Armando Córdova

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Catalytic Asymmetric Conjugate Reactions

Edited by Armando Córdova

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Preface

The stereoselective conjugate reaction is one of the most important transformations in organic synthesis to achieve asymmetric carbon–carbon and heteroatom-carbon bond-forming reactions. There is today no such book that is focused on this topic. In particular, there is need for a book that covers catalytic asymmetric methods. The last book on the general topic of conjugate reactions in organic synthesis was published in 1992 and the discussion of stereoselective reactions is a small part. This book covers catalytic asymmetric methods based on conjugate additions, which are catalyzed by organometallic complexes or small organic molecules. Significant efforts have been made in asymmetric catalysis during this decade and pioneers of this field were awarded the Nobel prize in 2001. Thus, a book that focuses on modern methods on catalytic stereoselective conjugate addition reactions is highly desirable for the chemistry community.

I would like to thank all the distinguished scientists and their coauthors for their rewarding and timely contributions. I gratefully acknowledge the Wiley-VCH editorial staff, in particular to Dr. Elke Maase for proposing to me this excellent topic and to Dr. Waltraud Wuest who was of precious help for the development of this project.

Stockholm, April 2010 *Armando Córdova*

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Rhodium- and Palladium-Catalyzed Asymmetric Conjugate Additions

Guillaume Berthon and Tamio Hayashi

1.1
Introduction

Since the seminal report by Uemura [1] in 1995 for palladium, and by Miyaura in 1997 for rhodium [2], the late transition metal-catalyzed conjugate addition of organoboron reagents to activated alkenes has emerged as one of the most functional group-tolerant and reliable carbon–carbon bond-forming processes. The maturity of this methodology is such that it has become an ideal testing ground for new ligand concepts and design, as will be illustrated throughout this chapter. A true statement to the robustness of this process is the application of Rh-catalyzed enantioselective conjugate addition (ECA) on a kilogram-scale for the manufacture of advanced pharmaceutical ingredients, and its use as a key step in the synthesis of complex natural products [3–5].

In this chapter, an overview will be provided – spanning from 2003 to mid-2009 – of the developments in the field of rhodium- and palladium-catalyzed ECA of organometallic reagents (B, Si, Zn, and Ti) to activated alkenes. The chapter is not intended to be comprehensive, and will include only selected examples of this powerful methodology. For more in-depth and comprehensive accounts, the reader should consult a number of excellent reviews that are available on this subject [6–16].

1.2
Rh-Catalyzed ECA of Organoboron Reagents

This section will include details of the state of the art for the rhodium-catalyzed ECA of organoboron reagents to activated olefins. Special emphasis will be placed on α,β-unsaturated ketones, as this substrate class has attracted the most attention and undergone thorough investigation with a plethora of different ligand systems. Many of the findings described for α,β-unsaturated ketones are also applicable to other olefin classes and other nucleophilic organometallic reagents, unless otherwise specified.

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