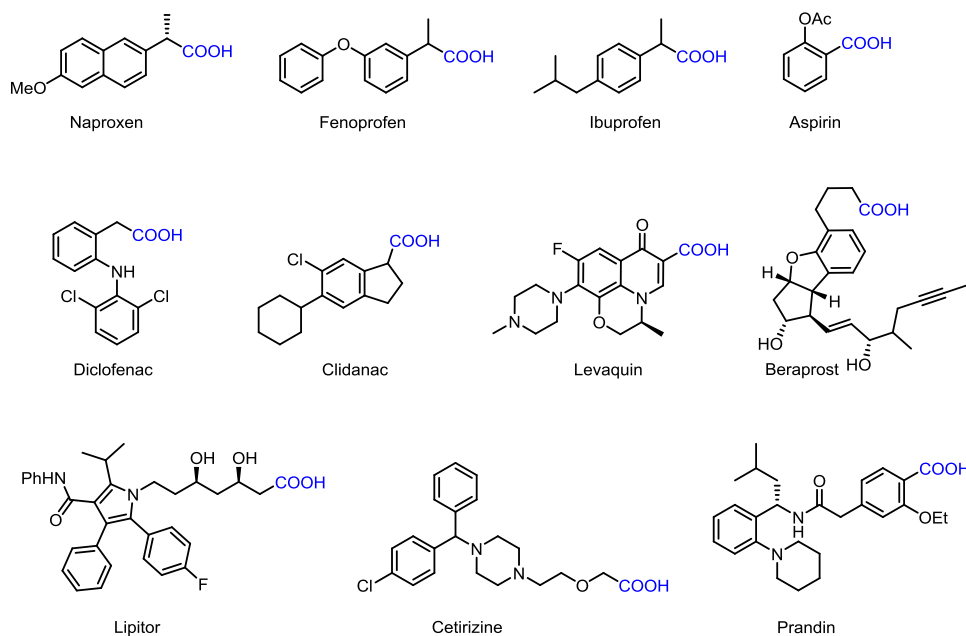


Fig. 1. Carboxylic acids in pharmaceuticals.

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