

Studies on the Palladium and Copper Catalysed Synthesis of Some Functionalised Carbocycles and Heterocycles

**A thesis submitted in part fulfillment of the requirements
for the degree of
Doctor of Philosophy**

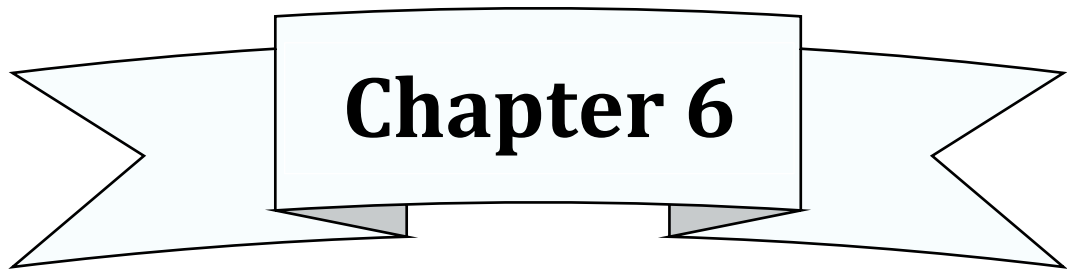
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Conclusion

And

Future Scope

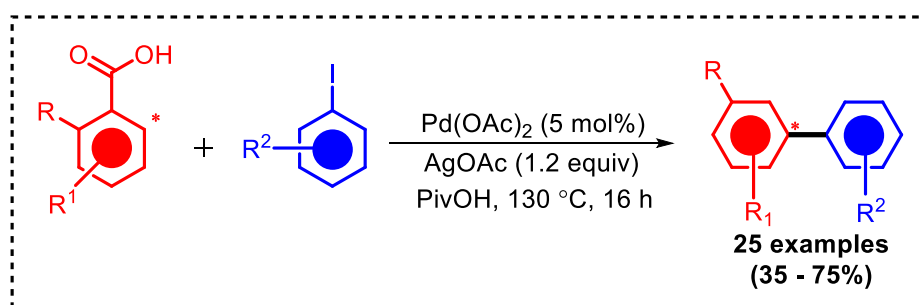
6.1. General Conclusion

The thesis focuses on the utilisation of transition metals namely palladium and copper in synthetic transformations and construction of carbon-carbon/carbon-heteroatom bonds that lead to the generation of functionalised carbocycles and heterocycles. The thesis consists of six chapters: general introduction (**Chapter 1**), four experimental chapters (**Chapter 2–5**), conclusion and future scope (**Chapter 6**). The significant findings of the experimental chapters are highlighted below.

6.2. Significant findings of the experimental works.

Chapter 2

Aryl carboxylate directed *ortho*-arylation decarboxylation cascade involving aryl iodides as coupling partners to obtain *meta*-substituted biphenyls under palladium (II) catalysis has been achieved. The reaction favours the presence of electron donating groups on the aryl carboxylic acid. The directing role of carboxylate group in the formation of a five membered palladacycle has been studied. Dual role of palladium (II) in C-H activation as well as decarboxylation, silver (I) center acting as a halide scavenger observed.

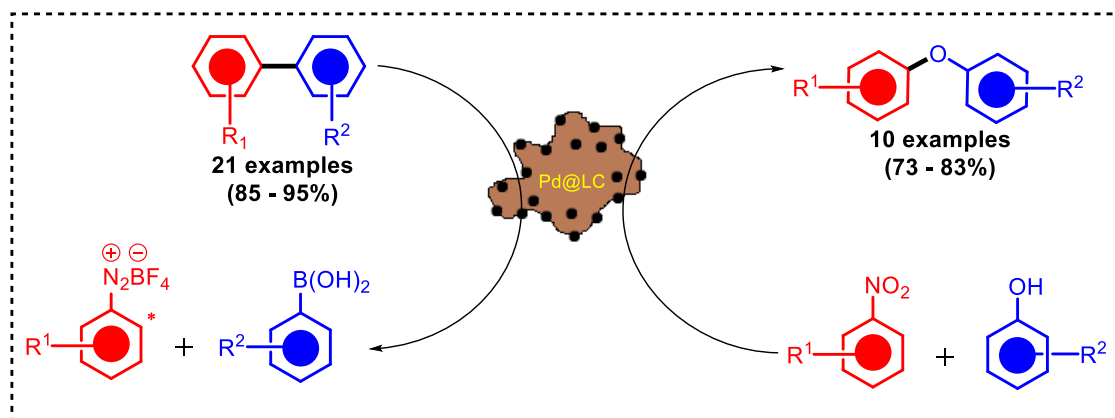


Scheme 6.1. Carboxylic acid directed *ortho*-arylation under Pd(II) catalysis

Chapter 3

A palladium nanocatalyst consisting of palladium nanoparticles supported on a lignocellulose bio-template derived from waste pomegranate peels has been employed as an efficient catalyst for two types of reactions. The first is a Suzuki-Miyaura type cross-coupling reaction of aryl diazonium salts with arylboronic acids, which is a heterogeneous process. The second is a de-nitrative cross-coupling reaction of nitroarenes with phenols to synthesise diaryl ethers, which requires the

presence of electron-withdrawing groups on the nitroarene and is semi-heterogeneous involving the initial leaching of the active palladium (0) centers to the reaction mixture.



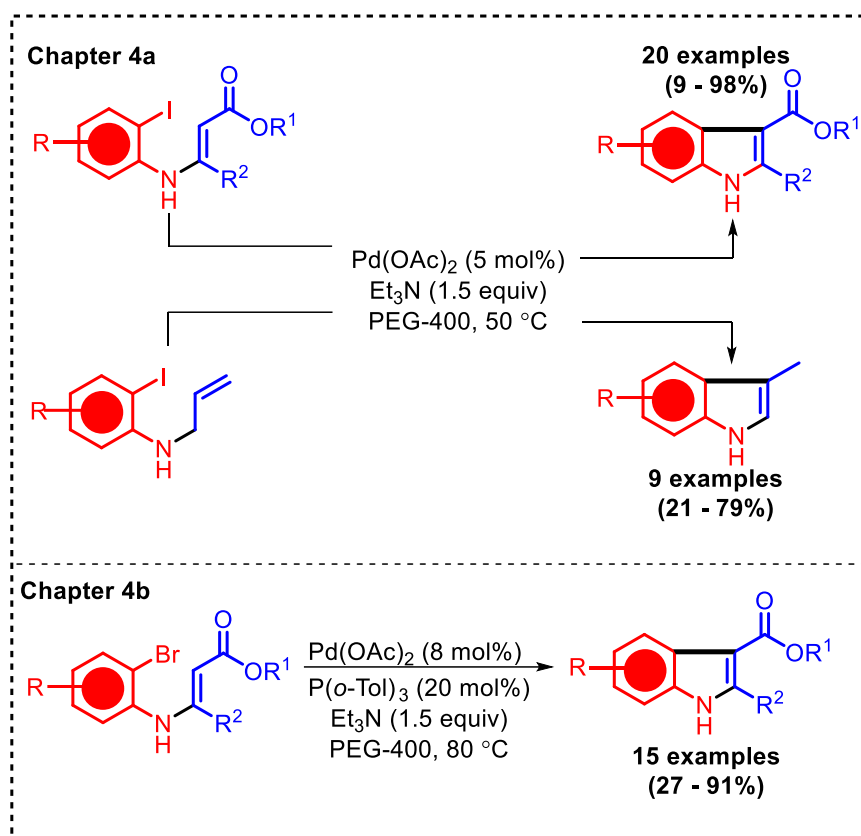
Scheme 6.2. Lignocellulose supported palladium nanomaterial catalysed Suzuki-Miyaura type cross-coupling and de-nitrative cross-coupling

Chapter 4

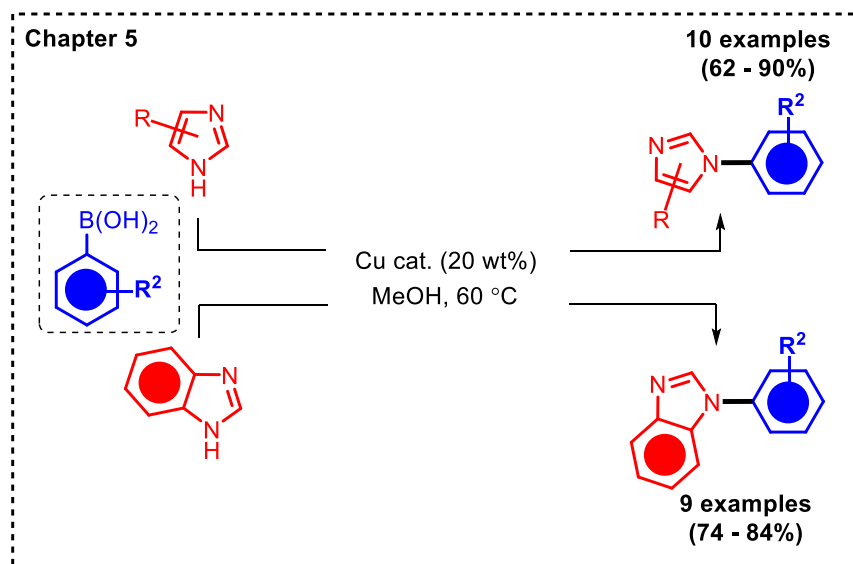
The cyclisation of *N*-vinyl-2-iodoanilines, and *N*-allyl-2-iodoanilines has been successfully carried out using Pd(II)/PEG-400 system, yielding indoles in good to excellent yields (**Chapter 4a**). The PEG-400 solvent acts as both a reducing agent and a stabiliser of palladium nanoparticles, facilitating the formation of catalytically active nanoparticles and rendering the system heterogeneous and reusable. This system also catalyses the cyclisation of *N*-vinyl-2-bromoanilines producing substituted indoles in good to excellent yields. The cyclisation of these however requires a sigma donor ligand (P(*o*-Tol)₃) for optimum conversion (**Chapter 4b**).

Chapter 5

A copper-based nanomaterial, consisting of copper oxide (Cu₂O) supported over copper, has been made through an eco-friendly approach using gas-phase H₂O/O₂ stimulation, that eliminates the need for conventional reducing agents. This hybrid Cu₂O/Cu nanostructure facilitates the efficient synthesis of a wide variety of *N*-arylated imidazole derivatives. The catalyst also exhibits excellent reusability, over multiple cycles for Chan-Lam arylation of imidazoles.



Scheme 6.3. Pd(II)/PEG system for intramolecular Heck cyclisation

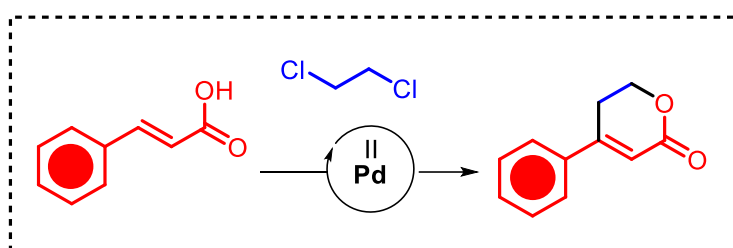


Scheme 6.4. Copper oxide nanomaterial supported over copper catalysed Chan-Lam arylation

6.3. Future scope

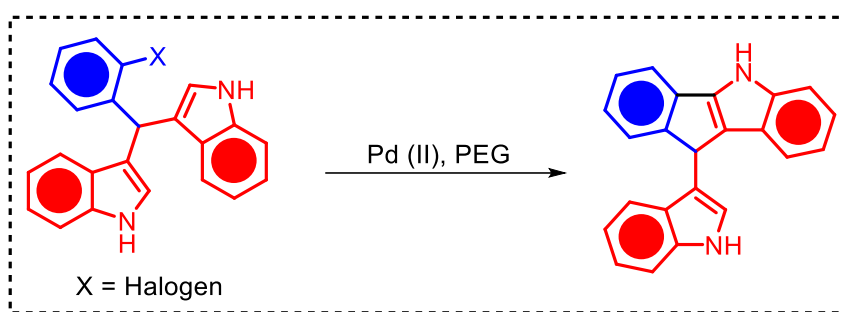
The work depicted in the thesis can further be utilised in synthetic transformations for the construction of important motifs. The future scope of the thesis can be given as follows:

(i) β -C-H Activation of cinnamic acids for the construction of cyclic esters: The directing ability of carboxylate group can be utilised in the formation of palladacycle at the β -sp² carbon which can then be used in cyclisation reactions with vicinal and geminal aliphatic dihalides *via* S_N2 reaction and carbon-halogen activation.



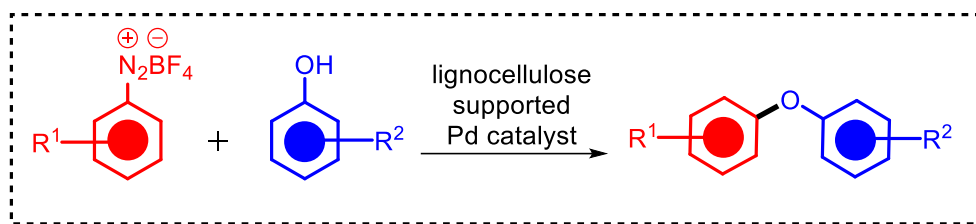
Scheme 6.5. Construction of 5,6-dihydro-2*H*-pyran-2-ones *via* β -C-H activation of cinnamic acids

(ii) *In-situ* generated palladium nanoparticle catalysed strategy can be employed for the intramolecular Heck cyclisation of 2-iodoarylbisindolylmethanes to generate indol-3-yl)-5,10-dihydroindeno[1,2-*b*]indoles which can then show biological potency.



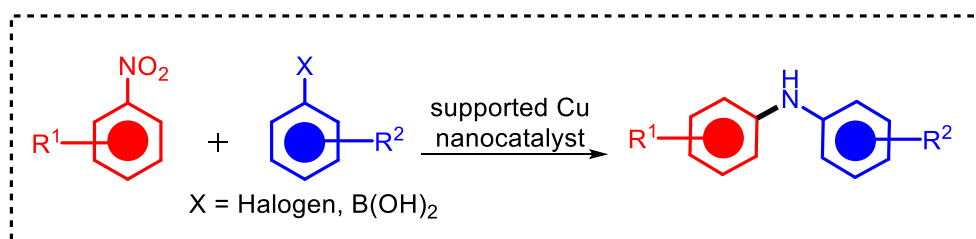
Scheme 6.6. Intramolecular Heck cyclisation involving indolyl systems for synthesis of π -extended heterocycles

(iii) Lignocellulose supported palladium nanomaterials can be developed and utilised for the cross-coupling of aryl diazoniums with phenols to synthesise diaryl ethers



Scheme 6.7. Lignocellulose supported palladium catalysed cross-coupling of aryl diazonium salts with phenols

(iv) Supported copper nanomaterials can be developed and utilised for the reductive cross-coupling of aryl nitrates with aryl donors such as aryl boronic acids and aryl halides to synthesise diaryl amines.



Scheme 6.8. Supported copper nanomaterials catalysed reductive cross-coupling of aryl nitrates