# *tert*-Butyl Hydroperoxide Mediated Development of Some New C-C And C-N Bond Formation

Thesis submitted in partial fulfillment for the award of degree

## Doctor of Philosophy


Submitted by

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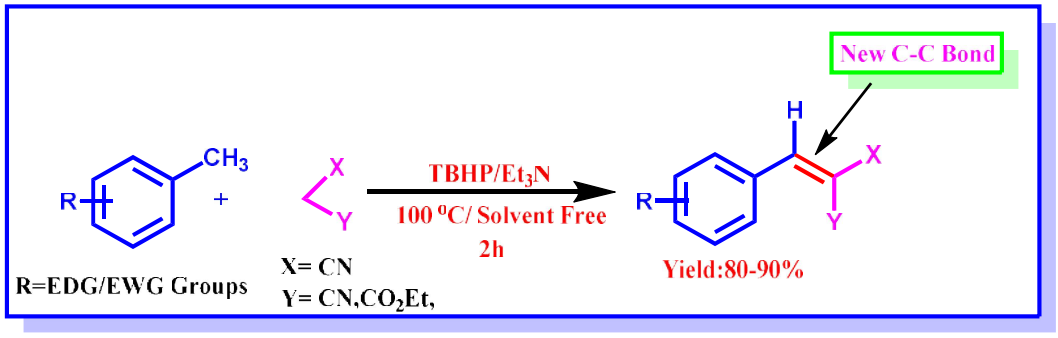
# *Chapter-6*

# Summary and Conclusion

The thesis entitled "***tert*-butyl hydroperoxide mediated development of some new C-C and C-N bond formation**" represents the efficient formation of C-C and C-N bonds via oxidative coupling using TBHP as the oxidant. The contents of the thesis have been divided into six chapters.

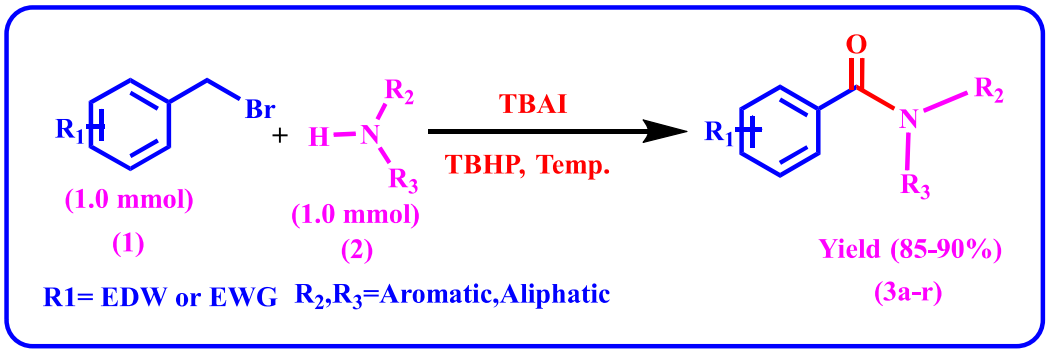
**Chapter 1** provides a general overview of TBHP and briefly discusses its application in C-C and C-N bond formation. The subsequent four chapters (**Chapters 2 to 5**) describe the investigations and findings. Each chapter is independently complete in itself and consists of an introduction, results and discussion, control experiment, mechanism, experimental section, and references.

**Chapter 2** explains a metal-free oxidative condensation of methyl arenes with malononitrile using trimethylamine (10%) as a catalyst and *tert*-butyl hydroperoxide (TBHP) (3equivalent) as an oxidant at 100ºC under solvent-free conditions **(Scheme A**). This method is metal-free, practical, inexpensive, non-toxic, and environmentally benign. This method involves metal-free C-C bond formation via C-H activation of methylarenes under mild reaction conditions.



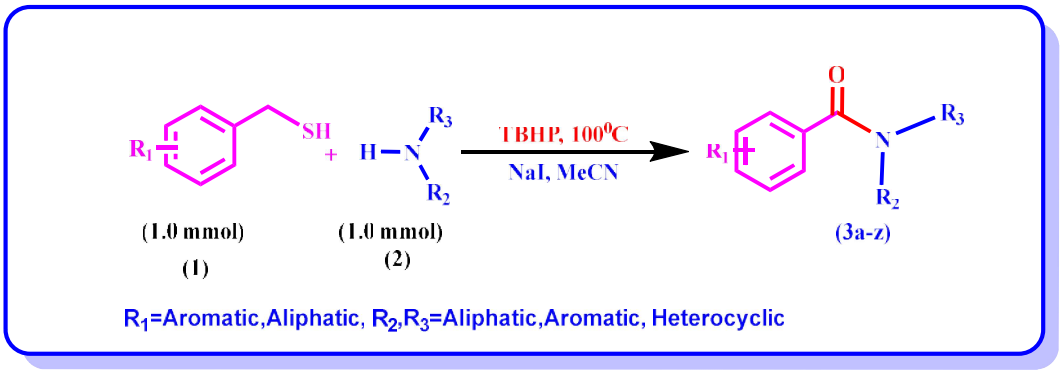

**Scheme A** C-C bond formation via oxidative coupling

**Chapter 3** describes a new, metal-free, and TBAI catalyzed synthesis of amide **3** in excellent yield (85-90% ) via oxidative coupling of benzyl halide **1** with various amines **2** in the presence of 3 equivalent of TBHP at 80ºC. (**Scheme B**). This approach involves metal-free C-O and C-N bond formation via oxidation of benzyl bromide under mild reaction conditions.



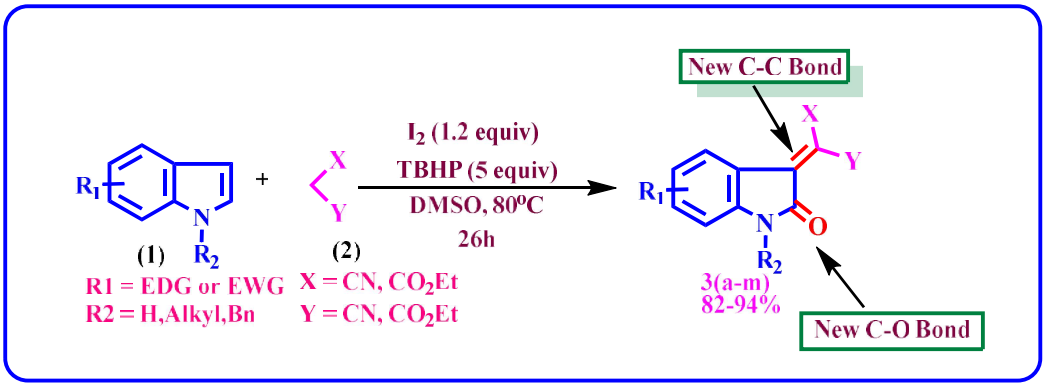

**Scheme B** Synthesis of amide via C-N bond formation

**Chapter 4** explores a facile, novel method for the direct amidation of benzyl mercaptan **1** through oxidative coupling with amine **2** using TBHP as an oxidant and NaI as a catalyst (**Scheme C**). All the reactions were accomplished without transition metal to provide product **3** with a good to excellent yield (84-90%). The current procedure performed adequately for various substrates, with electron releasing and an electron-withdrawing group containing benzyl mercaptan and various amines.




**Scheme C** Synthesis of amide from benzyl mercaptan and amine

**Chapter 5** describes a metal-free oxidative coupling of indole **1** and active methylene compound **2** into the corresponding 3-ylidene oxindole **3** via C-C and C-O bonds under mild reaction conditions(**Scheme D**). This method is the first report on the oxidative coupling of indole and active methylene compounds to corresponding 3-ylidene oxindoles under metal-free conditions. The current $I_2$ / TBHP mediated oxidative coupling is easy to get to a variety of 3-ylidene oxindoles derivatives in good to excellent yields(82-94%).




**Scheme D** Oxidative coupling of indole and active methylene compound

## Conclusion

1. We have demonstrated a new, facile, solvent-free, and efficient one-pot synthesis of 2-benzylidenemalononitrile using a resourceful TBHP catalyst and readily available starting materials. This approach allows the product to be easily isolated without column chromatography. This approach offers low catalyst loading, high yield, easy work-up, and broad substrate scope.
2. We have reported a practical and efficient protocol for the metal-free C-C & C-N bond formation via C-H activation of inexpensive Benzyl bromide. TBHP & TBAI has been exploited as a catalyst & oxidant for the green and environmentally benign

synthesis of amide & its derivatives by a one-pot reaction of Benzyl bromide & Amines.

3. We have developed a new and efficient protocol for the metal & catalyst-free C-N bond formation via C-H activation of inexpensive Benzyl mercaptan. TBHP has been exploited as an oxidant for the green and environmentally benign synthesis of amide & its derivatives by a one-pot reaction of Benzyl mercaptan & amines.
4. We have established a new and efficient one-pot oxidative coupling of indole under metal-free conditions for C-C bond formation via C-H activation of inexpensive indole. TBHP has been exploited as an oxidant & $I_2$ as a catalyst for the green and environmentally benign synthesis for developing C-C bond by one-pot reaction of Indole & Active methylene compound.

**Scope for further work**

1. Further, explore the methylarenes as a surrogate for the construction of some privileged compounds.
2. Development of different methodology like the metal-free, solvent-free reaction to synthesize N, S, and O containing biologically active compounds.
3. Further, explore the indole as a surrogate for the creation of some privileged isatin moieties.