ABSTRACT

Synthesis of novel [2.2]paracyclophane derivatives
as potential chiral substrates and chiral ligands

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This dissertation presents the work of two areas of research. The first area of study describes efficient syntheses of a unique amino acid, 4-amino-13-carboxy [2.2]paracyclophane **39** and its amino ester derivative **82**. Novel oxazolinyl [2.2]paracyclophane derivatives are used as intermediates and the oxazolinyl group is shown to be an excellent pseudo-*geminal* directing group for the electrophilic aromatic bromination reaction.

The unique transannular interaction in the [2.2]paracyclophane system was evidenced in the formation of the first [6.2.2]cyclophane **103**, described in this work.

The second body of work describes the synthesis of unique PHANEPHOS derivatives, which can be used as either chiral ligands or chiral catalysts. A new *ortho*-lithiation reaction of 4-*N,N*-diethylcarboxamido[2.2]paracyclophane **154** leading to the preparation of 4,5-disubstituted[2.2]paracyclophane derivatives is outlined. Pseudo-*geminal* bromination of 4-*N,N*-diethylcarboxamido [2.2]paracyclophane giving access to a variety of 4,13-disubstituted compounds is

also discussed. The *ortho*-lithiation and pseudo-*geminal* substitution reactions are used sequentially to give 4,5,13-trisubstituted compounds in which two ligand groups have the same geometrical relationship as in PHANEPHOS.

It is shown that *N,N*-diethylcarboxamido derivatives can be reduced to *N,N*-diethylaminomethyl and hydroxymethyl compounds thus increasing the variety of potential ligands available.

Finally, a preliminary study to explore the potential of a number of chiral oxazolinyl and *N,N*-diethylcarboxamido derivatives to catalyze the addition of diethylzinc to benzaldeyde is described.

Keywords: Alicia Reid, amino acid, chiral, catalyst, ligands, oxazolinyl, *N,N*-diethylcarboxamido, [2.2]paracyclophane, PHANEPHOS, pseudo-*geminal*, *ortho*-lithiation, transannular.