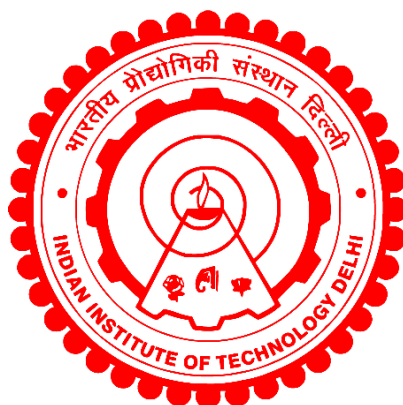


**SYNTHETIC APPLICATIONS OF PHENALENYL-
BASED MOIETY AS A POTENT PHOTOCATALYST
IN ORGANIC TRANSFORMATIONS**

VISHALI PATHANIA



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JULY 2025**

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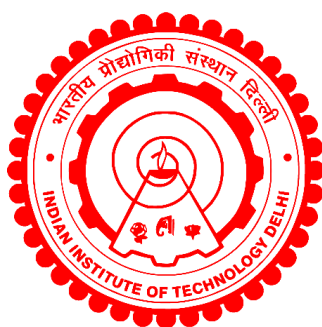
Department of Chemistry

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 Parents and Family Members

CERTIFICATE

This is to certify that the thesis entitled “*Synthetic Applications of Phenalenyl-Based Moiety as a Potent Photocatalyst in Organic Transformations*” being submitted by **Miss Vishali Pathania** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by her. **Miss Vishali Pathania** has worked under my supervision and guidance and has fulfilled all the necessary requirements for the submission of a Ph.D. thesis, which to my knowledge has reached the requisite standard and is worthy of consideration for the award of a **Doctor of Philosophy** degree.

The work embodied in this thesis has not been submitted, in part or full, to another university or institute for the award of any degree or diploma.

Dr. Sudipta Raha Roy

Research Supervisor,

Associate Professor,

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Indian Institute of Technology Delhi

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-Vishali Pathania

ABSTRACT

The thesis entitled "**Synthetic Applications of Phenalenyl-based Moiety as a Potent Photocatalyst in Organic Transformations**" is a comprehensive exploration towards the development of photocatalytic pathways towards the construction of C–C/P/B/O/N as well as S–O bonds which are essential in creating complex organic molecules. Initially, we have worked on unveiling the excited state properties of phenalenyl-based organic molecule by doing various photophysical studies and then it was implemented in the photoinduced cleavage of strong C–X bonds and thereby trapping the aryl radical with different reagents to achieve six different class of reactions. We have also developed the photoinduced oxidative formylation of tertiary anilines to get the formamide derivatives. Next, we were also able to employ the similar type of concept for oxidative dehydrogenation of a variety of saturated *N*-heterocycles under visible light irradiation. The synthesis of indole core was also carried out by utilizing diazoacetates as a one-carbon unit under the photochemical conditions by utilizing phenalenyl based photocatalyst. On the other hand, the divergent synthesis was achieved by tuning the excited state properties of the phenalenyl scaffold to construct sulfoxides and sulfones. In the last chapter, we have modified the phenalenyl photocatalyst to successfully oxidize the biarylcarboxylic acids to get the desired lactone product via the intramolecular lactonization.

Chapter 1: Introduction: Photochemistry is a fascinating and rapidly evolving field that has a significant influence on organic synthesis offering a distinctive approach for bond formation and creating intricate molecules by exploiting the light-matter interactions. More recently, photoredox catalysis began to flourish when various research groups revealed hitherto unknown facets of synthetic chemistry. So far, the synthetic community has experienced continuous and rapid progress in research, showcasing the versatility and potential of photoredox catalysis across academic and pharmaceutical fields. The utilization of light as a more environmentally friendly reagent in synthetic organic chemistry presents a broad array of benefits. Visible light serves as an exceptional reagent for catalytic transformations, offering several advantages: it is readily accessible, safe to handle, can be precisely delivered within a reaction mixture, and leaves no residue, even when used in excess. While photosynthetic organisms exploit these properties of visible light in natural photosynthesis, synthetic chemists employ visible light photocatalysis to efficiently synthesize high-value chemicals. A major benefit of generating radical intermediates through photochemistry is the capacity to precisely control reaction conditions. By manipulating parameters like intensity, wavelength, or exposure time, the reaction may be tightly controlled, as light triggers the generation of radicals. With such precise control, reaction conditions may be fine-tuned, leading to an increase in yield and selectivity of the targeted product. As photochemical techniques have been refined over decades, the range of photoredox reactions that can be accomplished through these methods has diversified. By revealing the interplay between photochemistry and catalysis, photoredox catalysis opens up new possibilities for organic

synthesis by facilitating the mild synthesis of radical intermediates. Therefore, in this thesis, we have explored the excited state properties of an odd alternant hydrocarbon, i.e., phenalenyl and used it as a potent photocatalyst in diverse synthetic transformations.

Chapter 2: Transforming Non-innocent Phenalenyl to a Potent Photoreductant through Visible-

Light-Induced Electron Transfer Processes: In this work, we have established a phenalenyl-based molecular scaffold which serves as a potent photoreductant utilizing the empty NBMO in the presence of a base to form a radical anion which, upon photoexcitation, behaves as a stronger reductant and accomplishes the cleavage of strong C–X (X = Cl, Br, I) bonds under milder reaction conditions. The base was found to be involved in a dual role of electron and hydrogen atom donor. Further, the aryl radical formed by the homolysis of C–X bonds in this technique was captured for the C_{sp2}–C_{sp2} coupling with unactivated arenes. The photoreductant potency of the phenalenyl-based catalytic system was further extended to C–P as well as C–B bond formation reactions. EPR and lifetime studies reveal the formation of a persistent radical having a sufficient lifetime to take part in the reaction by the PET mechanism. Different spectroscopic techniques combined with DFT calculations were utilized for the characterization of active catalytic species and for the elucidation of plausible mechanistic pathways. This not only is the initial report of the application of phenalenyl as a photoreductant but also provides a completely metal-free (alkali and transition metal) approach for the challenging reductive functionalization of aryl halides at room temperature.

Chapter 3: Photoinduced Direct Formylation of Anilines: A Greener Oxidation using a

Phenalenyl Photocatalyst: The rapidly expanding field of photocatalysis has revolutionized synthetic organic chemistry by establishing innovative pathways to functionalize organic molecules under mild conditions. This chapter is concerned with the sustainable approach for the photoinduced oxidative formylation of N,N-dimethylanilines using a phenalenyl-based photocatalyst. The methodology exhibits tolerance to a variety of electron-donating and electron-withdrawing groups as well as to diverse functional groups, specifically offering a selective and efficient pathway for the N-formylation. Using visible light, this photochemical technique proves to be environmentally friendly, scalable, and milder alternative strategy. The mechanistic insights were gained through a series of spectroscopic techniques, including electron paramagnetic resonance, steady-state fluorescence, and fluorescence lifetime studies. The post-functionalization was also completed and has the potential to be used in various applications.

Chapter 4: Phenalenyl-Based Photocatalyst for Oxidative Dehydrogenation of N-Heterocycles:

The environmental benefits of molecular oxygen as the oxidizing agent in oxidation reactions that synthesize fine chemicals cannot be overstated. Increased interest in developing robust photocatalysts is stimulated by the fact that the current photocatalytic transformation boom has made previously inaccessible synthetic approaches possible. By employing a phenalenyl-based photocatalyst, we have

successfully developed oxidative dehydrogenation utilizing molecular oxygen as a greener oxidant. Under photoinduced oxidative dehydrogenation conditions, different types of saturated *N*-heterocycles were successfully dehydrogenated. The versatility of this bioinspired protocol is demonstrated by the fact that a wide variety of *N*-heteroaromatics, such as quinoline, carbazole, quinoxaline, acridine, and indole derivatives, were successfully synthesized. Detailed mechanistic studies validate the proposed mechanism. Fluorescence lifetime and CV experiments revealed the crucial role of water on the efficiency of the reaction. The present protocol also provides scalability, and allowing for the functionalization of bioactive molecules at a late stage in a sustainable manner.

Chapter 5: Unraveling the Potential of Phenalenyl-based-Photocatalyst for the Indole Formation from Anilines and Diazoacetates: Indole and its derivatives are widespread in nature and have long been regarded as privileged structures in drug discovery due to their high affinity for binding to multiple receptors. As a result, a variety of effective approaches for building indoles have been established. Because of its flexibility and modularity, the method that uses diazoacetates as a one-carbon atom unit in position C3 of the indole backbone has been one of the most appealing research subjects among existing strategies. So, this chapter deals with the photochemical approach that has been developed proceeding under milder reaction conditions to synthesise indoles as well as pyrido-indoles. The reaction progresses without the use of metals or additional reagents, exhibiting a broad substrate scope with improved yields, including the natural product derivative obtained from (*L*)-menthol. Further, spectroscopic studies including UV-visible studies, fluorescence quenching studies as well as transient absorption spectroscopic studies were carried out to get into the mechanistic insights of the reaction.

Chapter 6: Tuning the Photocatalyst at Excited State: Captivating Photo Divergent Synthesis of Sulfoxides and Sulfones: By tuning the two different modes of the excited-state phenalenyl, a divergent approach is attained under the milder reaction conditions. While unraveling the excited-state photophysics of the phenalenyl catalyst using transient absorption spectroscopy, divergent catalysis has been exposed, which was made possible by modulating the formation of diverse photocatalytic species in different media. Delving into this deeper understanding has transformed how we can control and harness catalytic processes, pushing the frontiers of innovation in green chemistry. Further, spectroscopic as well as other mechanistic investigations were conducted to realize the insights of this divergent approach. Also, a variety of sulfoxides and sulfones were well tolerated under the current protocol. This was also diversified to post-functionalization as well as to the late-stage modification of molecules containing marketed drug scaffolds.

Chapter 7: Unveiling the Potency of a Phenalenyl-based Photocatalyst for Intramolecular Dehydrogenative Lactonization: Numerous attempts to create coumarin scaffolds have met with success owing to the extensive application of the benzo-3,4-coumarin skeletal unit in a broad range of pharmaceuticals, fluorescent materials, and other fine chemicals. Therefore, in this chapter, an

intramolecular dehydrogenative lactonization reaction has been accomplished by combining a phenalenyl-based organic photocatalyst and a Co(III) co-catalyst. Due to its extremely high excited state redox potential, the phenalenyl motif could directly oxidise carboxylic acid derivatives to generate carboxyl free radicals without the assistance of an external base. This protocol allows access to multiple 4-aryl-2*H*-chromen-2-ones by using the external oxidant K₂S₂O₈ and shows diverse functional group tolerance for biaryl-2-carboxylic acids. Moreover, the reaction was performed on a bulk scale with a very good yield.

सारांश

"कार्बनिक रूपांतरणों में एक शक्तिशाली फोटोकैटेलिस्ट के रूप में फेनालेनिल-आधारित मोइटी के सिंथेटिक अनुप्रयोग" शीर्षक वाली थीसिस, सी-सी/पी/बी/ओ/एन के साथ-साथ एस-ओ बॉन्ड के निर्माण की दिशा में फोटोकैटेलिटिक मार्गों के विकास की दिशा में एक व्यापक अन्वेषण है जो जटिल कार्बनिक अणुओं को बनाने में आवश्यक हैं। प्रारंभ में, हमने विभिन्न फोटोफिजिकल अध्ययनों के माध्यम से फेनालेनिल-आधारित कार्बनिक अणु के उत्तेजित अवस्था गुणों को उजागर करने पर काम किया है और फिर इसे मजबूत सी-एक्स बॉन्ड के फोटोइंज्यूड क्लीवेज में लागू किया गया और इस तरह छह अलग-अलग वर्ग की प्रतिक्रियाओं को प्राप्त करने के लिए एरिल रेडिकल को विभिन्न अभिकर्मकों के साथ फंसाया गया। हमने फॉर्माइड डेरिवेटिव प्राप्त करने के लिए तृतीयक एनिलिन के फोटोइंज्यूड ऑक्सीडेटिव फॉर्मिलेशन को भी विकसित किया है। इसके बाद, हम दृश्य प्रकाश विकिरण के तहत संतृप्त एन-हेट्रोसाइक्ल्स की एक किस्म के ऑक्सीडेटिव डिहाइड्रोजनेशन के लिए समान प्रकार की अवधारणा को नियोजित करने में भी सक्षम थे। इंडोल कोर का संश्लेषण भी फेनालेनिल आधारित फोटोकैटेलिस्ट का उपयोग करके फोटोकैमिकल स्थितियों के तहत एक-कार्बन इकाई के रूप में डायज़ोएसीटेट का उपयोग करके किया गया था। दूसरी ओर, सल्फोक्साइड और सल्फोन्स के निर्माण के लिए फेनालेनिल स्कैफोल्ड के उत्तेजित अवस्था गुणों को ट्यून करके डायवर्जेंट संश्लेषण प्राप्त किया गया था। पिछले अध्याय में, हमने इंटरमोलिकुलर लैक्टोनाइजेशन के माध्यम से वांछित लैक्टोन उत्पाद प्राप्त करने के लिए बायरिलकार्बोक्सिलिक एसिड को सफलतापूर्वक ऑक्सीकरण करने के लिए फेनालेनिल फोटोकैटेलिस्ट को संशोधित किया है।

अध्याय 1: परिचय: फोटोकैमिस्ट्री एक आकर्षक और तेजी से विकसित होने वाला क्षेत्र है जिसका कार्बनिक संश्लेषण पर महत्वपूर्ण प्रभाव है, जो प्रकाश-पदार्थ अंतःक्रियाओं का दोहन करके बंधन निर्माण और जटिल अणुओं के निर्माण के लिए एक विशिष्ट दृष्टिकोण प्रदान करता है। हाल ही में, फोटोरेडॉक्स कटैलिसिस तब पनपने लगा जब मैकमिलन, स्टीफेंसन और यून के नेतृत्व वाले शोध समूहों ने सिंथेटिक रसायन विज्ञान के अब तक अज्ञात पहलुओं का खुलासा किया। अब तक, सिंथेटिक समुदाय ने अनुसंधान में निरंतर और तेजी से प्रगति का अनुभव किया है, जो अकादमिक और फार्मास्युटिकल क्षेत्रों में फोटोरेडॉक्स कटैलिसिस की बहुमुखी प्रतिभा और क्षमता को प्रदर्शित करता है। सिंथेटिक ऑर्गेनिक केमिस्ट्री में अधिक पर्यावरण के अनुकूल अभिकर्मक के रूप में प्रकाश का उपयोग कई तरह के लाभ प्रदान करता है। दृश्यमान प्रकाश उत्प्रेरक परिवर्तनों के लिए एक असाधारण अभिकर्मक के रूप में कार्य करता है, जो कई लाभ प्रदान करता है: यह आसानी से सुलभ है, संभालने में सुरक्षित है, प्रतिक्रिया मिश्रण के भीतर सटीक रूप से वितरित किया जा सकता है, और अधिक उपयोग किए जाने पर भी कोई अवशेष नहीं छोड़ता है। जबकि प्रकाश संश्लेषक जीव प्राकृतिक प्रकाश संश्लेषण में दृश्यमान प्रकाश के इन गुणों का दोहन करते हैं, सिंथेटिक रसायनज्ञ उच्च-मूल्य वाले रसायनों को कुशलतापूर्वक संश्लेषित करने के लिए दृश्यमान प्रकाश फोटोकैटेलिसिस का उपयोग करते हैं। फोटोकैमिस्ट्री के माध्यम से रेडिकल इंटरमीडिएट्स

उत्पन्न करने का एक प्रमुख लाभ प्रतिक्रिया स्थितियों को सटीक रूप से नियंत्रित करने की क्षमता है। तीव्रता, तरंग दैर्घ्य या एक्सपोज़र समय जैसे मापदंडों में हेरफेर करके, प्रतिक्रिया को कसकर नियंत्रित किया जा सकता है, क्योंकि प्रकाश रेडिकल्स की पीढ़ी को ट्रिगर करता है। इस तरह के सटीक नियंत्रण के साथ, प्रतिक्रिया की स्थितियों को ठीक किया जा सकता है, जिससे लक्षित उत्पाद की उपज और चयनात्मकता में वृद्धि होती है। चूंकि फोटोकैमिकल तकनीकों को दशकों से परिष्कृत किया गया है, इसलिए इन विधियों के माध्यम से प्राप्त की जा सकने वाली फोटोरेडॉक्स प्रतिक्रियाओं की सीमा में विविधता आई है। फोटोकैमिस्ट्री और कटैलिसिस के बीच परस्पर क्रिया को प्रकट करके, फोटोरेडॉक्स कटैलिसिस रेडिकल इंटरमीडिएट्स के हल्के संश्लेषण की सुविधा देकर कार्बनिक संश्लेषण के लिए नई संभावनाओं को खोलता है। इसलिए, इस थीसिस में, हमने एक विषम वैकल्पिक हाइड्रोकार्बन, यानी फेनालेनिल के उत्तेजित अवस्था गुणों का पता लगाया है और इसे विविध सिंथेटिक परिवर्तनों में एक शक्तिशाली फोटोकैटलिस्ट के रूप में उपयोग किया है।

अध्याय 2: दृश्य-प्रकाश-प्रेरित इलेक्ट्रॉन स्थानांतरण प्रक्रियाओं के माध्यम से गैर-निर्दोष फेनालेनिल को एक शक्तिशाली फोटोरिडक्टेंट में बदलना: इस कार्य में, हमने एक फेनालेनिल-आधारित आणविक मचान स्थापित किया है जो एक शक्तिशाली फोटोरिडक्टेंट के रूप में कार्य करता है जो एक आधार की उपस्थिति में खाली NBMO का उपयोग करके एक रेडिकल आयन बनाता है, जो फोटोएक्साइटेशन पर, एक मजबूत रिडक्टेंट के रूप में व्यवहार करता है और हल्के प्रतिक्रिया स्थितियों के तहत मजबूत C-X (X = Cl, Br, I) बॉन्ड के दरार को पूरा करता है। यह पाया गया कि बेस इलेक्ट्रॉन और हाइड्रोजन परमाणु दाता की दोहरी भूमिका में शामिल है। इसके अलावा, इस तकनीक में C-X बॉन्ड के होमोलिसिस द्वारा गठित एरिल रेडिकल को निष्क्रिय एरेन्स के साथ Csp²-Csp² युग्मन के लिए कैप्चर किया गया था। फेनालेनिल-आधारित उत्प्रेरक प्रणाली की फोटोरिडक्टेंट क्षमता को C-P के साथ-साथ C-B बॉन्ड निर्माण प्रतिक्रियाओं तक आगे बढ़ाया गया था। ईपीआर और जीवनकाल अध्ययन से पता चलता है कि पीईटी तंत्र द्वारा प्रतिक्रिया में भाग लेने के लिए पर्याप्त जीवनकाल वाले एक स्थायी रेडिकल का निर्माण होता है। सक्रिय उत्प्रेरक प्रजातियों के लक्षण वर्णन और संभावित यांत्रिकी मार्गों की व्याख्या के लिए डीएफटी गणनाओं के साथ संयुक्त विभिन्न स्पेक्ट्रोस्कोपिक तकनीकों का उपयोग किया गया। यह न केवल फोटोरिडक्टेंट के रूप में फेनालेनिल के अनुप्रयोग की प्रारंभिक रिपोर्ट है, बल्कि कमरे के तापमान पर एरिल हैलाइड्स के चुनौतीपूर्ण रिडक्टिव फंक्शनलाइजेशन के लिए पूरी तरह से धातु-मुक्त (क्षार और संक्रमण धातु) दृष्टिकोण भी प्रदान करता है।

अध्याय 2: दृश्य-प्रकाश-प्रेरित इलेक्ट्रॉन स्थानांतरण प्रक्रियाओं के माध्यम से गैर-निर्दोष फेनालेनिल को एक शक्तिशाली फोटोरिडक्टेंट में बदलना: इस कार्य में, हमने एक फेनालेनिल-आधारित आणविक मचान स्थापित किया है जो एक शक्तिशाली फोटोरिडक्टेंट के रूप में कार्य करता है जो एक आधार की उपस्थिति में खाली NBMO का उपयोग करके एक रेडिकल आयन बनाता है, जो फोटोएक्साइटेशन पर, एक मजबूत रिडक्टेंट के रूप में व्यवहार करता है और हल्के प्रतिक्रिया स्थितियों के तहत मजबूत C-X (X = Cl, Br, I) बॉन्ड के दरार को पूरा करता है। यह पाया गया कि बेस इलेक्ट्रॉन और हाइड्रोजन परमाणु दाता की दोहरी भूमिका में शामिल है। इसके अलावा, इस तकनीक में C-X बॉन्ड के होमोलिसिस द्वारा गठित एरिल रेडिकल को निष्क्रिय एरेन्स के साथ

$C_{sp2}-C_{sp2}$ युग्मन के लिए कैप्चर किया गया था। फेनालेनिल-आधारित उत्प्रेरक प्रणाली की फोटोरिडक्टेंट क्षमता को C-P के साथ-साथ C-B बॉन्ड निर्माण प्रतिक्रियाओं तक आगे बढ़ाया गया था। ईपीआर और जीवनकाल अध्ययन से एक लगातार मूलक के गठन का पता चलता है जिसमें पीईटी तंत्र द्वारा प्रतिक्रिया में भाग लेने के लिए पर्याप्त जीवनकाल होता है। सक्रिय उत्प्रेरक प्रजातियों के लक्षण वर्णन और प्रशंसनीय यांत्रिकी मार्गों के स्पष्टीकरण के लिए डीएफटी गणनाओं के साथ संयुक्त विभिन्न स्पेक्ट्रोस्कोपिक तकनीकों का उपयोग किया गया था। यह न केवल एक फोटोरिडक्टेंट के रूप में फेनालेनिल के अनुप्रयोग की प्रारंभिक रिपोर्ट है, बल्कि कमरे के तापमान पर एरिल हैलाइडों के चुनौतीपूर्ण रिडक्टिव फंक्शनलाइजेशन के लिए पूरी तरह से धातु-मुक्त (क्षार और संक्रमण धातु) दृष्टिकोण भी प्रदान करता है।

अध्याय 3: एनिलीनों का प्रकाश-प्रेरित प्रत्यक्ष निर्माण: एक फेनालेनिल फोटोकैटेलिस्ट का उपयोग करके

एक हरित ऑक्सीकरण: फोटोकैटलिसिस के तेजी से विस्तार करने वाले क्षेत्र ने हल्की परिस्थितियों में कार्बनिक अणुओं को क्रियाशील बनाने के लिए अभिनव मार्ग स्थापित करके सिंथेटिक कार्बनिक रसायन विज्ञान में क्रांति ला दी है कार्यप्रणाली विभिन्न इलेक्ट्रॉन-दान करने वाले और इलेक्ट्रॉन-निकालने वाले समूहों के साथ-साथ विविध कार्यात्मक समूहों के प्रति सहिष्णुता प्रदर्शित करती है, विशेष रूप से एन-फॉर्मिलेशन के लिए एक चयनात्मक और कुशल मार्ग प्रदान करती है। दृश्य प्रकाश का उपयोग करते हुए, यह फोटोकैमिकल तकनीक पर्यावरण के अनुकूल, स्केलेबल और हल्की वैकल्पिक रणनीति साबित होती है। यांत्रिक अंतर्दृष्टि स्पेक्ट्रोस्कोपिक तकनीकों की एक श्रृंखला के माध्यम से प्राप्त की गई थी, जिसमें इलेक्ट्रॉन पैरामैग्नेटिक अनुनाद, स्थिर-अवस्था प्रतिदीप्ति और प्रतिदीप्ति जीवनकाल अध्ययन शामिल हैं। पोस्ट-फंक्शनलाइजेशन भी पूरा हो गया था और इसमें विभिन्न अनुप्रयोगों में उपयोग किए जाने की क्षमता है।

अध्याय 4: एन-हेट्रोसाइकल्स के ऑक्सीडेटिव डिहाइड्रोजनीकरण के लिए फेनालेनिल-आधारित

फोटोकैटेलिस्ट: फेनालेनिल-आधारित फोटोकैटेलिस्ट का उपयोग करके, हमने आणविक ऑक्सीजन को हरित ऑक्सीडेंट के रूप में उपयोग करते हुए ऑक्सीडेटिव डिहाइड्रोजनेशन को सफलतापूर्वक विकसित किया है। फोटोइंड्यूस्ड ऑक्सीडेटिव डिहाइड्रोजनेशन स्थितियों के तहत, विभिन्न प्रकार के संतृप्त एन-हेट्रोसाइकल्स को सफलतापूर्वक डिहाइड्रोजन किया गया। इस बायोइंस्पायर्ड प्रोटोकॉल की बहुमुखी प्रतिभा इस तथ्य से प्रदर्शित होती है कि किनोलिन, कार्बाज़ोल, किनॉक्सालिन, एक्रिडीन और इंडोल डेरिवेटिव जैसे कई प्रकार के एन-हेट्रोएरोमैटिक्स को सफलतापूर्वक संश्लेषित किया गया था। विस्तृत यांत्रिक अध्ययन प्रस्तावित तंत्र को मान्य करते हैं। प्रतिदीप्ति जीवनकाल और सीवी प्रयोगों ने प्रतिक्रिया की दक्षता पर पानी की महत्वपूर्ण भूमिका का खुलासा किया। वर्तमान प्रोटोकॉल स्केलेबिलिटी भी प्रदान करता है, और एक स्थायी तरीके से देर से चरण में बायोएक्टिव अणुओं के कार्यात्मककरण की अनुमति देता है।

अध्याय 5: एनिलीन और डायज़ोएसिटेट से इंडोल निर्माण के लिए फेनालेनिल-आधारित-फोटोकैटेलिस्ट

की क्षमता का पता लगाना: इंडोल और इसके व्युत्पन्न प्रकृति में व्यापक हैं और कई रिसेप्टर्स से बंधने के लिए

उनकी उच्च आत्मीयता के कारण लंबे समय से दवा की खोज में विशेषाधिकार प्राप्त संरचनाओं के रूप में माने जाते हैं। नतीजतन, इंडोल बनाने के लिए कई तरह के प्रभावी तरीके स्थापित किए गए हैं। इसकी लचीलेपन और मॉड्यूलरिटी के कारण, इंडोल बैकबोन की स्थिति C3 में एक-कार्बन परमाणु इकाई के रूप में डायज़ोएसीटेट का उपयोग करने वाली विधि मौजूदा रणनीतियों में सबसे आकर्षक शोध विषयों में से एक रही है। इसलिए, यह अध्याय फोटोकैमिकल दृष्टिकोण से संबंधित है जिसे इंडोल के साथ-साथ पाइरिडो-इंडोल को संश्लेषित करने के लिए हल्की प्रतिक्रिया स्थितियों के तहत आगे बढ़ते हुए विकसित किया गया है। प्रतिक्रिया धातुओं या अतिरिक्त अभिकर्मकों के उपयोग के बिना आगे बढ़ती है, जो बेहतर पैदावार के साथ एक व्यापक सबस्ट्रेट स्कोप प्रदर्शित करती है, जिसमें (एल)-मेन्थॉल से प्राप्त प्राकृतिक उत्पाद व्युत्पन्न शामिल है। इसके अलावा, प्रतिक्रिया की यांत्रिक अंतर्दृष्टि प्राप्त करने के लिए यूवी-दृश्य अध्ययन और प्रतिदीप्ति शमन अध्ययन सहित स्पेक्ट्रोस्कोपिक अध्ययन किए गए।

अध्याय 6: उत्तेजित अवस्था में फोटोकैटेलिस्ट को ट्यून करना: सल्फॉक्साइड और सल्फोन का मनोरम फोटो डायवर्जेंट संश्लेषण: उत्तेजित-अवस्था फेनालेनिल के दो अलग-अलग तरीकों को ट्यून करके, हल्की प्रतिक्रिया स्थितियों के तहत एक डायवर्जेंट दृष्टिकोण प्राप्त किया जाता है। क्षणिक अवशोषण स्पेक्ट्रोस्कोपी का उपयोग करके फेनालेनिल उत्प्रेरक के उत्तेजित-अवस्था फोटोफिजिक्स को सुलझाने के दौरान, डायवर्जेंट कटैलिसिस को उजागर किया गया है, जो विभिन्न मीडिया में विविध फोटोकैटलिटिक प्रजातियों के गठन को मॉड्यूलेट करके संभव बनाया गया था। इस गहरी समझ में आने से यह बदल गया है कि हम कैसे उत्प्रेरक प्रक्रियाओं को नियंत्रित और उपयोग कर सकते हैं, इसके अलावा, वर्तमान प्रोटोकॉल के तहत विभिन्न प्रकार के सल्फोक्साइड और सल्फोन को अच्छी तरह से सहन किया गया। इसे पोस्ट-फंक्शनलाइजेशन के साथ-साथ बाजार में उपलब्ध दवा स्कैफोल्ड वाले अणुओं के अंतिम चरण के संशोधन के लिए भी विविधतापूर्ण बनाया गया था।

अध्याय 7: इंटरमोलिकुलर डीहाइड्रोजनेटिव लैक्टोनाइजेशन के लिए फेनालेनिल-आधारित फोटोकैटलिस्ट की क्षमता का अनावरण: फार्मास्यूटिकल्स, फ्लोरोसेंट सामग्रियों और अन्य बढ़िया रसायनों की एक विस्तृत श्रृंखला में बेंजो-3,4-कौमरिन कंकाल इकाई के व्यापक अनुप्रयोग के कारण कूमारिन स्कैफोल्ड बनाने के कई प्रयासों को सफलता मिली है। इसलिए, इस अध्याय में, एक फेनालेनिल-आधारित कार्बनिक फोटोकैटलिस्ट और एक Co(III) सह-उत्प्रेरक के संयोजन से एक इंटरमोलिकुलर डीहाइड्रोजनेटिव लैक्टोनाइजेशन प्रतिक्रिया को पूरा किया गया है। अपनी अत्यंत उच्च उत्तेजित अवस्था रेडॉक्स क्षमता के कारण, फेनालेनिल मोटिफ बाहरी आधार की सहायता के बिना कार्बोक्सिल मुक्त मूलक उत्पन्न करने के लिए कार्बोक्सिलिक एसिड व्युत्पन्न को सीधे ऑक्सीकरण कर सकता है। यह प्रोटोकॉल बाहरी ऑक्सीडेंट $K_2S_2O_8$ का उपयोग करके कई 4-एरिल-2H-क्रोमेन-2-ओन्स तक पहुंच की अनुमति देता है और बायरिल-2-कार्बोक्सिलिक एसिड के लिए विविध कार्यात्मक समूह सहिष्णुता दिखाता है। इसके अलावा, प्रतिक्रिया बहुत अच्छी उपज के साथ बड़े पैमाने पर की गई थी।

LIST OF ABBREVIATIONS

PC	photocatalyst
PS	photosensitizer
SET	single electron transfer
EnT	energy transfer
PCET	proton-coupled electron transfer
PET	photoinduced electron transfer
4CzIPN	1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene
GC	gas chromatography
TLC	thin layer chromatography
δ	chemical shift
^1H NMR	proton nuclear magnetic resonance
^{13}C NMR	carbon nuclear magnetic resonance
Hz	Hertz
ppm	parts per million
HRMS	high-resolution mass spectra
ESI-TOF	electrospray ionization time-of-flight
HAT	hydrogen-atom transfer
DMA	dimethylacetamide
DMF	dimethylformamide
DMSO	dimethylsulfoxide
DCE	1,2-dichloroethane
$t\text{BuOH}$	tertiary butanol
TEMPO	2,2,6,6-tetramethylpiperidin-1-yl-oxidanyl
BHT	2,6-di- <i>tert</i> -butyl-4-methylphenol
OH^-	hydroxide anion
DFT	density functional theory
SMD	solvation model density
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
SOMO	singly occupied molecular orbital
LED	light emitting diode
PAH	polyaromatic hydrocarbon
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DABCO	1,4-diazabicyclo[2.2.2]octane
DIPEA	diisopropylethylamine

NSAID	non-steroidal anti-inflammatory drug
CV	cyclic voltammetry
BDE	bond-dissociation energy
LSF	late-stage functionalization
GC–MS	gas chromatography–mass spectrometry
H ₂ O ₂	hydrogen peroxide
KI	potassium iodide
MeCN	acetonitrile
EtOAc	ethyl acetate
H ₂	hydrogen
ISC	intersystem crossing
CDCl ₃	deuterated chloroform
DMSO- <i>d</i> ₆	deuterated dimethyl sulfoxide
DMAP	4-(dimethylamino)pyridine
DCC	dicyclohexyl carbodiimide
HPLC	high-performance liquid chromatography
SCE	saturated calomel electrode
IC	internal conversion
MeOH	methanol
EtOH	ethanol
DCM	dichloromethane
MO	molecular Orbital
KCl	potassium chloride
AgCl	silver chloride
OAH	odd alternant hydrocarbon
ADH	acceptorless dehydrogenation
ODH	oxidative dehydrogenation

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