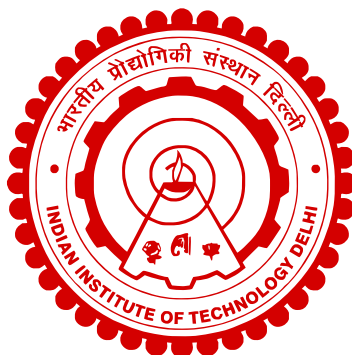


**PHOTOCATALYST-ASSISTED SINGLE ELECTRON  
TRANSFER-INDUCED HETEROCYCLE SYNTHESIS  
AND FUNCTIONALIZATION IN VISIBLE LIGHT**

**SHRUTI RAJPUT**



**DEPARTMENT OF CHEMISTRY  
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**July 2025**

**© Indian Institute of Technology Delhi (IITD), New Delhi, 2025**

**PHOTOCATALYST-ASSISTED SINGLE ELECTRON  
TRANSFER-INDUCED HETEROCYCLE SYNTHESIS AND  
FUNCTIONALIZATION IN VISIBLE LIGHT**

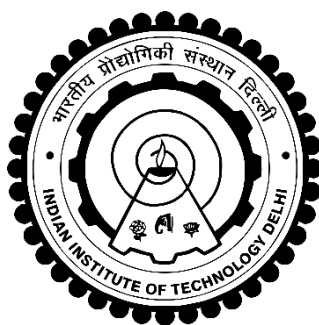
**by**

**SHRUTI RAJPUT**  
**Department of Chemistry**

**Submitted**

**In fulfillment of the requirements of the degree of  
Doctor of Philosophy**

**to the**



**Indian Institute of Technology Delhi**

**July 2025**

***Dedicated to my beloved family***

## CERTIFICATE

This is to certify that the thesis entitled, “*Photocatalyst-assisted single electron transfer-induced heterocycle synthesis and functionalization in visible light*” being submitted by **Ms. Shruti Rajput** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of Bonafide research work carried out by her. **Ms. Shruti Rajput** has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in whole or in part, to any other university or institute for award of any degree or diploma.



**Nidhi Jain**  
Professor  
Department of Chemistry  
Indian Institute of Technology Delhi  
New Delhi-110016

## ACKNOWLEDGEMENTS

*I am sincerely grateful to my supervisor, **Prof. Nidhi Jain** for her unwavering support, encouragement, and expert guidance throughout my Ph.D. journey. Her vast knowledge, insightful suggestions, and meticulous attention to detail have greatly enriched my research work. From the early stages of formulating ideas to the final stages of thesis writing, her continuous mentorship has been instrumental in keeping me focused and motivated. Her patience, understanding, and belief in my potential gave me the strength to navigate the challenges of research with confidence. I am especially thankful for her time and effort in reviewing my work and providing thoughtful feedback, which helped refine the quality of my work. It has been an immense privilege and honor to work under her supervision, and I will always remain grateful for the academic and personal growth I experienced under her guidance. I would like to extend my sincere thanks to the members of my **Student Research Committee (SRC)**, **Prof. Nalin Pant**, **Prof. Sudipta Raha Roy**, and **Prof. Josemon Jacob** for their valuable suggestions, constructive feedback, and constant encouragement throughout my research. I also thank all the past and present Head of the Department of Chemistry, IITD for the academic support and the facilities provided to carry out my research work. I also thank the administrative and technical staff members whose assistance and cooperation made my research experience smooth and hassle-free. I am also grateful to my institute for providing me with the necessary resources and financial support through the research fellowship, which enabled me to pursue my work without constraints. I am equally thankful to my seniors (**Dr. Sharvan Kumar**, **Dr. Ramandeep Kaur**, **Dr. Arun Sharma**, **Dr. Vipin Jain**, **Dr. Poonam Sharma**, **Dr. Alankrita Garia**, **Dr. Ritu**, and **Dr. Vikas**) whose guidance and camaraderie helped me in the initial phases of my work, and to my co-workers (**Rajat**, **Rohit Kumar**, **Harsha**, **Anirban Datta**, **Vijay Rahane**, **Shruti Sharma**, **Teja**, **Koyena** and **Suhel**) whose enthusiasm and support added positivity and energy to the lab environment. I sincerely thank the M.Sc. students I had the privilege to mentor (**Megha**, **Tanya**, **Dikshita**, and **Nitesh**) during my Ph.D. Their hard work, curiosity, and valuable contributions to my research have been truly appreciated, and it was a pleasure to guide and collaborate with them. I am grateful to **Prof. Harpal Singh** and **Ms. Priya Gupta** from the Centre of Biomedical Engineering, IITD for collaborating with me and performing the biological studies for my research work. The work done by them added an important aspect to my research. I am deeply thankful to my friends (**Mansi**, **Preeti Mishra**, **Shashank**, **Bhuvnesh**, **Smriti Mishra**, **Aparna Tyagi**, and **Debarshi Saha**) both within and outside the academic circle, for being my constant source of strength*

*and joy throughout this journey. Their unwavering support, understanding, and timely words of encouragement have helped me stay balanced and motivated during the most challenging phases of my Ph.D. I owe my deepest gratitude to my parents **Mr. Ramanand Rajput** and **Mrs. Malti Devi** for their unconditional love, constant support, endless sacrifices, and providing the best education possible, which has shaped the person I am today. I would also like to thank my parents **Mr. Sudhir Kumar**, and **Mrs. Shailza Rani** for their understanding, care, and encouragement. Their support, both emotionally and practically, has been invaluable in allowing me to focus on my research. I am grateful to my aunt **Mrs. Sarika Rajput** for her constant encouragement throughout this journey. My siblings **Mr. Mayank Rajput**, **Ms. Nidhi Rajput**, and **Ms. Gitika Singh** deserve my wholehearted thanks as well for always being by my side. Most importantly, I would like to extend my deepest gratitude to my life partner **Mr. Lakshya Dev Singh** for his unwavering love, support, and patience during the final phase of this journey. His belief in me, constant encouragement, and understanding during both the challenging and joyous moments have been a source of great strength. Lastly, I would like to express my deepest gratitude to God for blessing me with the strength, resilience, and wisdom to complete this journey. I am truly grateful for the gift of life, the opportunities I have received, and the ability to pursue my dreams. Without His grace, none of this would have been possible.*

*Shruti Rajput*

## ABSTRACT

The thesis entitled “**Photocatalyst-assisted single electron transfer-induced heterocycle synthesis and functionalization in visible light**” explores the application of homogeneous photocatalysts in promoting organic transformations. In recent years, visible light has emerged as an efficient tool to achieve chemical reactions, enabling the generation of highly reactive intermediates formed *in situ* without the need for stoichiometric reagents. It offers a greener and environmentally benign route for the construction and functionalization of organic heterocyclic molecules. We have developed novel protocols involving cyclization, oxidation, and C-H activation strategies for the synthesis of functionalized molecules, enabling the formation of analogous to biologically relevant compounds.

This dissertation comprises five chapters. **Chapter 1** explains the role of photochemistry, focusing on the sophisticated applications of photoredox and dual catalysis for the synthesis and functionalization of heterocycles. It outlines the classification of photocatalysts and an in-depth discussion of photocatalytic processes. A detailed study of homogeneous photocatalysts employed in our research work, and their application in facilitating organic transformations.

In **Chapter 2**, a photoinduced direct synthesis of 3-amino-1-indenones *via* radical cascade cyclization strategy is demonstrated. The methodology involves a domino reaction between 2-alkynylarylnitrile and *N*-aminopyridinium salt and captures the reactivity of *in situ* generated nitrogen-centered radical in visible light. Multiple bond-forming events including C-N, C-C, and C-O take place sequentially on 2-alkynylarylnitrile enabling construction of 3-amino-1-indenone core at room temperature. The transformation exhibits good substrate scope furnishing the products in good yields. A preliminary biological screening of the synthesized compounds is indicative of their potent anti-cancer property.

Building upon our efforts to develop novel strategies under visible light irradiation, in **Chapter 3** we report the visible light-assisted tandem oxidative 5-exo-dig cyclization of 1,6-enynes for the synthesis of aminated C-3 aryloylated benzofuran, furopyridine, benzothiophene, and indole derivatives. Nitrogen-centered radical generated *in situ* from *N*-aminopyridinium salt initiates the consecutive formation of C-N, C-C, and C-O bonds. The methodology exhibits good functional group tolerance and regio-selectivity, furnishing products in good to excellent yields at room temperature. Preliminary biological screening of synthesized molecules reveals their potential as anti-cancer agents.



In **Chapter 4**, a metal-free and photooxidative activation of 2-alkynylarylnitriles in the presence of pyrylium salt as a photocatalyst is reported. The 1,2-diketone intermediate generated in visible light demonstrates base-assisted *orthogonality* towards cyclization, furnishing 4-aryl-4-hydroxyisoquinoline-1,3-(2*H*,4*H*)-dione and 3-aryl-3-hydroxy-2,3-dihydroazanaphthoquinone derivatives. The reaction has a wide substrate scope, good functional group tolerance, uses an organic photocatalyst, and takes place at room temperature. Preliminary biological screening of synthesized molecules reveals their potential as anti-cancer agents.

In **Chapter 5**, we demonstrate a directing group-assisted decarboxylative *ortho*-benzoylation of *N*-aryl-7-azaindoles with  $\alpha$ -keto acids by synergistic visible light promoted photoredox and palladium catalysis. The approach tenders rapid entry to aryl ketone architectures from simple  $\alpha$ -keto acid precursors *via* the *in situ* generation of a benzoyl radical intermediate. The transformation provides a range of *ortho*-benzoylated *N*-aryl-7-azaindoles, with excellent site-selectivity and good functional group compatibility under mild reaction conditions. Biological target predictions indicate that these molecules may serve as potential anti-cancer and anti-viral agents.

## सार

“दृश्य प्रकाश में फोटोकैटेलिस्ट-सहायता प्राप्त एकल इलेक्ट्रॉन स्थानांतरण-प्रेरित हेट्रोसाइकिल संश्लेषण और क्रियाशीलता” शीर्षक वाली थीसिस कार्बनिक परिवर्तनों को बढ़ावा देने में सजातीय फोटोकैटेलिस्ट के अनुप्रयोग की खोज करती है। हाल के वर्षों में, दृश्य प्रकाश रासायनिक प्रतिक्रियाओं को प्राप्त करने के लिए एक कुशल उपकरण के रूप में उभरा है, जो स्टोइकोमेट्रिक अभिकर्मकों की आवश्यकता के बिना सीटू में गठित अत्यधिक प्रतिक्रियाशील मध्यवर्ती की पीढ़ी को सक्षम करता है। यह कार्बनिक हेट्रोसाइक्लिक अणुओं के निर्माण और क्रियाशीलता के लिए एक हरित और पर्यावरण के अनुकूल मार्ग प्रदान करता है। हमने क्रियाशील अणुओं के संश्लेषण के लिए चक्रीकरण, ऑक्सीकरण और C-H सक्रियण रणनीतियों को शामिल करते हुए नए प्रोटोकॉल विकसित किए हैं, जो जैविक रूप से प्रासंगिक यौगिकों के अनुरूप निर्माण को सक्षम करते हैं।

इस शोध प्रबंध में पाँच अध्याय शामिल हैं। **अध्याय 1** फोटोकैमिस्ट्री की भूमिका की व्याख्या करता है, जो हेट्रोसाइकिल के संश्लेषण और क्रियाशीलता के लिए फोटोरेडॉक्स और दोहरे कटैलिसीस के परिष्कृत अनुप्रयोगों पर ध्यान केंद्रित करता है। यह फोटोकैटेलिस्ट के वर्गीकरण और फोटोकैटेलिटिक प्रक्रियाओं की गहन चर्चा को रेखांकित करता है। हमारे शोध कार्य में उपयोग किए जाने वाले सजातीय फोटोकैटेलिस्ट का विस्तृत अध्ययन, तथा कार्बनिक परिवर्तनों को सुविधाजनक बनाने में उनका अनुप्रयोग।

**अध्याय 2** में रेडिकल कैस्केड साइक्लाइजेशन रणनीति के माध्यम से 3-एमिनो-1-इंडेनोन का फोटो-प्रेरित प्रत्यक्ष संश्लेषण प्रदर्शित किया गया है। कार्यप्रणाली में 2-एल्काइनिलरीलनाइट्राइल और एन-एमिनोपाइरिडिनियम नमक के बीच एक डोमिनो प्रतिक्रिया शामिल है तथा दृश्य प्रकाश में इन-सीटू उत्पन्न नाइट्रोजन-केंद्रित रेडिकल की प्रतिक्रियाशीलता को कैप्चर करता है। सी-एन, सी-सी, तथा सी-ओ सहित कई बॉन्ड-फॉर्मिंग घटनाएँ क्रमिक रूप से 2-एल्काइनिलरीलनाइट्राइल पर होती हैं, जिससे कमरे के तापमान पर 3-एमिनो-1-इंडेनोन कोर का निर्माण संभव होता है। परिवर्तन अच्छे सबस्ट्रेट स्कोप को प्रदर्शित करता है, जिससे उत्पाद अच्छी पैदावार देते हैं। संश्लेषित यौगिकों की प्रारंभिक जैविक जांच उनके शक्तिशाली कैंसर-रोधी गुण का संकेत देती है।

दृश्य प्रकाश विकिरण के तहत नई रणनीति विकसित करने के हमारे निरंतर प्रयासों के आधार पर, **अध्याय 3** में हम एमीनेटेड सी-3 एरिलोलेटेड बेंज़ोफ्यूरान, फ्यूरोपाइरीडीन, बेंज़ोथियोफीन और इंडोल डेरिवेटिव के संश्लेषण के लिए 1,6-एनीन के दृश्य प्रकाश से सहायता प्राप्त टेंडेम ऑक्सीडेटिव 5-एक्सो-डिग साइक्लाइजेशन की रिपोर्ट करते हैं। एन-एमिनोपाइरीडिनियम नमक से सीटू में उत्पन्न नाइट्रोजन-

केंद्रित रेडिकल सी-एन, सी-सी और सी-ओ बॉन्ड के क्रमिक गठन की शुरुआत करता है। कार्यप्रणाली अच्छी कार्यात्मक समूह सहिष्णुता और क्षेत्र-चयनात्मकता प्रदर्शित करती है, जो कमरे के तापमान पर अच्छे से उत्कृष्ट उपज वाले उत्पाद प्रदान करती है। संश्लेषित अणुओं की प्रारंभिक जैविक जांच से कैंसर विरोधी एजेंट के रूप में उनकी क्षमता का पता चलता है।

**अध्याय 4** में फोटोकैटैलिस्ट के रूप में पाइरिलियम नमक की उपस्थिति में 2-एल्काइनिलरीलनाइटाइल्स के धातु-मुक्त, फोटोऑक्सीडेटिव सक्रियण की रिपोर्ट की गई है। दृश्य प्रकाश में उत्पन्न 1,2-डाइकेटोन मध्यवर्ती चक्रीकरण की दिशा में आधार-सहायता प्राप्त ऑर्थोगोनैलिटी प्रदर्शित करता है, जो 4-एरिल-4-हाइड्रॉक्सीइसोक्विनोлин-1,3-(2*H*,4*H*)-डायऑन और 3-एरिल-3-हाइड्रॉक्सी-2,3-डायहाइड्रोएज़ानाफथोक्विनोन व्युत्पन्न प्रदान करता है। प्रतिक्रिया में व्यापक सबस्ट्रेट स्कोप, अच्छी कार्यात्मक समूह सहिष्णुता, एक कार्बनिक फोटोकैटैलिस्ट का उपयोग होता है, और यह कमरे के तापमान पर होता है। संश्लेषित अणुओं की प्रारंभिक जैविक जांच से कैंसर विरोधी एजेंट के रूप में उनकी क्षमता का पता चलता है।

**अध्याय 5** में हमने खुलासा किया कि  $\alpha$ -कीटो एसिड के साथ *N*-एरिल-7-एज़ैनडोल्स के निर्देशन समूह की सहायता से डीकार्बोक्सिलेटिव ऑर्थो-बेंज़ोयलेशन को सहक्रियात्मक दृश्य प्रकाश द्वारा प्रवर्तित फोटोरेडॉक्स और पैलेडियम कटैलिसीस द्वारा प्राप्त किया गया है। यह दृष्टिकोण सरल  $\alpha$ -कीटो एसिड अग्रदूतों से बेंज़ोयल रेडिकल इंटरमीडिएट की इन-सीटू पीढ़ी के माध्यम से एरिल कीटोन आर्किटेक्चर में तेजी से प्रवेश करता है। यह परिवर्तन ऑर्थो-बेंज़ोइलेटेड एन-एरिल-7-एज़ैनडोल्स की एक श्रृंखला प्रदान करता है, जिसमें हल्की प्रतिक्रिया स्थितियों के तहत उत्कृष्ट साइट-चयनात्मकता और अच्छी कार्यात्मक समूह संगतता होती है। जैविक लक्ष्य भविष्यवाणियों से संकेत मिलता है कि ये अणु संभावित कैंसर विरोधी और एंटी-वायरल एजेंट के रूप में काम कर सकते हैं।

## TABLE OF CONTENTS

|                                                                                                                                                                                       |          |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|
| CERTIFICATE .....                                                                                                                                                                     | I        |
| ACKNOWLEDGEMENTS .....                                                                                                                                                                | II       |
| ABSTRACT .....                                                                                                                                                                        | IV       |
| TABLE OF CONTENTS .....                                                                                                                                                               | VIII     |
| LIST OF SCHEMES .....                                                                                                                                                                 | XII      |
| LIST OF FIGURES .....                                                                                                                                                                 | XVI      |
| LIST OF TABLES .....                                                                                                                                                                  | XX       |
| GLOSSARY OF SYMBOLS AND ABBREVIATIONS .....                                                                                                                                           | XXIII    |
| <b>Chapter 1: Introduction .....</b>                                                                                                                                                  | <b>1</b> |
| 1.1. Introduction .....                                                                                                                                                               | 2        |
| 1.2. Photoredox catalysis .....                                                                                                                                                       | 2        |
| 1.2.1. The advent of photoredox catalysis .....                                                                                                                                       | 3        |
| 1.2.2. Photocatalyst .....                                                                                                                                                            | 4        |
| 1.2.3. Photophysical overview .....                                                                                                                                                   | 4        |
| 1.2.4. Photochemical processes .....                                                                                                                                                  | 5        |
| 1.2.4.1. Single electron transfer process (SET) .....                                                                                                                                 | 5        |
| 1.2.4.2. Energy transfer (ET) .....                                                                                                                                                   | 6        |
| 1.2.4.3. Hydrogen atom transfer (HAT) .....                                                                                                                                           | 7        |
| 1.2.4.4. Proton-coupled electron transfer (PCET) .....                                                                                                                                | 8        |
| 1.2.4.5. Electron-donor/acceptor (EDA) photoinduced electron transfer .....                                                                                                           | 8        |
| 1.2.5. Classification of photocatalyst .....                                                                                                                                          | 9        |
| 1.2.5.1. Homogeneous photocatalysts .....                                                                                                                                             | 9        |
| 1.2.5.2. Heterogenous photocatalysts .....                                                                                                                                            | 11       |
| 1.2.5.3. Photochemistry of photocatalysts .....                                                                                                                                       | 11       |
| 1.2.5.4. Transition-metal photoredox catalysts .....                                                                                                                                  | 11       |
| 1.2.5.5. Organophotoredox catalysts .....                                                                                                                                             | 13       |
| 1.2.6. Dual catalytic system .....                                                                                                                                                    | 15       |
| 1.2.6.1. Dual synergistic catalysis .....                                                                                                                                             | 16       |
| 1.3. Thesis overview .....                                                                                                                                                            | 18       |
| 1.3.1. Photoredox radical cascade cyclization of 2-alkynylarylnitriles in visible light: Direct access to 3-amino-1-indenones .....                                                   | 19       |
| 1.3.2. Synthesis of aminated C-3 aryloylated benzofuran, furopyridine, benzothiophene and indole derivatives from 1,6-enyne and <i>N</i> -aminopyridinium salt in visible light ..... | 19       |

|                                                                                                                                                                                           |            |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| 1.3.3. Base-assisted orthogonal synthesis of 4-arylisquinolinediones and aza-naphthoquinones from 2-alkynylarylnitriles <i>via</i> photoactivation by pyrylium salt in visible light..... | 20         |
| 1.3.4. Pd and photoredox dual catalysis assisted decarboxylative <i>ortho</i> -benzoylation of <i>N</i> -phenyl-7-azaindoles .....                                                        | 20         |
| 1.4. References .....                                                                                                                                                                     | 22         |
| <b>Chapter 2: Photoredox radical cascade cyclization of 2-alkynylarylnitriles in visible light: Direct access to 3-amino-1-indenones .....</b>                                            | <b>24</b>  |
| 2.1. Introduction .....                                                                                                                                                                   | 25         |
| 2.2. Results and Discussion.....                                                                                                                                                          | 28         |
| 2.3. Biological studies .....                                                                                                                                                             | 35         |
| 2.4. Conclusion.....                                                                                                                                                                      | 37         |
| 2.5. Experimental section .....                                                                                                                                                           | 38         |
| 2.5.1. General information .....                                                                                                                                                          | 38         |
| 2.5.2. General procedure .....                                                                                                                                                            | 39         |
| 2.5.3. Mechanistic investigation.....                                                                                                                                                     | 42         |
| 2.5.3.1. Free-radical trapping experiments .....                                                                                                                                          | 42         |
| 2.5.3.2. Electron paramagnetic resonance spectroscopic studies .....                                                                                                                      | 44         |
| 2.5.3.3. Stern-volmer study: Fluorescence quenching experiments .....                                                                                                                     | 45         |
| 2.5.3.4. Cyclic voltammetry .....                                                                                                                                                         | 46         |
| 2.5.3.5. Quantum Yield Determination.....                                                                                                                                                 | 46         |
| 2.5.3.6. Crystallographic description of compound <b>3c</b> .....                                                                                                                         | 49         |
| 2.5.4. Physical properties and characterization of compounds .....                                                                                                                        | 50         |
| 2.5.5. Copies of $^1\text{H}$ , $^{13}\text{C}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of synthesized compounds .....                                                | 63         |
| 2.6. References .....                                                                                                                                                                     | 104        |
| <b>Chapter 3: Synthesis of aminated C-3 aryloylated benzofuran, furopyridine, benzothiophene and indole derivatives from 1,6-enyne and N-aminopyridinium salt in visible light.....</b>   | <b>108</b> |
| 3.1. Introduction .....                                                                                                                                                                   | 109        |
| 3.2. Results and Discussion.....                                                                                                                                                          | 113        |
| 3.3. Biological studies .....                                                                                                                                                             | 121        |
| 3.4. Conclusion.....                                                                                                                                                                      | 122        |
| 3.5. Experimental section .....                                                                                                                                                           | 122        |
| 3.5.1. General Information .....                                                                                                                                                          | 122        |
| 3.5.2. General procedure .....                                                                                                                                                            | 123        |
| 3.5.3. Mechanistic investigation.....                                                                                                                                                     | 129        |
| 3.5.3.1 Free radical trapping experiments .....                                                                                                                                           | 129        |

|                                                                                                                                                                                               |     |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 3.5.3.2. Carbocation trapping by thiophenol (PhSH) .....                                                                                                                                      | 132 |
| 3.5.3.3. Electron paramagnetic resonance spectroscopic studies .....                                                                                                                          | 132 |
| 3.5.3.4 Stern-Volmer study: Fluorescence quenching experiments.....                                                                                                                           | 133 |
| 3.5.3.5. Cyclic voltammetry .....                                                                                                                                                             | 134 |
| 3.5.3.6. Quantum yield determination .....                                                                                                                                                    | 135 |
| 3.5.3.7. Detection of hydrogen gas by headspace-GC.....                                                                                                                                       | 138 |
| 3.5.3.8. <i>In situ</i> IR analysis .....                                                                                                                                                     | 138 |
| 3.5.3.9. Crystallographic description of compound <b>3a</b> .....                                                                                                                             | 140 |
| 3.5.4. Physical properties and characterization of compounds .....                                                                                                                            | 141 |
| 3.5.5. Copies of $^1\text{H}$ , $^{13}\text{C}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of synthesized compounds .....                                                    | 155 |
| 3.6. References .....                                                                                                                                                                         | 202 |
| <b>Chapter 4: Base-assisted orthogonal synthesis of 4-arylisquinolinediones and azanaphthoquinones from 2-alkynylarylnitriles via photoactivation by pyrylium salt in visible light</b> ..... | 204 |
| 4.1. Introduction .....                                                                                                                                                                       | 205 |
| 4.2. Result and Discussion .....                                                                                                                                                              | 207 |
| 4.3. Biological studies .....                                                                                                                                                                 | 216 |
| 4.4. Conclusion.....                                                                                                                                                                          | 217 |
| 4.5. Experimental section.....                                                                                                                                                                | 217 |
| 4.5.1. General information .....                                                                                                                                                              | 217 |
| 4.5.2. General Procedure .....                                                                                                                                                                | 218 |
| 4.5.3. Mechanistic investigation.....                                                                                                                                                         | 221 |
| 4.5.3.1. Free-radical trapping experiments .....                                                                                                                                              | 221 |
| 4.5.3.2. Detection of singlet oxygen by 1,3-diphenylisobenzofuran (DPBF) .....                                                                                                                | 221 |
| 4.5.3.3. Superoxide radical anion quenching experiment.....                                                                                                                                   | 221 |
| 4.5.3.4. Electron paramagnetic resonance spectroscopic studies .....                                                                                                                          | 222 |
| 4.5.3.5. Stern-Volmer study: Fluorescence quenching experiments.....                                                                                                                          | 222 |
| 4.5.3.6. Cyclic voltammetry .....                                                                                                                                                             | 223 |
| 4.5.3.7. Quantum yield determination .....                                                                                                                                                    | 224 |
| 4.5.3.8. D <sub>2</sub> O exchange experiment .....                                                                                                                                           | 226 |
| 4.5.3.9. Detection of intermediate <b>1a'</b> .....                                                                                                                                           | 228 |
| 4.5.3.10. <i>In situ</i> IR analysis .....                                                                                                                                                    | 228 |
| 4.5.3.11. Reaction of <b>3a</b> with KOH .....                                                                                                                                                | 229 |
| 4.5.3.12. Crystallographic description of compound <b>2b</b> .....                                                                                                                            | 230 |
| 4.5.4. Physical properties and characterization of compounds .....                                                                                                                            | 232 |
| 4.5.5. Copies of $^1\text{H}$ and $^{13}\text{C}\{^1\text{H}\}$ and $^{19}\text{F}$ NMR spectra of synthesized compounds.....                                                                 | 242 |

|                                                                                                                                                   |            |
|---------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| 4.6. References .....                                                                                                                             | 285        |
| <b>Chapter 5: Pd and photoredox dual catalysis assisted decarboxylative ortho-benzoylation of N-phenyl-7-azaindoles .....</b>                     | <b>287</b> |
| 5.1. Introduction .....                                                                                                                           | 288        |
| 5.2. Results and Discussion.....                                                                                                                  | 293        |
| 5.3. Biological target and binding affinity predictions.....                                                                                      | 298        |
| 5.4. Conclusion.....                                                                                                                              | 299        |
| 5.5. Experimental Section .....                                                                                                                   | 300        |
| 5.5.1. General Information .....                                                                                                                  | 300        |
| 5.5.2. General Procedure .....                                                                                                                    | 300        |
| 5.5.3. Mechanistic investigation.....                                                                                                             | 303        |
| 5.5.3.1. Free-radical trapping with TEMPO .....                                                                                                   | 303        |
| 5.5.3.2. Superoxide radical anion trapping experiment.....                                                                                        | 303        |
| 5.5.3.3. Quantum yield determination .....                                                                                                        | 304        |
| 5.5.3.3. Detection of carbon dioxide (Monitoring reaction by HSGC).....                                                                           | 306        |
| 5.5.3.4. Cyclic voltammetry .....                                                                                                                 | 306        |
| 5.5.3.5. Stern-Volmer study: Fluorescence quenching experiments.....                                                                              | 307        |
| 5.5.3.6. H <sub>2</sub> O <sub>2</sub> Detection Using hydrogen peroxide test strips <sup>40</sup> .....                                          | 308        |
| 5.5.3.7. Crystallographic description of compound <b>3r</b> .....                                                                                 | 308        |
| 5.5.4. Physical properties and characterization of compounds .....                                                                                | 310        |
| 5.5.5. Copies of <sup>1</sup> H, <sup>13</sup> C{ <sup>1</sup> H} and <sup>19</sup> F{ <sup>1</sup> H} NMR spectra of synthesized compounds ..... | 322        |
| 5.6. References .....                                                                                                                             | 356        |
| <i>Curriculum Vitae</i> .....                                                                                                                     | 360        |

## LIST OF SCHEMES

### Chapter 1

|                                                                                                                 |    |
|-----------------------------------------------------------------------------------------------------------------|----|
| Scheme 1.1. Reduction of phenacyl sulfonium salt .....                                                          | 3  |
| Scheme 1.2. Photocatalytic Pschorr reaction .....                                                               | 3  |
| Scheme 1.3. Reductive decarboxylation of redox-active esters .....                                              | 3  |
| Scheme 1.4. [2+2] Enone cycloaddition .....                                                                     | 4  |
| Scheme 1.5. State energy diagram .....                                                                          | 5  |
| Scheme 1.6. Single electron transfer process.....                                                               | 6  |
| Scheme 1.7. Energy transfer process .....                                                                       | 7  |
| Scheme 1.8. Hydrogen atom transfer process (a) Direct HAT; (b) Indirect HAT .....                               | 7  |
| Scheme 1.9. Proton-coupled electron transfer process .....                                                      | 8  |
| Scheme 1.10. Photoexcitation of electron donor-acceptor complexes.....                                          | 9  |
| Scheme 1.11. Homogeneous photocatalysts .....                                                                   | 10 |
| Scheme 1.12. Utilized homogeneous photocatalysts .....                                                          | 11 |
| Scheme 1.13. Simplified molecular orbital presentation of Ir(ppy) <sub>3</sub> photochemistry .....             | 12 |
| Scheme 1.14. Photochemistry of Eosin Y .....                                                                    | 13 |
| Scheme 1.15. Acid base reactions of Eosin Y .....                                                               | 14 |
| Scheme 1.16. Different pyrylium salts.....                                                                      | 15 |
| Scheme 1.17. The merger of Pd and photoredox catalysis enables arene C-H arylation with<br>diazonium salts..... | 17 |
| Scheme 1.18. General mechanism of metallaphotocatalysis .....                                                   | 18 |

### Chapter 2

|                                                                                                             |    |
|-------------------------------------------------------------------------------------------------------------|----|
| Scheme 2.1. Radical cascade cyclization of 2-alkynylarylnitriles with sulfonyl hydrazides ..                | 25 |
| Scheme 2.2. Radical cascade cyclization of <i>o</i> -alkynylbenzonitriles with sulfonyl hydrazides<br>..... | 26 |
| Scheme 2.3. Radical cascade cyclization of <i>o</i> -alkynylbenzonitriles with aryl sulfinates.....         | 26 |
| Scheme 2.4. Radical cascade cyclization of <i>o</i> -alkynylbenzonitriles with phosphine oxides ..          | 26 |



|                                                                                                   |    |
|---------------------------------------------------------------------------------------------------|----|
| Scheme 2.5. Radical cascade cyclization of <i>o</i> -alkynylarylnitriles with cyclic ethers ..... | 26 |
| Scheme 2.6. Bioactive drugs containing 1-indenone core .....                                      | 27 |
| Scheme 2.7. Synthesis of 3-amino-1-indenone.....                                                  | 27 |
| Scheme 2.8. Our work: Photoredox radical cascade cyclization of 2-alkynylarylnitriles .....       | 28 |
| Scheme 2.9. Substrate scope with 2-alkynylarylnitriles <sup>a,b</sup> .....                       | 32 |
| Scheme 2.10. Substrate scope with <i>N</i> -protected-1-aminopyridinium salt <sup>a,b</sup> ..... | 33 |
| Scheme 2.11. Control experiments .....                                                            | 34 |
| Scheme 2.12. Plausible mechanism .....                                                            | 35 |
| Scheme 2.13. Synthesized 2-alkynylarylnitriles <b>1a-1v</b> .....                                 | 40 |
| Scheme 2.14. Synthesis of <i>N</i> -protected-1-aminopyridinium salt .....                        | 40 |
| Scheme 2.15. Synthesized <i>N</i> -protected-1-aminopyridinium salts <b>2a-2j</b> .....           | 41 |

### Chapter 3

|                                                                                                     |     |
|-----------------------------------------------------------------------------------------------------|-----|
| Scheme 3.1. Bioactive drugs containing C-3 aryloylated core .....                                   | 109 |
| Scheme 3.2. Oxy-trifluoromethylation of 1,6-enynes with Langloi's reagent .....                     | 109 |
| Scheme 3.3. Trifluoromethylation of 1,6-enynes with Togni's reagent.....                            | 110 |
| Scheme 3.4. Difluoromethylation of 1,6-enynes with difluoromethyltriphenylphosphonium bromide ..... | 110 |
| Scheme 3.5. Visible light mediated cyclization of 1,6-enynes with bromomalonates .....              | 110 |
| Scheme 3.6. Visible light mediated [2+2+1] annulation of 1,6-enynes with bromomalonates .....       | 111 |
| Scheme 3.7. Visible light induced cyclization of 1,6-enynes with arylsulfonic acids.....            | 111 |
| Scheme 3.8. Visible light induced cyclization of 1,6-enynes with disulfides.....                    | 111 |
| Scheme 3.9. Visible light mediated cyclization of 1,6-enynes with arylsulfonyl azides .....         | 111 |
| Scheme 3.10. Visible light mediated cyclization of 1,6-enynes with thiosulfonates.....              | 112 |
| Scheme 3.11. Nitrate cyclization of 1,6-enynes using <i>tert</i> -butyl nitrile .....               | 112 |
| Scheme 3.12. Electrochemical annulation of 1,6-enynes and disulfonimides.....                       | 113 |

|                                                                                                                          |     |
|--------------------------------------------------------------------------------------------------------------------------|-----|
| Scheme 3.13. Our work: Photoredox radical cascade cyclization of 1,6-enynes with <i>N</i> -aminopyridinium salt .....    | 113 |
| Scheme 3.14. Substrate scope with 2-vinyloxy arylalkynes <sup>a,b</sup> .....                                            | 117 |
| Scheme 3.15. Substrate scope with benzenethiol-linked and <i>N</i> -tosyl (Ts) protected 1,6-enynes <sup>a,b</sup> ..... | 118 |
| Scheme 3.16. Substrate scope with <i>N</i> -protected 1-aminopyridinium salt <sup>a,b</sup> .....                        | 119 |
| Scheme 3.17. Plausible mechanism .....                                                                                   | 120 |
| Scheme 3.18. Synthesis of <b>1a</b> .....                                                                                | 123 |
| Scheme 3.19. Synthesized compounds <b>1b-1q</b> .....                                                                    | 124 |
| Scheme 3.20. Synthesis of <b>1r</b> .....                                                                                | 125 |
| Scheme 3.21. Synthesized compounds <b>1s-1x</b> .....                                                                    | 126 |
| Scheme 3.23. Synthesized compound <b>1z</b> .....                                                                        | 127 |
| Scheme 3.24. Synthesis of <i>N</i> -aminopyridinium salt .....                                                           | 128 |
| Scheme 3.25. Synthesized <i>N</i> -aminopyridinium salts <b>2a-2j</b> .....                                              | 128 |

## Chapter 4

|                                                                                                                                                                                             |     |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Scheme 4.1. Radical cascade cyclization of 2-alkynylarylnitrile under thermal conditions .                                                                                                  | 205 |
| Scheme 4.2. Radical cascade cyclization of 2-alkynylarylnitrile in visible light .....                                                                                                      | 205 |
| Scheme 4.3. Bioactive molecule containing isoquinoline-1,3-dione core .....                                                                                                                 | 206 |
| Scheme 4.4. Synthesis of 4-aryl-4-hydroxyisoquinoline-1,3-(2 <i>H</i> ,4 <i>H</i> )-dione.....                                                                                              | 206 |
| Scheme 4.5. Synthesis of 3-aryl-3-hydroxyisoquinoline-1,4-(2 <i>H</i> ,3 <i>H</i> )-dione.....                                                                                              | 206 |
| Scheme 4.6. Visible light-mediated synthesis of 4-aryl-4-hydroxyisoquinoline-1,3-(2 <i>H</i> ,4 <i>H</i> )-dione and 3-aryl-3-hydroxyisoquinoline-1,4-(2 <i>H</i> ,3 <i>H</i> )-dione ..... | 207 |
| Scheme 4.7. Substrate scope for 4-hydroxy-4-arylisoquinolinedione derivatives <sup>a,b</sup> .....                                                                                          | 212 |
| Scheme 4.8. Substrate scope for azanapthaquinone derivatives <sup>a,b</sup> .....                                                                                                           | 213 |
| Scheme 4.9. Control experiments .....                                                                                                                                                       | 214 |
| Scheme 4.10. Proposed mechanism.....                                                                                                                                                        | 215 |
| Scheme 4.11. Synthesized 2-alkynylarylnitriles <b>1a-1w</b> .....                                                                                                                           | 219 |

## Chapter 5

|                                                                                                                                          |     |
|------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Scheme 5.1. Bioactive compounds containing 7-azaindole core.....                                                                         | 288 |
| Scheme 5.2. Overview of literature reports on <i>ortho</i> -selective functionalization of <i>N</i> -phenyl-7-azaindoles .....           | 289 |
| Scheme 5.3. Ruthenium catalyzed <i>ortho</i> -selective cyanation and aminocarbonylation of <i>N</i> -aryl-7-azaindoles.....             | 289 |
| Scheme 5.4. Iridium catalyzed <i>ortho</i> -selective alkynylation, phosphoramidation and amidation of <i>N</i> -aryl-7-azaindoles ..... | 290 |
| Scheme 5.5. Rhodium catalyzed <i>ortho</i> -selective C-C bond formation of <i>N</i> -aryl-7-azaindoles .....                            | 290 |
| Scheme 5.6. Rhodium catalyzed <i>ortho</i> -selective C-C bond formation and functionalization of <i>N</i> -aryl-7-azaindoles.....       | 291 |
| Scheme 5.7. Rhodium catalyzed <i>ortho</i> -selective chalcogenation, amination and chlorination of <i>N</i> -aryl-7-azaindoles .....    | 292 |
| Scheme 5.8. Palladium catalyzed <i>ortho</i> -nitration of <i>N</i> -aryl -7-azaindoles.....                                             | 292 |
| Scheme 5.9. Our work: Photoredox assisted <i>ortho</i> -benzoylation of <i>N</i> -phenyl-7-azaindoles                                    | 293 |
| Scheme 5.10. Substrate scope with <i>N</i> -phenyl-7-azaindoles <sup>a,b</sup> .....                                                     | 296 |
| Scheme 5.11. Scope of $\alpha$ -keto acids <sup>a,b</sup> .....                                                                          | 296 |
| Scheme 5.12. Control experiments .....                                                                                                   | 297 |
| Scheme 5.13. Plausible mechanism .....                                                                                                   | 298 |
| Scheme 5.14. Synthesized <i>N</i> -phenyl-7-indoles <b>1a-1u</b> .....                                                                   | 301 |
| Scheme 5.15. Synthesis of $\alpha$ -keto carboxylic acids.....                                                                           | 301 |
| Scheme 5.16. Synthesized $\alpha$ -keto carboxylic acids <b>2a-2i</b> .....                                                              | 302 |

## LIST OF FIGURES

### Chapter 1

|                                                     |    |
|-----------------------------------------------------|----|
| Figure 1.1. Heterogeneous photocatalyst mpg-CN..... | 11 |
| Figure 1.2. Dual catalytic system.....              | 16 |
| Figure 1.3. Dual synergistic catalysis .....        | 17 |

### Chapter 2

|                                                                                                                                                                                                                                                         |    |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 2.1. <i>In-vitro</i> cytotoxicity studies. (A) % Cell growth inhibition plot of <b>3a</b> and <b>4h</b> on triple negative SUM-149 cells. (B) % Cell growth inhibition plot of <b>3a</b> and <b>4h</b> on triple negative MDA-MB-468 cells ..... | 36 |
| Figure 2.2. Biocompatibility evaluation of <b>3a</b> and <b>4h</b> on L929 cells .....                                                                                                                                                                  | 37 |
| Figure 2.3. HRMS of the reaction mixture .....                                                                                                                                                                                                          | 43 |
| Figure 2.4. HRMS of the reaction mixture .....                                                                                                                                                                                                          | 44 |
| Figure 2.5. EPR spectrum of <i>N</i> -aminopyridinium salt <b>2a</b> with spin trap (DMPO) .....                                                                                                                                                        | 44 |
| Figure 2.6. HRMS of the reaction mixture .....                                                                                                                                                                                                          | 45 |
| Figure 2.7. (A) Luminescence quenching of <i>fac</i> -Ir(ppy) <sub>3</sub> by <b>2a</b> ; (B) Luminescence quenching of <i>fac</i> -Ir(ppy) <sub>3</sub> by <b>1a</b> .....                                                                             | 45 |
| Figure 2.8. Stern-volmer plots of <i>fac</i> -Ir(ppy) <sub>3</sub> quenching with <b>2a</b> and <b>1a</b> .....                                                                                                                                         | 46 |
| Figure 2.9. (A) Cyclic Voltammetry curve for <b>1a</b> ; (B) Cyclic Voltammetry curve for <b>2a</b> .....                                                                                                                                               | 46 |
| Figure 2.10. UV-visible spectra of the irradiated and non-irradiated ferrioxalate solution after interacted with buffered solution of phenanthroline .....                                                                                              | 47 |
| Figure 2.11. UV-visible spectrum of ferrioxalate solution .....                                                                                                                                                                                         | 47 |
| Figure 2.12. UV-visible spectrum of <i>fac</i> -Ir(ppy) <sub>3</sub> .....                                                                                                                                                                              | 48 |
| Figure 2.13. ORTEP diagram of compound <b>3c</b> (with 20% probability ellipsoids).....                                                                                                                                                                 | 49 |

### Chapter 3

|                                                                                                                                                                                                                                            |     |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 3.1. % Cell growth inhibition plot of <b>3a</b> , <b>3n</b> , <b>4a</b> , <b>4h</b> , and <b>5c</b> on triple negative SUM-149, MDA-MB-468, MDA-MB-231 breast cancer cells, A549 lung cancer cells, MCF-7 breast cancer cells ..... | 121 |
| Figure 3.2. HRMS of the reaction mixture .....                                                                                                                                                                                             | 130 |

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |     |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 3.3. HRMS of the reaction mixture .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 131 |
| Figure 3.4. HRMS of the reaction mixture .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 131 |
| Figure 3.5. HRMS of the reaction mixture .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 132 |
| Figure 3.6. EPR spectrum of <i>N</i> -aminopyridinium salt <b>2a</b> with spin trap (DMPO) .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | 133 |
| Figure 3.7. HRMS of the reaction mixture .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 133 |
| Figure 3.8. (A) Luminescence quenching of <i>fac</i> -Ir(ppy) <sub>3</sub> by <b>2a</b> ; (B) Luminescence quenching of <i>fac</i> -Ir(ppy) <sub>3</sub> by <b>1a</b> .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 134 |
| Figure 3.9. Stern-volmer plots of <i>fac</i> -Ir(ppy) <sub>3</sub> quenching with <b>2a</b> and <b>1a</b> .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | 134 |
| Figure 3.10. (A) Cyclic voltammetry curve for <b>1a</b> under N <sub>2</sub> (IUPAC Convention); (B) Cyclic voltammetry curve for <b>2a</b> under N <sub>2</sub> (IUPAC plotting convention) voltammograms were recorded in 0.1 M n-Bu <sub>4</sub> NPF <sub>6</sub> solution at a scan rate of 100 mV/s with 2.0 mm circular glassy carbon (surface area = 3.14 mm <sup>2</sup> ) in DMSO, Pt wire as a counter electrode, and Ag/AgCl in saturated KCl as a reference electrode. ....                                                                                                                                                            | 135 |
| Figure 3.11. UV-visible spectra of the irradiated and non-irradiated ferrioxalate solution after interacted with buffered solution of phenanthroline .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 136 |
| Figure 3.12. UV-visible spectrum of Ferrioxalate solution .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | 136 |
| Figure 3.13. UV-visible spectrum of <i>fac</i> -Ir(ppy) <sub>3</sub> in DMSO .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | 137 |
| Figure 3.14. Headspace GC analysis for hydrogen gas (H <sub>2</sub> ) evolved during the reaction ....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | 138 |
| Figure 3.15. <i>In situ</i> IR monitoring of the reaction, reaction conditions = <b>1a</b> : <b>2a</b> (1:1.2) on a 0.1 mmol scale, <i>fac</i> -Ir(ppy) <sub>3</sub> (1.0 mol%), DMSO = 2 mL, 50 W blue LED, rt, open-air, 7 h. (a) Reaction progress with decreasing intensity of 1450 cm <sup>-1</sup> C=C stretching band for <b>1a</b> ; (b) Reaction progress with decreasing intensity of 1376 cm <sup>-1</sup> C-O stretching band for intermediate <b>F</b> ; (c) Reaction progress with increasing intensity of 1530 cm <sup>-1</sup> C=O stretching band for product <b>3a</b> ; (d) 2D representation of reaction profile for 7 h ..... | 139 |
| Figure 3.16. ORTEP diagram of compound <b>3a</b> (with 50% probability ellipsoids) .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 140 |

## Chapter 4

Figure 4.1. (A) Sigmoidal dose–response curves of all tested derivatives in triple-negative breast cancer MDA-MB-468 cells. (B) Comparative IC<sub>50</sub> values of the derivatives following

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |     |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| treatment at 100 $\mu$ M concentration in MDA-MB-468 cells. Data are presented as mean $\pm$ SD (n = 3). Statistical significance was determined with $p < 0.1$ considered non-significant ....                                                                                                                                                                                                                                                                                | 216 |
| Figure 4.2. EPR spectrum of reaction mixture with spin trap (DMPO) .....                                                                                                                                                                                                                                                                                                                                                                                                       | 222 |
| Figure 4.3. (A) Luminescence quenching of T( <i>p</i> -Me)PPT by <b>1a</b> ; (B) Stern-Volmer plot of T( <i>p</i> -Me)PPT quenching with <b>1a</b> .....                                                                                                                                                                                                                                                                                                                       | 223 |
| Figure 4.4. Luminescence quenching of T( <i>p</i> -Me)PPT by nitrogen and oxygen.....                                                                                                                                                                                                                                                                                                                                                                                          | 223 |
| Figure 4.5. Cyclic voltammetry curve (A) 2,4,6-tri- <i>p</i> -tolylpyrylium tetrafluoroborate (T( <i>p</i> -Me)PPT) and (B) 2-(phenylethynyl)benzonitrile <b>1a</b> under N <sub>2</sub> (IUPAC Plotting Convention) Voltammogram was recorded in 0.1 M n-Bu <sub>4</sub> NPF <sub>6</sub> solution at a scan rate of 0.1 V/s with 3.0 mm circular glassy carbon electrode in MeCN, Pt wire as a counter electrode, and Ag/AgCl in saturated KCl as a reference electrode..... | 224 |
| Figure 4.6. (A) UV-visible spectra of the irradiated and non-irradiated ferrioxalate solution after interacted with buffered solution of phenanthroline; (B) UV-visible spectra of Ferrioxalate solution. ....                                                                                                                                                                                                                                                                 | 225 |
| Figure 4.7. UV-visible spectra of T( <i>p</i> -Me)PPT .....                                                                                                                                                                                                                                                                                                                                                                                                                    | 226 |
| Figure 4.8. D <sub>2</sub> O exchange spectra for <b>2a</b> .....                                                                                                                                                                                                                                                                                                                                                                                                              | 227 |
| Figure 4.9. D <sub>2</sub> O exchange spectra for <b>3a</b> .....                                                                                                                                                                                                                                                                                                                                                                                                              | 227 |
| Figure 4.10. <i>In situ</i> IR monitoring of the reaction .....                                                                                                                                                                                                                                                                                                                                                                                                                | 229 |
| Figure 4.11. ORTEP diagram of compound <b>2b</b> (with 50% probability ellipsoids) .....                                                                                                                                                                                                                                                                                                                                                                                       | 230 |

## Chapter 5

|                                                                                                                                                                                                                 |     |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 5.1. LigTMap based binding target and affinity prediction of selected compounds..                                                                                                                        | 299 |
| Figure 5.2. HRMS of the reaction mixture .....                                                                                                                                                                  | 303 |
| Figure 5.3. (A) UV-visible spectra of the irradiated and non-irradiated ferrioxalate solution after interacting with buffered solution of phenanthroline; (B) UV-visible spectra of Ferrioxalate solution ..... | 304 |
| Figure 5.4. UV-visible spectra of Eosin Y .....                                                                                                                                                                 | 305 |
| Figure 5.5. Calibration curve for CO <sub>2</sub> estimation .....                                                                                                                                              | 306 |
| Figure 5.6. Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) show oxidation (A) and reduction (B) potential values of <b>1a</b> .....                                                           | 307 |

|                                                                                                                           |     |
|---------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 5.7. (A) Luminescence quenching of Eosin Y by <b>2a</b> ; (B) Luminescence quenching of Eosin Y by <b>1a</b> ..... | 307 |
| Figure 5.8. Stern-volmer plots of Eosin Y quenching with <b>2a</b> and <b>1a</b> .....                                    | 308 |
| Figure 5.9. H <sub>2</sub> O <sub>2</sub> detection using hydrogen peroxide strips.....                                   | 308 |
| Figure 5.10. ORTEP diagram of compound <b>3r</b> (with 40% probability ellipsoids).....                                   | 309 |

## LIST OF TABLES

### Chapter 1

|                                                                          |    |
|--------------------------------------------------------------------------|----|
| Table 1.1. Examples of homogeneous and heterogeneous photocatalysts..... | 9  |
| Table 1.2. Redox potentials of different homogeneous photocatalysts..... | 10 |

### Chapter 2

|                                                                       |    |
|-----------------------------------------------------------------------|----|
| Table 2.1. Selected optimization studies.....                         | 29 |
| Table 2.2. Optimization of photocatalyst .....                        | 30 |
| Table 2.3. Optimization of solvent.....                               | 30 |
| Table 2.4. Optimization of light source and reaction atmosphere ..... | 31 |
| Table 2.5. Optimization of additive .....                             | 31 |
| Table 2.6. Optimization of stoichiometry of substrates .....          | 31 |
| Table 2.7. IC <sub>50</sub> value for <b>3a</b> and <b>4h</b> .....   | 36 |
| Table 2.8. Crystallographic description of <b>3c</b> .....            | 49 |

### Chapter 3

|                                                                                                           |     |
|-----------------------------------------------------------------------------------------------------------|-----|
| Table 3.1. Selected optimization studies.....                                                             | 114 |
| Table 3.2. Optimization of photocatalyst .....                                                            | 115 |
| Table 3.3. Optimization of solvent.....                                                                   | 115 |
| Table 3.4. Optimization of light source and reaction atmosphere .....                                     | 116 |
| Table 3.5. Optimization of additive .....                                                                 | 116 |
| Table 3.6. Optimization of stoichiometry of substrates .....                                              | 116 |
| Table 3.7. IC <sub>50</sub> value for <b>3a</b> , <b>3n</b> , <b>4a</b> , <b>4h</b> , and <b>5c</b> ..... | 122 |
| Table 3.8. Crystallographic description of <b>3a</b> .....                                                | 140 |

### Chapter 4

|                                                                                               |     |
|-----------------------------------------------------------------------------------------------|-----|
| Table 4.1. Optimization studies .....                                                         | 208 |
| Table 4.2. Optimization of base for the formation of <b>3a</b> .....                          | 210 |
| Table 4.3. Optimization of time for intermediate formation.....                               | 211 |
| Table 4.4. IC <sub>50</sub> value for <b>2b</b> , <b>2d</b> , <b>3a</b> , and <b>3j</b> ..... | 217 |



|                                                            |     |
|------------------------------------------------------------|-----|
| Table 4.5. Crystallographic description of <b>2b</b> ..... | 230 |
|------------------------------------------------------------|-----|

## **Chapter 5**

|                                               |     |
|-----------------------------------------------|-----|
| Table 5.1. Selected optimization studies..... | 294 |
|-----------------------------------------------|-----|

|                                                            |     |
|------------------------------------------------------------|-----|
| Table 5.2. Crystallographic description of <b>3r</b> ..... | 309 |
|------------------------------------------------------------|-----|

## GLOSSARY OF SYMBOLS AND ABBREVIATIONS

|                                        |                                                 |
|----------------------------------------|-------------------------------------------------|
| Ac                                     | Acetyl                                          |
| Al <sub>2</sub> O <sub>3</sub>         | Aluminium oxide                                 |
| Ag                                     | Silver                                          |
| AgNO <sub>3</sub>                      | Silver nitrate                                  |
| AgSbF <sub>6</sub>                     | Silver hexafluoroantimonate                     |
| Ag <sub>2</sub> O                      | Silver oxide                                    |
| AgCl                                   | Silver chloride                                 |
| AgOTf                                  | Silver trifluoromethanesulfonate                |
| BHT                                    | Butylated hydroxytoluene                        |
| BQ                                     | Benzoquinone                                    |
| CCDC                                   | Cambridge crystallographic data centre          |
| CDCl <sub>3</sub>                      | Deuterated chloroform                           |
| CH <sub>3</sub> CN                     | Acetonitrile                                    |
| Cu(OTf) <sub>2</sub>                   | Copper triflate                                 |
| CuCl                                   | Copper (II) chloride                            |
| CV                                     | Cyclic voltammetry                              |
| Cu(OAc) <sub>2</sub>                   | Copper acetate                                  |
| CsOAc                                  | Cesium acetate                                  |
| Cs <sub>2</sub> CO <sub>3</sub>        | Cesium carbonate                                |
| CuCl <sub>2</sub>                      | Copper (II) chloride                            |
| CHCl <sub>3</sub>                      | Chloroform                                      |
| CF <sub>3</sub> CO <sub>2</sub> Ag     | Silver trifluoroacetate                         |
| CuI                                    | Copper (I) iodide                               |
| CIDNP                                  | Chemically Induced Dynamic Nuclear Polarization |
| CdS                                    | Cadmium sulfide                                 |
| DABCO                                  | 1,4-Diazabicyclo[2.2.2]octane                   |
| DBU                                    | 1,8-Diazabicyclo[5.4.0]undec-7-ene              |
| DCE                                    | Dichloroethane                                  |
| DCM or CH <sub>2</sub> Cl <sub>2</sub> | Dichloromethane                                 |
| DDQ                                    | 2,3-dichloro-5,6-dicyano-1,4-benzoquinone       |
| DIPEA                                  | Diisopropyl ethyl amine                         |

---

|                                |                                        |
|--------------------------------|----------------------------------------|
| DMA                            | Dimethyl acetamide                     |
| DMAP                           | 4-dimethylaminopyridine                |
| DMF                            | Dimethyl formamide                     |
| DMSO                           | Dimethyl sulfoxide                     |
| DMSO- <i>d</i> <sub>6</sub>    | Deuterated dimethyl sulfoxide          |
| DIPEA                          | Diisopropylethylamine                  |
| DMPO                           | 5,5-Dimethyl-1-pyrroline N-oxide       |
| DMA                            | Dimethylacetamide                      |
| DMEM                           | Dulbecco's modified Eagle's medium     |
| EPR                            | Electron paramagnetic resonance        |
| Equiv.                         | Equivalent                             |
| ET                             | Energy transfer                        |
| Et                             | Ethyl                                  |
| Et <sub>3</sub> N              | Triethylamine                          |
| EtOH                           | Ethanol                                |
| EtOAc                          | Ethylacetate                           |
| E                              | Electrophile                           |
| EY                             | Eosin Y                                |
| <i>fac</i>                     | Facial                                 |
| h                              | Hour                                   |
| H <sub>2</sub> O <sub>2</sub>  | Hydrogen peroxide                      |
| HAT                            | Hydrogen atom transfer                 |
| HCl                            | Hydrochloric acid                      |
| HOMO                           | Highest occupied molecular orbital     |
| HPLC                           | High performance liquid chromatography |
| HRMS                           | High resolution mass spectrometry      |
| Hz                             | Hertz                                  |
| HFIP                           | Hexafluoroisopropanol                  |
| H <sub>2</sub> O               | Water                                  |
| HSGC                           | Headspace gas chromatography           |
| H <sub>2</sub> SO <sub>4</sub> | Sulfuric acid                          |
| IC                             | Internal conversion                    |
| ISC                            | Intersystem crossing                   |

|                                              |                                     |
|----------------------------------------------|-------------------------------------|
| K <sub>2</sub> CO <sub>3</sub>               | Potassium carbonate                 |
| K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> | Potassium persulfate                |
| K <sub>3</sub> PO <sub>4</sub>               | Potassium phosphate                 |
| KOAc                                         | Potassium acetate                   |
| KCl                                          | Potassium chloride                  |
| KOH                                          | Potassium hydroxide                 |
| KO <sup>t</sup> Bu                           | Potassium <i>tert</i> -butoxide     |
| LED                                          | Light emitting diode                |
| LUMO                                         | Lowest unoccupied molecular orbital |
| LiI                                          | Lithium iodide                      |
| m/z                                          | Mass by charge ratio                |
| Mpg-CN                                       | Mesoporous graphitic carbon nitride |
| Me                                           | Methyl                              |
| mg                                           | Milligram                           |
| min                                          | Minutes                             |
| mL                                           | Mililitre                           |
| MLCT                                         | Metal to ligand charge transfer     |
| MeCN                                         | Acetonitrile                        |
| MHz                                          | Megahertz                           |
| MeOH                                         | Methanol                            |
| mmol                                         | Millimole                           |
| μM                                           | Micromolar                          |
| mV/s                                         | Milivolt per second                 |
| mA                                           | Miliampere                          |
| μL                                           | Microlitre                          |
| μs                                           | Microseconds                        |
| Na <sub>2</sub> SO <sub>4</sub>              | Sodium sulphate                     |
| NaPF <sub>6</sub>                            | Sodium hexafluorophosphate          |
| NaOAc                                        | Sodium acetate                      |
| NaOH                                         | Sodium hydroxide                    |
| NaHCO <sub>3</sub>                           | Sodium bicarbonate                  |
| NMR                                          | Nuclear magnetic resonance          |
| ND                                           | Not detected                        |

|                                   |                                              |
|-----------------------------------|----------------------------------------------|
| $n\text{BU}_4\text{NOAc}$         | Tetrabutylammonium acetate                   |
| $\text{Na}_2\text{S}_2\text{O}_8$ | Sodium persulfate                            |
| $\text{N}_2$                      | Nitrogen                                     |
| nm                                | Nanometre                                    |
| $\text{NH}_4\text{Cl}$            | Ammonium chloride                            |
| NCR                               | Nitrogen center radical                      |
| NHC                               | N-heterocyclic carbene                       |
| $\text{Na}_2\text{CO}_3$          | Sodium carbonate                             |
| Nu                                | Nucleophile                                  |
| Ox                                | Oxidation                                    |
| $\text{O}_2$                      | Oxygen                                       |
| Ph                                | Phenyl                                       |
| PCET                              | Proton-coupled electron transfer             |
| $\text{Pd}(\text{OAc})_2$         | Palladium acetate                            |
| $\text{PPh}_3\text{AuCl}$         | Chlorido(triphenylphosphine)gold(I)          |
| Pt                                | Platinum                                     |
| $\text{PPh}_3$                    | Triphenylphosphine                           |
| $\text{PdCl}_2(\text{PPh}_3)_2$   | Dichlorobis(triphenylphosphine)palladium(II) |
| $\text{PhSH}$                     | Thiophenol                                   |
| $\text{PdCl}_2$                   | Palladium chloride                           |
| $\text{Pd}_2(\text{dba})_3$       | Tris(dibenzylideneacetone)dipalladium        |
| $\text{PhCl}$                     | Chlorobenzene                                |
| rt                                | room temperature                             |
| RCR                               | Radical cascade reaction                     |
| Red                               | Reduction                                    |
| SCE                               | Standard calomel electrode                   |
| SET                               | Single electron transfer                     |
| Sub                               | Substrate                                    |
| SCXRD                             | Single-crystal X-ray diffraction             |
| TEMPO                             | 2,2,6,6-Tetramethylpiperinyloxy              |
| TLC                               | Thin layer chromatography                    |
| TBHP                              | <i>tert</i> -Butyl hydroperoxide             |
| Ts                                | Tosyl                                        |

|                      |                   |
|----------------------|-------------------|
| TiO <sub>2</sub>     | Titanium dioxide  |
| <i>tert</i>          | Tertiary          |
| THF                  | Tetrahydrofuran   |
| TMS                  | Tetramethylsilane |
| UV                   | Ultra-violet      |
| V                    | Volt              |
| W                    | Watt              |
| Zn(OTf) <sub>2</sub> | Zinc triflate     |
| ZnO                  | Zinc oxide        |
| ZnSe                 | Zinc selenide     |