

***VISIBLE LIGHT MEDIATED  
MULTICOMPONENT REACTIONS AND C-H  
FUNCTIONALIZATION BY SUBSTRATE  
PHOTOACTIVATION IN NEUTRAL, ACIDIC  
AND BASIC CONDITIONS***

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

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**VISIBLE LIGHT MEDIATED MULTICOMPONENT  
REACTIONS AND C-H FUNCTIONALIZATION BY  
SUBSTRATE PHOTOACTIVATION IN NEUTRAL, ACIDIC  
AND BASIC CONDITIONS**

by

**VIKAS**

**Department of Chemistry**

**Submitted**

**In fulfillment of requirements of the degree of**

**Doctor of Philosophy**

to the



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**February 2025**

*Dedicated to my beloved Parents and my wife*

## CERTIFICATE

This is to certify that the thesis entitled, “*Visible Light Mediated Multicomponent Reactions and C-H Functionalization by Substrate Photoactivation in Neutral, Acidic and Basic Conditions*” being submitted by **Mr. Vikas** 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 him. **Mr. Vikas** 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, titled "Visible Light Mediated Multicomponent Reactions and C-H Functionalization by Substrate Photoactivation in Neutral, Acidic, and Basic Conditions" focuses on the synthesis and functionalization of organic molecules under photocatalyst-free conditions. In recent years, the direct activation of substrates using visible light has emerged as a powerful tool for driving chemical transformations. This approach enables the generation of highly reactive intermediates in situ without the need for stoichiometric reagents. The work described in this thesis involves the design of multicomponent reactions and C-H functionalization strategies to synthesize biologically relevant compounds.

The thesis is organized into five chapters:

**Chapter 1** provides an introduction to photochemistry, photocatalysts, and photochemical processes. It also elaborates on substrate activation under visible light in the absence of photocatalysts, with a focus on mechanistic insights and applications.

**Chapter 2** describes a method for the synthesis of **2-(4-hydroxyphenyl)-substituted acetaldehydes** via the direct photoactivation of *para*-benzoquinone under visible light. This reaction was explored with various mono-nucleophiles, including indoles, anilines, and thiols, and demonstrated broad substrate compatibility. The process operates under mild conditions, leading to diarylated quaternary centers with a free keto group at the  $\alpha$ -position, offering potential for further reactivity exploration.

**Chapter 3** reports an efficient strategy for synthesizing **dihydroquinoxalines** bearing a tetrasubstituted carbon stereocenter. The reaction involves commercially available starting materials (*para*-benzoquinones, alkynes, and *ortho*-phenylenediamines/*ortho*-aminophenol) and requires ambient conditions. Direct photoactivation of *para*-benzoquinone initiates a [2+2] cycloaddition with alkynes, generating  $\delta,\delta$ -disubstituted *para*-quinone methide intermediates. These intermediates react with binucleophiles to produce dihydroquinoxalines, which exhibit amine-sensing properties in their protonated forms.

**Chapter 4** presents an acid-catalyzed visible-light-mediated activation of **quinoxalin-2(1H)-ones** for C-H functionalization under photocatalyst-free conditions. The photoactivated quinoxalin-2(1H)-one acts as a photosensitizer, transferring energy to oxygen to facilitate C-N cross-dehydrogenative coupling with carbazoles and amides. This reaction proceeds under

mild conditions, including sunlight exposure, yielding quinoxalin-2(1*H*)-one-carbazole scaffolds with fluorescent properties such as aggregation-induced emission (AIE) and intramolecular charge transfer (ICT).

**Chapter 5** demonstrates a base-catalyzed activation of **7-hydroxycoumarin**, and its use as a catalyst for C-C and C-N bond formation under visible light. Deprotonation of 7-hydroxycoumarin induces electronic changes that result in a bathochromic shift, generating 2-oxochrome-7-olate, which exhibits photoreductant properties. This system supports arylation, alkylation, and amination reactions with high functional group tolerance, without requiring metal or dye-based photocatalysts.

This work underscores the potential of visible-light-mediated, photocatalyst-free methodologies for developing efficient and sustainable synthetic strategies.

## सार

थीसिस, जिसका शीर्षक है "न्यूट्रल, एसिडिक और बेसिक कंडीशंस के तहत सबस्ट्रेट फोटोएक्टिवेशन द्वारा विजिबल लाइट मीडिएटेड मल्टीकंपोनेंट रिएक्शन्स और सी-एच फंक्शनलाइजेशन" फोटोकैटलिस्ट-मुक्त स्थितियों के तहत कार्बनिक अणुओं के संश्लेषण और क्रियाशीलता पर केंद्रित है। हाल के वर्षों में, दृश्य प्रकाश का उपयोग करके सबस्ट्रेट्स का प्रत्यक्ष सक्रियण रासायनिक परिवर्तनों को चलाने के लिए एक शक्तिशाली उपकरण के रूप में उभरा है। यह दृष्टिकोण स्टोइकोमेट्रिक अभिकर्मकों की आवश्यकता के बिना सीटू में अत्यधिक प्रतिक्रियाशील मध्यवर्ती उत्पन्न करने में सक्षम बनाता है। इस थीसिस में वर्णित कार्य में जैविक रूप से प्रासंगिक यौगिकों को संश्लेषित करने के लिए बहुघटक प्रतिक्रियाओं और सी-एच कार्यात्मकता रणनीतियों का डिज़ाइन शामिल है।

थीसिस पाँच अध्यायों में व्यवस्थित है:

**अध्याय 1** फोटोकैमिस्ट्री, फोटोकैटलिस्ट और फोटोकैमिकल प्रक्रियाओं का परिचय प्रदान करता है। यह यंत्रवत अंतर्दृष्टि और अनुप्रयोगों पर ध्यान देने के साथ फोटोकैटलिस्ट की अनुपस्थिति में दृश्य प्रकाश के तहत सबस्ट्रेट सक्रियण पर भी विस्तार से बताता है।

**अध्याय 2** दृश्य प्रकाश के तहत पैरा-बेंजोक्विनोन के प्रत्यक्ष फोटोएक्टिवेशन के माध्यम से 2-(4-हाइड्रॉक्सीफेनिल)-प्रतिस्थापित एसिटाल्डिहाइड के संश्लेषण के लिए एक विधि का वर्णन करता है। इस प्रतिक्रिया का पता इंडोल्स, एनिलिन और थिओल्स सहित विभिन्न मोनो-न्यूक्लियोफाइल के साथ लगाया गया और व्यापक सबस्ट्रेट संगतता का प्रदर्शन किया गया। यह प्रक्रिया हल्की परिस्थितियों में संचालित होती है, जिससे  $\alpha$ -स्थिति पर एक मुक्त कीटो समूह के साथ डायरीलेटेड चतुर्धातुक केंद्रों की ओर अग्रसर होता है, जो आगे की प्रतिक्रियाशीलता अन्वेषण की क्षमता प्रदान करता है।

**अध्याय 3** टेट्राप्रतिस्थापित कार्बन स्टीरियोसेंटर वाले डायहाइड्रोक्विनॉक्सालिन को संश्लेषित करने के लिए एक कुशल रणनीति की रिपोर्ट करता है। प्रतिक्रिया में परिवेशी परिस्थितियों में व्यावसायिक रूप से उपलब्ध प्रारंभिक सामग्री (पैरा-बेंजोक्विनोन, एल्काइन्स, और ऑर्थो-फेनिलिनेडियमाइंस/ऑर्थो-एमिनोफेनॉल) शामिल हैं। पैरा-बेंजोक्विनोन का प्रत्यक्ष फोटोएक्टिवेशन एल्काइन्स के साथ एक [2+2] साइक्लोडिशन शुरू करता है, जिससे  $\delta,\delta$ -विस्थापित पैरा-क्विनोन मेथाइड मध्यवर्ती उत्पन्न होता है। ये मध्यवर्ती बाइ-न्यूक्लियोफाइल के साथ प्रतिक्रिया करके डायहाइड्रोक्विनॉक्सालिन का उत्पादन करते हैं, जो अपने प्रोटोनेटेड रूपों में अमीन-सेंसिंग गुण प्रदर्शित करते हैं।

**अध्याय 4** फोटोकैटलिस्ट-मुक्त परिस्थितियों में सी-एच क्रियाशीलता के लिए किनॉक्सालिन-2(1एच)-ओन्स का एसिड-उत्प्रेरित दृश्य-प्रकाश-मध्यस्थ सक्रियण प्रस्तुत करता है। फोटोएक्टिवेटेड किनॉक्सालिन-2(1H)-वन एक फोटोसेंसिटाइज़र के रूप में कार्य करता है, जो कार्बोज़ोल और एमाइड्स

के साथ सी-एन क्रॉस-डीहाइड्रोजेनेटिव युग्मन की सुविधा के लिए ऊर्जा को ऑक्सीजन में स्थानांतरित करता है। यह प्रतिक्रिया हल्के परिस्थितियों में आगे बढ़ती है, जिसमें सूरज की रोशनी का जोखिम, एकत्रीकरण-प्रेरित उत्सर्जन (एआईई) और इंटरमोल्यूलर चार्ज ट्रांसफर (आईसीटी) जैसे फ्लोरोसेंट गुणों के साथ किनॉक्सालिन -2 (1 एच) - एक-कार्बाज़ोल मचान उत्पन्न करना शामिल है।

**अध्याय 5** 7-हाइड्रॉक्सीकौमरिन के आधार-उत्प्रेरित सक्रियण को प्रदर्शित करता है, जो दृश्य प्रकाश के तहत सी-सी और सी-एन बंधन निर्माण के लिए उत्प्रेरक के रूप में इसके उपयोग को सक्षम बनाता है। 7-हाइड्रॉक्सीकौमरिन का अवक्षेपण इलेक्ट्रॉनिक परिवर्तनों को प्रेरित करता है जिसके परिणामस्वरूप बाथोक्रोमिक बदलाव होता है, जिससे 2-ऑक्सोक्रोम-7-ओलेट उत्पन्न होता है, जो फोटोरिडक्टेंट गुणों को प्रदर्शित करता है। यह प्रणाली धातु या डार्क-आधारित फोटोकैटलिस्ट की आवश्यकता के बिना, उच्च कार्यात्मक समूह सहिष्णुता के साथ एरीलेशन, एल्किलेशन और एमिनेशन प्रतिक्रियाओं का समर्थन करती है।

यह कार्य कुशल और टिकाऊ सिंथेटिक रणनीतियों को विकसित करने के लिए दृश्य-प्रकाश-मध्यस्थता, फोटोकैटलिस्ट-मुक्त पद्धतियों की क्षमता को रेखांकित करता है।

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## GLOSSARY OF SYMBOLS AND ABBREVIATIONS

4-NO <sub>2</sub> BzOH	4-Nitrobenzoic acid
Ac	Acetyl
AIE	Aggregation Induced Emission
Al <sub>2</sub> O <sub>3</sub>	Aluminium oxide
BBr <sub>3</sub>	Boron tribromide
BCl <sub>3</sub>	Boron trichloride
BET	Back electron transfer
BF <sub>3</sub>	Boron trifluoride
BF <sub>3</sub> .Et <sub>2</sub> O	Boron trifluoride etherate
BHT	Butylated hydroxytoluene
CCDC	Cambridge crystallographic data centre
CDCl <sub>3</sub>	Deuterated chloroform
CH <sub>3</sub> CN	Acetonitrile
CH <sub>3</sub> OH	Methanol
CPA	Chiral phosphoric acid
Cs <sub>2</sub> CO <sub>3</sub>	Caesium carbonate
CsF	Caesium fluoride
Cu(OTf) <sub>2</sub>	Copper triflate
CuCl	Copper (II) chloride
CuCN	Copper (I) cyanide
CV	Cyclic voltammetry
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
EDA	Electron donor acceptor
EPR	Electron paramagnetic resonance
Equiv.	Equivalent
ET	Energy transfer
Et	Ethyl
Et <sub>3</sub> N	Triethyl amine
EtOH	Ethanol
FeCl <sub>2</sub>	Iron (II) chloride
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
ICT	Intramolecular charge transfer
InCl <sub>3</sub>	Indium (III) chloride
K <sub>2</sub> CO <sub>3</sub>	Potassium carbonate

$K_2S_2O_8$	Potassium persulfate
KI	Potassium iodide
KOAc	Potassium acetate
$La(OTf)_2$	Lanthanum triflate
LEDs	Light emitting diodes
LUMO	Lowest unoccupied molecular orbital
m/z	Mass by charge ratio
MCRs	Multi-component reactions
Me	Methyl
mg	Milligram
min	Minutes
mL	Mililitre
$MnO_2$	Manganese dioxide
Mpg-CN	Mesoporous Graphitic Carbon Nitride
MTBE	Methyl <i>tert</i> -butyl ether
$Na(BH_3)CN$	Sodium cyanoborohydride
NDI	Naphthalene-tetracarboxylic Diimide
$Na_2SO_4$	Sodium sulphate
$NaBH_4$	Sodium Borohydride
NaOAc	Sodium acetate
NaOH	Sodium hydroxide
$Ni(OTf)_2$	Nickle triflate
NMR	Nuclear magnetic resonance
NR	No Reaction
PBQ or <i>p</i> -BQ	<i>para</i> -benzoquinone
PCET	Proton coupled electron transfer