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**A study of new planar chiral monophosphine
ligands based on [2.2]paracyclophane and their
use in catalysis**

Jingjing Wang

**Chemistry – Institute of Fundamental Sciences,
Massey University**

**Masters Thesis under the supervision of Dr. Gareth
J. Rowlands**

2011

Abstract

The Suzuki-Miyaura coupling reaction is one of the most powerful methods for the construction of biaryls. The biaryl motif has great importance in pharmaceutical, agrichemical and material science industries, and is often axially chiral. The outcome of a Suzuki-Miyaura coupling reaction can be influenced by many factors, but the ligand plays the most vital role. A large number of ligands have been developed, including many chiral ligands for asymmetric reactions. While ligand design has focused on molecules containing either central or axial chirality, little has been focused on planar chiral ligands.

In this project, three new ligands based on the [2.2]paracyclophane backbone have been designed, *pseudo-ortho* substituted monophosphines (**L1** and **L2**), secondary phosphine oxide and arylindolyl phosphine ligands (**L3** and **L4**). Unfortunately, similar analogues of **L1** and **L2** were reported before our results, and a synthesis route to the secondary phosphine oxide ligands was not achieved. The use of **L1** in gold mediated cyclisation was investigated, which concluded that **L1** was not suitable for this kind of reaction. However, arylindolyl phosphine ligands were prepared successfully, and produced promising preliminary results in achiral Suzuki-Miyaura coupling reactions.

Interesting X-ray crystallography structure of brominated indole is discussed.

Acknowledgements

I would like to thank everyone who contributed to this project, and give a special thanks to my supervisor Gareth J. Rowlands, for the knowledge he passed on and his patience. I also wish to acknowledge that David Martin and Geoff B. Jameson collected and processed all the X-ray crystallography data for my molecules.

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Abbreviations

(<i>S</i>)-PEA	(<i>S</i>)-phenethylamine
AAA	Asymmetric Allylic Alkylation
Ac	Acetate
aryl-MOPFs	aryl-monophosphinoferrocene
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl
BINOL	1,1'-Bi-2,2-naphthol
Bz	Benzyl
Cbz	Carbobenzyloxy
Cy	Cyclohexyl
DCM	Dichloromethane
DMAP	4-Dimethylaminopyridine
DMF	Dimethylformamide
dppf	1,1'-bis(diphenylphosphino)ferrocene
ee	enantiomeric excess
HIV	Human immunodeficiency virus
NBS	N-bromosuccinimide
<i>n</i> -Bu	<i>n</i> -Butyl
Ph	Phenyl
r.t.	room temperature
SPO	Secondary phosphine oxide
<i>t</i> -Bu	<i>t</i> -Butyl
TDMPP	tri(2,6-dimethoxyphenyl)phosphine
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TON	Turnover number
TTMPP	tri(2,4,6-trimethoxyphenyl)phosphine