

# CONTENTS

---

---

	Page No.
Acknowledgements	vi
List of Titles	viii
List of Schemes	xiv
List of Figures	xv
List of Tables	xvi
List of Notations, Symbols and Abbreviations	xviii
General Experimental Considerations	xxii
Preface	xxiii

## LIST OF TITLES

Titles	CHAPTER-1	Page No.
	<b>Introduction</b>	
1.1	Brief Introduction of tert-Butyl hydroperoxide (TBHP)	1
1.2	Application of TBHP	4
1.2.1	TBHP Mediated C-C Bond Formation:	4
1.2.1.1	Synthesis of [6,6,5] tricyclic frameworks	5
1.2.1.2	Synthesis of 1H-indole derivatives	5
1.2.1.3	Synthesis of indole derivatives via cross-dehydrogenativecoupling	6
1.2.1.4	Oxidative Coupling of $\beta$ -ketoesters with carboxylic acids	6
1.2.1.5	Coupling of azoles with $\alpha$ -C(sp <sup>3</sup> )-H of ethers and thioethers	6
1.2.1.6	sp <sup>3</sup> C-H bond functionalizationof toluene derivatives	7
1.2.1.7	Synthesis of isoxazoline-functionalized phenanthridines	

1.2.1.8	Domino synthesis of 3-aryloindoles via two sp <sup>3</sup> C–H activation.	8
1.2.1.9	C-2-Alkylation of azoles	9
1.2.1.10	Preparation of double bond	9
1.2.1.11	Oxidative coupling of benzothiazoles with aldehydes	10
1.2.1.12	1,3-Dipolar cycloaddition/ oxidation/ aromatization cascade reaction	10
1.2.1.13	Tandem Michael addition/oxidative annulations	10
1.2.1.14	Regioselective synthesis of C-3 dicarbonyl indole derivatives	
1.2.2	TBHP Mediated C-N Bond formation	11
1.2.2.1	Oxidative imidation of ketones	12
1.2.2.2	Oxidative amidation of aldehyde	12
1.2.2.3	Coupling reaction between isocyanide and aryl methanes	13
1.2.2.4	Amination of benzylic C–H bonds	13
1.2.2.5	Amination of benzoxazoles with amines	14
1.2.2.6	Amide bond formation from aldehydes and aromatic tertiary amines	14
1.2.2.7	Alkylation of aryl tetrazoles	15
1.2.2.8	Synthesis of $\alpha$ -ketoamides from aryl methyl ketones	15
1.2.2.9	Synthesis of amides from alcohols and N,N-disubstituted formamides	16
1.2.2.10	Synthesis of tertiary amides from tertiary amines and anhydrides	16
1.2.2.11	Oxidative amidation of aldehydes using amine HCl salts	17
1.2.2.12	Oxidative aminations of benzoxazole	17

1.2.2.13	Amide bond formation from benzyl alcohols/aldehydes	18
1.2.2.14	Synthesis of N-sulfonyl formamide	19
1.2.2.15	Imidation of the C(sp <sup>3</sup> )-H bond	19
1.2.2.16	Synthesis of amide from methyl arenes and the HCl salt of amines	20
1.2.2.17	Cross-dehydrogenative amination	21
1.2.2.18	Intramolecular dehydrogenative cyclization of N-acyl dipeptide esters	22
1.2.2.19	The Synthesis of 4,3-fused 1,2,4-triazoles	22
1.2.2.20	N-Amidoalkylation of purine	22
1.2.2.21	The stereoselective Synthesis of trans-disubstituted aziridines	23
1.2.2.22	The Synthesis of [1,2,4]triazolo[3,4-c]quinoxaline scaffolds	23
1.2.3.1	Synthesis of $\alpha$ -ketoamides	24
1.2.3.2	Synthesis of $\beta$ -acylated enaminones	25
1.2.3.3	TBHP-Initiated Transamidation of secondary amides	25
1.2.3.4	Aqueous Domino synthesis of quinazolinones and quinoxalines	26
1.2.3.5	C-3 Functionalization of quinoxalin-2(1H)ones	26
1.2.3.6	Four component synthesis of enaminones	26
1.2.3.7	Synthesis of achiral axial 3, 3'-biindole-2, 2'-dibenzenesulfonothioate	27
1.2.3.8	Synthesis of 3,5-disubstituted-1,2,4-triazoles	27
1.2.3.9	Transition-metal-free synthesis of 3-sulfonylated thioflavones	28
1.2.3.10	One-pot synthesis of 2-amino-1,3,4-oxadiazoles	28

1.3	References	30
-----	------------	----

## CHAPTER-2

### **TBHP Mediated Solvent-Free Cascade Csp<sup>3</sup>-H Bond Functionalization of Methyl Arene with Active Methylene Compounds using Et<sub>3</sub>N- as a Catalyst**

2.1	Introduction	41
2.2	Results and Discussion	43
2.3	Control experiment	49
2.4	Mechanism of C-H functionalization	51
2.5	Conclusion	52
2.6	Experimental Section	52
2.6.1.	General experimental procedure	52
2.6.2	Physical and spectral data of representative compounds	52
2.6.3	Spectral Data of Product 2 Benzylidenemalononitrile 2a	56
2.6.4	Spectral Data of Product (Z)-Ethyl 3-(4-chlorophenyl)-2-cyanoacrylate 3n	58
2.7	References	60

## CHAPTER-3

### **TBHP initiated C-N Bond Formation via Oxidative Coupling of Benzyl Bromides with Amine using TBAI as a Catalyst**

3.1	Introduction	66
3.2	Results and Discussion	68
3.3	Control experiment	73
3.4	Mechanism of amide formation	74
3.5	Conclusion	76
3.6	Experimental Section	78
3.6.1	General experimental procedure for the synthesis of amide	78
3.6.2	Characterization data of synthesized compounds 3(a-r)	78
3.6.3	Spectral Data of Product N-phenylbenzamide (3a)	82
3.6.4	Spectral Data of Product N-Butyl-N-methylbenzamide (3n)	84

3.6.5 Spectral Data of Product phenyl(pyrrolidin-1-yl)methanone (3p)	86
3.7 References	88

#### CHAPTER-4

##### **NaI/TBHP-Promoted C-N Bond Formation Via Oxidative Coupling of Benzyl Mercaptan with Amine: A Facile Approach for The Synthesis of Amides**

4.1 Introduction	93
4.2 Results and Discussion	94
4.3 Control experiments to establish mechanism of the reaction	101
4.4 Mechanism of C-N Bond Formation Via Oxidative Coupling	103
4.5 Gram-scale synthesis of Benzamide with Benzylmercaptan & Aniline	104
4.6 Conclusion	105
4.7 Experimental Section	105
4.7.1 General experimental procedure for the synthesis of compound 3	105
4.7.2 Characterization data of synthesized compounds and 3(a-t)	106
4.7.3 Spectral Data of Product N-Phenylbenzamide 3a	110
4.7.4 Spectral Data of Product 1-(2 Naphthalenecarbonyl)piperidine(3m)	113
4.7.5 Spectral Data of Product piperidin-1-yl(pyridin-4-yl)methanone(3t)	115
4.8 References	117

#### CHAPTER-5

##### **I<sub>2</sub>/TBHP Mediated Oxidative Coupling of Indole with Active methylene Compounds Via C-C and C-O bond formation**

5.1 Introduction	121
5.2 Results and Discussion	122
5.3 Control Experiment	129
5.4 Mechanism for coupling of indole with active methylene groups	130
5.5 Conclusion	132
5.6 Experimental Section	132

5.6.1	General experimental procedure for the synthesis of the compound of 3a	132
5.6.2	Characterization data of the compounds	132
5.6.3	Spectrul data of Product 2-(2-oxoindolin-3-ylidene) malononitrile 4a	138
5.6.4	Spectrul data of Product Ethyl-2-cyano-2-(2-oxoindolin-3-ylidene) acetate 4g	140
5.6.5	Spectrul data of Product 5, 5-Dimethyl-2-(2-oxoindolin-3-ylidene) cyclohexane-1, 3-dione 4m	142
5.7	References	144

### **Summary and Conclusions**

### **List of Research Publications**