



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI  
PhD-17 SHORT ABSTRACT OF THESIS

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Thesis Title: **Light-Driven Molecular Complexity: Cascade Functionalization of Alkynes via Selenium and/or Sulfonyl Radicals**

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SHORT ABSTRACT

The contents of the present thesis, entitled “**Light-Driven Molecular Complexity: Cascade Functionalization of Alkynes via Selenium and/or Sulfonyl Radicals**” have been divided into five chapters. The first chapter contains a brief overview of photo-redox catalysis, the importance of organoselenium and heterocyclic sulfone compounds, and some relevant literature reports on organo-photocatalytic selenium or sulfonyl radical addition to alkyne systems, and the last four chapters were based on the results achieved from the experimental works performed during the entire course of the PhD research programme.

**Chapter I: A brief introduction to the visible light-induced photocatalytic selenium/sulfonyl radical mediated cascade reaction of alkynes**

Visible light-induced photo-redox catalysis has become a valuable tool for facilitating a wide range of organic transformations. Easy access to visible light, combined with its gentle and harmless nature, makes the entire process environmentally benign. The majority of organic compounds require an additional catalyst or photosensitizer, as they are unable to absorb visible light in their ground state. Examples of photocatalysts include organic dyes, semiconductors, and

catalysts based on precious metals, such as ruthenium and iridium-polypyridyl complexes. These metal-based compounds exhibit high redox potentials, advantageous photophysical characteristics, and significant absorption. Despite being important in terms of efficiency and photophysical characteristics, their low abundance, toxicity, and expense limit them. In **Chapter I**, we present a brief overview of photo-redox catalysis, the importance of organoselenium and heterocyclic sulfone compounds, and some relevant literature reports on organo-photocatalytic selenium or sulfonyl radical addition to alkyne systems.

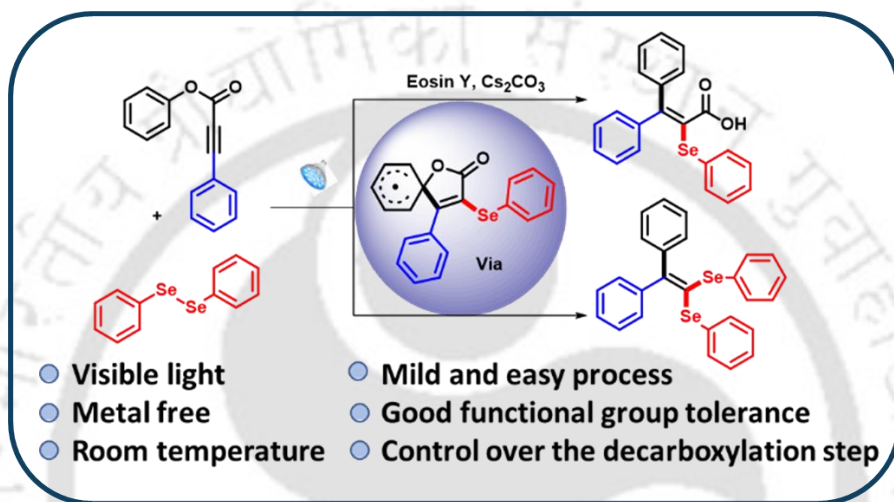
### **Aim of the Thesis:**

Over the last few decades, the increasing demand for photo-redox catalysis and the biological significance of organoselenium and heterocyclic sulfone compounds have inspired us to develop a sustainable photocatalytic approach for the construction of organoselenium and heterocyclic sulfone compounds. The primary goal of this thesis is the eosin Y photocatalytic selenium/sulfonyl radical-mediated cascade functionalization of alkynes. Here, we have developed a photocatalytic selenium radical-mediated 1,4-aryl migration process for the synthesis of selenium-containing  $\alpha$ ,  $\beta$ -unsaturated carboxylic acid and 1,1-diselenide compounds, sulfonyl radical-mediated 5-exo-dig cyclisation of 1,6-diyne and 1,6-enyne to construct the heterocyclic sulfones, and the synthesis of benzosultams from N-alkyl N-propargyl arylsulfonamide with sulfonyl radical addition.

### **Chapter II: Photocatalytic Selective Synthesis of 1,1-Diselenide Alkene Derivatives and Selenium-Containing $\alpha$ , $\beta$ -Unsaturated Carboxylic Acids**

Chemists are interested in organoselenides because they have several uses in synthetic organic chemistry, functional materials, probe imaging, catalysis, and fluorescence. In mice, bis-selenide alkene derivatives are effective antinociceptive and antioxidant agents. It is also known that certain polyselenide alkene derivatives may inhibit human erythrocyte aminolevulinic acid dehydratase (d-ALA-D). Derivatives of polyselenides have also been used in a molecular magnetic superconductor device. In **Chapter II**, we discussed how aryl alkynoates can undergo a domino reaction with selenium radicals produced by visible light, resulting in the selective production of 1,1-diselenide alkene derivatives and selenium-containing  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids,

depending on the photocatalytic conditions. The procedure is scalable, gentle, and metal-free. The selectivity was controlled by using a catalytic amount of Eosin Y dye and cesium carbonate as a base, which obstacle the room temperature decarboxylation step, helping to manage the product selectivity. The method produces respectable product yields and exhibits good functional group tolerance. Additionally, by creating the vinylic halides, allylic alcohol, and  $\alpha$ ,  $\beta$ -unsaturated ester, the synthetic usefulness of this approach was further increased.



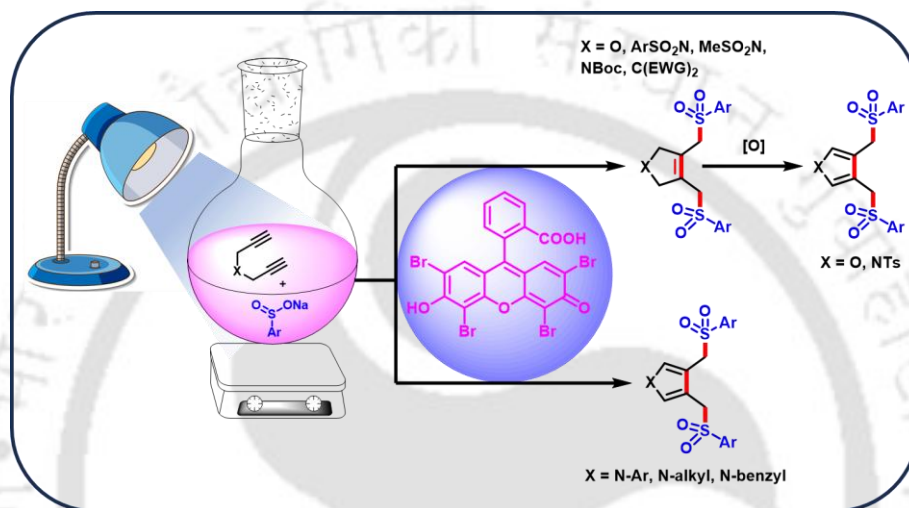
**Scheme 1:** Schematic representation of Chapter II.

**Publication:** *Org. Lett.* **2022**, *24*, 8180–8185.

### **Chapter III: Substituent-Dependent, Switchable Synthesis of Nonaromatic and Aromatic Heterocyclic Sulfones Using Visible Light**

In synthetic organic chemistry, heterocyclic molecules have long been desirable targets due to their diverse range of biological functions. Likewise, sulfone derivatives are a significant family of bioactive substances with a wide range of biological characteristics. Natural products, agrochemicals, medicinal, and organic functional materials frequently contain both heterocyclic and carbocyclic sulfones. In **Chapter III**, the switchable synthesis of aromatic and nonaromatic sulfonyl heterocycles was described by using visible light. Here, we reported an intriguing transition between pyrrole and 2,5-dihydropyrrole, which was influenced by the substitution on the N atom of the 1,6-diyne. First, disulfonylated 2,5-dihydropyrrole was produced by the

sulfonyl radical-mediated 5-exodig cyclization, which can then be converted to sulfonated pyrrole through photocatalytic dehydrogenative aromatization (PDA). Our analysis shows that the PDA process is impacted by the type of substituents on the N-atom. The product selectivity depending on the substituent of the N-atom of 1,6-diyne was supported with a strong mechanistic study. This advanced and gentle methodology shows high functional group tolerance and highlights its potential as a strong substitute for conventional synthetic methods.



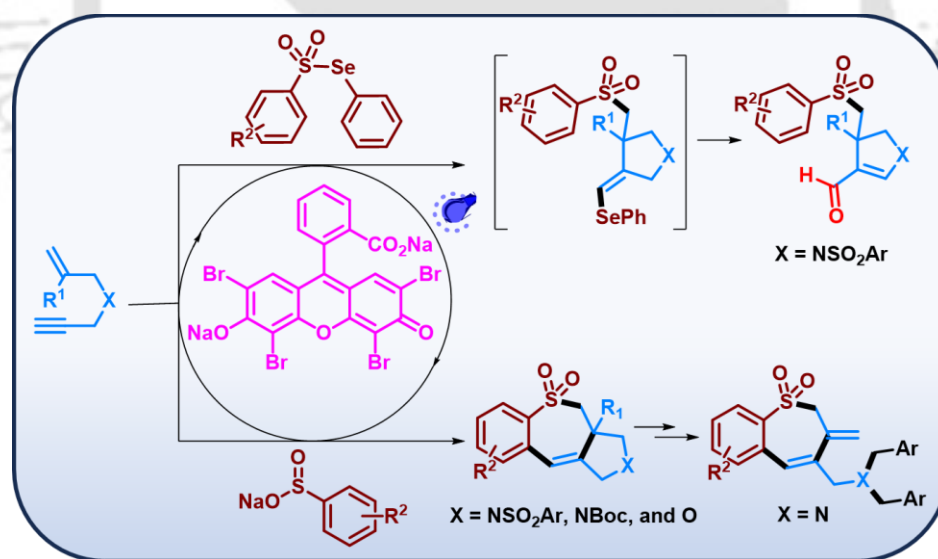
**Scheme 2:** Schematic representation of Chapter III.

**Publication:** *Org. Lett.* **2024**, *26*, 9357–9362.

#### **Chapter IV: Visible-Light Mediated Divergent Synthesis of Sulfonated Dihydropyrrole-3-Carboxaldehydes and Tricyclic Sulfones via Sulfonyl Radical Source Modulation**

Sulfones are important organosulfur compounds, have a wide range of uses as solvents, polymer constituents, and biopharmaceutical agents. Their usefulness in both industrial and medicinal contexts has been demonstrated by their use as synthetic intermediates in the manufacture of several chemical and physiologically active compounds, including protease and  $\beta$ -lactamase inhibitors. Therefore, developing novel pathways for visible light catalysis-based functionalized sulfone synthesis would be crucial. In **Chapter IV**, we documented a green and effective photocatalytic approach that selectively forms tricyclic benzofused seven-membered sulfones and sulfonated dihydropyrrole-3-carboxaldehydes by the cyclization of 1,6-enynes induced by

sulfonyl radicals. The switchable nature of the method depends on the selection of a sulfonyl radical source, which determines the selective control between radical cyclization and radical cascade cyclization. Under photocatalytic conditions, sodium aryl sulfinates produced tricyclic benzo-fused seven-membered sulfones, whereas selenosulfonates produced sulfonylated heterocyclic carboxaldehydes. Selenosulfonates on the exposers of blue LEDs get cleaved to produce sulfonyl and phenylselenyl radicals. Then chemoselective addition of sulfonyl radical to the alkene part, followed by 5-exo-dig cyclization, produces a vinyl radical, which is trapped by phenylselenyl radical. Further, selenosulfonylated intermediates undergo photocatalytic aerobic oxidation to produce sulfonylated 4,5-dihydropyrrole-3-carboxaldehydes. Tricyclic benzo-fused seven-membered sulfones are produced when sodium arylsulfinates react with 1,6-enynes in the presence of photocatalyst EY- $\text{Na}_2$  under blue LEDs in HFIP solvent. Furthermore, the tricyclic sulfone is easily converted into a special exocyclic double-bonded bicyclic seven-membered sulfone. The ring opening may be via quaternary ammonium salts (QAs) formation, followed by Hoffmann-type elimination.

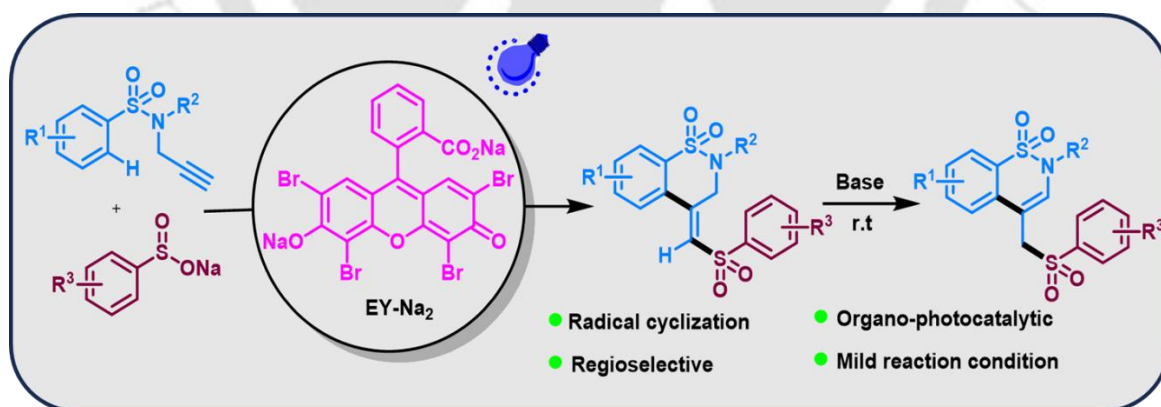


**Scheme 3:** Schematic representation of Chapter IV.

**Publication:** *Chem. Eur. J.* **2025**, *31*, e02052.

## Chapter V: Visible Light-Induced Access of Benzosultams via Sulfonyl Radical-Triggered 6-Exo-Dig Cyclization of N-Alkyl N-Propargyl Arylsulfonamide

Benzosultams are a subclass of bicyclic sulfonamides that are present in many medicines, agricultural agents, physiologically active substances, and OLEDs. They are essential in the synthesis of many drugs because they exhibit a variety of interesting pharmacological actions, including inhibitory, antibacterial, anticancer, anti-inflammatory, and anti-HIV properties. A variety of oxicams, including piroxicam, ampiroxicam, and meloxicam, are used as non-steroidal anti-inflammatory medicines (NSAIDs) to treat arthritis. In **Chapter V**, we show how to use Eosin Y as an active photocatalyst to perform a visible light-induced sulfonyl radical-triggered synthesis of the benzosultam derivatives at room temperature, from N-alkyl-N-propargyl arylsulfonamide and sodium aryl sulfinate salts. The reaction proceeds through a radical pathway via 6-exo-dig cyclization. The technique also exhibits good yields and a broad variety of substrate scope. As a direct alternative to the traditional synthetic methods for the synthesis of benzosultam derivatives, the procedure is gentle, metal-free, less sensitive, and environmentally benign. Further, the synthetic usefulness was extended by isomerizing benzosultams with an exocyclic double bond to the corresponding benzosultams with an endocyclic double bond via simple treatment of KOH at room temperature.



**Scheme 4:** Schematic representation of Chapter V.

**Publication:** *Org. Lett.* (accepted).