

## ABSTRACT

The Synthesis and Testing of Chiral Hydroxy- and Mercapto[2.2]paracyclophane Ligands as Potential Catalysts in the Addition of Diethylzinc to Benzaldehyde.

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This dissertation seeks to determine whether the enantiopure ligands: *R*- and *S*-enantiomers of the 4,5- or the 4,13- disubstituted[2.2]paracyclophane containing either a thiol or a hydroxydiphenylmethyl moiety, can act as efficient catalysts and enantioselectively catalyse the addition reaction of diethylzinc to benzaldehyde. Our tested ligands like 5-diethylcarboxamido-4-mercapto[2.2]paracyclophane (**98**), 5-piperidinylcarboxamido-4-mercapto[2.2]paracyclophane (**139**), 13-diethylcarboxamido-4-mercapto[2.2]paracyclophane (**99**), 13-piperidinylcarboxamido-4-mercapto[2.2]paracyclophane (**140**) and 13-hydroxydiphenylmethyl-4-*N,N*-diethylcarboxamido[2.2]paracyclophane (**100**) were synthesized starting from either a 4-bromo[2.2]paracyclophane moiety or an enantiopure form of 4-carboxy[2.2]paracyclophane (**16**). The appropriate parent

compound undergoes lithiation and subsequent trapping with either diisopropyl disulfide or dibenzyl disulfide followed by reduction to give the corresponding thiol while trapping with benzaldehyde gave us our hydroxydiphenylmethyl compounds. The potential of the tested ligands: *R*- and *S*- enantiomers of the 4,5- or the 4,13- disubstituted[2.2]paracyclophane containing either a thiol or a hydroxydiphenylmethyl moiety, to enantioselectively catalysed the addition reaction of diethylzinc to benzaldehyde on the basis of the results will also be discussed.

**CHAPTERS ONE AND TWO** provide, respectively, some brief background on chirality and asymmetric synthesis while **CHAPTERS THREE** discusses chirality and asymmetric synthesis in [2.2]paracyclophane systems along with the rationale for the study. **CHAPTERS FOUR AND FIVE** discuss the various experiments carried out to synthesize our ligands and to test their ability to catalyse the addition reaction of diethylzinc to benzaldehyde and induce chirality in the product. **CHAPTER SIX** gives the experimental procedures.

**Keywords:** asymmetric, chiral, chirality, catalyst, disulphides, enantiopure, ligands, lithiation, reduction, sulfur, [2.2]paracyclophane, transannular.