UNIVERSITAT ROVIRA I VIRGILI
SCREENING OF MODULAR CARBOHYDRATE LIGAND LIBRARIES
IN ASYMMETRIC METAL-CATALYZED C-C AND C-X BOND FORMATION REACTIONS
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Structure of the thesis

This thesis is based on ten papers published in international journals. These papers have been reedited to provide a uniform format throughout the thesis.

The thesis is divided into eight chapters.

- Chapter 1. *Introduction*. This chapter first presents the importance of metal asymmetric catalysis in the synthesis of enantiomerically pure compounds. An important step in this synthesis is the design and synthesis of chiral ligands. Among them, new chiral ligands derived from carbohydrate are presented. These ligands are applied to four asymmetric catalytic reactions, which are reviewed in detail in this chapter. For each reaction, the antecedents, performance and main achievements are discussed, with emphasis on the application of carbohydrate ligands. The state-of-the-art and current needs in this field justify the objectives of the thesis.

- Chapter 2. *Objectives*. Based on the aspects discussed in chapter 1, this chapter presents the objectives of the thesis. These involve the synthesis and application of new sugar ligands in asymmetric catalysis.

- Chapter 3. *Pd-catalyzed asymmetric allylic substitution*. This chapter contains three sections on the development and application of new phosphite-oxazoline, phosphite-phosphoroamidite and monophosphite ligand libraries in the asymmetric Pd-catalyzed allylic substitution reactions. The first section, *A carbohydrate-based phosphite-oxazoline ligand library for Pd-catalyzed allylic substitution reactions,* describes the synthesis and application of a phosphite-oxazoline ligand library in the asymmetric Pd-catalyzed allylic substitution of several substrates with different electronic and steric properties. This paper also discusses the synthesis and characterization of the Pd-π-allyl intermediates to provide greater insight into the origin of the enantioselectivity. The second section, *Pd-catalyzed asymmetric allylic substitution using pyranoside phosphite-*

phosphoroamidite ligands, includes the development and application of new a phosphite-phosphoroamidite ligand library in asymmetric allylic substitution. The third section, *Pd-catalyzed asymmetric allylic substitution using a sugar-based monophosphite ligand library*, presents the synthesis and application of a monophosphite sugar-based ligand library in the Pd-catalyzed allylic alkylation reactions.

- Chapter 4. *Pd-catalyzed asymmetric Heck reactions.* This chapter contains one section, *Screening of a modular sugar-based phosphite-oxazoline ligand library in asymmetric Pd-catalyzed Heck reactions*, which discusses the application for the first time of phosphite-oxazoline ligands (developed in Chapter 3) in the asymmetric Pd-catalyzed Heck reactions. The effects of various triflates sources and substrates types are also studied.

- Chapter 5. *Ni-catalyzed asymmetric addition of trialkylaluminium to aldehydes.* This chapter contains two sections on the application of the phosphite-oxazoline, phosphite-phosphoroamidite and monophosphite ligand libraries (developed in Chapter 3) in the asymmetric Ni-catalyzed 1,2-addition reactions. The first one, *Phosphite-oxazoline and phosphite-phosphoroamidite ligand libraries in the asymmetric Ni-catalyzed trialkylaluminium addition to aldehydes,* reports the investigations of the Ni-catalyzed trialkylaluminium 1,2-addition to aldehydes using the phosphite-oxazoline and phosphite-phosphoroamidite ligand libraries. The second section, *Screening of a modular sugar-based phosphite ligand library in the asymmetric Ni-catalyzed trialkylaluminium addition to aldehydes,* includes the application of the sugar-based monophosphite ligand library in the Ni-catalyzed trialkylaluminium 1,2-addition to several aldehydes types.

- Chapter 6. *Cu-catalyzed asymmetric 1,4-conjugated addition of trialkylaluminium reagents to enones.* This chapter contains two sections on the application of the phosphite-oxazoline, phosphite-phosphoroamidite and monophosphite ligand libraries (developed in Chapter 3) in the asymmetric Cu-catalyzed 1,4-addition reactions. The first one, *Sugar phosphite-oxazoline and*

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phosphtie-phosphoroamidite ligand libraries for Cu-catalyzed asymmetric 1,4-addition reactions, reports the investigations of the Cu-catalyzed 1,4-addition of organometallic reagents to enones using the phosphite-oxazoline and phosphite-phosphoroamidite ligand libraries. The second section, *Screening of a modular sugar-based phosphite ligand library in the Cu-catalyzed asymmetric 1,4-addition reactions*, includes the application of the sugar-based monophosphite ligand library in the Cu-catalyzed trialkylaluminium 1,4-addition to cyclic and linear enones.

- Chapter 7. *Conclusions*. This chapter presents the conclusions of the work presented in this thesis.

- The *Appendix* contains the list of papers and meeting presentations given by the author during the period of development of this thesis.