Visible-Light Mediated Synthesis of Nitrogen and Sulfur Containing Compounds: A Greener Approach

THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE AWARD OF DEGREE

DOCTOR OF PHILOSOPHY

By

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Dedicated to my loving family…

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List of Notations, Symbols and Abbreviations

Notations	Abbreviations
%	Percentage
<	Less than
>	More than
°	Degree
Å	Angstrom
Ac	Acetyl
Ac_2O	Acetic anhydride
AcOH	Acetic acid
Bn	Benzyl
Bz	Benzoyl group
Boc	Di-*tert*-butyl dicarbonate
brs	Broad singlet
Obser.	Observed
Calc.	Calculated
©	Copyright
$CHCl_3$	Chloroform
CD_3OD	Methanol-d4
$CDCl_3$	Deuterated chloroform
cm	Centimeter
J	Coupling constant
DMF	Dimethylformamide
DMSO-d_6	Deuterated dimethyl sulfoxide
D_2O	Deuterated water
ºC	Degree Celsius
d	Doublet
DMAP	4-Dimethylaminopyridine
DCE	Dichloroethane
DCM	Dichloromethane
dd	Doublet of doublet
ddd	Doublet of doublet of doublet

ddt	Doublet of doublet of triplet
DMSO	Dimethyl sulfoxide
dq	Doublet of quartet
dt	Doublet of triplet
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DABCO	1,4-Diazabicyclo[2.2.2]octane
equiv.	Equivalent
EtOH	Ethanol
EtOAc	Ethyl acetate
EDG	Electron donating group
EWG	Electron withdrawing group
equiv.	Equivalent
g	Gram; Gravitational force
BAs	Barbituric acids
h	Hour
$Sc(OTf)_3$	Scandium (III) Trifluoromethanesulfonate
H_2DEBA	Diethylbarbituric acid
Hz	Hertz
IR	Infra-Red
LDA	Lithium diisopropylamide
m	Multiplet
H_3BA	Barbituric acid
MeOH	Methanol
mg	Milligram
MHz	Megahertz
min	Minute
mL	Milliliter
mm	Millimeter
mmol	Millimole
µm	Micrometer
M.p.	Melting point
nm	Nanometer
NMR	Nuclear Magnetic Resonance

n-BuLi	*n*-Butyllithium
KOH	Potassium hydroxide
pH	Potential of hydrogen
ppm	Parts per million
RT	Room temperature
NaCl	Sodium chloride
s	Singlet
NMP	N-Methyl-2-pyrrolidone
t-Bu	Tertiary butyl
THF	Tetrahydrofuran
TLC	Thin-Layer Chromatography
TMS	Tetramethylsilane
CF_3COOH	Trifluoroacetic acid
UV	Ultraviolet
XRD	X-ray Diffraction
α	Alpha
β	Beta
γ	Gamma
δ	Chemical shift
[ox]	Oxidation
R_f	Refractive Index
i.e.	that is
o	Ortho
m	Meta
p	Para
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
Et_3N	Triethylamine
$Cu(OTf)_2$	Copper (II) trifluoromethanesulfonate
$Yb(OTf)_3$	Ytterbium (III) trifluoromethanesulfonate
TBHP	*tert*–Butylhydroperoxide
BHT	Butylatedhydroxytoluene
Ag_2O	Silver(I) oxide

$LiAlH_4$	Lithium aluminium hydride
$ZnCl_2$	Zinc chloride
$Ni(OTf)_2$	Nickel (II) trifluoromethanesulfonate
$KMnO_4$	Potassium permanganate
$K_2S_2O_8$	Potassium persulfate
TEMPO	(2,2,6,6-Tetramethylpiperidin-1-yl)oxidanyl
ZnO	Zinc oxide
CH_3COOH	Acetic acid
p-TSA	*p*-Toluenesulfonic acid
TiO_2	Titanium dioxide
CuCl	Copper (I) chloride
$AlCl_3$	Aluminium chloride
$NaBH_4$	Sodium borohydride
DTBP	Di-*tert*-butyl peroxide
et al.	et alia, Latin for “and others”
i.e.	that is
e.g.	Example
equiv.	Equivalents

General Experimental Considerations

All the chemicals were procured from Aldrich, USA, and E. Merck, Germany, and were used as received. The solvents were purchased from Merck, India, and Ranbaxy, India, and were purified before their use. The preparation and particulars of the substrates employed for the work undertaken are given in their respective chapters. **Melting points** were measured using Stuart Melting point apparatus SPM10 in open capillary tubes and are uncorrected. **UV-visible spectroscopy** of the reaction solution was recorded on a SHIMADZU UV-3600 UV-visible spectrophotometer. **Infrared (IR)** spectra were recorded on the Perkin-Elmer FT-IR-5300 spectrophotometer (ν_{max} expressed in cm^{-1}). The **^{1}H** (500 MHz) and **^{13}C** (126 MHz) **NMR** **^{19}F** (126 MHz) **NMR** spectra were run on a Bruker Advance 500 MHz FT-NMR at 500 MHz spectrometers. Chemical shifts are given in δ ppm, using tetramethylsilane (TMS) as an internal standard **HRMS (m/z) and** were recorded in an electron ionization or electrospray ionization (ESI) mode on Waters-Q-TOF Premier-HAB213 and Sciex X500R QTOF instruments. The **elemental microanalyses** were performed on Exeter Analytical Inc Model, CE-440 elemental analyzer.

Thin-layer Chromatography (TLC) was performed on glass plates (7.5 × 2.5 and 7.5 × 5.0 cm) coated with Merck silica gel GF 254 using various combinations of ethyl acetate and n-hexane as an eluent. Visualization of spots was accomplished either in an iodine chamber or by exposure to UV light. Merck silica gel (100-200 mesh) was used for column chromatography (approximately 15-20 g per 1 g of the crude product).

Preface

The fundamental goal of this thesis is to create novel synthetic methodologies that use visible light as a renewable, sustainable, and environmentally friendly source of energy. Light irradiation provides enough energy to perform the reaction without the disadvantages of thermal activation, such as high temperatures or harsh conditions. This thesis work focuses on developing novel visible-light-mediated organic transformation strategies for the synthesis of Nitrogen and Sulfur-containing compounds in distinct ways.

The effective green synthesis of nitrogen and sulfur-containing compounds is embodied in the thesis titled **"Visible Light Mediated Synthesis of Nitrogen and Sulfur-Containing Compounds: A Greener Approach"**. **Chapter 1** will provide a detailed explanation of visible light, its importance, and visible light-mediated synthesis of nitrogen and sulfur-containing compounds.

Chapter 2 will describe the visible-light-induced cu-catalyzed synthesis of schiff's base of 2- amino benzonitrile derivatives and acetophenones. **Chapter 3** will disclose the photo-triggered catalyst-free synthesis of sulfonamides in a sustainable solvent via an electron donor-acceptor (EDA) complex. **Chapter 4** will highlight visible-light-induced arylation via electron-donor-acceptor complex: a catalyst-free approach for the synthesis of n-(hetero)aryl sulfonamides. **Chapter 5** will present a visible-light-driven synthesis of amine–sulfonate salt derivatives: a step towards a green approach finally, **Chapter 6** will summarize and conclude the total thesis work.