

Table of Contents

Content	Page Number
Abstract	i – xi
Keywords	xii
Declaration by the Candidate	xiii
Certificate from the Supervisor	xiv
Certificate from the External examiner and ODEC	xv
Acknowledgements	xvi – xvii
Table of contents	xviii – xxii
List of Schemes	xxiii – xxvii
List of Figures	xxviii – xxx
List of Tables	xxxii – xxxiii
Abbreviations and Symbols	xxxiv – xxxv
Chapter 1. General Introduction	1.1 – 1.50
1.1. Transition metal catalysis	1.1 – 1.3
1.2. Transition metal catalysed cross-coupling reactions	1.3 – 1.5
1.3. Palladium in C–C and C–heteroatom cross-couplings	1.6– 1.22
1.3.1. Oxidative addition to Palladium (0)	1.8 – 1.9
1.3.2. The Suzuki–Miyaura cross-coupling reaction	1.9 – 1.15
1.3.3. The Heck reaction	1.15 – 1.22
1.4. Palladium in C–H functionalisation	1.22 – 1.29
1.5. Copper in cross-coupling reactions	1.29 – 1.36
1.5.1. Copper in C–N bond formations and the Chan–Lam reaction	1.30 – 1.36
1.6. Mechanistic pathway from Chan–Lam cross-coupling	1.36 – 1.37
1.7. Thesis overview and objectives	1.37 – 1.38
1.8. Bibliography	1.39 – 1.50
Chapter 2. Palladium (II) Catalysed Access to <i>meta</i>-Substituted Biphenyls via Carboxylic acid Directed <i>ortho</i>-Arylation–Decarboxylation Cascade	2.1 – 2.29
2.1. Introduction	2.1 – 2.2
2.2. Experimental section	2.2 – 2.17
2.2.1. General information	2.2 – 2.3

Table of Contents

2.2.2. Optimisation of the reaction conditions	2.3 – 2.5
2.2.3. General procedure for C6 arylation of <i>ortho</i> -substituted benzoic acids	2.5
2.2.4. Substrate Scope Studies	2.5 – 2.8
2.2.5. X Ray Crystallography	2.9 – 2.11
2.2.6. Control Experiments	2.11 – 2.12
2.2.7. Plausible Reaction Mechanism	2.12 – 2.14
2.2.8. Computational studies	2.15 – 2.17
2.3. Conclusion	2.17
2.4. ¹ H and ¹³ C NMR Data	2.18 – 2.23
2.5. Representative NMR Spectra	2.24 – 2.25
2.6. Bibliography	2.26 – 2.29
Chapter 3. Utilising Palladium (0)-Supported Lignocellulosic Biomass Catalyst for C-C and C-O Bond Formations	3.1 – 3.41
3.1. Introduction	3.1 – 3.5
3.1.1. Suzuki-Miyaura cross-coupling	3.2
3.1.2. De-nitrative cross-coupling	3.2 – 3.5
3.2. Objectives of the present work	3.5 – 3.6
Chapter 3a. Utilising Palladium (0)-Supported Lignocellulosic Biomass Catalyst for Suzuki-Miyaura Type Cross-Coupling of Aryl Diazonium Salts with Arylboronic acids	3.7 – 3.18
3.3. Introduction	3.7 – 3.8
3.4. Experimental Section	3.8 – 3.9
3.4.1. General information	3.8
3.4.2. General procedure for the synthesis of lignocellulose supported palladium catalyst	3.8 – 3.9
3.4.3. General procedure for the synthesis aryl diazonium tetrafluoroborates	3.9
3.5. Results and Discussion	3.9 – 3.17
3.5.1. Characterisation of the synthesised nanomaterial	3.10
3.5.2. Optimisation of the reaction conditions	3.10 – 3.11

3.5.3. General procedure for Suzuki–Miyaura type cross-coupling reaction	3.11 – 3.12
3.5.4. Substrate Scope Studies	3.12 – 3.14
3.5.5. Reusability studies	3.14 – 3.15
3.5.6 Plausible reaction mechanism	3.16 – 3.17
3.5.7. Conclusion	3.17 – 3.18
Chapter 3b. Utilising Palladium (0)-Supported Lignocellulosic Biomass Catalyst for De-nitrative Cross-Coupling of Nitroarenes with Phenols	3.19 – 3.41
3.6. Introduction	3.19 – 3.22
3.7. Optimisation of the reaction conditions	3.22 – 3.23
3.8 General procedure for the <i>O</i> -arylation reaction	3.24
3.9. Substrate scope studies	3.24 – 3.25
3.10. Heterogeneity studies	3.25
3.11. Reaction mechanism	3.25
3.12. Conclusion	3.27
3.13. ¹ H and ¹³ C NMR Data	3.28 – 3.34
3.14. Representative NMR Spectra	3.35 – 3.36
3.15. Bibliography	3.37 – 3.41
Chapter 4. Palladium (II)–PEG System for the Efficient Synthesis of Indoles <i>via</i> Intramolecular Heck Cyclisation	4.1 – 4.55
4.1. Introduction	4.1 – 4.4
4.2. Objectives of the present work	4.4
4.3. Experimental section	4.4 – 4.8
4.3.1. General information	4.4
4.3.2. Single crystal X-ray diffraction studies	4.5
4.3.3. General procedure for the Michael addition of 2-Haloanilines with propiolate esters	4.5
4.3.4. General procedure for the <i>N</i> -functionalisation of the adducts	4.5 – 4.6
4.3.5. General procedure for the <i>N</i> -allylation of 2-iodoanilines	4.6
4.3.6. General procedure for the synthesis of <i>N</i> -alkyl- <i>N</i> -allyl-2-iodoanilines from <i>N</i> -allyl-2-iodoanilines	4.6

Chapter 4a. <i>In-Situ</i> Generated Palladium Nanoparticles Catalysed Synthesis of Indoles via Intramolecular Heck Cyclisation of <i>N</i>-vinyl and <i>N</i>-allyl-2- iodoanilines	
4.4. Introduction	4.9 – 4.12
4.5. Results and discussion	4.13 – 4.24
4.5.1. Optimisation of the reaction conditions for the cyclisation of 2-iodo- <i>N</i> -vinylanilines	4.13 – 4.15
4.5.2. Substrate scope studies	4.15 – 4.19
4.5.3. One pot sequential cyclisation attempt	4.20
4.5.4. Scale-up experiments	4.20 – 4.21
4.5.5. X-Ray crystallographic studies	4.21 – 4.23
4.5.6. Mechanistic studies	4.23 – 4.24
4.6. Reusability studies	4.24 – 4.25
4.7. Reaction mechanism	4.26 – 4.27
4.7.1. Cyclisation of <i>N</i> -vinyl-2-iodoanilines	4.26
4.7.2. Cyclisation of <i>N</i> -allyl-2-iodoanilines	4.27
4.8. Conclusion	4.28
Chapter 4b. Palladium (II) – PEG System for the Efficient Synthesis of Indoles via Intramolecular Heck Cyclisation of <i>N</i>-vinyl-2-bromoarenes	
4.9. Introduction	4.29 – 4.31
4.10. Optimisation of reaction conditions for the cyclisation of 2-bromo- <i>N</i> -vinylanilines	4.31 – 4.32
4.11. Substrate scope studies	4.33 – 4.35
4.11.1. General procedure for the cyclisation of <i>N</i> -vinyl-2-bromoanilines	4.33
4.11.2. Substrate scope for the cyclisation of <i>N</i> -vinyl-bromoanilines	4.33- 4.35
4.11.3. One pot sequential cyclisation attempt	4.36
4.11.4. Scale-up experiments	4.37
4.11.5. Reaction mechanism	4.37 – 4.38
4.12. Conclusion	4.38
4.13. ¹ H and ¹³ C NMR Data	4.39 – 4.46

Table of Contents

4.14. Representative NMR Spectra	4.47 – 4.48
4.15. Bibliography	4.49 – 4.55
Chapter 5. Biogenic Cu₂O/Cu Nanomaterial Catalysed <i>N</i>-arylation of Imidazoles and Benzimidazoles with Arylboronic acids Under External Base Free Conditions	5.1 – 5.33
5.1. Introduction	5.1 – 5.3
5.2. Experimental Section	5.3 – 5.5
5.2.1. Fabrication of the nanomaterial	5.3
5.2.2. Characterisation techniques	5.3 – 5.4
5.2.3. Experimental Procedure for the <i>N</i> -arylation of imidazoles and benzimidazoles with arylboronic acids	5.4 – 5.5
5.3. Results and discussion	5.5 – 5.20
5.3.1. Characterisation of the Cu-nanomaterial	5.5 – 5.12
5.3.2. Optimisation of the reaction conditions	5.12 – 5.14
5.3.3. Substrate scope studies	5.14 – 5.16
5.3.4. Catalyst reusability studies	5.16 – 5.17
5.3.5. Catalyst analysis post reuse	5.17 – 5.19
5.3.6. Reaction Mechanism	5.20
5.4. Conclusion	5.20 – 5.21
5.5. ¹ H and ¹³ C NMR Data	5.22 – 5.27
5.6. Representative NMR Spectra	5.28 – 5.29
5.7. Bibliography	5.30 – 5.33
Chapter 6. Conclusion and Future Scope	6.1 – 6.5
6.1. General Conclusion	6.1
6.2. Significant findings of the experimental works	6.1 – 6.3
6.3. Future scope	6.3 – 6.5
Appendix	A – F
Annexure A	A – D
Annexure B	E – F