

Dedicated to...

*Maa-Denta, Mantu Peha-Manju Pehi
& Luo-Kush*

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Date: 08/05/2024

Place: Tezpur University



(Sudhamoyee Katakya)

TZ203913 of 2022



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CERTIFICATE FROM SUPERVISOR

This is to certify that the thesis entitled "*Exploration of Synthetic Methodologies for Carbon-Carbon and Carbon-Heteroatom (N, O, S) Bond Formation Reaction Catalysed by Cu & Pd*" submitted to the School of Sciences, Tezpur University in partial fulfillment for the award of the degree of Doctor of Philosophy in Chemical Sciences is a record of research work carried out by **Miss Sudhamoyee Katakya** under my supervision and guidance. She has been duly registered (Registration No. **TZ203913 of 2022**), and the thesis presented is worthy of being considered for Ph.D. Degree.

All help received by her from various sources have been duly acknowledged. No part of this thesis has been submitted elsewhere for award of any other degree.

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CERTIFICATE OF THE EXTERNAL EXAMINER AND ODEC

This is to certify that the thesis entitled “*Exploration of Synthetic Methodologies for Carbon-Carbon and Carbon-Heteroatom (N, O, S) Bond Formation Reaction Catalysed by Cu & Pd*” submitted by **Miss Sudhamoyee Katak**y to the School of Sciences, Tezpur University in partial fulfillment of the award of the degree of Doctor of Philosophy in the Department of Chemical Sciences has been examined by us on _____ and found to be satisfactory.

The committee recommends for the award of the degree of Doctor of Philosophy.

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Abbreviations, Acronyms and Symbols

%	Percentage
δ	Chemical shift
J	Coupling constant
λ	Wavelength
Ar	Aryl
Ac	Acetyl
ACN	Acetonitrile
Å	Angstrom
BET	Brunauer-Emmett-Teller
°C	degree Centigrade
CAN	Ceric Ammonium Nitrate
DCE	Dichloroethane
DMAc	Dimethylacetamide
DMAP	4-Dimethylaminopyridine
DMF	N,N-dimethylformamide
DMSO	Dimethylsulfoxide
EDX	Energy Dispersive X-ray
EDGs	Electron donating groups
EWGs	Electron withdrawing groups
Equiv.	Equivalent (s)
ESI-MS	Electro Spray Ionization-Mass Spectrometry
FT-IR	Fourier transformed infra-red
FDA	Food and Drug Administration
g	gram
HFIP	Hexafluoro-2-isopropanol
HRMS	High Resolution Mass Spectrometry
h	hour
ICP-OES	Inductively Coupled Plasma - Optical Emission spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standards
MeOH	Methanol
MOF	Metal Organic Framework

MHz	Mega-Hertz
mmol	milli mole
mg	milligram
mL	milli Liter
m	multiplet
m/z	Atomic mass units per charge
nm	Nanometer
NMR	Nuclear Magnetic Resonance
NPs	Nanoparticles
PEG	Polyethylene Glycol
ppm	parts-per-million
<i>p</i> -TsOH	<i>p</i> -toluene sulphonic acid
PEG	Polyethylene glycol 400
p-XRD	Powder X-ray diffraction
rt	Room temperature
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscope
^t Bu	<i>tert</i> -butyl
Tz	Tetrazole
TEM	Transmission Electron Microscope
TMB	3,3',5,5'-Tetramethylbenzidine
TBAB	Tetrabutylammonium bromide
TLC	Thin Layer Chromatography
TM	Transition metal
TMEDA	Tetramethylethylenediamine
TMS	Tetramethylsilane
UV-Vis	Ultra violet-visible
XPS	X-ray Photoelectron Spectroscopy

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General Experimental Information

All the chemicals were purchased commercially and used directly without any purification. The progress of the reactions was monitored by analytical thin layer chromatography (TLC) on Merck silica gel F₂₅₄ plates and visualised using UV light ($\lambda=254$ nm). UV-Visible spectra were recorded in a UV-visible spectrophotometer (Shimadzu Corporation, UV-2550). Column Chromatographic separations were done by distilled solvents (hexane: ethyl acetate) over silica gel (60-120 or 100-200 mesh). ¹H and ¹³C NMR spectra were recorded on a JEOL JNM ECS NMR (400 MHz & 600 MHz) spectrometer using CDCl₃ and DMSO as solvent and TMS as an internal standard. Chemical shifts are reported in parts-per-million (ppm) and NMR spectra are plotted using MestReNova software (14.2.26256). HRMS data were obtained from the electro spray ionization (ESI) technique on a Q-TOF mass analyzer. The characterization of the synthesized catalysts was done by using Fourier transformed infra-red (FT-IR), Powder X-ray diffraction (p-XRD), Scanning Electron Microscope-Elemental dispersive X-ray (SEM-EDX), Transmission Electron Microscope (TEM), and X-ray photoelectron spectroscopy (XPS) analyses. FT-IR spectra were recorded on a PerkinElmer Frontier MIR FT-IR spectrometer. Powder XRD studies were carried out using a Rigaku Miniflex X-ray diffractometer (D8 FOCUS and MINIFLEX, BRUKER AXS, Germany and Rigaku Corporation, Japan), equipped with Cu K α radiation ($\lambda = 0.1542$ nm, scanning rate = 0.05 s⁻¹) at 30 kV and 15 mA, where the data obtained was in the 2θ range of 10° to 100°. TEM (JEM-2100, Jeol, Japan), SEM (JEOL-JSM-6390LV, Japan), and EDX analysis techniques (JEOL-JSM-6390LV, Japan) were employed for morphological and elemental analyses. The SEM and TEM analyses were carried out using ImageJ software. The amount of metal incorporation was determined by Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES) analysis (Perkin Elmer, Optima 5300 DV). The elemental composition and chemical bonding information were analyzed by high resolution XPS measurements (Thermo-Scientific ESCALAB Xi+ spectrometer) with a monochromatic Al K α X-ray source (1486.6 eV) and a spherical energy analyzer that operates in the CAE (constant analyzer energy) mode. The CAE for high-resolution spectra was recorded at 50 eV.