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

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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.

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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 |