Formation of Carbon-Sulfur Bonds with Sp^2 and Sp^3-Carbons Under Metal and Metal-Free Conditions

Thesis submitted in partial fulfillment for the

Award of Degree

Doctor of Philosophy

by

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Dedicated to my loving

Parents...

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GENERAL EXPERIMENTAL CONSIDERATIONS

All the reactions were carried out in oven dried glasswares. Starting materials were prepared using modified literature procedures and modified procedures as described in the experimental sections. Solvents, Chemicals were purchased from commercial sources (Aldrich, Alfa Aesar, SD fine and Avra) and used without further purifications, unless otherwise stated. **Melting points** of products were measured Staurt SMP10 melting point apparatus using in open capillary tubes. **FT-IR** for the products were recorded on ALPHA BRUKER Eco-ATR fitted out on ZnSe ATR crystal in the range of 500-3000 cm^{-1}. **^{1}HNMR** and **^{13}C NMR** spectra were recorded on Bruker Avance 500 MHz NMR spectrometer using deuterated solvents. Chemical shifts are given in ppm, using tetramethylsilane (TMS) as an internal standard. **Mass spectra (HRMS)** were measured on water's Quattro Micro V 4.1. Electronic absorption spectra were recorded on Shimadzu UV-2450 spectrophotometer. **Thin layer chromatography (TLC)** was performed using pre-coated plates obtained from E. Merck (TLC silica gel 60 F254). The TLCs were visualized in UV Chamber with 254 nm wavelength lamp, then further analyzed by charring in stain solution (5% H_2SO_4 in MeOH) and also sometimes in iodine chamber. **Column chromatography** was performed on silica gel (60-120 or 100-200 mesh) using different eluents. **IR spectra** of the new compounds have been recorded using PerkinElmer instrument. The details of other fine chemicals, reaction conditions, substrate preparation etc. are given in respective chapters.

PREFACE

Organosulfur compounds have received significant interest due to the presence in commonly found in foods, vegetables, and dietary items, providing various health benefits. Moreover, broad applications in different fields, including modern organic synthesis, medicinal chemistry, drug discovery, materials science, etc. It is worth noting that more than 300 sulfur-containing FDA-approved drugs are available in the market. Organosulfur compounds can be categorized according to different sulfur-based functional groups. Some of the common functional groups in organosulfur compounds include thiol, sulfide, sulfoxide, thioacetic acid, sulfonic acid, thioamide, sulfonamide, sulfoximine, sulfinic acid, thioimidates, dithiocarbamates, sulfone, etc.

In this context, the thesis entitled **"Formation of Carbon-Sulfur Bonds with Sp^2 and Sp^3-Carbons Under Metal and Metal-Free Conditions."** has focused on the development of routes for C-S bond formation under mild conditions. **Chapter 1** will present a comprehensive overview of several C-S bond-formation methods and their significance in both biological and synthetic domains. **Chapter 2** will highlight the procedure of synthesizing (3)-S-arylthioindoles from indole and thiophenols in water using potassium persulfate-glucose mediators. **Chapter 3**, will cover the methods of synthesizing thioimidates from thioamides and arylboronic acids using copper as a catalyst under mild conditions. **Chapter 4** will highlight a straightforward and efficient method for the synthesizing of various functionalized *S*-benzyl dithiocarbamates from α-aryl diazo esters via a multicomponent reaction involving carbon disulfide and amines. **Chapter 5**, will

discuss the process of synthesizing α-aryl sulfone propanamide from arylsulfinates using α-halohydroxamates at room temperature. In the end, **Chapter 6** will summarize and conclude the entire thesis work.

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LIST OF NOTATIONS, SYMBOLS AND ABBREVIATIONS

Notations	Abbreviations
%	Percentage
<	Less than
>	More than
°	Degree
°C	Degree Celsius
©	Copyright
Å	Angstrom
1,10-Phen.	1, 10-phenanthroline
2,2-Bipy	2, 2-Bipyridine
Ac	Acetyl group
Ac_2O	Acetic anhydride
AIBN	Azobisisobutyronitrile
AcOH	Acetic acid
Aq.	Aqueous
atm.	Atmosphere
brs	Broad Singlet
Bn	Benzyl
Bz	Benzoyl group
Calc.	Calculated
calcd	Calculated
$CHCl_3$	Chloroform
cm	Centimeter
$CDCl_3$	Deuterated Chloroform
CD_3OD	Methanol-d_4
c	Concentration
cc	Column chromatography
CSA	Camphorsulfonic acid
COSY	^1H-^1H Correlation Spectroscopy
D_2O	Deuterated water
DCE	1,2-Dichloroethane
DMAP	4-Dimethylaminopyridine
DMF	Dimethylformamide
DCM	Dichloromethane
DEPT	Distortionless enhancement by polarization transfer
d	Doublet
dd	Doublet of doublet

ddd	Doublet of doublet of doublet
ddt	Doublet of doublet of triplet
dq	dq
dt	Doublet of triplet
DNA	Deoxyribonucleic acid
DABCO	1,4-Diazabicyclo[2.2.2]octane
Dppe	1,2-Bis(diphenylphosphino)ethane
EDG	Electron donating group
EWG	Electron withdrawing group
equiv.	Equivalent
EtOH	Ethanol
EtOAc	Ethyl acetate
Et_3N	Triethylamine
ESI	Electrospray ionization
g	Gram; Gravitational force
GC-MS	Gas Chromatography Mass Spectrometry
h	Hour
HRMS	High Resolution Mass Spectrometry
HPLC	High-performance liquid chromatography
Hz	Hertz
HSQC	Heteronuclear single quantum coherence spectroscopy
i-Pr	*Iso*-propyl
IR	Infra Red
J	Coupling constant
KI	Potassium iodide
KOH	Potassium hydroxide
LG	Leaving group
lit.	Literature
m	Multiplet
m/z	Mass to charge ratio
MeOH	Methanol
mg	Milligram
MHz	Megahertz
min	Minute
mL	Milliliter
mm	Millimeter
mmol	Milli Mole
µm	Micrometer
m.p.	Melting Point
MOM	Methoxymethyl

MS	Molecular sieve
MeOD	Dutereted methanol
nm	Nanometer
NaCl	Sodium chloride
NMR	Nuclear Magnetic Resonance
n-BuLi	*n*-Butyllithium
NMP	N-Methyl-2-pyrrolidone
nr	Not reported
nd	Not determined
NBS	N-Bromosuccinimide
NIS	N-Iodosuccinimide
NCS	N-Chlorosuccinimide
NOESY	Nuclear Overhauser Effect Spectroscopy
Obser.	Observed
PDC	Pyridinium dichromate
PG	Protectin group
pH	Potential of hydrogen
ppm	Parts per million
Py	Pyridine
PTSA	*p*-Toluenesulfonic acid
Pd-C	Palladiun on carbon
Quant.	Quantitative
RT	Room Temperature
RNA	Ribonucleic acid
R*f*	Retardation Factor
s	Singlet
t-Bu	Tertiary butyl
TBN	*tert*-Butyl nitrite
THF	Tetrahydrofuran
TLC	Thin-Layer Chromatography
TMS	Tetramethylsilane
TMEDA	Tetramethylethylenediamine
TBAI	Tetran-n-Butyl Ammonium Iodide
TBAF	Tetran-n-Butyl Ammonium Fluoride
TBAB	Tetran-n-Butyl Ammonium Bromide
TBS	*tert*-Butyldimethylsilyl
TBDMS	*tert*-Butyldimethylsilyl
TBDPS	*tert*-Butyldiphenylsilyl
TEMPO	(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl
TFA	Trifluoroacetic acid

TfOH	Trifluoromethanesulfonic acid
t	Triplet
TMSOTf	Trimethylsilyl trifluoromethanesulfonate
TsCl	4-Toluenesulfonyl chloride
UV	Ultraviolet
XRD	X-ray diffraction
α	Alpha
β	Beta
δ	Chemical shift
δ	Delta
[ox]	Oxidation
[α]	Specific rotation
i.e.	that is
o	*Ortho*
m	*Meta*
p	*Para*

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