

Table of Contents

	Page No.
Abstract	i
Keywords	vii
Declaration	viii
Certificate from Supervisor	ix
Certificate of the External Examiner and ODEC	x
Acknowledgements	xi
Table of Contents	xiii
List of Schemes	xviii
List of Figures	xxi
List of Tables	xxv
Abbreviations and Symbols	xxvii
Chapter 1. General Introduction	1-36
1.1 Heterocyclic Compounds	1
1.2 N-Heterocycles: The Molecules of Diverse Biological Functions	1
1.3 Indole-Based Heterocyclic Compounds	3
1.4 Synthetic Approaches to Indoles	5
1.5 Introduction to C–H Activation and Functionalization	7
1.6 Site-Selective Functionalization of Indole C–H Bonds	9
1.7 Functionalization at the C3 Position of Indoles	10
1.7.1 Transition Metal-Catalyzed C3-Functionalization of Indoles	11
1.7.2 Metal-Free Protocols for C3-Functionalization of Indoles	13
1.8 Transition Metal-Catalyzed C2-Functionalization of Indoles	15
1.8.1 Directing Group Guided C2-Functionalization of Indoles	17
1.8.2 Directing Group-Free C2-Functionalization of Indoles	20
1.9 C–C Coupling of Pre-Functionalized Positions of N-Heterocycles	23
1.10 Towards Sustainability of Synthetic Developments	25
1.10.1 Heterogeneous Catalysis	26
1.10.2 Choosing Greener Solvents	27
1.10.3 Biomass-Based Renewable Materials	28

1.11 Thesis Outline and Objectives	28
1.12 Bibliography	29
Chapter 2. Molecular Iodine Catalyzed Selective C3-Benzylolation of Indoles with Benzyl Alcohol	37-57
2.1 Introduction	37
2.2 Results and Discussion	38
2.2.1 Optimization of Reaction Conditions	38
2.2.2 Substrate Scope Study	40
2.2.3 Mode of Iodine Catalysis	42
2.2.4 Plausible Mechanism	43
2.3 Summary	44
2.4 Experimental Section	44
2.4.1 General Information	44
2.4.2 Synthesis of Primary and Secondary Benzyl Alcohols	45
2.4.3 General Procedure for C3-Benzylolation of Indoles with Benzyl Alcohols	45
2.5 Characterization Data of the Products	46
2.6 X-Ray Crystallography Details	51
2.7 Representative HRMS spectra	52
2.8 Representative ¹ H and ¹³ C{ ¹ H} NMR spectra	53
2.9 Bibliography	55
Chapter 3. Molecular Iodine Catalyzed Selective Construction of Cyclopenta[<i>b</i>]indoles from Indoles and Acetone	58-84
3.1 Introduction	58
3.2 Results and Discussion	59
3.2.1 Optimization of Reaction Conditions	59
3.2.2 Substrate Scope Study	61
3.2.3 Investigations on Reaction Mechanism	64
3.2.4 Plausible Mechanism	65
3.3 Summary	66

3.4 Experimental Section	67
3.4.1 General Information	67
3.4.2 Synthesis of <i>N</i>-Substituted Indoles	68
3.4.3 General Procedure for the Synthesis of Indolyl-cyclopenta[<i>b</i>]indole Derivatives	68
3.4.4 General Procedure for the Synthesis of Bis(indolyl)alkane Derivatives	68
3.5 Characterization Data of the Products	69
3.6 X-Ray Crystallography Details	77
3.7 Representative HRMS spectra	78
3.8 Representative ¹H and ¹³C{¹H} NMR spectra	79
3.9 Bibliography	82
Chapter 4. Studies on Heterogeneous Pd-Based Catalytic System for C–H Bond Functionalization at C2 Position of Indoles	85-138
<i>Section A. Palladium-on-Carbon as a Reusable Heterogeneous Catalyst for C2-Arylation of <i>N</i>-Alkylated Indoles with Arylboronic Acids</i>	85-102
4A.1 Introduction	85
4A.2 Results and Discussion	86
4A.2.1 Optimization of Reaction Conditions	86
4A.2.2 Substrate Scope Study	88
4A.2.3 Hot-Filtration Test	90
4A.2.4 Reusability Test	91
4A.2.5 Characterization of Recovered Catalyst	91
4A.2.6 Plausible Mechanism	93
4A.3 Summary	94
4A.4 Experimental Section	94
4A.4.1 General Information	94
4A.4.2 Synthesis of <i>N</i>-Substituted Indoles	95
4A.4.3 General Procedure for C2-Arylation of Indoles with Arylboronic Acids	95
4A.5 Characterization Data of the Products	96
4A.6 Representative ¹H and ¹³C{¹H} NMR spectra	101

Section B. Pd(0)-Embedded-Lignocellulosic Nanomaterials: A Bio-Tailored Reusable Catalyst for Selective C2-Arylation of Free N-H Indoles	103-131
4B.1 Introduction	103
4B.2 Results and Discussion	105
4B.2.1 Preparation of Lignocellulose-Supported Pd Nanomaterials	105
4B.2.2 Characterization of Pd NPs@LCpp	105
4B.2.3 Optimization of Reaction Conditions	110
4B.2.4 Substrate Scope Study	113
4B.2.5 Extension of Scope of the Reaction	115
4B.2.6 Recyclability Study	116
4B.2.7 Characterization of the Recovered Catalyst	117
4B.2.8 Nature of Active Catalyst Species	119
4B.2.9 Plausible Mechanism	119
4B.3 Summary	120
4B.4 Experimental Section	121
4B.4.1 General Information	121
4B.4.2 Preparation of Catalysts	121
4B.4.2.1 Preparation of LCpp	121
4B.4.2.2 Preparation of Pd NPs@LCpp	122
4B.4.3 Characterization of Catalysts	122
4B.4.4 Synthesis of N-Substituted Indoles	123
4B.4.5 General Procedure for C2-Arylation of Indoles with Arylboronic Acids	123
4B.4.6 Procedure of One-Pot C2-Functionalization-Suzuki-Miyaura Coupling Reaction	123
4B.5 Characterization Data of the Products	124
4B.6 Representative ¹H and ¹³C{¹H} NMR spectra	130
4.1 Bibliography	132
Chapter 5. Bimetallic Pd-Ag Nanoclusters Decorated Micro-Cellulose Bio-Template for Catalytic Suzuki-Miyaura Coupling Reaction of N-Rich Heterocycles	139-176
5.1 Introduction	139
5.2 Results and Discussion	141

5.2.1 Green Synthesis of Cellulose Supported Pd-Ag Bi-Metallic Nanoclusters	141
5.2.2 Characterization of Pd-Ag@PMFC	141
5.2.3 Optimization of Reaction Conditions	148
5.2.4 Substrate Scope Study	150
5.2.5 Hot-Filtration Test	153
5.2.6 Reusability Test	154
5.2.7 Characterization of the Recovered Catalyst	155
5.2.8 Catalytic Role of Pd-Ag@PMFC in SMCR	156
5.2.9 Plausible Mechanism	158
5.2.10 Comparative Literature Analysis of Heterogeneous Catalysts Explored in SMCR of Heterocyclic Compounds	159
5.3 Summary	161
5.4 Experimental Section	161
5.4.1 General Information	161
5.4.2 Preparation of Catalysts	162
5.4.2.1 Preparation of PMFC	162
5.4.2.2 Preparation of Pd-Ag@PMFC	162
5.4.2.3 Preparation of Pd@PMFC and Ag@PMFC	163
5.4.3 Characterization of Catalysts	163
5.4.4 General Procedure for SMCR of Heteroaryl Compounds	163
5.5 Characterization Data of the Products	164
5.6 Representative ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra	169
5.7 Bibliography	171
Chapter 6. Conclusion and Future Scopes	177-180
6.1 Conclusion	177
6.2 Significant Findings of the Experimental Works	178
6.3 Future Scopes of the Works	179
Annexure	
List of Publications	A1-A2
List of Conferences	A3