Photocatalytic Functionalization of Olefins *via* Redox Net-Neutral and Singlet Oxygen Mediated Strategies

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Dedicated to my beloved Parents

CERTIFICATE

This is to certify that the thesis entitled, **"Photocatalytic Functionalization of Olefins *via* Redox Net-Neutral and Singlet Oxygen Mediated Strategies"** being submitted by **Mr. Rohit Kumar** 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. Rohit Kumar** 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.

N. Jain

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Rohit Kumar

ABSTRACT

The thesis entitled "**Photocatalytic Functionalization of Olefins *via* Redox Net-Neutral and Singlet Oxygen Mediated Strategies**" aims at developing sustainable strategies for olefin functionalization under mild conditions. The work described in the thesis demonstrates visible light assisted methods that enable olefin functionalization and oxidative conversions leading to the synthesis of useful heterocyclic scaffolds.

This thesis is divided into five chapters. **Chapter 1** provides an introduction to photochemistry, classification of photocatalysts, and mechanism of various photocatalytic processes. A detailed overview of photoredox-assisted net-neutral radical-polar pathways and singlet oxygen generation *via* photosensitization is presented, since both these form a part of the studies performed in subsequent chapters.

In **Chapter 2**, we report a photoredox assisted α-acylation of enol acetates with acyl chlorides using $Ir(ppy)_3$ as the catalyst. The reaction proceeds *via* net-redox neutral radical-polar crossover pathway and furnishes 1,3-diketones in moderate to high yields under mild conditions without an external oxidant. The application of this method is demonstrated in the synthesis of Avobenzone (main ingredient in sunscreens), one-pot synthesis of *anti*-bacterial 4*H*-1,4-benzothiazines and organic-laser dye boron difluoride hemicurcuminoid complex.

Chapter 3 describes a mild and efficient ruthenium-catalyzed hydroxy-arylation of the terminal double bond of *N*-substituted 3-methyleneisoindolin-1-ones. The reaction takes place with aryl diazonium salt as the arylating reagent and water as the hydroxyl source in visible light at ambient temperature. The strategy entails vicinal difunctionalization of alkene and enables construction of 3-benzyl-3-hydroxyisoindolin-1-one heterocyclic scaffolds in moderate to good yields. C-C and C-O bonds are formed in one pot without any external additive and oxidant through an *in situ* generation of a carbocation intermediate in green light.

In **Chapter 4**, we demonstrate a one-step approach for the conversion of β-enaminonitriles to synthetically versatile α-keto amides in moderate to high yields under visible light irradiation photosensitized by porphyrins. The method is mild, cost-effective, and sustainable and requires air as the sole reagent/oxidant. The reaction is believed to proceed *via* an ene-type pathway initiated by $^1O_2$, followed by dehydration, imine hydrolysis, and subsequent nucleophilic substitution of the cyanide group by amine. The method offers a broad substrate

scope and has also been extended for synthesis of *α*-keto esters with aliphatic alcohols as nucleophiles. The porphyrin recovered after the reaction can be reused multiple times.

In **Chapter 5,** singlet oxygen ($^1O_2$) and base assisted conversion of *β*-enaminoesters to *α*-acyloxy-*β*-ketoesters is demonstrated under visible light irradiation. The reaction involves formation of an imine intermediate *via* ene-type pathway initiated by $^1O_2$ followed by base promoted dimerization and hydrolysis steps. The method is mild, environmentally friendly, requires air as the oxidant, and gives the products in moderate to high yields.

सार

"रेडॉक्स नेट-न्यूट्रल और सिंगलेट ऑक्सीजन मध्यस्थता रणनीतियों के माध्यम से ओलेफिन्स का फोटोकैटेलिटिक कार्यात्मककरण" शीर्षक वाली थीसिस, हेट्रोसाइक्लिक अणुओं को हरित, अधिक पर्यावरण के अनुकूल तरीके से संश्लेषित करने के लिए कार्बनिक परिवर्तन विकसित करने पर केंद्रित है। हाल के वर्षों में, दृश्य प्रकाश रासायनिक प्रतिक्रियाओं को संचालित करने के लिए एक शक्तिशाली उपकरण के रूप में उभरा है, जो स्टोइकोमेट्रिक अभिकर्मकों की आवश्यकता के बिना अत्यधिक प्रतिक्रियाशील मध्यवर्ती पदार्थों के निर्माण को सक्षम बनाता है। हमने ओलेफिन के मोनो और डिफंक्शनलाइजेशन और ओलेफिन सिस्टम के ऑक्सीडेटिव रूपांतरणों को डिज़ाइन किया है, जिससे संभावित चिकित्सीय अनुप्रयोगों के साथ जैविक रूप से प्रासंगिक एनालॉग्स का निर्माण होता है।

इस शोध प्रबंध में पाँच अध्याय शामिल हैं। **अध्याय 1** में फोटोकैमिस्ट्री के महत्व, फोटोकैटेलिस्ट के वर्गीकरण और फोटोकैटेलिटिक प्रक्रियाओं का विस्तृत अवलोकन किया गया है। यह फोटोरेडॉक्स-सहायता प्राप्त नेट-न्यूट्रल रेडिकल-पोलर मार्गों और फोटोसेंसिटाइजेशन के माध्यम से सिंगलेट ऑक्सीजन उत्पादन की गहन चर्चा भी प्रदान करता है, जिनमें से दोनों का उपयोग हमारी परियोजनाओं में किया जाता है।

अध्याय 2 में, हम Ir(ppy)3 की उत्प्रेरक मात्रा का उपयोग करके एसाइल क्लोराइड के साथ एनोल एसीटेट के फोटोरेडॉक्स सहायता प्राप्त α-एसाइलेशन की रिपोर्ट करते हैं। प्रतिक्रिया नेट-रेडॉक्स न्यूट्रल रेडिकल-पोलर क्रॉसओवर मार्ग के माध्यम से आगे बढ़ती है और बाहरी ऑक्सीडेंट के बिना हल्के परिस्थितियों में मध्यम से उच्च पैदावार में 1,3-डाइकेटोन प्रदान करती है। इस पद्धति का अनुप्रयोग एवोबेनज़ोन (सनस्क्रीन में मुख्य घटक) के संश्लेषण, एंटी-बैक्टीरियल *4H*-1,4-बेंजोथियाज़िन के एक-पॉट संश्लेषण और कार्बनिक-लेजर डाई बोरान डिफ्लुओराइड हेमिकर्कुमिनोइड कॉम्प्लेक्स के संश्लेषण में प्रदर्शित होता है।

दृश्य प्रकाश के तहत ओलेफिन क्रियाशीलता के लिए नवीन रणनीतियों को विकसित करने के हमारे प्रयासों को आगे बढ़ाते हुए, **अध्याय 3** में, *N*-प्रतिस्थापित 3-मेथिलीनआइसोइंडोलिन-1-ओन्स के टर्मिनल डबल बॉन्ड के एक हल्के और कुशल रूथेनियम-उत्प्रेरित हाइड्रॉक्सी-आरिलीकरण का वर्णन किया गया है। यह प्रतिक्रिया एरिल डाइज़ोनियम लवण के साथ एरिलेटिंग अभिकर्मक के रूप में और हाइड्रॉक्सिल स्रोत के रूप में पानी के साथ परिवेश के तापमान पर दृश्य प्रकाश में होती है। इस रणनीति में एल्केन का विसिनल डिफंक्शनलाइज़ेशन शामिल है और मध्यम से अच्छी पैदावार में 3-बेंज़िल-3-हाइड्रॉक्सीआइसोइंडोलिन-1-वन हेट्रोसाइक्लिक स्कैफोल्ड का निर्माण सक्षम बनाता है। C–C

और C–O बॉन्ड बिना किसी बाहरी योजक और ऑक्सीडेंट के एक पॉट में हरे प्रकाश में कार्बोकेशन इंटरमीडिएट की इन-सीटू पीढ़ी के माध्यम से बनते हैं।

अध्याय 4 में, हम पॉरफिरिन द्वारा फोटोसेंसिटाइज्ड दृश्य प्रकाश विकिरण के तहत मध्यम से उच्च पैदावार में β-एनामिनोनाइट्राइल्स को सिंथेटिक रूप से बहुमुखी α-कीटो एमाइड में बदलने के लिए एक-चरणीय दृष्टिकोण की रिपोर्ट करते हैं। यह विधि हल्की, लागत प्रभावी और टिकाऊ है और इसके लिए एकमात्र अभिकर्मक/ऑक्सीडेंट के रूप में हवा की आवश्यकता होती है। माना जाता है कि प्रतिक्रिया $^1O_2$ द्वारा शुरू किए गए ईन-प्रकार के मार्ग के माध्यम से आगे बढ़ती है, इसके बाद निर्जलीकरण, इमाइन हाइड्रोलिसिस और उसके बाद साइनाइड समूह का एमाइन द्वारा न्यूक्लियोफिलिक प्रतिस्थापन होता है। यह विधि एक व्यापक सब्सट्रेट स्कोप प्रदान करती है और इसे न्यूक्लियोफाइल के रूप में एलिफैटिक अल्कोहल के साथ α-कीटो एस्टर के संश्लेषण के लिए भी बढ़ाया गया है। प्रतिक्रिया के बाद बरामद पॉरफिरिन का कई बार पुन: उपयोग किया जा सकता है।

अध्याय 5 में, दृश्य प्रकाश विकिरण के तहत β-एनामिनोएस्टर के α-एसाइलॉक्सी-β-कीटोएस्टर में सिंगलेट ऑक्सीजन ($^1O_2$) और बेस असिस्टेड रूपांतरण का प्रदर्शन किया गया है। इस अभिक्रिया में $^1O_2$ द्वारा आरंभ किए गए ईन-प्रकार मार्ग के माध्यम से इमीन मध्यवर्ती का निर्माण शामिल है, जिसके बाद बेस द्वारा प्रवर्तित द्विगुणन और हाइड्रोलिसिस चरण होते हैं। यह विधि हल्की, पर्यावरण के अनुकूल है, ऑक्सीडेंट के रूप में हवा की आवश्यकता होती है, और मध्यम से उच्च उपज में उत्पाद देती है।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

Ac	Acetyl
Ar	Aryl
$BF_3.Et_2O$	Boron trifluoride etherate
BPY	Bipyridyl
Bu	Butyl
Bz	Benzoyl
Calcd	Calculated
CCD	Charge-coupled device
CCDC	Cambridge crystallographic data entre
$CDCl_3$	Deuterated chloroform
CFL	Compact Fluorescent Lamp
CH_2Cl_2	Chloroform
CT	Charge transfer
CV	Cyclic voltammetry
D_2O	Deuterium oxide
DABCO	1,4-diazabicyclo[2.2.2]octane
DBM	Dibenzoyl methane
DHPS	Dihydropyridines
DMF	Dimethylformamide
DMPO	5,5-Dimethyl-1-pyrroline *N*-oxide
DMSO	Dimethyl sulfoxide
DPBF	1,3-diphenylisobenzofuran
DPV	Differential pulse voltammetry
DTBBPY	Di-*tert*-butyl-2,20-bipyridyl
DTBPY	4,4′-*Bis*(1,1-dimethylethyl)-2,2′-bipyridyl
EDA	Electron donor acceptor
Equiv.	Equivalent
ESI	Electrospray ionization
ESR	Electron spin resonance
ET	Energy transfer
Et	Ethyl

EtOAc	Ethyl acetate
EtOH	Ethanol
FL	Fluorescence
GC-MS	Gas chromatography-mass spectrometry
H	hour
HAT	Hydrogen atom transfer
HCl	Hydrochloric acid
HRMS	High-resolution mass spectrometry
Hz	Hertz
^{i}Pr	Isopropyl
IR	Infrared
ISC	Intersystem crossing
LED	Light emitting diode
Lit.	Literature
m/z	Mass by charge ratio
Max	Maximum
Me	Methyl
MeOH	Methanol
Mg	Milligram
MHz	Megahertz
Min.	Minimum
mL	Millilitre
MLCT	Metal to ligand charge transfer
Na_2SO_4	Sodium sulphate
NMR	Nuclear magnetic resonance
Nu	Nucleophile
OAc	Acetoxy
ORPCO	Oxidative radical polar crossover
ORTEP	Oak Ridge Thermal Ellipsoid Plot
PC	Photocatalyst
PCET	Proton coupled electron transfer
PFP	Pentafluorophenyl
Ph	Phenyl

Piv	Pivaloyl
Ppm	Parts per million
PPY	2-phenylpyridyl
Pr	Propyl
Pt	Platinum
Rf	Retention factor
Rh	Rhodium
RPC	Radical polar crossover
RRPCO	Reductive radical polar crossover
S_0	Singlet ground state
S_1	Singlet excited state
SCE	Standard calomel electrode
SCXRD	Single crystal X-ray diffraction
SET	Single electron transfer
T_1	Triplet energy state
TBS	*tert*-Butyldimethylsilyl
TEMCT	Thermoelectrically cooled mercury cadmium telluride
TEMP	2,2,6,6-tetramethyl-4-piperidone
Temp.	Temperature
TEMPO	2,2,6,6-Tetramethylpiperidinyloxy
TFA	Trifluoro acetyl
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMS	Trimethylsilyl
TMSCl	Trimethylsilyl chloride
TOF	Time of flight
TPP	Tetraphenyl porphyrin
TTAD	*n*-Tritriacontane-16,18-dione
UV	Ultraviolet