

# Preface

Homogenous catalyst plays an important role in modern organic synthesis, especially now that more focus is being placed the development of sustainable chemistry. With the assistance of catalysis, many organic reactions can be carried out under much milder conditions and in a more selective manner. One branch of homogenous catalysts is carbonylation, which has significant industrial importance and is of academic interest. Several distinguishable advantages of carbonylation reactions are: (1) the carbon chain can be easily increased after the insertion of carbon monoxide; (2) carbonyl-containing compounds are important synthetic intermediates in organic synthesis, which hold imperative applications in advanced materials, dyes, pharmaceuticals, and so on; and (3) carbon monoxide as one of the most important C1 sources can be applied and incorporated into the parent molecules which give more complex compounds. As a result of these advantages, the field of carbonylation research has received much attention during the past decades and this attention is still increasing. When I joined Matthias Beller's group in 2009 and began to work on "Carbonylative Transformation of C–X Bonds," it was difficult for me to find a general textbook on this topic. As a new student with limited knowledge in coupling chemistry, it was even more difficult. Gradually I began to collect the literature on this topic, which was quite a time-consuming process. Even after I had finished my Ph.D. studies in 2012, we still could not find a general textbook available. In this context, and with Matthias's encouragement and support, we began to prepare a book on this topic by ourselves in order to fill the gap and provide a general overview for new researchers who wish to work in this area.

This book is divided into 12 chapters and organized according to the various nucleophiles. In [Chap. 1](#), we give a general introduction and compare and describe the advantages and differences between homogenous and heterogeneous catalysts. We then include a definition of carbonylation and describe mechanisms for different transition metals on carbonylation reactions together with their differences in activities. The following chapters are based on the different properties of nucleophiles applied, chapters are given. Water, alcohols, and amines as nucleophiles are described in [Chap. 2](#), as they go through the same reaction mechanism. [Chapter 3](#) focusses on reductive carbonylation, which give aldehydes as their product. All the reactions that include organometallic reagents as nucleophiles,

where ketones are the main product, are discussed in [Chap. 4](#). In [Chap. 5](#), we discuss the combination of carbon monoxide, alkynes, and organo-halides to give alkynones as the terminal product, which is the so-called carbonylative Sonogashira reaction. In [Chap. 6](#), we focus on carbonylative C–H activation reactions. Carbonylative Heck reactions partly go through the Heck mechanism and give alkenones as the product; these results are mentioned in [Chap. 7](#). The carbonylative coupling of two different nucleophiles that need additional oxidants is called oxidative carbonylation and we summarize this in [Chap. 8](#). Furthermore, nitro as an interesting functional group can be reduced by CO to ureas, isocyanates, and related compounds. As an important sub-branch in carbonylation reactions, we discuss the reduction of C–NO<sub>2</sub> with CO in [Chap. 9](#). The applications of carbonylation reactions in total synthesis are presented in [Chap. 10](#). The *Taiji* among carbonylation, noncarbonylation, and decarbonylation is the difficulty in developing carbonylation reactions. A successful carbonylation reaction needs to suppress the noncarbonylation pathway and avoid the decarbonylation reaction. We discuss this topic in [Chap. 11](#) within the context of our own understanding. The book ends with our personal outlook on the field in [Chap. 12](#).

We truly hope that this book can help researchers who are new to the field understand and gain an overview of carbonylation. We also hope that it will be a useful general reference book for more senior scientists.

Xiao-Feng Wu

Transition Metal Catalyzed Carbonylation Reactions

Carbonylative Activation of C-X Bonds

Beller, M.; Wu, X.-F.

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