ABSTRACT

Synthesis and investigation of homochiral [2.2]paracyclophane derived
ligands as potential catalysts for the enantioselective addition
of diethylzinc to benzaldehyde.

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This dissertation describes the synthesis of selected planar homochiral ligands derived from *N,N*-diethylcarboxamido[2.2]paracyclophane **49 (**shown overleaf) and studies done to determine their ability to catalyze the addition of diethylzinc to benzaldehyde. This reaction is a model for enantioselective addition to aldehydes.

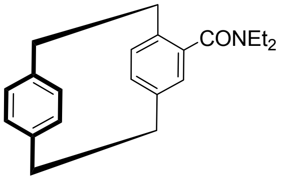
Initial synthetic work focused on the replacement of the *N,N*-diethylcarboxamido moiety with a different amide group which, while retaining its C-13 and C-5 directing properties, would be more susceptible to hydrolysis or reduction. This approach was not successful.

Subsequent to this, disubstituted [2.2]PC derivatives possessing the *N*,*N*-diethylcarboxamido group (**45, 46, 47, 48, 83** and **84**) were synthesized and efforts were made to optimize their reduction to the corresponding tertiary amine and / or alcohol functionalities using traditional reducing agents $LiAlH_4$, BH_3 and $LiBH_4/BF_3.OEt_2$, under suitably modified conditions.

Preliminary screenings of the reduced compounds as well as their parent amides in racemic form were done to determine their potential as catalysts for the addition of diethylzinc to benzaldehyde.

It was discovered that the compounds possessing hydroxyl groups in addition to the amine moiety (**94** and **97**) along with one compound possessing the hydroxyl and amide functionalities (**47**) were successful catalysts, even in racemic form. The position of the hydroxyl and amide groups relative to each other on the [2.2]PC framework was shown to have a great effect on the catalytic efficacy of the ligand.

The successful ligands **47** and **94** were synthesized in homochiral form and tested for their ability to enantioselectively direct the course of the addition reaction. Under the reaction conditions, excellent yields of the product, 1-phenylpropanol were achieved but the catalysts showed poor enantioselectivity.



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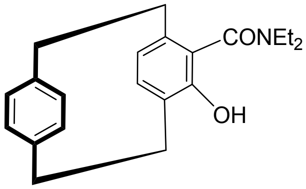

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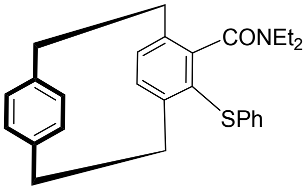

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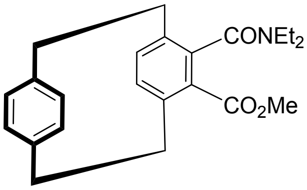

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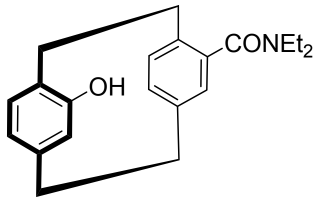

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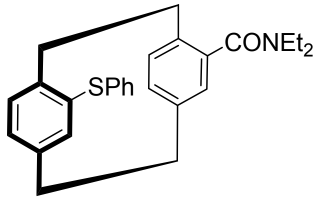

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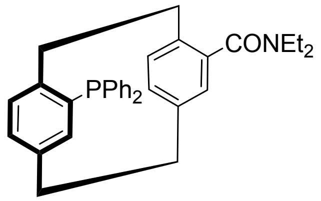

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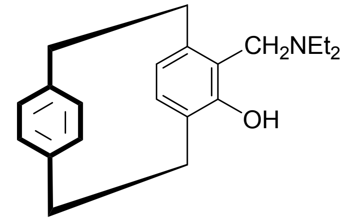

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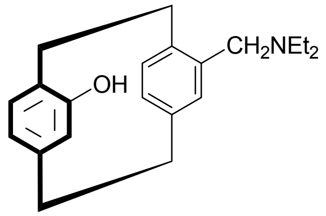

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Keywords: [2.2]paracyclophane, catalyst, planar chiral, ligands, reduction, amine, phenol, diethylzinc, benzaldehyde.