

**VISIBLE LIGHT MEDIATED FUNCTIONALIZATIONS THROUGH DUAL
METALLAPHOTOREDOX CATALYSIS OR PHOTOCATALYST-
FREE STRATEGIES**

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**DEPARTMENT OF CHEMISTRY
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**Visible Light Mediated Functionalizations Through Dual
Metallaphotoredox Catalysis or Photocatalyst-Free Strategies**

by

RAJAT

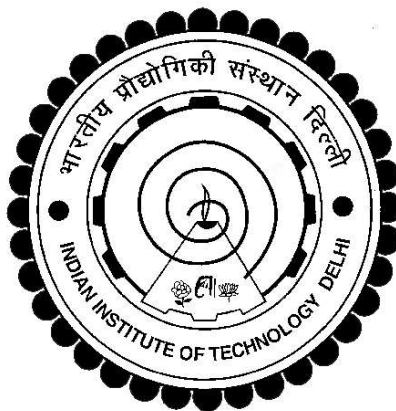
Department of Chemistry

Submitted

In fulfillment of the requirements of the degree of

Doctor of Philosophy

to the



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Dedicated to my Father

CERTIFICATE

This is to certify that the thesis entitled, “**Visible Light Mediated Functionalizations Through Dual Metallaphotoredox Catalysis or Photocatalyst-Free Strategies**” being submitted by **Ms. Rajat** 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. Rajat** 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 part or full, to any other university or institute for award of any degree or diploma.

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ABSTRACT

The thesis entitled “**Visible Light Mediated Functionalizations Through Dual Metallaphotoredox Catalysis or Photocatalyst-Free Strategies**” explores the development of sustainable synthetic methodologies for the construction of heterocyclic molecules. By harnessing visible light as a green and renewable energy source, this work aims to enable diverse chemical transformations *via* the generation of reactive intermediates under mild conditions, either through dual catalytic systems or photocatalyst-free pathways. A range of C-H functionalization and alkyne cleavage reactions have been developed to synthesize molecules of biological and synthetic relevance.

The dissertation is divided into four chapters:

Chapter 1 introduces the fundamental concepts of photochemistry, highlighting the advantages of visible light over traditional energy sources. It also provides a detailed discussion on the classification of photocatalysts, mechanistic aspects of photoredox catalysis, and the specific homogeneous catalyst employed in this work.

In **Chapter 2A** and **Chapter 2B**, an unprecedented site-selective C-1 selective monoarylation and monoacylation of *N*-protected carbazoles using a dual catalytic system based on Eosin Y and palladium under visible light irradiation has been demonstrated. Diazonium salts and phenyl glyoxylic acid were employed as arylating and acylating agents, respectively, enabling regioselective C-C bond formation. The methodology has good functional group tolerance, high regioselectivity, and furnishes the monosubstituted products in moderate to good yields at room temperature.

In **Chapter 3**, we report a regioselective sulfonamidation of *N*-(2-hydroxyaryl)amides with iminoiodinanes and iodine in visible light at room temperature. The method does not require a strong oxidant, metal or photocatalyst and enables direct functionalization of C-H bond to C-N bond. Mechanistic investigations suggest an *in-situ* generation of *N*-centered radical from *N,N*-diiodo-sulfonamide by homolytic N-I bond cleavage followed by its site-specific addition to *N*-(2-hydroxyaryl)amides to furnish *para*-sulfonamide derivatives.

Chapter 4 focuses on the transition-metal and photocatalyst-free oxidative cleavage of alkynes with PIDA/iminoiodinanes in visible light. The method provides efficient access to aryl ketones from both terminal and internal alkynes, with iminoiodinane playing a dual role

as both a nitrene and an aryl source. The methodology is operationally simple, does not require expensive transition metal catalysts, or strong oxidants, and gives the products in moderate to good yields. The experimental evidence and literature reports suggest generation of triplet nitrenes as key reaction intermediates, and subsequent tandem radical migration and oxidative cleavage of alkynes.

Overall, the thesis underscores the power and versatility of visible-light-mediated transformations in modern organic synthesis. Through the strategic use of both metallaphotoredox catalysis and photocatalyst-free strategies, it offers practical and environmentally conscious routes to valuable molecular scaffolds.

सार

"द्विधात्विक मेटालफोटोरेडॉक्स उत्प्रेरण या प्रकाश उत्प्रेरक-मुक्त रणनीतियों के माध्यम से दृश्य प्रकाश-मध्यस्थ क्रियाशीलता" शीर्षक वाला शोध-प्रबंध विषमचक्रीय अणुओं के निर्माण हेतु स्थायी संश्लेषणात्मक पद्धतियों के विकास की पड़ताल करता है। दृश्य प्रकाश को एक हरित और नवीकरणीय ऊर्जा स्रोत के रूप में उपयोग करके, इस कार्य का उद्देश्य द्वैध उत्प्रेरक प्रणालियों या प्रकाश उत्प्रेरक-मुक्त मार्गों के माध्यम से, सौम्य परिस्थितियों में प्रतिक्रियाशील मध्यवर्ती पदार्थों के निर्माण के माध्यम से विविध रासायनिक परिवर्तनों को संभव बनाना है। जैविक और संश्लेषणात्मक प्रासंगिकता वाले अणुओं तक पहुँचने के लिए C-H क्रियाशीलता और एल्काइन विदलन अभिक्रियाओं की एक श्रृंखला विकसित की गई है।

शोध-प्रबंध चार अध्यायों में विभाजित है: **अध्याय 1** प्रकाश रसायन विज्ञान की मूलभूत अवधारणाओं का परिचय देता है, पारंपरिक ऊर्जा स्रोतों की तुलना में दृश्य प्रकाश के लाभों पर प्रकाश डालता है। यह प्रकाश उत्प्रेरकों के वर्गीकरण, प्रकाश रेडॉक्स उत्प्रेरण के यांत्रिक पहलुओं और इस कार्य में प्रयुक्त विशिष्ट समरूप उत्प्रेरक पर भी विस्तृत चर्चा प्रदान करता है।

अध्याय 2A और **अध्याय 2B** में, दृश्य प्रकाश विकिरण के अंतर्गत ईओसिन Y और पैलेडियम पर आधारित द्वि-उत्प्रेरक प्रणाली का उपयोग करके *N*-संरक्षित कार्बाज़ोल्स का अभूतपूर्व स्थल-चयनात्मक *C*-1 चयनात्मक मोनोएरिलेशन और मोनोएसिलेशन किया गया है। डायज़ोनियम लवण और फेनिल ग्लाइऑक्सीलिक अम्ल का उपयोग क्रमशः एरिलेटिंग और एसिलेटिंग एजेंट के रूप में किया गया, जिससे रीजियोसेलेक्टिव *C*-*C* बंध निर्माण संभव हुआ। इस पद्धति में अच्छी कार्यात्मक समूह सहनशीलता, उच्च रीजियोसेलेक्टिविटी है, और यह कमरे के तापमान पर मध्यम से अच्छी उपज में मोनोप्रतिस्थापित उत्पाद प्रदान करती है।

अध्याय 3 में, हम कमरे के तापमान पर दृश्य प्रकाश में इमिनोआयोडिनैन्स और आयोडीन के साथ *N*-(2-हाइड्रॉक्सीएरिल)एमाइड्स के एक क्षेत्र-चयनात्मक सल्फोनामाइडेशन की रिपोर्ट करते हैं। इस विधि में किसी प्रबल ऑक्सीडेंट, धातु या प्रकाश उत्प्रेरक की आवश्यकता नहीं होती है और यह *C*-*H* बंध को *C*-*N* बंध में सीधे क्रियाशील बनाने में सक्षम बनाता है। यांत्रिक जाँच से पता चलता है कि समअपघटनी *N*-*I* बंध विदलन द्वारा *N,N*-डायआयोडो-सल्फोनामाइड से *N*-केंद्रित मूलक का स्थानीय उत्पादन होता है, जिसके बाद पैरा-सल्फोनामाइड व्युत्पन्न बनाने के लिए *N*-(2-हाइड्रॉक्सीएरिल)एमाइड्स में इसका स्थान-विशिष्ट योग होता है।

इसके अलावा, दृश्य प्रकाश में नई रणनीतियाँ विकसित करने के हमारे प्रयासों के क्रम में, **अध्याय 4** दृश्य प्रकाश में PIDA/इमिनोआयोडिनैन के साथ एल्काइनों के संक्रमण धातु और प्रकाश उत्प्रेरक-मुक्त ऑक्सीडेटिव विदलन पर केंद्रित है। यह विधि टर्मिनल और आंतरिक दोनों एल्काइनों से एरिल कीटोन्स तक कुशल पहुँच प्रदान करती है, जिसमें इमिनोआयोडिनैन नाइट्रिन और एरिल स्रोत, दोनों के रूप में दोहरी भूमिका निभाता है। यह कार्यप्रणाली संचालन की दृष्टि से सरल है, इसके लिए महंगे संक्रमण धातु उत्प्रेरकों या प्रबल ऑक्सीडेंटों की आवश्यकता नहीं होती है, और यह मध्यम से अच्छी उपज वाले उत्पाद प्रदान करती है। प्रायोगिक साक्ष्य और साहित्यिक रिपोर्टें बताती हैं कि इस अभिक्रिया क्रम के पहले चरण में त्रिक नाइट्रिन प्रमुख मध्यवर्ती के रूप में शामिल होते हैं, और एक अद्वितीय यांत्रिक मार्ग के साथ एल्काइनों के अग्रानुक्रम मूलक प्रवास और ऑक्सीडेटिव विदलन अभिक्रिया में शामिल होते हैं।

कुल मिलाकर, यह शोध-प्रबंध आधुनिक कार्बनिक संश्लेषण में दृश्य-प्रकाश-मध्यस्थ परिवर्तनों की शक्ति और बहुमुखी प्रतिभा को रेखांकित करता है। मेटालाफोटोरेडॉक्स उत्प्रेरण और प्रकाश-उत्प्रेरक-मुक्त रणनीतियों, दोनों के रणनीतिक उपयोग के माध्यम से, यह मूल्यवान आणविक ढाँचों के लिए व्यावहारिक और पर्यावरण-सचेत मार्ग प्रदान करता है।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

ACN	Acetonitrile
AcOH	Acetic acid
Ac ₂ O	Acetic anhydride
AgNO ₃	Silver nitrate
Ag ₂ CO ₃	Silver carbonate
Ag ₂ O	Silver oxide
AgOAc	Silver acetate
AgSbF ₆	Silver hexafluoroantimonate
AgCl	Silver chloride
Ag	Silver
Ar	Aryl
BNAH	1-Benzyl-1,4-dihydronicotinamide
BQ	benzoquinone
BHT	Butylated hydroxytoluene
Calcd.	Calculated
CCDC	Cambridge crystallographic data centre
Cat.	Catalyst
CsF	Caesium fluoride
CDCl ₃	Deuterated chloroform
CHCl ₃	Trichloromethane
CH ₂ Cl ₂	Dichloromethane
CT	Charge transfer
CuSO ₄	Copper sulphate
CuCl	Copper chloride
Cu	Copper
CV	Cyclic voltammeter

DPV	Differential pulse voltammetry
D ₂ O	Deuterium oxide
DCE	Dichloroethane
DG	Directing group
DMF	Dimethylformamide
DCM	Dichloromethane
DMSO	Dimethylsulfoxide
EtOH	Ethanol
EI-MS	Electron ionization mass <i>spectrometry</i>
Et	Ethyl
EtOAc	Ethyl acetate
ESI	Electron spray ionization
EDG	Electron withdrawing group
Equiv.	Equivalent
ET	Energy transfer
EDA	Electron donor-acceptor
EPR	Electron paramagnetic resonance
FCC	Flash column chromatography
FTIR	Fourier transform infrared spectroscopy
FID	Flame ionization detector
GC-MS	Gas chromatography-mass spectrometry
H	Hour
Hz	Hertz
HOMO	Highest occupied molecular orbital
HRMS	High resolution mass spectroscopy
HS-GC	Headspace gas chromatography

HAT	Hydrogen atom transfer
ISC	Inter-system crossing
Ir	iridium
I ₂	Iodine
LEDs	Light emitting diodes
LiBF ₄	Lithium tetrafluoroborate
K ₂ CO ₃	Potassium carbonate
KCl	Potassium chloride
MeOH	Methanol
ml	Mililitre
Mg	Milligram
MgSO ₄	Magnesium sulphate
Mpg-CN	Graphitic carbon nitride
mm	Milimetre
max	Maximum
min	Minutes
Me	Methyl
MHz	Megahertz
m/z	Mass by charge ratio
Na ₂ SO ₄	Sodium sulphate
Na ₂ S ₂ O ₃	Sodium thiosulphate
NaBH ₄	Sodium tetrahydridoborate
NaOH	Sodium hydroxide
(NH ₄) ₂ S ₂ O ₈	Ammonium persulfate
NaHCO ₃	Sodium hydrogen carbonate
NBS	<i>N</i> -Bromosuccinimide

NHPI	<i>N</i> -Hydroxyphthalimide
NBS	<i>N</i> -Bromosuccinimide
NFSI	<i>N</i> -Fluorobenzenesulfonimide
NMR	Nuclear magnetic resonance
ORTEP	Oak Ridge Thermal Ellipsoid Plot
PET	Photoinduced electron transfer
Pd(OAc) ₂	Palladium acetate
PCET	Proton-coupled electron transfer
Ph	Phenyl
Py	Pyridine
Pym	Pyrimidine
Ppm	Parts per million
PXRD	Powder x-Ray crystallography
Ru	Ruthenium
Rf	Retention factor
RT	Room temperature
SET	Single electron transfer
SCE	Standard calomel electrode
TEMPO	(2,2,6,6-tetramethylpiperidin-1-yl) oxidanyl
THF	Tetrahydrofuran
TM	Transition metal
TBHP	<i>tert</i> -butyl hydroperoxide
T ₁	Triplet energy state
Temp.	Temperature
TLC	Thin layer chromatography
Ts	<i>para</i> -toluenesulfonyl

TOF	Time of flight
^t Bu	<i>tert</i> -butyl
TMS	Tetramethylsilane
UV	Ultraviolet