Contents

Chapter 1: introduction 1

1.1 Introduction 2

1.2 Preconditions for axial chirality and mechanism of atropisomerization
The phenomenon of axial chirality 5

1.3 Atropisomerization by physical rotation 7

1.3.1 Effects of nonbonding substituents 7

1.3.2 Bridged biaryl systems 9

1.4 Diphosphine ligand 10

1.4.1 BINAP in asymmetric catalysis 10

Chapter 2: 2-(2-Hydroxyaryl)cinnamic amides: a new class of axially chiral molecules 20

2.1 Non-biaryl classes of atropisomeric molecules 21

2.2 2-(2-Hydroxyaryl)cinnamic amides: a new class of axially chiral molecules 25

2.3 Results and discussion 25

2.4 Barriers to rotation 31

2.5 Conclusions 37

2.6 Experimental section 38

Chapter 3: Monodentate Phosphorus Ligands 52

3.1 Homogeneous catalysis using transition metal complexes 53

3.2 Monodentate phosphines 56

3.3 Monodentate phosphonites 58

3.4 Monodentate phosphites 59

3.5 Monodentate phosphoramidites 61

3.6 The monodentate ligand combination approach 63

3.7 *Tropos* monodentate phosphites and phosphoramidites 65

3.8 Experimental section 74

Chapter 4: Catalytic, Enantioselective Preparation of Diarylmethanols 95

4.1 Introduction 96

4.2 Biologically active diarylmethanols derivates 97

4.3 Catalytic enantioselective preparation of diarylmethanols Nucleophilic addition of organometallic compounds to aldehydes 98

4.3.1 Phenyl transfer reactions to aromatic aldehydes using diphenylzinc as aryl source 98

4.3.2 Other aryl sources in the aryl transfer reactions to aldehydes 106

4.3.3 Rh-, Ti-, and Cu-catalysed enantioselective aryl transfer reactions 114

4.4 Rhodium-catalysed addition of arylboronic acids to aldehydes 117

4.5 Experimental section 126

Chapter 5: Asymmetric Aryl Transfer to Imines: Synthesis of Diarylmethylamines 129

5.1 Introduction 130

5.2 Enantioselective rhodium-catalysed addition of arylboronic acids to *N*-tosylarylimines 138

5.3 Experimental section 145

Summary 153