

## CHAPTER 1

**ELECTROPHILIC AMINATION OF CARBANIONS, ENOLATES,  
AND THEIR SURROGATES**

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## CHAPTER 1

## ALLYLBORATION OF CARBONYL COMPOUNDS

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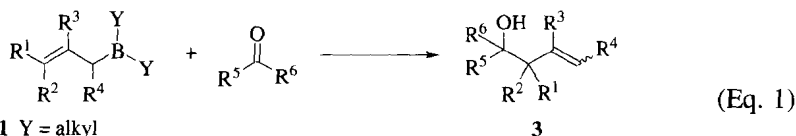
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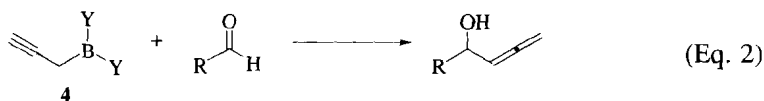
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### INTRODUCTION

Allylic boron compounds have gained a prominent position as a useful class of synthetic reagents in the past 25 years. Their general structures, **1** and **2**, and their utility in carbonyl additions are shown in Eq. 1. The main use of these reagents is in the stereoselective synthesis of homoallylic alcohols **3** by an allyl-transfer reaction to carbonyl compounds. In this process, a new carbon-carbon bond is formed, and up to two new stereogenic centers are created. Moreover, the residual allylic unit can be manipulated through a number of different transformations such as oxidative cleavage, olefin metathesis, and many others. Although less prevalent, the propargyl and allenyl reagents typified by **4** and **5** have also been described (Eqs. 2 and 3). Most examples of allylic boron reagents used in carbonyl additions belong to one of two main classes, boranes (structure **1**, Y = alkyl) and boronate derivatives (structure **2**, Y = OR or NR<sub>2</sub> for bis(sulfonamide) derivatives). This chapter focuses on describing and comparing both classes, and when needed, they will be discussed separately. A chart of ligand structures with the acronyms used in this text can be found preceding the Tables.



- 1** Y = alkyl  
**2** Y = O-alkyl(aryl)  
 or N-alkyl(aryl)



## CHAPTER 1

**CATALYTIC ASYMMETRIC HYDROGENATION OF C=N  
FUNCTIONS**

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## INTRODUCTION

Chiral amines are important targets for synthetic chemists and attempts to prepare such compounds via enantioselective hydrogenation of an appropriate C=N function date back to 1941.<sup>1</sup> Originally, only heterogeneous hydrogenation catalysts such as Pt black, Pd/C, or Raney nickel were employed. These classical hydrogenation catalysts were modified with chiral additives in the hope that some asymmetric induction in the delivery of dihydrogen to the reactant might occur. Only very few substrates were studied and not surprisingly, enantioselectivities were low and results could not always be reproduced.<sup>2</sup> The first reports on the use of homogeneous ruthenium<sup>3</sup> and rhodium<sup>4,5</sup> diphosphine complexes appeared in 1975, but useful enantioselectivities were not reported until 1984.<sup>6</sup> Remarkable progress has been made since the 1990's and a variety of very selective catalysts are now available for the enantioselective reduction of different types of C=N functions.<sup>7-15</sup> Moreover, the first industrial application was announced in 1996.<sup>16</sup> Despite this progress, the enantioselective hydrogenation of prochiral C=N groups such as imines, oximes, or hydrazones to the corresponding chiral amines still represents a major challenge.