

UNIVERSITI TEKNOLOGI MARA

**Ni(II), Cu(II), AND Pd(II)
SCHIFF BASE COMPLEXES:
SYNTHESIS,
CHARACTERIZATION, DFT,
ANTIBACTERIAL STUDY, AND
APPLICATION AS HOMOGENEOUS
CATALYSTS IN STILLE REACTION**

NUR NABIHAH BINTI MUZAMMIL

PhD

March 2026

UNIVERSITI TEKNOLOGI MARA

**Ni(II), Cu(II), AND Pd(II)
SCHIFF BASE COMPLEXES:
SYNTHESIS,
CHARACTERIZATION, DFT,
ANTIBACTERIAL STUDY, AND
APPLICATION AS HOMOGENEOUS
CATALYSTS IN STILLE REACTION**

NUR NABIHAH BINTI MUZAMMIL

Thesis submitted in fulfilment
of the requirements for the degree of
**Doctor of Philosophy
(Science)**

Faculty of Applied Sciences

March 2026

CONFIRMATION BY PANEL OF EXAMINERS

I certify that a Panel of Examiners has met on 5 November 2025 to conduct the final examination of Nur Nabihah binti Muzammil on her Doctors of Philosophy thesis entitled “Ni(II), Cu(II), and Pd(II) Schiff Base Complexes: Synthesis, Characterization, DFT, Antibacterial Study, and Application as Homogeneous Catalysts in Stille Reaction” in accordance with Universiti Teknologi MARA Act 1976 (Akta 173). The Panel of Examiners recommends that the student be awarded the relevant degree. The Panel of Examiners was as follows:

Norizan Ahmat @ Abdul Hamid, PhD
Professor
Faculty of Applied Sciences
Universiti Teknologi MARA
(Chairman)

Karimah Kassim, PhD
Associate Professor
Faculty of Applied Sciences
Universiti Teknologi MARA
(Internal Examiner)

Wan Mohd Khairul Wan Mohamed Zin, PhD
Professor
Faculty of Science and Marine Environment
Universiti Malaysia Terengganu
(External Examiner)

PROF DR HJH ZURAEDA IBRAHIM
Dean
Institute of Postgraduates Studies
Universiti Teknologi MARA

Date: 30 March 2026

AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

Name of Student : Nur Nabihah binti Muzammil

Student ID. No. : 2021309269

Programme : Doctor of Philosophy (Science) – AS950

Faculty : Applied Sciences

Thesis Title : Ni(II), Cu(II), and Pd(II) Schiff Base Complexes:
Synthesis, Characterization, DFT, Antibacterial Study,
and Application as Homogeneous Catalysts in Stille
Reaction

Signature of Student :

Date : March 2026

ABSTRACT

The Stille reaction, a vital palladium-catalyzed cross-coupling method, has significantly advanced organic synthesis, yet challenges related to catalyst stability, reagent toxicity, and selectivity drive ongoing research toward improved efficiency and sustainability. This thesis presents the synthesis, characterization, catalytic evaluation in Stille reaction, DFT analysis, and antibacterial activity of Ni(II), Cu(II), and Pd(II) Schiff base complexes. Two Schiff base series, B1 and B2, were successfully prepared via condensation of *ortho*-vanillin and salicylaldehyde with *para*-substituted phenylamine derivatives in a 1:1 ratio, followed by complexation with Ni(II), Cu(II), and Pd(II) salts in a 2:1 ratio to afford 30 metal complexes. All ligands and complexes were characterized using elemental analysis, melting point, molar conductivity, magnetic susceptibility, NMR, FTIR, and UV-Visible spectroscopy. Low molar conductivity values confirmed their non-electrolytic nature. FTIR spectra showed shifts of the $\nu(\text{C}=\text{N})$ band from 1603-1618 cm^{-1} (ligands) to 1602-1618 cm^{-1} (complexes), $\nu(\text{C}-\text{N})$ from 1340-1367 cm^{-1} (ligands) to 1341-1394 cm^{-1} (complexes), and $\nu(\text{C}-\text{O})$ from 1241-1260 cm^{-1} (ligands) to 1211-1247 cm^{-1} (complexes), indicating coordination through azomethine nitrogen and phenolic oxygen. Weak M-N and M-O bands appeared at 548-703 cm^{-1} and 437-543 cm^{-1} , respectively. In the ^1H NMR spectra, the phenolic OH signal at 12.91-13.89 ppm disappeared upon complexation, and the $\text{HC}=\text{N}$ proton shifted from 8.61-8.67 ppm in the ligand to 7.69-7.72 ppm in the complexes. Corresponding ^{13}C NMR signals for the $\text{C}=\text{N}$ carbon shifted from 160.4-161.4 ppm to 161.6-165.4 ppm, further supporting coordination. UV-Visible spectra showed $\pi-\pi^*$ and $n-\pi^*$ transitions at 201-316 nm and 300-430 nm for the free ligands, shifting to 208-366 nm and 334-443 nm in the complexes, consistent with metal-ligand interaction. Additionally, 11 single crystals of compounds were successfully obtained through slow evaporation, consisting of ligands (B1H, B1Me, B2H, B2Me) and complexes (CuB1Me, CuB2H, CuB2C, PdB1OMe, PdB2Me, PdB2OMe, PdB2C) and were analysed using single crystal X-ray diffraction. Six of them are new compounds, reflecting the novelty of this study. Pd(II) complexes from the B1 series were used to optimize the reaction conditions for Stille reaction by varying temperatures (30 $^\circ\text{C}$, 60 $^\circ\text{C}$, 80 $^\circ\text{C}$, and 100 $^\circ\text{C}$), bases types (KOH, triethylamine, and K_2CO_3), and amounts of catalysts (0.5, 1.0, 1.5, and 2.0 mmol%), with the best performance achieved using KOH, 2.0 mmol%, and 100 $^\circ\text{C}$. Pd(II) Schiff base complexes have the best catalytic performance compared to Ni(II) and Cu(II) Schiff base complexes, with conversion rates of 90.8% and 50.1% after 60 minutes, respectively. PdB1OMe was the most effective catalyst, giving 100% conversion under optimized conditions afforded isolated biphenyl product of 41.9% yield, confirmed by NMR and FTIR spectroscopy. DFT calculations further supported high catalytic efficiency of PdB1OMe using B3LYP method with basis set of LANL2DZ, showing a small value of HOMO-LUMO gap (1.939 eV) and high electrophilicity (7.039 eV), consistent with strong electron-accepting ability and enhanced reactivity in catalytic activity. Furthermore, all synthesized compounds underwent antibacterial screening using the disk diffusion method against four bacterial strains, with 1% ciprofloxacin serving as positive control. The study assessed their antibacterial efficacy against Gram-positive strains; *Staphylococcus aureus* (*S. aureus*) and *Bacillus subtilis* (*B. subtilis*) and Gram-negative strains; *Escherichia coli* (*E. coli*) and *Salmonella typhimurium* (*S. typhimurium*) for both ligand series.

ACKNOWLEDGEMENT

With profound gratitude, I begin by expressing my deepest appreciation to Allah, whose endless mercy and guidance have granted me the strength, perseverance, and opportunity to complete this PhD journey. Through every challenge, His blessings have been my source of resilience and wisdom.

I am immensely grateful to my main supervisor, Associate Professor Dr Amalina Mohd Tajuddin, for her unwavering guidance, patience, and invaluable insights throughout this research. Her mentorship has been instrumental in shaping both my academic growth and research direction. My sincere thanks also go to my co-supervisor, Associate Professor Dr Mohd Tajudin Mohd Ali, whose thoughtful advice and encouragement have been a cornerstone of this study. A special appreciation is extended to Associate Professor Dr Sharifah Aminah Syed Mohamad, whose expertise and support in conducting the antibacterial studies have greatly contributed to this work.

To my labmates, Balqis Auni, Siti Solihah, Nur Husnina, Muhammad Azwan, Umami Liyana, Siti Sufiana, and Arif Naim, your companionship, support, and shared experiences have made the laboratory a place of learning, discovery, and friendship. I am equally grateful to the Coordination Chemistry Group members, lab assistants, and science officers of the Faculty of Applied Sciences, whose dedication ensured the availability of essential resources and facilities that made this research possible. I sincerely acknowledge the financial support provided by Universiti Teknologi MARA (UiTM) and the scholarship provided by the Ministry of Higher Education through MyBrainSc program, which have allowed me to pursue this academic endeavor with determination and focus.

My deepest and most heartfelt gratitude is reserved for my family and friends, who have stood by me unwaveringly, offering encouragement, love, and belief in my potential. To my beloved father, Muzammil Mokhtar, and my wonderful mother, your sacrifices, prayers, and boundless love have shaped every step of this journey. Your unwavering faith in me has been my greatest motivation, and every success I achieve is a reflection of the values you have instilled in me. To my beloved siblings, Nur Athirah, Nurul Izzah, and Ahmad Imran, and to my dear husband, Ahmad Najmi Muhammad Zaki, your unwavering support, patience, and faith in my journey have been my greatest source of strength. I am deeply grateful for your encouragement, which has uplifted me through every challenge and triumph.

This thesis marks the culmination of years of perseverance, dedication, and collaboration. I am sincerely grateful for the unwavering support and guidance I have received throughout this journey, and I remain committed to pursuing knowledge and excellence in my academic and professional endeavors.

TABLE OF CONTENTS

	Page
CONFIRMATION BY PANEL OF EXAMINERS	ii
AUTHOR'S DECLARATION	iii
ABSTRACT	iv
ACKNOWLEDGEMENT	v
TABLE OF CONTENTS	vi
LIST OF TABLES	x
LIST OF FIGURES	xiii
LIST OF SYMBOLS	xvii
LIST OF ABBREVIATIONS	xix
CHAPTER 1 INTRODUCTION	1
1.1 Research Background	1
1.1.1 Schiff Base Ligands	1
1.1.2 Schiff Base Complexes	3
1.1.3 Stille Reaction	4
1.1.4 Density Functional Theory (DFT)	5
1.1.5 Antibacterial Activity	6
1.2 Problem Statement	7
1.3 Objectives	9
1.4 Scope and Limitation	10
1.5 Significance of Study	14
1.6 Research Flow Chart	15
CHAPTER 2 LITERATURE REVIEW	17
2.1 Schiff Base Ligands	17
2.1.1 Framework of Schiff Base Ligands	17
2.1.2 Schiff Base Complexes	20
2.2 Catalysis	26
2.2.1 Carbon-Carbon Coupling Reaction	28
2.2.2 Stille Reaction	30

2.2.3	Catalytic Optimization of Stille Reaction Between Organotin and Aryl Halides using Palladium Catalyst	33
2.2.4	Reactivity of Aryl Halides in Stille Reaction	37
2.2.5	Catalytic Optimization of Stille Reaction using Copper and Nickel as Catalysts	38
2.3	Density Functional Theory (DFT)	43
2.3.1	Basis Set in Schiff Base Compounds	45
2.3.2	DFT-Based Insights into Cross-Coupling Catalysis	49
2.4	Antibacterial Activity	50
CHAPTER 3 RESEARCH METHODOLOGY		56
3.1	Chemicals and Materials	56
3.2	Instrumentations	57
3.2.1	CHN Elemental Analyzer	57
3.2.2	Molar Conductometer	58
3.2.3	Melting Point	58
3.2.4	Magnetic Susceptibility	58
3.2.5	¹ H and ¹³ C Nuclear Magnetic Resonance (NMR) Spectrometer	59
3.2.6	Fourier Transform Infrared Spectrometer	60
3.2.7	UV-Visible Spectrometer	60
3.2.8	Single Crystal X-ray Diffraction	61
3.2.9	Gas Chromatography-Flame Ionization Detector (GC-FID)	62
3.3	Synthesis of Ligands	62
3.3.1	Synthesis of B1 Series of Ligands	62
3.3.2	Synthesis of B2 Series of Ligands	64
3.4	Synthesis of Metal Complexes	65
3.4.1	Synthesis of Ni(II) B1 Series of Complexes	66
3.4.2	Synthesis of Ni(II) B2 Series of Complexes	67
3.4.3	Synthesis of Cu(II) B1 Series of Complexes	69
3.4.4	Synthesis of Cu(II) B2 Series of Complexes	71
3.4.5	Synthesis of Pd(II) B1 Series of Complexes	72
3.4.6	Synthesis of Pd(II) B2 Series of Complexes	74
3.5	Homogeneous Catalysis of Stille Reaction	76
3.5.1	General Procedure of Stille Reaction	76

3.5.2	Screening of the Best Catalysts	76
3.5.3	Optimum of Reaction Conditions	76
3.5.4	Effect of using Different Catalysts in Stille Reaction	77
3.5.5	Isolation of Stille Product	78
3.6	Density Functional Theory (DFT)	78
3.6.1	Frontier Molecular Orbitals (FMO)	79
3.6.2	Global Chemical Reactivity Descriptors (GCRD)	79
3.7	Antibacterial Activity	80
3.7.1	Bacterial Strains	81
3.7.2	Solubility Study	81
3.7.3	Experimental Method	81
CHAPTER 4 RESULTS AND DISCUSSION		83
4.1	Investigation Pathways	83
4.2	Characterization of Ligands and Ni(II), Cu(II), and Pd(II) Complexes	84
4.2.1	Elemental Analysis (C, H, N), Melting Point, and Molar Conductivity	84
4.2.2	Magnetic Susceptibility	88
4.2.3	FTIR	91
4.2.4	¹ H NMR	96
4.2.5	¹³ C NMR	102
4.2.6	UV-Visible	107
4.2.7	Single Crystal X-ray Diffraction	112
4.3	Catalytic Activity of Stille Reaction	139
4.3.1	Screening of the Best Catalyst Series	139
4.3.2	Optimization of Catalytic Activity	139
4.3.3	Effect of using Different Catalysts in Stille Reaction	150
4.3.4	Isolation of Stille Product	153
4.4	Density Functional Theory (DFT)	157
4.4.1	Frontier Molecular Orbitals (FMO)	158
4.4.2	Global Chemical Reactivity Descriptors (GCRD)	162
4.4.3	Molecular Electrostatic Potential (MEP)	166
4.5	Antibacterial Activity	167
4.5.1	Solubility Study	168

4.5.2	Interpretation of Antibacterial Results	171
4.5.3	Toxicity Assessment	173
CHAPTER 5	CONCLUSION	175
5.1	Conclusion	175
5.2	Recommendations	178
REFERENCES		180
APPENDICES		204
AUTHOR'S PROFILE		299

LIST OF TABLES

Tables	Title	Page
Table 1.1	Structure of B1 Series of Ligands and Their Complexes	12
Table 1.2	Structure of B2 Series of Ligands and Their Complexes	13
Table 2.1	Previous Studies of Schiff Base Ligands and Their Complexes	22
Table 2.2	The Catalytic Activities of Palladium in Stille Reaction between Various Aryl Halide and Tributylphenyltin	34
Table 2.3	The Catalytic Activities of Copper and Nickel Transition Metal Catalysts in Stille Reaction	39
Table 2.4	Theoretical Methods in Schiff Base Compounds	47
Table 2.5	Antibacterial Study for Schiff Base Compounds	53
Table 3.1	List of Solvents and Chemicals	56
Table 3.2	List of Instruments for the Synthesis and Characterization of Compounds	57
Table 3.3	Spin-Only Magnetic Moment for Complexes	59
Table 4.1	Physicochemical Data of the B1 Series Ligand and Its Respective Metal Complexes	86
Table 4.2	Physicochemical Data of the B2 Series Ligand and Its Respective Metal Complexes	87
Table 4.3	Magnetic Susceptibility of Ni(II), Cu(II), and Pd(II) Complexes	90
Table 4.4	FTIR Data of B1 Series Ligands and Its Respective Metal Complexes	94
Table 4.5	FTIR Data of B2 Series Ligands and Its Respective Metal Complexes	95
Table 4.6	¹ H NMR Data of B1 Series Ligands and Its Respective Metal Complexes	100
Table 4.7	¹ H NMR Data of B2 Series Ligands and Its Respective Metal Complexes	101
Table 4.8	¹³ C NMR Data of B1 Series Ligands and Its Respective Metal Complexes	105

Table 4.9	¹³ C NMR Data of B2 Series Ligands and Its Respective Metal Complexes	106
Table 4.10	UV-Visible Data of B1 Series Ligands and Its Respective Metal Complexes	110
Table 4.11	UV-Visible Data of B2 Series Ligands and Its Respective Metal Complexes	111
Table 4.12	Crystallographic Data Collections Parameters for B1 Series Compounds	113
Table 4.13	Crystallographic Data Collections Parameters for B2 Series Compounds	114
Table 4.14	Selected Bond Lengths (Å) and Bond Angles (°) of B1H	116
Table 4.15	Intermolecular and Intramolecular Hydrogen Bonds of B1H (Å, °)	117
Table 4.16	Selected Bond Lengths (Å) and Bond Angles (°) of B1Me	119
Table 4.17	Intermolecular and Intramolecular Hydrogen Bonds of B1Me (Å, °)	119
Table 4.18	Selected Bond Lengths (Å) and Bond Angles (°) of B2H	121
Table 4.19	Intramolecular Hydrogen Bond of B2H (Å, °)	121
Table 4.20	Selected Bond Lengths (Å) and Bond Angles (°) of B2Me	122
Table 4.21	Intramolecular Hydrogen Bond of B2Me (Å, °)	123
Table 4.22	Selected Bond Lengths (Å) and Bond Angles (°) of CuB1Me	125
Table 4.23	Intermolecular Hydrogen Bonds of CuB1Me (Å, °)	125
Table 4.24	Selected Bond Lengths (Å) and Bond Angles (°) of CuB2H	127
Table 4.25	Selected Bond Lengths (Å) and Bond Angles (°) of CuB2C	129
Table 4.26	Selected Bond Lengths (Å) and Bond Angles (°) of PdB1OMe	131
Table 4.27	Selected Bond Lengths (Å) and Bond Angles (°) of PdB2Me	133
Table 4.28	Selected Bond Lengths (Å) and Bond Angles (°) of PdB2OMe	135
Table 4.29	Selected Bond Lengths (Å) and Bond Angles (°) of PdB2C	137
Table 4.30	Percent Conversion of Iodobenzene of Stille Reaction	139
Table 4.31	Selectivity of Product in Stille Reaction	141
Table 4.32	Effect of Different Amounts of Catalysts on Stille Reaction	150
Table 4.33	Percent Conversion of Iodobenzene using Different Catalysts	152
Table 4.34	Physicochemical Data of Biphenyl	154
Table 4.35	The Main FTIR Data of Biphenyl	154

Table 4.36	¹ H NMR Chemical Shifts, δ (ppm) of Aromatic Protons of Biphenyl	155
Table 4.37	¹³ C NMR Chemical Shifts δ (ppm) of Biphenyl	156
Table 4.38	HOMO, LUMO, and Energy Gap of Compounds	158
Table 4.39	Global Chemical Reactivity Descriptors (GCRD) Values for Compounds	163
Table 4.40	Solubility Test for B1 Series Ligands and Its Respective Metal Complexes	169
Table 4.41	Solubility Test for B2 Series Ligands and Its Respective Metal Complexes	170
Table 4.42	Relative Diameter of Inhibition Zone Exhibit by B1 Series Ligands and Its Metal Complexes	172
Table 4.43	Relative Diameter of Inhibition Zone Exhibit by B2 Series Ligands and Its Metal Complexes	173
Table 4.44	Toxicity Test of Acetic Acid with Different Concentrations against <i>B. subtilis</i> and <i>S. typhimurium</i>	174
Table 4.45	Toxicity Test of TEA with Different Concentrations against <i>S. aureus</i> and <i>E. coli</i>	174

LIST OF FIGURES

Figures	Title	Page
Figure 1.1	Formation of Schiff Base	1
Figure 1.2	Mechanism for Formation of Schiff Base	2
Figure 1.3	General Reaction Formation of Metal Complex	4
Figure 1.4	General Reaction of Stille Reaction	5
Figure 1.5	Flow of Research Work	16
Figure 2.1	Activation Energy in Catalysis	27
Figure 2.2	Examples of Cross-Coupling Types	29
Figure 2.3	Times Cited and Publications Over Time on Stille Reaction	31
Figure 2.4	General Reaction and Mechanism of Pd-Catalyzed Stille Reaction	33
Figure 2.5	Plausible Mechanistic Pathway for the CuI Catalyzed <i>E</i> -Selective Stille Reaction	41
Figure 2.6	Plausible Mechanism for the Ni-Catalyzed Carbonylative Stille Reaction	43
Figure 3.1	Synthesis Reaction of B1 Series of Ligands	63
Figure 3.2	Synthesis Reaction of B2 Series of Ligands	64
Figure 3.3	Synthesis Reaction of Ni(II) Complexes with B1 Ligands Series	66
Figure 3.4	Synthesis Reaction of Ni(II) Complexes with B2 Ligands Series	68
Figure 3.5	Synthesis Reaction of Cu(II) Complexes with B1 Ligands Series	69
Figure 3.6	Synthesis Reaction of Cu(II) Complexes with B2 Ligands Series	71
Figure 3.7	Synthesis Reaction of Pd(II) Complexes with B1 Ligands Series	73
Figure 3.8	Synthesis Reaction of Pd(II) Complexes with B2 Ligands Series	74
Figure 3.9	Catalytic Reaction of Iodobenzene with Tributylphenyltin	76

Figure 4.1	Crystal Field Splitting Diagram for Ni(II), Cu(II), and Pd(II) Complexes	88
Figure 4.2	FTIR Spectra of B1H and Its Metal Complexes	91
Figure 4.3	FTIR Spectra of B2H and Its Metal Complexes	93
Figure 4.4	^1H NMR Spectra for (a) B1H and (b) PdB1H	96
Figure 4.5	^1H NMR Spectra for (a) B2H and (b) PdB2H	97
Figure 4.6	The Numbering System for ^1H and ^{13}C NMR of (a) B1 Series Schiff Base Complexes and (b) B2 Series Schiff Base Complexes	98
Figure 4.7	^{13}C NMR Spectra for (a) B1H and (b) PdB1H	102
Figure 4.8	^{13}C NMR spectra for (a) B2H and (b) PdB2H	103
Figure 4.9	UV-Visible Spectra of B1H and Its Metal Complexes	107
Figure 4.10	UV-Visible Spectra of B2H and Its Metal Complexes	108
Figure 4.11	The ORTEP Diagram of B1H, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level	116
Figure 4.12	Crystal Packing of B1H View Down Crystallographic <i>b</i> -Axis	117
Figure 4.13	The ORTEP Diagram of B1Me, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level	118
Figure 4.14	Crystal Packing of B1Me View Down Crystallographic <i>b</i> -Axis	119
Figure 4.15	The ORTEP Diagram of B2H with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level	120
Figure 4.16	Crystal Packing of B2H View Down Crystallographic <i>a</i> -Axis	121
Figure 4.17	The ORTEP Diagram of B2Me, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level	122
Figure 4.18	Crystal Packing of B2Me View Along Crystallographic <i>c</i> -Axis	123
Figure 4.19	The ORTEP Diagram of CuB1Me, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level	124
Figure 4.20	Crystal Packing of CuB1Me View Down Crystallographic <i>c</i> -Axis	125
Figure 4.21	The ORTEP Diagram of CuB2H, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level	127
Figure 4.22	Crystal Packing of CuB2H View Down Crystallographic <i>c</i> -Axis	128

Figure 4.23	The ORTEP Diagram of CuB2C, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level	129
Figure 4.24	Crystal Packing of CuB2C View Down Crystallographic <i>a</i> -Axis	130
Figure 4.25	The ORTEP Diagram of PdB1OMe, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level	131
Figure 4.26	Crystal Packing of PdB1OMe View Down Crystallographic <i>a</i> -Axis	132
Figure 4.27	The ORTEP Diagram of PdB2Me, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level	133
Figure 4.28	Crystal Packing of PdB2Me View Down Crystallographic <i>b</i> -Axis	134
Figure 4.29	The ORTEP Diagram of PdB2OMe, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level	135
Figure 4.30	Crystal Packing of PdB2OMe View Down Crystallographic <i>a</i> -Axis	136
Figure 4.31	The ORTEP Diagram of PdB2C, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level	137
Figure 4.32	Crystal Packing of PdB2C View Down Crystallographic <i>a</i> -Axis	138
Figure 4.33	GC Chromatogram of Reaction Mixture for Stille Reaction	140
Figure 4.34	Effect of Temperatures on % Conversion of Iodobenzene	143
Figure 4.35	Effect of Types of Bases on % Conversion of Iodobenzene	146
Figure 4.36	Effect of Amounts of Catalysts on % Conversion of Iodobenzene	149
Figure 4.37	GC Chromatogram of Negative Control for Stille Reaction	153
Figure 4.38	FTIR Spectra of Isolated Biphenyl and Standard Biphenyl	154
Figure 4.39	¹ H NMR of Biphenyl	155
Figure 4.40	¹³ C NMR of Biphenyl	156
Figure 4.41	Mechanism of Stille Reaction using Pd(II) Schiff Base as Catalyst and KOH as Base	157
Figure 4.42	HOMO, LUMO and Energy Gap Representation of Ligands	159

Figure 4.43	HOMO, LUMO and Energy Gap Representation of Pd(II) Schiff Base Complexes	161
Figure 4.44	The MEP Map of the Compounds Calculated from DFT Approach	167
Figure 4.45	Toxicity Test of 5% TEA against <i>S. aureus</i> and <i>E. coli</i>	174

LIST OF SYMBOLS

Symbols

α	Alpha
$\text{\AA}$	Angstrom
β	Beta
B.M.	Bohr magneton
cm	Centimeter
ΔE	Change in energy
η	Chemical hardness
μ	Chemical potential
S	Chemical softness
J	Coupling constants
Δ	Crystal field splitting energy
$^{\circ}$	Degree angle
$^{\circ}\text{C}$	Degree Celcius
δ	Delta
eV	Electron volt
χ	Electronegativity
ω	Electrophilicity index
ν	Frequency

γ	Gamma
g	Gram
g/mol	Gram per mole
Hz	Hertz
K	Kelvin
λ	Lambda
μL	Microliter
mL	Milliliter
mm	Millimeter
mmol	Millimole
mmol%	Millimole percent
M	Molarity
nm	Nanometer
Ω	Ohm
ppm	Part per million
%	Percentage
π	Pi
θ	Theta

LIST OF ABBREVIATIONS

Abbreviations

^{13}C NMR	Carbon Nuclear Magnetic Resonance
^1H NMR	Proton Nuclear Magnetic Resonance
ACN	Acetonitrile
B3LYP	Becke's Three-Parameter Hybrid Functional
C-C	Carbon-Carbon
CDCl_3	Chloroform
CHN	Carbon Hydron Nitrogen
CFSE	Crystal Field Stabilization Energy
DFT	Density Functional Theory
DMA	Dimethylacetamide
DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide
TEA	Triethylamine
EtOH	Ethanol
FID	Flame Ionization Detector
FMO	Frontier Molecular Orbital
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
GCRD	Global Chemical Reactivity Descriptors

GGA	Generalized Gradient Approximation
HOMO	Highest Occupied Molecular Orbital
LDA	Local Density Approximation
LMCT	Ligand Metal Charge Transfer
LUMO	Lowest Unoccupied Molecular Orbital
M	Metal Ion
MEP	Molecular Electrostatic Potential
MSB	Magnetic Susceptibility Balance
ORTEP	Oak Ridge Thermal Ellipsoid Plot
PEG	Polyethylene Glycol
RT	Room Temperature
TEA	Triethylamine
TLC	Thin Layer Chromatography
TON	Turnover Number
UV-Visible	Ultraviolet-Visible
XC	Exchange-Correlation

CHAPTER 1

INTRODUCTION

1.1 Research Background

1.1.1 Schiff Base Ligands

This research focused on the reaction of *ortho*-vanillin or salicylaldehyde with *para*-substituted aniline derivatives bearing hydrogen (-H), electron-donating groups (-CH₃, -OCH₃), and electron-withdrawing groups (-Cl, -NO₂). The molecular design was based on an N,O-bidentate coordination motif, incorporating an imine nitrogen and a phenolic oxygen as donor sites. The *ortho*-hydroxyl group on the aldehyde moiety was essential in contributing the structural rigidity to the ligand backbone, positioning the donor atoms into an optimal geometry for the formation of stable five-membered chelate rings upon coordination.

The general reaction of the Schiff base is shown in Figure 1.1 (Buta et al., 2022). Schiff base are classified as organic compounds containing imine (azomethine) functional group with formula (R-C=N), where R denotes as alkyl or aryl group and this group is formed from condensation of primary amines and carbonyl group of the aldehydes or ketones in the presence or absence of acids or bases in organic solvents such alcohols, where, the hydrogen atoms of the primary amines react with oxygen atom of the carbonyl group to form water molecule and the other product named a Schiff base (Aboura et al., 2018).

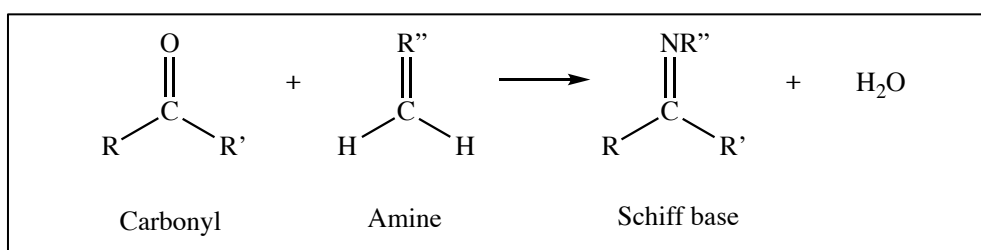


Figure 1.1 Formation of Schiff Base

The general mechanism of Schiff base formation in Figure 1.2 requires a nucleophilic addition of primary amine and the water molecule elimination reaction. An unstable intermediate, called carbinolamine is formed in nucleophilic addition reaction

when amine acts as a nucleophilic attack on carbonyl carbon (Ghorbani-Choghamarani et al., 2016). This carbinolamine will then undergo a rate-determining step reaction known as an acid catalyzed dehydration reaction. Due to the weak base properties of the amine, the acid concentration used in the reaction should not be too concentrated. The amine may be protonated and become non-nucleophilic without the formation of carbinolamine. The condensation reaction of Schiff base can be influenced by several factors, such as solution pH, steric substituent hindrance, and the electronic effect of the starting materials (Aboura et al., 2018).

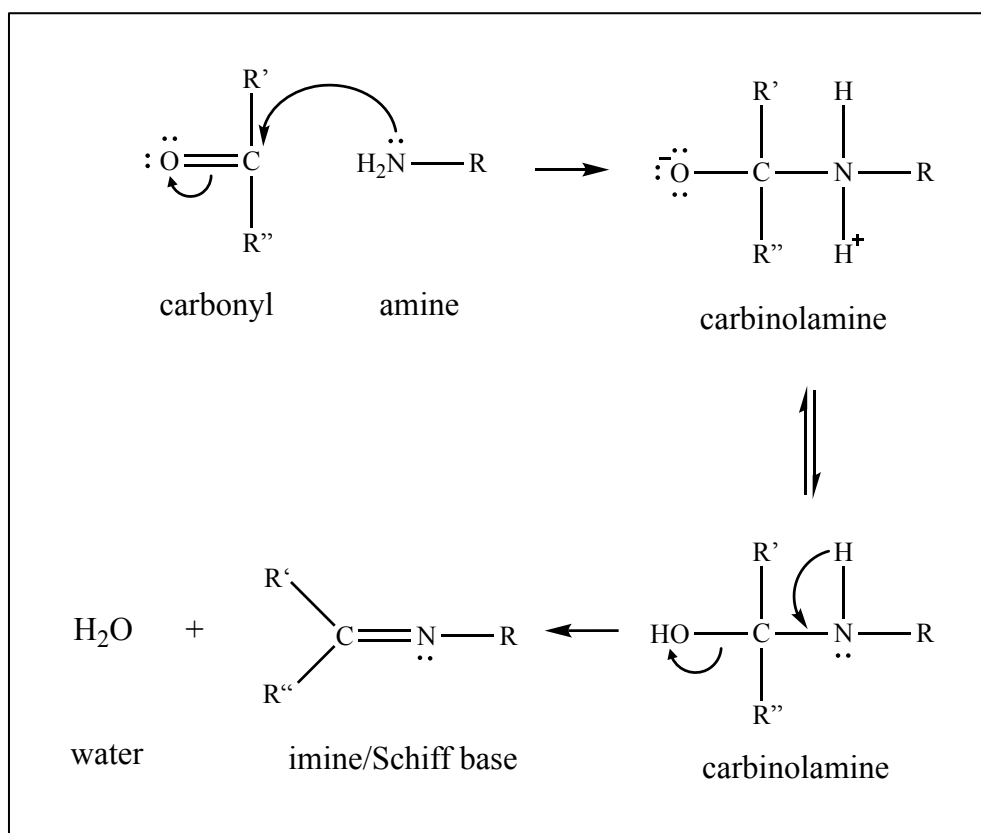


Figure 1.2 Mechanism for Formation of Schiff Base

Schiff base, which are effective as coordinating ligands and widely used in coordinating chemistry due to the relative preparation easiness, synthetic flexibility, and special property of the C=N group, are particularly excellent chelating agents, especially when there is a functional group such as -OH or -SH present close to the imine group for the formation of a five- or six- membered ring with the metal ion (Prakash & Adhikari, 2011). O-H and S-H groups can form ionic bonds with metal upon complexation, increasing the chelating ability of the ligand. The compounds can function as mono-, di-, or polydentate ligands depending on the number of coordinating

atoms number present in the molecule. A chelate ring with less than five or more than six atoms will be unstable due to the steric factor (Gupta & Sutar, 2008). Generally, imines are bi- or tridentate ligands that can form very stable complexes with metal ions.

1.1.2 Schiff Base Complexes

Schiff base complexes are a significant class of coordination compounds that have attracted considerable attention in various fields of chemistry due to their versatility, stability, and diverse applications (Abu-khadra et al., 2016). Compounds with a metal centre coordinated to donor atoms of the ligand, such as nitrogen and oxygen via a dative covalent bond, are known as metal complexes (Kargar et al., 2021). In this study, Ni(II), Cu(II), and Pd(II) ions were selected as coordinating metal centers due to their ability to form stable chelate complexes with Schiff base ligands. Ni(II) exhibits versatile coordination behavior, often adopting square planar or tetrahedral geometries depending on the ligand environment, Cu(II) and Pd(II) typically favors square planar coordination and plays a prominent role in catalytic and organometallic chemistry. The ligands employed in this work contain ONNO donor atoms, which donate their lone pairs of electrons to the empty *d*-orbitals of the metal ion. This strong coordination capability facilitates the generation of well-defined and thermodynamically stable complexes with predictable geometries. The complexes were synthesized *via* complexation method using different molar ratios of ligands and metal salts.

The formation of a metal complex between a ligand with a lone pair of electrons and a metal ion with vacant orbitals known as dative covalent bond formation (Figure 1.3). In this process, the ligand, which has at least one atom with a lone pair of electrons (such as nitrogen, oxygen, or sulphur), acts as a donor and donates these electrons to the metal ion, which has vacant *d* orbitals capable of accepting electron pairs (Singh et al., 2016). The metal ion, often a transition metal, has a specific electronic configuration with vacant *d* orbitals that allow it to form coordination bonds with ligands. When the ligand approaches the metal ion, the lone pair on the donor atom overlaps with the vacant orbitals of the metal, leading to the formation of a coordinate covalent bond (Szklarzewicz et al., 2021). This results in the metal ion being surrounded by a set of ligands, creating a metal-ligand complex.

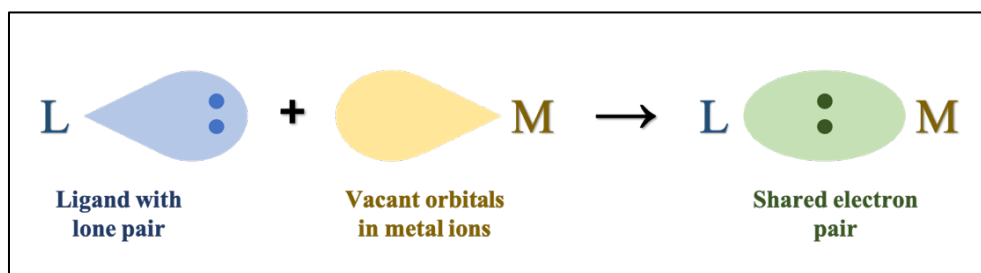


Figure 1.3 General Reaction Formation of Metal Complex

The ability of metal ion to accept electron density from the ligand depends on its charge, size, and the availability of vacant orbitals, while the ability of ligand to donate electron density is influenced by its electronic structure and the nature of the donor atom (El-Ajaily et al., 2018). The overall stability and geometry of the complex are determined by the coordination number of the metal and the spatial arrangement of the ligands, which is influenced by both the metal and the properties of ligand. This process, where the metal ion accepts electron density from the ligand to form a stable complex, is central to coordination chemistry and underpins many catalytic, biological, and material processes.

1.1.3 Stille Reaction

The Stille reaction has made a major contribution to various applications in the total synthesis of complex natural products due to the chemical stability of the coupling partners, the mild reaction conditions and the functional group compatibility (Jani & Bahrami, 2020). In the art of organic synthesis, Stille reaction is one of the most prevalent, efficient and selective Pd-catalyzed cross-coupling reactions for the construction of C-C bonds. Discovered by John K. Stille in the late 1970s, this reaction involves the coupling of organotin (stannane) reagents with organic electrophiles, such as aryl, vinyl, or alkyl halides or pseudohalides, in the presence of a palladium-based catalyst (Aleena et al., 2021). Figure 1.4 demonstrates the general reaction of Stille reaction and the well-established Stille reaction mechanism. The reaction is between an organostannane also called organotin and an organic electrophile in the presence of palladium catalyst to generate a new C-C single bond.

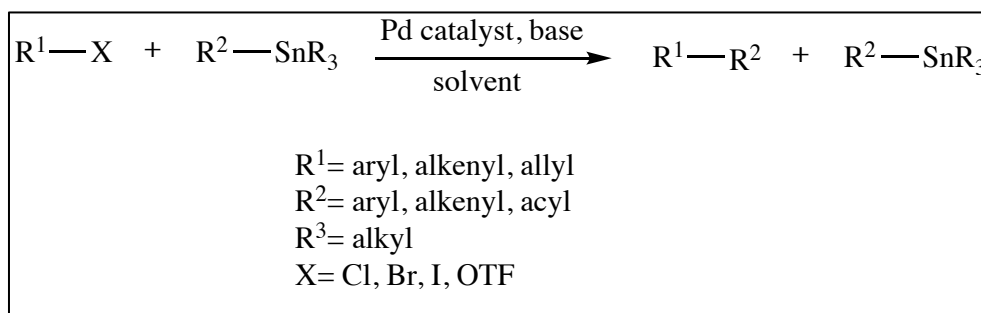


Figure 1.4 General Reaction of Stille Reaction

Stille reaction has been chosen in this study because it offers several advantages such as relative thermal stability, air or moisture insensitivity and reaction conditions that are highly tolerant of many organic functional groups, including alcohols, esters, amines, and nitriles, which remain intact during the reaction (Li et al., 2016). This feature has made the Stille reaction particularly valuable in the synthesis of pharmaceuticals, natural products, and complex organic materials, where precise control over molecular structure is paramount. In addition, organotin reagents used in Stille coupling reactions can be commercially available or readily synthesized, more stable and purified, making Stille reaction an easily accessible method for synthesis (Wang et al., 2019).

1.1.4 Density Functional Theory (DFT)

Density functional theory (DFT) is a powerful and widely used computational approach in quantum chemistry and materials science for investigating the electronic structure of atoms, molecules, and condensed matter systems (Reeves et al., 2020). Introduced in its modern form through the foundational work of Hohenberg, Kohn, and Sham in the 1960s, DFT has become an indispensable tool for understanding and predicting the properties of chemical systems (Xu et al., 2020). At its core, DFT is based on the principle that the ground-state properties of a many-electron system can be uniquely determined by its electron density, rather than the complex many-body wavefunction. This simplification dramatically reduces the computational cost while maintaining a high degree of accuracy, making it feasible to study systems with a large number of electrons. The central equation in DFT is the Kohn-Sham equation, which describes a system of non-interacting electrons that reproduce the same electron density as the real interacting system (Russell et al., 2019).

The utility of DFT lies in its ability to calculate a variety of electronic properties, including molecular geometries, energies, charge distributions, and vibrational frequencies (Russell et al., 2019). It has been instrumental in studying reaction mechanisms, chemical bonding, and the stability of transition states, providing insights into processes that are challenging to access experimentally. Additionally, DFT is used to interpret spectroscopic data and predict the outcomes of catalytic and electronic materials design. The success of DFT can also be attributed to the development of numerous exchange-correlation functionals, which approximate the complex many-body interactions within a system. These functionals range from the simpler Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) to hybrid functionals like B3LYP, which incorporate a fraction of exact exchange from Hartree-Fock theory (McMullin et al., 2010). Advanced methods, such as meta-GGA and range-separated functionals, further enhance its accuracy for specific applications.

In the context of coordination chemistry, DFT is particularly valuable for studying the electronic properties of metal complexes, elucidating their structure-function relationships, and predicting catalytic behavior. By providing detailed insights into electronic structures, DFT complements experimental techniques, aiding in the rational design of new materials and catalysts. Overall, combination of accuracy, efficiency, and versatility of DFT has solidified its position as a cornerstone of computational chemistry, enabling researchers to tackle complex problems across diverse scientific disciplines.

1.1.5 Antibacterial Activity

Antibacterial studies are an essential area of research in the fight against bacterial infections, which pose a significant threat to global public health (Kondori et al., 2020). With the rising prevalence of antibiotic-resistant bacteria, such as *S. aureus*, *B. subtilis*, *E. coli*, and *S. typhimurium*, the development of new and effective antibacterial agents has become a critical priority. These studies aim to explore, design, and evaluate compounds with the potential to inhibit bacterial growth or kill pathogenic microorganisms, providing innovative solutions to combat infectious diseases.

Antibacterial agents work by targeting specific processes essential for bacterial survival, such as cell wall synthesis, protein production, DNA replication, or metabolic pathways (Tsacheva et al., 2023). Traditional antibiotics like penicillin, tetracyclines,

and fluoroquinolones have been highly successful; however, the overuse and misuse of these drugs have accelerated the emergence of multidrug-resistant (MDR) strains, rendering many antibiotics ineffective (Abu-khadra et al., 2016). This growing resistance crisis underscores the urgency for novel therapeutic strategies.

Metal-based compounds, including transition metal complexes, have gained significant attention in antibacterial studies due to their unique modes of action. Transition metals such as nickel, copper, and palladium when coordinated with biologically active ligands like Schiff base, exhibit enhanced antimicrobial properties (Silva et al., 2011). These metal complexes can disrupt bacterial membranes, interfere with essential enzymes, and generate reactive oxygen species that induce oxidative stress, leading to bacterial death.

The use of Schiff base ligands in antibacterial studies is particularly promising because of their versatility in chelating metal ions and forming stable complexes (Kondori et al., 2020). The imine ($C=N$) functional group in Schiff base plays a pivotal role in biological interactions, enhancing the antibacterial activity of the complexes. By modifying the Schiff base structure or the metal centre, researchers can tune the activity and specificity of these complexes against a broad spectrum of bacterial strains.

Antibacterial studies often involve a combination of experimental and computational approaches to evaluate the efficacy, mechanism of action, and structure-activity relationships of potential agents (Hangan et al., 2023). Methods such as disk diffusion, minimum inhibitory concentration (MIC) assays, and time-kill studies provide quantitative data on the antibacterial potency of compounds (Abu-khadra et al., 2016). Antibacterial studies play a vital role in addressing the global challenge of antibiotic resistance. They provide a foundation for discovering innovative therapies that leverage the unique properties of metal complexes and other emerging agents, paving the way for effective treatments against resistant bacterial pathogens.

1.2 Problem Statement

Although Schiff base ligands containing the azomethine ($-CH=N-$) functionality are well-known for their strong chelating ability with transition metals, systematic comparative studies of Ni(II), Cu(II), and Pd(II) complexes derived from the same bidentate Schiff base under identical synthetic conditions are lacking. The identity of the metal center can significantly influence coordination geometry, ligand field

strength, and bonding parameters due to differences in ionic radius, preferred coordination number, and electronic configuration. For instance, Cu(II) and Pd(II) often favors square planar geometry, whereas Ni(II) may adopt tetrahedral or square planar arrangements, resulting in variations in metal-ligand bond lengths, angles, and electronic properties, which in turn strongly influence catalytic activity by affecting substrate coordination, activation barriers, and reaction pathways. Using a consistent Schiff base framework allows these differences to be attributed solely to the metal center, providing a controlled platform to evaluate structure–activity relationships. However, no studies have systematically prepared Ni(II), Cu(II), and Pd(II) complexes from the same Schiff base, characterized them comprehensively through elemental analysis, FTIR, NMR, UV-Visible, and single crystal X-ray diffraction, and correlated these structural differences with catalytic performance. This gap prevents a clear understanding of how metal identity affects electronic structure, coordination behavior, and reactivity, limiting the rational design of Schiff base complexes as efficient catalysts.

The Stille reaction is a widely applied palladium-catalyzed cross-coupling method that provides a straightforward and reliable route for forming carbon-carbon bonds, making it valuable for the synthesis of pharmaceuticals, natural products, and advanced materials (Sharma et al., 2020). Although Pd(II) complexes are the standard catalysts for the Stille reaction, their use is associated with several limitations, including the high cost of palladium, concerns regarding metal scarcity, and environmental challenges related to the recovery and disposal of toxic heavy-metal residues. In contrast, Ni(II) and Cu(II) complexes offer potential advantages due to their lower toxicity, greater earth abundance, and reduced environmental burden associated with catalyst waste and metal contamination. However, despite these advantages, the use of Ni(II) and Cu(II) complexes as homogeneous catalysts for the Stille reaction remains significantly underexplored, and their catalytic mechanisms and efficiencies are not well elucidated when compared with established Pd(II) systems. This gap limits the development of more sustainable and cost-effective catalytic alternatives. Therefore, a systematic investigation of Ni(II), Cu(II), and Pd(II) complexes derived from Schiff base ligands is required to evaluate their catalytic performance and to better understand structure–activity relationships in the Stille reaction.

Although Ni(II), Cu(II), and Pd(II) catalysts have been extensively studied in the Stille reaction, there is a significant lack of integrated computational and

experimental investigations that systematically examine their electronic and catalytic behavior. Specifically, there are no detailed density functional theory (DFT) investigations employing the B3LYP functional with the 6-311++G(d,p) basis set for ligands and LANL2DZ for metal complexes to compute frontier molecular orbital (FMO), global chemical reactivity descriptors (GCRD), and molecular electrostatic potential (MEP). This lack of computational insight prevents a detailed understanding of the mechanistic roles of different metal centers in the oxidative addition, transmetalation, and reductive elimination steps of the Stille catalytic cycle. Consequently, the effect of metal identity and ligand structure on catalytic efficiency and selectivity remains poorly defined, limiting the rational design of more effective and sustainable Schiff base catalysts. Therefore, there is a clear need for a comprehensive study combining DFT calculations with experimental evaluation to predict electronic properties, clarify mechanistic pathways, and guide the development of catalysts with enhanced performance in the Stille reaction.

Antibiotic resistance is a growing problem that makes it difficult to treat infections with standard antibiotics, creating an urgent need for new antibacterial drugs. Metal complexes, particularly those with transition metals like Ni(II), Cu(II), and Pd(II), are promising candidates because they can interact with biological systems in unique ways. When these complexes are derived from Schiff bases, they may have enhanced antibacterial properties. Although metal complexes have shown potential in this area, the antibacterial activities of Ni(II), Cu(II), and Pd(II) complexes derived from Schiff bases have not been thoroughly investigated. New antibacterial agents may be developed as a result of determining their effectiveness.

1.3 Objectives

The objectives of this study were:

- i. To synthesize and characterize the bidentate Schiff base ligands derived from *ortho*-vanillin and salicylaldehyde with *para*-substituted phenylamines and their Ni(II), Cu(II), and Pd(II) complexes.
- ii. To investigate the catalytic activity of Ni(II), Cu(II), and Pd(II) complexes as homogeneous catalysts for Stille reaction and to optimize the key reaction parameters, including reaction temperatures, bases types, and catalysts amounts.

- iii. To calculate the electronic properties of the synthesized compounds using density functional theory (DFT) in order to understand how electronic structure influences their catalytic activity and efficiency in the Stille reaction.
- iv. To investigate the antibacterial potential of Ni(II), Cu(II) and Pd(II) complexes using disk diffusion method against *S. aureus*, *B. subtilis*, *E. coli*, and *S. typhimurium*.

1.4 Scope and Limitation

This research centered on ten bidentate Schiff base ligands, categorized into two series: B1 and B2, along with their Ni(II), Cu(II), and Pd(II) complexes. The B1 ligands were synthesized from *ortho*-vanillin, whereas the B2 ligands originated from salicylaldehyde. Each ligand was formed through condensation with phenylamine derivatives bearing *para*-positioned substituents, specifically H, CH₃, OCH₃, Cl, and NO₂. The structure of ligands and metal complexes are shown in Table 1.1 and Table 1.2, respectively. All synthesized ligands and their metal complexes were characterized by CHN elemental analysis, molar conductivity, melting point, magnetic susceptibility, FTIR, ¹H and ¹³C NMR, UV-Visible, and single crystal X-ray diffraction. A total of 40 compounds were synthesized in this study, comprising 20 newly identified compounds using Cambridge Crystallographic Data Centre (CCDC). 11 crystals structures were successfully harvested, six of which are new compounds (B2Me, CuB1Me, PdB1OMe, PdB2Me, PdB2OMe, and PdB2C) demonstrating the novelty of this research. B1H (Yu, 2011), B1Me (Yeap et al., 2003), B2H (Ahmed et al., 2021), CuB2H (Wei et al., 1964), and CuB2C (Xiao & Cao, 2020) are previously published compounds.

Screening for the best catalytic series was performed prior to the optimization process by comparing the percent conversion of the reactant after 60 minutes of reaction. For a detailed investigation, five Pd(II) complexes of B1 series were used as catalysts for optimization by varying three reaction parameters which were the temperatures (30 °C, 60 °C, 80 °C, 100 °C), types of bases (KOH, K₂CO₃, triethylamine (TEA)), and amounts of catalysts (0.5, 1.0, 1.5, 2.0 mmol%). Gas chromatography-flame ionization detector (GC-FID) was used to monitor the progress of the Stille reaction.

The electronic structure interaction in compounds was explained and displayed using the frontier molecular orbitals which include the difference between the highest occupied molecular energy (HOMO) and lowest unoccupied molecular energy (LUMO) via Gaussian09w and GaussView16 software. Other than that, global chemical reactivity descriptors comprising chemical potential, chemical hardness, chemical softness, electronegativity and electrophilicity were utilized in evaluating the stability and reactivity of the synthesized compounds. As an additional part of this study, an antibacterial activity screening was also carried out on representative synthesized Schiff base ligands and their Ni(II), Cu(II), and Pd(II) complexes using the disk diffusion method.

However, there are potential limitations that may impact the research outcomes. Certain constraints were encountered in terms of structural elucidation. Theoretical studies were primarily limited, as only selected complexes could be calculated using density functional theory (DFT) due to restricted access to specialized high-performance computers, potentially constraining the depth of the study.

Furthermore, a significant challenge in performing NMR spectroscopy is the solubility of certain complexes in deuterated solvents. Some metal complexes, coordination compounds, or highly stable crystalline structures exhibit low solubility, making it difficult to obtain clear spectral data. When a complex does not dissolve properly, signal intensity weakens, or peaks may not appear at all, preventing accurate structural characterization.

Table 1.1
Structure of B1 Series of Ligands and Their Complexes

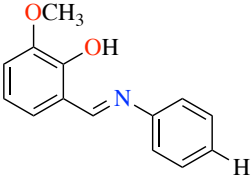
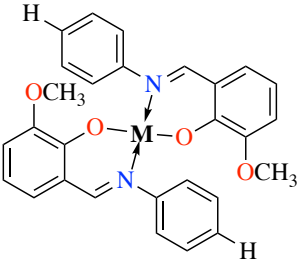
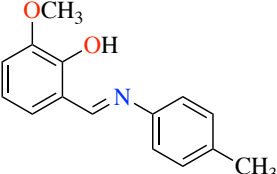
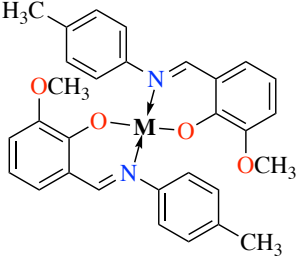
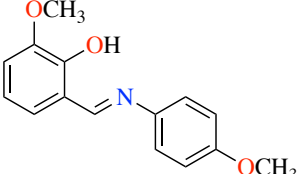
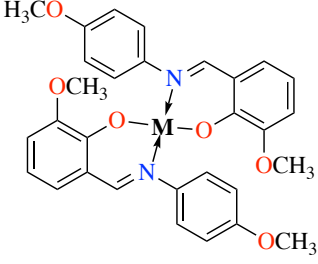
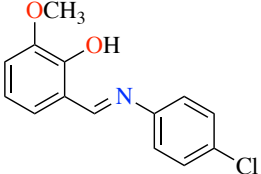
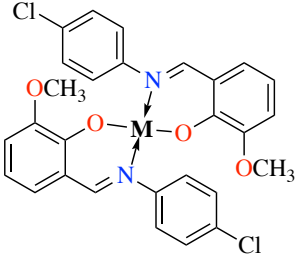
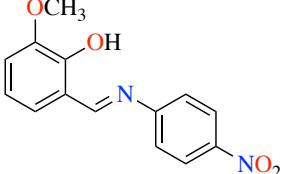
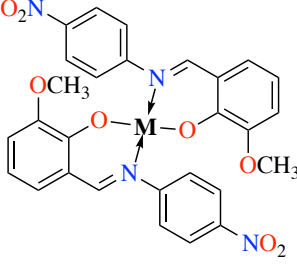
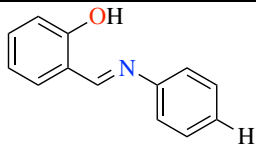
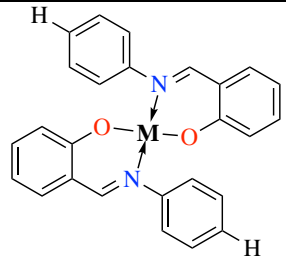
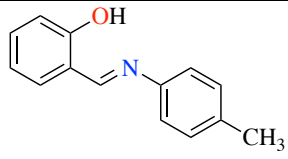
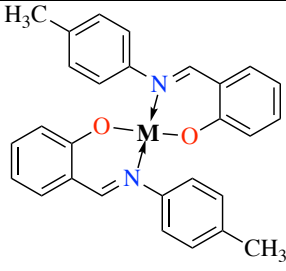
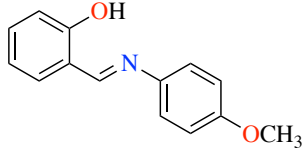
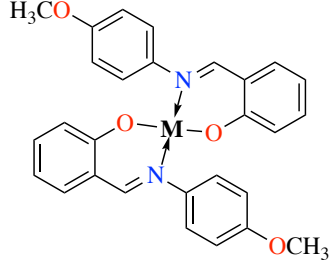
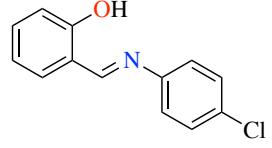
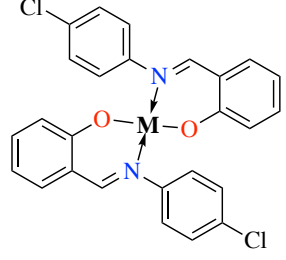
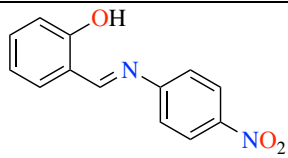
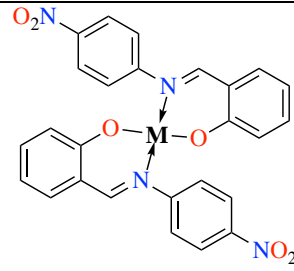
Ligands	Complexes (M: Ni, Cu, Pd)
 B1H	 MB1H
 B1Me	 MB1Me
 B1OMe	 MB1OMe
 B1C	 MB1C
 B1N	 MB1N

Table 1.2
Structure of B2 Series of Ligands and Their Complexes

Ligands	Complexes (M: Ni, Cu, Pd)
 B2H	 MB2H
 B2Me	 MB2Me
 B2OMe	 MB2OMe
 B2C	 MB2C
 B2N	 MB2N

1.5 Significance of Study

This research contributed to the development of novel coordination compounds, highlighting the versatility of Schiff base ligands in stabilizing metal centers and expanding their applications in catalysis and computational chemistry. The study of the Stille reaction in this research was driven by its relatively underexplored potential when catalyzed by Schiff base complexes. The Stille reaction was a powerful and widely used method for forming carbon-carbon bonds, which were fundamental to organic synthesis, particularly in the development of pharmaceuticals, agrochemicals, and advanced materials. However, despite its significance, there was limited research on how novel coordination compounds, such as Ni(II), Cu(II), and Pd(II) Schiff base complexes, could function as efficient homogeneous catalysts for this reaction. This gap highlights the novelty of the present research, which investigates these complexes to expand the scope of Schiff base complexes in catalysis.

Additionally, the utilisation of Density Functional Theory (DFT) in this research extends significantly beyond the structural characterization of the synthesized complexes. The study employs DFT as a mechanistic and predictive tool to deepen the understanding of catalytic pathways involved in the Stille reaction. Specifically, DFT calculations are used to model the key steps of the catalytic cycle as such oxidative addition, transmetalation, and reductive elimination to estimate activation energy barriers and identify the most energetically feasible pathways for each metal complex. Frontier molecular orbital analyses (HOMO-LUMO distributions), energy gap evaluations, molecular electrostatic potential (MEP) mapping, and global reactivity descriptors such as chemical hardness, chemical softness, chemical potential, electronegativity, electrophilicity index, and maximum additional electric charge are examined to elucidate how Schiff base ligands modulate the electronic environment at the metal center. These parameters provide insight into charge distribution, nucleophilicity/ electrophilicity patterns, and the overall reactivity of the complexes, thereby influencing substrate binding and catalytic performance. Through these analyses, the computational results can be correlated with experimental observations, ultimately supporting the rational design of improved Schiff base catalysts. The integration of DFT at this deeper mechanistic level responds directly to a notable gap

in the literature, where computational confirmation of catalytic efficiency for Schiff base catalysts remains limited.

With the rise of drug-resistant bacteria, there was a critical need for new antimicrobial agents. This study explored the antibacterial potential of the synthesized metal complexes against representative bacterial strains using the disk diffusion method, which might potentially serve as alternative antimicrobial agents with significant potential in both medicine and environmental science. The finding would provide useful information towards developing new antibiotics.

This research supports Sustainable Development Goal 7 (Affordable and Clean Energy) by developing energy-efficient and environmentally friendly Schiff base catalysts for organic synthesis, enhanced through DFT-based optimization to reduce energy input and chemical waste. It also aligns with Sustainable Development Goal 12 (Responsible Consumption and Production) by promoting greener catalytic processes that minimize hazardous byproducts, optimize resource utilization, and encourage sustainable practices in chemical manufacturing. Furthermore, it contributes to national policy priorities on sustainable energy and green chemistry by advancing cleaner technologies that support industrial innovation and reduce environmental impact. In the Malaysian context, this research is directly aligned with the National Science, Technology and Innovation Policy (DSTIN 2021-2030) and the 10-10 MySTIE framework, which aim to elevate the nation from a consumer to a creator of high-tech innovation in science and technology. By developing locally synthesized, well-characterized Ni(II), Cu(II), and Pd(II) Schiff base catalysts and advancing computational insight into their electronic structures, this work supports national goals of fostering indigenous research and development capabilities and cultivating economic value from scientific discovery.

1.6 Research Flow Chart

The flowchart illustrates the research process for synthesizing and characterizing Schiff base ligands and their metal complexes, highlighting the key steps from synthesis to applications. The flow of research work for this research is given in Figure 1.5.

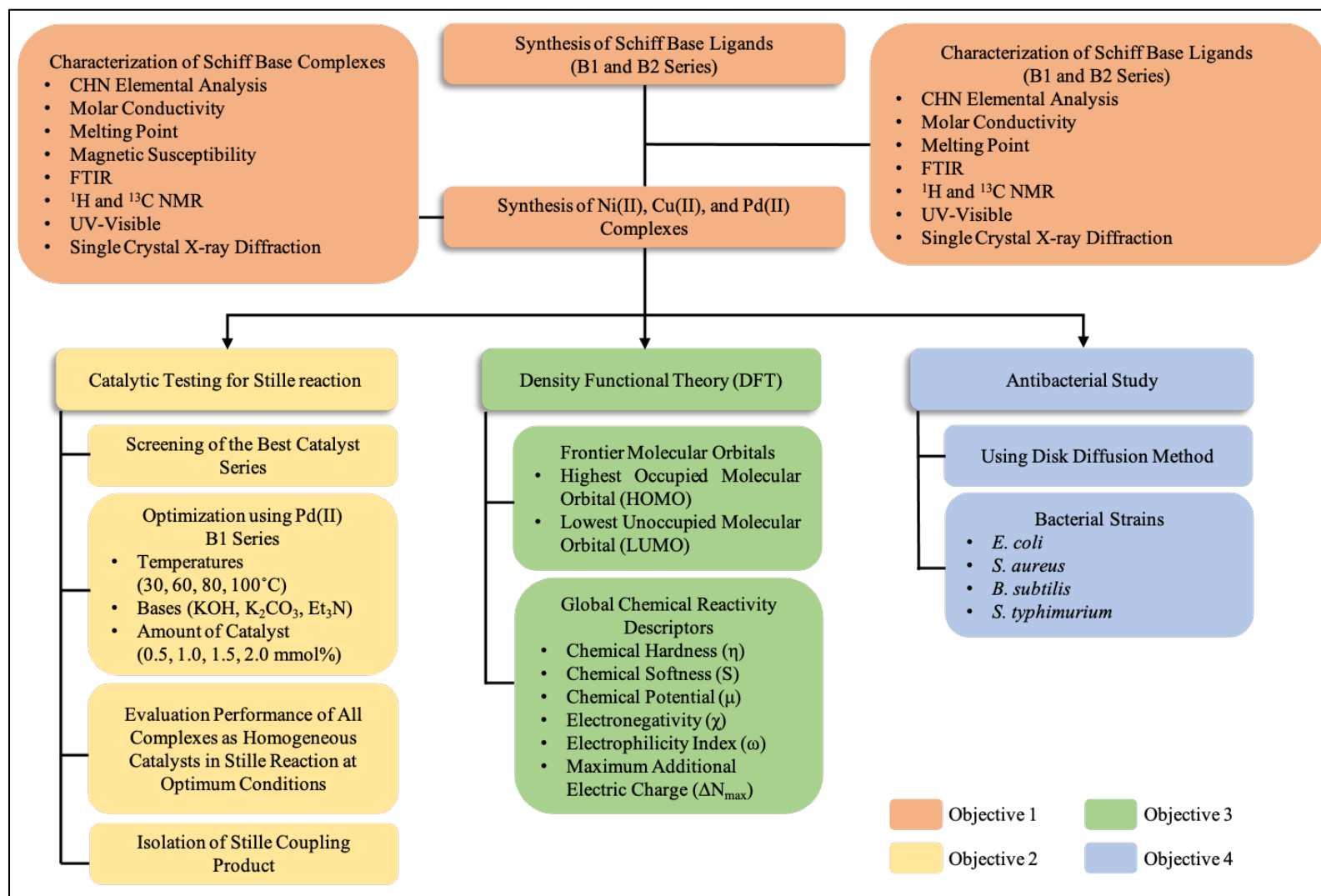


Figure 1.5 Flow of Research Work

CHAPTER 2

LITERATURE REVIEW

2.1 Schiff Base Ligands

Schiff base is a good class of chelating organic compounds capable of binding to different metal ions with interesting medicinal and non-medicinal properties (Berhanu et al., 2019), particularly in the presence of nearby oxygen or sulfur donor atoms. The two common donor atoms, N and O, of the chelated Schiff base exert two opposite electronic effects: the phenolate oxygen is a hard donor which stabilizes the higher oxidation state of the metal atom; whereas the imine nitrogen is a soft donor which stabilizes the lower oxidation state of the metal ion (Kumar, 2020). These nitrogen and oxygen donor atom ligands are excellent chelating agents for transition and non-transition metals, forming stable compounds with most transition metals (Kondori et al., 2020).

The classic synthesis method of Schiff base is a condensation of carbonyl compound with primary amine carried out in solution where solvents are usually organic compounds forming azeotropic mixtures (Kılınç & Şahin, 2019). The mixture of amine and carbonyl are refluxed and the water elimination is occasionally carried out in a Dean Stark apparatus. Water is regarded as a hindering factor that inhibits the progress of chemical reaction, which can be eliminated using molecular sieves or dehydrating agents functioning as catalysts such as phosphorous(V) oxide supported on silica, titanium(IV) chloride, magnesium perchlorate, aluminum chloride and hydrobromic acid (Mirosław, 2020).

2.1.1 Framework of Schiff Base Ligands

The structural versatility of Schiff base ligands arises primarily from the wide range of aldehydes and amines that can be employed in their synthesis, allowing systematic modification of both the electronic and steric environment around the imine functionality (Aboura et al., 2018). Variations in the aldehyde component, particularly in aromatic systems, play a crucial role in defining the overall ligand framework, conformational rigidity, and coordination behavior toward metal ions (Nandaniya et al.,

2024). As a result, comparative studies involving different aldehydes have been extensively used to correlate ligand structure with coordination geometry, stability, and functional properties of the resulting metal complexes in Section 2.1.1.1.

Substituent effects on the aromatic aldehyde ring further influence the physicochemical properties of Schiff base ligands and it will be discussed in Section 2.1.1.2. Electron-donating and electron-withdrawing groups can modulate the electron density at the imine nitrogen, thereby affecting metal-ligand bond strength and ligand field strength (Lei et al., 2023). In addition, the position of substitution (*ortho*, *meta*, or *para*) has a pronounced impact on steric hindrance and ligand planarity. *Para*-substituted Schiff base ligands are frequently preferred in ligand design, as substitution at the *para* position minimizes steric congestion near the coordination site, promotes greater planarity, and facilitates more effective metal-ligand interactions compared to *ortho*-substituted analogues (Yeap et al., 2003).

Consequently, the use of *para*-substituted aldehydes provides an effective strategy for isolating electronic effects while reducing steric interference, enabling clearer structure–property correlations (Sarah et al., 2024). Such comparative aldehyde and substituent studies are therefore essential for understanding how subtle modifications in Schiff base frameworks influence coordination geometry, electronic structure, and reactivity, forming a rational basis for the design of metal complexes with tailored structural and catalytic properties.

2.1.1.1 Effect of Aldehydes on Schiff Base Ligands

Ortho-vanillin and salicylaldehyde differ in both their electronic and steric profiles, leading to distinct influences on metal-ligand behaviour and catalytic performance. *Ortho*-vanillin possesses three functional groups: an aldehyde, an *ortho*-hydroxy group, and a methoxy group positioned meta to the hydroxyl. The methoxy group is a strong electron-donating substituent, contributing electron density to the aromatic ring via resonance and inductive effects. This increased electron density strengthens the ability of the ligand to donate electrons to a coordinated metal center, which can help stabilize higher oxidation states, and influencing reactivity toward electrophiles (Hijas et al., 2019). In addition, the extra substituent, methoxy group also subtly increases steric bulk, which can affect selectivity by controlling substrate approach to the metal center.

In contrast, salicylaldehyde contains only an aldehyde and an *ortho*-hydroxy group, lacking the methoxy substituent. This gives it a simpler, more electron-neutral framework that keeps the coordinated metal center relatively electron-deficient, thereby increasing its electrophilicity, potentially favoring binding of nucleophilic substrates or promoting oxidative addition steps in catalytic cycles (Wang et al., 2024). The resulting metal complexes are more Lewis acidic, which can promote nucleophilic substrate binding, facilitate oxidative addition steps, and potentially accelerate turnover rates in catalytic cycles where substrate association is rate-limiting.

By organizing the study into two series, a systematic comparison was created: B1 series (*ortho*-vanillin derivatives) explores the effect of increased electron donation and slight steric modification, while the other, B2 series (salicylaldehyde derivatives) serves as a more electron-neutral, less sterically hindered baseline. This allows clearer evaluation of how electron-donating substituents and steric effects influence catalytic performance, stability, and selectivity.

2.1.1.2 Effect of Substituents on Schiff Base Ligands

Moreover, the structure of the chosen ligands in this study, which incorporates both electron-withdrawing (-Cl and -NO₂) and electron-donating substituents (-CH₃ and -OCH₃) at the *para* position, offers several advantages in tuning its chemical behavior. When placed at the *para* position on an aromatic ring, these substituents exert strong resonance and inductive effects without introducing significant steric hindrance near the binding site, allowing for efficient and predictable electronic modulation (Hameed & Azad, 2024). This “push-pull” electronic balance can improve catalytic activity, stability, and selectivity by stabilizing reactive intermediates while maintaining an accessible and symmetrical coordination environment. Additionally, the combination of both substituent types may enhance the solubility of ligand and oxidative stability, further supporting its performance in various catalytic systems.

The electron-donating group such as methyl (-CH₃) and methoxy (-OCH₃) increase electron density at the imine nitrogen and phenolic oxygen donor sites through inductive and mesomeric effects. This strengthens metal-ligand σ -interactions, enriching the electron density of the coordinated metal center. In catalysis, this electron enrichment enhances the activation of electrophilic substrates, promotes nucleophilic attack, and stabilizes higher oxidation states of the metal. Such stabilization lowers the

energy barrier for key steps, particularly reductive elimination, thereby accelerating catalytic turnover and improving overall efficiency (Liang & Chen, 2018).

In contrast, the electron-withdrawing group such as chloro (-Cl) and nitro (-NO₂) decrease electron density at the donor atoms by inductive and resonance effects, thereby reducing the basicity of the ligand and the electron density at the coordinated metal center. This can be advantageous in catalytic reactions where a more electrophilic metal center enhances substrate activation, particularly in processes involving oxidative addition or electrophilic activation steps. Thus, the systematic variation of *para*-substituents provides a means to fine-tune the electronic properties of the Schiff base ligands, enabling control over metal-centered reactivity and offering a rational approach to optimizing catalytic efficiency (Lei et al., 2023).

2.1.2 Schiff Base Complexes

Due to excellent ligating properties and relatively facile synthesis methods, the Schiff base ligands are widely used in transition metal coordination chemistry (Abdel-Rahman et al., 2019). In addition, the solid compounds of Schiff base are stable and can be stored at room temperature without any extra special precautions. Steric and electronic effects around the metal core can be finely tuned by an appropriate selection of bulky and/or electron-withdrawing or electron-donating substituents incorporated into the Schiff base. Schiff base ligands can coordinate with the metal centres due to the presence of lone pair electrons in donor atoms. The interaction of the Lewis acid-base is responsible for the coordination of Schiff base to a metal centre where electron-rich moieties, such as imine nitrogen, donate electrons to the metal centre to form dative covalent bonds (İnci et al., 2021).

Normally, the preparation of Schiff base complexes is conducted through the reaction of Schiff base ligands with metal acetate under reflux reactions. Basically, the synthesized Schiff base ligands or complexes will undergo purification step to confirm the purity of the compound. Column chromatography technique on silica gel is one of the common purification techniques used in synthesis laboratory. The technique however, has the potential to degrade on the compounds. Hence, recrystallizations are the most preferable way of purifying the compounds.

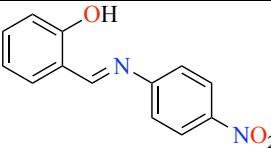
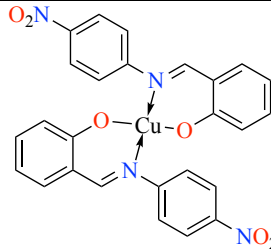
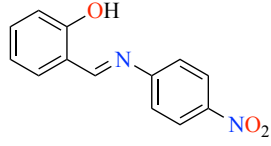
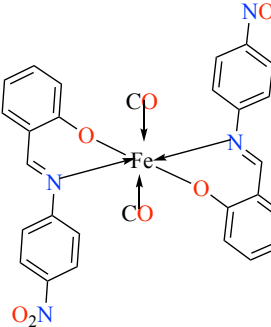
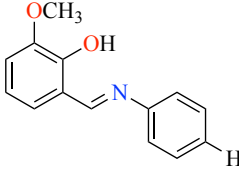
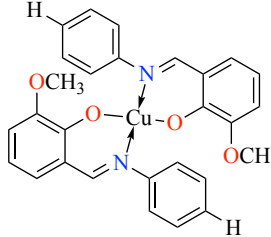
Over recent years, Schiff base ligands and their metal complexes have gained considerable attention. These compounds have been used in different areas, such as

heterogeneous and homogeneous catalysis for organic compound oxidation and polymerization (Zulu et al., 2020). Metal complexes containing Schiff base ligands have demonstrated attractive properties such as interesting magnetism and strong catalytic activities (Gholizadeh et al., 2017). By changing their structural architecture, as well as electronic properties, the physical and chemical properties of imines can be altered. By manipulating chemical structures, the application of Schiff base and their metal complexes can be significantly diversified, infiltrating diverse fields such as catalysis, corrosion safety, sensor systems, and a wide range of bioactivity (Khosa et al., 2015). Bidentate Schiff base are well known to coordinate with various metal ions where have gained a lot of interest in recent years because of their rich coordination chemistry (Sakhare et al., 2015), and have remarkable behaviors of stability and thermal degradation (Al-Zaidi et al., 2019). Metal complexes have been proven to be effective stereospecific catalysts for oxidation, reduction, hydrolysis, biological activity, and other organic and inorganic chemistry transformations. Schiff base complexes play a vital role in designing metal complexes related to synthetic and natural oxygen carriers. Transition metal-catalyzed C-C bond formation reactions are acknowledged to be a powerful method for synthesis and an important emphasis on many organic transformations for academic and industrial processes (Sarwar et al., 2018).

Previous studies as shown in Table 2.1 have reported Schiff base ligands with similar designs to those in this research, but their applications have largely been limited to biological studies, typically involving copper and iron complexes. However, there is limited information on the use of nickel and palladium with these ligands, particularly in the context of catalytic applications. To address this gap, the present research focuses on the development and investigation of nickel, copper, and palladium Schiff base complexes, aiming to evaluate their catalytic potential and establish structure-activity relationships.

Table 2.1

Previous Studies of Schiff Base Ligands and Their Complexes

Schiff Base Ligand	Metal Complexes	Application	Reference
		Antibacterial Study	(Kondori et al., 2020)
		Antimicrobial and anticancer Study	(Kupwade & Sawant, 2020)
		Antimicrobial Study	(Sobola et al., 2014)

2.1.2.1 Nickel Schiff Base Complexes

Nickel was discovered by Axel Fredrik Cronstedt in 1754, is a transition metal with atomic number 28 and an atomic mass of 58.71. It appears as a silver-white, ductile metal and is positioned in Group 10, Period 4 of the periodic table. The electronic structure of nickel is $[\text{Ar}]3d^8 4s^2$, which enables it to access a range of oxidation states, most commonly 0, +1, +2, +3, and +4. This versatility in oxidation state is central to its catalytic activity, particularly in cross-coupling reactions, where nickel can participate in both two-electron and single-electron redox processes (Wu et al., 2023). Nickel complexes exhibit diverse geometries, including square planar, tetrahedral, and octahedral, with coordination numbers typically ranging from two to six depending on the ligands and oxidation state (Michael et al., 2014).

In cross-coupling catalysis, the ability of nickel to stabilize multiple oxidation states (Ni(0), Ni(I), Ni(II), Ni(III), and even Ni(IV)) allows for unique mechanistic pathways, such as radical and non-radical cycles, that are not always accessible to other

transition metals like palladium (Han, 2013). This flexibility enables nickel catalysts to activate a broad spectrum of substrates, including traditionally inert aryl ethers and alkyl electrophiles, and to facilitate challenging C-C and C-heteroatom bond formations under mild conditions (Adhikary & Guan, 2014). The structural diversity and redox properties of nickel complexes, combined with their earth abundance and cost-effectiveness, have made nickel a highly attractive and practical catalyst for modern cross-coupling reactions.

Nickel Schiff base complexes rely heavily on geometry and oxidation state to determine catalytic behavior, particularly because nickel readily accesses Ni(0), Ni(I), Ni(II), and Ni(III) states. Tetradentate Schiff bases enforce square planar Ni(II) geometries, stabilizing low-spin d^8 configurations that support predictable and selective catalytic reactions such as olefin oligomerization, epoxide opening, and cross-coupling (Cozzi, 2004; Yamabe & Yamazaki, 2003). The rigid ligand environment suppresses high-spin states and limits access to Ni(I)/Ni(III) intermediates, which increases selectivity but reduces overall reactivity. By contrast, bidentate Schiff bases often give rise to tetrahedral or octahedral Ni(II) geometries that are high-spin and flexible, enabling easier changes in coordination number during catalysis (Rani & Singh, 2018). These geometries facilitate redox cycling involving Ni(I) and Ni(III), which is essential for modern Ni-catalyzed C-C bond formation, hydrogenation, and C-H activation. While this flexibility enhances catalytic turnover, it also makes complexes more susceptible to decomposition. Thus, nickel catalysis benefits from tetradentate square planar complexes for stable, selective catalysis, whereas bidentate tetrahedral/octagonal complexes support redox-intensive, high-activity pathways.

2.1.2.2 Copper Schiff Base Complexes

Copper was one of the first metals discovered and used by humans, with evidence of its use dating back to ancient civilizations, though its formal recognition as an element is attributed to early chemists in antiquity. Copper has the atomic number 29 and an atomic mass of approximately 63.55. Physically, it is a reddish-orange, malleable, and ductile metal with high thermal and electrical conductivity. In the periodic table, copper is located in Group 11 and Period 4, classified as a transition metal. Its electronic structure is $[\text{Ar}] 3d^{10} 4s^1$, which allows copper to access multiple

oxidation states, most commonly +1 (cuprous) and +2 (cupric), but also 0 and, less frequently, +3.

Copper complexes can adopt a variety of geometries, including linear, trigonal planar, tetrahedral, square planar, and octahedral, depending on the oxidation state and ligand environment. The coordination number for copper typically ranges from 2 to 6. The ability of copper to cycle between different oxidation states and form diverse coordination environments underpins its effectiveness as a catalyst in cross-coupling reactions. In recent years, copper has emerged as a versatile and cost-effective alternative to precious metals like palladium for catalyzing C-C and C-heteroatom bond-forming cross-coupling reactions, often under mild and ligand-free conditions (Liu & Wan, 2011). Copper catalysts are particularly valued for their abundance, low toxicity, and unique reactivity patterns, enabling efficient coupling of a wide range of organometallic reagents and electrophiles, including challenging substrates such as unactivated alkyl halides and heteroaryl compounds (Thapa et al., 2015). This versatility has led to the widespread adoption of copper-catalyzed cross-coupling in both academic and industrial organic synthesis (Afsina et al., 2021).

Copper Schiff base complexes show pronounced geometry-reactivity relationships because copper frequently cycles between Cu(I), Cu(II), and occasionally Cu(III) during catalysis. Tetradentate N₂O₂ Schiff bases typically stabilize Cu(II) in square planar or square pyramidal geometries that restrict geometric reorganization and favor oxidative processes such as alcohol oxidation, phenol oxidation, and biomimetic oxygen activation (Kayan et al., 2010; Sundberg & Martell, 1978). These complexes maintain the Cu(II)/Cu(III) redox couple more efficiently due to their rigid coordination environment, giving high selectivity in oxygen-transfer reactions. In contrast, bidentate Schiff bases often produce tetrahedral Cu(I) or distorted Cu(II) complexes that are highly flexible, enabling rapid ligand exchange and making them ideal for catalytic reactions such as azide-alkyne cycloaddition (CuAAC), radical transformations, and polymerization (Gupta & Sutar, 2008). The ability of bidentate ligands to stabilize both Cu(I) and Cu(II) is critical for redox cycling, providing fast turnover but lower resistance to oxidation. Therefore, copper catalysis relies on tetradentate square planar complexes for controlled oxidative processes, while bidentate tetrahedral complexes enhance flexibility and support fast Cu(I)/Cu(II) redox cycling.

2.1.2.3 Palladium Schiff Base Complexes

Palladium was discovered in 1803 by the English chemist William Hyde Wollaston. It has an atomic number of 46 and an atomic mass of approximately 106.42. Physically, palladium is a lustrous, silvery-white, malleable, and ductile metal. In the periodic table, it is positioned in Group 10 and Period 5, classified as a transition metal. The electronic structure of palladium is $[\text{Kr}] 4d^{10}$, which allows it to access multiple oxidation states, most commonly 0 and +2, but also +1 and +4 in certain complexes. Palladium complexes exhibit a variety of geometries, including square planar especially for Pd(II), tetrahedral, and less commonly octahedral, with coordination numbers typically ranging from 2 to 6 depending on the ligands and oxidation state (Rúa-Sueiro et al., 2022).

The uniqueness of palladium electronic configuration and ability to cycle between oxidation states underpin its exceptional catalytic activity in cross-coupling reactions. It serves as the central catalyst in a wide range of C-C and C-heteroatom bond-forming reactions, such as the Suzuki-Miyaura, Heck, Stille, Sonogashira, and Buchwald-Hartwig couplings, which are fundamental in organic synthesis for pharmaceuticals, agrochemicals, and materials science (Manabe, 2015; Zhang et al., 2023). The versatility of palladium catalysts is further enhanced by the use of various ligands, including phosphines and N-heterocyclic carbenes, which allow for fine-tuning of the catalyst's stability, reactivity, and selectivity (Chakraborty et al., 2021; Marion & Nolan, 2008). Advances in palladium catalysis include the development of well-defined complexes, nanoparticles, and single-atom catalysts, all of which have demonstrated high efficiency, recyclability, and the ability to catalyze challenging cross-coupling reactions under mild conditions (Christmann & Vilar, 2005; Elhampour & Nemati, 2017). As a result, palladium remains the most widely studied and utilized transition metal for cross-coupling catalysis in both academic and industrial settings (Colacot, 2012).

Palladium Schiff base complexes display catalytic behavior that is strongly influenced by ligand geometry and oxidation state. Tetradentate Schiff bases commonly stabilize Pd(II) in a square planar d^8 geometry, creating a rigid coordination sphere ideal for oxidative addition and reductive elimination steps in cross-coupling reactions such as Suzuki, Heck, and Sonogashira (Tsuji, 2006; Cozzi, 2004). This geometry not only enhances the stability of the Pd(II) active species but also minimizes unwanted side

reactions caused by ligand dissociation. In contrast, Gupta & Sutar (2008) reported that bidentate Schiff bases often yield more flexible square planar or pseudo-tetrahedral geometries, generating complexes with higher ligand-exchange rates that can increase catalytic turnover but reduce catalyst lifetime. Oxidation state plays a critical role: Pd(0)/Pd(II) cycling is essential in most catalytic cycles, and Schiff base rigidity influences how easily the metal transitions between these states. Tetradentate complexes stabilize Pd(II) and slow reduction to Pd(0), improving selectivity, whereas bidentate ligands facilitate faster Pd(II) $\rightarrow$ Pd(0) conversion, enhancing activity at the cost of stability. Thus, for palladium catalysis, geometry and oxidation state control are tightly coupled, with tetradentate square planar complexes favoring controlled, selective catalysis, and bidentate complexes promoting faster but less robust catalytic cycles.

2.2 Catalysis

The Swedish chemist Jöns Jacob Berzelius has introduced the idea of catalysis more than 180 years ago and describes a catalyst as any material that increases the rate of a chemical reaction without consumption (Ludwig & Schindler, 2017). Many years later in 1895 Ostwald, who won the coveted Nobel Prize in Chemistry in 1909 came up with the definition that is used until today: “A catalyst is a substance that accelerates a chemical reaction without affecting the position of the equilibrium.” Due to the presence of catalyst in a chemical reaction, the reaction rate has proven to increase without affecting reaction equilibrium (Agostini & Radnik, 2020). Figure 2.1 displays the activation energy in catalysis as reported by Mashuri et al. (2020). Catalysts are not only essential in small-scale laboratory applications but also in a wider industry (Deraz, 2018).

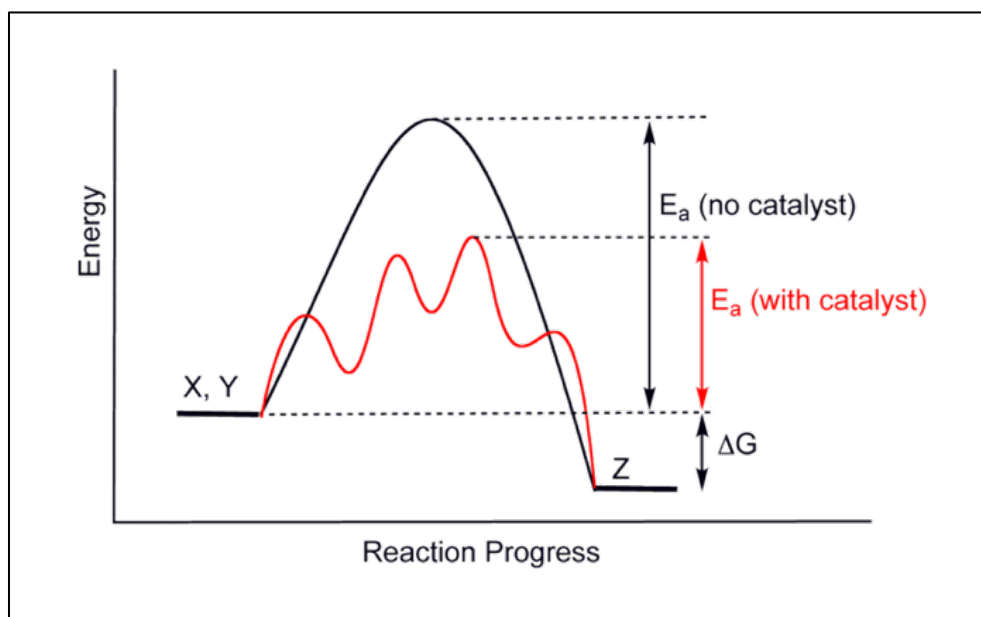


Figure 2.1 Activation Energy in Catalysis

Two types of catalysis, namely homogenous and heterogeneous catalysts, rely on the aggregation phase during which the catalyst works. Homogeneous catalysts are both the catalyst and the reactants are in the same phase, for example, all are molecules in gas phase or more commonly in liquid phase. Heterogeneous catalysts exist in different phase in which, for example, catalysts and reactants form separate physical phases in a solid state while the reaction mixture may be in either gaseous or liquid form (Vincent et al., 2016). Heterogeneous catalysts have a significant advantage over homogeneous catalysts, it makes easier and cheaper to separate and reuse of heterogeneous catalysts (Argyle & Bartholomew, 2015). The recyclable, reusable of the catalyst as well as low separation degree after it has been used in a reaction can be very costly for homogeneous catalysts.

However, Krishna et al. (2020) argue that despite understanding the advantages of heterogeneous catalysts in terms of separation and recyclability, homogeneous catalysts are actually more prevalence in chemical reactions because each catalytic entity can function as a single active site making homogeneous catalysts more active and selective than conventional heterogeneous catalysts such as oxides or supported metal particles. On the other hand, the heterogeneity of the surface sites is a common feature of heterogeneous catalysts that would impede a clear understanding of its mechanism of action. With its excellent selectivity, simple preparation, and ability to proceed under mild conditions, the homogeneous catalyst is more preferable. Moreover, homogeneous catalyst is more suitable to achieve a green chemistry because of the

processes that are very environmental compared to heterogeneous catalysts (Grison & Barrault, 2018).

Transition metal is the most common metal used as a catalyst in chemical reactions. Transition metal has the potential to improve the reaction rate by assisting through single or multiple steps to produce the end product (Dell'Anna et al., 2006). Transition metals and their compounds have been the key catalysts for chemical reactions such as coupling reactions as these metals have the ability to activate an array of organic compounds in which new bonds can be catalyzed (Lima et al., 2020). The application of the transition metal complexes can be found in most well-known cross-coupling reactions. These metals are used in the form of complexes along with ligands, as the presence of the ligands has an enormous role in stabilizing and improving the reaction rate and selectivity (Rendón-López et al., 2019).

2.2.1 Carbon-Carbon Coupling Reaction

Carbon-carbon coupling reactions are essential in organic synthesis, allowing chemists to build complex molecules by forming new C-C bonds. The most widely used methods are transition metal-catalyzed cross-coupling reactions, with palladium catalysts being central to classic processes like Suzuki, Heck, and Negishi couplings, which efficiently join organic halides and organometallic reagents (Chang et al., 2020; Huang et al., 2020; Nasrollahzadeh et al., 2018). Figure 2.2 shows the examples of cross coupling types. Advances in catalyst design have led to the use of other metals such as nickel, copper, iron, and manganese, which offer benefits in cost, toxicity, and sustainability, and have enabled new strategies like reductive and dehydrogenative coupling (Waiba & Maji, 2020; Xue & Lin, 2010).

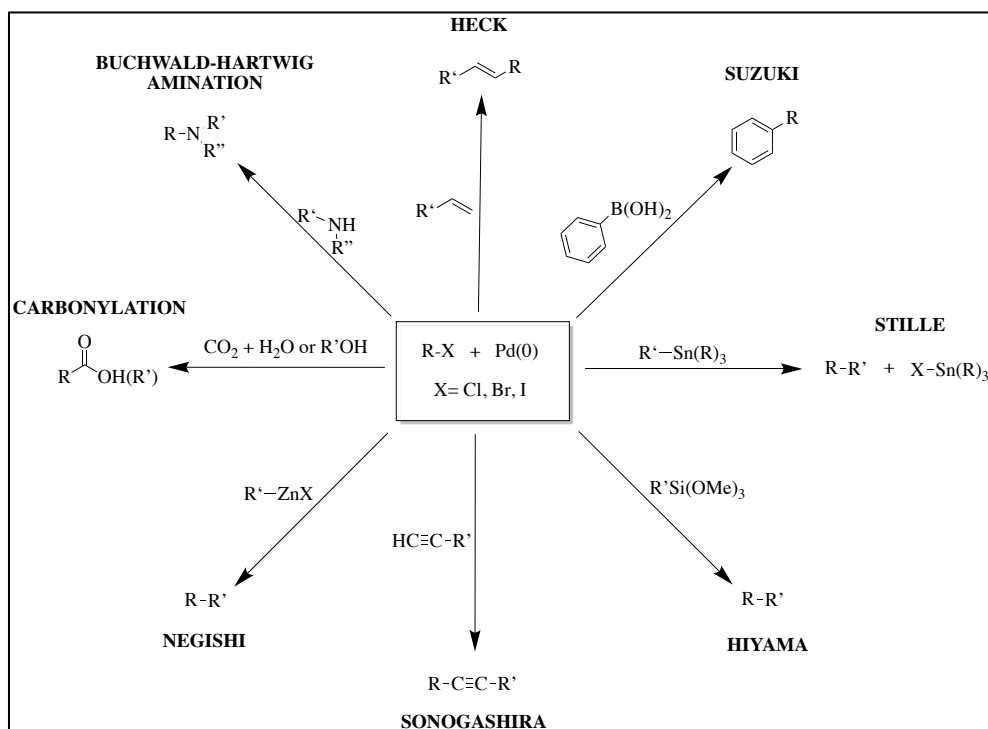


Figure 2.2 Examples of Cross-Coupling Types

Homogeneous catalysts are widely used in carbon-carbon coupling reactions, especially in traditional cross-coupling methods. Palladium(II) acetate is a widely used precursor for homogeneous palladium catalysts. When combined with phosphine ligands such as triphenylphosphine (PPh_3), dialkylbiaryl phosphines, or bidentate ligands, it forms active catalytic species for cross-coupling reactions like Suzuki, Heck, and Stille couplings (Martin & Buchwald, 2008; Yilmaz, 2018). The choice of phosphine ligand significantly influences the catalyst's activity, selectivity, and stability. Bulky and electron-rich phosphines, such as dialkylbiaryl phosphines and ylide-substituted phosphines (YPhos), enhance the rate of oxidative addition and reductive elimination, expanding the substrate scope to include challenging aryl chlorides and hindered systems (Newman & Lautens, 2011). Bidentate phosphine-imine ligands and ferrocenyl phosphine ligands have also been developed to improve solubility and performance in specific media, such as supercritical CO_2 (Matsheku et al., 2021). Mechanistic studies, both experimental and theoretical, continue to deepen understanding of these reactions, guiding the development of more selective and sustainable processes (Andrade & Martins, 2020). Overall, carbon-carbon coupling reactions remain a cornerstone of modern synthetic chemistry, with ongoing innovations expanding their scope and efficiency.

Transition metals play a central role in carbon-carbon coupling reactions, serving as catalysts that enable the formation of new C-C bonds with high efficiency and selectivity. Palladium (Pd) is the most widely used transition metal for classic cross-coupling reactions such as Suzuki, Heck, and Sonogashira couplings, due to its exceptional catalytic activity and broad substrate compatibility (Tsuji & Fujihara, 2012). However, Shang & Liu (2011) state that other transition metals including nickel (Ni), copper (Cu), iron (Fe), platinum (Pt), gold (Au), and silver (Ag) have also been developed as effective catalysts, each offering unique advantages in terms of cost, reactivity, and environmental impact. First-row transition metals like nickel and copper are especially attractive for their abundance and lower toxicity, and have enabled new reductive and decarboxylative coupling strategies (Dyker, 1999). Overall, the choice of transition metal catalyst depends on the specific reaction, desired selectivity, and practical considerations such as cost and sustainability (Kostas, 2021).

2.2.2 Stille Reaction

Stille reaction is an organic reaction of an organohalide with an organotin compound that uses palladium catalyst to give the coupled product. It has been shown that this type of reaction is an effective technique for construction of C-C bonds. Gholamian & Hajjami (2019) state that the selective C-C bond formation reactions are also essential steps in a broad variety of organic processes from supramolecular chemistry to natural products synthesis. There are therefore various research groups around the world are designed to expand new methodologies and various catalysts for forming C-C bonds. The important structural motifs that can be prepared by Stille reaction are biaryl compounds (Jana et al., 2009). Stille reactions have been used in the syntheses of various biaryl compounds, which are important intermediates in the syntheses of natural products, functionalized polymers, and pharmaceuticals (Yano et al., 2013).

Figure 2.3 displays the time cited and publications over time on Stille reaction from 1970 to 2025. The graph illustrates the research trajectory of the Stille reaction, highlighting both publication output and citation trends over time. Initially, before the 1980s, there were minimal contributions, reflecting its early-stage development. However, from the mid-1980s to the early 2000s, publications increased sharply, coinciding with advancements in palladium-catalyzed cross-coupling methodologies.

A notable peak around 2006 indicates extensive exploration and optimization of the reaction, making it a widely adopted synthetic tool. Following this peak, citation rates gradually declined, suggesting a shift toward alternative coupling strategies, such as Suzuki and Sonogashira reactions, which offer improved sustainability and efficiency. Although research on the Stille reaction is still being published consistently, fewer studies are referencing these works.

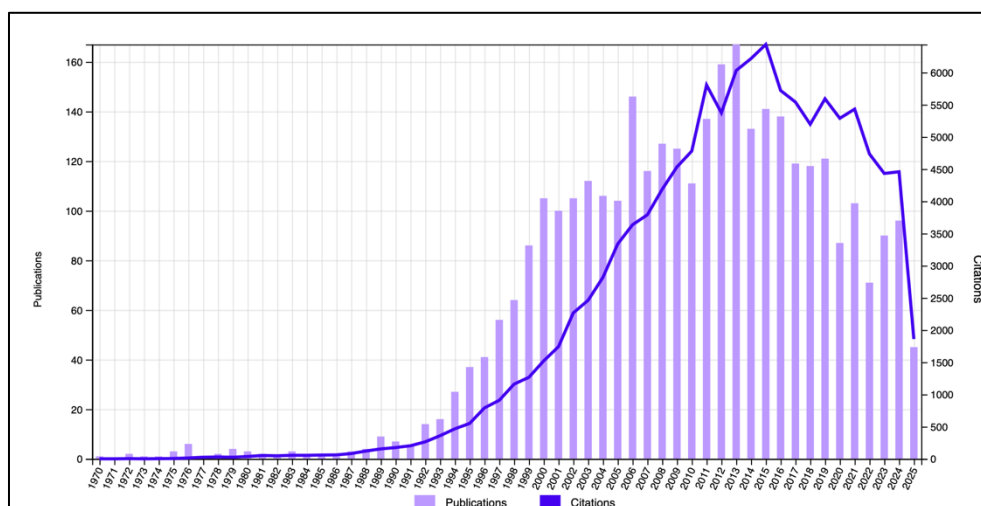


Figure 2.3 Times Cited and Publications Over Time on Stille Reaction

An American chemist, John Kenneth Stille (May 8, 1930-July 19, 1989) discovered the Stille reaction, which is a key part of palladium-catalyzed reaction chemistry in 1977. The main advantages of the Stille reaction include the stability and functional group tolerance of stannanes, the broad reaction scope of aryl halides and pseudo-halides, and its chemoselectivity (Brain et al., 2010). The optimization could be done by varying parameters such as solvents, reaction time, bases, catalyst loadings and temperature. The synthesis is compatible with the electronic effects and the steric effects exerted by the substituents on the aryl halides. Therefore, this reaction has been widely applied in natural product synthesis, biological research, and for pharmaceutical purposes.

2.2.2.1 Palladium-Catalyzed Stille Reaction

The palladium-catalyzed reaction of aryl halides or pseudo-halides with organostannanes, known as the Stille reaction, is one of the most powerful methods for the straightforward construction of carbon-carbon bonds in synthetic chemistry

(Chrétien et al., 2007). Significant progress in the preparation and characterization of variety of ligands and catalysts has been made to avoid protection and deprotection procedures, which therefore allow synthesis to be carried out in fewer steps (Pattenden & Sinclair, 2002). Transition metal-catalyzed reactions involve catalytic cycles which are a succession of elemental steps in which the metal is present as different catalytic species. John Kenneth Stille developed his work in 1980s on the synthesis of a multitude of ketones using this versatile mild process and suggested a mechanism for the transformation (De Cattelle et al., 2019).

Figure 2.4 demonstrates the general reaction of Stille reaction and the well-established Stille reaction mechanism as reported by Espinet & Echavarren (2004). The reaction is between an organostannane also called organotin and an organic electrophile in the presence of palladium catalyst to generate a new C-C single bond (Nielsen et al., 2005). The active Pd(0) species may be generated from Pd(II) precursor that is reduced by the organotin before entering the catalytic cycle. Three key basic steps involved in the catalytic cycle are oxidative addition, transmetalation and reductive elimination. The mechanism begins with oxidative addition of the organohalide to Pd(0) to form a Pd(II) complex. In the following transmetalation with the organotin, the R group of the organotin reagent replaces the halide anion on the palladium complex. Reductive elimination then gives the final coupled product, regenerates the palladium catalyst, thus the catalytic cycle can begin again. Theoretical studies indicate that the steric and electronic properties of ligands are both significant in catalysis to control catalytic performance (Heravi & Mohammadkhani, 2018). In general, oxidative addition is controlled by electronic factors, while a combination of electronic and steric effects regulates the transmetalation and reductive elimination processes (Jutand, 2004).

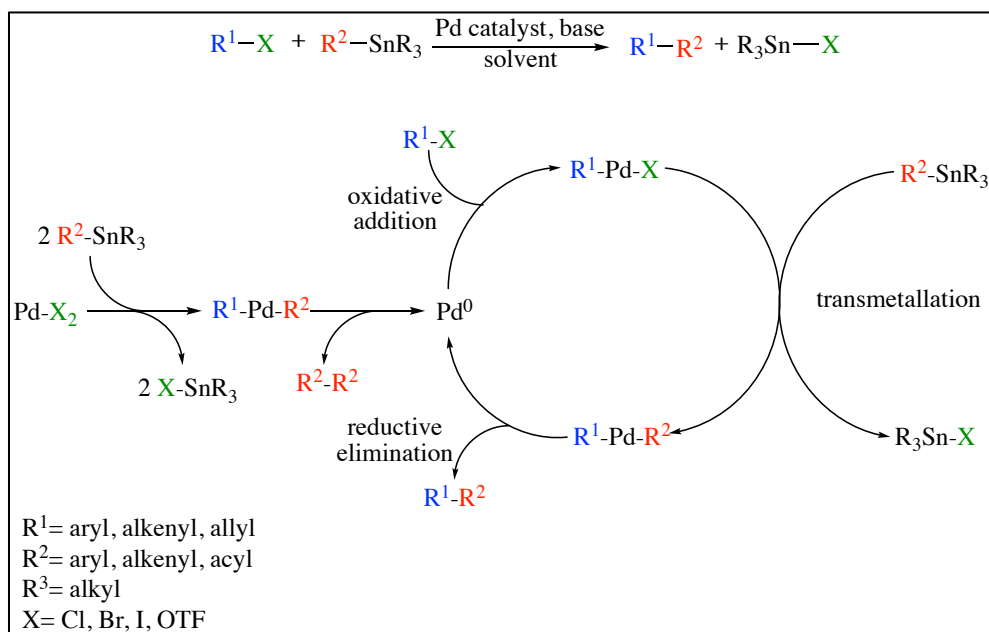


Figure 2.4 General Reaction and Mechanism of Pd-Catalyzed Stille Reaction

Palladium complexes are mostly used to catalyze this coupling reaction as they offer high product yields, high regioselectivity, high stereoselectivity and compatibility with many functional moieties. The activity of other transition metal catalysts such as nickel and copper have also been investigated as nickel and copper catalysts offer cost-effective, sustainable, and mechanistically versatile alternatives to palladium, broadening the scope of modern C-C bond formation and advancing greener synthetic methodologies (Neetha et al., 2020). However, in addition to the findings reported by Scrivanti et al. (2002), the scope and functional group tolerance of the palladium catalysts are far wider than those of any other metal species. The reaction of triorganostannyl ions as nucleophiles with haloarenes has long been known, with the products obtained depending on the nucleophile, solvent, base, and the amount of catalyst used in the reaction (Kantam et al., 2007).

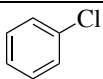
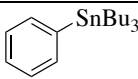
2.2.3 Catalytic Optimization of Stille Reaction Between Organotin and Aryl Halides using Palladium Catalyst

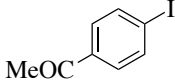
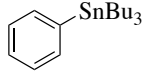
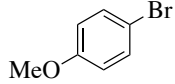
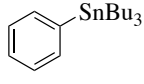
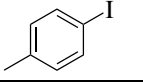
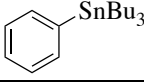
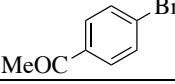
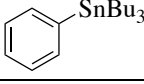
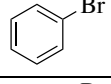
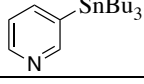
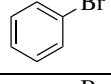
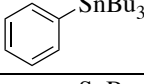
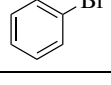
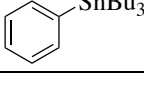
Stille reaction can be initiated by reacting an aryl halide with organotin. The palladium-catalyzed Stille reaction of aryl halides (or halide equivalents) with organotin reagents have been widely applied in natural product synthesis (Sun et al., 2014), carbohydrate chemistry (Sawoo et al., 2009) and biological research (Pereira et al.,

2001). The popularity is due, in part, to the ease of handling of organotin reagents and their excellent functional group tolerance (Tamoradi et al., 2018). The effect of bases, different amounts of catalysts, temperatures and types of solvents were observed to find optimum reaction conditions. There are many substrates reported in the literature but the most common are aryl iodides and tributylphenyltin (Hernán et al., 2003; Lau & Chiu, 2007; Naghipour et al., 2017). However, the optimum reaction conditions for certain substrates cannot be determined easily, thus optimization need to be carried out (McMullin et al., 2010). In addition, the optimization is essential because optimum reaction conditions directly influence the yield of product formed but there are no specific protocols for different kinds of reaction. Carter et al. (2002) pointed that this needs to be carried out prior to the catalytic testing of the synthesized complexes in the reaction. The optimization could be done by varying parameters such as solvents, reaction time, bases, catalyst loadings and temperatures. To narrow down the scope of this research, the optimum reaction conditions compiled below are focused on the types of bases, catalyst loadings, reaction temperatures and effect of solvents to produce biphenyl as the main products (Table 2.2).

Previous studies in Table 2.2 have highlighted the efficiency of palladium complexes as catalysts in the Stille reaction. Although palladium complexes are well established as efficient catalysts in the Stille reaction, the role of Schiff base complexes in modulating their catalytic performance has not been thoroughly investigated. In particular, there is a lack of detailed investigations linking the molecular structure of Schiff base-palladium catalysts to their catalytic efficiency which highlights a critical research gap. This study addresses this gap by evaluating newly developed bidentate Schiff base complexes as potential catalysts, combining experimental and computational approaches to establish structure-activity relationships.

Table 2.2
The Catalytic Activities of Palladium in Stille Reaction between Various Aryl Halide and Tributylphenyltin

Aryl Halide	Organotin	Reaction conditions	Catalyst	% GC Yield	Reference
		DMF, K ₂ CO ₃ , 120 °C, 48 h	Pd/Al(OH) ₃ (0.7 mol%)	80	(Alamgholiloo et al., 2020)
	Ph ₃ SnCl	PEG, NA ₂ CO ₃ , 80 °C, 1h	BNP@Cur-Pd (0.05 mol%)	96	(Jani & Bahrami, 2020)

		H ₂ O, NaHCO ₃ , 110 °C, 3 h	PdCl ₂ (NH ₃) ₂ /L (1 mol%)	98	(Li et al., 2016)
		Toluene, CsF, 60 °C, 10 h	Pd ₂ (dba) ₃ /pyrazolyl tethered phosphine ligand (1:1) (2 mol%)	90	(Wu et al., 2016)
		NMP/DMF, 120 °C, 15 h	Pd NCs (0.1 mol%)	86	(Ma et al., 2013)
		DMF, LiCl, 100 °C, 20 h	Pd(0)-MCM-41 (5 mol%)	97	(Yano et al., 2013)
		DMF, CsF, CuI, 110 °C, 16 h	Cyclopalladated ferrocenylimines (1 mol%)	99	(Pal et al., 2010)
		DMF/H ₂ O, 60 °C, 6 h	MCM-41-2P-Pd(0) (0.5 mol%)	86	(Jana et al., 2009)
		THF, NMP, 80 °C, 12 h	Pd ₂ (dba) ₃ /iminophosp hine- <i>n</i> -butyl-lithium ligand (1:1) (5 mol%)	92	(Zhao et al., 2008)

2.2.3.1 Effect of Temperatures in Stille Reaction

Temperature variation significantly influences catalyst efficiency in Stille reactions, with both the rate and selectivity of the reaction being affected by the chosen temperature and catalyst system. Studies have shown that certain catalysts, such as dendrimer-encapsulated palladium nanoparticles and novel succinimide-based Pd complexes, can achieve high efficiency and selectivity at room temperature, enabling the Stille reaction to proceed rapidly and with minimal catalyst loading under mild, aqueous conditions (Garcia-Martinez et al., 2005; Zhang et al., 2018). Lower temperatures can help preserve catalyst integrity and prevent deactivation, while also favoring selectivity for sensitive substrates. Conversely, Ronson et al. (2015) revealed that increasing the temperature generally accelerates the reaction rate by providing more kinetic energy to the reactants, but excessively high temperatures may risk catalyst deactivation or unwanted side reactions, thus reducing overall efficiency. Therefore, the optimal temperature for catalyst efficiency in the Stille reaction is highly dependent on the specific catalyst and substrate, and careful temperature control is essential to maximize both yield and catalyst longevity (Lv et al., 2020). Optimum reaction temperature for Stille reaction can go as low as 60 °C and as high as 120 °C as displayed in Table 2.2. With regards to the table, it can be concluded that reactions with higher temperatures achieved good yields. In order to find the most suitable temperature for

the catalyst, it is crucial to find the range of temperatures to obtain the best yield of result.

2.2.3.2 Effect of Types of Bases in Stille Reaction

The choice of base also affects the solubility of reactants and intermediates, the formation of byproducts, and the overall reaction environment, which in turn impacts the efficiency of the catalyst (Khanmoradi et al., 2017; Neo et al., 2018). Prabhu & Pal (2015) stated that a base is important in palladacycle formation as it facilitates the reaction forward by removing a proton from the coordination of organotin to the metal in the mechanism of the Stille reaction. Additionally, the interaction between the base and the catalyst or support such as in immobilized Schiff base complexes can influence metal leaching and catalyst reuse (Chiappe et al., 2006). Therefore, selecting the appropriate base balancing strength, compatibility with the catalyst, and reaction conditions is crucial for optimizing catalyst efficiency in Stille reaction. The type of base used in Stille reactions whether a hard base like KOH or K_2CO_3 , or a softer base like triethylamine can significantly affect catalyst efficiency by influencing both the stability of the catalyst and the rate of the coupling process. Kalay et al. (2020) pointed that hard bases such as KOH and K_2CO_3 are strong, inorganic, and can promote deprotonation and facilitate the transmetalation step, but they may also risk deactivating sensitive catalysts or causing side reactions, especially in water or polar solvents. However, Wu et al. (2016) reported that softer, organic bases like triethylamine are milder and can help maintain catalyst integrity, often leading to higher selectivity and better yields with less risk of catalyst degradation, particularly in reactions involving sensitive ligands or substrates. Table 2.2 shows various optimum bases commonly used which include K_2CO_3 , $NaHCO_3$, CsF, NaOAc and Na_2CO_3 .

2.2.3.3 Effect of Amounts of Catalysts in Stille Reaction

The amounts of catalysts used in Stille reaction have a direct impact on catalyst efficiency, product yield, and the practicality of the process. Studies show that highly active palladium catalysts can achieve excellent yields even at extremely low loadings as little as 0.0001 mol% to 0.1 mol%, making the reaction more economical and environmentally friendly while maintaining high turnover numbers and allowing for

catalyst reuse (Yu et al., 2020). However, for less reactive substrates or less active catalyst systems, higher catalyst amounts (up to 1 mol% or more) may be necessary to achieve satisfactory yields (Ayala et al., 2021). The optimal catalyst amount depends on factors such as substrate type, catalyst structure, and reaction conditions; using more catalyst than needed does not always improve efficiency and can increase costs or complicate product purification (Śpiewak et al., 2021). In nanoparticle and supported catalyst systems, low catalyst loadings are often sufficient due to high surface area and accessibility, and these systems can be reused multiple times without significant loss of activity (Śpiewak et al., 2021). Overall, minimizing catalyst amount while maintaining high efficiency is a key goal in Stille reaction, and advances in catalyst design have enabled significant reductions in required catalyst loading without sacrificing performance. Table 2.2 displays the amount of catalyst of 0.1 mol% to 5 mol%.

2.2.4 Reactivity of Aryl Halides in Stille Reaction

A wide range of electron-withdrawing and electron-donating substituted aryl halides are converted to their corresponding biphenyl products by Stille reaction and all biphenyls are prepared in good to excellent yields (Coates et al., 2009). To expand the scope of the reaction substrate, various organohalides are used in the Stille reaction as listed in Table 2.2. The reaction rate of different halides follows the conventional trend of $\text{ArI} > \text{ArBr} > \text{ArCl}$ (Coates et al., 2009). The reactions of organohalides bearing both electron-donating and electron-withdrawing substituents, such as $-\text{OCH}_3$, COCH_3 and $-\text{CH}_3$ with organotin give the corresponding products in good yields. The strengths of the vinyl analogue are $\text{COCH}_3 > \text{OCH}_3 > \text{CH}_3$ (Shoeb et al., 2018). When 4-iodoacetophenone and 4-bromoacetophenone, which are aryl halides of iodide and bromide with an electron-withdrawing group ($-\text{COCH}_3$) at the *para*-position is coupled with tributylphenyltin under 1.0 mol% (Li et al., 2016) and 5.0 mol% (Yano et al., 2013) catalyst loading, their corresponding Stille coupling products are obtained in 98% and 97% yields, respectively. The yield of 4-iodoacetophenone is slightly higher than the yield of 4-bromoacetophenone with a shorter reaction time of 3 hours compared to 20 hours for 4-bromoacetophenone. Thus, as expected, aryl halides bearing electron-withdrawing groups show a better reactivity and give the higher yields of the biphenyl products.

Iodobenzene and bromobenzene showed a slightly lower rate compared with those having electron-withdrawing substituents, but still resulted in excellent yields by prolonging the reaction time (Mukherjee & Sarkar, 2003). Conversely, aryl halides bearing an electron-donating group at the *para*-position which is -CH₃ yielded a lower yield of 86% even with a long reaction time (15 hours). Therefore, it can be concluded that the presence of electron-withdrawing moieties improves the product yields and take shorter reaction times compared to those with electron-donating ones (Jani & Bahrami, 2020). As listed in Table 2.2, the temperatures used in the Stille reactions that gave high yields of products are in the range of 100-120 °C.

2.2.5 Catalytic Optimization of Stille Reaction using Copper and Nickel as Catalysts

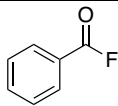
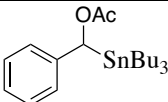
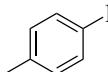
The use of transition metals in cross-coupling reactions has been verified as a powerful tool in synthetic organic chemistry to access valuable pharmaceutical intermediates and functional organic molecules (Yabe et al., 2010). Palladium-catalyzed reactions of aryl halides for the formation of new carbon-carbon bonds have huge potential in fine organic synthesis, with particular emphasis (Coccia et al., 2013). The activity of other transition metal catalysts such as nickel and copper have also been investigated. Nickel and copper are increasingly important as catalysts in organic synthesis, offering distinct advantages and unique reactivity compared to palladium. Copper compounds are described to be a significant tool in building a variety of carbon-carbon and carbon-heteroatom bonds more than a century ago (Yoon et al., 2022). Whereas nickel catalyst reaction had emerged in 1972 (Cho et al., 2005). The catalytic optimization for Stille reaction using copper and nickel catalysts follow similar optimization as that of palladium catalyst i.e. types of bases, catalysts amounts, temperatures and solvents as shown in Table 2.3. Copper and nickel catalysts reactions of different electrophiles and nucleophiles or two types of nucleophiles are alternative synthetic procedures to Pd(II)-based processes to access functional organic molecules and heterocycles (Aleena et al., 2021). Furthermore, various proposed reaction mechanisms covering radical path or through the involvement of metal complexes in different oxidation states are highlighted and discussed.

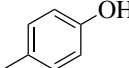
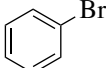
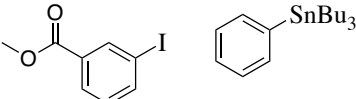
Despite the great advances in utilizing palladium as catalyst, copper is still very much used as one of the important catalysts; being a non-noble metal, copper is cheap

and available in many organic synthetic laboratories globally (Baqi, 2021). Nickel catalyzed cross-coupling of electrophiles (organic halides and pseudohalides) with carbon nucleophiles (organometallic compounds) has had a prominent impact on organic synthesis (Xu et al., 2014). The selection of ligands has made it possible to utilize a variety of reagents with very simple and inexpensive catalyst precursors. Diverse reactivity and cost efficiency have been the valuable driving force behind the remarkable progress of nickel catalysts in this area, with more challenges in the modern design of process equipment (Ananikov, 2015). Nickel has a significant cost advantage compared to palladium (Tao & Wang, 2016). Hence, it is important to explore the possibility of using nickel and copper as catalysts for the cross-coupling.

Based on previous studies, palladium complexes are widely recognized as efficient catalysts in the Stille reaction. However, the use of alternative metals such as nickel and copper has received comparatively less attention. Despite their potential advantages, there is a lack of detailed investigations linking the molecular structure of nickel and copper-based catalysts to their catalytic performance, leaving structure-activity relationships in this area poorly understood. Notably, this gap is further underscored by the absence of significant contributions in the literature since 2020 as shown in Table 2.3, highlighting the need for further investigation. To address this gap, the present study investigates the catalytic potential of nickel and copper Schiff base complexes, with the aim of evaluating their efficiency and providing insights into how ligand structure influences their activity.

Table 2.3
The Catalytic Activities of Copper and Nickel Transition Metal Catalysts in Stille Reaction

Entry	Aryl Halide	Organotin	Reaction conditions	Catalyst	% GC Yield	Reference
1		Bu ₃ Sn-SiMe ₃	CsF, toluene, 140 °C, 24 h	NiCl ₂ (10 mol%)	94	(Wang et al., 2019)
2		Ph ₃ SnCl	Na ₂ CO ₃ , PEG, 80 °C, 20 min	SBA-Cu ²⁺ (0.379 mol %)	93	(Ghorbani-Choghamarani et al., 2016)
3			THF, PhCH ₃ , 60 °C, 48 h	CuCN (8 mol%)	50	(Thapa et al., 2015)
4		Ph ₃ SnCl	DMF, K ₂ CO ₃ , 100 °C, 2.7 h	NiBr ₂ (16 mol%)	89	(Iranpoor et al., 2015)

5		Ph ₃ SnCl	TEA, Et ₂ O, 60 °C, 30 h	Cu(OAc) ₂ (40 mol%)	62	(Iranpoor et al., 2013)
6		Ph ₃ SnCl	CsF, H ₂ O, 60 °C, 2h	G ₃ DenP-Ni (2 mol%)	99	(Wu et al., 2012)
7			NMP, NaCl, 100 °C, 20 h	CuI (10 mol%)	89	(Kang et al., 1998)

2.2.5.1 Copper-Catalyzed Stille Reaction

The palladium-free copper catalyzed Stille-like reactions found in the literature are likely to operate via a Cu(I)/Cu(III) cycle similar to the Pd(0)/Pd(II) classic Stille cycle (Cordovilla et al., 2015). The detailed investigation on a possible mechanism is shown in Figure 2.5 for CuI along with Cs₂CO₃ additive as the best catalyst for the coupling of allyl bromide and functionalized furanyl stannyl derivative with minimal catalyst loading at ambient temperature was identified by Ghosh and co-workers (Ghosh et al., 2020). The improvement of *E/Z* ratio is presumably due to solvent ligation on the metal center, resulting in a square planar transition state. The proposed Cu(III) η³ allyl complexation prompted the *Z*-isomer or the γ-alkylated intermediate to be less stable or to not form, thus resulting in the major (*E*)-isomer. The *E*-isomer was obtained in an excellent yield of up to 94%. The significance of this reaction lies in the applicability of the *E*-isomer in the synthesis of anticancer therapeutic, spliceostatin derivatives.

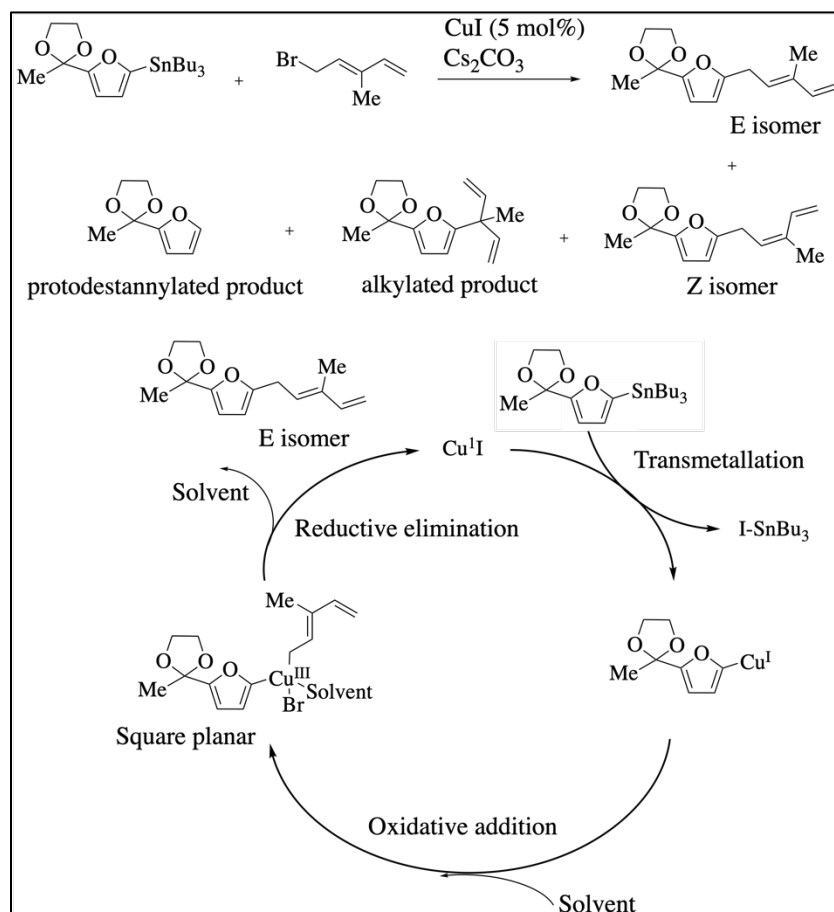


Figure 2.5 Plausible Mechanistic Pathway for the CuI Catalyzed *E*-Selective Stille Reaction

Copper has been explored as both a promoting transition metal and a catalyst over years in conducting stereospecific Stille couplings (Lange et al., 2008). A novel Schiff base-alumoxane reinforced mesoporous Cu nano-catalyst (SBA-Cu²⁺) has been synthesized and well-characterized. It catalyzed the coupling of triphenyltin chloride with aryl/heteroaryl halides in a medium of polyethylene glycol (PEG) and Na₂CO₃ as the base within a short time, as reported by Ghorbani-Choghamarani and co-workers (Table 2.3, Entry 2). The desired biphenyls are acquired in moderate to excellent yields with minor loadings of nano-copper catalyst (0.379 mol%) at high temperatures of about 80 °C. The use of low-boiling (Et₂O) solvents resulted in lower yields of biphenyl product. Thapa and co-workers described that a CuCN-catalyzed coupling between α -heteroatom-substituted alkyltributyltin and iodobenzene in THF and less polar solvent, PhCH₃ in 60 °C for 48 hours yielded a product in low yield of 50% (Table 2.3, Entry 3). This proved that less polar solvent produced low product yields.

The preliminary efforts towards such a process focused on optimizing the reaction of Ph₃SnCl and 4-methylphenol which has reported to have a low yield of 62%

in 60 °C using Cu(OAc)₂ as the catalyst for 30 hours in TEA and Et₂O as the solvent (Table 2.3, Entry 5). An earlier study on Cu(I)-catalyzed Stille cross-coupling and carbonylative coupling using hypervalent iodide as the electrophile and tributylphenyltin with NaCl as the additive in *N*-methyl-2-pyrrolidone (NMP) for 20 hours in 100 °C gave 89% of the product yield, as reported by Kang and co-workers (Table 2.3, Entry 7).

2.2.5.2 Nickel-Catalyzed Stille Reaction

The plausible mechanism of Ni-catalyzed Stille carbonylative coupling of aryl halides with metal carbonyls as solid source of CO is outlined in Figure 2.6 (Iranpoor et al., 2015). Carbonylative Stille reaction is a three-component reaction of diverse organotin with aryl or vinyl electrophiles which have been applied in the presence of carbon monoxide to give unsymmetrical diaryl ketones (Wang et al., 2016). The mechanism begins with Ni(II) pre-catalyst being reduced by the generated CO to Ni(0). Oxidative addition of the carbon-iodide bond to the generated Ni(0) generates the intermediate (I) which followed by CO insertion to generate the intermediate (II). The attack of base to Ph₃SnX followed by migration of a phenyl group generates the intermediate (III). Eventually, after reductive elimination, the corresponding unsymmetrical diaryl ketones and Ni(0) are produced. In addition, a base such as K₂CO₃ or OH⁻ is able to react with Ph₃SnCl to migrate the Ph group.

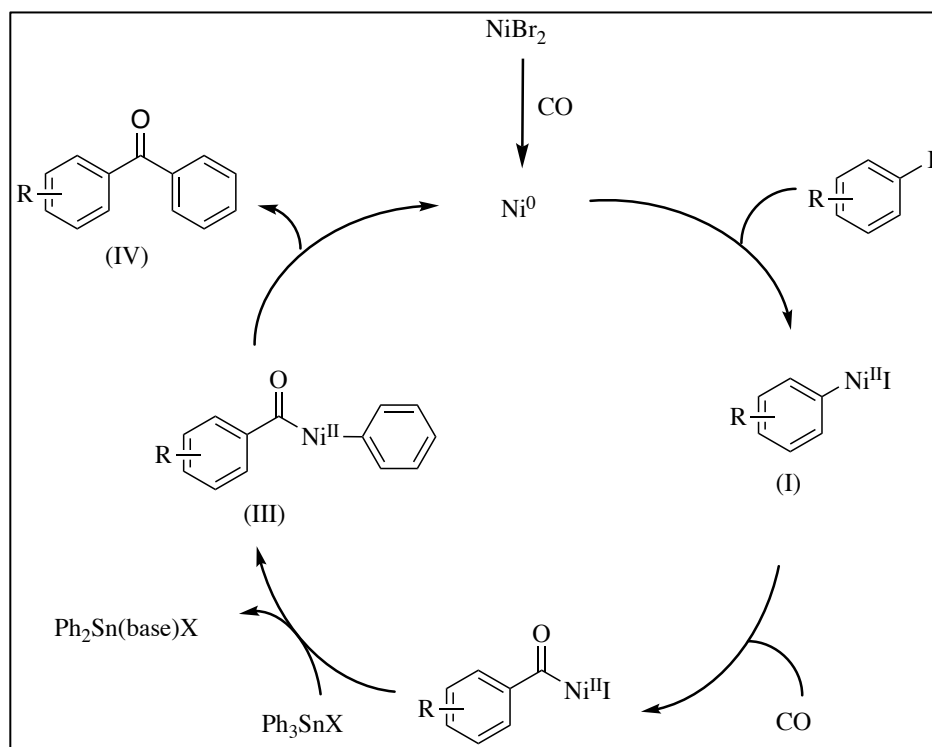


Figure 2.6 Plausible Mechanism for the Ni-Catalyzed Carbonylative Stille Reaction

The reaction between aryl fluoride and tributylstannyltrimethylsilane in the presence of 10 mol% NiCl_2 catalyst and CsF as the base in toluene as the solvent at 140°C yielded 94% of the product (Table 2.3, Entry 1). Iranpoor *et. al.* reported that the reaction of 4-iodotoluene, NiBr_2 , $\text{Cr}(\text{CO})_6$, K_2CO_3 as the base and Ph_3SnCl in DMF as the solvent at 100°C yielded 89% of the desired product (Table 2.3, Entry 4). Coupling triphenyltin chloride with bromobenzene in H_2O as the solvent and CsF as the base for 60°C for 2 hours afforded the desired biaryls in decent to excellent yields of 99% (Table 2.3, Entry 6).

2.3 Density Functional Theory (DFT)

Density Functional Theory (DFT) has become a foundational tool in computational chemistry due to its efficiency and reasonable accuracy across a wide range of chemical systems. Originally developed by Hohenberg and Kohn (1964), who demonstrated that the ground-state energy of a many-electron system is a unique functional of the electron density, DFT was made computationally practical through the Kohn-Sham (1965) formalism (Hohenberg & Kohn, 1964). Central to DFT is the challenge of approximating the exchange-correlation (XC) functional, which captures the complex many-body effects (Verma & Truhlar, 2020). The evolution of XC

functionals has followed a systematic progression known as "Jacob's Ladder," ranging from the Local Density Approximation (LDA) to more sophisticated hybrid and double hybrid functionals (Perdew & Schmidt, 2003). The Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA), such as PBE and BLYP, are popular for their balance of accuracy and computational efficiency, especially in solid-state and molecular calculations (Motamarri et al., 2019).

Hybrid functionals, like B3LYP and PBE0, incorporate a portion of exact exchange from Hartree-Fock theory and are widely used for molecular systems, providing improved accuracy for thermochemistry and electronic properties (Janesko, 2021). B3LYP, in particular, has become the standard for many quantum chemistry applications due to its reliable performance across a broad range of molecular systems, while PBE0 is favored for its parameter-free construction and consistent results (Feng et al., 2025). Long-range corrected and range-separated hybrid functionals, such as CAM-B3LYP and ω B97X, address delocalization errors and are particularly effective for excited states and charge-transfer systems (Körzdörfer & Brédas, 2014). The accuracy of DFT calculations is highly dependent on the choice of basis set, as the basis set determines how well the electronic wavefunctions are represented. Using a more complete or larger basis set generally improves accuracy, especially for properties like charge densities, reaction energies, and spectroscopic parameters, but also increases computational cost (Gubler et al., 2025). For many applications, medium-sized basis sets such as 6-31G+ (2d) or DZVP-DFT can offer a good balance between accuracy and efficiency.

Density Functional Theory (DFT) calculations provide a range of important molecular properties that are widely used in chemistry and materials science. From DFT, one can obtain the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which are crucial for understanding a molecule's electronic structure and reactivity (Costa et al., 2017). The difference between these energies, known as the HOMO-LUMO energy gap, offers insight into the molecule's chemical stability and potential for electronic transitions (Aslantaş et al., 2009). DFT also allows for the calculation of global chemical reactivity descriptors (GCRD), which help predict how a molecule might behave in chemical reactions (Ojha et al., 2023). Molecular electrostatic potential (MEP) maps can be generated to visualize regions of electron density, highlighting sites susceptible to electrophilic or nucleophilic attack (Kanchana et al., 2023). Additional properties

accessible through DFT include optimized molecular geometries, vibrational frequencies, thermodynamic parameters, and charge distribution analyses, all of which contribute to a comprehensive understanding of molecular behavior (Mehmet & Fermin, 2023). These computational results are often validated by comparison with experimental data, making DFT a powerful tool for predicting and interpreting chemical phenomena.

2.3.1 Basis Set in Schiff Base Compounds

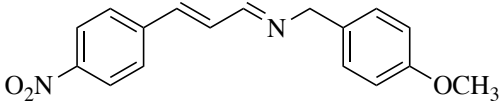
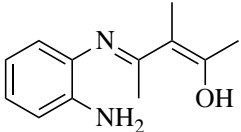
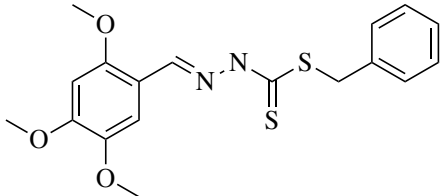
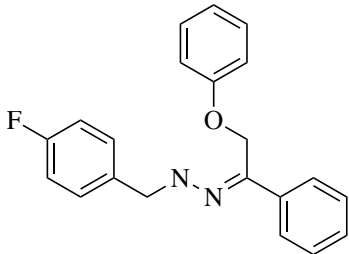
For DFT calculations involving Schiff base, commonly used and recommended basis sets include 6-31+G(d,p), 6-311G(d), 6-311+G(2d,p), and cc-pVDZ, often paired with the B3LYP functional for reliable results in geometry optimization, vibrational analysis, and electronic property calculations (Beytur & Yuksek, 2021). The 6-31+G(d,p) and 6-311G(d) basis sets provide a good balance between computational cost and accuracy for organic molecules like Schiff base, while the addition of diffuse functions (+) and polarization functions (d,p) is important for accurately describing electronic distributions and non-covalent interactions (Tyagi et al., 2017). For systems containing heavier atoms (such as iodine), mixed basis sets like cc-pVDZ for lighter atoms and LANL2DZ for heavier elements are used to ensure proper treatment of core and valence electrons (Ani et al., 2021). For more precise property calculations, especially for (hyper)polarizabilities, larger and more flexible basis sets such as aug-cc-pVDZ or aug-cc-pVTZ are recommended, though they require more computational resources (Zalešny et al., 2015). Ultimately, the choice of basis set should be guided by the size of the Schiff base, the properties of interest, and available computational resources, but 6-31+G(d,p) and 6-311G(d) are widely accepted starting points for most studies.

Moreover, for DFT calculations on Schiff base complexes with Ni(II), Cu(II), and Pd(II), a common and effective approach is to use a mixed basis set: LANL2DZ for the transition metal centers (Ni, Cu, Pd) and 6-31++G(or 6-31G(d,p)) for the lighter atoms (C, H, N, O) in the ligand (Guechtouli et al., 2023). This combination balances computational efficiency and accuracy, as LANL2DZ includes effective core potentials suitable for heavy metals, while 6-31++G provides good flexibility for organic frameworks. This setup is widely used for geometry optimizations, vibrational analyses, and electronic property calculations of such complexes (Geeta et al., 2010). For even

greater accuracy, especially in property calculations or when dealing with subtle electronic effects, larger basis sets like Def2-TZVP or SDD for metals and 6-311G(d,p) or Def2-TZVP for non-metals can be considered, though at higher computational cost. The choice of basis set should also be guided by the specific goals of the study and available computational resources, but the LANL2DZ/6-31++G combination is a well-established starting point for Schiff base complexes of Ni(II), Cu(II), and Pd(II).

DFT calculations have been widely used in previous studies to analyze HOMO-LUMO gaps and global chemical reactivity descriptors (GCRD) as shown in Table 2.4. However, their application in confirming the catalytic efficiency of Schiff base complexes remains limited. Specifically, few studies have explored the relationship between the molecular structure of Schiff base complexes and their catalytic performance through computational methods. To bridge this gap, the present research utilizes DFT calculations to examine the electronic properties and validate the catalytic potential of newly designed Schiff base complexes.

Table 2.4
Theoretical Methods in Schiff Base Compounds

Compounds	Methods and Basis Sets	Uses	References
	B3LYP/6-31+G(d,p)	• Frontier Molecular Orbital (FMO) • Natural Bond Orbital (NBO) • Chemical Reactivity Analysis	(Ani et al., 2021)
	B3LYP/6-31G(d,p)	• Frontier Molecular Orbital (FMO) • Natural Bond Orbital (NBO) • Chemical Reactivity Analysis	(Guechtouli et al., 2023)
	B3LYP/6-31+G(d,p)	• Frontier Molecular Orbital (FMO) • Natural Bond Orbital (NBO) • Molecular Electrostatic Potential (MEP) • Infrared, UV-Visible, bond length and bond angle	(Mumit et al., 2020)
	B3LYP/6-311+G(d,p)	• Frontier Molecular Orbital (FMO) • Chemical Reactivity Analysis	(Elmacı et al., 2018)

	B3LYP/LANL2DZ	• Frontier Molecular Orbital (FMO) • Natural Bond Orbital (NBO)	(Alwi et al., 2023)
	B3LYP/LANL2DZ	• Frontier Molecular Orbital (FMO) • Natural Bond Orbital (NBO) • Chemical Reactivity Analysis	(Guechtouli et al., 2023)

2.3.2 DFT-Based Insights into Cross-Coupling Catalysis

Density Functional Theory (DFT) plays a crucial role in understanding and advancing cross-coupling reaction catalysis by providing detailed insights into reaction mechanisms, energetics, and selectivity that are often inaccessible through experiment alone. DFT calculations allow researchers to map out the full catalytic cycle including key steps like oxidative addition, transmetalation, and reductive elimination by characterizing intermediates and transition states, and by comparing alternative mechanistic pathways for different catalysts such as palladium, nickel, iron, and copper (Fromm et al., 2014; García-Melchor et al., 2013). These studies revealed how factors like ligand environment, oxidation state changes, and the presence of bases or co-catalysts influence the efficiency and selectivity of cross-coupling reactions (Braga et al., 2006). DFT has clarified the origins of enantioselectivity, regioselectivity, and chemoselectivity, and has explained how subtle changes in catalyst structure or reaction conditions can shift the reaction outcome (Nieves-quinones et al., 2019).

Density Functional Theory (DFT) has become a cornerstone in understanding and predicting the reactivity and selectivity of cross-coupling reactions. The parameter of DFT-derived descriptors, which are frontier molecular orbitals (FMO), global chemical reactivity descriptors (GCRD), and molecular electrostatic potential (MEP) provide mechanistic insights into catalytic activity. The highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals whose energy gap (ΔE) is a key indicator of chemical reactivity of a molecule and kinetic stability in Frontier Molecular Orbitals (FMO). The small energy gap excites electrons from the HOMO orbital to the LUMO orbital, indicating that the molecule is reactive (Lai et al., 2019). A smaller HOMO-LUMO gap generally correlates with higher reactivity and lower kinetic stability, facilitating facilitates electron transfer during key catalytic steps, such as oxidative addition and reductive elimination in cross-coupling reactions (Ahmad et al., 2017).

Beyond FMO, global chemical reactivity descriptors (GCRD) derived from DFT, such as chemical hardness (η), chemical softness (S), chemical potential (μ), electrophilicity index (ω), and maximum additional electric charge ($\Delta N_{\max}$) offer deeper mechanistic insights. Chemical softness, the inverse of chemical hardness, reflects the ease with which a catalyst can redistribute its electron density in response to changes in

its environment (Pal & Kumar, 2021); higher softness (with higher S , the inverse of η) is associated with greater adaptability and enhanced catalytic performance, as soft catalysts can better stabilize transition states and reaction intermediates (Trevor et al., 2021). Chemical hardness (η) is a good indicator of the chemical stability. The molecules having a large energy gap are known as hard and having a small energy gap are known as soft molecules (Adejumo et al., 2020). The soft molecules are more polarizable than the hard ones because they need little energy for excitation. Conversely, chemical hardness measures resistance to electron density change. Higher hardness of catalysts (with larger η) are less reactive resulting in lower catalytic performance in cross-coupling reactions.

Chemical potential (μ), related to the tendency of a molecule to donate electrons, and electrophilicity (ω), quantifying the stabilization energy upon acquiring additional electronic charge, further distinguish the roles of catalysts and substrates in cross-coupling (Liu et al., 2021). Higher (less negative) chemical potential can promote steps like oxidative addition by making electron transfer more favourable. High electrophilicity and electronegativity values indicate strong electron-accepting (Lewis acid) character, which can enhance catalytic performance (Shaikh et al., 2012). MEP analysis is particularly valuable for identifying sites susceptible to electrophilic and nucleophilic attacks: regions with negative potential (often coloured red in MEP maps) are favourable for electrophilic attack, while positive potential regions (blue) are prone to nucleophilic attack (Suresh et al., 2022). This mapping enables the prediction of reactive sites, hydrogen bonding capabilities, and the directionality of intermolecular interaction (Ojha et al., 2023). For example, in catalysis, MEP helps pinpoint binding hotspots and rationalize ligand–receptor interactions. Overall, DFT-guided mechanistic understanding enables the rational design of more efficient, selective, and versatile cross-coupling catalysts.

2.4 Antibacterial Activity

Schiff base, organic compound containing an azomethine ($C=N$) functional group, have attracted considerable interest in medicinal chemistry due to their broad spectrum of biological activities, particularly their antibacterial potential. These compounds exhibit activity against both Gram-positive and Gram-negative bacteria, including common clinical pathogens such as *S. aureus*, *B. subtilis*, *E. coli*, and

S. typhimurium (Ali et al., 2017). The mechanism of antibacterial action of Schiff base involves multiple pathways, including interference with bacterial enzyme systems, disruption of membrane integrity, and interaction with nucleic acids, which inhibit replication and transcription (Gomha et al., 2015). Schiff base are also known to act as ligands that form metal complexes, which often enhance antibacterial activity due to increased lipophilicity and redox potential (Patel et al., 2021).

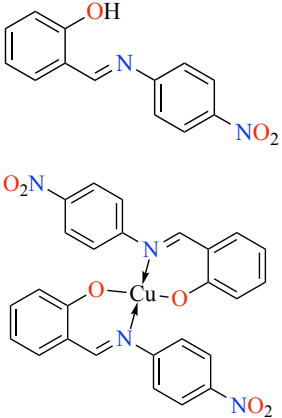
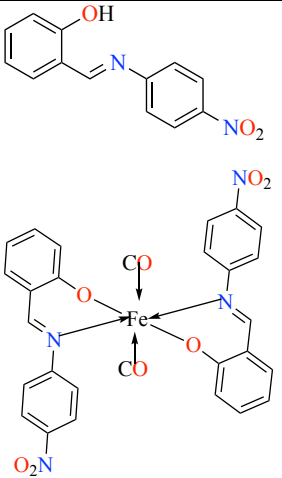
Structurally, Schiff base containing electron-withdrawing groups such as nitro or halogen substituents have demonstrated improved antibacterial efficacy, likely due to increased electrophilicity and better interaction with bacterial targets (Kavitha et al., 2016). For instance, benzimidazole-derived Schiff base have shown minimum inhibitory concentration (MIC) values as low as 31.25 µg/mL against *S. aureus*, outperforming some standard antibiotics like streptomycin (El-Gohary et al., 2019). Similarly, Schiff base incorporating thiazole or indole rings exhibited large inhibition zones against *B. subtilis* and *E. coli*, with certain derivatives producing zones up to 37 mm, which were notably higher than those produced by ciprofloxacin (Ahmed et al., 2022). The antibacterial performance against *S. typhimurium* was found to be more variable, although certain Schiff base complexes showed promising activity, particularly when coordinated with transition metals such as Cu(II) and Ag(I) (Jain et al., 2018). Overall, Schiff base remain a versatile and potent class of antibacterial agents, and ongoing research continues to explore their structural optimization and potential therapeutic applications.

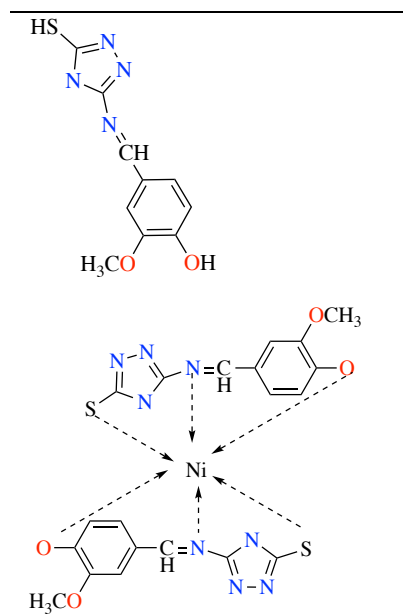
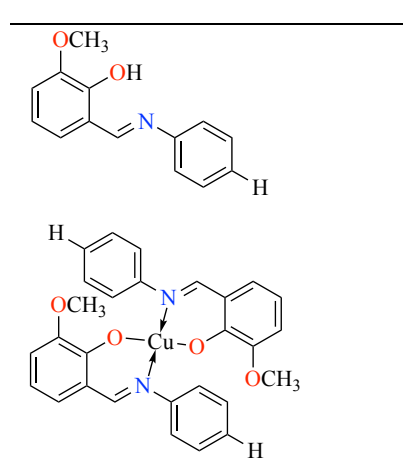
The structural characteristics of Schiff base significantly influence their antibacterial activity, with various studies emphasizing the role of functional groups, molecular geometry, and metal coordination. Electron-withdrawing groups such as nitro (-NO₂), chloro (-Cl), and fluoro (-F) on the aromatic ring have been reported to enhance antibacterial potency by increasing the electrophilic character of the azomethine carbon, facilitating better interaction with bacterial targets (Feng et al., 2014). Conversely, electron-donating groups like methyl (-CH₃) or methoxy (-OCH₃) tend to reduce activity by stabilizing the azomethine linkage and decreasing its reactivity (Zoubi, 2013). Additionally, the planarity and aromaticity of the Schiff base structure are critical, as these features facilitate intercalation with bacterial DNA and improve cell wall penetration (Fonkui et al., 2019). Metal complexation, particularly with transition metals like Cu(II), Zn(II), or Ag(I), often enhances

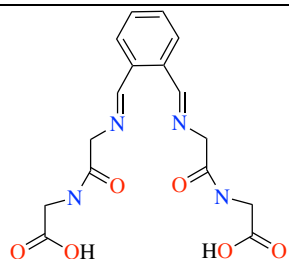
antibacterial activity due to increased lipophilicity and the ability to generate reactive oxygen species, which disrupt microbial membranes (Kadhim et al., 2022).

Currently, Schiff base and their metal complexes have demonstrated comparable or superior activity to some conventional antibiotics in in vitro assays, particularly against *S. aureus* and *E. coli* as shown in Table 2.5. However, variability in activity against more resistant strains, such as *S. typhimurium*, highlights the need for structure-activity relationship (SAR) studies to optimize these compounds for broader-spectrum efficacy. Future research should focus on high-throughput synthesis of Schiff base with diverse substituents, computational modelling to predict bioactivity, and in vivo testing to evaluate therapeutic potential and toxicity. The integration of nanotechnology, such as Schiff base-loaded nanoparticles, and exploration of synergistic effects with existing antibiotics may also pave the way for more effective antibacterial therapies (Idrish et al., 2018). Thus, while current studies establish Schiff base as promising antimicrobial agents, their translation into clinical use will depend on deeper mechanistic insights and comprehensive pharmacological evaluation.

Table 2.5
Antibacterial Study for Schiff Base Compounds

Compound	Bacterial strain tested	Method	Findings	Reference
	<i>S. aureus</i> <i>E. faecalis</i> <i>E. coli</i> <i>P. aeruginosa</i>	Disk diffusion	Cu(II) complex exhibit more profound antibacterial activity than free ligand	(Kondori et al., 2020)
	<i>S. aureus</i> <i>Kleb.</i> <i>E. coli</i>	Agar well disk diffusion	Fe(III) complex shows higher activity than Schiff base, especially on Gram-positive bacteria, higher activity was estimated than Gram-negative bacteria	(Kupwade & Sawant, 2020)

	• <i>B. cereus</i> • <i>S. aureus</i> • <i>E. coli</i> • <i>Kleb.</i>	Disk diffusion	Ni(II) complex exhibited the more potent antibacterial activity when compared to the ligand	(Vinusha et al., 2019)
	• <i>S. aureus</i> • <i>B. subtilis</i> • <i>E. coli</i>	Disk diffusion	Cu(II) complexes exhibited lower activity than the Schiff base ligands.	(Sobola et al., 2014)

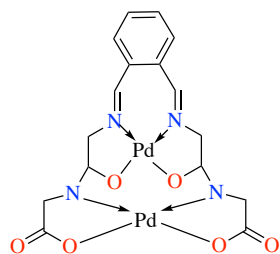


- *S. aureus*
- *B. subtilis*
- *E. coli*
- *K. pneumonia*

Disk diffusion

Pd(II) complex has higher antibacterial activity compared to ligand

(Geeta et al., 2010)



CHAPTER 3

RESEARCH METHODOLOGY

3.1 Chemicals and Materials

All chemicals and solvents used are listed in Table 3.1. They were used as purchased without any purification. The glassware used in the synthesis of all compounds were washed, rinsed with washing acetone and dried in a 50 °C drying cabinet before use.

Table 3.1
List of Solvents and Chemicals

Solvents	Grade	Supplier	Country of Origin
Ethanol Absolute (EtOH) 99%	A.R.	HmBG Chemicals	Australia
Acetonitrile	A.R.	Sigma-Aldrich	Germany
Dimethyl sulfoxide (DMSO)	A.R.	Merck	USA
Dichloromethane	A.R.	Sigma-Aldrich	Germany
Petroleum ether	A.R.	Chemiz	Malaysia
Hexane	A.R.	Sigma-Aldrich	Germany
<i>Ortho</i> -vanillin	A.R.	Sigma-Aldrich	Germany
Salicylaldehyde	A.R.	Sigma-Aldrich	Germany
Aniline	A.R.	Sigma-Aldrich	Germany
4-methylaniline	A.R.	Sigma-Aldrich	Germany
4-methoxyaniline	A.R.	Sigma-Aldrich	Germany
4-chloroaniline	A.R.	Sigma-Aldrich	Germany
4-nitroaniline	A.R.	Sigma-Aldrich	Germany
Nickel(II) acetate tetrahydrate	A.R.	Sigma-Aldrich	Germany
Copper(II) acetate monohydrate	A.R.	Sigma-Aldrich	Germany
Palladium(II) acetate	A.R.	Sigma-Aldrich	Germany
Iodobenzene	A.R.	Sigma-Aldrich	Germany
Tributylphenyltin	A.R.	Thermo Scientific	USA
Biphenyl	A.R.	Sigma-Aldrich	Germany
Triethylamine	A.R.	Chemiz	Malaysia
Potassium hydroxide (KOH)	A.R.	Friedemann Schmidt	Australia
Potassium carbonate (K ₂ CO ₃)	A.R.	Friedemann Schmidt	Australia

3.2 Instrumentations

In the course of this research, nine instruments were used to synthesize and characterize the compounds. All of the instruments used were available in UiTM. The list of instruments is displayed in Table 3.2.

Table 3.2

List of Instruments for the Synthesis and Characterization of Compounds

Instrument	Model	Lab/Institution
CHN elemental analyzer	Thermo Scientific Flash 2000 CHNS-O Analyser	Coordination Chemistry Lab, UiTM
Molar conductometer	Mettler Toledo 730	Chemistry Lab (MK1), Block D, FSG UiTM
Melting point	Buchi Melting Point M-560	Coordination Chemistry Lab, UiTM
Magnetic Susceptibility	Sherwood Auto	Coordination Chemistry Lab, UiTM
^1H and ^{13}C NMR spectrometer	Bruker Varian Spectrometer (600 MHz)	Atta-ur-Rahman Institute for Natural Product (AuRIns), UiTM
FTIR spectrometer	Perkin Elmer Spectrum One FT- IR Spectrometer	Instrumental Lab A306, Faculty of Applied Science UiTM
UV-Visible spectrometer	Perkin Elmer UV-Vis Lambda 35	Instrumental Lab A307, Faculty of Applied Science UiTM
Single crystal X-ray diffractometer	Bruker D8-QUEST CCD diffractometer	Atta-ur-Rahman Institute for Natural Product (AuRIns), UiTM
GC-FID	Agilent 7890A Network GC System	Instrumental Lab WB304, UiTM

3.2.1 CHN Elemental Analyzer

Elemental analysis (C, H, N) was conducted using Thermo Scientific Flash 2000 Elemental Analyzer. 2.5-3.0 mg of dry powdered sample was weighed and crimped in a tin container and introduced in the auto sampler. The sample was combusted at 950 °C in the reactor. The elemental analysis was carried out to determine the percentage of carbon, hydrogen, and nitrogen present in the compound.

3.2.2 Molar Conductometer

Molar conductivity was used to measure electrolytic property of the complex solution and to check the presence of ions in the complexes. The molar conductivity of the complexes was determined using Mettler Toledo 730 conductivity meter. All complexes were dissolved in acetonitrile to give solutions with concentration of 10^{-4} M at room temperature. It was recorded in the unit of $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$.

3.2.3 Melting Point

The purity of the compound was assessed based on its melting point, as a pure compound typically exhibits a narrow melting range from the initial melting point to complete liquefaction. The presence of impurities tends to broaden this melting range. Melting point of the synthesized compounds were determined using Buchi Melting Point M-560. A small amount of sample in the form of fine powder was introduced in a capillary tube. A heating rate of $5\text{ }^{\circ}\text{C}/\text{min}$ was applied during the melting point measurement to ensure consistent thermal equilibration. The temperature at which the solid started to melt until it completely molten was recorded. Melting point determination was performed to ascertain the purity of the synthesized compounds. Each compound was conducted in triplicates.

3.2.4 Magnetic Susceptibility

The magnetic moment of complexes was determined using magnetic susceptibility balance (MSB). The complexes were crushed finely, weighed and introduced in a tube to the length of 15-45 mm. The sample in tube was placed in the balance and the mass in the presence of magnetic field were recorded. Magnetic moment of the complexes was determined to obtain the information on the number of unpaired electrons in the d orbitals of the metal. The number of unpaired electrons were used to predict the geometry of complexes. The magnetic moment, μ_{eff} , was calculated according to the formula in (3.1).

$$\mu_{\text{eff}} = 2.83[(\chi_M')(T)]^{\frac{1}{2}} \quad (3.1)$$

Where X is diamagnetic corrections and T is temperature.

High-spin and low-spin configurations in transition metal complexes are determined by the interaction between the *d*-orbitals of metal ion and the ligand field, as explained by crystal field theory. When ligands surround a metal ion, they cause the *d*-orbitals to split into two sets of energy levels: the lower-energy *t_{2g}* orbitals and the higher-energy *e_g* orbitals. The energy gap between these levels, called the crystal field splitting energy (Δ), determines whether electrons pair up in the lower-energy orbitals or occupy the higher-energy orbitals. Weak-field ligands create a small splitting (Δ) and lead to high-spin complexes with maximum unpaired electrons. In contrast, strong-field ligands create a large splitting, causing electrons to pair in the lower-energy orbitals, resulting in low-spin complexes. The number of unpaired electrons determines the magnetic properties: high-spin complexes with unpaired electrons are paramagnetic, while low-spin complexes with all electrons paired are diamagnetic. Thus, the spin state and ligand field strength dictate whether a complex exhibits paramagnetism or diamagnetism. Generally, tetrahedral complexes are high spin, while square planar complexes are low spin. Table 3.3 shows the spin-only magnetic moment for Ni(II), Cu(II), and Pd (II) complexes.

Table 3.3
Spin-Only Magnetic Moment for Complexes

Central metal	High spin complexes				Low spin complexes		
	Number of d electrons	Number of unpaired electrons	μ (exp.) B.M.	μ (cal.) B.M.	Number of unpaired electrons	μ (exp.) B.M.	μ (cal.) B.M.
Ni ²⁺	8	2	2.80-3.50	2.83	0	0	0
Cu ²⁺	9	1	1.70-2.20	1.73	-	-	-
Pd ²⁺	8	-	-	-	0	0	0

3.2.5 ¹H and ¹³C Nuclear Magnetic Resonance (NMR) Spectrometer

¹H and ¹³C NMR were carried out to determine the proton and carbon in the compounds. The chemical shift was recorded in the unit of δ , ppm. The nature of the protons and carbons analysed based on their multiplicity. The multiplicity is described using terms like singlet, doublet, triplet, quartet, etc. Each term indicates the number of

peaks and their relative intensities in the NMR spectrum. The number of atoms present in the compound was verified by the intensity of the peak appeared in the spectrum. The coupling constant (J) is determined by measuring the distance between the peaks within a multiplet and converting it into a frequency in Hertz (Hz). ^1H and ^{13}C NMR spectroscopy analysis were carried out using Bruker Varian-600 MHz spectrometer. The measurements were performed in deuterated chloroform (CDCl_3) or deuterated DMSO ($\text{DMSO-}d_6$). The NMR sample was prepared by filling the 4 cm length of a regular 5 mm outer diameter, tube that holds a 10-20 mg of sample dissolved in 700 μL of deuterated solvent and introduced into NMR tube through cotton wool for filtration. The instrument worked based on spinning of nuclei in the sample.

3.2.6 Fourier Transform Infrared Spectrometer

The vibrational characteristics of the functional groups in the molecule were measured at various frequencies based on the intensity and polarity of the bonds. Infrared Spectrometry analysis was carried out using Perkin Elmer Spectrum One FT-IR Spectrometer. A small amount of sample was ground with dry powdered potassium bromide in a 1:10 ratio, then pressed to form a translucent pellet. Infrared radiation was allowed to pass through the pellet. A background spectrum was first necessary to obtain an infrared transmission spectrum. The spectrum was recorded in the range of $4000\text{--}400\text{ cm}^{-1}$. The scanning process was repeated four times, and the resulting infrared bands were categorized as strong (s), medium (m), or weak (w).

3.2.7 UV-Visible Spectrometer

UV-Visible spectroscopy analysis was carried out using Perkin Elmer Lambda 35 UV-Vis Spectrometer. Ligands and complexes were dissolved in acetonitrile to give the solutions with the concentration of 10^{-4} M . The UV-Visible spectra were obtained in the range of 200-900 nm using 1 cm pathlength quartz cuvette. UV-Visible analysis was performed to determine the type of electronic transition that occurred from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), within the ligands and between ligands and their corresponding complexes. Shifting in wavelength (bathochromic and hypsochromic) and change in intensity (hypochromic and hyperchromic) were observed. The measurement absorption was

used a linear relationship between absorbance and concentration which follows Beer-Lambert's Law to indicate how strongly a compound absorbs light at a particular wavelength. The molar absorptivity was calculated according to the formula in (3.2).

$$\varepsilon = \frac{A}{cl} \quad (3.2)$$

Where A = absorbance, c = sample concentration in L, l = length of light path through the sample in cm.

3.2.8 Single Crystal X-ray Diffraction

The single crystal of compounds obtained were analysed using single crystal X-ray diffractometer, Bruker D8 QUEST CCD diffractometer with PHOTON III 7 detector, using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 298 K. A crystal suitable for single crystal X-ray diffraction was selected under a microscope and carefully mounted on a nylon loop for stability. The sample was positioned with a precise distance of 40 mm from the detector to ensure optimal data collection during the experiment. The data was collected using APEX4 and reduced using the software SAINT. Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the Olex-2 software package. Mercury software was utilized for the graphical representation of the X-ray results. The formation of crystals indicates the high purity of the synthesized compounds. Single crystal X-ray diffraction was carried out to elucidate the chemical structure of the proposed compounds. To confirm the geometry of the crystal structure, if $\tau_4 = 1$, the hybridization of metal ion is sp^3 for a perfect tetrahedron, while for a perfect square planar, $\tau_4 = 0$, corresponding to dsp^2 hybridization for square planar. The formula for geometrical index is in (3.3).

$$\tau_4 = \left[\frac{360^\circ - (\alpha + \beta)}{141^\circ} \right] \quad (3.3)$$

3.2.9 Gas Chromatography-Flame Ionization Detector (GC-FID)

The catalytic investigation of Stille reaction was observed using Gas Chromatography-Flame Ionization Detection (GC-FID) Agilent 6890N. 0.5-1.0 mL sample of each entry of catalytic system was pipetted from the reaction tube into a GC vial, taken at 0, 15, 30, 45 and 60 minutes. The samples will be injected at 50 °C. The temperatures increment at 15 °C per minute and the final temperature of 300 °C. Gas chromatographic analysis was carried out using split injection with a 0.2 µL injection volume. *n*-dodecane was used as standard. The standard solution concentration was 50 ppm (50 µg/mL). Split ratio and split flow used were 20:1 and 18.9 mL/min, respectively. The column used is HP-5 capillary column. The percentage conversion of iodobenzene in this reaction was calculated using (3.4).

$$\% \text{ Conversion} = \frac{(A_{\text{int}}/A_{\text{ext. std}}) - (A_{\text{final}}/A_{\text{ext. std}})}{(A_{\text{int}}/A_{\text{ext. std}})} \quad (3.4)$$

A_{int} = peak area of reactant before reaction

A_{final} = peak area of reactant after reaction

$A_{\text{ext. std}}$ = peak area of external standard

3.3 Synthesis of Ligands

Ten ligands were synthesized and characterized, comprising five ligands from the B1 series and five ligands from the B2 series, using the conventional method as described in the 3.3.1 and 3.3.2 and the chemical reactions are shown in Figure 3.1 and Figure 3.2. The method was adapted from Sobola et al. (2014) with some modification of reaction time. All the reaction progress was monitored by TLC using a hexane:ethanol (3:6) as solvent system to ensure completion and product purity.

3.3.1 Synthesis of B1 Series of Ligands

The synthesis reaction of B1 series of ligands in 1:1 molar ratio is shown in Figure 3.1, where X is referred to H, CH₃, OCH₃, Cl and NO₂. In this reaction, *ortho*-vanillin was used as primary aldehyde reacted with five phenylamine derivatives.

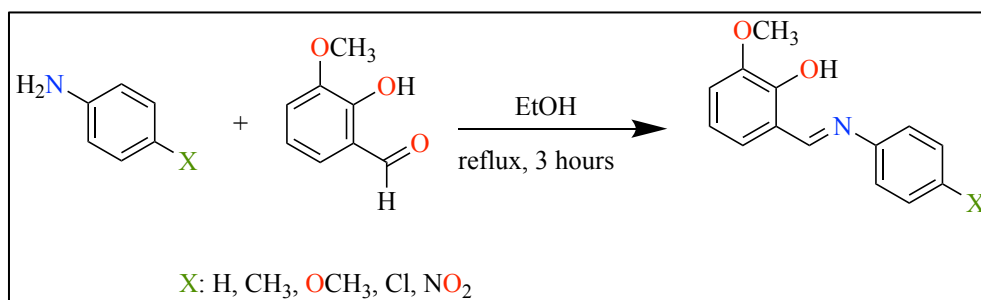


Figure 3.1 Synthesis Reaction of B1 Series of Ligands

3.3.1.1 Synthesis of (E)-2-methoxy-6-((phenylimino)methyl)phenol [B1H]

An ethanolic solution of *ortho*-vanillin (0.760 g, 5 mmol, 1 equiv.) and aniline (0.465 g, 5 mmol, 1 equiv.) were heated to boil (10 mL) separately. The two hot solutions were mixed in a 100 mL round-bottom flask to give an orange solution. The mixture was refluxed for 3 hours. The orange solid was appeared when the solution was allowed to cool slowly to room temperature. The solid was filtered off, washed with ice-cold ethanol and air-dried at room temperature to give 80.8% yield. The solid was recrystallized from the filtrate yielding orange block crystals.

3.3.1.2 Synthesis of (E)-2-methoxy-6-((*p*-tolylimino)methyl)phenol [B1Me]

The preparation of B1Me was similar as described in 3.3.1.1. *Ortho*-vanillin (0.760 g, 5 mmol, 1 equiv.) and 4-methylaniline (0.535 g, 5 mmol, 1 equiv.) in ethanol was resulted in formation of orange precipitate affording a yield of 78.9%. Orange block crystals were obtained by recrystallization of the solid from the filtrate.

3.3.1.3 Synthesis of (E)-2-methoxy-6-(((4-methoxyphenyl)imino)methyl)phenol [B1OMe]

B1OMe was prepared using the same protocol described in 3.3.1.1. *Ortho*-vanillin (0.760 g, 5 mmol, 1 equiv.) and 4-methoxyaniline (0.616 g, 5 mmol, 1 equiv.) afforded the orange precipitate resulting in 67.4% yield.

3.3.1.4 Synthesis of (E)-2-(((4-chlorophenyl)imino)methyl)-6-methoxyphenol [B1C]

B1C was synthesised according to the method described in 3.3.1.1 by treating *ortho*-vanillin (0.760 g, 5 mmol, 1 equiv.) with 4-chloroaniline (0.638 g, 5 mmol, 1 equiv.). An orange precipitate was obtained in this reaction to obtain 80.9% yield.

3.3.1.5 Synthesis of (E)-2-methoxy-6-(((4-nitrophenyl)imino)methyl)phenol [B1N]

B1N was prepared according to the same method described in 3.3.1.1. The condensation reaction between *ortho*-vanillin (0.760 g, 5 mmol, 1 equiv.) and 4-nitroaniline (0.691 g, 5 mmol, 1 equiv.) yielded the brown precipitate, resulting in 88.9% yield.

3.3.2 Synthesis of B2 Series of Ligands

The synthesis reaction of B2 series of ligands in 1:1 molar ratio is shown in Figure 3.2, where X is referred to H, CH₃, OCH₃, Cl and NO₂. In this reaction, salicylaldehyde was used as primary aldehyde reacted with five phenylamine derivatives.

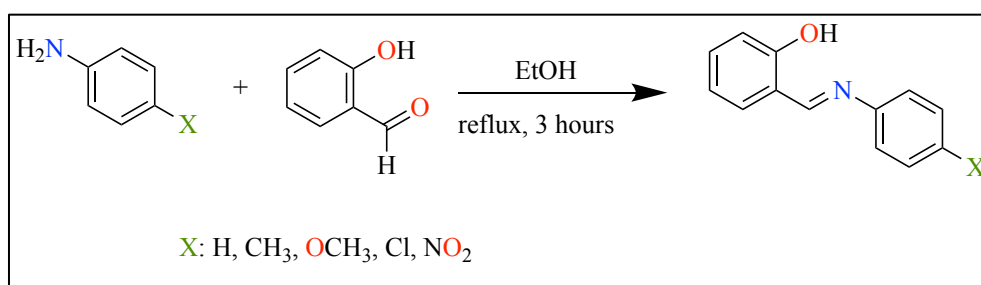


Figure 3.2 Synthesis Reaction of B2 Series of Ligands

3.3.2.1 Synthesis of (E)-2-((phenylimino)methyl)phenol [B2H]

An ethanolic solution of salicylaldehyde (0.611 g, 5 mmol, 1 equiv.) was heated to boil. Aniline (0.465 g, 5 mmol, 1 equiv.) was also boiled in ethanol (10 mL). The two hot solutions were mixed in a 100 mL round-bottom flask to give a yellow solution. The mixture was refluxed for 3 hours. Upon cooling, yellow solid was appeared. The solid was filtered off, washed with ice-cold ethanol and air-dried at room temperature with

85.4% yield. Recrystallization of the solid form from the filtrate afforded yellow block crystals.

3.3.2.2 Synthesis of (E)-2-((p-tolylimino)methyl)phenol [B2Me]

The preparation of B2Me was similar as described in 3.3.2.1. Salicylaldehyde (0.611 g, 5 mmol, 1 equiv.) and 4-methylaniline (0.535 g, 5 mmol, 1 equiv.) in ethanol was resulted in formation of yellow precipitate afforded the product in 81.0% yield. The solid obtained was recrystallized from the filtrate to give yellow block crystals.

3.3.2.3 Synthesis of (E)-2-(((4-methoxyphenyl)imino)methyl)phenol [B2OMe]

B2OMe was prepared using the same protocol described in 3.3.2.1. Salicylaldehyde (0.611 g, 5 mmol, 1 equiv.) and 4-methoxyaniline (0.616 g, 5 mmol, 1 equiv.) afforded the green precipitate with 76.7% yield.

3.3.2.4 Synthesis of (E)-2-(((4-chlorophenyl)imino)methyl)phenol [B2C]

B2C was synthesised according to the method described in 3.3.2.1 by treating salicylaldehyde (0.611 g, 5 mmol, 1 equiv.) and 4-chloroaniline (0.638 g, 5 mmol, 1 equiv.). A yellow precipitate was obtained in this reaction with a yield of 66.1%.

3.3.2.5 Synthesis of (E)-2-(((4-nitrophenyl)imino)methyl)phenol [B2N]

B2N was prepared according to the same method described in 3.3.2.1. The condensation reaction between salicylaldehyde (0.611 g, 5 mmol, 1 equiv.) and 4-nitroaniline (0.691 g, 5 mmol, 1 equiv.) yielded the brown precipitate in 87.4% yield.

3.4 Synthesis of Metal Complexes

In this study, a total of 30 complexes were synthesized and characterized by reacting the ligands with Ni(II), Cu(II), and Pd(II) metal centres, all employing conventional methods. The methodology was adapted from the work of Xiao & Cao, (2020) and Sobola et al., (2014) with some modifications of reaction time and

concentrations. All reaction progress was monitored by TLC using a hexane:ethanol (3:6) as solvent system to ensure completion and product purity.

3.4.1 Synthesis of Ni(II) B1 Series of Complexes

The synthesis reaction of nickel(II) acetate tetrahydrate with the B1 Schiff base ligand series in 1:2 molar ratio in EtOH is represented in Figure 3.3.

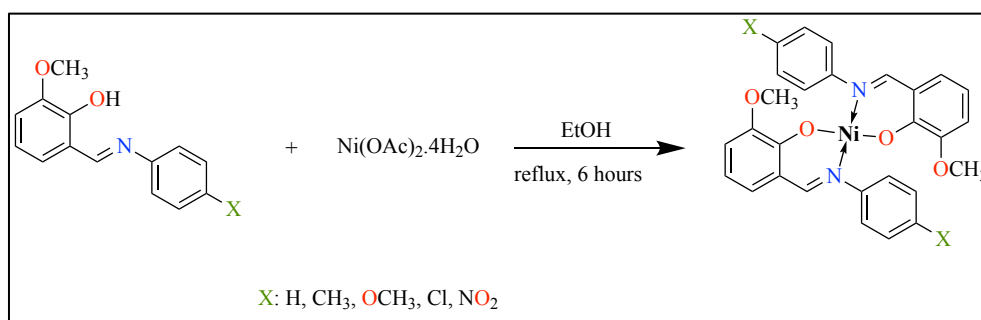


Figure 3.3 Synthesis Reaction of Ni(II) Complexes with B1 Ligands Series

3.4.1.1 Synthesis of bis(2-methoxy-6-((E)-(phenylimino)methyl)phenoxy)nickel [NiB1H]

The ligand, B1H, (2.273 g, 10 mmol, 2 equiv.) was dissolved in hot ethanol in a 100 mL round-bottom flask. Nickel(II) acetate tetrahydrate (1.244 g, 5 mmol, 1 equiv.) was dissolved separately in hot ethanol and added into the flask containing the ligand solution. The mixture was stirred and refluxed for 6 hours upon which brown solid was formed. The solid was filtered off, washed with ice-cold ethanol and air-dried at room temperature with 61.7% yield.

3.4.1.2 Synthesis of bis(2-methoxy-6-((E)-(p-tolylimino)methyl)phenoxy)nickel [NiB1Me]

The preparation of NiB1Me was similar as described 3.4.1.1. The reaction of B1Me ligand (2.413 g, 10 mmol, 2 equiv.) and nickel(II) acetate tetrahydrate (1.244 g, 5 mmol, 1 equiv.) was resulted in formation of green precipitate, resulting in 71.3% yield.

3.4.1.3 Synthesis of bis(2-methoxy-6-((E)-((4-methoxyphenyl)imino)methyl)phenoxy)nickel [NiB1OMe]

NiB1OMe was prepared using the same protocol described in 3.4.1.1. The reaction of B1OMe ligand (2.573 g, 10 mmol, 2 equiv.) and nickel(II) acetate tetrahydrate (1.244 g, 5 mmol, 1 equiv.) afforded green solid in 60.8% yield.

3.4.1.4 Synthesis of bis(2-((E)-((4-chlorophenyl)imino)methyl)-6-methoxyphenoxy)-nickel [NiB1C]

NiB1C was synthesised according to the method described in 3.4.1.1 by treating B1C ligand (2.617 g, 10 mmol, 2 equiv.) and nickel(II) acetate tetrahydrate (1.244 g, 5 mmol, 1 equiv.). A green solid was formed in this reaction giving a 66.0% yield.

3.4.1.5 Synthesis of bis(2-methoxy-6-((E)-((4-nitrophenyl)imino)methyl)phenoxy)-nickel [NiB1N]

NiB1N was prepared according to the same method described in 3.4.5.1. The condensation reaction between B1N ligand (2.723 g, 10 mmol, 2 equiv.) and nickel(II) acetate tetrahydrate (1.244 g, 5 mmol, 1 equiv.) afforded brown precipitate with a yield of 92.6%.

3.4.2 Synthesis of Ni(II) B2 Series of Complexes

The reaction of nickel(II) acetate tetrahydrate with the B2 Schiff base ligand series in 1:2 molar ratio in EtOH is represented in Figure 3.4.

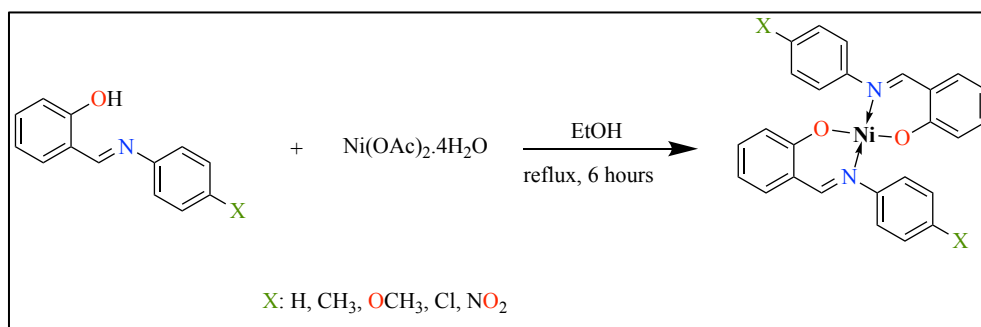


Figure 3.4 Synthesis Reaction of Ni(II) Complexes with B2 Ligands Series

3.4.2.1 Synthesis of bis(2-((E)-(phenylimino)methyl)phenoxy)nickel [NiB2H]

The ligand, B2H, (1.972 g, 10 mmol, 2 equiv.) was dissolved in hot ethanol in a 100 mL round-bottom flask. Nickel(II) acetate tetrahydrate (1.244 g, 5 mmol, 1 equiv.) was dissolved separately in hot ethanol and added into the flask containing the ligand solution. The mixture was stirred and refluxed for 6 hours upon which green solid was formed. The solid was filtered off, washed with ice-cold ethanol and air-dried at room temperature with 72.9% yield.

3.4.2.2 Synthesis of bis(2-((E)-(p-tolylimino)methyl)phenoxy)nickel [NiB2Me]

The preparation of NiB2Me was similar as described in 3.4.2.1. The reaction of B2Me ligand (2.113 g, 10 mmol, 2 equiv.) and nickel(II) acetate tetrahydrate (1.244 g, 5 mmol, 1 equiv.) in ethanol was resulted in formation of green precipitate with 84.0% of yield.

3.4.2.3 Synthesis of bis(2-((E)-((4-methoxyphenyl)imino)methyl)phenoxy)nickel [NiB2OMe]

NiB2OMe was prepared using the same protocol described in 3.4.6.1. The reaction of B2OMe ligand (2.273 g, 10 mmol, 2 equiv.) and nickel(II) acetate tetrahydrate (1.244 g, 5 mmol, 1 equiv.) afforded the green precipitate in 80.9% of yield.

3.4.2.4 Synthesis of bis(2-((E)-((4-chlorophenyl)imino)methyl)phenoxy)nickel [NiB2C]

NiB2C was synthesised according to the method described in 3.4.2.1 by treating B2C ligand (2.317 g, 10 mmol, 2 equiv.) and nickel(II) acetate tetrahydrate (1.244 g, 5 mmol, 1 equiv.). A brown precipitate was obtained in this reaction affording 65.3% yield.

3.4.2.5 Synthesis of bis(2-((E)-((4-nitrophenyl)imino)methyl)phenoxy)nickel [NiB2N]

NiB2N was prepared according to the same method described in 3.4.2.1. The condensation reaction between B2N ligand (2.422 g, 10 mmol, 2 equiv.) and nickel(II) acetate tetrahydrate (1.244 g, 5 mmol, 1 equiv.) yielded the brown precipitate of 77.7% yield.

3.4.3 Synthesis of Cu(II) B1 Series of Complexes

The reaction of copper(II) acetate monohydrate with the B1 Schiff base ligand series in 1:2 molar ratio in EtOH is represented in Figure 3.5.

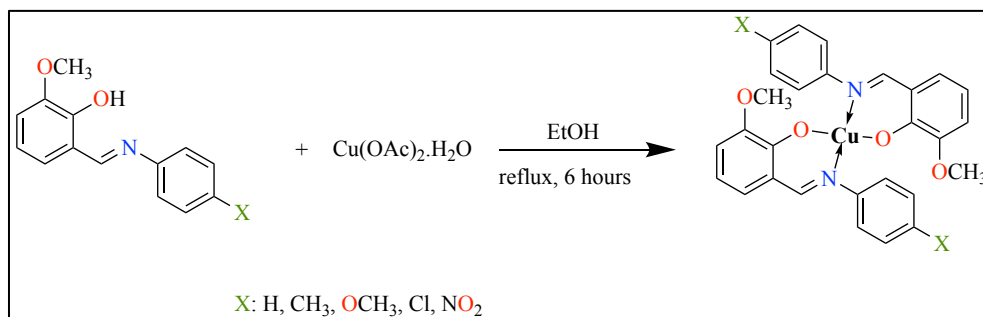


Figure 3.5 Synthesis Reaction of Cu(II) Complexes with B1 Ligands Series

3.4.3.1 Synthesis of bis(2-methoxy-6-((E)-(phenylimino)methyl)phenoxy)copper [CuB1H]

B1H ligand (2.273 g, 10 mmol, 2 equiv.) was dissolved in hot ethanol in a 100 mL round-bottom flask. Copper(II) acetate monohydrate (0.988 g, 5 mmol,

1 equiv.) was dissolved separately in hot ethanol and added into the flask containing the ligand solution. The mixture was stirred and refluxed for 6 hours upon which black solid was formed. The solid was filtered off, washed with ice-cold ethanol and air-dried at room temperature with 76.5% yield.

3.4.3.2 Synthesis of bis(2-methoxy-6-((E)-(p-tolylimino)methyl)phenoxy)copper [CuB1Me]

The preparation of CuB1Me was similar as described 3.4.3.1. The reaction of B1Me ligand (2.413 g, 10 mmol, 2 equiv.) and copper(II) acetate monohydrate (0.988 g, 5 mmol, 1 equiv.) was resulted in formation of brown precipitate, giving the yield of 78.3%. The solid was recrystallized from the filtrate yielding brown block crystals.

3.4.3.3 Synthesis of bis(2-methoxy-6-((E)-((4-methoxyphenyl)imino)methyl)-phenoxy)copper [CuB1OMe]

CuB1OMe was prepared using the same protocol described in 3.4.3.1. The reaction of B1OMe ligand (2.573 g, 10 mmol, 2 equiv.) and copper(II) acetate monohydrate (0.988 g, 5 mmol, 1 equiv.) afforded black solid to give 61.4% yield.

3.4.3.4 Synthesis of bis(2-((E)-((4-chlorophenyl)imino)methyl)-6-methoxyphenoxy)-copper [CuB1C]

CuB1C was synthesised according to the method described in 3.4.3.1 by treating B1C ligand (2.617 g, 10 mmol, 2 equiv.) and copper(II) acetate monohydrate (0.988 g, 5 mmol, 1 equiv.). A brown solid was formed in this reaction, affording 84.4% yield.

3.4.3.5 Synthesis of bis(2-methoxy-6-((E)-((4-nitrophenyl)imino)methyl)phenoxy)-copper [CuB1N]

CuB1N was prepared according to the same method described in 3.4.3.1. The condensation reaction between B1N ligand (2.723 g, 10 mmol, 2 equiv.) and

copper(II) acetate monohydrate (0.988 g, 5 mmol, 1 equiv.) yielded brown precipitate and was obtained 98.2% yield.

3.4.4 Synthesis of Cu(II) B2 Series of Complexes

The reaction of copper(II) acetate monohydrate with the B2 Schiff base ligand series in 1:2 molar ratio in EtOH is represented in Figure 3.6.

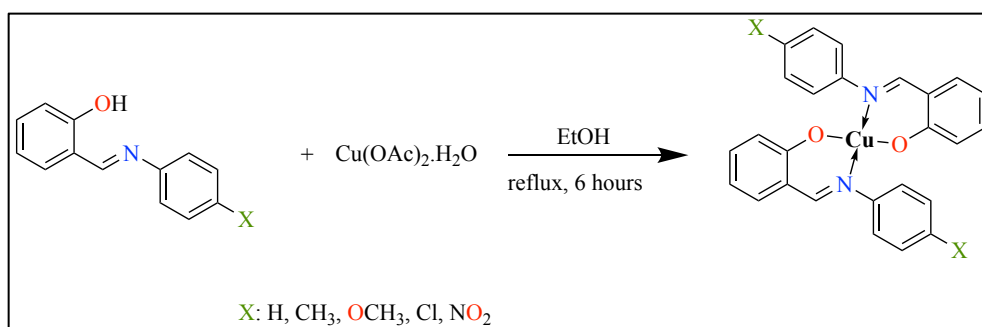


Figure 3.6 Synthesis Reaction of Cu(II) Complexes with B2 Ligands Series

3.4.4.1 Synthesis of bis(2-((E)-(phenylimino)methyl)phenoxy)copper [CuB2H]

B2H ligand (1.972 g, 10 mmol, 2 equiv.) was dissolved in hot ethanol in a 100 mL round-bottom flask. Copper(II) acetate monohydrate (0.988 g, 5 mmol, 1 equiv.) was dissolved separately in hot ethanol and added into the flask containing the ligand solution. The mixture was stirred and refluxed for 6 hours upon which brown solid was formed. The solid was filtered off, washed with ice-cold ethanol and air-dried at room temperature with 75.2% yield. Recrystallization of the crude solid from the filtrate afforded brown block crystals.

3.4.4.2 Synthesis of bis(2-((E)-(p-tolylimino)methyl)phenoxy)copper [CuB2Me]

The preparation of CuB2Me was similar as described in 3.4.4.1. The reaction of B2Me ligand (2.113 g, 10 mmol, 2 equiv.) and copper(II) acetate monohydrate (0.988 g, 5 mmol, 1 equiv.) in ethanol was resulted in formation of brown precipitate, giving the yield of 84.6%.

3.4.4.3 Synthesis of bis(2-((E)-((4-methoxyphenyl)imino)methyl)phenoxy)copper [CuB2OMe]

CuB2OMe was prepared using the same protocol described in 3.4.4.1. The reaction of B2OMe ligand (2.273 g, 10 mmol, 2 equiv.) and copper(II) acetate monohydrate (0.988 g, 5 mmol, 1 equiv.) afforded the brown precipitate with 77.0% yield.

3.4.4.4 Synthesis of bis(2-((E)-((4-chlorophenyl)imino)methyl)phenoxy)copper [CuB2C]

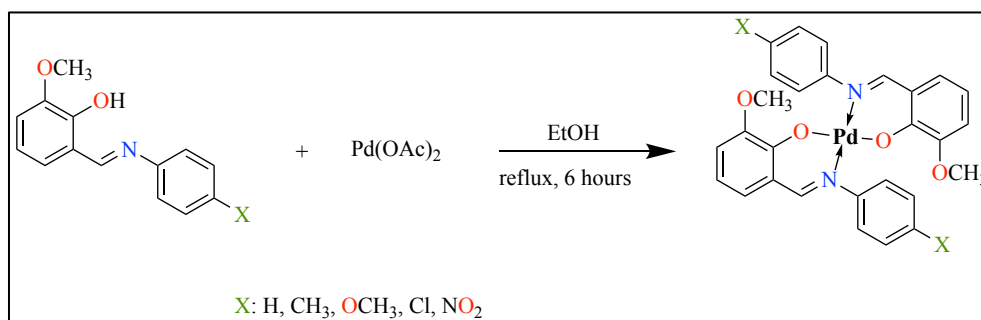
CuB2C was synthesised according to the method described in 3.4.4.1 by treating B2C ligand (2.317 g, 10 mmol, 2 equiv.) and copper(II) acetate monohydrate (0.988 g, 5 mmol, 1 equiv.). A brown precipitate was obtained in this reaction in 88.6% yield. The solid was recrystallized from the filtrate yielding brown block crystals.

3.4.4.5 Synthesis of bis(2-((E)-((4-nitrophenyl)imino)methyl)phenoxy)copper [CuB2N]

CuB2N was prepared according to the same method described in 3.4.4.1. The condensation reaction between B2N ligand (2.422 g, 10 mmol, 2 equiv.) and copper(II) acetate monohydrate (0.988 g, 5 mmol, 1 equiv.) yielded the brown precipitate and obtained 87.1% yield.

3.4.5 Synthesis of Pd(II) B1 Series of Complexes

The reaction of palladium(II) acetate with the B1 Schiff base ligand series in 1:2 molar ratio in EtOH is represented in Figure 3.7.



3.4.5.1 Synthesis of bis(2-methoxy-6-((E)-(phenylimino)methyl)phenoxy)palladium [PdB1H]

The ligand, B1H (2.273 g, 10 mmol, 2 equiv.) was dissolved in hot ethanol in a 100 mL round-bottom flask. Palladium(II) acetate (1.123 g, 5 mmol, 1 equiv.) was dissolved separately in hot ethanol and added into the flask containing the ligand solution. The mixture was stirred and refluxed for 6 hours upon which brown solid was formed. The solid was filtered off, washed with ice-cold ethanol and air-dried at room temperature with 90.0% yield.

3.4.5.2 Synthesis of bis(2-methoxy-6-((E)-(p-tolylimino)methyl)phenoxy)palladium [PdB1Me]

The preparation of PdB1Me was similar as described 3.4.5.1. The reaction of B1Me ligand (2.413 g, 10 mmol, 2 equiv.) and palladium(II) acetate (1.123 g, 5 mmol, 1 equiv.) was resulted in formation of brown precipitate to afford 96.0% yield.

3.4.5.3 Synthesis of bis(2-methoxy-6-((E)-((4-methoxyphenyl)imino)methyl)-phenoxy)palladium [PdBIOMe]

PdB1OMe was prepared using the same protocol described in 3.4.5.1. The reaction of B1OMe ligand (2.573 g, 10 mmol, 2 equiv.) and palladium(II) acetate (1.123 g, 5 mmol, 1 equiv.) afforded brown solid in 91.6% yield. The solid was recrystallized from chloroform yielding brown block crystals.

3.4.5.4 Synthesis of bis(2-((E)-((4-chlorophenyl)imino)methyl)-6-methoxyphenoxy)-palladium [PdB1C]

PdB1C was synthesised according to the method described in 3.4.5.1 by treating B1C ligand (2.617 g, 10 mmol, 2 equiv.) and palladium(II) acetate (1.123 g, 5 mmol, 1 equiv.). A brown solid was formed in this reaction, affording 84.7% yield.

3.4.5.5 Synthesis of bis(2-methoxy-6-((E)-((4-nitrophenyl)imino)methyl)phenoxy)-palladium [PdB1N]

PdB1N was prepared according to the same method described in 3.4.5.1. The condensation reaction between B1N ligand (2.723 g, 10 mmol, 2 equiv.) and palladium(II) acetate (1.123 g, 5 mmol, 1 equiv.) yielded brown precipitate to obtain 74.8% yield.

3.4.6 Synthesis of Pd(II) B2 Series of Complexes

The reaction of palladium(II) acetate with the B2 Schiff base ligand series in 1:2 molar ratio in EtOH is represented in Figure 3.8.

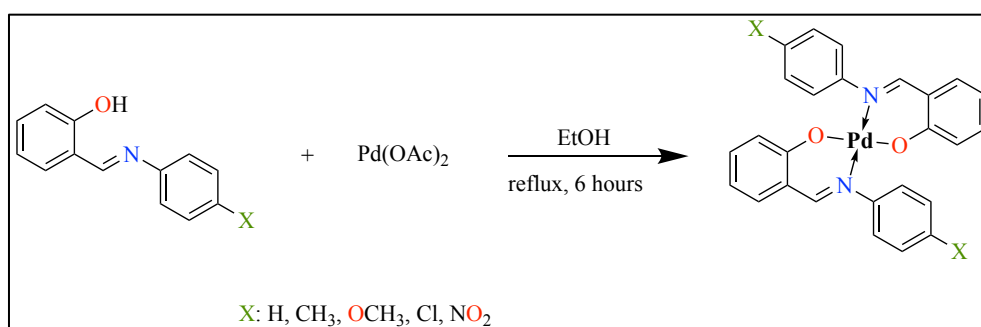


Figure 3.8 Synthesis Reaction of Pd(II) Complexes with B2 Ligands Series

3.4.6.1 Synthesis of bis(2-((E)-(phenylimino)methyl)phenoxy)palladium [PdB2H]

The ligand, B2H, (1.972 g, 10 mmol, 2 equiv.) was dissolved in hot ethanol in a 100 mL round-bottom flask. Palladium(II) acetate (1.123 g, 5 mmol, 1 equiv.) was dissolved separately in hot ethanol and added into the flask containing the ligand solution. The mixture was stirred and refluxed for 6 hours upon which brown solid was

formed. The solid was filtered off, washed with ice-cold ethanol and air-dried at room temperature with 93.9% yield.

3.4.6.2 Synthesis of bis(2-((E)-(p-tolylimino)methyl)phenoxy)palladium [PdB2Me]

The preparation of PdB2Me was similar as described in 3.4.6.1. The reaction of B2Me ligand (2.113 g, 10 mmol, 2 equiv.) and palladium(II) acetate (1.123 g, 5 mmol, 1 equiv.) in ethanol was resulted in formation of brown precipitate and was obtained 92.4% yield. Brown block crystals were obtained by recrystallization of the solid from chloroform.

3.4.6.3 Synthesis of bis(2-((E)-((4-methoxyphenyl)imino)methyl)phenoxy)palladium [PdB2OMe]

PdB2OMe was prepared using the same protocol described in 3.4.6.1. The reaction of B2OMe ligand (2.273 g, 10 mmol, 2 equiv.) and palladium(II) acetate (1.123 g, 5 mmol, 1 equiv.) afforded the brown precipitate of 93.3% yield. Upon recrystallization from chloroform, brown block crystals were formed.

3.4.6.4 Synthesis of bis(2-((E)-((4-chlorophenyl)imino)methyl)phenoxy)palladium [PdB2C]

PdB2C was synthesised according to the method described in 3.4.6.1 by treating B2C ligand (2.317 g, 10 mmol, 2 equiv.) and palladium(II) acetate (1.123 g, 5 mmol, 1 equiv.). A brown precipitate was obtained in this reaction, giving 86.9% yield. The solid was recrystallized from chloroform yielding brown block crystals.

3.4.6.5 Synthesis of bis(2-((E)-((4-nitrophenyl)imino)methyl)phenoxy)palladium [PdB2N]

PdB2N was prepared according to the same method described in 3.4.6.1. The condensation reaction between B2N ligand (2.422 g, 10 mmol, 2 equiv.) and palladium(II) acetate (1.123 g, 5 mmol, 1 equiv.) yielded the brown precipitate, giving 78.5% yield.

3.5 Homogeneous Catalysis of Stille Reaction

3.5.1 General Procedure of Stille Reaction

In a 12-Radley's carousel containing iodobenzene (0.20 g, 1 mmol, 1 equiv.) and 7 mL of DMSO was added in tributylphenyltin (0.55 g, 1.5 mmol, 1.5 equiv.). Subsequently, Pd(II) Schiff base complexes (1.0 mmol%) was then added to the reaction mixture, followed by triethylamine, TEA (0.20 g, 2.0 mmol, 2.0 equiv.). The mixture was refluxed at 80 °C for 60 minutes (Jani & Bahrami, 2020). The reaction progress was monitored by GC-FID for every 0, 15, 30, 45 and 60 minutes to determine the percentage of conversion of iodobenzene. The general procedure for Stille reaction is shown in Figure 3.9.

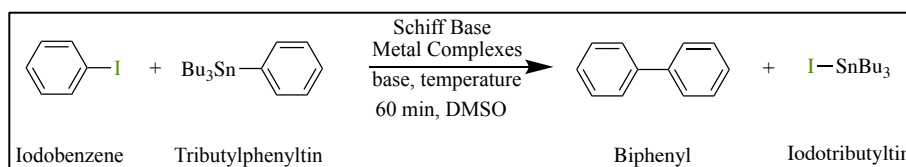


Figure 3.9 Catalytic Reaction of Iodobenzene with Tributylphenyltin

3.5.2 Screening of the Best Catalysts

The screening of the best catalysts was carried out using the procedure as described under 3.5.1. For screening purposes, Pd(II) complexes from B1 and B2 series was used as catalyst. The mixture was heated at 80 °C for 60 minutes (Jani & Bahrami, 2020). The reaction progress was monitored by GC-FID for every 0, 15, 30, 45 and 60 minutes to determine the percentage of conversion of iodobenzene. Each sample were run in triplicates. The best catalyst series was determined based upon the highest percentage conversion of iodobenzene.

3.5.3 Optimum of Reaction Conditions

The optimization of reaction conditions for Stille reaction was carried out using procedure described under 3.5.1. Three reaction parameters namely the reaction temperatures, types of bases, and amounts of catalysts were varied to find the optimum reaction conditions between iodobenzene and tributylphenyltin. Five Pd(II) complexes

from B1 series were employed as catalysts as the complexes were found to be the most active catalyst during the screening process. The optimization process began with temperatures, followed by bases and amounts of catalysts. The optimum reaction conditions were determined based on the highest percentage conversion of iodobenzene after 60 minutes of reaction.

3.5.3.1 Optimization using Different Temperatures

The optimization process was begun with the optimization for different temperatures. The reaction described under 3.5.1 was repeated using triethylamine as base with 1.0 mmol% amount of catalyst. The temperatures were varied at 30 °C, 60 °C, 80 °C and 100 °C.

3.5.3.2 Optimization using Different Types of Bases

After the most optimum temperature obtained, the optimization process was proceeded to seek the most optimum type of base used. The reaction described under 3.5.1 was repeated using three different bases which are KOH, K₂CO₃ and TEA. The temperature was kept constant at 100 °C with 1.0 mmol% amount of catalyst.

3.5.3.3 Optimization using Different Amounts of Catalysts

After the most optimum reaction temperature and base obtained, the optimization process was proceeded to seek the most optimum amount of catalyst used. The reaction described under 3.5.1 was repeated using KOH as base. The temperature was kept constant at 100 °C. The amounts of catalysts were varied at 0.5, 1.0, 1.5 and 2.0 mmol%.

3.5.4 Effect of using Different Catalysts in Stille Reaction

The reactions catalyzed by various Ni(II), Cu(II), and Pd(II) complexes as catalysts were carried out under optimized conditions, using KOH as the base at 100 °C with a catalyst loading of 2.0 mmol%, as detailed in the Section 3.5.3.1 - 3.5.3.3.

3.5.5 Isolation of Stille Product

Upon reaction completion, the mixture was cooled down, diluted with distilled water and extracted with dichloromethane, CH_2Cl_2 for three times. The organic phase was collected and dried with a drying agent, Na_2SO_4 and concentrated using rotary evaporator. Thin Layer Chromatography (TLC) technique was used to find the most suitable solvent system for further purification of the crude product. Then, the product was purified by column chromatography using petroleum ether:hexane (v/v 3:2) as solvent system. The solid white product, biphenyl, was obtained by evaporation of the eluent in a fume hood. It was characterized via CHN elemental analysis, FTIR and ^1H and ^{13}C NMR spectroscopy.

3.6 Density Functional Theory (DFT)

Density functional theory (DFT) calculations were carried out to understand the electronic structure, reactivity, and global chemical descriptors of the Schiff base ligands and their metal complexes. The CIF files obtained from single crystal X-ray diffraction were used only as starting geometries. Each structure was then fully optimized in the gas phase to obtain its minimum-energy form in vacuum, with the understanding that the optimized structures may differ from the solid-state models due to the absence of crystal-packing effects.

All computations were performed using Gaussian 09 program package. Geometry optimization was carried out using the B3LYP hybrid functional, which is widely applied for organic ligands and transition-metal complexes. For the ligand atoms (H, C, N, O), the 6-311++G(d,p) basis set was selected because it provides reliable accuracy for optimized geometries, charge distribution, electrostatic potentials, and frontier orbital analyses.

For the metal centers (Ni, Cu, and Pd), the LANL2DZ effective core potential (ECP) and its associated basis set were employed. The GEN keyword in Gaussian was used solely to assign different basis sets to ligand atoms and metal atoms but it is not part of the basis-set name. The combination of B3LYP/6-311++G(d,p) for ligand atoms and LANL2DZ for metal atoms is widely used in computational studies of transition-metal complexes, as it provides a practical balance between computational efficiency and the accurate description of metal–ligand interactions.

From the optimized geometries, several electronic properties were calculated, including HOMO–LUMO energy gaps, molecular electrostatic potential (MEP), and global chemical reactivity descriptors such as chemical hardness, chemical softness, chemical potential, electronegativity, electrophilicity index, and maximum additional electric charge ($\Delta N_{\max}$). These parameters were used to complement the experimental findings and to assess the intrinsic electronic factors that may influence the catalytic behavior of the metal complexes in the Stille reaction.

3.6.1 Frontier Molecular Orbitals (FMO)

Frontier molecular orbitals (FMO) were a cornerstone of coordination chemistry and were essential in understanding the electronic structure and reactivity of coordination compounds. FMO referred to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a molecule or complex. These orbitals were crucial in predicting the chemical properties and reactivity of coordination compounds. The HOMO was predominantly connected with the electron-rich regions of the ligands in coordination compounds. It reflected the location of accessible electrons for donation to the metal center. Coordination bond formation frequently involved the HOMO. In contrast, the LUMO was often centered around the metal atom. It denoted the electron-deficient zone in which the metal could accept electrons from the ligands and establish coordinate bonds. The energy gap, which was the difference in energy between the HOMO and LUMO, helps determine the kinetic stability of compound and chemical reactivity in catalytic activity (Ahmad et al., 2017). The energy gap was calculated from the equation (3.5).

$$\text{Energy gap} = E_{LUMO} - E_{HOMO} \quad (3.5)$$

3.6.2 Global Chemical Reactivity Descriptors (GCRD)

Global chemical reactivity descriptors were deduced from FMOs to investigate the kinetic and the reactivity of molecular systems. General chemical parameters such as chemical hardness (η), chemical softness (S), chemical potential (μ), electronegativity (χ), electrophilicity index (ω), and maximum additional electric charge

($\Delta N_{\max}$) were used to define the descriptors. The calculations for GCRD values were obtained using (3.6) to (3.11).

$$\text{Chemical hardness } (\eta) = \left[\frac{(E_{LUMO} - E_{HOMO})}{2} \right] \quad (3.6)$$

$$\text{Chemical softness } (S) = \left[\frac{1}{(2\eta)} \right] \quad (3.7)$$

$$\text{Chemical potential } (\mu) = \left[\frac{(E_{LUMO} + E_{HOMO})}{2} \right] \quad (3.8)$$

$$\text{Electronegativity } (\chi) = \left[\frac{(I + A)}{2} \right] \quad (3.9)$$

$$\text{Electrophilicity index } (\omega) = \left[\frac{\mu^2}{2\eta} \right] \quad (3.10)$$

$$\text{Maximum additional electric charge } (\Delta N_{\max}) = \left[-\frac{\mu}{\eta} \right] \quad (3.11)$$

Where ionisation energy (I) is equal to $-E_{HOMO}$ and electron affinity (A) is equal to $-E_{LUMO}$.

3.7 Antibacterial Activity

The method to study antibacterial activity of all the ligands and complexes was described herein. A standardised disk diffusion method was carried out.

3.7.1 Bacterial Strains

A total of four species of bacteria were used in this study, which were *S. aureus*, *B. subtilis*, *E. coli*, and *S. typhimurium*. Each bacterial strain was sub-cultured and inoculated priorly on a nutrient agar and incubated for 24 hours before it being used.

3.7.2 Solubility Study

Different solvents used to perform solubility study which are acetonitrile, triethylamine, dimethyl sulfoxide, ethyl acetate, dimethylformamide, acetone, tetrahydrofuran and acetic acid. Several clean test tubes were prepared and placed in the test tube racks to ensure their stability of the test tubes. An amount of 1 mg compounds was transferred into the test tubes using a toothpick. Following that, 1 mL of solvent was pipetted into the test tube that contain the compound. The stopper was placed on the test tube, and the solution was completely dissolved using a vortex mixer. If the solution was not completely dissolved, the solution will be sonicated in a water bath sonicator to ensure complete dissolution.

3.7.3 Experimental Method

3.7.3.1 Sample Preparation (crude/fraction)

An amount of 1 mg of compound was weighed and transferred into a sterile micro centrifuge tube. The compound was dissolved in 1 mL of the respective solvent in the micro-centrifuge. The compounds were dissolved in DMF at 10% concentration.

3.7.3.2 Preparation of Inoculum

Four bacterial strains were used in this study. Two to four well-isolated colonies from bacteria growing on Nutrient Agar plate were picked with a sterile loop and transferred into a tube containing 10 mL of Mueller-Hinton Broth (MHB). The broth culture was placed in an incubator shaker which set to 70 rpm at 37 °C for 18-24 hours.

3.7.3.3 Disk Diffusion Assay

The MHA agar plates were labelled accordingly including the sample, date, and the bacteria used for antimicrobial study. The overnight grown bacteria were adjusted using a spectrophotometer to a standardized final 625 nm of approximately 0.08-0.10 to meet the 0.5 McFarland standard. Sterile disks were placed in a sterile petri dish according to the sample used in this test. Each disk was saturated with 50 μ L of the sample and put it aside to allow air-dry. Optimally, a sterile cotton swab was dipped into the adjusted suspension within 15 minutes after adjusting the turbidity of the inoculum suspension. The swab should be rotated several times and pressed firmly on the inside wall of the tube above the fluid level to remove excess inoculum from the swab. The entire agar surface swabbed with the prepared inoculum. The procedure was repeated by rotating the plate to ensure even distribution of bacteria including the rim of the agar as well. Aseptically, the saturated disk was transferred onto the MHA accordingly. The disks must be distributed evenly and not too close to each other. The complete plate was covered and incubated at 37 °C for 18-24 hours (to identify formation of bacterial strains). The clear zone of diameter (inhibition zone) was measured using a ruler and the result was recorded. The assay was conducted in triplicates.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Investigation Pathways

This study commenced with the synthesis of two series imine ligands, referred as B1 and B2. The B1 series of Schiff base were prepared by reacting *ortho*-vanillin with phenylamines and their respective derivatives, incorporating electron-withdrawing and electron-donating groups at the *para* position. These substituents, H, CH₃, OCH₃, Cl, and NO₂ yielded ligands designated as B1H, B1Me, B1OMe, B1C, and B1N. Similarly, the B2 series was synthesized via condensation between salicylaldehyde and phenylamines with identical functional groups, producing B2H, B2Me, B2OMe, B2C, and B2N. In total, ten ligands were successfully obtained.

Comprehensive characterization was performed using elemental analysis (C, H, N), melting point, FTIR, ¹H and ¹³C NMR and UV-Visible spectroscopy. Following characterization, the ligands were complexed with nickel(II) acetate tetrahydrate (Ni(OAc)₂·4H₂O), copper(II) acetate monohydrate (Cu(OAc)₂·H₂O), and palladium(II) acetate (Pd(OAc)₂), leading to the formation of Ni(II), Cu(II), and Pd(II) complexes. The assignment of each complex aligned with its parent ligand, resulting in 10 complexes per metal center across both series. These complexes were further analyzed via elemental analysis (C, H, N), melting point determination, molar conductivity measurements, magnetic susceptibility balance (MSB), FTIR spectroscopy, ¹H and ¹³C NMR spectroscopy, and UV-Visible spectroscopy.

Additionally, 11 single crystals were successfully grown using the slow evaporation technique, consisting of ligands (B1H, B1Me, B2H, B2Me) and complexes (CuB1Me, CuB2H, CuB2C, PdB1OMe, PdB2Me, PdB2OMe, PdB2C). Their structures were elucidated using single crystal X-ray diffraction analysis.

The catalytic potential of Pd(II) complexes from both series was screened in the Stille reaction. The B1 series of Pd(II) complexes demonstrated better catalytic efficiency compared to the B2 series of Pd(II) complexes, leading to their selection for optimization studies. The reaction conditions were optimized by varying the temperatures, types of bases, and the amounts of catalysts. The catalytic performance was evaluated using GC-FID to determine the percentage of iodobenzene conversion.

The optimum conditions were used in the catalytic investigation, employing all Ni(II), Cu(II), and Pd(II) complexes from B1 series and B2 series. The coupling product, biphenyl, was isolated via column chromatography and characterized through CHN elemental analysis, FTIR, ^1H and ^{13}C NMR spectroscopy, and compared with a standard biphenyl.

The crystal structures obtained employed to run density functional theory (DFT). The optimization of the geometries of the compounds were conducted using the B3LYP method with a 6-311++G(d,p) basis set for the ligands and LANL2DZ basis set for the complexes.

4.2 Characterization of Ligands and Ni(II), Cu(II), and Pd(II) Complexes

4.2.1 Elemental Analysis (C, H, N), Melting Point, and Molar Conductivity

The condensation of *ortho*-vanillin with *para*-substituted phenylamines (1:1) in ethanol resulted in B1 Series ligands, yielding between 67.4-88.9%. Similarly, the condensation of salicylaldehyde with *para*-substituted phenylamines (1:1) in ethanol produced B2 ligands with yields ranging from 66.1% to 87.4%. The *para*-substituted system was chosen due to its minimal steric hindrance, resulting in a more favorable molecular geometry and improved structural stability, which also contributed to the high percent yield (Sarah et al., 2024). The synthesis of Ni(II) complexes with both ligands series, (ligand:metal) in 2:1 ratio were achieved with good yields between 60.8% and 92.5%, while the synthesis of Cu(II) complexes resulted in yields from 61.4% to 98.2%. Pd(II) complexes derived from both ligand series exhibited favorable yields, varying from 74.8% to 96.0%. All % yield was recorded in Table 4.1 for B1 Series compounds and Table 4.2 for B2 Series compounds.

All synthesized compounds were solids under ambient conditions and exhibited stability against air and moisture. The ligands and complexes of B1 and B2 series displayed different colours, as listed in Table 4.1 and Table 4.2, respectively. In terms of physical properties, the B1 series ligands displayed orange and brown colours, while B2 ligands were observed in yellow, green, and brown colours. The metal complexes of B1 Series exhibited green, black, and brown colours, whereas those of B2 Series were green and brown. All synthesized compounds were solid at ambient conditions and showed stability against air and moisture.

Micro-elemental analysis of B1 and B2 Series compounds were presented in Table 4.1 and Table 4.2, respectively, confirmed that the percentage of carbon, hydrogen, and nitrogen matched the expected molecular composition. The melting points of metal complexes were notably higher than those of their corresponding ligands, likely due to the increase in molecular weight following complexation and the strong dative covalent and ionic interactions between the metal ions and ligands. Melting points were recorded as temperature ranges, marking the transition from the initial melting point to complete liquefaction. This analysis remains a reliable approach for assessing the purity of the synthesized compounds.

The nitrogen atom in the imine group plays a central role in its chemical behavior, particularly in terms of dative covalent bonding and Lewis acid-base interactions (Rabelo et al., 2024). The nitrogen has a lone pair of electrons, making it a Lewis base capable of donating electron density to electron-deficient species. This allows Schiff base to form dative covalent bonds with Lewis acids, such as metal ions, where the metal acts as the electron acceptor. This property is especially significant in coordination chemistry, where Schiff base serve as ligands, stabilizing metal ions through their electron-donating nitrogen. This combination of dative bonding and acid-base interactions make Schiff base highly versatile in catalysis, material science, and biological systems.

The molar conductance values for the synthesized complexes were determined using the concentration of 10^{-3} M acetonitrile solutions at room temperature. For Schiff base complexes, the significant value is generally low molar conductivity, typically less than $20 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$, indicating non-electrolytic behavior (Chandra et al., 2015). From Table 4.1 and Table 4.2, the molar conductivity value less than $1 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ was found for all Ni(II), Cu(II), and Pd(II) complexes reflecting the non-conductive nature of the solution at room temperature. This indicates the absence of any electrolytes in the solutions where, there are no ions or counter ions existing in the outer sphere coordination of the complexes (Raman et al., 2001).

Table 4.1
Physicochemical Data of the B1 Series Ligand and Its Respective Metal Complexes

Compounds	Molecular Formula (RMM)	Mw (g/mol)	Colour	Yield (%)	Melting point (°C)	Molar Conductivity ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	Elemental Analysis % Calculated (Found)		
							C	H	N
B1H	C ₁₄ H ₁₃ NO ₂	227.26	Orange	80.8	86-87	-	73.99 (73.29)	5.77 (5.68)	6.16 (6.05)
NiB1H	C ₂₈ H ₂₄ N ₂ NiO ₄	511.20	Green	61.7	149-150	0.620	65.79 (64.34)	4.73 (5.11)	5.48 (4.95)
CuB1H	C ₂₈ H ₂₄ CuN ₂ O ₄	516.06	Black	76.5	208-209	0.529	65.17 (65.01)	4.69 (4.45)	5.43 (5.40)
PdB1H	C ₂₈ H ₂₄ N ₂ O ₄ Pd	558.93	Brown	90.0	264-265	0.275	60.17 (59.39)	4.33 (4.19)	5.01 (4.84)
B1Me	C ₁₅ H ₁₅ NO ₂	241.29	Orange	78.9	103-104	-	74.67 (73.79)	6.27 (6.24)	5.81 (5.71)
NiB1Me	C ₃₀ H ₂₈ N ₂ NiO ₄	538.26	Green	71.3	124-125	0.207	66.82 (66.20)	5.23 (5.29)	5.19 (4.31)
CuB1Me	C ₃₀ H ₂₈ CuN ₂ O ₄	544.11	Brown	78.3	232-234	0.054	66.22 (66.80)	5.19 (5.16)	5.15 (5.15)
PdB1Me	C ₃₀ H ₂₈ N ₂ O ₄ Pd	586.98	Brown	96.0	290-291	0.874	61.39 (60.55)	4.81 (4.74)	4.77 (4.58)
B1OMe	C ₁₅ H ₁₅ NO ₃	257.29	Orange	67.4	95-97	-	70.02 (69.57)	5.88 (5.80)	5.44 (5.33)
NiB1OMe	C ₃₀ H ₂₈ N ₂ NiO ₆	571.26	Green	60.8	179-180	0.782	63.08 (62.01)	4.94 (4.94)	4.90 (3.31)
CuB1OMe	C ₃₀ H ₂₈ CuN ₂ O ₆	576.11	Black	61.4	192-194	0.326	62.55 (61.32)	4.90 (4.74)	4.86 (4.71)
PdB1OMe	C ₃₀ H ₂₈ N ₂ O ₆ Pd	618.98	Brown	91.6	290-291	0.333	58.21 (57.70)	4.56 (4.46)	4.53 (4.38)
B1C	C ₁₄ H ₁₂ ClNO ₂	261.71	Orange	80.9	111-113	-	64.25 (63.73)	4.62 (4.43)	5.35 (5.29)
NiB1C	C ₂₈ H ₂₂ Cl ₂ N ₂ NiO ₄	580.09	Green	66.0	221-222	0.182	57.98 (56.74)	3.82 (3.73)	4.83 (4.50)
CuB1C	C ₂₈ H ₂₂ Cl ₂ CuN ₂ O ₄	584.94	Green	84.4	203-204	0.979	57.49 (57.32)	3.79 (3.69)	4.79 (4.78)
PdB1C	C ₂₈ H ₂₂ Cl ₂ N ₂ O ₄ Pd	627.81	Brown	84.7	289-290	0.294	53.57 (52.39)	3.53 (3.36)	4.46 (4.27)
B1N	C ₁₄ H ₁₂ N ₂ O ₄	272.26	Brown	88.9	172-173	-	61.88 (61.76)	4.67 (4.44)	10.32 (10.29)
NiB1N	C ₂₈ H ₂₂ N ₄ NiO ₈	601.20	Brown	92.6	304-305	0.960	56.04 (55.94)	3.94 (3.69)	9.43 (9.32)
CuB1N	C ₂₈ H ₂₂ CuN ₄ O ₈	606.05	Brown	98.2	300-301	0.684	55.75 (55.49)	4.52 (3.66)	8.90 (9.24)
PdB1N	C ₂₈ H ₂₂ N ₄ O ₈ Pd	648.92	Brown	74.8	317-318	0.148	50.92 (51.83)	3.74 (3.42)	8.60 (8.63)

Table 4.2

Physicochemical Data of the B2 Series Ligand and Its Respective Metal Complexes

Compounds	Molecular Formula (RMM)	Mw (g/mol)	Colour	Yield (%)	Melting point (°C)	Molar Conductivity ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	Elemental Analysis % Calculated (Found)		
							C	H	N
B2H	C ₁₃ H ₁₁ NO	197.24	Yellow	85.4	51-52	-	79.17 (77.49)	5.62 (5.53)	7.10 (6.95)
NiB2H	C ₂₆ H ₂₀ N ₂ NiO ₂	451.15	Green	72.9	272-273	0.309	69.22 (68.47)	4.47 (4.50)	6.21 (5.73)
CuB2H	C ₂₆ H ₂₀ CuN ₂ O ₂	456.00	Brown	75.2	239-240	0.179	68.48 (67.47)	4.42 (4.26)	6.14 (6.01)
PdB2H	C ₂₆ H ₂₀ N ₂ O ₂ Pd	498.88	Brown	93.9	233-235	0.261	62.60 (61.82)	4.04 (3.91)	5.62 (5.46)
B2Me	C ₁₄ H ₁₃ NO	211.26	Yellow	81.0	96-98	-	79.59 (78.26)	6.20 (6.14)	6.63 (6.50)
NiB2Me	C ₂₈ H ₂₄ N ₂ NiO ₂	479.21	Green	84.0	276-277	0.862	70.18 (69.78)	5.05 (5.20)	5.85 (5.84)
CuB2Me	C ₂₈ H ₂₄ CuN ₂ O ₂	484.06	Brown	84.6	208-209	0.334	69.48 (68.80)	5.00 (4.90)	5.79 (5.71)
PdB2Me	C ₂₈ H ₂₄ N ₂ O ₂ Pd	526.93	Brown	92.4	321-322	0.220	63.82 (62.94)	4.59 (4.48)	5.32 (5.17)
B2OMe	C ₁₄ H ₁₃ NO ₂	227.26	Green	76.7	83-85	-	73.99 (73.00)	5.77 (5.70)	6.16 (6.01)
NiB2OMe	C ₂₈ H ₂₄ N ₂ NiO ₄	511.20	Green	80.9	256-257	0.425	65.79 (63.17)	4.73 (4.77)	5.48 (5.18)
CuB2OMe	C ₂₈ H ₂₄ CuN ₂ O ₄	516.06	Brown	77.0	179-180	0.137	65.17 (63.90)	4.69 (4.54)	5.43 (5.28)
PdB2OMe	C ₂₈ H ₂₄ N ₂ O ₄ Pd	558.93	Brown	93.3	263-264	0.213	60.17 (60.44)	4.33 (4.38)	5.01 (4.99)
B2C	C ₁₃ H ₁₀ ClNO	231.68	Yellow	66.1	106-107	-	67.40 (66.20)	4.35 (4.12)	6.05 (6.03)
NiB2C	C ₂₆ H ₁₈ Cl ₂ N ₂ NiO ₂	520.04	Green	65.3	283-284	0.309	60.05 (59.94)	3.49 (3.62)	5.39 (5.34)
CuB2C	C ₂₆ H ₁₈ Cl ₂ CuN ₂ O ₂	524.89	Brown	88.6	241-243	0.116	59.50 (57.29)	3.46 (3.17)	5.34 (5.11)
PdB2C	C ₂₆ H ₁₈ Cl ₂ N ₂ O ₂ Pd	567.76	Brown	86.9	314-315	0.277	55.00 (54.05)	3.20 (3.10)	4.93 (5.00)
B2N	C ₁₃ H ₁₀ N ₂ O ₃	242.23	Brown	87.4	161-162	-	64.19 (64.46)	4.35 (4.16)	11.59 (11.56)
NiB2N	C ₂₆ H ₁₈ N ₄ NiO ₆	541.15	Green	77.7	323-324	0.644	54.67 (57.71)	3.65 (3.35)	8.61 (10.35)
CuB2N	C ₂₆ H ₁₈ CuN ₄ O ₆	546.00	Brown	87.1	317-318	0.714	57.15 (57.20)	3.50 (3.32)	10.39 (11.64)
PdB2N	C ₂₆ H ₁₈ N ₄ O ₆ Pd	588.87	Brown	78.5	360-361	0.519	51.77 (53.03)	3.31(3.08)	9.41 (9.51)

4.2.2 Magnetic Susceptibility

The magnetic properties of the complexes were analyzed to determine the number of unpaired electrons in the partially occupied *d*-orbitals. These measurements provided valuable insight into the electron configuration of the metal ions, contributing to a deeper understanding of their electronic structures and magnetic behaviours. Magnetic susceptibility values of the complexes were shown in Table 4.3. The preferred geometries of Ni(II), Cu(II), and Pd(II) complexes can be understood in terms of their electronic configurations and the resulting crystal field stabilization energy (CFSE) as shown in Figure 4.1.

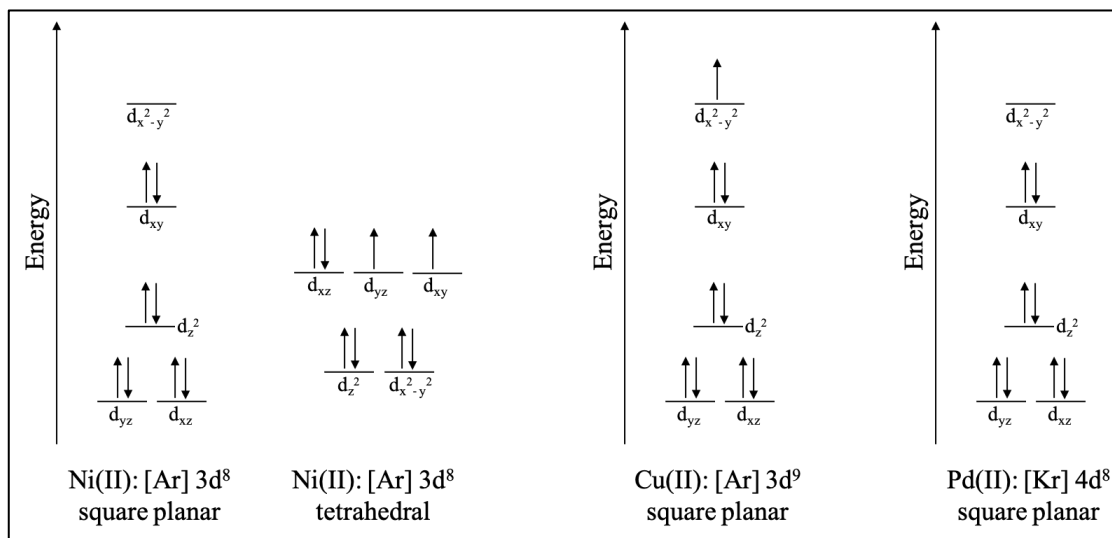


Figure 4.1 Crystal Field Splitting Diagram for Ni(II), Cu(II), and Pd(II) Complexes

Transition-metal complexes commonly adopt either square planar or tetrahedral geometries, and the preference for one over the other is governed primarily by the *d*-electron configuration of the metal and the strength of the surrounding ligand field (Rabelo et al., 2024). Square planar complexes arise when the ligand field is sufficiently strong to generate a large crystal field splitting, stabilizing a low-spin electronic configuration with high CFSE; this arrangement is particularly favored by *d*⁸ metal ions, where *dsp*² hybridization allows optimal in-plane orbital overlap and typically produces diamagnetic species (Chen et al., 2018). In contrast, tetrahedral complexes experience much smaller crystal field splitting, making high-spin configurations more favorable and resulting in lower CFSE and commonly paramagnetic behavior (Boča et al., 2017).

These principles govern the structural chemistry of Ni(II), Pd(II), and Cu(II). Ni(II) with a $3d^8$ electron configuration can adopt either geometry: strong-field ligands generate square planar, low-spin Ni(II) with no unpaired electrons, while weak-field ligands stabilize tetrahedral Ni(II) containing two unpaired electrons (Blanchard et al., 2005). Cu(II) ($3d^9$) often forms square planar complexes, but the presence of a single unpaired electron in the degenerate for example the orbitals induces a Jahn-Teller distortion, elongating or compressing axial bonds to relieve electronic degeneracy (Boshaala et al., 2021). This distortion further stabilizes the square planar geometry and enhances in-plane metal-ligand interactions (Rehman et al., 2009). In contrast, Pd(II) has a $4d^8$ configuration, and in a square planar geometry, the crystal field splitting is significant, with the dx^2-y^2 orbital remaining unoccupied, leading to high stabilization (Monger et al., 2021). This makes square planar geometry the preferred structure for Pd(II).

These geometric and electronic characteristics directly influence catalytic performance. Square planar complexes, with their low-spin configuration and accessible coordination sites, excel in two-electron pathways such as oxidative addition and reductive elimination (Dawson et al., 2023). This is exemplified in the Stille reaction, a palladium-catalyzed cross-coupling between an organostannane ($R-SnR_3$) and an organic halide ($R'-X$). The catalytic cycle proceeds via three main steps: (1) oxidative addition of the organic halide to the square planar Pd(0) complex, enabled by effective overlap between the metal dx^2-y^2 orbital and the σ^* orbital of the C-X bond; (2) transmetalation, where the organostannane transfers its organic group to Pd(II), facilitated by the coplanar arrangement of ligands; and (3) reductive elimination, where the two organic groups couple in-plane to regenerate Pd(0) (Espinete & Echavarren, 2004). The square planar geometry is crucial at every step, stabilizing the intermediate oxidation states and aligning orbitals for efficient C-C bond formation (Banerjee et al., 2025). In contrast, tetrahedral complexes, such as high-spin Ni(II), favor single-electron transfer and radical pathways, making them suitable for photoredox or radical-mediated transformations rather than two-electron cross-coupling reactions (Diccianni et al., 2020).

Table 4.3

Magnetic Susceptibility of Ni(II), Cu(II), and Pd(II) Complexes

Compounds	Bohr Magneton	Number of unpaired electrons	Magnetism	Geometry
NiB1H	3.183	2	Paramagnetic	Tetrahedral
NiB1Me	3.053	2	Paramagnetic	Tetrahedral
NiB1OMe	3.329	2	Paramagnetic	Tetrahedral
NiB1C	0	0	Diamagnetic	Square planar
NiB1N	0	0	Diamagnetic	Square planar
NiB2H	2.548	2	Paramagnetic	Tetrahedral
NiB2Me	3.224	2	Paramagnetic	Tetrahedral
NiB2OMe	3.342	2	Paramagnetic	Tetrahedral
NiB2C	3.114	2	Paramagnetic	Tetrahedral
NiB2N	2.291	2	Paramagnetic	Tetrahedral
CuB1H	1.766	1	Paramagnetic	Square planar
CuB1Me	1.623	1	Paramagnetic	Square planar
CuB1OMe	1.745	1	Paramagnetic	Square planar
CuB1C	1.753	1	Paramagnetic	Square planar
CuB1N	1.904	1	Paramagnetic	Square planar
CuB2H	1.736	1	Paramagnetic	Square planar
CuB2Me	1.676	1	Paramagnetic	Square planar
CuB2OMe	1.683	1	Paramagnetic	Square planar
CuB2C	1.815	1	Paramagnetic	Square planar
CuB2N	1.736	1	Paramagnetic	Square planar
PdB1H	0	0	Diamagnetic	Square planar
PdB1Me	0	0	Diamagnetic	Square planar
PdB1OMe	0	0	Diamagnetic	Square planar
PdB1C	0	0	Diamagnetic	Square planar
PdB1N	0	0	Diamagnetic	Square planar
PdB2H	0	0	Diamagnetic	Square planar
PdB2Me	0	0	Diamagnetic	Square planar
PdB2OMe	0	0	Diamagnetic	Square planar
PdB2C	0	0	Diamagnetic	Square planar
PdB2N	0	0	Diamagnetic	Square planar

4.2.3 FTIR

FTIR spectroscopy was employed to identify new peaks corresponding to metal-ligand interactions, specifically through phenolic oxygen and azomethine nitrogen. Additionally, shifts in the azomethine band and the disappearance of the hydroxyl peak in the metal complexes, compared to their respective ligands, were observed. These spectral changes provided evidence for ligand formation as well as successful coordination between the ligands and metal centers. Figure 4.2 shows the representative FTIR spectra of B1H and its corresponding complexes while Figure 4.3 displays the representative FTIR spectra of B2H and its corresponding complexes. The infrared data of B1 series compounds and B2 series compounds are recorded in Table 4.4 and Table 4.5, respectively. The FTIR spectra for the compounds can be found in APPENDIX A.

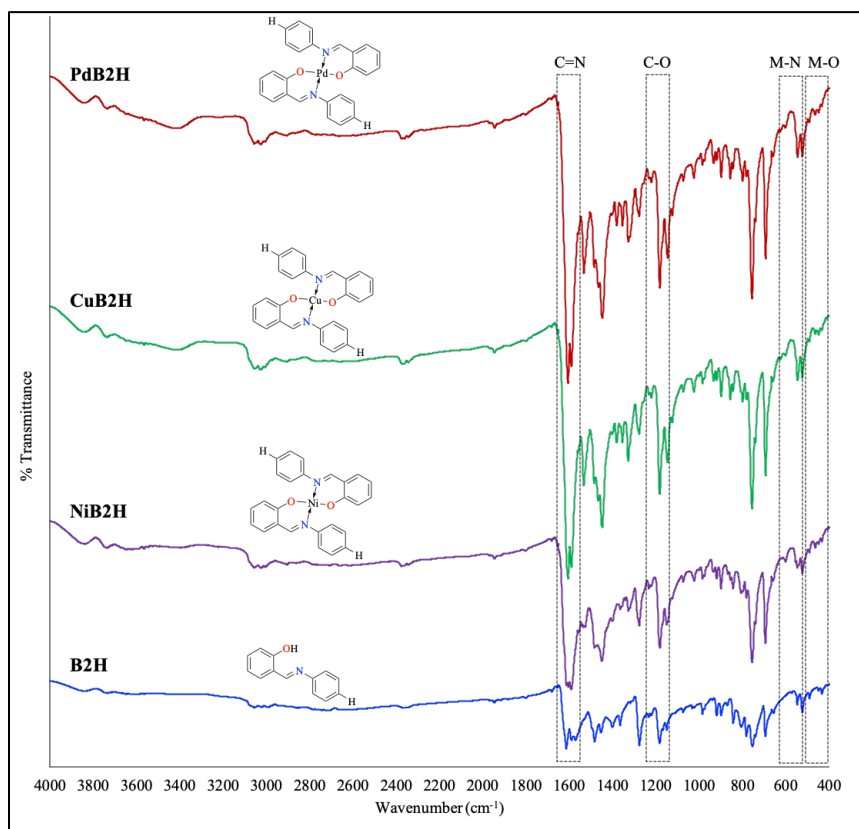


Figure 4.2 FTIR Spectra of B1H and Its Metal Complexes

The infrared spectra of the B1 ligands exhibit strong bands at range of 1603-1618 cm⁻¹ assignable to C=N stretching of the imine/azomethine. These bands shifted to lower frequency, 1602-1618 cm⁻¹ upon coordination to metal centres,

indicating the involvement of the azomethine nitrogen in the complexation (Şenol et al., 2011; Nair et al., 2012). This observation can be explained by the donation of lone pair of electrons from the nitrogen to the empty d-orbitals of the transition metals, lowering the electron density of the C=N and reducing the energy of the bond. The infrared spectra of all metal complexes exhibit bands at 1340-1394 cm^{-1} assignable to $\nu(\text{C-N})$ corresponding to those appearing in the lower region 1340-1367 cm^{-1} for the free ligands. The shifting to higher wavenumbers supports the discussion above on the involvement of azomethine nitrogen in the complexation to metal centres.

The $\nu(\text{C-O})$ bands in the region 1241-1260 cm^{-1} of the free ligands shifted to lower wavenumbers of 1211-1247 cm^{-1} in the complexes, indicating that the phenolic oxygen is also involved in complexation. This suggestion is further corroborated below. Broad OH bands are observed in the range of 3384-3402 cm^{-1} in free ligands, but not observed in the spectra of the complexes. This further suggests that the phenolic moieties in the ligands underwent deprotonation upon complexation, forming ionic bonds between the metal centre and the phenolic oxygen.

The O-H stretching peak was absent or significantly reduced for some ligands in the FTIR spectrum. This can be attributed to intramolecular hydrogen bonding, where the OH group forms a hydrogen bond with a nearby electronegative atom (such as nitrogen or oxygen) within the same molecule; $\text{O}-\text{H}\cdots\text{N}$ (Borho et al., 2006). This interaction can reduce the intensity and shift the position of the OH stretching band in FTIR spectra, sometimes making it very broad, weak, or even unobservable in the typical OH region (3200-3600 cm^{-1}).

The appearance of new bands at 440-577 cm^{-1} and 548-703 cm^{-1} attributable to M-O and M-N vibrations, respectively, supports the suggestion above of the participation of the nitrogen atoms of the azomethine group and oxygen atoms of the phenolic group of the ligand in the complexation with metal ions (Shebl, 2009; Ouf et al., 2010). Accordingly, one can deduce that the ligands bind to the metal ion as bidentate fashion (N, O) in 2:1 ratio at azomethine nitrogen and the oxygen atoms (Nair et al., 2012).

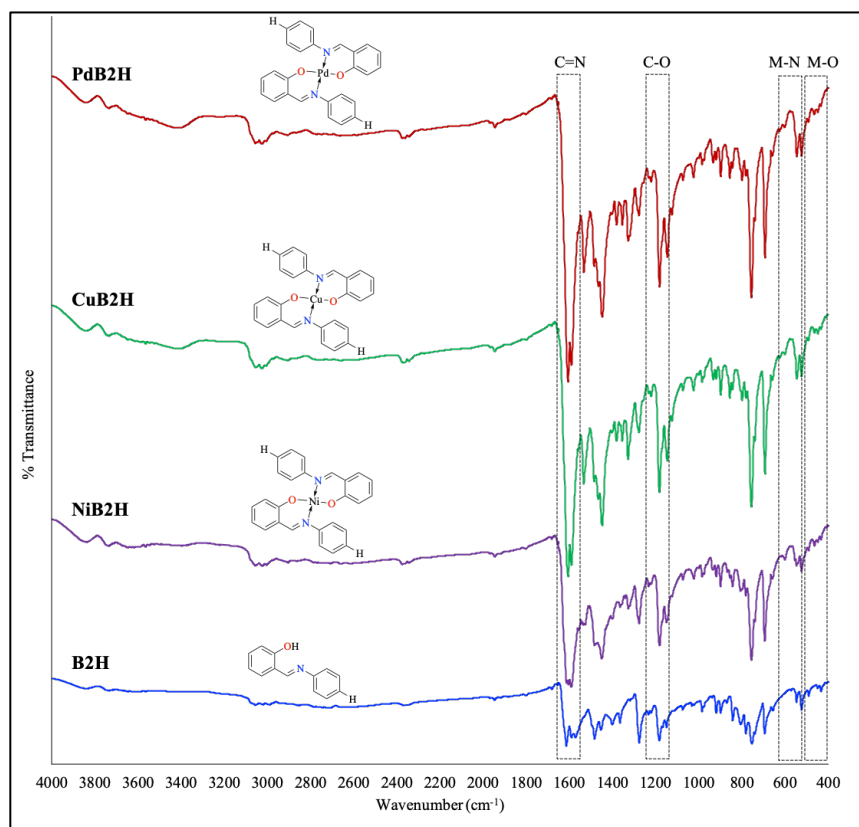


Figure 4.3 FTIR Spectra of B2H and Its Metal Complexes

Similar observations as those for the B1 series of compounds are also observed for the B2 series. It can be clearly shown that the appearance of the C=N of azomethine in the range $1610\text{--}1620\text{ cm}^{-1}$, indicates the formation of Schiff base. The azomethine C=N bands shifted to lower frequencies, $1594\text{--}1614\text{ cm}^{-1}$ in all complexes due to the withdrawal of electron density from the nitrogen atom owing to coordination (Bartyzel, 2017). A similar effect was observed in the stretching vibration of the Schiff base phenolic C-O ($1257\text{--}1336\text{ cm}^{-1}$), with respect to the same group in the complexes where it was shifted to lower frequency ($1244\text{--}1322\text{ cm}^{-1}$), confirming oxygen coordination to the metal. The nature of this interaction is such that it reduces the electron density on the C=N and C-N moieties as shown by the reduction of the frequency implying the reducing strength of the C=N and C-N bonds. The appearance of new bands at $408\text{--}523\text{ cm}^{-1}$ and $524\text{--}590\text{ cm}^{-1}$, that ascribed M-O and M-N vibrations supporting the participation of the nitrogen atom of the azomethine group and oxygen atom of the of OH group of the ligand in the complexation with metal ions (Ouf et al., 2010).

Table 4.4
FTIR Data of B1 Series Ligands and Its Respective Metal Complexes

Compound	Wavenumber, ν (cm ⁻¹)					
	OH	C=N	C-N	C-O	M-N	M-O
B1H	-	1615 (s)	1362 (s)	1253 (s)	-	-
NiB1H	-	1632 (s)	1388 (m)	1211 (s)	697 (w)	537 (w)
CuB1H	-	1605 (s)	1394 (s)	1231 (s)	692 (w)	537 (w)
PdB1H	-	1602 (s)	1386 (s)	1240 (s)	695 (w)	543 (w)
B1Me	3384 (w)	1618 (s)	1364 (s)	1258 (s)	-	-
NiB1Me	-	1615 (s)	1380 (m)	1237 (s)	548 (w)	494 (w)
CuB1Me	-	1615 (s)	1389 (s)	1232 (s)	606 (w)	487 (w)
PdB1Me	-	1601 (s)	1375 (s)	1237 (s)	607 (w)	498 (w)
B1OMe	3402 (w)	1618 (s)	1367 (s)	1241 (s)	-	-
NiB1OMe	-	1616 (s)	1340 (s)	1233 (s)	618 (w)	468 (w)
CuB1OMe	-	1612 (s)	1392 (s)	1233 (s)	608 (w)	456 (w)
PdB1OMe	-	1611 (s)	1380 (m)	1237 (s)	606 (w)	474 (w)
B1C	3395 (w)	1614 (s)	1355 (s)	1257 (s)	-	-
NiB1C	-	1605 (s)	1358 (m)	1245 (m)	582 (w)	458 (w)
CuB1C	-	1603 (s)	1363 (s)	1235 (s)	586 (w)	440 (w)
PdB1C	-	1603 (s)	1359 (m)	1240 (s)	581 (w)	450 (w)
B1N	-	1603 (s)	1340 (s)	1260 (s)	-	-
NiB1N	-	1608 (s)	1341 (s)	1247 (s)	703 (w)	573 (w)
CuB1N	-	1607 (s)	1341 (s)	1239 (s)	699 (w)	577 (w)
PdB1N	-	1604 (s)	1341 (s)	1240 (m)	701 (w)	572 (w)

Note: s = strong; m = medium; w = weak.

Table 4.5
FTIR Data of B2 Series Ligands and Its Respective Metal Complexes

Compound	Wavenumber, ν (cm ⁻¹)					
	OH	C=N	C-N	C-O	M-N	M-O
B2H	3392 (w)	1615 (s)	1366 (m)	1326 (s)	-	-
NiB2H	-	1603 (s)	1356 (m)	1322 (s)	540 (w)	465 (w)
CuB2H	-	1608 (s)	1355 (s)	1280 (s)	544 (w)	445 (w)
PdB2H	-	1607 (s)	1353 (m)	1315 (s)	548 (w)	468 (w)
B2Me	3415 (w)	1619 (s)	1399 (s)	1332 (s)	-	-
NiB2Me	-	1611 (s)	1367 (s)	1320 (s)	524 (w)	459 (w)
CuB2Me	-	1612 (s)	1386 (s)	1283 (s)	531 (w)	425 (w)
PdB2Me	-	1597 (s)	1381 (m)	1314 (s)	542 (w)	449 (w)
B2OMe	3414 (w)	1620 (s)	1397 (s)	1257 (s)	-	-
NiB2OMe	-	1614 (s)	1362 (m)	1244 (m)	579 (w)	487 (w)
CuB2OMe	-	1611 (s)	1380 (m)	1251 (s)	590 (w)	488 (w)
PdB2OMe	-	1609 (s)	1378 (m)	1248 (s)	555 (w)	459 (w)
B2C	3394 (w)	1610 (s)	1360 (s)	1322 (s)	-	-
NiB2C	-	1608 (s)	1348 (m)	1317 (s)	561 (w)	426 (w)
CuB2C	-	1607 (s)	1345 (s)	1272 (s)	585 (w)	408 (w)
PdB2C	-	1603 (s)	1350 (s)	1313 (s)	574 (w)	438 (w)
B2N	-	1613 (s)	1344 (s)	1272 (s)	-	-
NiB2N	-	1606 (s)	1338 (s)	1260 (m)	585 (w)	427 (w)
CuB2N	-	1594 (s)	1342 (s)	1258 (m)	583 (w)	523 (w)
PdB2N	-	1607 (s)	1327 (s)	1251 (m)	578 (w)	424 (w)

Note: s = strong; m = medium; w = weak.

4.2.4 ^1H NMR

The ^1H NMR spectra of the free ligands and complexes were recorded in CDCl_3 . The ^1H NMR data of the compounds from both series are shown in Table 4.6 and Table 4.7. Figure 4.4 shows the representative ^1H NMR spectra of B1H and its PdB1H while Figure 4.5 displays the representative ^1H NMR spectra of B2H and PdB2H . The ^1H NMR spectra for other compounds can be found in APPENDIX B.

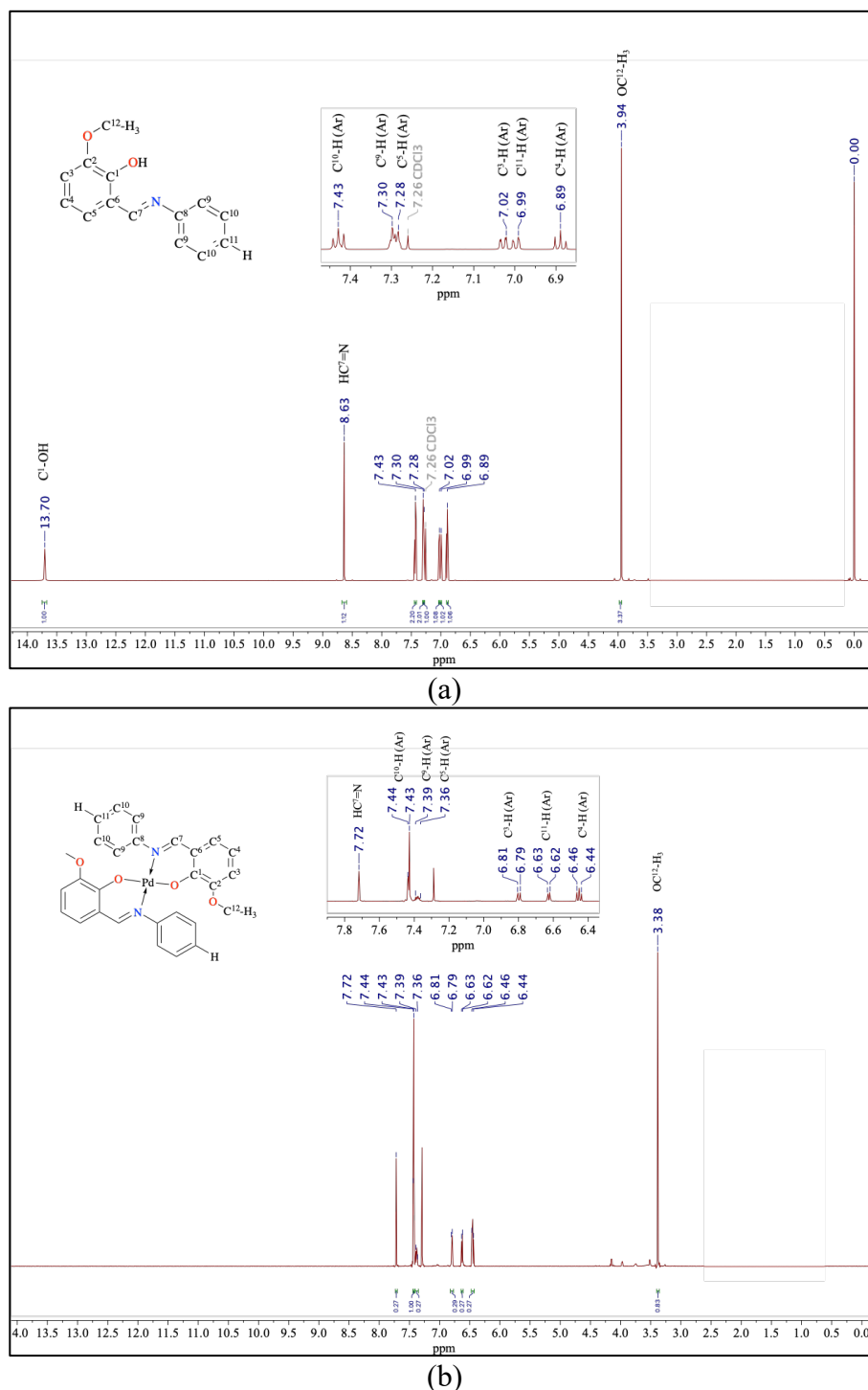


Figure 4.4 ^1H NMR Spectra for (a) B1H and (b) PdB1H

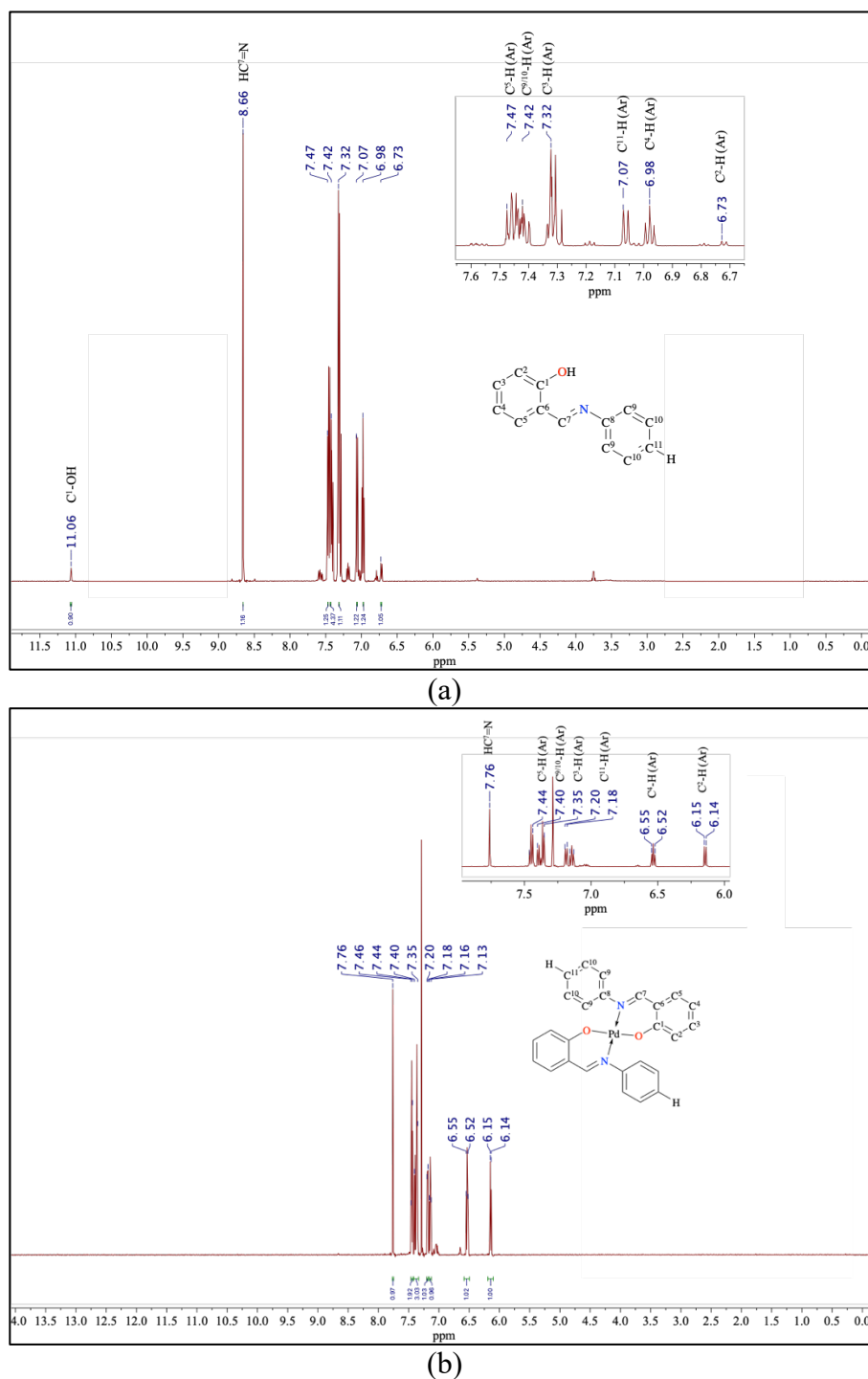


Figure 4.5 ^1H NMR Spectra for (a) B2H and (b) PdB2H

The proton numbering was assigned as shown in Figure 4.6 for B1 and B2 series respectively. The number of hydrogens obtained from the integration is in conformance with the proposed chemical structures. Since the compounds are symmetrical, the integration only displayed half of the total number of hydrogens.

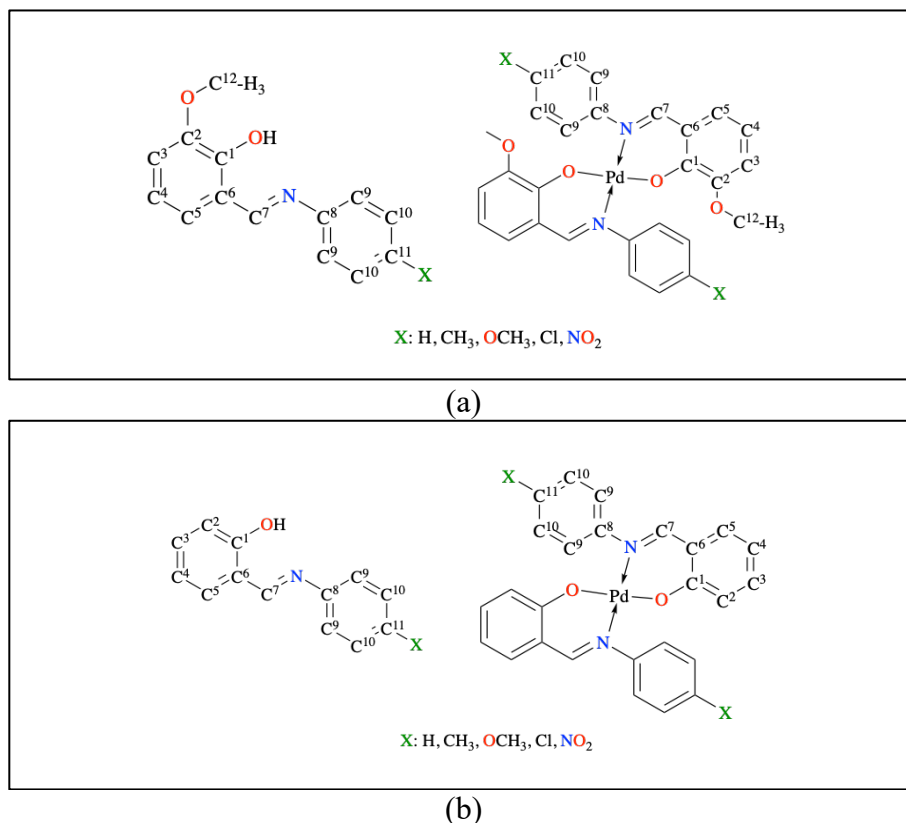


Figure 4.6 The Numbering System for ^1H and ^{13}C NMR of (a) B1 Series Schiff Base Complexes and (b) B2 Series Schiff Base Complexes

OH appears as singlet at 12.91-13.89 ppm in free ligands of B1 series and at 11.06-13.45 ppm in ligands of B2 series. These hydroxyl protons were found in the downfield region likely due to the formation of hydrogen bonding with azomethine nitrogen as well as the deshielding effect of oxygen (Aranha et al., 2006).

The absence of OH peak in all spectra of complexes supported the infrared evidence that the coordination to metal centres was established through deprotonation of the hydroxyl groups (Raman et al., 2001). Azomethine proton, $\text{HC}^7=\text{N}$ appears as singlet in the region of 8.61-8.67 ppm for all free ligands of B1 series and at 8.61-8.66 ppm in free ligands of B2 series. This signal was found in the upfield region for all Pd(II) complexes of B1 and B2 series, ranging from 7.69-7.72 ppm and 7.70-7.76 ppm, respectively. This supports the shifting of azomethine peak in FTIR spectra as explained in section 4.2.3, which suggested the involvement of azomethine nitrogen in the coordination to metal centres (Maity et al., 2010). The donation of electron density from the nitrogen atom to the metal weakens the $\text{C}=\text{N}$ bond, which is observed as a lower stretching frequency (ν) in the FTIR spectrum. This electron

redistribution also increases the electron density on the ligand, leading to greater proton shielding and resulting in an upfield shift in the ^1H NMR signals.

The chemical shifts of aromatic protons of free ligands appeared in the range of 6.88-8.34 ppm and at 6.71-8.34 ppm for B1 and B2 series, respectively. This is in agreement with the chemical shifts reported by Tajuddin et al. (2014). These hydrogens experience the shielding effect of diamagnetic anisotropy caused by circulating π electrons in the aromatic rings (Ahmad et al., 2020). The signals of these aromatic protons were found at 6.41-8.30 ppm and 6.14-7.44 ppm in the complexes of B1 and B2 series, respectively. The shifting in chemical shift of these protons indicates that the complexation has been established between metal ions and the ligands.

The presence of methyl, CH_3 at $\text{C}^{11}\text{-H(Ar)}$, in B1Me, B2Me and in their corresponding complexes was detected at 2.38 to 2.45 ppm while the presence of methoxy, $-\text{OCH}_3$ at $\text{C}^{11}\text{-H(Ar)}$, in B1OMe, B2OMe and in their corresponding complexes were detected at 3.44 to 3.84 ppm. The chemical shift of $\text{C}^2\text{-OCH}_3$ proton in B1 series compounds was found further upfield with respect to methyl group attached to aromatic carbon as the former was more shielded in the range of 3.37-3.94 ppm in free ligands and complexes of B1 series.

Table 4.6
¹H NMR Data of B1 Series Ligands and Its Respective Metal Complexes

Compound	Chemical shift, δ (ppm)								
	C ¹ -OH	HC ⁷ =N	C ³ -H (Ar)	C ⁴ -H (Ar)	C ⁵ -H (Ar)	C ⁹ -H (Ar)	C ¹⁰ -H (Ar)	C ¹¹ -H (Ar)	C ² -OCH ₃ (Ar)
B1H	13.70 (s, 1H)	8.63 (s, 1H)	7.02-7.04 (dd, J = 8.1, 1.4 Hz, 1H)	6.88-6.90 (t, J = 7.88, 7.88 Hz, 1H)	7.28 (m, 1H)	7.30 (d, J = 1.06 Hz, 2H)	7.42-7.44 (t, J = 7.87, 7.87 Hz, 2H)	6.99-7.00 (dd, J = 8.00, 1.26 Hz, 1H)	3.94 (s, 3H)
PdB1H	-	7.72 (s, 1H)	6.79-6.81 (dd, J = 8.1, 1.5 Hz, 1H)	6.44-6.46 (m, 1H)	7.36 (dd, J = 4.1, 3.0 Hz, 1H)	7.39 (d, J = 3.9 Hz, 2H)	7.43-7.44 (m, 2H)	6.62-6.63 (dd, J = 7.5, 1.5 Hz, 1H)	3.38 (s, 3H)
B1Me	13.84 (s, 1H)	8.63 (s, 1H)	6.97-6.99 (dd, J = 7.97, 1.14 Hz, 1H)	6.86-6.89 (t, J = 7.88 Hz, 1H)	7.01-7.02 (dd, J = 7.76, 1.28 Hz, 1H)	7.20-7.23 (m, 4H)		2.38 (s, 3H)	3.94 (s, 3H)
PdB1Me	-	7.69 (s, 1H)	6.61-6.64 (dd, J = 7.6, 1.5 Hz, 1H)	6.41-6.46 (t, J = 7.8 Hz, 1H)	6.77-6.80 (dd, J = 8.0, 1.5 Hz, 1H)	7.28-7.32 (m, 4H)		2.45 (s, 3H)	3.38 (s, 3H)
B1OMe	13.89 (s, 1H)	8.62 (s, 1H)	6.97-6.98 (dd, J = 8.1, 1.3 Hz, 1H)	6.86-6.89 (t, J = 7.9 Hz, 1H)	7.00-7.01 (dd, J = 7.8, 1.3 Hz, 1H)	7.28-7.29 (d, J = 8.9 Hz, 2H)	6.94-6.96 (d, J = 8.9 Hz, 2H)	3.84 (s, 3H)	3.94 (s, 3H)
PdB1OMe	-	7.71 (s, 1H)	6.78-6.80 (dd, J = 8.1, 1.4 Hz, 1H)	6.44-6.46 (t, J = 7.8 Hz, 1H)	6.95-6.96 (m, 1H)	7.33-7.35 (d, J = 8.6 Hz, 2H)	6.62-6.64 (d, J = 7.6 Hz, 1H)	3.44 (s, 3H)	3.90 (s, 3H)
B1C	13.42 (s, 1H)	8.61 (s, 1H)	7.03 (m, 1H)	6.89-6.91 (t, J = 7.9 Hz, 1H)	7.22-7.23 (m, 1H)	7.00-7.02 (d, J = 8.6 Hz, 2H)	7.38-7.40 (d, J = 8.5 Hz, 2H)	-	3.94 (s, 3H)
PdB1C	-	7.70 (s, 1H)	6.77-6.80 (dd, J = 8.1, 1.6 Hz, 1H)	6.45-6.50 (t, J = 7.8 Hz, 1H)	7.30-7.33 (m, 1H)	6.63-6.66 (m, 2H)	7.38-7.41 (d, J = 8.6 Hz, 2H)	-	3.51 (s, 1H)
B1N	12.91 (s, 1H)	8.67 (s, 1H)	7.08-7.10 (m, 1H)	6.95-6.98 (t, J = 7.9 Hz, 1H)	7.29 (m, 1H)	7.39-7.41 (d, J = 9.0 Hz, 2H)	8.32-8.34 (d, J = 9.0 Hz, 2H)	-	3.98 (s, 3H)
PdB1N	-	7.71 (s, 1H)	6.62-6.64 (m, 1H)	6.48-6.51 (m, 1H)	6.79-6.80 (m, 1H)	7.52-7.53 (d, J = 8.9 Hz, 2H)	8.29-8.30 (d, J = 8.8 Hz, 2H)	-	3.37 (s, 3H)

Note: s = singlet; d = doublet; t = triplet; dd = doublet of doublet; m = multiplet.

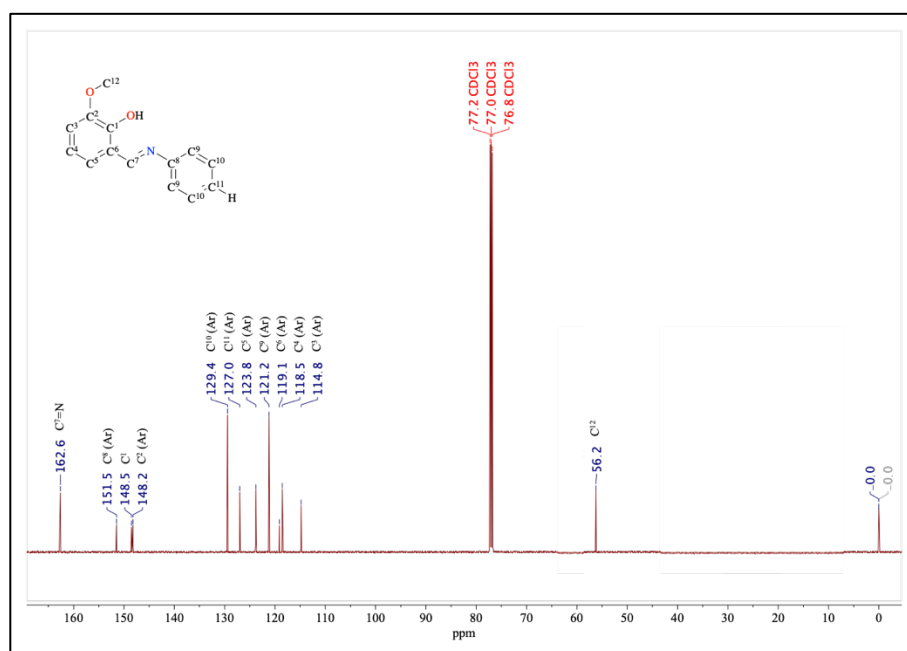
Table 4.7
¹H NMR Data of B2 Series Ligands and Its Respective Metal Complexes

Compound	Chemical shift, δ (ppm)								
	C ¹ -OH	HC ⁷ =N	C ³ -H (Ar)	C ⁴ -H (Ar)	C ⁵ -H (Ar)	C ⁹ -H (Ar)	C ¹⁰ -H (Ar)	C ¹¹ -H (Ar)	C ² -H (Ar)
B2H	11.06 (s, 1H)	8.66 (s, 1H)	7.31-7.35 (m, 1H)	6.96-6.99 (td, J = 7.5, 1.1 Hz, 1H)	7.46-7.47 (m, 1H)		7.42-7.44 (m, 4H)	7.07 (m, 1H)	6.71-6.73 (dd, J = 8.5, 1.0 Hz, 1H)
PdB2H	-	7.76 (s, 1H)	7.13-7.16 (m, 1H)	6.52-6.55 (m, 1H)	7.44-7.46 (m, 1H)		7.35-7.40 (m, 4H)	7.18-7.20 (dd, J = 7.9, 1.8 Hz, 1H)	6.14-6.15 (m, 1H)
B2Me	13.41 (s, 1H)	8.62 (s, 1H)	7.01-7.03 (m, 1H)	6.92-6.95 (m, 1H)	7.35-7.37 (m, 1H)		7.19-7.23 (m, 4H)	2.38 (s, 3H)	7.38-7.39 (dd, J = 7.4, 1.4 Hz, 1H)
PdB2Me	-	7.73 (s, 1H)	7.14-7.16 (m, 1H)	6.50-6.55 (m, 1H)	7.11-7.12 (m, 1H)		6.17-6.20 (m, 4H)	2.45 (s, 3H)	7.18-7.19 (m, 1H)
B2OMe	13.45 (s, 1H)	8.61 (s, 1H)	7.34-7.35 (m, 1H)	7.01-7.02 (m, 1H)	7.37-7.38 (m, 1H)	7.27-7.28 (d, J = 8.9 Hz, 2H)	6.94-6.96 (d, J = 8.2 Hz, 2H)	3.84 (s, 3H)	6.92-6.93 (d, J = 8.8 Hz, 1H)
PdB2OMe	-	7.72 (s, 1H)	7.13-7.15 (m, 1H)	6.49-6.52 (m, 1H)	7.25-7.26 (m, 1H)	6.93-6.94 (d, J = 8.8 Hz, 2H)	6.55-6.56 (d, J = 6.9 Hz, 2H)	3.88 (s, 3H)	6.22-6.23 (d, J = 8.5 Hz, 2H)
B2C	11.06 (s, 1H)	8.62 (s, 1H)	7.40 (m, 1H)	6.96-6.99 (td, J = 7.5, 1.1 Hz, 1H)	7.43-7.44 (m, 1H)	7.24-7.26 (d, J = 8.8 Hz, 2H)	7.41-7.42 (d, J = 8.7 Hz, 2H)	-	7.04-7.06 (d, J = 8.8 Hz, 1H)
PdB2C	-	7.70 (s, 1H)	7.16-7.19 (m, 1H)	6.52-6.55 (m, 1H)	7.38-7.39 (m, 1H)	7.03-7.06 (d, J = 8.2 Hz, 2H)	7.25-7.26 (d, J = 6.2 Hz, 2H)	-	6.18-6.19 (d, J = 8.6 Hz, 2H)
B2N	12.59 (s, 1H)	8.66 (s, 1H)	7.29 (m, 1H)	7.46-7.48 (m, 1H)	7.01-7.03 (m, 1H)	7.39-7.40 (d, J = 8.6 Hz, 2H)	8.33-8.34 (d, J = 8.6 Hz, 2H)	-	7.08-7.09 (d, J = 8.2 Hz, 1H)
PdB2N	-	7.74 (s, 1H)	6.56-6.59 (m, 1H)	7.18-7.21 (m, 1H)	6.07-6.08 (m, 1H)	7.49-7.50 (d, J = 8.8 Hz, 2H)	8.32-8.33 (d, J = 8.8 Hz, 2H)	-	6.62-6.63 (m, 1H)

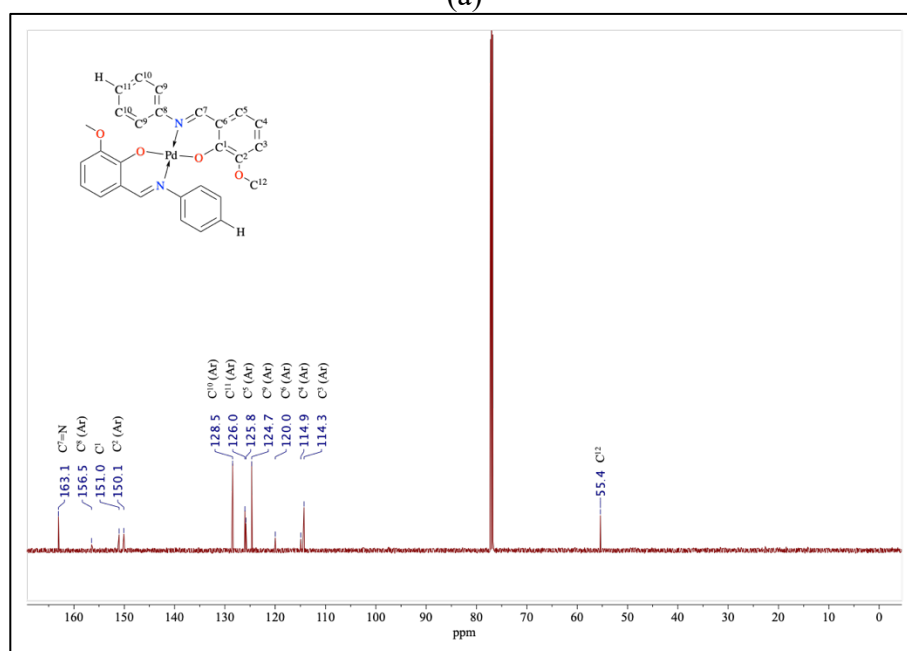
Note: s = singlet; d = doublet; dd = doublet of doublet; td = triplet of double; m = multiplet.

4.2.5 ^{13}C NMR

The ^{13}C NMR spectra of the free ligands and complexes were recorded in CDCl_3 . The chemical shifts are as tabulated in Table 4.8 for B1 series and Table 4.9 for B2 series. Figure 4.7 shows the representative ^{13}C spectra of B1H and PdB1H while Figure 4.8 shows the representative ^{13}C spectra of B2H and PdB2H . The ^{13}C NMR spectra for other compounds can be found in APPENDIX C.



(a)



(b)

Figure 4.7 ^{13}C NMR Spectra for (a) B1H and (b) PdB1H

The azomethine carbon, $C^7=N$ was found in the range of 161.6-165.4 ppm and 160.4-161.4 ppm in all free ligands of B1 and B2 series, respectively with no significant influence of substituents. It appeared in downfield regions for complexes in the range of 162.7-163.1 ppm in all Pd(II) complexes. This indicates that the complexation has taken place between metal centre and azomethine nitrogen (Shanker et al., 2009) and further supports FTIR data as explained in Section 4.2.3.

The complexation between metal centres and phenolic oxygen, on the other hand, can be seen through the shifting of C-OH/C-O signals (C^1). The signal of C-OH at C^1 was observed to be higher than that of $C=N$ at C^7 due to higher electronegativity of oxygen (3.44) as compared to nitrogen (3.04) on Pauling's scale.

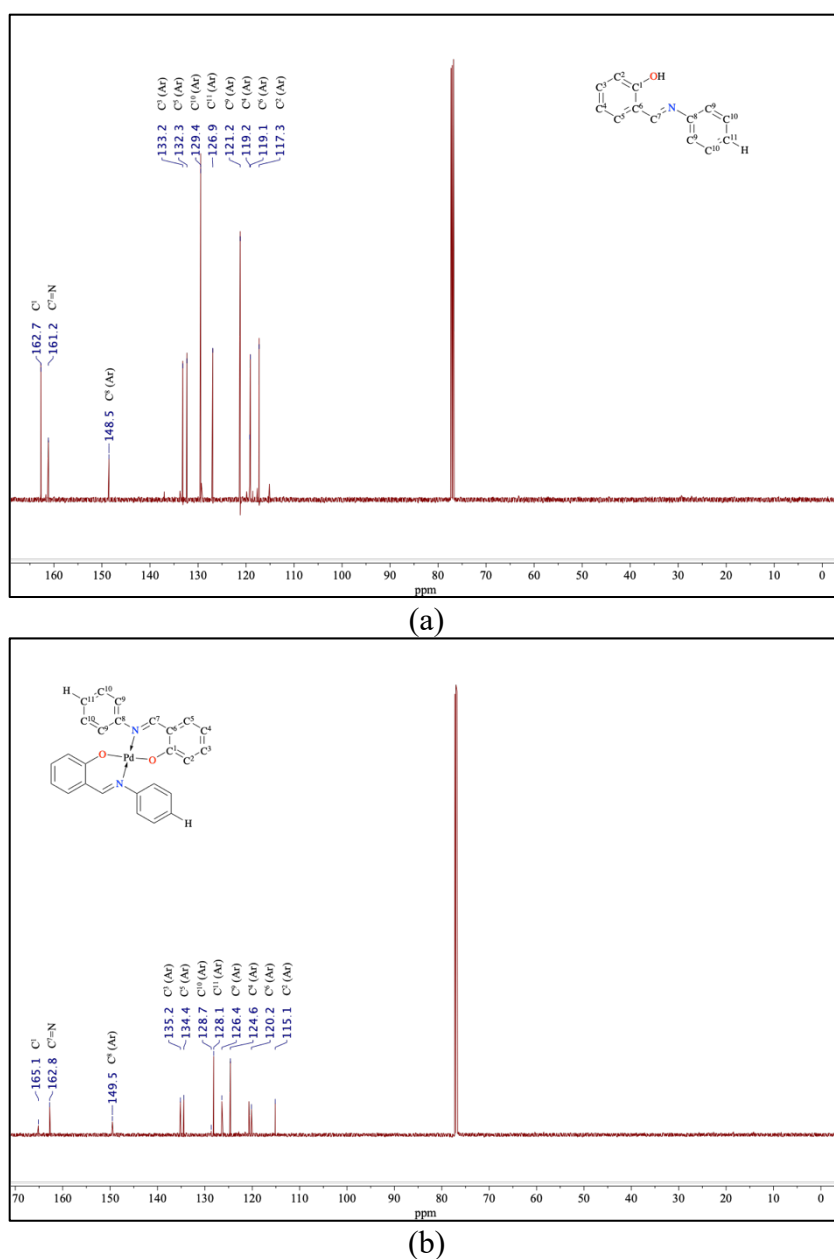


Figure 4.8 ^{13}C NMR spectra for (a) B2H and (b) PdB2H

Aromatic carbons of B1 series compounds were seen in the range of 114.4-158.9 ppm in free ligands and in the region of 113.6-158.0 ppm in complexes. While for B2 series compounds, the aromatic carbons were detected at 114.6-158.8 ppm in free ligands and 115.1-154.7 ppm in their complexes. The peak of aromatic carbon, C¹¹ (Ar) was found further downfield in B1C and B1OMe with respect to its peak in other ligands owing to the presence of electronegative element of chlorine, Cl attached at B1C with electronegative value of 3.16 and oxygen, O (3.44) attached next to the carbon at B1OMe. The shifting of aromatic carbons to downfield and upfield suggested the complexation between metal and ligands (Hazani et al., 2018).

The presence of methyl group at C¹³ (-CH₃) and methoxy group at C¹⁴ (-OCH₃) in B1Me, and B1OMe was detected at 21.1 ppm and 55.6 ppm, respectively. While for B2Me and B2OMe, methyl (C¹⁴) and methoxy groups (C¹³) were seen at 21.1 ppm and 55.5 ppm, respectively. These values are in agreement with the values previously reported by Senol et al., (2011). The number of carbons seen on the spectra are equal to the number of carbons in the proposed structures.

Table 4.8
¹³C NMR Data of B1 Series Ligands and Its Respective Metal Complexes

Compound	Chemical shift, δ (ppm)													
	C ¹	C ⁷ =N	C ³ (Ar)	C ⁴ (Ar)	C ⁵ (Ar)	C ⁶ (Ar)	C ⁸ (Ar)	C ⁹ (Ar)	C ¹⁰ (Ar)	C ¹¹ (Ar)	C ¹²	C ¹³	C ¹⁴	C ² (Ar)
B1H	148.5	162.6	114.8	118.5	123.8	119.1	151.5	121.2	129.4	127.0	56.2	-	-	148.2
PdB1H	150.1	163.1	114.3	114.9	125.8	120.0	156.5	124.7	128.5	126.0	55.4	-	-	150.1
B1Me	151.5	161.6	114.6	118.4	130.0	121.0	148.5	123.7	137.0	145.5	56.2	-	21.1	148.5
B1OMe	151.3	160.4	114.4	118.4	123.5	119.3	141.0	122.3	114.6	158.9	56.2	55.6	-	148.5
PdB1OMe	156.4	162.8	113.6	114.4	125.6	120.0	143.3	125.6	114.2	158.0	55.5	55.2	-	151.2
B1C	151.4	163.0	115.1	118.7	123.9	119.0	146.8	122.5	129.6	132.6	56.2	-	-	148.5
PdB1C	156.4	163.0	114.2	114.6	126.1	119.5	148.2	125.5	128.6	131.6	55.2	-	-	151.1
B1N	151.6	165.4	116.0	118.7	124.3	119.1	154.0	121.9	125.2	146.2	56.3	-	-	148.6
PdB1N	154.9	163.1	114.5	115.2	124.2	119.3	156.4	125.7	125.9	126.4	55.0	-	-	150.8

Table 4.9
¹³C NMR Data of B2 Series Ligands and Its Respective Metal Complexes

Compound	Chemical shift, δ (ppm)												
	C ¹	C ⁷ =N	C ³ (Ar)	C ⁴ (Ar)	C ⁵ (Ar)	C ⁶ (Ar)	C ⁸ (Ar)	C ⁹ (Ar)	C ¹⁰ (Ar)	C ¹¹ (Ar)	C ¹³	C ¹⁴	C ² (Ar)
B2H	162.7	161.2	133.2	119.2	132.3	119.1	148.5	121.2	129.4	126.9	-	-	117.3
PdB2H	165.1	162.8	135.2	124.6	134.4	120.2	149.5	126.4	128.7	128.1	-	-	115.2
B2Me	161.7	161.1	132.9	119.3	132.1	119.0	145.9	121.0	130.0	136.9	-	21.1	117.2
PdB2Me	165.2	162.7	135.0	120.7	134.4	120.3	147.1	124.4	128.6	136.1	-	30.9	115.1
B2OMe	161.0	160.4	132.7	119.4	131.9	119.0	141.4	122.3	114.6	158.8	55.5	-	117.2
PdB2OMe	165.1	162.7	135.1	120.6	134.4	115.1	142.8	125.6	113.2	158.1	55.6	-	122.3
B2C	163.1	161.2	132.6	122.2	132.5	119.3	147.1	122.6	129.6	133.6	-	-	117.4
PdB2C	165.1	163.0	134.6	120.8	128.2	119.9	147.8	122.5	126.0	135.7	-	-	115.5
B2N	165.4	161.4	134.5	119.6	133.0	118.7	154.2	121.9	125.2	146.2	-	-	117.6
PdB2N	169.2	163.1	136.5	120.9	134.9	119.6	154.7	123.9	125.9	146.2	-	-	116.1

4.2.6 UV-Visible

The electron transitions of the ligands and metal complexes were carried out through UV-Visible spectroscopy. All of the compounds were dissolved in acetonitrile at a concentration of 10^{-4} M. There are three main electronic excitations that are to be observed; $\pi\text{--}\pi^*$ (C=C), $\pi\text{--}\pi^*$ (C=N) and $n\text{--}\pi^*$ (C=N). The data of B1 and B2 series are tabulated in Table 4.10 and Table 4.11, respectively. Figure 4.9 shows the representative UV-Visible spectra of B1H and its corresponding complexes while Figure 4.10 shows the representative UV-Visible spectra of B2H and its corresponding complexes. The UV-Visible spectra for other compounds can be found in APPENDIX D.

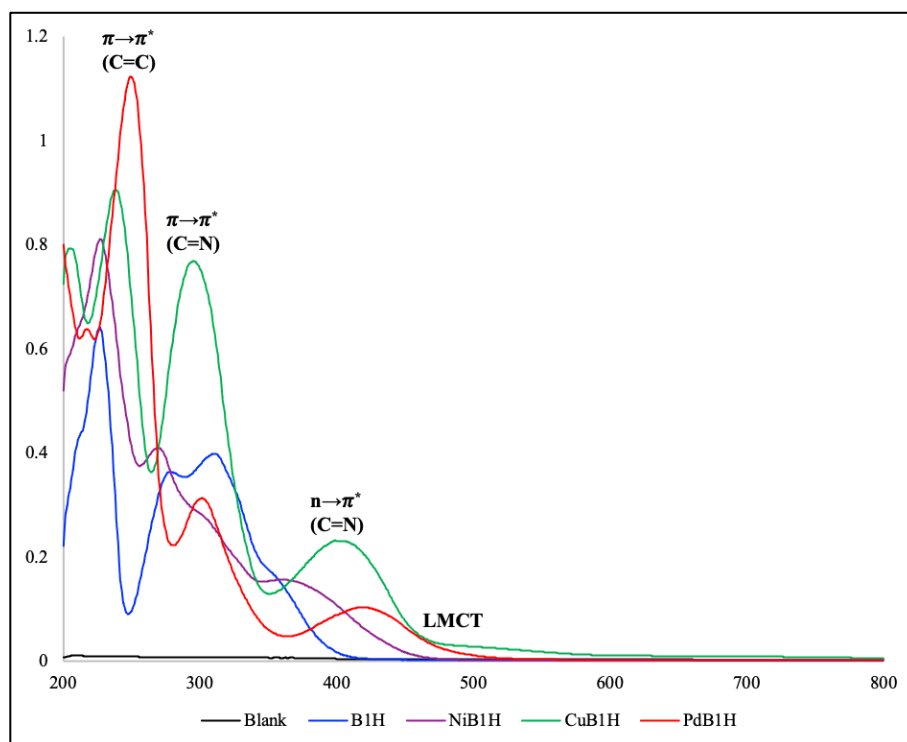


Figure 4.9 UV-Visible Spectra of B1H and Its Metal Complexes

The spectra of all free ligands and complexes exhibited a high intensity band at the region 201-316 nm assignable to $\pi\text{--}\pi^*$ (C=C) of aromatic benzene and $\pi\text{--}\pi^*$ (C=N) of azomethine group. While $n\text{--}\pi^*$ (C=N) was observed as a weak to medium peak at range 300-430 nm similarly reported by Vilches et al., (2020). These peaks were observed to be slightly at higher wavelength probably due to conjugation by aromatic benzene. In conjugated systems, the p electrons are delocalized over a larger molecular

orbital network. This delocalization leads to a reduction in the energy levels of the p electrons, correspond to longer wavelengths. Therefore, an increase in conjugation results in a shifting towards longer wavelengths (redshift) in the absorption spectrum.

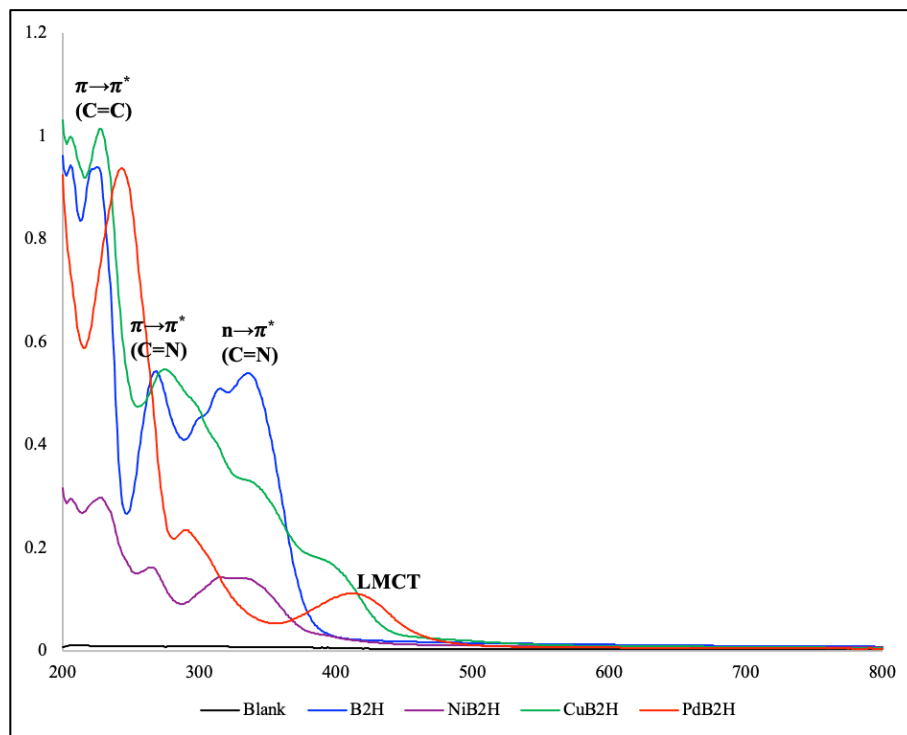


Figure 4.10 UV-Visible Spectra of B2H and Its Metal Complexes

Upon complex formation, both the B1 and B2 series exhibited a bathochromic shift (red shift) for both the $\pi\text{--}\pi^*$ at the range of 208-366 nm and $n\text{--}\pi^*$ at 334-443 nm transition bands. This observation aligns with FTIR spectroscopy results (Section 4.2.3), which showed a decrease in the wavenumber. This finding suggests that the C=N bond experiences a decrease in strength upon forming a complex containing metal centers. The donation of lone pair electrons on the imine N induces an effect that reduces the electron density on the C=N bond. Subsequently weaken the C=N bond. The interaction between donor atoms and metal ions enhances the conjugation and delocalization of the entire electronic system, leading to alterations in the energy levels of the $\pi\text{--}\pi^*$ and $n\text{--}\pi^*$ transitions of the conjugated chromophore.

All complexes were expected to exhibit a weak broad band in the region 407-527 nm due to ligand to metal charge transfer (LMCT) that arise due to the charge transfer from the p-orbitals of the ligand to the d-orbitals of metals (Aranha et al., 2007; Ahmad et al., 2018). Coordination of oxygen atoms to the metal can affect the electron

density around the metal center, potentially influencing the position and intensity of LMCT transitions. Laporte's Rule states that if a system is centrosymmetric, transitions between states with same inversion symmetry are forbidden, but transitions between states of different inversion symmetry are allowed (Bahron, 2019). As a results, the d-d transition peak of complexes was not detected as the peak is very weak due to forbidden by the Laporte's selection rule for centrosymmetric compounds (Karmakar et al., 2022).

Molar absorptivity (ϵ), also known as the molar extinction coefficient, is a fundamental parameter in UV-Visible spectroscopy that indicates how strongly a compound absorbs light at a particular wavelength and is expressed in Beer-Lambert's law (Haleem et al., 2019). A higher molar absorptivity value implies that even at low concentrations, the compound exhibits strong absorbance, making it easier to detect and quantify (Lotfy & Saleh, 2019). Conversely, a low ϵ value suggests weak absorption, requiring higher concentrations for accurate detection. Thus, molar absorptivity is essential for assessing the sensitivity of spectrophotometric measurements, comparing electronic transitions among compounds, and providing insights into the electronic structure of molecules.

Table 4.10
UV-Visible Data of B1 Series Ligands and Its Respective Metal Complexes

Compound	Band Assignment, λ_{max} , nm, (Molar Absorptivity, ϵ , Lmol ⁻¹ cm ⁻¹)			
	$\pi-\pi^*$ (benzene)	$\pi-\pi^*$ (C=N)	n- π^*	LMCT
B1H	210 (4,265), 225 (6,333)	279 (3,624)	315 (3,930)	-
NiB1H	234 (8,027) 269 (3,973)	308 (2,642)	370 (1,529)	498 (64)
CuB1H	241 (8,947)	300 (7,545)	400 (2,312)	527 (28)
PdB1H	252 (16,573)	306 (4,537)	432 (1,492)	512 (118)
B1Me	213 (7,324), 229 (9,169)	268 (4,468)	320 (6,091)	-
NiB1Me	231 (7,984)	284 (3,756), 318 (4,413)	361 (2,187)	489 (108)
CuB1Me	214 (8,134), 233 (8,252)	295 (5,772)	395 (1,398)	500 (245)
PdB1Me	221 (3,518), 252 (6,024)	303 (1,908)	418 (572)	488 (104)
B1OMe	228 (6,487)	270 (3,396)	328 (4,656)	-
NiB1OMe	231 (6,387)	275 (3,396)	335 (4,603)	524 (157)
CuB1OMe	242 (9,046)	310 (6,118)	394 (2,799)	520 (251)
PdB1OMe	252 (5,555)	302 (2,068)	430 (677)	526 (138)
B1C	228 (6,378)	268 (3,425)	319 (4,622)	-
NiB1C	234 (8,345)	281 (4,796), 310 (4,897)	370 (1,894)	477 (108)
CuB1C	234 (5,796)	289 (4,182)	371 (103)	519 (136)
PdB1C	251 (9,541)	304 (3,025)	425 (918)	511 (143)
B1N	203 (7,110)	223 (8,457)	333 (7,618)	-
NiB1N	218 (4,110)	250 (4,110)	339 (2,899)	506 (102)
CuB1N	245 (5,656)	313 (5,697)	437 (1,284)	540 (106)
PdB1N	252 (5,270)	311 (2,451)	443 (727)	526 (212)

Table 4.11
UV-Visible Data of B2 Series Ligands and Its Respective Metal Complexes

Compound	Band Assignment, λ_{max} , nm, (Molar Absorptivity, ϵ , Lmol ⁻¹ cm ⁻¹)			
	$\pi-\pi^*$ (benzene)	$\pi-\pi^*$ (C=N)	n- π^*	LMCT
B2H	205 (9,206), 227 (9,255)	270 (5,337)	319 (5,021)	-
NiB2H	208 (2,899), 234 (2,932)	273 (1,581)	334 (1,401)	490 (103)
CuB2H	210 (9,669), 231 (9,905)	303 (4,496)	405 (1,493)	578 (173)
PdB2H	245 (9,275)	292 (2,284)	419 (1,086)	501 (107)
B2Me	210 (1,144), 230 (1,313)	271 (492)	316 (956), 342 (1,075)	-
NiB2Me	216 (417), 233 (540)	274 (173)	348 (510)	507 (108)
CuB2Me	232 (6,717)	294 (4,067)	394 (1,957)	527 (114)
PdB2Me	247 (9,404)	295 (2,677)	416 (1,264)	508 (101)
B2OMe	212 (3,653), 231 (3,675)	272 (1,659)	349 (3,622)	-
NiB2OMe	234 (5,861)	276 (2,739)	355 (4,621)	510 (208)
CuB2OMe	236 (4,025)	280 (2,420)	410 (590)	499 (77)
PdB2OMe	246 (8,262)	288 (3,749)	418 (1,109)	507 (111)
B2C	209 (6,153), 229 (6,609)	262 (4,300)	321 (4,340)	-
NiB2C	233 (2,410)	275 (1,348)	342 (1,491)	511 (108)
CuB2C	234 (7,420)	283 (5,513)	385 (1,953)	502 (106)
PdB2C	251 (9,059)	294 (2,794)	418 (1,211)	505 (105)
B2N	215 (8,194)	316 (5,033)	353 (4,933)	-
NiB2N	251 (6,731)	366 (3,481)	430 (1,531)	507 (103)
CuB2N	271 (5,751)	353 (3,017)	400 (2,562)	507 (103)
PdB2N	257 (7,554)	305 (3,804)	425 (1,312)	508 (155)

4.2.7 Single Crystal X-ray Diffraction

The single crystal X-ray diffraction was carried out to confirm the chemical structure of the compound obtained from spectroscopic studies. All crystallographic data collections parameters for compounds B1H, B1Me, B2H, B2Me, CuB1Me, CuB2H, CuB2C, PdB1OMe, PdB2Me, PdB2OMe, and PdB2C are presented in two separate tables: Table 4.12 for B1 Series Schiff base compounds and Table 4.13 for B2 Series Schiff base compounds. Among them, B1H, B1Me, B2H, CuB2H, and CuB2C are previously published compounds, whereas the remaining six compounds; B2Me, CuB1Me, PdB1OMe, PdB2Me, PdB2OMe, and PdB2C are newly synthesized compounds. The CIF file data the crystal compounds can be found in APPENDIX E.

Table 4.12

Crystallographic Data Collections Parameters for B1 Series Compounds

Crystal data	B1H	B1Me	CuB1Me	PdB1OMe
CCDC Deposition Number	2233459	2233467	2283136	2286173
Empirical Formula	C ₁₄ H ₁₃ NO ₂	C ₁₅ H ₁₅ NO ₂	C ₃₀ H ₂₈ N ₂ O ₄ Cu	C ₃₀ H ₂₆ N ₂ O ₆ Pd
Formula weight	227.25	241.28	544.08	616.93
Temperature (K)	298.50	299.50	298.90	299.20
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal System	orthorhombic	orthorhombic	monoclinic	triclinic
Space Group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	C ₂ /c	P-1
Unit Cell Dimensions (Å)				
a	6.0879 (2)	5.9101 (14)	14.1948 (10)	7.123 (3)
b	9.1847 (2)	9.235 (2)	14.2903 (12)	8.326 (4)
c	21.0661 (5)	23.303 (6)	13.8653 (10)	11.625 (5)
α (°)	90.0	90.0	90.0	98.14 (3)
β (°)	90.0	90.0	107.74 (2)	103.81 (3)
Volume (Å ³)	1177.92 (5)	1271.9 (5)	2678.8 (4)	658.4 (5)
Z	4	4	4	1
Density (calculated) (Mg/m ³)	1.281	1.260	1.349	1.556
Absorption coefficient (mm ⁻¹)	0.086	0.084	0.853	0.753
Crystal Size (mm ³)	0.50×0.32×0.15	0.39×0.27×0.13	0.31×0.17×0.11	0.06×0.12×0.26
F (0 0 0)	480	512	1132	314
Theta range for data collection	3.483 to 28.301°	3.427 to 28.291°	3.085 to 28.308°	3.323 to 32.509°
Index ranges	-7 ≤ h ≤ 8, -12 ≤ k ≤ 12, -27 ≤ l ≤ 28	-7 ≤ h ≤ 7, -10 ≤ k ≤ 12, -29 ≤ l ≤ 30	-18 ≤ h ≤ 18, -18 ≤ k ≤ 19, -18 ≤ l ≤ 17	-9 ≤ h ≤ 10, -11 ≤ k ≤ 11, -15 ≤ l ≤ 15
Reflections Collected	35437	22568	31118	17448
Independent Reflections (R _{int})	2933 [R(int)= 0.0603]	3145 [R(int)= 0.0532]	3340 [R(int)= 0.0645]	3582 [R(int)= 0.0934]
Completeness to theta = 25.24°	99.7%	99.8%	99.8%	98.9%

Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	2933 / 0 / 159	3145 / 0 / 166	3340 / 12 / 174	3582 / 0 / 180
Goodness-of-fit on F ²	1.059	1.014	1.088	1.061
Final R Indices	R1 = 0.0359, wR2 = 0.0873	R1 = 0.0392, wR2 = 0.1017	R1 = 0.0403, wR2 = 0.0899	R1 = 0.0511, wR2 = 0.1045
R Indices (All Data)	R1 = 0.0485, wR2 = 0.0943	R1 = 0.0542, wR2 = 0.1110	R1 = 0.0650, wR2 = 0.1043	R1 = 0.0901, wR2 = 0.1198
Extinction coefficient	n/a	n/a	n/a	n/a
Largest diff. peak and hole	0.129 and -0.136 e.Å ⁻³	0.142 and -0.139 e.Å ⁻³	0.379 and -0.231 e.Å ⁻³	1.118 and -1.059 e.Å ⁻³

Table 4.13

Crystallographic Data Collections Parameters for B2 Series Compounds

Crystal data	B2H	B2Me	CuB2H	CuB2C	PdB2Me	PdB2OMe	PdB2C
CCDC Deposition Number	2233449	2233464	2233455	2233451	2286186	2270997	2289230
Empirical Formula	C ₁₃ H ₁₁ NO	C ₁₄ H ₁₃ NO	C ₂₆ H ₂₀ N ₂ O ₂ Cu	C ₂₆ H ₁₈ C ₁₂ N ₂ O ₂ Cu	C ₂₈ H ₂₄ N ₂ O ₂ Pd	C ₂₈ H ₂₄ N ₂ O ₄ Pd	C ₂₆ H ₁₈ C ₁₂ N ₂ O ₂ Pd
Formula weight	197.23	211.25	455.98	524.86	526.89	558.89	567.72
Temperature (K)	299.00	300.70	299.60	299.00	299.40	300.40	299.60
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal System	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c	P2 ₁ /n	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
Unit Cell Dimensions (Å)							
a	6.107 (9)	19.3199 (7)	11.932 (2)	9.8226 (12)	9.941 (3)	13.396 (3)	9.858 (4)
b	11.622 (19)	4.7654 (2)	7.9722 (15)	11.1394 (16)	10.952 (3)	11.231 (2)	11.122 (5)
c	14.46 (2)	12.2275 (4)	12.204 (2)	10.8118 (15)	10.969 (3)	7.8603 (14)	10.702 (5)
α (°)	90.0	90.0	90.0	90.0	90.0	90.0	90.0
β (°)	90.0	102.14 (1)	112.22 (8)	105.41 (4)	105.34 (8)	97.07 (6)	104.54 (15)
Volume (Å ³)	1026 (3)	1100.57 (7)	1074.7 (3)	1140.5 (3)	1151.8 (5)	1173.6 (4)	1135.8 (9)
Z	4	4	2	2	2	2	2
Density (calculated) (Mg/m ³)	1.276	1.275	1.409	1.528	1.519	1.582	1.660

Absorption coefficient (mm ⁻¹)	0.081	0.080	1.041	1.219	0.834	0.829	1.079
Crystal Size (mm ³)	0.44×0.30×0.07	0.50×0.40×0.13	0.35×0.23×0.21	0.4×0.14×30.08	0.17×0.23×0.27	0.16×0.19×0.23	0.10×0.15×0.25
F (0 0 0)	416	448	470	534	536	568	568
Theta range for data collection	2.817 to 28.855°	3.236 to 28.307°	3.127 to 28.381°	2.823 to 28.442°	3.721 to 28.311°	3.387 to 28.217°	3.664 to 28.229°
Index ranges	-6 ≤ h ≤ 8, -13 ≤ k ≤ 15, -18 ≤ l ≤ 19	-25 ≤ h ≤ 25, -6 ≤ k ≤ 6, -16 ≤ l ≤ 16	-15 ≤ h ≤ 15, -10 ≤ k ≤ 10, -16 ≤ l ≤ 16	-13 ≤ h ≤ 12, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14	-17 ≤ h ≤ 17, -14 ≤ k ≤ 14, -10 ≤ l ≤ 10	-12 ≤ h ≤ 13, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14
Reflections Collected	16153	30092	57286	42112	28336	35828	36184
Independent Reflections (R _{int})	2645 [R(int)= 0.086]	2749 [R(int)= 0.071]	2593 [R(int)= 0.134]	2844 [R(int)= 0.0896]	2867 [R(int)= 0.0405]	2904 [R(int)= 0.0431]	2793 [R(int)= 0.057]
Completeness to theta = 25.24°	99.8%	99.8%	95.3%	99.8%	99.6%	99.8%	99.8%
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	2645 / 0 / 127	2749 / 0 / 149	2593 / 0 / 142	2844 / 0 / 151	2867 / 0 / 152	2904 / 0 / 161	2793 / 0 / 151
Goodness-of-fit on F ²	1.000	1.074	1.045	1.174	1.272	1.122	1.109
Final R Indices	R1 = 0.0616, wR2 = 0.1419	R1 = 0.0560, wR2 = 0.1623	R1 = 0.0314, wR2 = 0.0764	R1 = 0.0578, wR2 = 0.1426	R1 = 0.0444, wR2 = 0.0951	R1 = 0.0251, wR2 = 0.0626	R1 = 0.0249, wR2 = 0.0584
R Indices (All Data)	R1 = 0.1446, wR2 = 0.1788	R1 = 0.0833, wR2 = 0.1925	R1 = 0.0531, wR2 = 0.0829	R1 = 0.1020, wR2 = 0.1808	R1 = 0.0631, wR2 = 0.1109	R1 = 0.0322, wR2 = 0.0682	R1 = 0.0378, wR2 = 0.0659
Extinction coefficient	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Largest diff. peak and hole	0.151 and -0.148 e.Å ⁻³	0.270 and -0.235 e.Å ⁻³	0.240 and -0.172 e.Å ⁻³	0.803 and -0.779 e.Å ⁻³	0.826 and -0.479 e.Å ⁻³	0.376 and -0.623 e.Å ⁻³	0.386 and -0.489 e.Å ⁻³

4.2.7.1 Crystal Structure of B1H

Orange crystals of the established compound B1H were obtained through slow evaporation from ethanol at room temperature. It crystallized in an orthorhombic crystal system with the space group of $P2_12_12_1$, cell parameter $a = 6.0879$ (2) Å, $b = 9.1847$ (2) Å, $c = 21.0661$ (5) Å, $\alpha = \beta = \gamma = 90^\circ$, $Z = 4$, and $V = 1177.92$ (5) Å³. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 , resulting in a good $R(\text{int}) = 6.03\%$ with 99.7% completeness. A CCDC search confirmed that this compound is not novel, as it has been previously reported by Yu (2011) (refcode: UNUWEG). Their structure exhibits the same crystal system and space group as the present crystal structure, and the bond length and bond angle values are also in close agreement, further supporting the consistency between both structures (Table 4.14). The ORTEP diagram of B1H is shown in Figure 4.11.

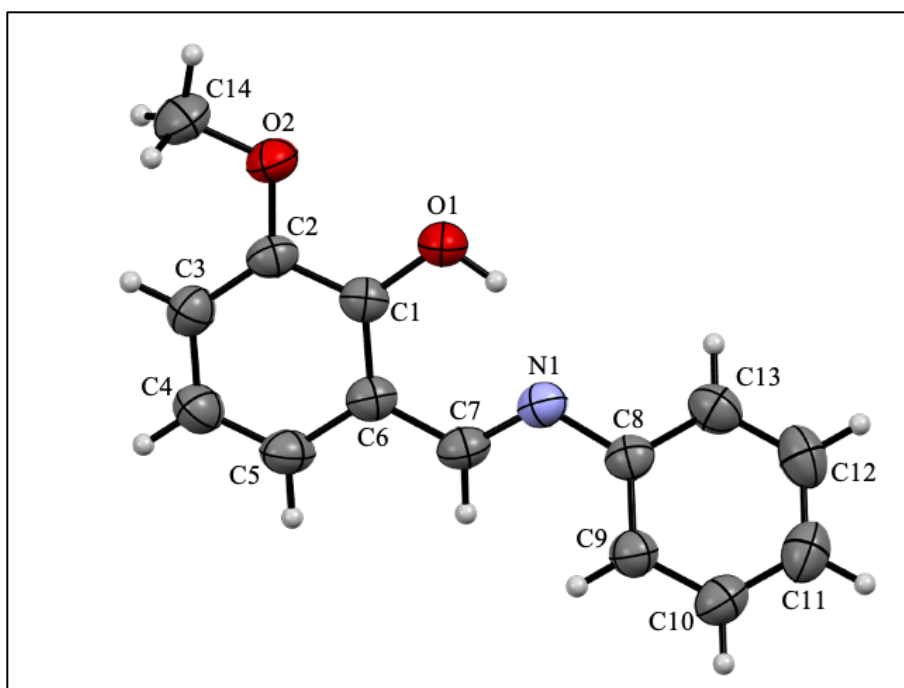


Figure 4.11 The ORTEP Diagram of B1H, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level

Table 4.14

Selected Bond Lengths (Å) and Bond Angles (°) of B1H

	Experimental	DFT (B3LYP/ 6-311++G(d,p))	(Yu, 2011)
Bond Lengths (Å)			
O1-C1	1.352 (2)	1.337	1.350 (4)
O2-C2	1.368 (2)	1.359	1.374 (4)
O2-C14	1.419 (3)	1.420	1.419 (4)

N1-C7	1.279 (2)	1.288	1.285 (4)
N1-C8	1.396 (3)	1.409	1.428 (4)
Bond Angles (°)			
C2-O2-C14	117.12 (16)	118.37	116.6 (3)
C7-N1-C8	120.64 (15)	121.16	120.1 (3)

Table 4.15

Intermolecular and Intramolecular Hydrogen Bonds of B1H (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.90 (3)	1.83 (3)	2.619 (2)	146 (2)
C10—H10···O2(a)	0.93	2.57	3.488 (2)	167

Symmetry code= (a): $-x, 1/2+y, 3/2-z$

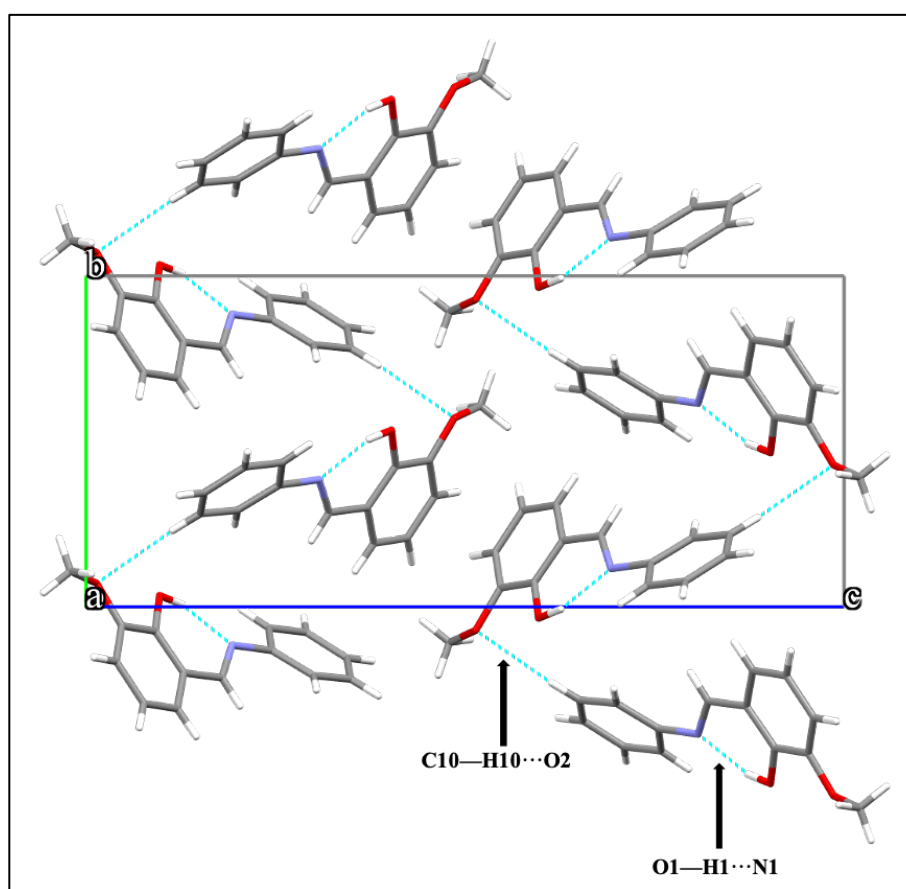


Figure 4.12 Crystal Packing of B1H View Down Crystallographic *b*-Axis

The two benzene rings of C1-C6 and C8-C13, are planar with maximum deviation of 0.015 (1) Å and 0.010 (2) Å for atom C6 and C10, respectively from their mean square planes. The plane makes dihedral angle of 30.58°. The C-O bond length range from 1.352 (2) Å to 1.419 (3) Å, while the C-N and C=N distances are 1.396 (3) Å and 1.279 (2) Å, respectively (Table 4.14). These values are consistent with previously reported data. A comparison of selected geometrical parameters with DFT

calculations at the B3LYP/6-311++G(d,p) level is presented in Table 4.14, showing excellent agreement between the optimized and experimental structures.

In the crystal packing, each of the molecule is stabilized by intermolecular C10—H10 $\cdots$ O2 hydrogen bond and intramolecular O1—H1 $\cdots$ N1 hydrogen bond (Table 4.15) as illustrated in Figure 4.12.

4.2.7.2 Crystal Structure of B1Me

The known compound, B1Me was obtained as orange crystals by slow evaporation of ethanol at room temperature. It crystallized in an orthorhombic crystal system with the space group of P2₁2₁2₁, cell parameter $a = 5.9101(14) \text{ \AA}$, $b = 9.235(2) \text{ \AA}$ and $c = 23.303(6) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $Z = 4$, and $V = 1271.9(5) \text{ \AA}^3$. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 , giving a good $R(\text{int}) = 5.32\%$ with 99.7% completeness. A search of the CCDC database confirmed that this structure has been previously reported by Yeap et al., (2003) (refcode: EKUGIA). The crystal system, space group, bond lengths, and bond angles match closely with the earlier report, indicating structural consistency.

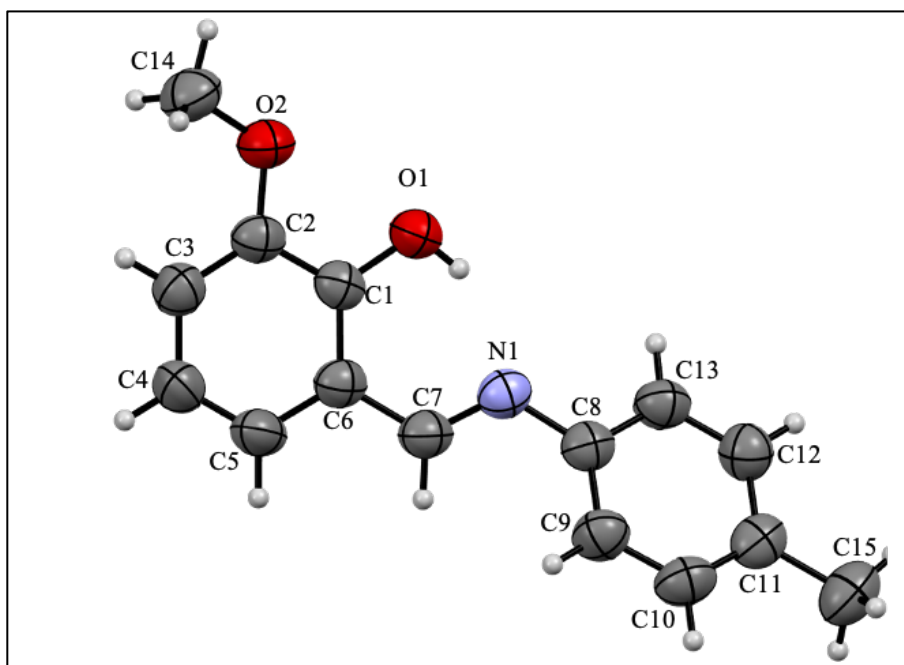


Figure 4.13 The ORTEP Diagram of B1Me, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level

Table 4.16
Selected Bond Lengths (Å) and Bond Angles (°) of B1Me

	Experimental	DFT (B3LYP/ 6-311++G(d,p))	(Yeap et al., 2003)
Bond Lengths (Å)			
O1-C1	1.348 (2)	1.338	1.335 (4)
O2-C2	1.362 (2)	1.360	1.364 (4)
O2-C14	1.420 (3)	1.419	1.438 (6)
N1-C7	1.275 (3)	1.288	1.272 (5)
N1-C8	1.414 (2)	1.408	1.419 (4)
Bond Angles (°)			
C2-O2-C14	117.03 (18)	118.36	116.4 (4)
C7-N1-C8	121.31 (16)	121.30	120.3 (3)

Table 4.17
Intermolecular and Intramolecular Hydrogen Bonds of B1Me (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.82	1.90	2.621 (2)	146
C10—H10···O1 ^(b)	0.93	2.47	3.365 (3)	162

Symmetry code= (b): 1-x,-1/2+y,1/2-z

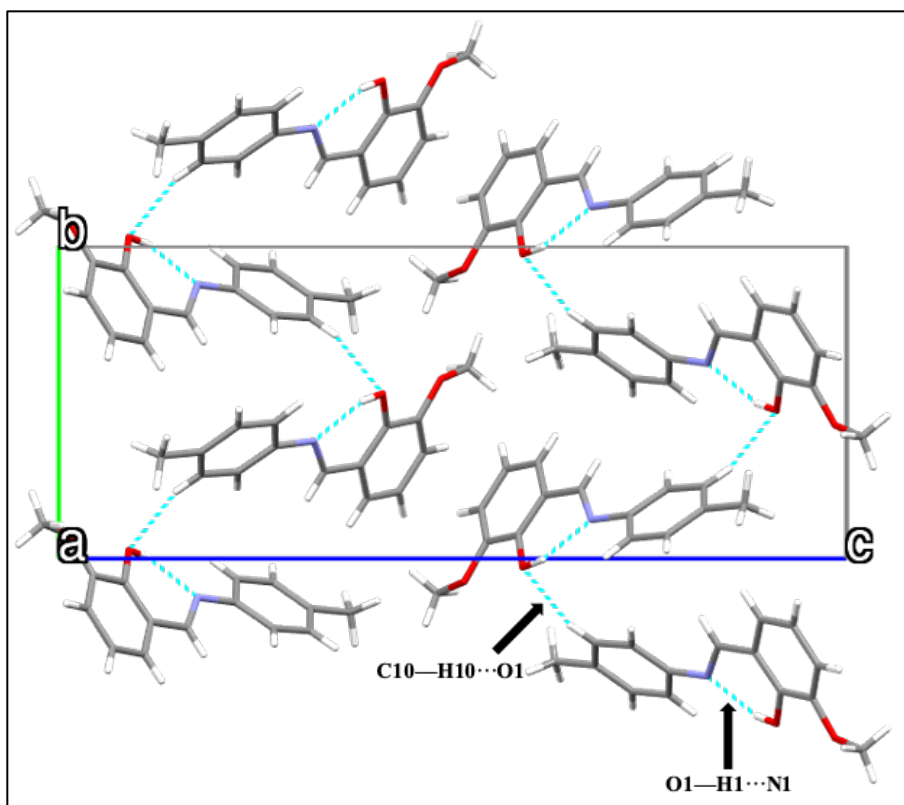


Figure 4.14 Crystal Packing of B1Me View Down Crystallographic *b*-Axis

The ORTEP diagram of B1Me in Figure 4.13 illustrates the two benzene rings C1-C6 and C8-C13, which exhibit slight deviations from planarity 0.015 (2) Å for atom C4 and 0.016 (2) Å for atom C8 and form a dihedral angle of 26.84°. The C-O, C-N,

and C=N bonds measure 1.348 (2) Å to 1.420 (3) Å, 1.414 (2) Å, and 1.275 (3) Å, respectively, consistent with both experimental and DFT-optimized geometries. The packing diagram for B1Me view down *b*-axis is shown in Figure 4.14. In the crystal packing, each of the molecule is stabilized by intermolecular C10—H10 $\cdots$ O1 hydrogen bond and intramolecular O1—H1 $\cdots$ N1 hydrogen bond (Table 4.17), as shown in Figure 4.14.

4.2.7.3 Crystal Structure of B2H

Slow evaporation of ethanol at room temperature yielded orange crystals of the established compound B2H. The ORTEP diagram of B2H is shown in Figure 4.15. It crystallized in an orthorhombic crystal system with the space group of $P2_12_12_1$, cell parameter $a = 6.107$ (9) Å, $b = 11.622$ (19) Å and $c = 14.46$ (2) Å, $\alpha = \beta = \gamma = 90^\circ$, $Z = 4$, and $V = 1026$ (3) Å³. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 , resulting in a good $R(\text{int}) = 6.03\%$ with 99.7% completeness. A CCDC search shows that this compound has already been reported by Ahmed et al. (2021) with a refcode: SALCAN08, confirming its lack of novelty. Both the crystal system and space group correspond to those of the published structure. Bond lengths and bond angles could not be evaluated comparatively because the data were published as a private communication.

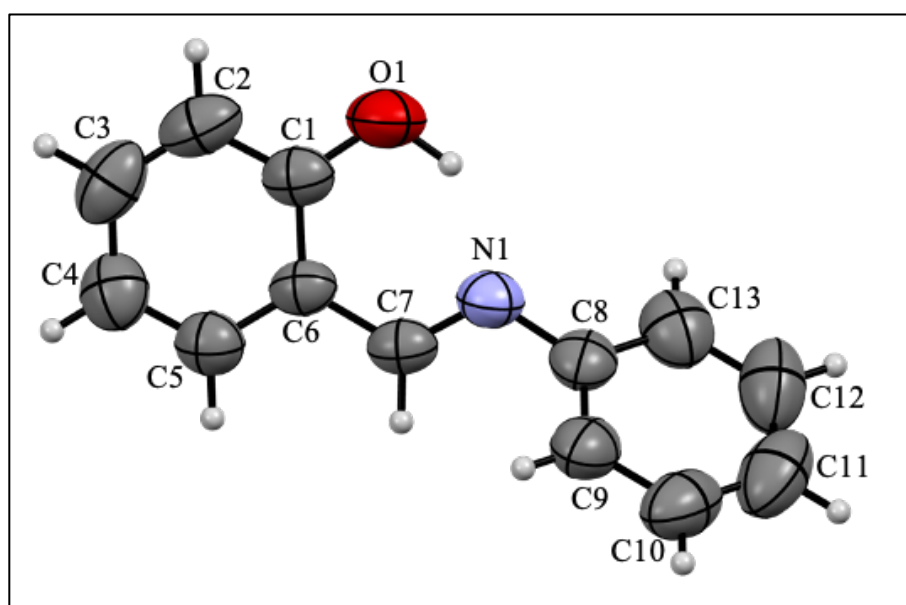


Figure 4.15 The ORTEP Diagram of B2H with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level

Table 4.18
Selected Bond Lengths (Å) and Bond Angles (°) of B2H

	Experimental	DFT (B3LYP/6-311++G(d,p))
Bond Lengths (Å)		
O1-C1	1.329 (6)	1.341
N1-C7	1.245 (6)	1.288
N1-C8	1.388 (5)	1.409
Bond Angles (°)		
C7-N1-C8	119.54 (3)	121.16

Table 4.19
Intramolecular Hydrogen Bond of B2H (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.97 (6)	1.75 (7)	2.580 (6)	141 (5)

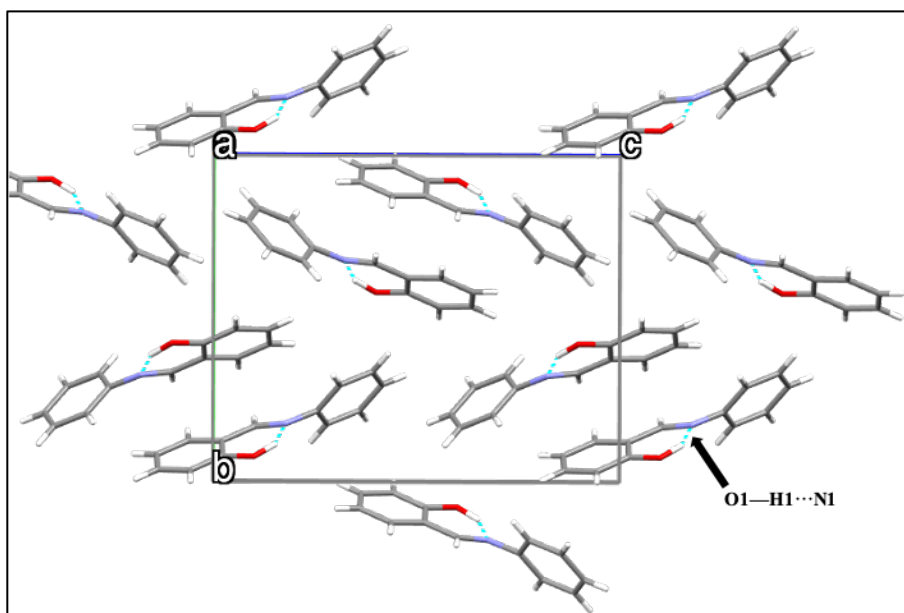


Figure 4.16 Crystal Packing of B2H View Down Crystallographic *a*-Axis

Rings C1-C6 and C8-C13 are planar, showing maximum deviation of 0.004 (4) at atom C3 and 0.001 (3) at atom C7. The plane makes dihedral angle of 51.26°. The C-O bond length is 1.329 (6) Å. The C=N and C-N bond lengths are 1.245 (6) Å and 1.388 (5) Å, respectively as shown in Table 4.18. The comparison of selected geometrical parameters of the experimental values and computational calculations by DFT at B3LYP/6-311++G(d,p) basis set level is given in Table 4.18. All bond lengths and angles of the optimized structure were compared to the experimental values and both results fall within the expected ranges. The packing diagram for B2H view down *a*-axis is shown in Figure 4.16. Molecular stabilization in the crystal packing arises from

an intramolecular O1—H1···N1 hydrogen bond (Table 4.19), as illustrated in Figure 4.16.

4.2.7.4 Crystal Structure of B2Me

Orange crystals of B2Me were obtained through slow evaporation from ethanol at room temperature. The ORTEP diagram of B2Me is shown in Figure 4.17. It crystallized in a monoclinic crystal system with the space group of $P2_12_12_1$, cell parameter $a = 19.3199$ (7) Å, $b = 4.7654$ (2) Å and $c = 12.2275$ (4) Å, $\alpha = \gamma = 90^\circ$, $\beta = 102.14^\circ$ (1), $Z=4$, and $V=1026$ (3) Å³. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1 = 0.0560$ and $wR2 = 0.1623$.

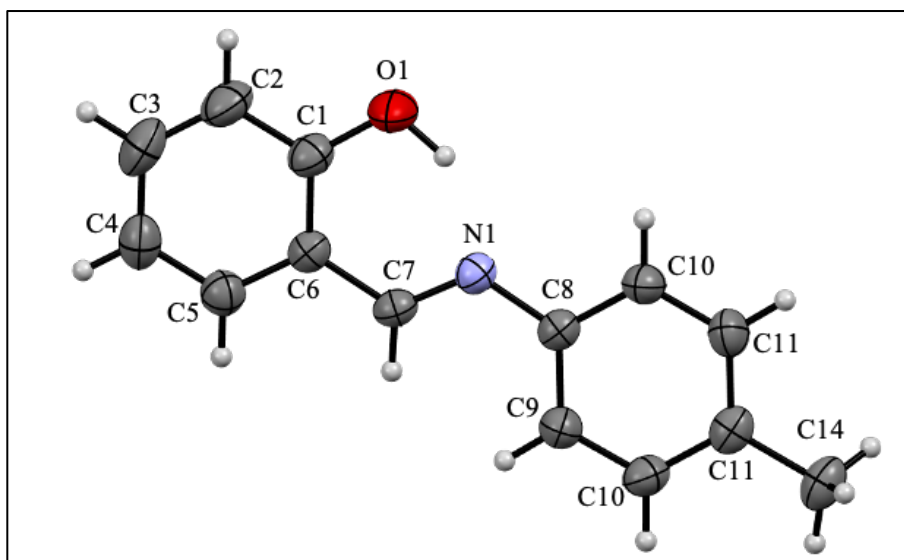


Figure 4.17 The ORTEP Diagram of B2Me, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level

Table 4.20

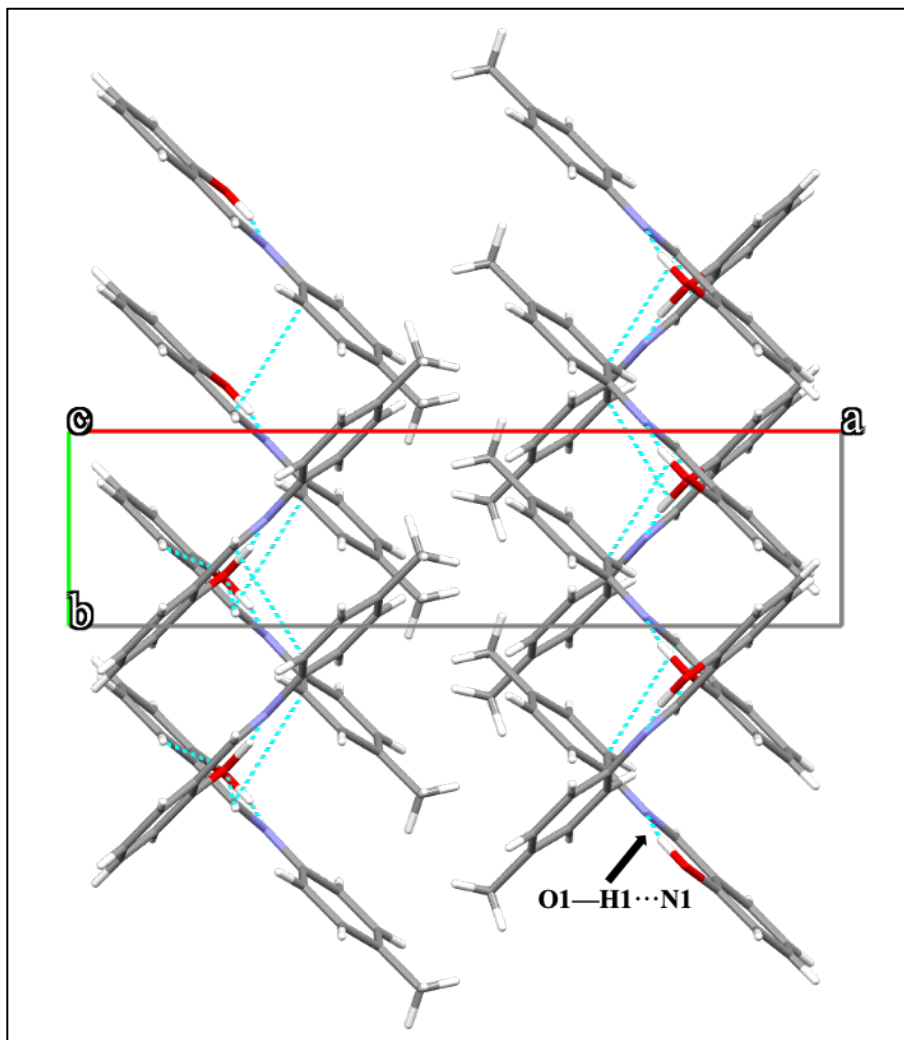
Selected Bond Lengths (Å) and Bond Angles (°) of B2Me

	Experimental	DFT (B3LYP/ 6-311++G(d,p))
Bond Lengths (Å)		
O1-C1	1.351 (2)	1.341
N1-C7	1.278 (2)	1.288
N1-C8	1.418 (2)	1.409
Bond Angles (°)		
C7-N1-C8	121.44 (13)	121.34

Table 4.21

Intramolecular Hydrogen Bond of B2Me ($\text{\AA}$, $^\circ$)

$\text{D}-\text{H}\cdots\text{A}$	$\text{D}-\text{H}$	$\text{H}\cdots\text{A}$	$\text{D}\cdots\text{A}$	$\text{D}-\text{H}\cdots\text{A}$
$\text{O1}-\text{H1}\cdots\text{N1}$	0.97 (3)	1.73 (2)	2.594 (19)	146 (2)

Figure 4.18 Crystal Packing of B2Me View Along Crystallographic *c*-Axis

Both benzene rings C1-C6 and C8-C13 are planar with maximum deviation from their mean square planes of 0.003 (2) for atom C3 and 0.008 (2) for atom C9. The plane makes dihedral angle of 6.46° . The C-O bond length is 1.351 (2) $\text{\AA}$. The C=N and C-N bond lengths are 1.278 (2) $\text{\AA}$ and 1.418 (2) $\text{\AA}$, respectively (Table 4.20). The bond length and angles are in normal ranges and the values are similar to previous study (Yeap et al., 2003). The comparison of selected geometrical parameters of the experimental values and computational calculations by DFT at B3LYP/6-311++G(d,p) basis set level is given in Table 4.20. All bond lengths and angles of the optimized structure were compared to the experimental values and both results fall within the

expected ranges. The packing diagram for B2Me view along *c*-axis is shown in Figure 4.18. Stabilization of each molecule in the crystal packing is achieved through an intramolecular O1—H1···N1 hydrogen bond (Table 4.21), as shown in Figure 4.18.

4.2.7.5 Crystal Structure of CuB1Me

Orange crystals of the novel copper complex, CuB1Me were obtained by slow evaporation of an ethanolic solution at room temperature. The ORTEP diagram of CuB1Me is shown in Figure 4.19. Atom C14 was found to be disordered over two positions with equal occupancy (0.5 each), as depicted in the ORTEP representation. It crystallized in a monoclinic crystal system with the space group of *C2/c*, cell parameter $a = 14.1948$ (10) Å, $b = 14.2903$ (12) Å and $c = 13.8653$ (10) Å, $\alpha = \gamma = 90^\circ$, $\beta = 107.74^\circ$ (2), $Z = 4$, and $V = 2678.8(4)$ Å³. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 , yielding a good $R(\text{int}) = 6.45\%$ with 99.8% completeness. The calculated value of τ_4 for CuB1Me is 0, indicating a square planar geometry, consistent with the paramagnetic property revealed by the magnetic susceptibility measurement.

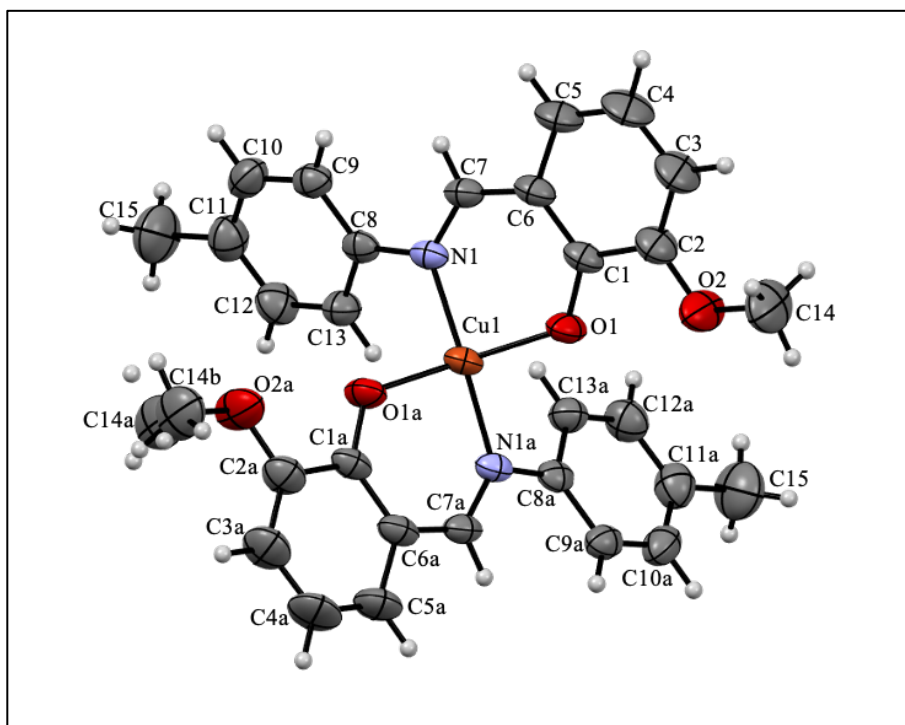


Figure 4.19 The ORTEP Diagram of CuB1Me, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level

Table 4.22

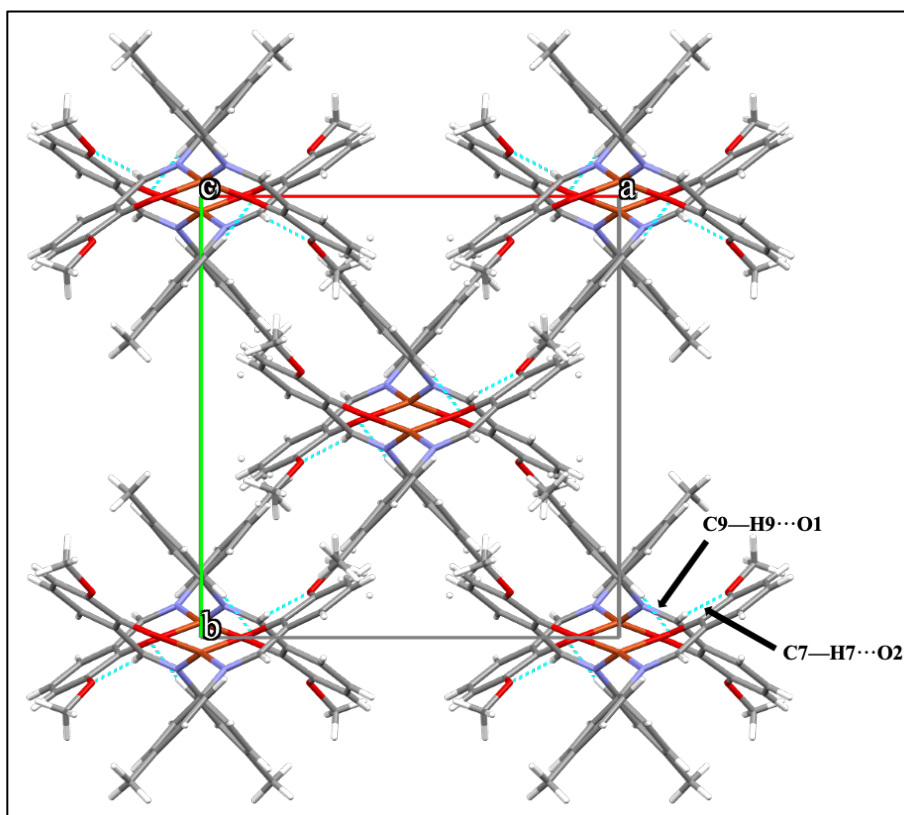
Selected Bond Lengths (Å) and Bond Angles (°) of CuB1Me

	Experimental	DFT (B3LYP/LANL2DZ)
Bond Lengths (Å)		
Cu1-O1	1.901 (16)	2.007
O1-C1	1.304 (3)	1.307
Cu1-N1	1.963 (18)	2.010
N1-C7	1.294 (3)	1.327
N1-C8	1.428 (3)	1.429
O2-C2	1.363 (3)	1.397
O2-C14	1.426 (2)	1.451
Bond Angles (°)		
Cu1-O1-C1	124.05 (14)	126.40
N1-Cu1-O1	94.20 (7)	94.59
Cu1-N1-C7	121.04 (15)	121.58
Cu1-N1-C8	118.73 (14)	118.95
C11-O2-C14	117.30 (9)	118.03

Table 4.23

Intermolecular Hydrogen Bonds of CuB1Me (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···O2	0.93	2.52	3.412 (3)	161
C9—H9···O1	0.93	2.41	3.288 (3)	157

Figure 4.20 Crystal Packing of CuB1Me View Down Crystallographic *c*-Axis

The planar benzene rings C1-C6 and C8-C13 exhibit maximum deviation of -0.011 (2) and 0.005 (2) for atom C1 and C13, respectively and form a dihedral angle of 16.68°. The C-O bond length range from 1.304 (3) Å to 1.426 (2) Å. The C=N and C-N bond lengths are 1.294 (3) Å and 1.428 (3) Å, respectively (Table 4.22). The comparison of selected geometrical parameters of the experimental values and computational calculations by DFT at B3LYP/LANL2DZ basis set level is given in Table 4.22. All bond lengths and angles of the optimized structure were compared to the experimental values and both results fall within the expected ranges. The packing diagram for CuB1Me view down *c*-axis is shown in Figure 4.20. Each molecule in the crystal packing is stabilized by an intermolecular C7—H7···O2 hydrogen bond and an C9—H9···O1 hydrogen bonds as illustrated in Figure 4.20 and summarized in Table 4.23.

4.2.7.6 Crystal Structure of CuB2H

Orange crystals of the known compound CuB2H were grown by slow evaporation from ethanol at room temperature. The ORTEP diagram of CuB2H is shown in Figure 4.21. It crystallized in a monoclinic crystal system with the space group of P21/n, cell parameter *a* = 11.932 (2) Å, *b* = 7.9722 (15) Å and *c* = 12.204 (2) Å, $\alpha = \gamma = 90^\circ$, $\beta = 112.22^\circ$ (8), *Z* = 2, and *V* = 1074.7 (3) Å³. The crystal structure was solved by direct methods and refined by full-matrix least-squares on *F*², leading to a satisfactory *R*(int) = 13.40% with 95.3% completeness. According to CCDC, this compound is not novel and has been previously reported ((Wei et al., 1964); refcode: PSALCU). Both the crystal system and space group correspond to those of the published structure. Bond lengths and bond angles values are very similar, supporting overall agreement as shown in Table 4.24. The τ_4 value of 0 for CuB2H confirms a square planar geometry, in agreement with its paramagnetic properties measured by magnetic susceptibility in Section 4.2.2.

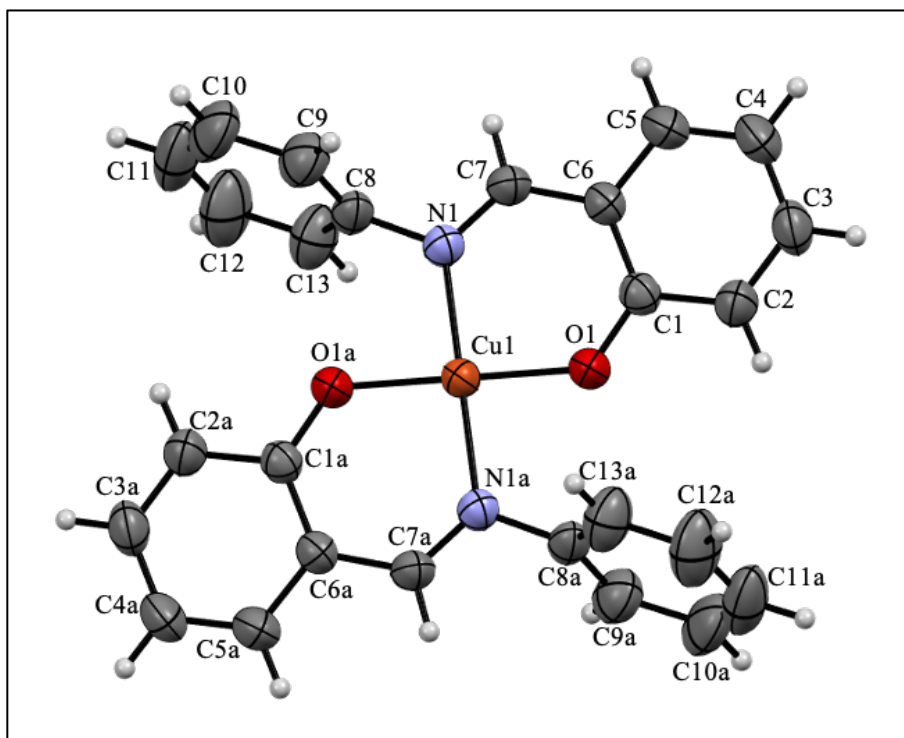


Figure 4.21 The ORTEP Diagram of CuB2H, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level

Table 4.24

Selected Bond Lengths (Å) and Bond Angles (°) of CuB2H

	Experimental	DFT (B3LYP/ LANL2DZ)	(Wei et al., 1964)
Bond Lengths (Å)			
Cu1-O1	1.881 (14)	1.920	1.878
O1-C1	1.303 (2)	1.330	1.313
Cu1-N1	2.003 (14)	2.043	1.993
N1-C7	1.289 (2)	1.322	1.302
N1-C8	1.440 (2)	1.448	1.438
Bond Angles (°)			
Cu1-O1-C1	127.92 (12)	131.31	128.0
N1-Cu1-O1	91.57 (6)	90.73	91.4
Cu1-N1-C7	123.27 (12)	123.76	123.4
Cu1-N1-C8	119.56 (11)	119.54	119.6

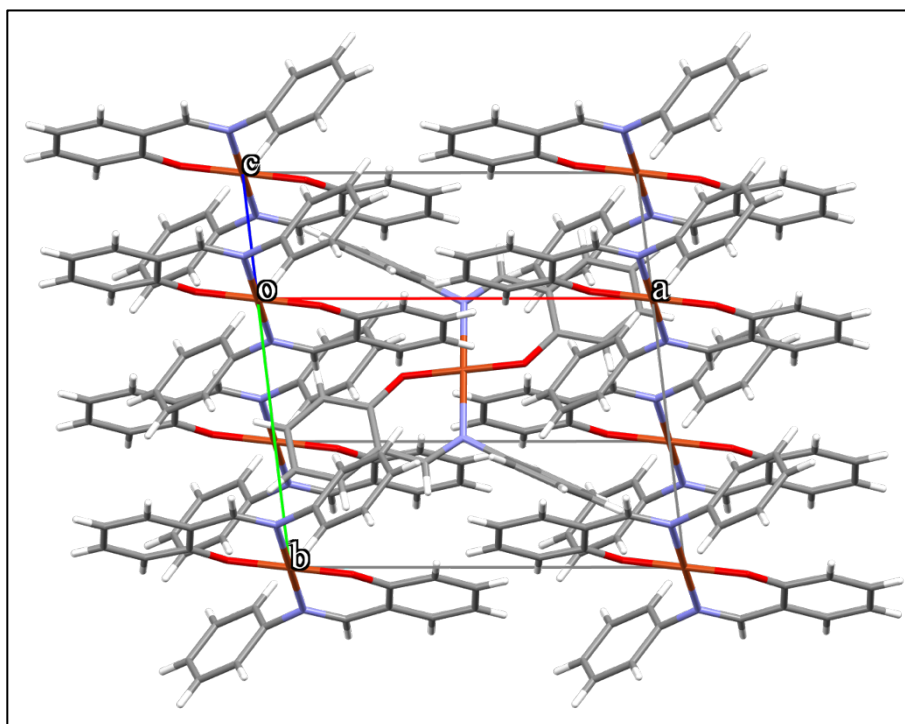


Figure 4.22 Crystal Packing of CuB2H View Down Crystallographic *c*-Axis

The benzene rings C1–C6 and C8–C13, which are planar with maximum deviations of 0.106 (2) Å and 0.007 (2) Å for atom C6 and C8, forming a dihedral angle of 64.76°. The bond length of C–O is 1.303 (2) Å, while the bond lengths of C–N and C=N are 1.440 (2) Å and 1.289 (2) Å, respectively (Table 4.24). Comparison with DFT-calculated geometrical parameters confirms the experimental values fall within expected ranges. The packing diagram for CuB2H view down *c*-axis is shown in Figure 4.22.

4.2.7.7 Crystal Structure of CuB2C

Slow evaporation of ethanol at room temperature afforded orange crystals of CuB2C, a previously published compound. The ORTEP diagram of CuB2C is shown in Figure 4.23. It crystallized in a monoclinic crystal system with the space group of P21/c, cell parameter $a = 9.8226$ (12) Å, $b = 11.1394$ (16) Å and $c = 10.8118$ (15) Å, $\alpha = \gamma = 90^\circ$, $\beta = 105.414^\circ$ (4), $Z = 2$, and $V = 1140.5$ (3) Å³. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 producing a good $R(\text{int}) = 8.96\%$ with 99.8% completeness. A CCDC search indicated that this compound has been previously reported (Xiao & Cao, 2020) with IHARIS01 refcode confirming that it is not novel. The published structure exhibits the same crystal system

and space group as observed here, and the bond lengths and bond angles parameters are in close agreement, supporting structural consistency. For CuB₂C, a calculated τ_4 of 0 indicates a square planar structure, consistent with paramagnetism observed experimentally (Section 4.2.2).

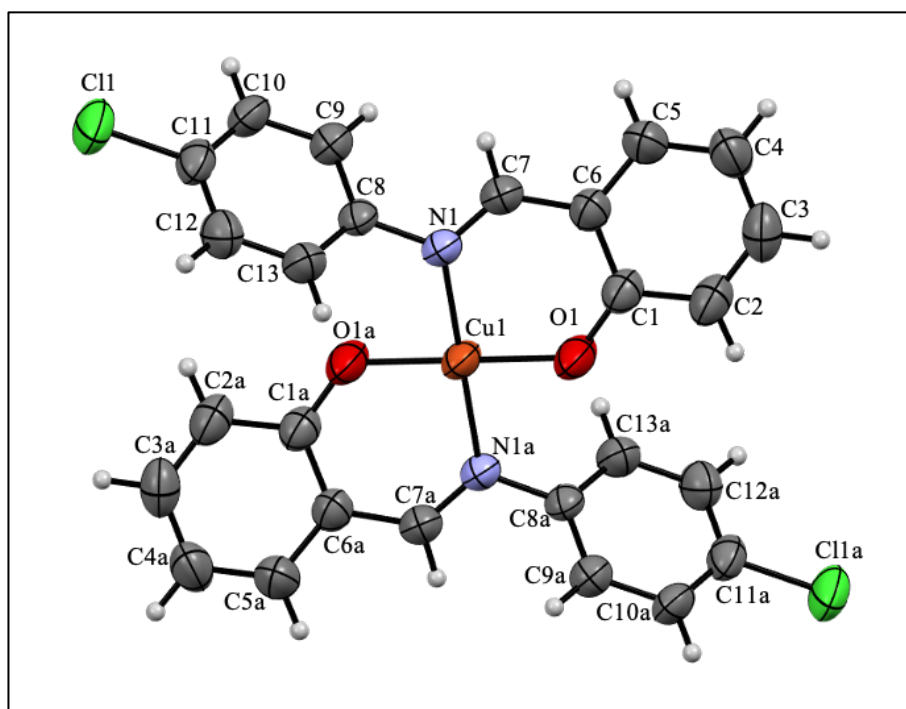


Figure 4.23 The ORTEP Diagram of CuB₂C, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level

Table 4.25

Selected Bond Lengths (Å) and Bond Angles (°) of CuB₂C

	Experimental	DFT (B3LYP/ LANL2DZ)	(Xiao & Cao, 2020)
Bond Lengths (Å)			
Cu1-O1	1.880 (3)	1.920	1.881 (4)
O1-C1	1.304 (5)	1.330	1.322 (8)
Cu1-N1	2.004 (2)	2.043	2.019 (5)
N1-C7	1.288 (4)	1.324	1.299 (7)
N1-C8	1.434 (4)	1.446	1.439 (7)
Bond Angles (°)			
Cu1-O1-C1	127.60 (3)	131.42	126.1 (4)
N1-Cu1-O1	90.72(14)	90.73	89.23 (19)
Cu1-N1-C7	122.79 (2)	123.83	122.4 (4)
Cu1-N1-C8	120.64 (2)	119.43	

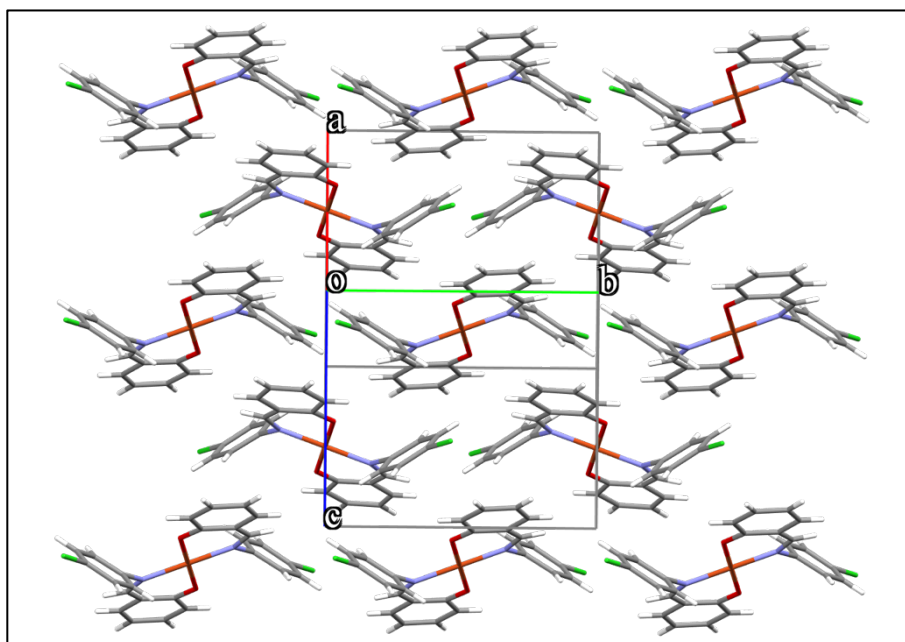


Figure 4.24 Crystal Packing of CuB2C View Down Crystallographic *a*-Axis

The two benzene rings (C1–C6 and C8–C13) show slight deviations from planarity, with maximum deviation of 0.006 (4) Å for C3 and 0.009 (4) Å for C11. The rings form a dihedral angle of 48.83°. The C–O bond lengths is 1.304 (5) Å, and the C–N and C=N distances are 1.434 (4) Å and 1.288 (4) Å, respectively (Table 4.25). Comparison with DFT-optimized geometrical parameters at the B3LYP/LANL2DZ shows excellent agreement with the experimental structure. The packing diagram for CuB2C view down *a*-axis is shown in Figure 4.24.

4.2.7.8 Crystal Structure of PdB1OMe

The novel compound, PdB1OMe was crystallized as orange crystals via slow evaporation from chloroform at room temperature. The ORTEP diagram of PdB1OMe is shown in Figure 4.25. It crystallized in a monoclinic crystal system with the space group of C2/c, cell parameter $a = 7.123$ (3) Å, $b = 8.326$ (4) Å and $c = 11.625$ (5) Å, $\alpha = 98.14$ (3), $\beta = 103.81^\circ$ (3), $\gamma = 90^\circ$, $Z = 1$, and $V = 658.4$ (5) Å³. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 , giving a good $R(\text{int}) = 9.34\%$ with 98.9% completeness. The calculated value of τ_4 for PdB1OMe is 0, indicating a square planar geometry, consistent with the diamagnetic property revealed by the magnetic susceptibility measurement (Section 4.2.2).

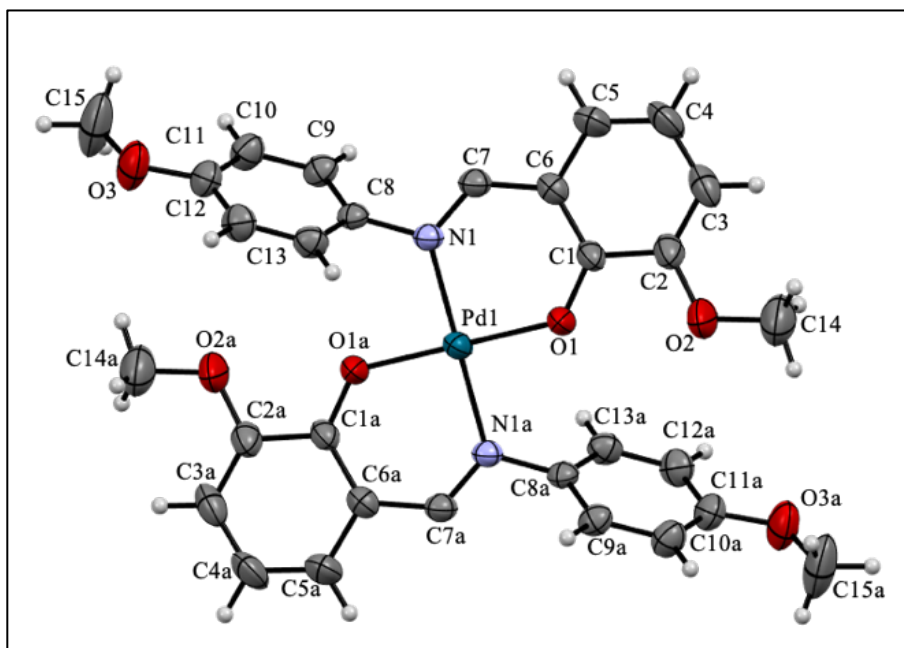


Figure 4.25 The ORTEP Diagram of PdB1OMe, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level

Table 4.26

Selected Bond Lengths (Å) and Bond Angles (°) of PdB1OMe

	Experimental	DFT (B3LYP/LANL2DZ)
Bond Lengths (Å)		
Pd1-O1	1.954 (3)	2.128
O1-C1	1.310 (4)	1.308
Pd1-N1	2.038 (3)	2.243
N1-C7	1.301 (4)	1.249
N1-C8	1.429 (5)	1.438
O2-C2	1.388 (6)	1.395
O2-C14	1.379 (7)	1.455
O3-C11	1.363 (5)	1.394
O3-C15	1.426 (7)	1.457
Bond Angles (°)		
Pd1-O1-C1	125.66 (3)	123.25
N1-Pd1-O1	91.57 (12)	83.61
Pd1-N1-C7	123.64 (3)	111.37
Pd1-N1-C8	120.99 (2)	114.79
C2-O2-C14	117.69 (4)	118.15
C11-O3-C15	117.35 (4)	118.83
O1-Pd1-O1a	180.00	180.00
N1-Pd1-N1a	180.00	180.00

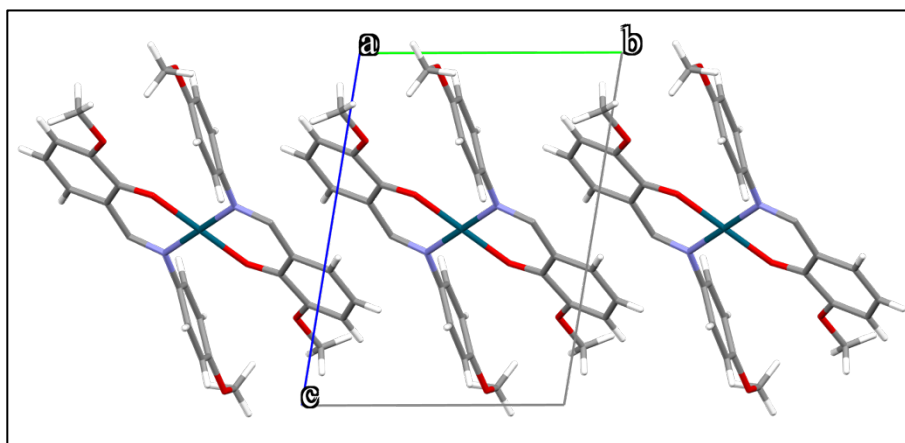


Figure 4.26 Crystal Packing of PdB1OMe View Down Crystallographic *a*-Axis

The two benzene rings C1-C6 and C8-C13, are planar with maximum deviation of 0.017 (3) and 0.009 (4) for atom C1 and C12, respectively from their mean square planes. The plane makes dihedral angle of 49.76°. The C-O bond length range from 1.310 (4) to 1.426 (7) Å. The C=N and C-N bond lengths are 1.301 (4) Å and 1.429 (5) Å, respectively (Table 4.26). The comparison of selected geometrical parameters of the experimental values and computational calculations by DFT at B3LYP/LANL2DZ basis set level is given in Table 4.26. All bond lengths and angles of the optimized structure were compared to the experimental values and both results fall within the expected ranges. The packing diagram for PdB1OMe view down *a*-axis is shown in Figure 4.26.

4.2.7.9 Crystal Structure of PdB2Me

Crystallization of the novel PdB2Me complex from slow evaporation from chloroform at room temperature yielded orange crystals. The ORTEP diagram of PdB2Me is shown in Figure 4.27. It crystallized in a monoclinic crystal system with the space group of P21/c, cell parameter $a = 9.941$ (3) Å, $b = 10.952$ (3) Å and $c = 10.969$ (3) Å, $\alpha = \gamma = 90^\circ$, $\beta = 105.337^\circ$ (8), $Z = 2$, and $V = 1151.8$ (5) Å³. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 , resulting in a good $R(\text{int}) = 4.05\%$ with 99.6% completeness. The geometry of PdB2Me is square planar, as indicated by a τ_4 of 0, consistent with magnetic susceptibility measurements showing diamagnetism.

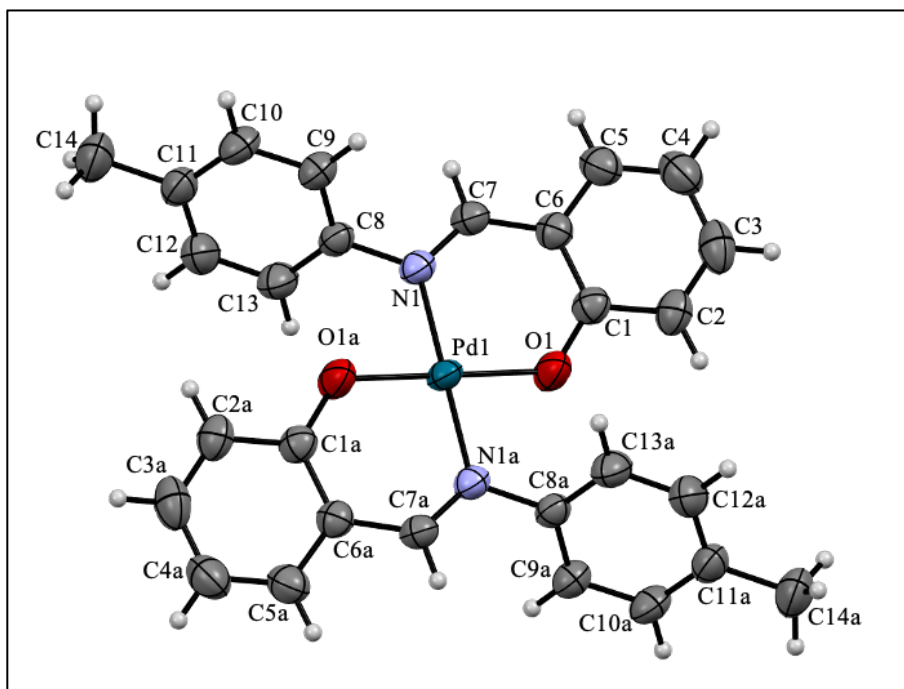


Figure 4.27 The ORTEP Diagram of PdB2Me, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level

Table 4.27

Selected Bond Lengths (Å) and Bond Angles (°) of PdB2Me

	Experimental	DFT (B3LYP/LANL2DZ)
Bond Lengths (Å)		
Pd1-O1	1.970 (3)	2.020
O1-C1	1.316 (5)	1.332
Pd1-N1	2.023 (3)	2.064
N1-C7	1.291 (5)	1.320
N1-C8	1.443 (5)	1.449
Bond Angles (°)		
Pd1-O1-C1	125.42 (3)	127.83
N1-Pd1-O1	91.44 (13)	91.56
Pd1-N1-C7	123.45 (3)	123.29
Pd1-N1-C8	120.00 (2)	119.73

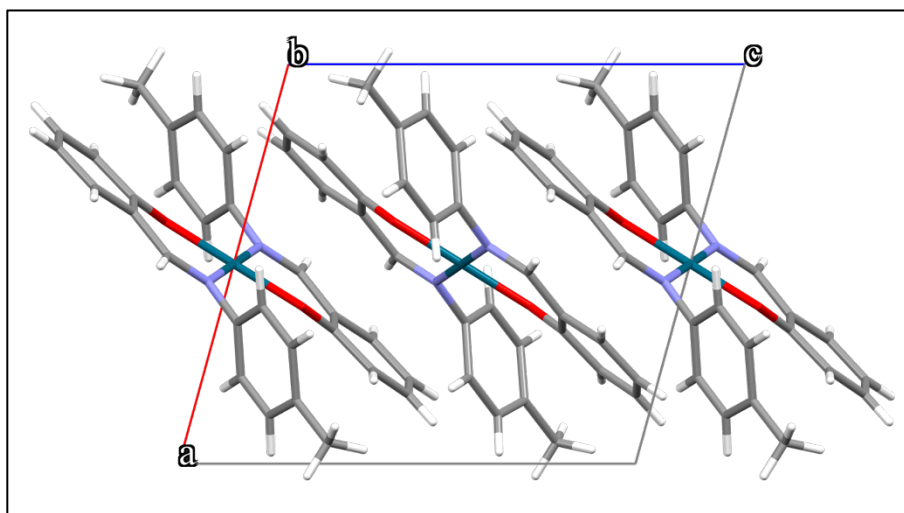


Figure 4.28 Crystal Packing of PdB2Me View Down Crystallographic *b*-Axis

The C1-C6 and C8-C13 benzene rings are planar with maximum deviation of 0.009 (5) and 0.008 (3) for atom C5 and C8, respectively, with a dihedral angle of 52.03° between them. The C-O bond length is 1.316 (5) Å. The C=N and C-N bond lengths are 1.291(5) Å and 1.443(5) Å, respectively (Table 4.27). The comparison of selected geometrical parameters of the experimental values and computational calculations by DFT at B3LYP/LANL2DZ basis set level is given in Table 4.27. All bond lengths and angles of the optimized structure were compared to the experimental values and both results fall within the expected ranges. The packing diagram for PdB2Me view down *b*-axis is shown in Figure 4.28.

4.2.7.10 Crystal Structure of PdB2OMe

Upon slow evaporation from ethanol at room temperature, the new compound PdB2OMe crystallized as orange crystals. The ORTEP diagram of PdB2OMe is shown in Figure 4.29. It crystallized in a monoclinic crystal system with the space group of P21/c, cell parameter $a = 13.396(3)$ Å, $b = 11.231(2)$ Å and $c = 7.8603(14)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 97.07^\circ(6)$, $Z = 2$, and $V = 1173.6(4)$ Å³. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 , giving a good $R(\text{int}) = 4.31\%$ with 99.8% completeness. Calculated $\tau_4 = 0$ for PdB2OMe reveals a square planar geometry, supporting the diamagnetic properties observed experimentally in Section 4.2.2.

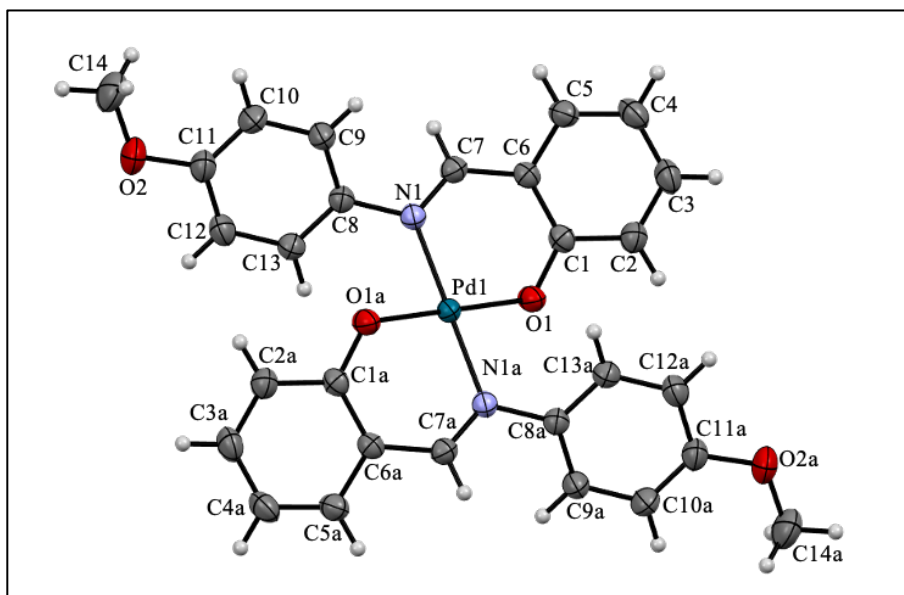


Figure 4.29 The ORTEP Diagram of Pd(B2OMe), with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level

Table 4.28

Selected Bond Lengths (Å) and Bond Angles (°) of Pd(B2OMe)

	Experimental	DFT (B3LYP/LANL2DZ)
Bond Lengths (Å)		
Pd1-O1	1.983 (16)	2.020
O1-C1	1.318 (2)	1.332
Pd1-N1	2.043 (16)	2.066
N1-C7	1.290 (2)	1.321
N1-C8	1.440 (3)	1.449
O2-C11	1.377 (3)	1.398
O2-C14	1.419 (4)	1.456
Bond Angles (°)		
Pd1-O1-C1	121.08 (13)	128.02
N1-Pd1-O1	90.58 (6)	91.57
N1-Pd1-O1a/ N1a-Pd1-O1	89.42 (6)	90.21
Pd1-N1-C7	121.67 (13)	123.29
Pd1-N1-C8	120.81 (11)	119.81
C11-O2-C14	116.92 (2)	118.56

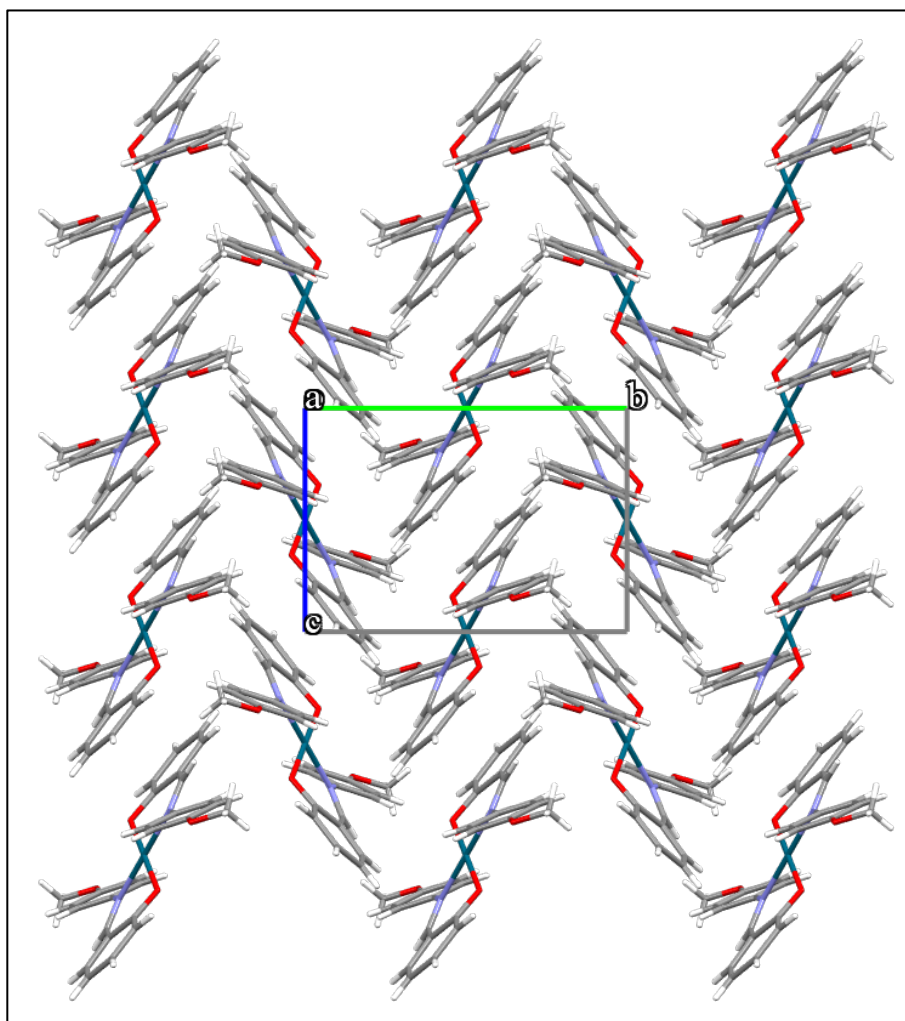


Figure 4.30 Crystal Packing of PdB2OMe View Down Crystallographic *a*-Axis

The two benzene rings C1-C6 and C8-C13, are planar with maximum deviation of 0.012 (2) and 0.008 (2) for atom C5 and C10, respectively from their mean square planes and the dihedral angle between the rings is 27.73°. The C-O bond length range from 1.318 (2) Å to 1.419 (4) Å. The C=N and C-N bond lengths are 1.290 (2) Å and 1.440 (3) Å, respectively (Table 4.28). The comparison of selected geometrical parameters of the experimental values and computational calculations by DFT at B3LYP/LANL2DZ basis set level is given in Table 4.28. All bond lengths and angles of the optimized structure were compared to the experimental values and both results fall within the expected ranges. The packing diagram for PdB2OMe view down *a*-axis is shown in Figure 4.30.

4.2.7.11 Crystal Structure of PdB2C

The newly synthesized PdB2C crystallized as orange crystals following slow evaporation from ethanol at room temperature. The ORTEP diagram of PdB2C is shown in Figure 4.31. It crystallized in a monoclinic crystal system with the space group of $P2_1/c$, cell parameter $a = 9.858$ (4) Å, $b = 11.122$ (5) Å and $c = 10.702$ (5) Å, $\alpha = \gamma = 90^\circ$, $\beta = 104.54^\circ$ (15), $Z = 2$, and $V = 1135.8$ (9) Å³. The crystal structure was solved by direct methods and refined by full-matrix least-squares resulting in a good $R(\text{int}) = 5.70\%$ with 99.8% completeness. The PdB2C complex has a square planar geometry with $\tau_4 = 0$, consistent with diamagnetic properties indicated by magnetic susceptibility data in Section 4.2.2.

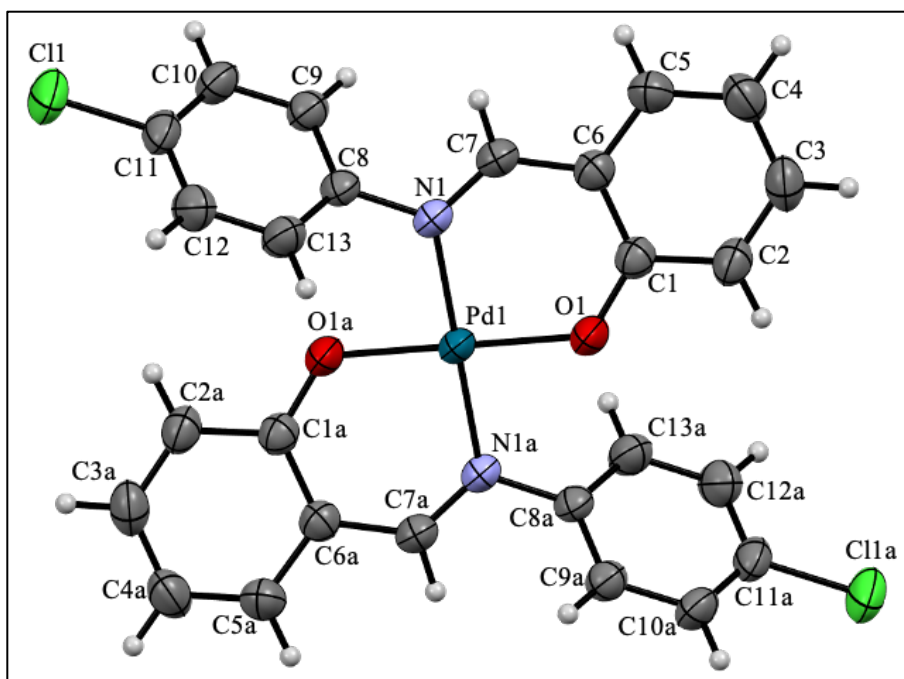


Figure 4.31 The ORTEP Diagram of PdB2C, with the Atom Labelling and Displacement Ellipsoids Drawn at the 50% Probability Level

Table 4.29

Selected Bond Lengths (Å) and Bond Angles (°) of PdB2C

	Experimental	DFT (B3LYP/LANL2DZ)
Bond Lengths (Å)		
Pd1-O1	1.979 (18)	2.020
O1-C1	1.316 (3)	1.333
Pd1-N1	2.025 (18)	2.063
N1-C7	1.294 (3)	1.322
N1-C8	1.439 (3)	1.447
Bond Angles (°)		

Pd1-O1-C1	124.78 (14)	127.92
N1-Pd1-O1	91.20 (7)	91.54
Pd1-N1-C7	123.01 (14)	123.45
Pd1-N1-C8	120.25 (12)	119.50

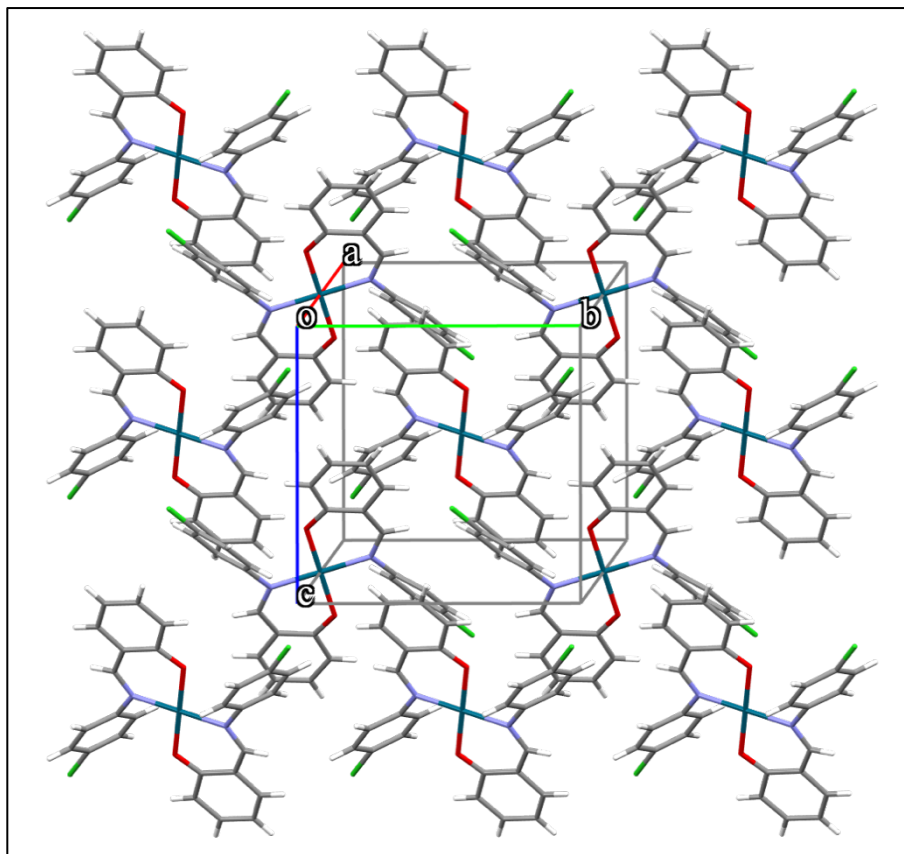


Figure 4.32 Crystal Packing of PdB2C View Down Crystallographic *a*-Axis

The two benzene rings C1-C6 and C8-C13, are planar with maximum deviation of 0.004 (2) and 0.007 (2) for atom C5 and C11, respectively from their mean square planes. The plane makes dihedral angle of 48.08°. The C-O bond length is 1.316 (3) Å. The C=N and C-N bond lengths are 1.294 (3) Å and 1.439 (3) Å, respectively (Table 4.29). The comparison of selected geometrical parameters of the experimental values and computational calculations by DFT at B3LYP/LANL2DZ basis set level is given in Table 4.29. All bond lengths and angles of the optimized structure were compared to the experimental values and both results fall within the expected ranges. The packing diagram for PdB2C view down *a*-axis is shown in Figure 4.32.

4.3 Catalytic Activity of Stille Reaction

4.3.1 Screening of the Best Catalyst Series

The Pd(II) complexes from the PdB1 and PdB2 series were evaluated to identify the most effective catalyst. Initially, the reaction mixture containing the catalyst, TEA, tributylphenyltin, and iodobenzene exhibited a light orange color, which gradually darkened to brown as the reaction progressed. A summary of the percent conversion of iodobenzene to Stille product after 60 minutes of reaction for selected complexes was presented in Table 4.30. The findings indicated that the Pd(II) complexes from the B1 series demonstrated the highest catalytic performance, leading to their selection for further optimization studies.

Table 4.30
Percent Conversion of Iodobenzene of Stille Reaction

Series	Compounds	% Conversion of Iodobenzene
PdB1	PdB1H	42.4
	PdB1Me	44.0
	PdB1OMe	69.3
	PdB1C	65.8
	PdB1N	66.4
PdB2	PdB2H	29.2
	PdB2Me	31.4
	PdB2OMe	42.7
	PdB2C	40.8
	PdB2N	54.7

The superior catalytic performance of the PdB1 series is attributed to the presence of an additional electron-donating substituent, which increases electron density around the active center and thereby enhances the catalytic activity (Shimada et al., 2019). Therefore, the PdB1 series of complexes namely PdB1H, PdB1Me, PdB1OMe, PdB1C and PdB1N, were chosen as catalysts for the Stille reaction.

4.3.2 Optimization of Catalytic Activity

The Stille reaction between iodobenzene and tributylphenyltin was optimized by varying reaction temperatures, types of bases, and amounts of catalysts. The reaction was monitored using GC-FID by percentage conversion of iodobenzene at every 15 minutes and sampling was done at 15, 30, 45 and 60 minutes.

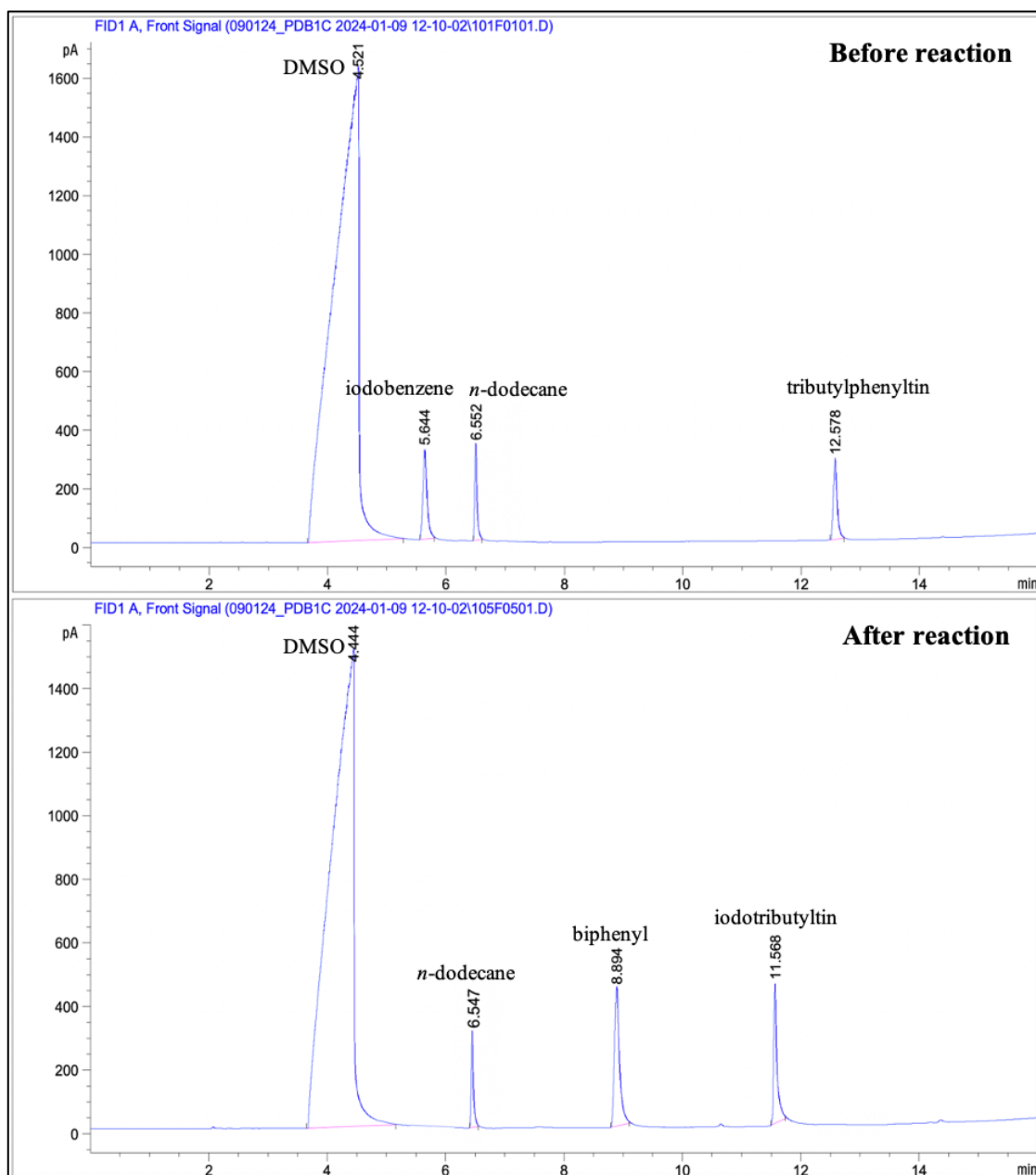


Figure 4.33 GC Chromatogram of Reaction Mixture for Stille Reaction

The reaction mixture of Stille reaction consisted of tributylphenyltin, iodobenzene, DMSO, and Pd(II) complex of B1 series. *n*-Dodecane was used as standard for this reaction. The presence of DMSO, iodobenzene, and tributylphenyltin could be detected at 4.521, 5.644, and 12.578 min respectively on the GC chromatogram (Figure 4.33). From the chromatogram, the biphenyl product appeared between the substrates because the tributylphenyltin is a more polar and non-volatile compound compared to biphenyl which is non-polar and moderate volatile compound. Since a non-polar HP-5 column was used, the non-polar compound, biphenyl eluted earlier, while the more polar, tributylphenyltin interacted more strongly with the stationary

phase, resulting in a longer retention time and eluting last. Additionally, the molecular weight of tributylphenyltin (367.2 g/mol) is heavier than biphenyl (154.21 g/mol).

Table 4.31
Selectivity of Product in Stille Reaction

Series	Catalyst	Selectivity of Product	
		% of biphenyl	% of iodotributyltin
NiB1	NiB1H	63.6	36.4
	NiB1Me	63.9	36.1
	NiB1OMe	67.6	32.4
	NiB1C	65.0	35.0
	NiB1N	68.2	31.8
NiB2	NiB2H	56.9	43.1
	NiB2Me	71.9	28.1
	NiB2OMe	63.3	36.7
	NiB2C	65.7	34.3
	NiB2N	60.4	39.6
CuB1	CuB1H	72.4	27.6
	CuB1Me	74.1	25.9
	CuB1OMe	77.3	22.7
	CuB1C	71.6	28.4
	CuB1N	67.0	33.0
CuB2	CuB2H	60.7	39.3
	CuB2Me	61.1	38.9
	CuB2OMe	61.3	38.7
	CuB2C	62.5	37.5
	CuB2N	62.1	37.9
PdB1	PdB1H	61.9	38.1
	PdB1Me	62.9	37.1
	PdB1OMe	62.3	37.7
	PdB1C	60.7	39.3
	PdB1N	60.5	39.5
PdB2	PdB2H	60.7	39.3
	PdB2Me	61.1	38.9
	PdB2OMe	61.3	38.7
	PdB2C	62.5	37.5
	PdB2N	62.1	37.9

There were two products appeared in the end of the reaction. The reaction proceeded with high selectivity toward the formation of biphenyl as the major product, while iodotributyltin was observed as a minor byproduct (Table 4.31). The position of the products was confirmed with their standard. The presence of the biphenyl, the major coupling product could be seen at 8.894 min. Whereas, iodotributyltin appeared as minor product for this reaction at 11.568 min. The position of the product was confirmed with standard biphenyl and iodotributyltin.

4.3.2.1 Effect of Temperatures

The optimization of reaction conditions for the Stille reaction of iodobenzene and tributylphenyltin was carried out by varying temperatures (30 °C, 60 °C, 80 °C, and 100 °C) while maintaining TEA as the base and catalyst amount of 1.0 mmol%. As illustrated in Figure 4.34, the highest conversion of iodobenzene was observed at 100 °C after 60 minutes, making it the optimal reaction temperature for this catalytic system. The most performing catalyst at this temperature was PdBIOMe while the least active one was PdBIH. The order of catalytic activity in descending order was as followed; PdBIOMe > PdBIN > PdBI Me > PdBIC > PdBIH. Based on the studies carried out in investigating the effect of temperatures on the catalytic activity of PdBI series complexes, it can be seen that complexes bearing electron-donating substituents (PdBIOMe) performed better than ones with electron-withdrawing substituents (PdBIN) because electron-donating group increase electron density at the active site, enhancing substrate activation and stabilizing reaction intermediates (Shimada et al., 2019). This facilitates key steps in many catalytic cycles, making the catalyst more effective.

In contrast, the lowest efficiency was recorded at 30 °C, yielding only 16.2-21.5% conversion within the same time frame. These results demonstrate that higher temperatures enhance the catalytic activity of the Stille reaction by increasing molecular collisions and reaction rates (Matata, 2024). Nevertheless, optimal performance requires balancing temperature to prevent catalyst deactivation and side reactions. The reaction was attempted at 120 °C, however, the formation of palladium black was observed, suggesting the catalyst decomposition and preventing further progression of the reaction (Jacks et al., 2004).

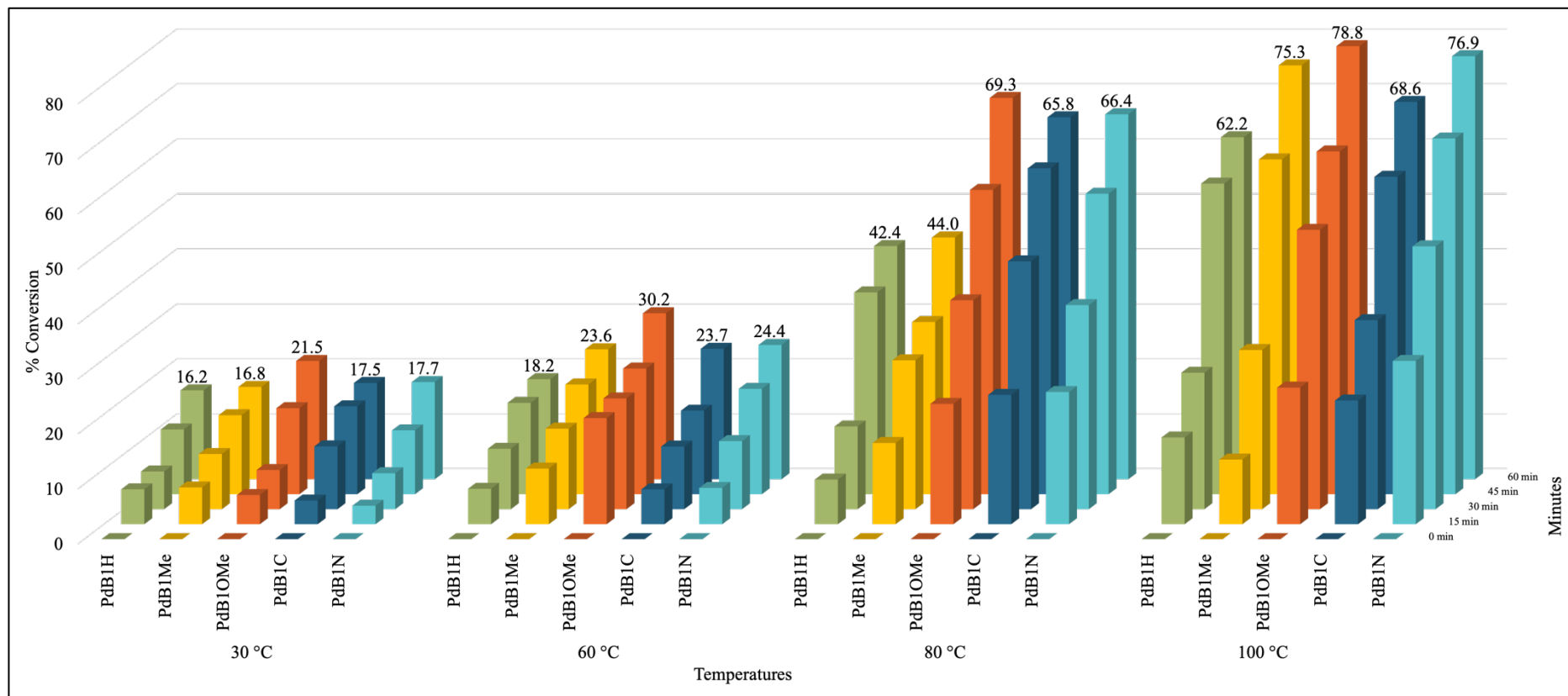


Figure 4.34 Effect of Temperatures on % Conversion of Iodobenzene

4.3.2.2 Effect of Types of Bases

To determine the most effective base for the Stille reaction, KOH, K₂CO₃, and TEA were evaluated under standardized conditions, with the temperature set at 100 °C and catalyst amount of 1.0 mmol%. The reaction mixture initially appeared light orange but gradually transitioned to a dark brown at the end of reaction, a consistent trend observed across all three bases. This study highlights the significant role of base selection in influencing reaction efficiency in the Stille reaction.

In the optimization of the Stille reaction, the choice of base plays a crucial role in facilitating the transmetalation step and maintaining catalyst stability. Among the bases studied which are KOH, triethylamine (TEA), and potassium carbonate (K₂CO₃), KOH was found to be the most effective, followed by TEA and then K₂CO₃. Although KOH is a hard base, which typically mismatches with the soft palladium center according to hard and soft acids and bases (HSAB) theory, its strong basicity and high nucleophilicity enhance the deprotonation of intermediate species and accelerate the reaction rate (Fantoni et al., 2025). KOH can also promote the activation of organostannanes by facilitating the formation of a more reactive tin species, thereby improving the efficiency of the transmetalation step (Dennis et al., 2019). Triethylamine, a soft organic base, aligns better with HSAB principles and helps stabilize the palladium center, reducing side reactions such as protodestannylation. However, its weaker basic strength can limit its ability to activate substrates as effectively as KOH (Lima et al., 2014). Potassium carbonate, though commonly used due to its mild nature and compatibility with various systems, demonstrated the least activity in this comparison, likely due to its relatively low basicity and poor solubility in organic solvents, which may hinder its ability to effectively engage in the reaction (Borhade & Waghmode, 2011). Thus, despite its hard character, KOH outperforms the other bases by accelerating the reaction kinetics and improving yields in the Stille coupling (Xiao et al., 2022). Figure 4.34 shows that KOH was the most effective base in this catalytic system by converting the highest percent of iodobenzene after 60 minutes of reaction time.

As seen in Figure 4.35, the most active complex when KOH was used as base was PdBIOMe and the least active one was PdBIH. The sequence of catalytic activity for the catalyst, in descending order with KOH as base was as followed; PdBIOMe > PdBIN > PdBIC > PdBIMe > PdBIH.

Based on the observations made on the effect of bases on the catalytic performance of metal complexes, it can be seen that catalysts with electron-donating substituents, PdB1OMe (-OCH₃) showed better catalytic activity than ones with electron-withdrawing substituents PdB1N (-NO₂), PdB1C (-Cl). This indicates that electronic profile of the complex played a pronounced role in activating the catalytic site of catalyst, hence converting higher percentage of iodobenzene in Stille reaction.

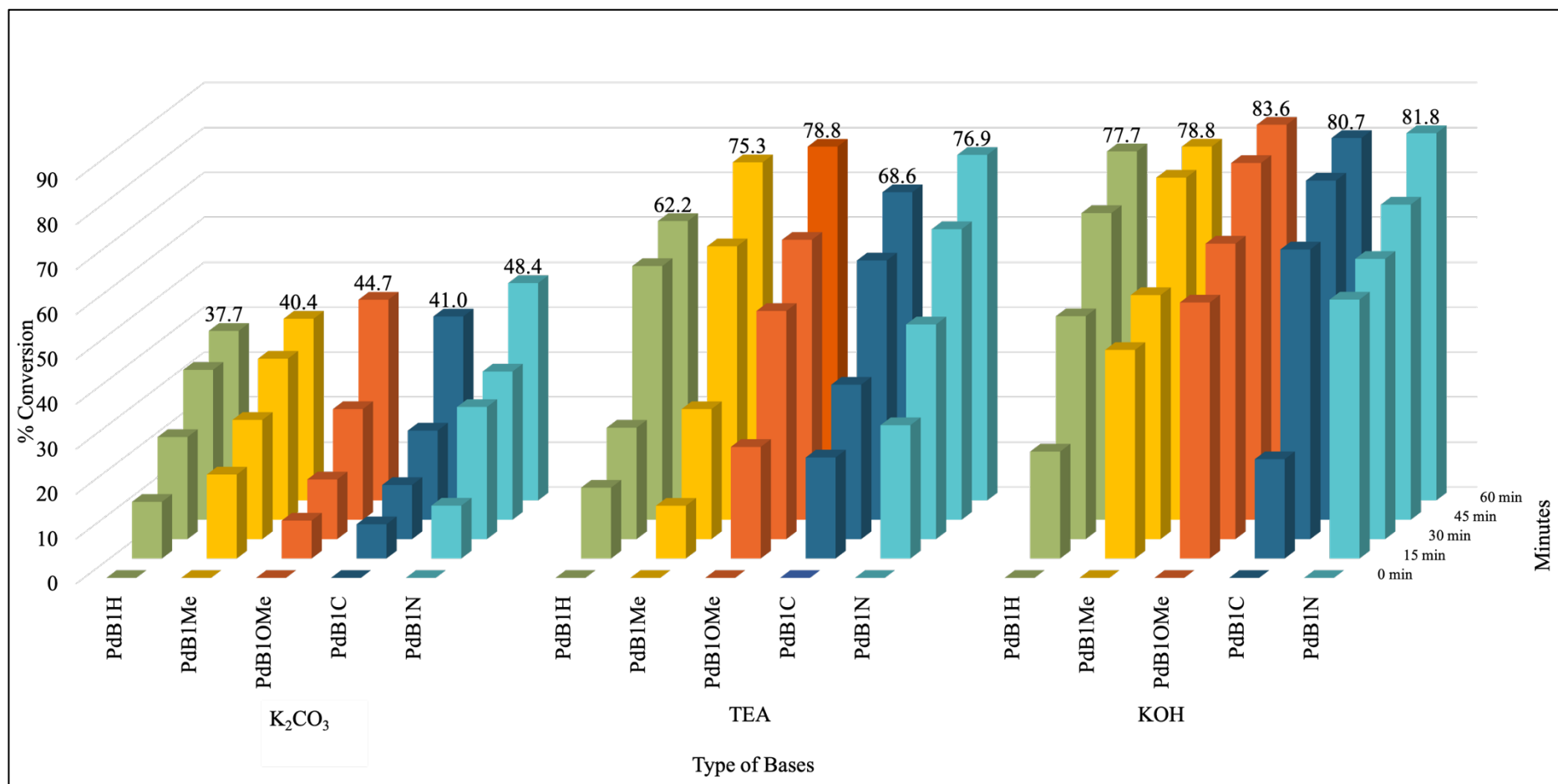


Figure 4.35 Effect of Types of Bases on % Conversion of Iodobenzene

4.3.2.3 Effect of Amounts of Catalysts

The catalytic efficiency of the system was investigated by varying the amount of catalyst of palladium complexes at four different concentrations, 0.5, 1.0, 1.5, and 2.0 mmol%, while maintaining KOH as the base and maintaining a reaction temperature of 100 °C.

At 0.5 mmol%, the Pd catalyst is present in a minimal quantity, likely resulting in lower active species availability, reducing overall conversion rates. The reaction may proceed sluggishly due to insufficient catalytic sites to facilitate oxidative addition and reductive elimination steps efficiently (Ayala et al., 2021). With 1.0 mmol%, there is an appreciable improvement, as the increased palladium presence enhances substrate activation and turnover. However, conversion rates remain suboptimal compared to higher catalyst amount, indicating possible limitations in intermediate stability or reaction kinetics (Śpiwak et al., 2021a). At 1.5 mmol%, the catalytic cycle appears to be sufficiently populated with active Pd species, showing notable enhancement in reaction rate. This suggests an improvement in surface coverage and electron transfer dynamics, though not yet maximizing efficiency. Although three of the catalysts achieved 100% conversion at 1.5 mmol% amount of catalyst, but not all catalysts were fully active under these conditions.

The optimum catalyst amount was determined to be 2.0 mmol%, as all catalysts were active at this concentration and achieved 100% conversion of iodobenzene within 60 minutes as illustrated in Figure 4.36 and Table 4.32, establishing it as the optimum amount of catalyst for this reaction to ensure consistent performance and reproducibility across all catalysts.

Based on the discussion made above, it is quite difficult to tell the significance of electronic profile on the catalytic performance of Pd(II) complexes in Stille reaction especially at the highest amount of catalyst. However, based on other amounts of catalysts parameters, it is apparent that complex bearing electron-donating substituent, PdB1OMe (-OCH₃) play an important role in enhancing the catalytic activity. This concentration likely ensures maximum substrate interaction, with palladium species well-dispersed and highly active in facilitating C-C bond formation. Excess catalyst beyond this amount could potentially lead to side reactions, metal aggregation, or wasted material without significant additional benefit (Kumar et al., 2024). In catalytic processes, selecting a catalyst that ensures a high yield and acceptable purity is a priority

before considering turnover number (TON), as a high-TON system that does not meet yield or purity standards is impractical for efficient catalysis (Matsheku et al., 2021). Therefore, this study determined the ideal amount catalyst based on percentage conversion rather than TON.

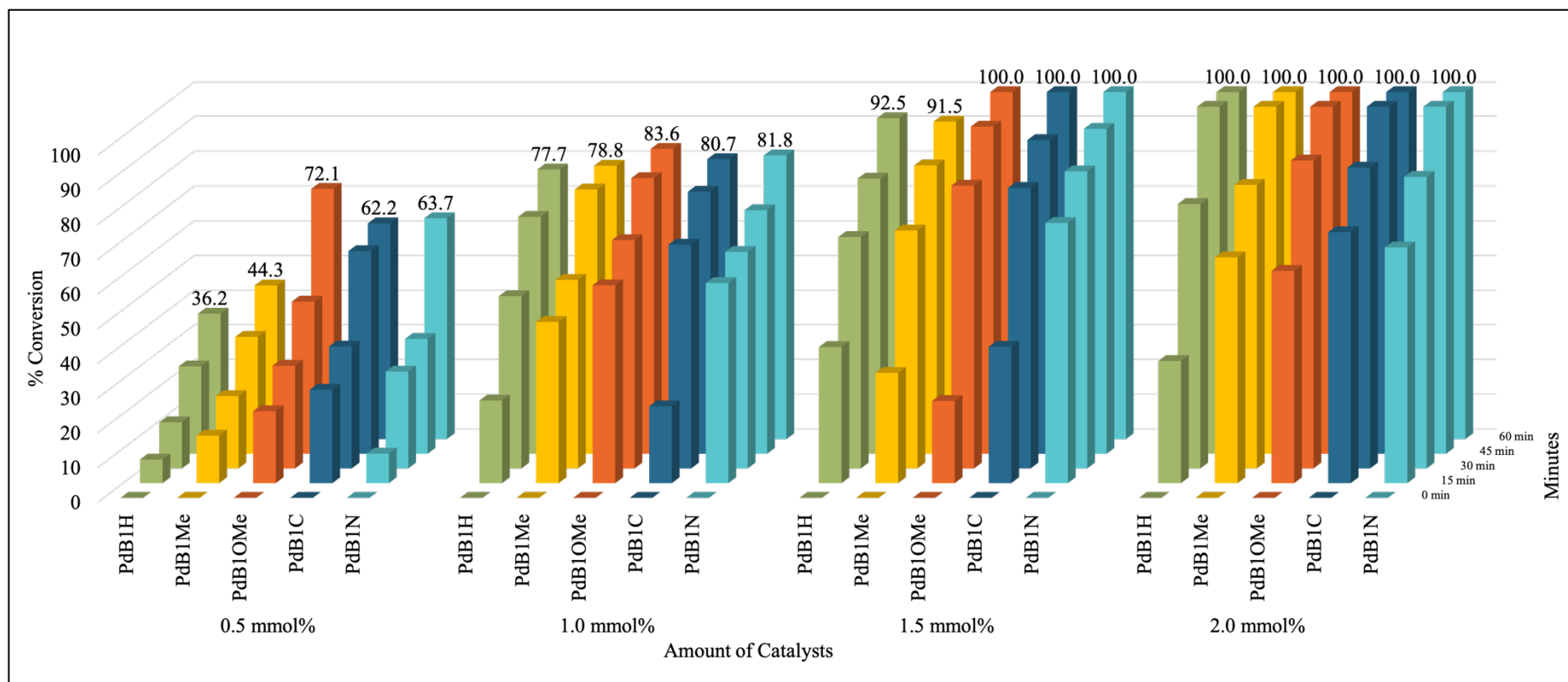


Figure 4.36 Effect of Amounts of Catalysts on % Conversion of Iodobenzene

Table 4.32

Effect of Different Amounts of Catalysts on Stille Reaction

Catalyst Loading	Catalyst	Conversion of Iodobenzene, %, (TON)			
		15 minutes	30 minutes	45 minutes	60 minutes
0.5 mmol%	PdB1H	6.8 (13.6)	13.3 (26.6)	25.2 (50.4)	36.2 (72.4)
	PdB1Me	13.7 (27.4)	20.9 (41.8)	33.7 (67.4)	44.3 (88.6)
	PdB1OMe	20.7 (41.4)	29.6 (59.2)	43.9 (87.8)	72.1 (144.2)
	PdB1C	26.9 (53.8)	35.1 (70.2)	58.4 (116.8)	62.2 (124.4)
	PdB1N	8.5 (17.0)	27.9 (55.8)	33.1 (66.2)	63.7 (127.4)
1.0 mmol%	PdB1H	23.8 (23.8)	49.6 (49.6)	68.3 (68.3)	77.7 (77.7)
	PdB1Me	46.4 (46.4)	54.3 (54.3)	76.2 (76.2)	78.8 (78.8)
	PdB1OMe	57.0 (57.0)	65.8 (65.8)	79.4 (79.4)	83.6 (83.6)
	PdB1C	22.1 (22.1)	64.5 (64.5)	75.5 (75.5)	80.7 (80.7)
	PdB1N	57.7 (57.7)	62.4 (62.4)	70.2 (70.2)	81.8 (81.8)
1.5 mmol%	PdB1H	39.2 (26.1)	66.7 (44.5)	79.3 (52.9)	92.5 (61.7)
	PdB1Me	31.8 (21.2)	68.6 (45.7)	83.1 (55.4)	91.5 (61.0)
	PdB1OMe	23.7 (15.8)	81.5 (54.3)	94.3 (62.9)	100.0 (66.7)
	PdB1C	39.3 (26.2)	80.9 (53.9)	90.4 (60.3)	100.0 (66.7)
	PdB1N	75.0 (50.0)	85.6 (57.1)	93.6 (62.4)	100.0 (66.7)
2.0 mmol%	PdB1H	55.0 (27.5)	79.8 (39.9)	100.0 (50.0)	100.0 (50.0)
	PdB1Me	65.1 (32.6)	81.7 (40.9)	100.0 (50.0)	100.0 (50.0)
	PdB1OMe	62.2 (31.3)	88.8 (44.4)	100.0 (50.0)	100.0 (50.0)
	PdB1C	55.7 (27.9)	82.1 (41.1)	100.0 (50.0)	100.0 (50.0)
	PdB1N	65.2 (32.6)	84.6 (42.3)	100.0 (50.0)	100.0 (50.0)

Note: Value in parenthesis is turnover number (TON) = mmol product/mmol catalyst used mmol% = 1 mmol of catalyst in 100 mmol of iodobenzene

4.3.3 Effect of using Different Catalysts in Stille Reaction

The reactions catalyzed by various Ni(II), Cu(II), and Pd(II) complexes were carried out smoothly under the optimized reaction conditions (KOH, 100 °C and 2.0 mmol%) affording the product, in moderate to high yields. The results were reported in Table 4.33. Pd(II) complexes, both from B1 and B2 series performed the best compared to Ni(II) and Cu(II) complexes. This is consistent with the results reported by Esmaeilpour, Javidi, Dodeji, and Abarghoui (2014) who found that palladium converted a higher percentage of reactant than nickel and copper. The lowest percent conversion for Ni(II) and Cu(II) were 62.7% and 28.8%, respectively and the highest conversion were 90.8% and 50.1%, respectively. Therefore, the catalytic performance of Ni(II)

complexes was quite decent and better than Cu(II) complexes (Esmaeilpour et al., 2014).

Nickel catalysts often outperform copper catalysts due to differences in their electronic structure, redox flexibility, and ability to undergo key catalytic steps, particularly oxidative addition and transmetalation. Nickel is a first-row transition metal that can exhibit reactivity analogous to palladium in cross-coupling catalysis. Although Ni(0) possesses a d^{10} electronic configuration, similar to Pd(0), differences in orbital energies and metal–ligand interactions allow nickel to access a broader range of oxidation states, allowing it to mimic reactivity of palladium in cross-coupling mechanisms (Bismuto et al., 2021). However, nickel offers greater redox flexibility, readily catalytic cycling between Ni(0), Ni(I), Ni(II), and even Ni(III) oxidation states. This makes it highly efficient in facilitating oxidative addition of aryl halides, especially challenging ones such as aryl chlorides (Zhou et al., 2022). Furthermore, stronger binding of nickel to electron-deficient substrates can enhance substrate activation and accelerate the transmetalation step with organostannanes (Liu et al., 2023).

On the other hand, copper complexes generally show lower efficiency in the Stille reaction. Copper tends to favor one-electron redox pathways and is more prone to forming side products, such as through homocoupling or oxidation reactions (McCann & Stahl, 2015). Moreover, Cu(II) complexes often lack the oxidative addition capability required to activate aryl halides effectively under typical Stille conditions, especially in the absence of ligands or additional oxidants (Patel & Singh, 2021). As a result, copper-catalyzed Stille reactions often require harsher conditions or additives, and still give lower yields and selectivity compared to nickel. Thus, the superior performance of nickel over copper in the Stille reaction is primarily due to its ability to access multiple oxidation states, promote key steps like oxidative addition and transmetalation more efficiently, and tolerate a broader range of substrates, while copper is often limited by its redox profile and reactivity scope.

There was no significant difference of catalytic activity of Pd(II) complexes between B1 series and B2 series despite their distinctive architectural differences. This implies that metal centers play a more important role in catalytic activities than the ligands. Nonetheless, the presence of ligands should not be neglected as ligands play a huge role in accustoming the rate of some or all of the catalytic steps, like oxidative addition, insertion, transmetalation and reductive elimination (Farina, 2004). In fact, the deposition of palladium black, a marker of deactivation of catalytic site of the metal, is

known to deposit rather quickly in ligandless catalysis (Farina, 2004). There was no formation of palladium black in any of the reactions catalyzed by the B1 and B2 series of complexes at temperature of 100 °C. This showed that B1 and B2 ligands acted as effective stabilizers to the catalytic active sites of Ni(II), Cu(II), and Pd(II).

Table 4.33
Percent Conversion of Iodobenzene using Different Catalysts

Series	Catalyst	% Conversion of Iodobenzene				
		0 min	15 min	30 min	45 min	60 min
NiB1	NiB1H	0	22.7	48.4	72.6	80.7
	NiB1Me	0	29.1	55.1	72.5	87.8
	NiB1OMe	0	22.8	48.7	73.8	85.7
	NiB1C	0	23.3	52.6	73.8	90.8
	NiB1N	0	18.6	48.8	74.3	83.1
NiB2	NiB2H	0	29.3	37.6	48.0	64.7
	NiB2Me	0	31.6	32.7	42.2	62.7
	NiB2OMe	0	29.9	42.7	51.1	70.5
	NiB2C	0	25.0	31.9	41.4	72.4
	NiB2N	0	26.8	40.4	45.3	67.0
CuB1	CuB1H	0	3.3	14.9	36.4	44.7
	CuB1Me	0	4.5	9.8	33.7	43.7
	CuB1OMe	0	17.3	21.2	32.1	46.0
	CuB1C	0	19.8	20.4	40.1	50.1
	CuB1N	0	12.1	12.4	34.2	48.1
CuB2	CuB2H	0	14.3	16.1	16.3	36.9
	CuB2Me	0	6.3	6.8	23.0	33.3
	CuB2OMe	0	7.4	16.7	17.6	28.8
	CuB2C	0	7.1	8.3	14.6	31.3
	CuB2N	0	9.8	11.5	13.9	34.6
PdB1	PdB1H	0	35.2	76.2	100.0	100.0
	PdB1Me	0	65.1	81.7	100.0	100.0
	PdB1OMe	0	61.2	88.8	100.0	100.0
	PdB1C	0	72.3	86.7	100.0	100.0
	PdB1N	0	67.9	84.0	100.0	100.0
PdB2	PdB2H	0	24.5	55.0	100.0	100.0
	PdB2Me	0	47.5	80.3	100.0	100.0
	PdB2OMe	0	35.8	72.1	100.0	100.0
	PdB2C	0	41.7	55.7	100.0	100.0
	PdB2N	0	65.2	84.6	100.0	100.0
Positive Control	Pd(OAc) ₂	0	68.6	83.1	100.0	100.0

There were two control experiments in this investigation. The reaction without any Ni(II), Cu(II), and Pd(II) species i.e. the negative control showed no conversion of the iodobenzene (Figure 4.37). The positive control using palladium(II) acetate (Pd(OAc)₂) as catalyst showed the highest conversion of 100% after 60 minutes of

reaction time (Table 4.33). However, the formation of palladium black was detected after 30 minutes of reaction, signaling the decomposition of palladium(II) acetate.

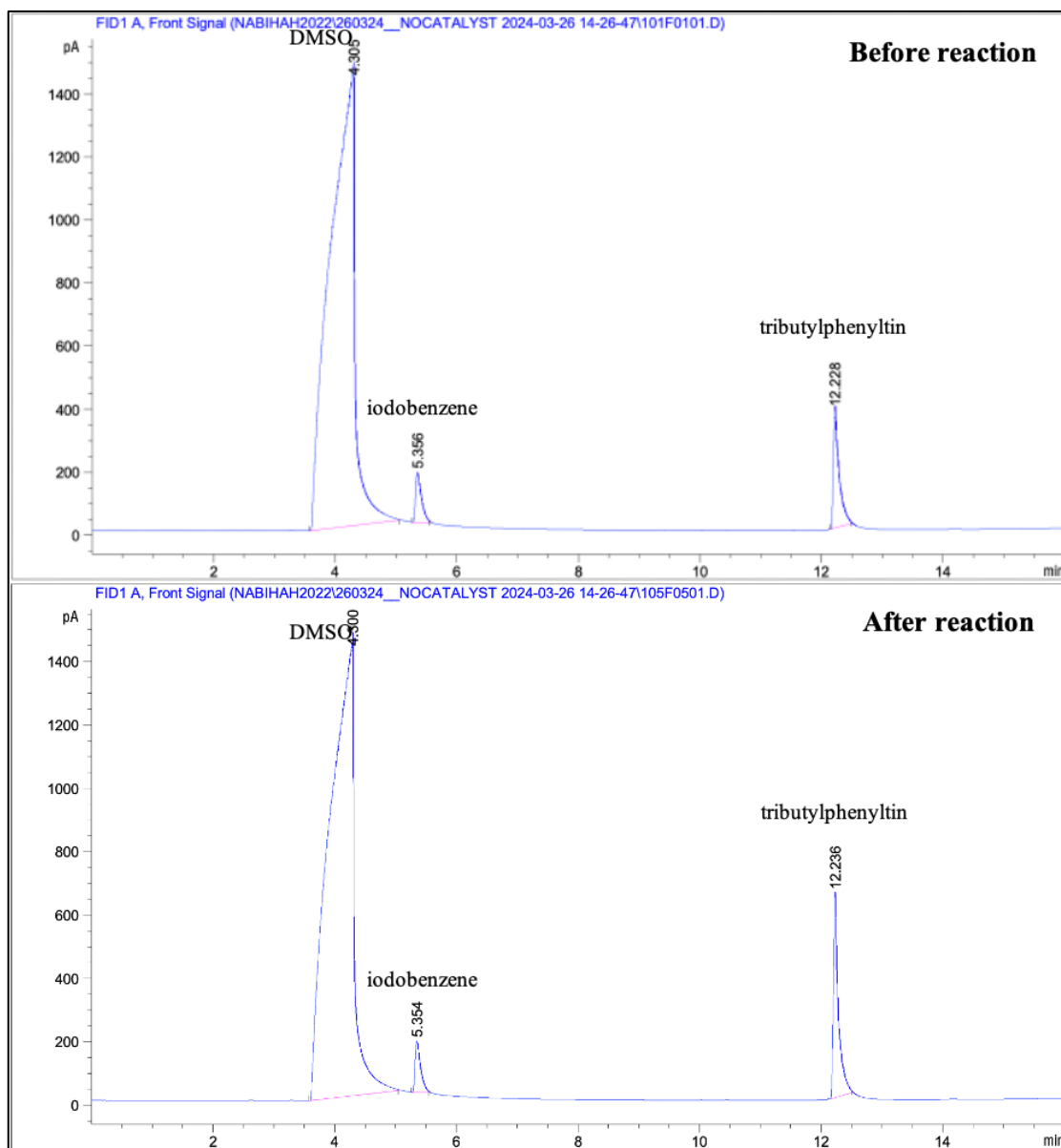


Figure 4.37 GC Chromatogram of Negative Control for Stille Reaction

4.3.4 Isolation of Stille Product

The Stille reaction between iodobenzene and tributylphenyltin using the optimum reaction conditions (KOH, 100 °C, and 2.0 mmol%) within 60 minutes of reaction catalyzed by the best catalyst namely PdBIOMe afforded a white solid of biphenyl with a yield of 41.9%. The physicochemical data of the compounds are reported in Table 4.34. The percentage of C and H were in concordance with the

proposed structure. The chemical structure of the product was elucidated using elemental analysis, FTIR and ^1H NMR and ^{13}C NMR.

Table 4.34
Physicochemical Data of Biphenyl

Compound	RMM	Mw (g/mol)	Colour	Yield (%)	Elemental Analysis %		
					Calculated (Found)		
					C	H	N
Isolated biphenyl	$\text{C}_{12}\text{H}_{10}$	154.21	White	41.9	93.46 (92.91)	6.54 (6.47)	-

The main peaks of the functional groups in FTIR spectrum are tabulated in Table 4.35. The characteristic band for C-C coupled stretching vibrations was found at 1876 cm^{-1} . The characteristic bands of benzene were detected at 3033 cm^{-1} for CH sp^2 stretching vibrations and at 1568 cm^{-1} for C=C stretching vibrations. The presence of CH sp^2 out of plane (oop) bending vibrations at 728 cm^{-1} and 695 cm^{-1} and CH sp^2 bending vibrations at 1429 cm^{-1} in the spectra further corroborates the existence of benzene in the chemical structure. These observations are in good agreement with the standard biphenyl (Figure 4.38).

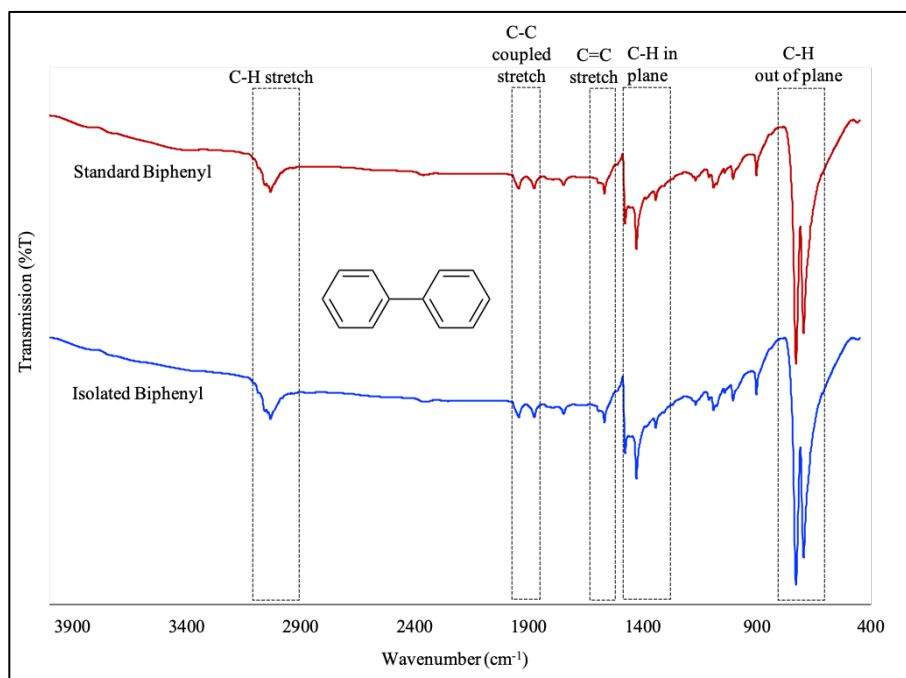


Figure 4.38 FTIR Spectra of Isolated Biphenyl and Standard Biphenyl

Table 4.35
The Main FTIR Data of Biphenyl

Compound	Wavenumber, ν (cm^{-1})				
	=C-H stretch	C-C coupled	C=C stretch	=C-H	=C-H

		stretch		in plane	(out of plane)
Standard biphenyl	3033	1876	1568	1428	728, 696
Isolated biphenyl	3033	1876	1568	1429	728, 695

The characteristic peaks of biphenyl were observed in ^1H NMR spectra and tabulated in Table 4.36. All aromatic protons were found at 7.40-7.65 ppm. The number of protons integrated was in concordance with the number of hydrogens in the proposed chemical structure. The spectrum for the isolated biphenyl was shown in Figure 4.39.

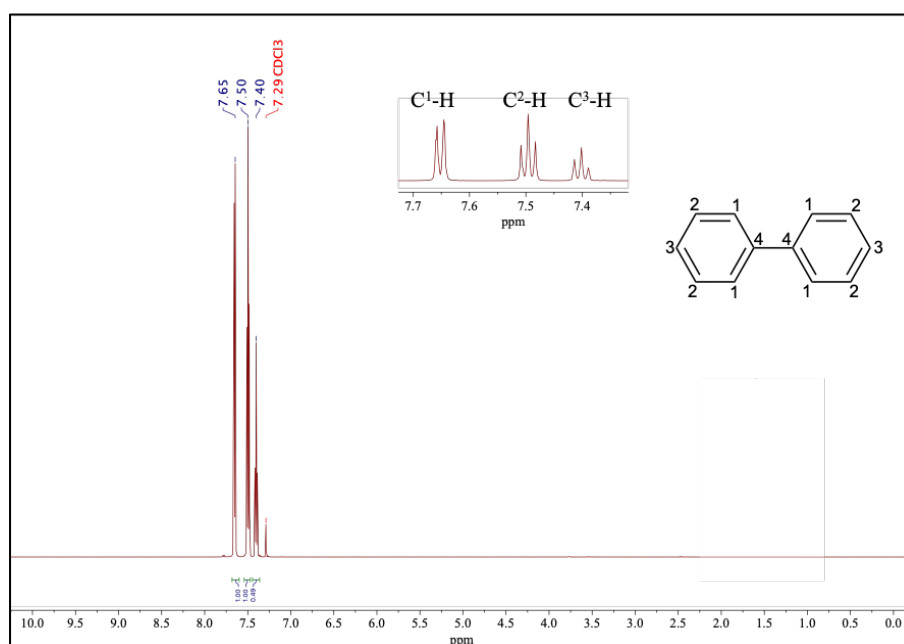


Figure 4.39 ^1H NMR of Biphenyl

Table 4.36

^1H NMR Chemical Shifts, δ (ppm) of Aromatic Protons of Biphenyl

Assignment	Chemical Shift, δ (ppm)
C ¹ -H (Ar)	7.65 (dd) 1H
C ² -H (Ar)	7.50 (td) 1H
C ³ -H (Ar)	7.40 (tt) 0.5H

Note: dd = doublet of doublet; td = triplet of doublet; tt = triplet of triplet.

^{13}C NMR spectral data of biphenyl is tabulated in Table 4.37 and the spectrum of ^{13}C NMR for isolated biphenyl is shown in Figure 4.40. The chemical shift of C-C was discovered at 141.3 ppm and aromatic carbons were found in the range of 127.2-128.8 ppm. The number of carbons integrated from the spectrum tallies with the number of carbons in the proposed chemical structure.

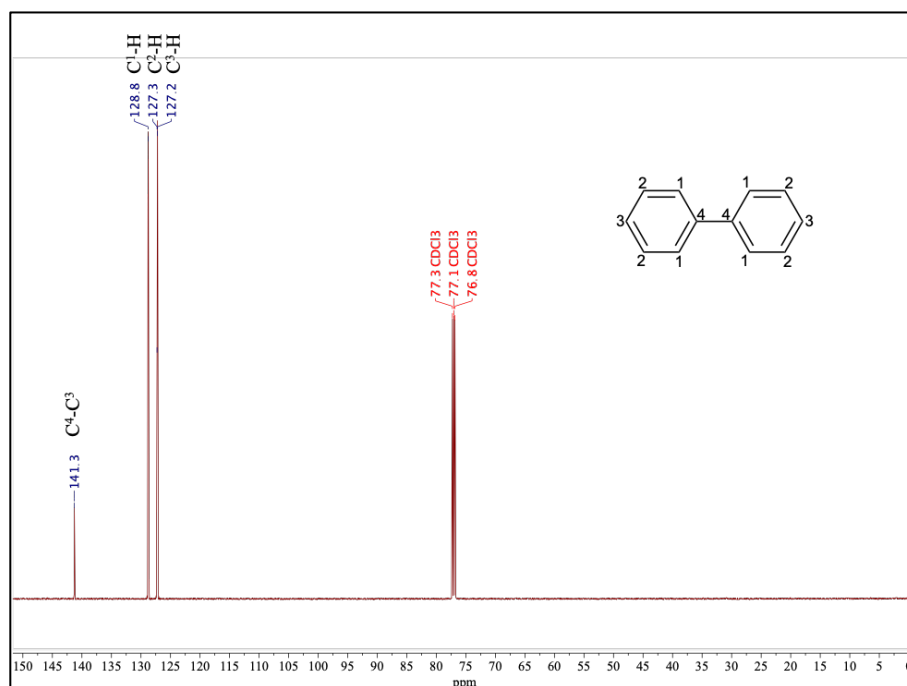


Figure 4.40 ^{13}C NMR of Biphenyl

Table 4.37

^{13}C NMR Chemical Shifts δ (ppm) of Biphenyl

Assignment	Chemical Shift, δ (ppm)
C^1 (Ar)	127.3 (s)
C^2 (Ar)	128.8 (s)
C^3 (Ar)	127.2 (s)
$\text{C}^4\text{-C}^3$	141.3 (s)

Based on the characterization from FTIR, ^1H and ^{13}C NMR of the isolated product, it can be concluded that the conversion of iodobenzene to biphenyl was successful. Figure 4.41 shows the mechanism of Stille reaction using KOH as base and Pd(II) Schiff base as catalyst (Espinet & Echavarren, 2004). KOH which is a strong base, also helps to facilitate the hydrolyze of Ar-SnBu₃ bond through the solubilization and C-Sn bond activation (Rai et al., 1995). This is crucial for the formation of a palladacycle intermediate, a key step in the reaction mechanism. The activation of the Ar-Pd-I intermediate can be enhanced by the presence of electron-donating groups on the ligand (Walther et al., 2023). For example, the methoxy group (-OCH₃) in PdBIOMe increases the electron density on the palladium center, which weakens the Ar-Pd bond and makes the intermediate more reactive. This facilitates the transmetalation and reductive elimination steps, improving the overall efficiency of the catalytic cycle.

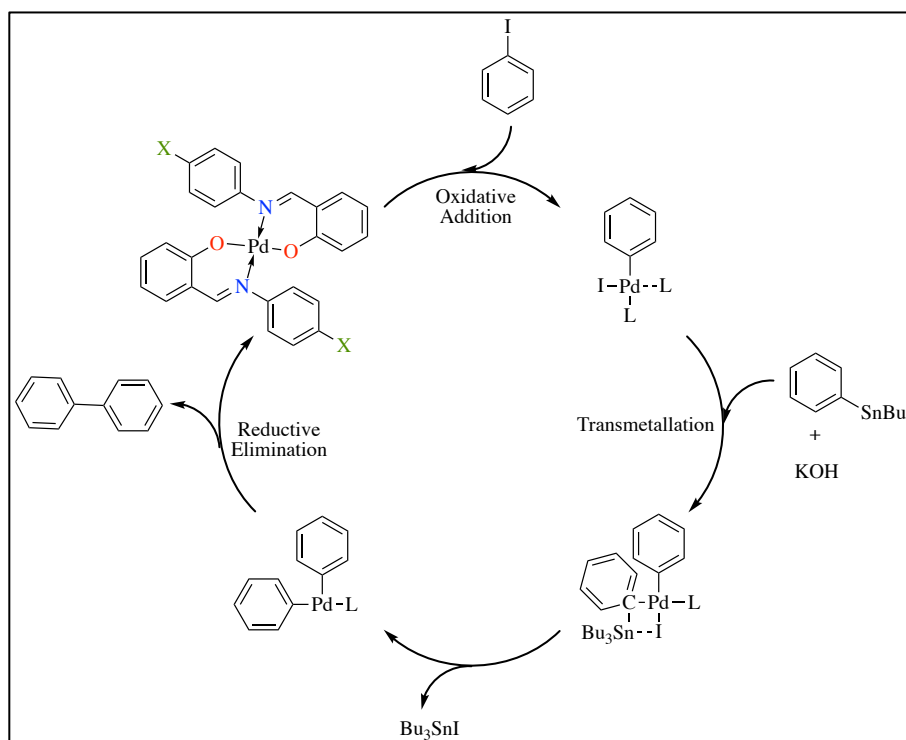


Figure 4.41 Mechanism of Stille Reaction using Pd(II) Schiff Base as Catalyst and KOH as Base

4.4 Density Functional Theory (DFT)

The theoretical findings were generated using the Gaussian09W software, and the compounds were built using GaussView 6.0 using the B3LYP method with a basis set of 6-311++G(d,p) for ligands and LANL2DZ method for metal atoms. The CIF files obtained from single crystal X-ray diffraction for B1H, B1Me, B2H, B2Me, CuB1Me, CuB2H, CuB2C, PdB1OMe, PdB2Me, PdB2OMe, and PdB2C were employed to run the density functional theory (DFT). In this context, the discussion focuses on the ligands, with particular emphasis on the intrinsic electronic stability and reactivity of their substituents, along with a comparative analysis of the corresponding Cu(II) and Pd(II) metal complexes. Electronic stability is assessed using the HOMO-LUMO energy gap, defined as the energy difference between the highest occupied and lowest unoccupied molecular orbitals. Reactivity is evaluated through global chemical descriptors including electrophilicity, chemical potential, and hardness, which reflect the tendency of the molecule to accept or donate electrons. These electronic features are critical for catalysis, as they influence the ability of the ligands and complexes to interact with substrates, facilitate electron transfer, and stabilize reaction intermediates, ultimately impacting catalytic efficiency and selectivity.

4.4.1 Frontier Molecular Orbitals (FMO)

The analysis of frontier molecular orbitals (FMO) plays an important role to study the stability of a molecule (Yu et al., 2022). The highest occupied molecular orbital (HOMO) represents electron donor ability while the lowest unoccupied molecular orbital (LUMO) represents the electron acceptor ability of the molecule (Shukla & Yadava, 2020). The electronic properties of ligands are significantly influenced by the nature of their substituents, particularly in terms of electron-withdrawing and electron-donating effects. In general, electron-donating groups decrease the HOMO-LUMO energy gap, while electron-withdrawing groups increase it due to their opposing electronic effects (El Ouafy et al., 2022). However, in the case of B2C, CuB2C, and PdB2C, the chloro substituent exhibits electron-donating behavior based on the calculated energy gap values, which is consistent with the statement by Joshi & Srivastava (2023) that chlorine can act as either an electron-donating or an electron-withdrawing group depending on the molecular environment. These HOMO-LUMO interactions are significant parameters indicating specific electron transfer in molecules, which are fundamental in catalytic reactions.

In general, molecules with large HOMO-LUMO energy gaps are generally stable with low chemical reactivity while those with small energy gaps are more conducting and polarizable, having high chemical reactivity and low kinetic stability (Hadigheh Rezvan, 2024). In contrast, in the context of catalysis, smaller HOMO-LUMO gaps become advantageous, as Ahmad et al. (2017) reported a correlation between reduced energy gaps and enhanced catalytic efficiency. Table 4.38 showed the value of HOMO, LUMO, and energy gap of the compounds, providing insights into their potential catalytic behavior.

Table 4.38
HOMO, LUMO, and Energy Gap of Compounds

Compound	Dipole moment (Debye)	E _{LUMO} (eV)	E _{HOMO} (eV)	Energy gap (eV)
B1H	2.241	-1.994	-5.890	3.896
B1Me	2.073	-1.928	-5.830	3.902
B2H	2.351	-2.089	-6.234	4.145
B2Me	2.598	-2.023	-6.110	4.087
B2C	1.951	-2.343	-6.025	3.682
CuB1Me	8.525	-2.804	-4.084	1.280

CuB2H	0.000363	-1.809	-5.504	3.695
CuB2C	0.000138	-2.085	-5.748	3.663
PdB1OMe	1.116	-2.841	-4.780	1.939
PdB2Me	0.000087	-1.796	-5.209	3.413
PdB2OMe	0.000009	-1.771	-5.191	3.420
PdB2C	0.00156	-2.118	-5.520	3.402

The calculated HOMO-LUMO energy gaps of the free ligands (B1H, B1Me, B2H, B2Me, and B2C) fall within the range of 3.682-4.145 eV as shown in Table 4.38 and Figure 4.42, indicating that the ligands possess relatively rigid and electronically stable frontier orbital structures. Among these, B2H exhibits the largest gap (4.145 eV), followed closely by B2Me (4.087 eV), whereas B2C shows the smallest gap (3.682 eV). The B1 series ligands display intermediate values, with B1H at 3.896 eV and B1Me at 3.902 eV. The calculated energy gaps suggest that the ligands have relatively rigid and electronically stable frameworks, resulting in limited reactivity in the absence of metal coordination.

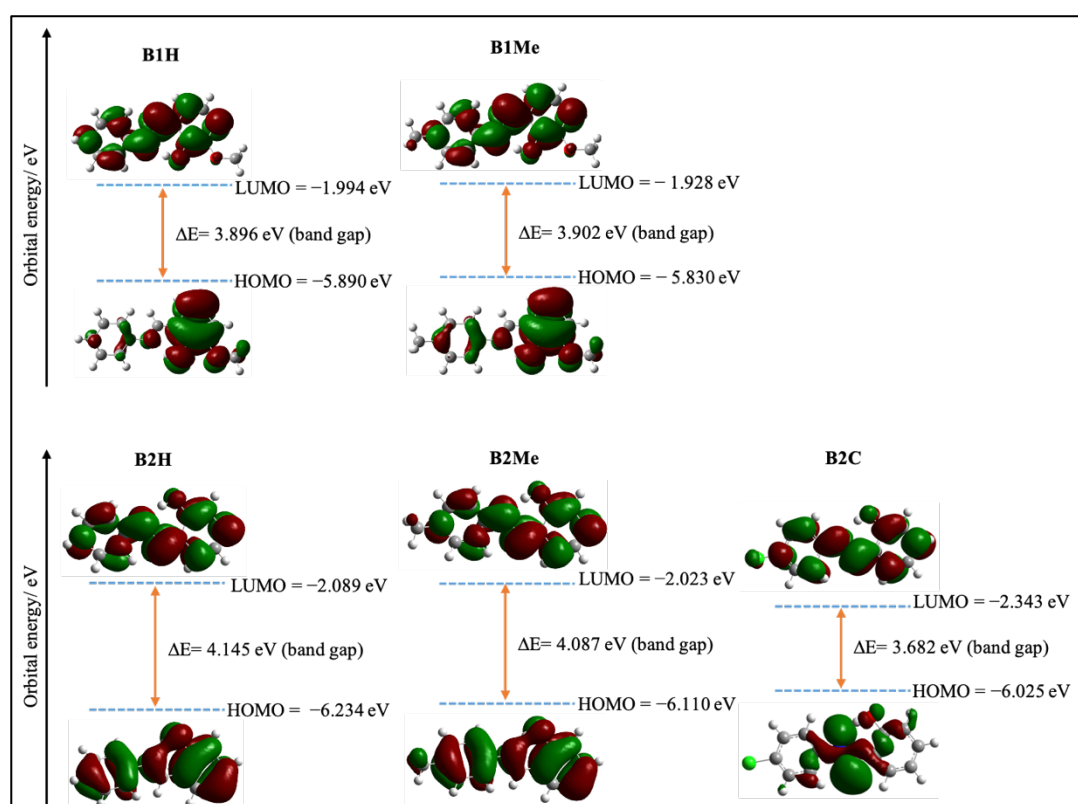


Figure 4.42 HOMO, LUMO and Energy Gap Representation of Ligands

However, the coordination to Cu(II) and Pd(II) leads to a significant reduction in the HOMO-LUMO energy gaps, which fall within the range of 1.280-3.695 eV as presented in Table 4.38, indicating enhanced electronic flexibility and reactivity of the metal complexes compared to the free ligands. This significant reduction in the HOMO-LUMO gap clearly demonstrates the strong electronic influence of metal-ligand coordination, which enhances orbital mixing, increases electronic polarizability, and facilitates charge-transfer interactions between the metal center and the ligand framework (Ahmad et al., 2017). The reduced energy gaps of the metal complexes indicate that the coordinated systems are electronically more reactive than the free ligands, and therefore better suited to participate in catalytic processes. These observations confirm that metal coordination plays a decisive role in lowering the energy gap, thereby activating the ligand structure and enabling catalytic activity that is not accessible in the free ligand state. The comparative analysis further supports the correlation between lower HOMO-LUMO gaps and higher catalytic activity observed experimentally.

In the context of Cu(II) and Pd(II) catalysts, FMO analysis allows for the correlation of computed electronic parameters with experimentally observed catalytic activities. By examining how substituents influence orbital energies and narrowing or widening the HOMO-LUMO gap, valuable insights can be gained into the structure-property relationships governing catalytic performance (Turaeva, 2020). The following discussion therefore explores the calculated frontier orbital energies of the studied complexes and evaluates how these electronic descriptors contribute to their catalytic efficiencies in Section 4.4.2. The catalytic performance of the metal complexes was partially rationalized using the calculated HOMO-LUMO energy gaps. In general, a smaller HOMO-LUMO gap is associated with higher electronic polarizability and easier participation in electron-transfer processes, which can enhance the reactivity of the complex in catalytic cycles (Miar et al., 2021).

For the Cu(II) series, the copper complex bearing both methoxy and methyl substituents which is CuB1Me has a particularly low gap (1.280 eV), while the unsubstituted (CuB2H) and chloro-substituted copper complexes (CuB2C) have much larger gaps (3.695 and 3.663 eV, respectively). The very low gap of would nominally predict high reactivity; however, the experimentally observed catalytic performance indicates that the metal identity and other factors beyond the HOMO-LUMO gap influence activity.

Therefore, although the HOMO-LUMO energy gap serves as a useful electronic descriptor for catalytic behavior, its relevance is best interpreted in terms of how energy gap magnitude influences reactivity. In particular, a smaller HOMO-LUMO gap reflects increased electronic softness and enhanced polarizability of the metal center, which facilitates charge transfer between the catalyst and reacting substrates (Ahmad et al., 2017). This effect lowers the energetic barriers for key elementary steps in the catalytic cycle such as oxidative addition and reductive elimination, thereby promoting higher catalytic activity. Consistent with this interpretation, within each metal series the complexes exhibiting the smallest HOMO-LUMO gaps show the highest catalytic activity.

Figure 4.43 shows the HOMO, LUMO and energy gap of represented Pd(II) Schiff base complexes. Within the Pd(II) series, the palladium complex bearing two methoxy substituents, which is PdB1OMe exhibits the smallest gap (1.939 eV) and accordingly shows the highest catalytic activity among the palladium derivatives, a trend that is consistent with the results discussed in Section 4.3.2. By contrast, palladium complexes with single methyl, methoxy, or chloro substituents show substantially larger gaps (PdB2Me: 3.413 eV, PdB2OMe: 3.420 eV, and PdB2C: 3.402 eV) and correspondingly lower activity. In this study Pd(II) complexes overall delivered superior catalytic results relative to Cu(II) complexes despite some copper species having comparable or smaller calculated gaps, which supports the result of catalytic study in Section 4.3.3.

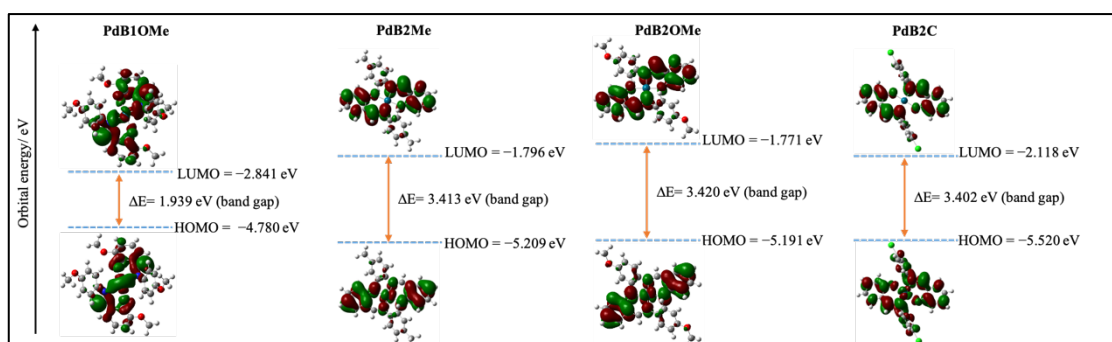


Figure 4.43 HOMO, LUMO and Energy Gap Representation of Pd(II) Schiff Base Complexes

However, the HOMO-LUMO gap alone cannot fully account for activity trends across different metal centers, since catalytic efficiency is also governed by factors such as the spatial distribution and metal character of the frontier orbitals, metal–substrate

binding strength, redox accessibility, steric constraints around the active site, and the specific rate-determining step of the reaction mechanism. To further support the structure–activity relationship, DFT-optimized geometries and key structural parameters (bond lengths and bond angles). The detailed bond length and bond angle values obtained from DFT calculations are presented in Section 4.2.7.1-4.2.7.11.

4.4.2 Global Chemical Reactivity Descriptors (GCRD)

Global Chemical Reactivity Descriptors (GCRD) method is another vital technique to understand the chemical properties of a molecule such as chemical hardness (η), chemical softness (S), chemical potential (μ), electronegativity (χ), electrophilicity index (ω), and maximum additional electric charge ($\Delta N_{\max}$), calculated from the energies of frontier molecular orbitals using density functional theory (Silva et al., 2014). The effect of substituents on the electronic properties of ligands plays a crucial role in determining their reactivity and stability in coordination chemistry. Electron-donating groups, tend to increase electron density on the ligand, thereby reducing electronegativity and chemical hardness while increasing chemical softness, whereas, electron-withdrawing groups decrease electron density on the ligand, thereby increasing electronegativity and chemical hardness while reducing chemical softness. (Dulla, 2024). On the other hand, in the context of B2C, CuB2C, and PdB2C, the chloro substituent exhibits electron-donating behavior based on the calculated values of the global chemical reactivity descriptors (GCRD). This observation aligns with the findings of Joshi & Srivastava (2023), who reported that chlorine can function as either an electron-donating or electron-withdrawing group depending on the molecular environment. Among these, chemical hardness and softness are particularly relevant to catalysis: harder molecules are less polarizable and interact less readily with substrates, while softer molecules can more easily adjust their electron density, facilitating electron transfer, stabilizing reaction intermediates, and enhancing catalytic activity (Chen et al., 2025). Table 4.39 displays the global chemical reactivity descriptors (GCRD) values of the compounds.

The ligands exhibit systematic electronic variations depending on their substituents. B1H, containing one methoxy group, shows moderate hardness and high softness, reflecting effective electron donation from the methoxy substituent. B1Me, bearing both a methyl and a methoxy group, maintains similar hardness but slightly

enhanced softness and electrophilicity, indicating a balanced electron-donating effect from the mixed substituents. B2H, which lacks substituents, is comparatively harder and more electronegative, reflecting a less electron-rich ligand framework. B2Me, with one methyl substituent, shows reduced hardness and slightly increased softness relative to B2H, consistent with the weak electron-donating nature of the methyl group. In contrast, B2C, containing a chloro substituent, exhibits the lowest softness and the highest electrophilicity and electronegativity.

Table 4.39
Global Chemical Reactivity Descriptors (GCRD) Values for Compounds

Compound	Chemical hardness, η	Chemical softness, S	Chemical potential, μ	Electronegativity, χ	Electrophilicity index, ω	$\Delta N_{\max}$
B1H	1.948	0.974	-3.942	3.942	3.989	2.024
B1Me	1.951	0.976	-3.879	3.879	3.856	1.988
B2H	2.073	1.036	-4.162	4.162	4.178	2.008
B2Me	2.044	1.022	-4.067	4.067	4.046	1.990
B2C	1.841	0.921	-4.184	4.184	4.754	2.273
CuB1Me	0.640	0.320	-3.444	3.444	9.267	5.381
CuB2H	1.848	0.924	-3.657	3.657	3.618	1.979
CuB2C	1.332	0.666	-3.917	3.917	5.759	2.941
PdB1OMe	0.970	0.485	-3.811	3.811	7.486	3.929
PdB2Me	1.707	0.854	-3.503	3.503	3.594	2.052
PdB2OMe	1.710	0.855	-3.481	3.481	3.543	2.036
PdB2C	1.701	0.851	-3.819	3.819	4.287	2.245

The catalytic performance of metal complexes in the Stille reaction is strongly governed by their electronic characteristics, which control the efficiency of oxidative addition, transmetalation, and reductive elimination (Blanchard et al., 2005). A comparison of Cu(II) Schiff base complexes (CuB1Me, CuB2H, CuB2C) and Pd(II) Schiff base complexes (PdB1OMe, PdB2Me, PdB2OMe, PdB2C) shows that palladium complexes are clearly superior as catalysts, consistent with palladium's well-known role in cross-coupling reactions.

Pd(II) complexes exhibit consistently higher global softness values ($S = 0.485$ - 0.855 eV) than the corresponding Cu(II) complexes ($S = 0.320$ - 0.924 eV), indicating a more polarizable and electronically flexible metal center (Adejumo et al., 2020). This enhanced softness is critical for efficient catalysis in the Stille cross-coupling reaction, as it enables the catalyst to readily accommodate electron

density fluctuations that occur during the catalytic cycle. In particular, soft metal centers favor strong yet reversible interactions with π -systems and organometallic intermediates, facilitating oxidative addition of the organic halide, stabilizing transmetalation intermediates, and promoting smooth reductive elimination to form the C-C bond (Ahmad et al., 2017).

The enhanced softness of palladium originates in part from relativistic effects that lead to contraction and stabilization of its d orbitals, thereby improving metal-ligand backbonding and lowering the energetic cost of interconversion between Pd(II) and Pd(0) oxidation states (Pal et al., 2021). This electronic flexibility allows palladium to stabilize both electron-rich oxidative addition intermediates and reduced Pd(0) species, which are essential for sustained catalytic cycle. In contrast, copper complexes possess higher hardness and more localized frontier orbitals, limiting their ability to accommodate the electron density fluctuations inherent in C-C bond forming reactions. As a result, Cu(II) complexes are less capable of accommodating the continuous electron flow required for oxidative addition and transmetalation steps, which limits their participation in classical cross-coupling pathways.

The electrophilicity index provides additional insight into how efficiently a complex will promote oxidative addition, the typical rate-determining step in the Stille mechanism (Shaikh et al., 2012). Palladium complexes show moderate to high electrophilicity ($\omega = 3.543\text{--}7.486$ eV), placing them in the optimal range for activating aryl halides without becoming overly electron-deficient. In contrast, copper complexes exhibit a much broader range of electrophilicity. Notably, CuB1Me shows a very high electrophilicity value ($\omega = 9.267$ eV). However, the combination of extreme electrophilicity with high chemical hardness makes this species poorly suited for subsequent steps in the catalytic cycle. Consequently, even when Cu(II) complexes exhibit high electrophilicity, their relatively low electronic softness limits their ability to stabilize the soft organometallic intermediates formed during the transmetalation step. This electronic mismatch increases activation barriers, slows catalytic turnover, and ultimately leads to reduced catalytic efficiency compared with palladium-based systems. Consequently, even when Cu(II) complexes exhibit high electrophilicity, their relatively low electronic softness limits their ability to stabilize the soft organometallic intermediates formed during the transmetalation step. This electronic mismatch increases activation barriers, slows catalytic turnover, and ultimately leads to reduced catalytic efficiency compared with palladium-based systems. As a result, while such a

copper complex may initially favor oxidative addition, it struggles to adapt electronically during later stages of the catalytic cycle. In particular, its limited softness hampers efficient transmetalation with soft organotin reagents and destabilizes key intermediates, leading to sluggish progression toward product formation.

Palladium complexes, by comparison, achieve a favorable balance between electrophilicity and softness. This balance enables efficient oxidative addition followed by smooth transmetalation and low barrier for reductive elimination (Liu et al., 2021). The suitability of palladium for these sequential steps is further supported by their chemical potential values ($\mu = -3.48$ to -3.82 eV), which indicate a strong yet flexible ability to accept electron density. Importantly, this electronic flexibility facilitates reversible redox transformation between Pd(0) and Pd(II) oxidation states, allowing palladium catalysts to sustain continuous turnover and high catalytic efficiency.

Among the palladium catalysts examined, PdBIOMe emerges as the most effective, and its superior performance is directly reflected by its optimized electronic parameters. PdBIOMe possesses the highest electrophilicity index ($\omega = 7.486$ eV) among the Pd series, supporting rapid oxidative addition and strong activation of aryl halide substrates. At the same time, its softness ($S = 0.485$ eV) remains within the ideal range, balancing intermediate stabilization and efficient organostannane transmetalation. Additionally, PdBIOMe exhibits the highest $\Delta N_{\max}$ value (3.929 eV) of all palladium complexes, signifying an excellent capacity to accept electron density during oxidative addition and then release it during reductive elimination. $\Delta N_{\max}$ parameter, which represents the maximum number of electrons a ligand can accept, influences the stability of the catalytic intermediate (Kaya & Putz, 2022). This redox flexibility is essential for maintaining high turnover frequency in catalytic cycles. The methoxy substituent plays a key role as well: its electron-donating resonance effect enriches electron density at the metal center, which accelerates reductive elimination, where the final and product-forming step of the Stille reaction. Thus, PdBIOMe achieves an optimal electronic balance through a synergistic combination of moderate softness, high electrophilicity, a favorable chemical potential, and effective ligand-derived electron donation, supporting the findings presented in Section 4.3.2.

4.4.3 Molecular Electrostatic Potential (MEP)

The molecular electrostatic potential (MEP) analysis is one of the useful tools to predict the electrophilic and nucleophilic sites in a molecule and their intermolecular interactions (Shukla & Yadava, 2020). The MEP surface of the compounds were generated from their optimized structure obtained by B3LYP/6-311++G(d,p) for the ligands and B3LYP/LANL2DZ level of the theory for the complexes. The different colour code in the plot represents the electrostatic potential regions in which the red colour is nucleophilic (electron rich) and the blue colour is electrophilic (electron deficient) (Uzun et al., 2019). The blue region typically represents region of positive potential, while the red region represents areas of negative potential. In the MEP diagram shown in Figure 4.44, the reactive sites of all the compounds are found at the oxygen atom bonded with the metal centre which is represented in red and holds the most negative potential spots. This nucleophilic site is distributed at the oxygen atom indicates the strongest attraction for electrophilic attack. In catalysis, electron-rich metal centers (negative MEP) promote oxidative addition by attacking electrophilic substrates like aryl halides (Suresh et al., 2022). It resulted in improving the catalytic activity.

The most positive potential spots in blue coloured regions of which are found in B2C, CuB2C and PdB2C are located on the hydrogen atom of the carbon attached to nitrogen atom in the ligands, representing electrophilic sites that possess the most attractive region for nucleophilic attacks due to the presence of the chloro substituent. Chlorine is a highly electronegative atom, meaning it strongly attracts electrons. When chlorine is attached to a molecule, it tends to draw electron density away from the surrounding atoms, creating a region of lower electron density (positive potential, blue) around the chlorine atom. However, the blue coloured regions are not seen at the compounds with methyl and methoxy groups. This absence can be attributed to the lack of regions with low electron density, which are typically associated with positive electrostatic potential (Raftani et al., 2021). A molecule, where electron density is relatively high or the charge distribution is more delocalized, the MEP map may predominantly show red, yellow, or green regions corresponding to negative and intermediate electrostatic potentials, while blue regions may be absent or very faint (Kaavin et al., 2024).

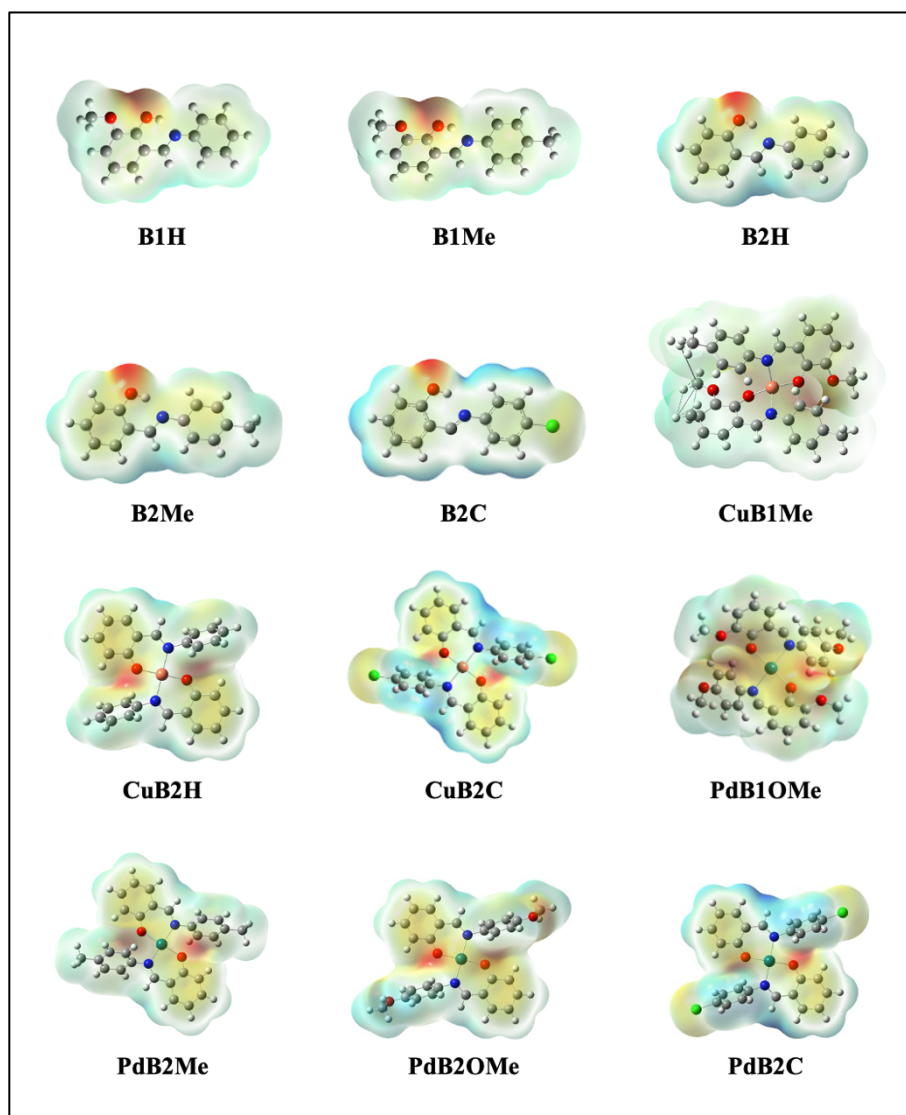


Figure 4.44 The MEP Map of the Compounds Calculated from DFT Approach

4.5 Antibacterial Activity

B1 and B2 series ligands and its respective complexes were screened for antibacterial properties by using disk diffusion method. A total of four bacteria strains were used and 1% ciprofloxacin was used as positive control. The Gram-positive bacteria; *S. aureus* and *B. subtilis* and Gram-negative bacteria; *E. coli* and *S. typhimurium* were used for both series of compounds. The zone of inhibition formed due to the synthesized compounds being introduced to the bacteria strain determine the potency of its antibacterial properties (Hossain, 2024).

4.5.1 Solubility Study

Both B1 and B2 series of Schiff base compounds have been tested in the solubility test to determine the ability of the compounds to dissolve in a solvent. Various solvents which are acetonitrile (ACN), triethylamine (TEA), dimethyl sulfoxide (DMSO), ethyl acetate (EA), dimethylformamide (DMF), acetone, tetrahydrofuran (THF), and acetic acid (AA) have been used to identify the best solvent for conducting antimicrobial studies. In Table 4.40, the best solvents for B1 series Schiff base complexes which demonstrated the highest solubility or partial solubility were selected for antibacterial study (10% DMF, 5% DMF, ACN, THF, AA). Meanwhile, the best solvents for B2 series of Schiff base compounds which demonstrated the highest solubility or partial solubility were selected for antibacterial study (10% DMF, 5% TEA, 10% AA) as shown in Table 4.41. Antibacterial study was done in triplicate and result were taken after 24 hours incubation by the average of the three readings.

Table 4.40
Solubility Test for B1 Series Ligands and Its Respective Metal Complexes

Compounds	Solvents															
	ACN		TEA		DMSO		EA		DMF		Acetone		THF		AA	
	100%	10%	100%	10%	100%	10%	100%	10%	100%	10%	100%	10%	100%	10%	100%	10%
B1H	SS	SS	SS	IS	SS	SS	SS	IS	SS	PS	SS	SS	SS	SS	SS	SS
NiB1H	SS	SS	SS	IS	SS	PS	SS	IS	SS	PS	PS	PS	SS	PS	SS	SS
CuB1H	SS	PS	SS	IS	SS	PS	SS	IS	PS	PS	SS	PS	SS	PS	SS	SS
PdB1H	SS	PS	SS	IS	SS	PS	SS	IS	SS	PS	SS	PS	SS	PS	SS	SS
B1Me	SS	PS	SS	IS	PS	PS	SS	IS	SS	PS	SS	PS	SS	PS	SS	SS
NiB1Me	SS	SS	SS	IS	SS	PS	SS	IS	SS	PS	SS	PS	SS	PS	SS	SS
CuB1Me	SS	PS	SS	IS	SS	PS	SS	IS	PS	PS	SS	PS	SS	PS	SS	SS
PdB1Me	SS	PS	SS	IS	PS	PS	SS	IS	PS	PS	PS	PS	SS	PS	SS	SS
B1OMe	SS	PS	SS	IS	PS	PS	SS	IS	SS	PS	SS	PS	SS	PS	SS	SS
NiB1OMe	PS	PS	SS	IS	SS	PS	SS	IS	PS	PS	PS	PS	PS	PS	SS	SS
CuB1OMe	PS	PS	SS	IS	PS	PS	SS	IS	PS	PS	SS	PS	SS	PS	SS	SS
PdB1OMe	SS	PS	SS	IS	PS	PS	SS	IS	SS	PS	PS	PS	SS	PS	SS	SS
B1C	SS	PS	SS	IS	PS	PS	SS	IS	SS	PS	SS	PS	SS	PS	SS	SS
NiB1C	SS	PS	SS	IS	PS	PS	SS	IS	SS	PS	SS	PS	SS	PS	SS	SS
CuB1C	SS	PS	SS	IS	PS	PS	SS	IS	PS	PS	SS	PS	SS	PS	SS	SS
PdB1C	SS	PS	SS	IS	PS	PS	SS	IS	SS	PS	PS	PS	SS	PS	SS	SS
B1N	SS	PS	SS	IS	SS	PS	SS	IS	SS	PS	SS	PS	SS	PS	SS	SS
NiB1N	SS	PS	SS	IS	PS	PS	SS	IS	PS	PS	PS	PS	PS	PS	SS	SS
CuB1N	SS	SS	SS	IS	PS	PS	SS	IS	PS	PS	PS	PS	PS	PS	SS	SS
PdB1N	SS	PS	SS	IS	PS	PS	SS	IS	PS	PS	PS	PS	PS	PS	SS	SS

Note: SS = Soluble Solution; PS = Partial Soluble; IS = Insoluble Solution.

Table 4.41

Solubility Test for B2 Series Ligands and Its Respective Metal Complexes

Compounds	Solvents															
	ACN		TEA		DMSO		EA		DMF		Acetone		THF		AA	
	100%	10%	100%	10%	100%	10%	100%	10%	100%	10%	100%	10%	100%	10%	100%	10%
B2H	SS	PS	SS	SS	SS	PS	SS	IS	SS	SS	SS	SS	SS	SS	SS	SS
NiB2H	SS	SS	PS	PS	SS	PS	SS	IS	IS	IS	PS	PS	PS	PS	SS	IS
CuB2H	SS	SS	PS	PS	SS	PS	SS	IS	SS	PS	SS	PS	SS	SS	SS	SS
PdB2H	SS	SS	PS	PS	SS	PS	SS	IS	SS	IS	SS	PS	SS	PS	SS	PS
B2Me	PS	PS	SS	SS	SS	PS	SS	IS	SS	IS	SS	PS	SS	SS	SS	SS
NiB2Me	SS	SS	PS	PS	SS	PS	SS	IS	IS	IS	PS	SS	SS	PS	SS	SS
CuB2Me	SS	SS	SS	PS	SS	PS	SS	IS	IS	IS	PS	PS	SS	PS	SS	SS
PdB2Me	SS	SS	PS	PS	SS	PS	SS	IS	SS	PS	PS	SS	SS	PS	SS	SS
B2OMe	SS	PS	SS	SS	SS	PS	SS	IS	SS	PS	SS	PS	SS	SS	SS	SS
NiB2OMe	SS	PS	PS	PS	SS	PS	SS	IS	SS	PS	SS	PS	SS	PS	SS	SS
CuB2OMe	PS	PS	PS	PS	SS	PS	SS	IS	SS	PS	IS	PS	SS	PS	SS	SS
PdB2OMe	PS	PS	PS	PS	SS	PS	SS	IS	SS	PS	PS	PS	SS	PS	SS	IS
B2C	SS	SS	SS	SS	SS	SS	SS	IS	SS	SS	SS	PS	SS	SS	SS	SS
NiB2C	SS	PS	PS	PS	SS	PS	SS	SS	SS	PS	SS	PS	SS	PS	SS	IS
CuB2C	PS	PS	PS	PS	SS	PS	SS	IS	SS	SS	IS	IS	SS	PS	SS	SS
PdB2C	PS	PS	PS	PS	SS	PS	SS	IS	SS	PS	PS	PS	SS	PS	IS	IS
B2N	SS	SS	SS	PS	SS	PS	SS	IS	SS	PS	SS	SS	SS	SS	SS	SS
NiB2N	SS	SS	PS	PS	SS	SS	SS	IS	SS	PS	SS	SS	SS	PS	SS	SS
CuB2N	PS	PS	PS	PS	SS	PS	SS	IS	PS	PS	SS	IS	SS	PS	SS	SS
PdB2N	PS	PS	PS	PS	SS	PS	SS	IS	SS	PS	PS	PS	SS	PS	IS	IS

Note: SS = Soluble Solution; PS = Partial Soluble; IS = Insoluble Solution.

4.5.2 Interpretation of Antibacterial Results

The result of inhibition against the B1 and B2 series compounds was shown in Table 4.42 and Table 4.43, respectively. Based on the diameter of the inhibition, it was noted that none of the compounds demonstrated any zone of inhibition. For positive control, 1% ciprofloxacin was used, in which the average zone of inhibition was $29 \pm 2.8\text{mm}$.

The absence of antibacterial activity in Schiff base compounds can be attributed to several interrelated structural and chemical factors. One major reason was different types of bacteria have different mechanism of resistance thus the Schiff base complexes reacted differently to different types of bacteria; Gram-positive and Gram-negative (Soliman et al., 2014). The presence of metal ions in the ligands somehow gives effect to the solubility of these complexes (Santos et al., 2014). Therefore, this factor of insolubility directly influences the ability to exert their antibacterial properties. Moreover, even though the compounds were soluble in respective solvents, the interaction between the metal complexes with solvent disturbed the ability to inhibit the tested bacteria (Woznicka et al., 2025). Despite the different polarity used the solubility of these compounds were still not satisfactory. In which most compounds did not dissolve in these solvents or dissolve partially or even demonstrated inconsistent solubility.

Breijyeh et al. (2020) stated that structural differences between Gram-positive and Gram-negative microorganisms affect their sensitivity to the extract. Typically, Gram-positive bacteria result in a larger zone of inhibition compared to Gram-negative bacteria. This discrepancy arises from the complex structures of Gram-negative bacteria, such as the outer membrane and thin peptidoglycan layer, which contribute to the resistance in the zone of inhibition diameter observed for Gram-negative bacteria.

Schiff base ligands can form complexes with various metal ions. The antibacterial activity can vary depending on the type of metal ion and the stability of the resulting complex. The solubility in lipids plays a crucial role in determining the antibacterial effectiveness (Arellano et al., 2023). When a chelation process occurs, the polarity of metal ion decreases because of the overlapping orbitals of the ligand and the partial sharing of the metal ion's positive charge with the donor groups (Uivarosi, 2013). This leads to greater dispersion of π -electrons throughout the chelate ring, consequently augmenting the lipid friendly nature of the metal complexes.

The presence of bulky groups in the ligand structure might hinder the binding or interaction with microbial targets, potentially affecting their antibacterial properties. Previous study by Naqvi et al. (2019) suggested that smaller particles normally have larger surface to volume ratio which offers more efficient mean for antibacterial activities. The mode of action of antibacterial compounds can vary. Some compounds may disrupt cell membranes, interfere with metabolic pathways, or inhibit crucial enzymes in microorganisms.

Table 4.42
Relative Diameter of Inhibition Zone Exhibit by B1 Series Ligands and Its Metal Complexes

Compounds	Diameter of inhibition (mm)			
	Gram-negative		Gram-positive	
	<i>E. coli</i>	<i>S. typhimurium</i>	<i>S. aureus</i>	<i>B. subtilis</i>
B1H	0	0	0	0
NiB1H	0	0	0	0
CuB1H	0	0	0	0
PdB1H	0	0	0	0
B1Me	0	0	0	0
NiB1Me	0	0	0	0
CuB1Me	0	0	0	0
PdB1Me	0	0	0	0
B1OMe	0	0	0	0
NiB1OMe	0	0	0	0
CuB1OMe	0	0	0	0
PdB1OMe	0	0	0	0
B1C	0	0	0	0
NiB1C	0	0	0	0
CuB1C	0	0	0	0
PdB1C	0	0	0	0
B1N	0	0	0	0
NiB1N	0	0	0	0
CuB1N	0	0	0	0
PdB1N	0	0	0	0

Table 4.43
Relative Diameter of Inhibition Zone Exhibit by B2 Series Ligands and Its Metal Complexes

Compounds	Diameter of inhibition (mm)			
	Gram-negative		Gram-positive	
	<i>E. coli</i>	<i>S. typhimurium</i>	<i>S. aureus</i>	<i>B. subtilis</i>
B2H	0	0	0	0
NiB2H	0	0	0	0
CuB2H	0	0	0	0
PdB2H	0	0	0	0
B2Me	0	0	0	0
NiB2Me	0	0	0	0
CuB2Me	0	0	0	0
PdB2Me	0	0	0	0
B2OMe	0	0	0	0
NiB2OMe	0	0	0	0
CuB2OMe	0	0	0	0
PdB2OMe	0	0	0	0
B2C	0	0	0	0
NiB2C	0	0	0	0
CuB2C	0	0	0	0
PdB2C	0	0	0	0
B2N	0	0	0	0
NiB2N	0	0	0	0
CuB2N	0	0	0	0
PdB2N	0	0	0	0

4.5.3 Toxicity Assessment

Toxicity tests were conducted using acetic acid against *B. subtilis* and *S. typhimurium* and triethylamine (TEA) against *S. aureus* and *E. coli*. The antibacterial study using this solvent at 10% concentration showed some activity. All concentrations of the acetic acid showed inhibition activity except 0.05% concentration which exhibited no inhibition. Table 4.44 shows the toxicity test of acetic acid with different concentrations against *B. subtilis* and *S. typhimurium* and it shows the lowest concentration that did not inhibit the tested bacteria was 0.05% acetic acid.

Meanwhile, the antibacterial study of triethylamine at 10% concentration showed some activity in Table 4.45. The toxicity test of TEA is demonstrated in Figure 4.45 for showing the zone of inhibition against the selected bacteria. The lowest concentration that did not inhibit the tested bacteria was 5% TEA. The average zone of inhibition for 5% TEA on *S. aureus* and *E. coli* that could be seen on the plate is 11.33 ± 0.58 mm.

However, the negative control also exhibited a zone of inhibition using these solvents did not show any activity. Therefore, this test was conducted to determine the toxicity of the solvent against the tested bacteria.

Table 4.44

Toxicity Test of Acetic Acid with Different Concentrations against *B. subtilis* and *S. typhimurium*

The concentration of acetic acid (%)	Bacteria	
	<i>B. subtilis</i> (Gram-positive bacteria)	<i>S. typhimurium</i> (Gram-negative bacteria)
10	Form ZOI: Successfully inhibit.	Form ZOI: Successfully inhibit.
5	Form ZOI: Successfully inhibit.	Form ZOI: Successfully inhibit.
2.5	Form ZOI: Successfully inhibit.	Form ZOI: Partially inhibit.
1.0	Form ZOI: Successfully inhibit.	Form ZOI: Partially inhibit.
0.5	Form ZOI: Successfully inhibit.	Form ZOI: Partially inhibit.
0.1	-	-
0.05	-	-

Note: ZOI = Zone of inhibition.

Table 4.45

Toxicity Test of TEA with Different Concentrations against *S. aureus* and *E. coli*

The concentration of TEA (%)	Bacteria	
	<i>S. aureus</i> (Gram-positive bacteria)	<i>E. coli</i> (Gram-negative bacteria)
10	Form ZOI: Successfully inhibit.	Form ZOI: Successfully inhibit.
5	Form ZOI: Successfully inhibit.	Form ZOI: Successfully inhibit.
2.5	-	-
1.0	-	-
0.5	-	-
0.1	-	-
0.05	-	-

Note: ZOI = Zone of inhibition.

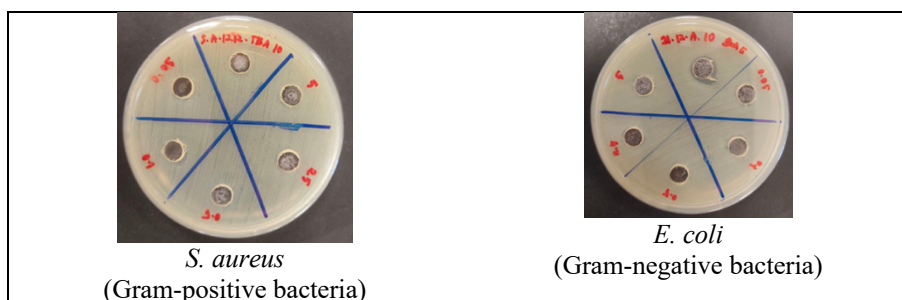


Figure 4.45 Toxicity Test of 5% TEA against *S. aureus* and *E. coli*

CHAPTER 5

CONCLUSION

5.1 Conclusion

In summary, ten bidentate Schiff base ligands (one new) were successfully synthesized and characterized, namely two series of ligands; B1 series derived from *ortho*-vanillin (B1H, B1Me, B1OMe, B1C, and B1N) and B2 series derived from salicylaldehyde (B2H, B2Me, B2OMe, B2C, and B2N). These ligands, incorporating various substituents (H, CH₃, OCH₃, Cl, and NO₂), were coordinated with Ni(II), Cu(II), and Pd(II) salts, resulting in the formation of 10 Ni(II) complexes (nine new), 10 Cu(II) complexes (four new), and 10 Pd(II) complexes (six new) using conventional technique and had a moderate to good percentage yield of 60.8-98.2%. Both the ligands and their respective metal complexes were intensely colored and exhibited stability under ambient conditions. Their characterization was performed using elemental analysis (C, H, N), melting point determination, molar conductivity, magnetic susceptibility balance (MSB) studies, FTIR, ¹H and ¹³C NMR, as well as UV-Visible spectroscopy.

All synthesized compounds were comprehensively characterized using physicochemical and spectroscopic techniques. The experimental CHN values for carbon, hydrogen, and nitrogen for elemental analysis were in close agreement with the calculated percentages, supporting the successful synthesis of the complexes and validating the proposed structure. All compounds exhibited non-electrolytic behaviour, as evidenced by their low molar conductivity values. In FTIR spectra, the $\nu(\text{C}=\text{N})$, $\nu(\text{C}-\text{N})$, and $\nu(\text{C}-\text{O})$ stretching frequencies of the ligands shifted to lower wavenumbers upon complexation, indicative of electron donation from the azomethine nitrogen and phenolic oxygen atoms to the vacant metal orbitals. The appearance of weak absorptions attributable to M-N and M-O vibrations provided further confirmation of coordination for these findings. ¹H NMR spectra revealed the disappearance of the phenolic -OH signal and a downfield shift of the HC⁷=N signals, corroborating the involvement of both donor sites in complexation. In addition, the UV-Visible spectra of the complexes exhibited bathochromic shifts in the $\pi-\pi^*$ and $n-\pi^*$ transitions of the C=N chromophore, consistent with metal-ligand interaction through the azomethine nitrogen and phenolic oxygen donors.

Single crystal X-ray diffraction confirmed eleven structures, comprising four ligands (B1H, B1Me, B2H, B2Me) and seven complexes (CuB1Me, CuB2H, CuB2C, PdB1OMe, PdB2Me, PdB2OMe, PdB2C), of which six of them are new compounds. It was revealed that all Cu(II) and Pd(II) complexes adopted square planar geometry. These results are in good agreement with the magnetic susceptibility measurements, which confirmed the paramagnetic nature of the Cu(II) complexes and the diamagnetic behavior of the Pd(II) complexes. In the case of Ni(II), complexes with unpaired electrons exhibited paramagnetic behavior and adopted a tetrahedral geometry, whereas Ni(II) complexes with no unpaired electrons were diamagnetic and favored a square planar geometry.

The synthesized Ni(II), Cu(II), and Pd(II) complexes were evaluated as catalysts in the Stille reaction between iodobenzene and tributylphenyltin in DMSO, using KOH as the base at 100 °C with a catalyst loading of 2.0 mmol%. These conditions were established following optimization studies, which involved varying different parameters, including temperatures (30 °C, 60 °C, 80 °C, and 100 °C), bases selection (K₂CO₃, KOH, and triethylamine), and amounts of catalysts (0.5, 1.0, 1.5, and 2.0 mmol%). The reaction afforded two products with high selectivity toward biphenyl as the major product and iodotributyltin as a minor byproduct. Biphenyl was detected at 8.894 min and iodotributyltin at 11.566 min in chromatogram, consistent with their standards. The highest conversion of iodobenzene was obtained under optimized conditions of KOH, 2.0 mmol%, and 100 °C.

Among the metal complexes, Pd(II) complexes exhibited superior catalytic performance, achieving complete conversion of iodobenzene within 60 minutes compared to Ni(II) and Cu(II) complexes. While Ni(II) complexes demonstrated reasonable catalytic efficiency, they outperformed Cu(II) complexes. Despite the limited research on the role of transition metals in the Stille reaction, this research provides evidence that catalysts other than palladium can act as effective alternatives. These findings not only expand the scope of the reaction but also open new opportunities for developing cost-effective and sustainable catalytic systems. These findings expand the scope of the Stille reaction and offer new opportunities for more sustainable and sustainable catalytic activity.

Complexes bearing electron-donating group namely, PdB1OMe was found to be the most effective catalyst than those bearing electron-withdrawing groups, achieving 100% conversion under optimized conditions. A slower catalytic activity was

also observed in the unsubstituted complex, PdBIH. Furthermore, characterization of the isolated biphenyl product revealed no traces of unwanted byproducts or contaminants. The Stille reaction between iodobenzene and tributylphenyltin using the optimum reaction conditions (KOH, 100 °C, and 2.0 mmol%) at 60 minutes catalyzed by PdBIOMe afforded a white solid of biphenyl with a yield of 41.9%.

The optimized geometries and electronic parameters obtained through DFT calculations were consistent with the single crystal X-ray diffraction data, confirming the reliability of the computational approach. Analysis of the HOMO-LUMO energy gaps provided insights into the relative stability and reactivity of the compounds, with narrower gaps indicating higher reactivity. These electronic features were directly correlated with the catalytic studies, supporting the experimental observation that compound effects significantly influence catalytic efficiency. DFT supported that PdBIOMe was the most effective catalyst by indicating a small value of HOMO-LUMO gap (1.939 eV) and high value of electrophilicity (7.039 eV) indicating a greater ability to accept electrons, which can enhance catalytic activity. The bond lengths and angles of the optimized structures were compared to the experimental values, and both datasets fell within the expected ranges. Overall, the DFT results complemented the experimental findings and contributed to a deeper understanding of the structure-activity relationships influencing the catalytic performance of the complexes.

The antibacterial evaluation of the synthesized Schiff base complexes revealed that none of the compounds produced a measurable inhibition zone against any of the tested bacterial strains, whereas the positive control, ciprofloxacin (1%), exhibited a strong inhibitory effect with an average zone of 29 ± 2.8 mm. The absence of antibacterial activity among the Schiff base derivatives can be attributed to a combination of chemical and biological factors. Variations in resistance mechanisms between Gram-positive and Gram-negative bacteria likely affected their susceptibility, while coordination of Ni(II), Cu(II), and Pd(II) ions to the ligands altered essential physicochemical parameters. In particular, the formation of neutral, less polar complexes reduced aqueous solubility and overall bioavailability, limiting membrane permeability and hindering penetration into bacterial cells. These characteristics, together with deviations from Lipinski's Rule of Five such as increased molecular weight, elevated lipophilicity, and an imbalanced hydrogen-bonding profile may have further restricted interaction with vital biomolecular targets, including bacterial

enzymes and nucleic acids. Collectively, these factors account for the lack of observable antibacterial activity and indicate that structural modification or ligand optimization will be necessary to improve the biological potential of these metal-Schiff base complexes.

5.2 Recommendations

There are a few recommendations that can be made to improve and make further progress in this study. One of the recommended approaches for synthesizing Schiff base and their metal complexes is the utilization of microwave-assisted techniques. This method significantly reduces the reaction time compared to conventional heating processes while requiring little to no solvent, making it a more environmentally friendly option. Additionally, the microwave-assisted technique eliminates the necessity for direct external heating, thereby preventing excessive thermal stress on reactants, and removes the need for water chilling systems, which simplifies the overall experimental setup. As a result, this approach enhances efficiency, improves reproducibility, and aligns with green chemistry principles, making it a viable strategy for sustainable synthetic applications and is directly parallel with Sustainable Development Goal 7 (Affordable and Clean Energy) and Sustainable Development Goal 12 (Responsible Consumption and Production) as mentioned in 1.5, which emphasizes resource efficiency, waste reduction, and the adoption of cleaner production methods.

Due to the partial solubility of compound in the deuterated solvent, some NMR data could not be fully collected, resulting in incomplete spectral resolution and limiting structural characterization. The limited solubility resulted in weak signal intensity, or peaks may not appear at all, making peak identification and analysis more difficult. To overcome this drawback, solid-state NMR can be considered as an alternative analytical technique, as it allows direct analysis of the compound in its crystalline or solid form without requiring complete dissolution.

Future research should focus on systematically investigating earth-abundant transition metals as potential substitutes for palladium in the Stille reaction. More detailed studies are needed to better understand how these metals actually work in the reaction, while optimization of reaction conditions including solvents, ligands, and temperature that could help improve their performance. Moreover, further work should evaluate the environmental and economic advantages of adopting non-palladium

catalysts, particularly in large-scale applications, and explore an expanded substrate scope to assess the generality and limitations of these alternative catalytic study.

The optimization process can be refined by adjusting reaction conditions, such as using water or a water-organic solvent mixture at ambient temperature. This approach aligns with the growing emphasis on greener synthetic methods. To enhance the catalytic aspect, immobilizing the catalyst onto solid supports like MCM-41, zeolite, graphene, or chitosan offers a practical solution. Heterogenization improves catalyst recyclability and reusability by facilitating easier separation from the reaction mixture, which is particularly advantageous when employing costly metals like palladium.

The isolation of Stille coupling products can be performed for all complexes to establish the correlation between the reactant consumption and product formation. A kinetic study of the catalyst can provide insights into the reaction order and any intermediate species formed during the reaction. Additionally, these complexes can be evaluated for their catalytic potential as catalyst in other coupling reactions, including carbonylation, Heck, Suzuki, Kumada, Hiyama, Negishi, and Sonogashira.

Future studies should focus on modifying the Schiff base ligands to improve solubility, membrane permeability, and compliance with Lipinski's Rule of Five, thereby enhancing the biological activity of their metal complexes. Exploration of alternative metal ions, mixed-ligand systems, and computational approaches such as molecular docking and ADMET prediction may help guide the design of more effective derivatives. Additionally, expanding antibacterial testing to include a wider range of pathogenic and drug-resistant strains, along with mechanistic studies on membrane interaction, DNA binding, and ROS generation, is recommended to gain deeper insight into the biological potential of these complexes.

REFERENCES

- Abdel-Rahman, L. H., Adam, M. S. S., Abu-Dief, A. M., & Abdel-Mawgoud, A. A. H. (2019). Catalytic Potential of Mononuclear Cr(III)-Imine Complexes for Selective Oxidation of Benzyl Alcohol by Aqueous H₂O₂. *Journal of Transition Metal Complexes*, 2, 1–14. <https://doi.org/10.32371/jtmc/236077>
- Aboura, W., Benabdallah, T., Zhang, F., & Therrien, B. (2018). Alkoxylation of the Imine Carbon Atom of a Schiff- Base Ligand upon Coordination to Arene Ruthenium. *Inorganica Chimica Acta*, 483, 93–97. <https://doi.org/10.1016/j.ica.2018.07.025>
- Abu-khadra, A. S., Farag, R. S., & Abdel-hady, A. E. M. (2016). Synthesis, Characterization and Antimicrobial Activity of Schiff Base Phenylsulfonyl Acetamide Metal Complexes. *American Journal of Analytical Chemistry*, 7, 233–245.
- Adejumo, T. T., Tzouras, N. V, Zorba, L. P., Radanovi, D., Pevec, A., & Grubiši, S. (2020). DFT Calculations of Zn (II) Hydrazone Complexes. *Molecules*, 25, 1–18.
- Adhikary, A., & Guan, H. (2014). *Nickel-Catalyzed Cross-Coupling Reactions*.
- Afsina, C. M. A., Aneja, T., Neetha, M., & Anilkumar, G. (2021). Copper-Catalyzed Cross-Dehydrogenative Coupling Reactions. *European Journal of Organic Chemistry*, 2021, 1776–1808. <https://doi.org/10.1002/ejoc.202001549>
- Agostini, G., & Radnik, J. (2020). Spectroscopy in catalysis. *Catalysts*, 10(4), 12–14. <https://doi.org/10.3390/catal10040408>
- Ahmad, G., Rasool, N., Ikram, H. M., Khan, S. G., Mahmood, T., Akhtar, M. N., & Alitheen, N. B. (2017). Efficient Synthesis of Novel Pyridine-Based Derivatives via Suzuki Cross-Coupling Reaction of Commercially Available 5-Bromo-2-methylpyridin-3- amine: Quantum Mechanical Investigations and Biological Activities. *Molecules*, 22, 190. <https://doi.org/10.3390/molecules22020190>
- Ahmad, S. N., Anouar, E. H., Tajuddin, A. M., Ramasamy, K., Yamin, B. M., & Bahron, H. (2020). Synthesis, characterization, quantum chemical calculations and anticancer activity of a Schiff base NNOO chelate ligand and Pd(II) complex. *PLOS ONE*, 15(4), 1–17. <https://doi.org/10.1371/journal.pone.0231147>

- Ahmed, N., Krause, J. A., & Gundmundsdottir, A. D. (2021). *CCDC 2114711: Experimental Crystal Structure Determination*.
<https://doi.org/10.5517/ccdc.csd.cc28zjh9>
- Al-Zaidi, B. H., Hasson, M. M., & Ismail, A. H. (2019). New complexes of chelating Schiffbase: Synthesis, spectral investigation, antimicrobial, and thermal behavior studies. *Journal of Applied Pharmaceutical Science*, 9(4), 45–57.
<https://doi.org/10.7324/JAPS.2019.90406>
- Alamgholiloo, H., Rostamnia, S., & Pesyan, N. N. (2020). Anchoring and stabilization of colloidal PdNPs on exfoliated bis-thiourea modified graphene oxide layers with super catalytic activity in water and PEG. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 602, 125130.
<https://doi.org/10.1016/j.colsurfa.2020.125130>
- Aleena, M. B., Philip, R. M., & Anilkumar, G. (2021). Advances in non-palladium-catalysed Stille couplings. *Applied Organometallic Chemistry*, 35(12), 1–15.
<https://doi.org/10.1002/aoc.6430>
- Alwi, N. S. M., Hamali, M. A., Rosnizam, A. N., Low, A. L. M., Anouar, E. H., Nassar, A. A., & Tajuddin, A. M. (2023). Crystallographic, antibacterial, and in silico studies of Ni(II) and Cu(II) Schiff base complexes derived from 2-acetylpyridine. *Inorganica Chimica Acta*, 558, 121742.
<https://doi.org/10.1016/j.ica.2023.121742>
- Andrade, M. A., & Martins, L. M. D. R. S. (2020). New trends in c–c cross-coupling reactions: The use of unconventional conditions. *Molecules*, 25(23).
<https://doi.org/10.3390/molecules25235506>
- Ani, F. E., Ibeji, C. U., Obasi, N. L., Kelani, M. T., Ukogu, K., Tolufashe, G. F., Ogundare, S. A., Oyeneyin, O. E., Maguire, G. E. M., & Kruger, H. G. (2021). Crystal, spectroscopic and quantum mechanics studies of Schiff bases derived from 4-nitrocinnamaldehyde. *Scientific Reports*, 11(1), 1–11.
<https://doi.org/10.1038/s41598-021-87370-0>
- Arellano, H., Nardello, V., Szunerits, S., Boukherroub, R., & Fameau, A. L. (2023). Saturated long chain fatty acids as possible natural alternative antibacterial agents: opportunities and challenges. *Advances in Colloid and Interface Science*, 318, 102952.

- Argyle, M. D., & Bartholomew, C. H. (2015). Heterogeneous catalyst deactivation and regeneration: A review. *Catalysts*, 5(1), 145–269. <https://doi.org/10.3390/catal5010145>
- Aslantaş, M., Kendi, E., Demir, N., Şabik, A. E., Tümer, M., & Kertmen, M. (2009). Synthesis, Spectroscopic, Structural Characterization, Electrochemical and Antimicrobial Activity Studies of the Schiff Base Ligand and its Transition Metal Complexes. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 74(3), 617–624. <https://doi.org/10.1016/j.saa.2009.07.006>
- Ayala, P., Giesriegl, A., Nandan, S. P., Myakala, S. N., Wobrauschek, P., & Cherevan, A. (2021). Isolation Strategy towards Earth-Abundant Single-Site Co-Catalysts for Photocatalytic Hydrogen Evolution Reaction. *Catalysts*, 11, 417.
- Banerjee, S., Chakrabarti, S., Bouley, B. S., Wahlmeier, A. J., & Mirica, L. M. (2025). Mononuclear palladium (I) and palladium (III) coordination compounds. *Coordination Chemistry Reviews*, 535, 216605. <https://doi.org/10.1016/j.ccr.2025.216605>
- Bartyzel, A. (2017). Synthesis, Thermal Study and Some Properties of N₂O₄—Donor Schiff Base and its Mn(III), Co(II), Ni(II), Cu(II) and Zn(II) Complexes. *Journal of Thermal Analysis and Calorimetry*, 127(3), 2133–2147. <https://doi.org/10.1007/s10973-016-5804-0>
- Berhanu, A. L., Gaurav, Mohiuddin, I., Malik, A. K., Aulakh, J. S., Kumar, V., & Kim, K. H. (2019). A review of the applications of Schiff bases as optical chemical sensors. *Trends in Analytical Chemistry*, 116, 74–91. <https://doi.org/10.1016/j.trac.2019.04.025>
- Beytur, M., & Yuksek, H. (2021). In Silico Calculations of 2-Methoxy-6-[(3-methyl-5-oxo-4,5-dihydro-1H-1,2,4-triazol-4-yl)-iminomethyl] Phenyl Benzoate. *The Eurasia Proceedings of Science Technology Engineering and Mathematics*, 15, 54–62.
- Bismuto, A., Finkelstein, P., Müller, P., & Morandi, B. (2021). The Journey of Ni(I) Chemistry. *Helvetica Chimica Acta*, 104. <https://doi.org/10.1002/hlca.202100177>
- Blanchard, S., Neese, F., Bothe, E., Bill, E., Weyhermuller, T., & Wieghardt, K. (2005). Square planar vs tetrahedral coordination in diamagnetic complexes of nickel(II) containing two bidentate π -radical monoanions. *Inorganic Chemistry*, 44(10), 3636–3656. <https://doi.org/10.1021/ic040117e>

- Boča, R., Rajnák, C., Titiš, J., & Valigura, D. (2017). Field Supported Slow Magnetic Relaxation in a Mononuclear Cu(II) Complex. *Inorganic Chemistry*, 56(3), 1478–1482. <https://doi.org/10.1021/acs.inorgchem.6b02535>
- Borhade, S. R., & Waghmode, S. B. (2011). Studies on Pd/NiFe₂O₄ catalyzed ligand-free Suzuki reaction in aqueous phase: Synthesis of biaryls, terphenyls and polyaryls. *Beilstein Journal of Organic Chemistry*, 7, 310–319. <https://doi.org/10.3762/bjoc.7.41>
- Borho, N., Suhm, M. A., Le Barbu-Debus, K., & Zehnacker, A. (2006). Intra- vs. intermolecular hydrogen bonding: Dimers of alpha-hydroxyesters with methanol. *Physical Chemistry Chemical Physics*, 8(38), 4449–4460. <https://doi.org/10.1039/b609725a>
- Boshaala, A., Abraham, A. F., Almughery, A. A., Al-Zaqri, N., Zarrouk, A., Lgaz, H., & Warad, I. (2021). Spectroscopic Insight into Tetrahedrally Distorted Square Planar Copper(II) Complex: XRD/HSA, Physicochemical, DFT, and Thermal Investigations. *Crystals*, 11(10). <https://doi.org/10.3390/cryst11101179>
- Braga, A. A. C., Ujaque, G., & Maseras, F. (2006). A DFT study of the full catalytic cycle of the Suzuki-Miyaura cross-coupling on a model system. *Organometallics*, 25(15), 3647–3658. <https://doi.org/10.1021/om060380i>
- Brejyeh, Z., Jubeh, B., & Karaman, R. (2020). Resistance of Gram-Negative Bacteria to Current Antibacterial Agents and Approaches to Resolve It. *Molecules*, 25, 1340–1363.
- Buta, I., Shova, S., Ilies, S., Manea, F., Andruh, M., & Costisor, O. (2022). Mono- and Oligonuclear Complexes based on a o-vanillin Derived Schiff-base Ligand: Synthesis, Crystal Structures, Luminescent and Electrochemical Properties. *Journal of Molecular Structure*, 1248, 131439. <https://doi.org/10.1016/j.molstruc.2021.131439>
- Chakraborty, S., Kaur, M., Adhikari, M., Manar, K. K., & Singh, S. (2021). A Bis (BICAAC) Palladium(II) Complex: Synthesis and Implementation as Catalyst in Heck-Mizoroki and Suzuki-Miyaura Cross Coupling Reactions. *Inorganic Chemistry*, 60(9), 6209–6217. <https://doi.org/10.1021/acs.inorgchem.0c03614>
- Chandra, S., Gautam, S., Rajor, H. K., & Bhatia, R. (2015). Syntheses, spectroscopic characterization, thermal study, molecular modeling, and biological evaluation of novel Schiff's base benzil bis(5-amino-1,3,4-thiadiazole-2-thiol) with Ni(II),

- and Cu(II) metal complexes. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*. <https://doi.org/10.1016/j.saa.2014.08.046>
- Chang, X., Malkani, A., Yang, X., & Xu, B. (2020). Mechanistic Insights into Electroreductive C-C Coupling between CO and Acetaldehyde into Multicarbon Products. *Journal of the American Chemical Society*, 142(6), 2975–2983. <https://doi.org/10.1021/jacs.9b11817>
- Chen, Z., Zheng, L., Tong, Y., Wang, J., Yang, D., Gao, X., & Wang, Y. (2025). *Effect of introducing electron-donating and electron-withdrawing substituents on the ES IPT process and fluorescence properties of 2-hydroxy-3-phenyliminomethyl-10-butyl phenothiazine derivatives: A DFT/TD-DFT study*.
- Chiappe, C., Pieraccini, D., Zhao, D., Fei, Z., & Dyson, P. J. (2006). Remarkable anion and cation effects on stille reactions in functionalised ionic liquids. *Advanced Synthesis and Catalysis*, 348, 68–74. <https://doi.org/10.1002/adsc.200505271>
- Christmann, U., & Vilar, R. (2005). Monoligated palladium species as catalysts in cross-coupling reactions. *Angewandte Chemie - International Edition*, 44(3), 366–374. <https://doi.org/10.1002/anie.200461189>
- Colacot, T. J. (2012). Commercial development of palladium(0) catalysts for highly selective cross-coupling reactions. *Platinum Metals Review*, 56(2), 110–116. <https://doi.org/10.1595/147106712X634774>
- Costa, R. A., Pitt, P. O., Pinheiro, M. L. B., Oliveira, K. M. T., Salomé, K. S., Barison, A., & Costa, E. V. (2017). Spectroscopic investigation, vibrational assignments, HOMO-LUMO, NBO, MEP analysis and molecular docking studies of oxoaporphine alkaloid liriodenine. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 174, 94–104. <https://doi.org/10.1016/j.saa.2016.11.018>
- Da Silva, C. M., Da Silva, D. L., Modolo, L. V., Alves, R. B., De Resende, M. A., Martins, C. V. B., & De Fátima, Â. (2011). Schiff Bases: A Short Review of Their Antimicrobial Activities. *Journal of Advanced Research*, 2(1), 1–8. <https://doi.org/10.1016/j.jare.2010.05.004>
- Dawson, G. A., Spielvogel, E. H., & Diao, T. (2023). Nickel-Catalyzed Radical Mechanisms: Informing Cross-Coupling for Synthesizing Non-Canonical Biomolecules. *Accounts of Chemical Research*, 56, 3640–3653. <https://doi.org/10.1021/acs.accounts.3c00588>

- Dell'Anna, M. M., Lofù, A., Mastrorilli, P., Mucciante, V., & Nobile, C. F. (2006). Stille coupling reactions catalysed by a polymer supported palladium complex. *Journal of Organometallic Chemistry*, 691, 131–137. <https://doi.org/10.1016/j.jorganchem.2005.07.104>
- Dennis, J. M., White, N. A., Liu, R. Y., & Buchwald, S. L. (2019). Pd-Catalyzed C-N Coupling Reactions Facilitated by Organic Bases: Mechanistic Investigation Leads to Enhanced Reactivity in the Arylation of Weakly Binding Amines. *ACS Catalysis*, 9(5), 3822–3830. <https://doi.org/10.1021/acscatal.9b00981>
- Deraz, N. M. (2018). The importance of catalyst preparation. *Journal of Industrial and Environmental Chemistry*, 2(1), 16–18. <http://www.alliedacademies.org/journal-industrial-environmental-chemistry/%0Ahttp://www.alliedacademies.org/articles/the-importance-of-catalyst-preparation-9694.html>
- Diccianni, J., Lin, Q., & Diao, T. (2020). Mechanisms of Nickel-Catalyzed Coupling Reactions and Applications in Alkene Functionalization. *Accounts of Chemical Research*. <https://doi.org/10.1021/acs.accounts.0c00032>
- Dulla, H. (2024). The Effect of Global and Local Chemical Reactivity Descriptors in the Determination of Properties of Transition Metal Clusters. *SINET: Ethiopian Journal of Science*, 46(3), 296–305. <https://doi.org/10.4314/sinet.v46i3.6>
- Dyker, G. (1999). Transition metal catalyzed coupling reactions under C-H activation. *Angewandte Chemie - International Edition*, 38(12), 1698–1712. [https://doi.org/10.1002/\(sici\)1521-3773\(19990614\)38:12<1698::aid-anie1698>3.0.co;2-6](https://doi.org/10.1002/(sici)1521-3773(19990614)38:12<1698::aid-anie1698>3.0.co;2-6)
- El-Ajaily, M. M., Maihub, A. A., Mahanta, U. K., Badhei, G., Mohapatra, R. K., & Das, P. K. (2018). Mixed ligand complexes containing schiff bases and their biological activities: A short review. *Rasayan Journal of Chemistry*, 11(1), 166–174. <https://doi.org/10.7324/RJC.2018.1111988>
- El Ouafy, H., Aamor, M., Oubenali, M., Mbarki, M., El Haimouti, A., & El Ouafy, T. (2022). Molecular Structure, Electrostatic Potential and HOMO, LUMO Studies of 4-Aminoaniline, 4-Nitroaniline and 4-Isopropylaniline by DFT. *Science and Technology Asia*, 27(1), 9–19. <https://doi.org/10.14456/scitechasia.2022.2>
- Elhampour, A., & Nemati, F. (2017). Palladium Nanoparticles Supported on Modified Hollow-Fe₃O₄@TiO₂: Catalytic Activity in Heck and Sonogashira Cross

- Coupling Reactions. *Organic Preparations and Procedures International*, 49(5), 443–458. <https://doi.org/10.1080/00304948.2017.1374101>
- Elmacı, G., Duyar, H., Aydiner, B., Seferoğlu, N., Naziri, M. A., Şahin, E., & Seferoğlu, Z. (2018). The syntheses, molecular structure analyses and DFT studies on new benzil monohydrazone based Schiff bases. *Journal of Molecular Structure*, 1162, 37–44. <https://doi.org/10.1016/j.molstruc.2018.02.035>
- Espinet, P., & Echavarren, A. M. (2004). The mechanisms of the Stille reaction. *Angewandte Chemie - International Edition*, 43, 4704–4734. <https://doi.org/10.1002/anie.200300638>
- Fantoni, T., Palladino, C., Grigolato, R., Muzzi, B., Ferrazzano, L., Tolomelli, A., & Cabri, W. (2025). Mastering palladium-catalyzed cross-coupling reactions: the critical role of in situ pre-catalyst reduction design. *Organic Chemistry Frontiers*, 12, 1982–1991. <https://doi.org/10.1039/d4qo02335h>
- Feng, R., Zhang, I. Y., & Xu, X. (2025). A cross-entropy corrected hybrid multiconfiguration pair-density functional theory for complex molecular systems. *Nature Communications*, 16(1), 1–14. <https://doi.org/10.1038/s41467-024-55524-z>
- Feng, Z. Q., Yang, X. L., Ye, Y. F., & Hao, L. Y. (2014). The effect of electron-withdrawing group functionalization on antibacterial and catalytic activity of palladium(II) complexes. *Bulletin of the Korean Chemical Society*, 35(4), 1121–1127. <https://doi.org/10.5012/bkcs.2014.35.4.1121>
- Fonkui, T. Y., Ikhile, M. I., Njobeh, P. B., & Ndinteh, D. T. (2019). Benzimidazole schiff base derivatives: Synthesis, characterization and antimicrobial activity. *BMC Chemistry*, 13(1), 1–11. <https://doi.org/10.1186/s13065-019-0642-3>
- Fromm, A., Van Wüllen, C., Hackenberger, D., & Gooßen, L. J. (2014). Mechanism of Cu/Pd-catalyzed decarboxylative cross-couplings: A DFT investigation. *Journal of the American Chemical Society*, 136(28), 10007–10023. <https://doi.org/10.1021/ja503295x>
- Garcia-Martinez, J. C., Lezutekong, R., & Crooks, R. M. (2005). Dendrimer-encapsulated Pd nanoparticles as aqueous, room-temperature catalysts for the Stille reaction. *Journal of the American Chemical Society*, 127(14), 5097–5103. <https://doi.org/10.1021/ja042479r>
- García-Melchor, M., Braga, A. A. C., Lledós, A., Ujaque, G., & Maseras, F. (2013). Computational perspective on Pd-catalyzed C-C cross-coupling reaction

- mechanisms. *Accounts of Chemical Research*, 46(11), 2626–2634. <https://doi.org/10.1021/ar400080r>
- Geeta, B., Shravankumar, K., Reddy, P. M., Ravikrishna, E., Sarangapani, M., Reddy, K. K., & Ravinder, V. (2010). Binuclear cobalt(II), nickel(II), copper(II) and palladium(II) complexes of a new Schiff-base as ligand: Synthesis, structural characterization, and antibacterial activity. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 77(4), 911–915. <https://doi.org/10.1016/j.saa.2010.08.004>
- Gholamian, F., & Hajjami, M. (2019). Synthesis of Pd immobilized on functionalized hexagonal mesoporous silica (HMS–CPTMS–Cy–Pd) for coupling Suzuki–Miyaura and Stille reactions. *Polyhedron*, 170, 649–658. <https://doi.org/10.1016/j.poly.2019.06.006>
- Gholizadeh, D. S., Khanmohammadi, H., & Sañudo, E. C. (2017). A new trinuclear N–N bridged Cu(II) complex with an asymmetric Schiff base ligand derived from hydrazine. *Polyhedron*, 133, 48–53. <https://doi.org/10.1016/j.poly.2017.05.010>
- Ghorbani-Choghamarani, A., Derakhshan, A. A., Hajjami, M., & Rajabi, L. (2016). Copper-Schiff base alumoxane: A new and reusable mesoporous nano catalyst for Suzuki-Miyaura and Stille C-C cross-coupling reactions. *RSC Advances*, 6(97), 94314–94324. <https://doi.org/10.1039/c6ra19725f>
- Grisson, C., & Barrault, J. (2018). Editorial overview: Green catalysis. *Green and Sustainable Chemistry*, 10, A1–A3. <https://doi.org/10.1016/j.cogsc.2018.04.016>
- Gubler, M., Schäfer, M. R., Behler, J., & Goedecker, S. (2025). Accuracy of charge densities in electronic structure calculations. *Journal of Chemical Physics*, 162(9), 1–10. <https://doi.org/10.1063/5.0251833>
- Guechtouli, N., Kichou, N., Bouzaheur, A., & Adjal, C. (2023). DFT Study of a Schiff Base Ligand and Its Nickel and Copper Complexes: Structure, Vibration, Chemical Reactivity and in Silico Biological. *Eurasia Proceedings of Science, Technology, Engineering and Mathematics*, 23, 548–555. <https://doi.org/10.55549/epstem.1374930>
- Gupta, K. C., & Sutar, A. K. (2008). Catalytic Activities of Schiff Base Transition Metal Complexes. *Coordination Chemistry Reviews*, 252(12–14), 1420–1450. <https://doi.org/10.1016/j.ccr.2007.09.005>

- Hadigheh Rezvan, V. (2024). Molecular structure, HOMO–LUMO, and NLO studies of some quinoxaline 1,4-dioxide derivatives: Computational (HF and DFT) analysis. *Results in Chemistry*, 7(March), 101437. <https://doi.org/10.1016/j.rechem.2024.101437>
- Haleem, M., Warwick, P., & Evans, N. D. M. (2019). Spectrophotometric determination of uranium with arsenazo-III in perchloric acid. *Elsevier*. <https://hdl.handle.net/2134/3082>.
- Han, F. S. (2013). Transition-metal-catalyzed suzuki–miyaura cross-coupling reactions: A remarkable advance from palladium to nickel catalysts. *Chemical Society Reviews*, 42(12), 5270–5298. <https://doi.org/10.1039/c3cs35521g>
- Hangan, A. C., Lucaciu, R. L., Turza, A., Dican, L., Sevastre, B., Páll, E., Oprean, L. S., & Borodi, G. (2023). New Copper Complexes with Antibacterial and Cytotoxic Activity. *International Journal of Molecular Sciences*, 24(18). <https://doi.org/10.3390/ijms241813819>
- Hazani, N. N., Dzulkifli, N. N., Ghazali, S. A. I. S. M., Mohd, Y., Farina, Y., & Jamion, N. A. (2018). Synthesis, Characterisation and Effect of Temperature On Corrosion Inhibition by Thiosemicarbazone Derivatives and its Tin(IV) Complexes. *Malaysian Journal of Analytical Sciences*, 22(5), 758–767.
- Hernán, A. G., Guillot, V., Kuvshinov, A., & Kilburn, J. D. (2003). Polymer-supported organotin reagents in the catalytic Stille reaction. *Tetrahedron Letters*, 44(47), 8601–8603. <https://doi.org/10.1016/j.tetlet.2003.09.143>
- Hohenberg, P., & Kohn, W. (1964). Inhomogeneous Electron Gas. *Integral Equations and Operator Theory*, 136(3), 864–871. <https://doi.org/10.1007/BF01198136>
- Hossain, T. J. (2024). Methods for screening and evaluation of antimicrobial activity: A review of protocols, advantages, and limitations. *European Journal of Microbiology and Immunology*, 14, 97–115. <https://doi.org/10.1556/1886.2024.00035>
- Huang, L., Ji, T., & Rueping, M. (2020). Remote Nickel-Catalyzed Cross-Coupling Arylation via Proton-Coupled Electron Transfer-Enabled C–C Bond Cleavage. *Journal of the American Chemical Society*, 142(7), 3532–3539. <https://doi.org/10.1021/jacs.9b12490>
- Idrish Ali, M., Nupur, S. A., . A., & Hoque, M. (2018). Synthesis and Antibacterial Property of Schiff Bases Derived from Toluidine and Benzaldehydes. *American*

- Journal of PharmTech Research*, 8(1), 282–288.
<https://doi.org/10.46624/ajptr.2018.v8.i1.019>
- İnci, D., Aydın, R., & Zorlu, Y. (2021). NOO-type tridentate Schiff base ligand and its one-dimensional Cu(II) coordination polymer: Synthesis, crystal structure, biomacromolecular interactions and radical scavenging activities. *Inorganica Chimica Acta*, 514, 119994. <https://doi.org/10.1016/j.ica.2020.119994>
- Iranpoor, N., Firouzabadi, H., Elham, E. D., Rostami, A., & Nematollahi, A. (2013). Triphenyltin chloride as a new source of phenyl group for C-heteroatom and C-C bond formation. *Journal of Organometallic Chemistry*, 740, 123–130. <https://doi.org/10.1016/j.jorganchem.2013.04.053>
- Iranpoor, N., Firouzabadi, H., & Etemadi-Davan, E. (2015). Phosphine-free NiBr₂-catalyzed synthesis of unsymmetrical diaryl ketones via carbonylative cross-coupling of aryl iodides with Ph₃SnX (X = Cl, OEt). *Journal of Organometallic Chemistry*, 794, 282–287. <https://doi.org/10.1016/j.jorganchem.2015.05.038>
- Jacks, T. E., Belmont, D. T., Briggs, C. A., Horne, N. M., Kanter, G. D., Karrick, G. L., Krikke, J. J., McCabe, R. J., Mustakis, X. J. G., Nanninga, T. N., Risedorph, G. S., Seamans, R. E., Skeean, R., Winkle, D. D., Zennie, T. M., De, V., Road, P., & Arbor, A. (2004). Development of a Scalable Process for CI-1034 , an Endothelin Antagonist. *Organic Process Research & Development*, 8, 201–212.
- Jana, S., Halder, S., & Koner, S. (2009). Heterogeneous Suzuki and Stille coupling reactions using highly efficient palladium(0) immobilized MCM-41 catalyst. *Tetrahedron Letters*, 50(34), 4820–4823. <https://doi.org/10.1016/j.tetlet.2009.05.098>
- Janesko, B. G. (2021). Replacing hybrid density functional theory: Motivation and recent advances. *Chemical Society Reviews*, 50(15), 8470–8495. <https://doi.org/10.1039/d0cs01074j>
- Jani, M. A., & Bahrami, K. (2020). BNPs@Cur-Pd as a versatile and recyclable green nanocatalyst for Suzuki, Heck and Stille coupling reactions. *Journal of Experimental Nanoscience*, 15(1), 182–201. <https://doi.org/10.1080/17458080.2020.1761959>
- Joshi, S., & Srivastava, R. (2023). Effect of “magic chlorine” in drug discovery: an in silico approach. *RSC Advances*, 13, 34922–34934. <https://doi.org/10.1039/d3ra06638j>

- Kaavin, K., Naresh, D., Yogeshkumar, M. R., Krishna, P. M., Janarthanan, S., Murali, K. M., & Malathi, M. (2024). In-silico DFT studies and molecular docking evaluation of benzimidazo methoxy quinoline-2-one ligand and its Co, Ni, Cu and Zn complexes as potential inhibitors of Bcl-2, Caspase-3, EGFR, mTOR, and PI3K, cancer-causing proteins. *Chemical Physics Impact*, 8, 100418. <https://doi.org/10.1016/j.chphi.2023.100418>
- Kadhim, G. N., Dim, I., Ahmad, H. F. S., Abood, A. S. A., Hanoon, M. M., Kadhum, A. A. H., Shaker, L. M., Alamiery, A. A., & Isahak, W. N. R. W. (2022). Bacterial inhibitory activity of a new Schiff base derived from thiazole complemented with gravimetric and theoretical investigations. *International Journal of Corrosion and Scale Inhibition*, 11(1), 307–321. <https://doi.org/10.17675/2305-6894-2022-11-1-18>
- Kalay, E., Cetin, S., Kolemen, S., & Metin, Ö. (2020). A facile synthesis of mesoporous graphitic carbon nitride supported palladium nanoparticles as highly effective and reusable catalysts for Stille coupling reactions under mild conditions. *New Journal of Chemistry*, 44(17), 6714–6723. <https://doi.org/10.1039/d0nj00546k>
- Kanchana, S., Kaviya, T., Rajkumar, P., Kumar, M. D., Elangovan, N., & Sowrirajan, S. (2023). Computational investigation of solvent interaction (TD-DFT, MEP, HOMO-LUMO), wavefunction studies and molecular docking studies of 3-(1-(3-(5-((1-methylpiperidin-4-yl)methoxy)pyrimidin-2-yl)benzyl)-6-oxo-1,6-dihydropyridazin-3-yl)benzonitrile. *Chemical Physics Impact*, 7, 100263. <https://doi.org/10.1016/j.chphi.2023.100263>
- Kang, S. K., Kim, J. S., Yoon, S. K., Lim, K. H., & Yoon, S. S. (1998). Copper-catalyzed coupling of polymer bound iodide with organostannanes. *Tetrahedron Letters*, 39(19), 3011–3012. [https://doi.org/10.1016/S0040-4039\(98\)00446-8](https://doi.org/10.1016/S0040-4039(98)00446-8)
- Kargar, H., Ardakani, A. A., Tahir, M. N., Ashfaq, M., & Munawar, K. S. (2021). Synthesis, Spectral Characterization, Crystal Structure and Antibacterial Activity of Nickel(II), Copper(II) and Zinc(II) Complexes Containing ONNO Donor Schiff Base Ligands. *Journal of Molecular Structure*, 1233, 130112. <https://doi.org/10.1016/j.molstruc.2021.130112>
- Kaya, S., & Putz, M. V. (2022). Atoms-In-Molecules' Faces of Chemical Hardness by Conceptual Density Functional Theory. *Molecules*, 27(24). <https://doi.org/10.3390/molecules27248825>

- Khanmoradi, M., Nikoorazm, M., & Ghorbani-Choghamarani, A. (2017). Synthesis and Characterization of Pd Schiff Base Complex Immobilized onto Functionalized Nanoporous MCM-41 and its Catalytic Efficacy in the Suzuki, Heck and Stille Coupling Reactions. *Catalysis Letters*, 147(5), 1114–1126. <https://doi.org/10.1007/s10562-016-1957-5>
- Khosa, M. K., Jamal, M. A., Saif, M. J., Muneer, M., Ur-Rehman, F., Farman, M., Shoaib, H. M., Shahid, M., & Hameed, S. (2015). Synthesis, Spectral investigation (¹H, ¹³C) and Anti-microbial Screening of benzophenone imines. *Pakistan Journal of Pharmaceutical Sciences*, 28(6), 2167–2171.
- Kılınç, D., & Şahin, Ö. (2019). Al₂O₃ based Co-Schiff Base complex catalyst in hydrogen generation. *International Journal of Hydrogen Energy*, 44(53), 28391–28401. <https://doi.org/10.1016/j.ijhydene.2019.08.053>
- Kondori, T., Akbarzadeh-t, N., Fazli, M., & Mir, B. (2020). A Novel Schiff Base Ligand and its Copper Complex: Synthesis, Characterization, X-ray Crystal Structure and Biological Evaluation. *Journal of Molecular Structure*, 1226, 129395. <https://doi.org/10.1016/j.molstruc.2020.129395>
- Körzdörfer, T., & Brédas, J. L. (2014). Organic electronic materials: Recent advances in the dft description of the ground and excited states using tuned range-separated hybrid functionals. *Accounts of Chemical Research*, 47(11), 3284–3291. <https://doi.org/10.1021/ar500021t>
- Kostas, I. D. (2021). Editorial catalysts: Special issue on transition metal catalyzed cross-coupling reactions. *Catalysts*, 11, 473. <https://doi.org/10.3390/catal11040473>
- Krishna, Kumari, S., Yadav, D., & Sharma, S. K. (2020). Cu(II) Schiff base complex grafted guar gum: Catalyst for benzophenone derivatives synthesis. *Applied Catalysis A, General*, 601, 117529. <https://doi.org/10.1016/j.apcata.2020.117529>
- Kumar, D. N. (2020). Spectral characterization of tetradentate Schiff base complexes of N₂O₂ donor groups. *Indian Journal of Chemistry -Section A*, 59(2), 200–206. <https://doi.org/10.56042/ijca.v59i2.25787>
- Kumar, R., Nayak, J., Chowdhury, S., Nayak, S., Banerjee, S., Basak, B., Siddiqui, M. R., Khan, M. A., Chatterjee, R. P., Singh, P. K., Chung, W. J., Jeon, B. H., Chakraborty, S., & Tripathy, S. K. (2024). Optimizing methanol synthesis from CO₂ using graphene-based heterogeneous photocatalyst under RSM and ANN-

- driven parametric optimization for achieving better suitability. *RSC Advances*, 14(18), 12496–12512. <https://doi.org/10.1039/d4ra00578c>
- Kupwade, R. V., & Sawant, V. J. (2020). Carbonyl releasing Schiff base complex of Fe(III): synthesis, physicochemical characterization, antimicrobial and anticancer studies. *Journal of Chemical Sciences*, 134(44), 1–12. <https://doi.org/10.1007/s12039-020-1746-y>
- Lai, T. Y., Guo, J., Fetting, J. C., & Power, P. P. (2019). Facile insertion of ethylene into a group 14 element-carbon bond: effects of the HOMO–LUMO energy gap on reactivity. *Chemcomm*, 55, 405–407. <https://doi.org/10.1039/c8cc08488b>
- Lange, H., Fröhlich, R., & Hoppe, D. (2008). Cu(I)-catalyzed stereospecific coupling reactions of enantioenriched α -stannylated benzyl carbamates and their application. *Tetrahedron*, 64(38), 9123–9135. <https://doi.org/10.1016/j.tet.2008.06.092>
- Lau, K. C. Y., & Chiu, P. (2007). The application of non-cross-linked polystyrene-supported triphenylarsine in Stille coupling reactions. *Tetrahedron Letters*, 48(10), 1813–1816. <https://doi.org/10.1016/j.tetlet.2007.01.005>
- Lei, X. P., Wu, Q. Y., Wang, C. Z., Lan, J. H., Chai, Z. F., Nie, C. M., & Shi, W. Q. (2023). Theoretical Insights into the Substitution Effect of Phenanthroline Derivatives on Am(III)/Eu(III) Separation. *Inorganic Chemistry*, 62(6), 2705–2714. <https://doi.org/10.1021/acs.inorgchem.2c03823>
- Li, X., Zhu, T., Shao, Z., Li, Y., Chang, H., Gao, W., Zhang, Y., & Wei, W. (2016). Newly-generated Al(OH)₃-supported Pd nanoparticles-catalyzed Stille and Kumada coupling reactions of diazonium salts, (Het)aryl chlorides. *Tetrahedron*, 72(1), 69–75. <https://doi.org/10.1016/j.tet.2015.10.069>
- Lima, J. C., Nascimento, R. D., Vilarinho, L. M., Borges, A. P., Silva, L. H. F., Souza, J. R., Dinelli, L. R., Deflon, V. M., da Hora, M. A. E., Bogado, A. L., & Maia, P. I. S. (2020). Group 10 metal complexes with a tetradentate thiosemicarbazone ligand: Synthesis, crystal structures and computational insights into the catalysis for C–C coupling via Mizoroki-Heck reaction. *Journal of Molecular Structure*, 1199. <https://doi.org/10.1016/j.molstruc.2019.126997>
- Lima, Rodrigues, A., Silva, V. L. M., Silva, A. M. S., & Santos, L. (2014). Role of the base and control of selectivity in the Suzuki-Miyaura cross-coupling reaction. *ChemCatChem*, 6(5), 1291–1302. <https://doi.org/10.1002/cctc.201301080>

- Liu, B., Romine, A. M., Rubel, C. Z., Engle, K. M., & Shi, B. (2021). Transition-Metal-Catalyzed , Coordination-Assisted Functionalization of Nonactivated C (sp³)–H Bonds. *Chemical Reviews*, 121, 14957–15074. <https://doi.org/10.1021/acs.chemrev.1c00519>
- Liu, Y., & Wan, J. P. (2011). Tandem reactions initiated by copper-catalyzed cross-coupling: A new strategy towards heterocycle synthesis. *Organic and Biomolecular Chemistry*, 9(20), 6873–6894. <https://doi.org/10.1039/c1ob05769c>
- Lotfy, H. M., & Saleh, S. S. (2019). Investigating advanced approaches based on iso-absorptivity coefficient in unresolved spectral signals of binary mixtures. *Journal of Analytical Methods in Chemistry*, 2019. <https://doi.org/10.1155/2019/7924821>
- Ludwig, J. R., & Schindler, C. S. (2017). Catalyst: Sustainable Catalysis. *Chem*, 2(3), 313–316. <https://doi.org/10.1016/j.chempr.2017.02.014>
- Lv, C., Xu, L., Chen, M., Cui, Y., Wen, X., Li, Y., Wu, C. E., Yang, B., Miao, Z., Hu, X., & Shou, Q. (2020). Recent Progresses in Constructing the Highly Efficient Ni Based Catalysts With Advanced Low-Temperature Activity Toward CO₂ Methanation. *Frontiers in Chemistry*, 8, 1–32. <https://doi.org/10.3389/fchem.2020.00269>
- Ma, G., Leng, Y., Wu, Y., & Wu, Y. (2013). Facile synthesis of 3-arylpyridine derivatives by palladacycle-catalyzed Stille cross-coupling reaction. *Tetrahedron*, 69(2), 902–909. <https://doi.org/10.1016/j.tet.2012.10.080>
- Manabe, K. (2015). Palladium catalysts for cross-coupling reaction. *Catalysts*, 5, 38–39. <https://doi.org/10.3390/catal5010038>
- Marion, N., & Nolan, S. P. (2008). Well-defined N-heterocyclic carbenes-palladium(II) precatalysts for cross-coupling reactions. *Accounts of Chemical Research*, 41(11), 1440–1449. <https://doi.org/10.1021/ar800020y>
- Martin, R., & Buchwald, S. L. (2008). Palladium-catalyzed suzuki-miyaura cross-coupling reactions employing dialkylbiaryl phosphine ligands. *Accounts of Chemical Research*, 41(11), 1461–1473. <https://doi.org/10.1021/ar800036s>
- Mashuri, S. I. S., Ibrahim, M. L., Kasim, M. F., Mastuli, M. S., Rashid, U., Abdullah, A. H., Islam, A., Asikin-Mijan, N., Tan, Y. H., Mansir, N., Kaus, N. H. M., & Hin, T. Y. (2020). Photocatalysis for Organic Wastewater Treatment: From the Basis to Current Challenges for Society. *Catalysts*, 10, 1–29.

- Matata, S. (2024). Impact of Temperature on the Rate of Chemical Reactions in Tanzania. *European Journal of Physical Sciences*, 7(1), 12–22.
- Matsheku, A. C., Tia, R., Maumela, M. C., & Makhubela, B. C. E. (2021). Ferrocenylimine palladium(II) complexes: Synthesis, characterization and application in mizoroki-heck and suzuki-miyaura cross-coupling reactions. In *Catalysts* (Vol. 11). <https://doi.org/10.3390/catal11070755>
- Mccann, S. D., & Stahl, S. S. (2015). Copper-Catalyzed Aerobic Oxidations of Organic Molecules: Pathways for Two-Electron Oxidation with a Four-Electron Oxidant and a One-Electron Redox-Active Catalyst. *Accounts of Chemical Research*, 48, 1756–1766. <https://doi.org/10.1021/acs.accounts.5b00060>
- McMullin, C. L., Rühle, B., Besora, M., Orpen, A. G., Harvey, J. N., & Fey, N. (2010). Computational study of PtBu₃ as ligand in the palladium-catalysed amination of phenylbromide with morpholine. *Journal of Molecular Catalysis A: Chemical*, 324, 48–55. <https://doi.org/10.1016/j.molcata.2010.02.030>
- Mehmet, H. K., & Fermin, A. (2023). Molecular Structure, Geometry Properties, HOMO-LUMO, and MEP Analysis of Acrylic Acid Based on DFT Calculations. *Journal of Physical Chemistry and Functional Materials*, 6(2), 92–100. <https://doi.org/10.54565/jphcfum.1343235>
- Miar, M., Shiroudi, A., Pourshamsian, K., Oliaey, A. R., & Hatamjafari, F. (2021). Theoretical investigations on the HOMO–LUMO gap and global reactivity descriptor studies, natural bond orbital, and nucleus-independent chemical shifts analyses of 3-phenylbenzo[d]thiazole-2(3H)-imine and its para-substituted derivatives: Solvent and subs. *Journal of Chemical Research*, 45(1–2), 147–158. <https://doi.org/10.1177/1747519820932091>
- Michael I. Lipschutz, & Tilley, T. D. (2014). Carbon-carbon cross-coupling reactions catalyzed by a two- coordinate nickel(II) bis(amido) complex via observable Ni(I) , Ni(II) and Ni(III) intermediates. *Angew Chem Int Ed Engl.*, 53(28), 7290–7204. <https://doi.org/10.1002/anie.201404577>
- Mirosław, B. (2020). Homo-and hetero-oligonuclear complexes of platinum group metals (PGM) coordinated by imine schiff base ligands. *International Journal of Molecular Sciences*, 21(10). <https://doi.org/10.3390/ijms21103493>
- Monger, L. J., Razinkov, D., Bjornsson, R., & Suman, S. G. (2021). Synthesis, Characterization, and Reaction Studies of Pd(II) Tripeptide Complexes. *Molecules*, 26, 1–20. <https://doi.org/10.3390/molecules26175169>

- Motamarri, P., Das, S., Rudraraju, S., Ghosh, K., Davydov, D., & Gavini, V. (2019). DFT-FE – A massively parallel adaptive finite-element code for large-scale density functional theory calculations. *Computer Physics Communications*, 246. <https://doi.org/10.1016/j.cpc.2019.07.016>
- Mumit, M. A., Pal, T. K., Alam, M. A., Islam, M. A. A., Paul, S., & Sheikh, M. C. (2020). DFT studies on vibrational and electronic spectra, HOMO-LUMO, MEP, HOMA, NBO and molecular docking analysis of benzyl-3-N-(2,4,5-trimethoxyphenylmethylene)hydrazinecarbodithioate. *Journal of Molecular Structure Journal*, 1220.
- Naghipour, A., Ghorbani-Choghamarani, A., Babaee, H., Hashemi, M., & Notash, B. (2017). Crystal structure of a novel polymorph of trans-dichlorobis (triphenylphosphine) palladium(II) and its application as a novel, efficient and retrievable catalyst for the amination of aryl halides and stille cross-coupling reactions. *Journal of Organometallic Chemistry*, 841, 31–38. <https://doi.org/10.1016/j.jorganchem.2016.10.002>
- Nandaniya, B. K., Das, S. P., Chhuchhar, D. R., Pithiya, M. G., Khatariya, M. D., Jani, D., & Kiran, B. (2024). Schiff base metal complexes: Advances in synthesis, characterization , and exploration of their biological potential. *International Journal of Chemical Studies*, 12(5), 131–134.
- Naqvi, Q. A., Kanwal, A., Qaseem, S., Naeem, M., Ali, S. R., Shaffique, M., & Maqbool, M. (2019). Size-dependent inhibition of bacterial growth by chemically engineered spherical ZnO nanoparticles. *Journal of Biological Physics*, 45, 147–159.
- Nasrollahzadeh, M., Issaabadi, Z., Tohidi, M. M., & Sajadi, S. M. (2018). Recent Progress in Application of Graphene Supported Metal Nanoparticles in C–C and C–X Coupling Reactions. *Chemical Record*, 18(2), 165–229. <https://doi.org/10.1002/tcr.201700022>
- Neo, W. T., Ye, Q., Shi, Z., Chua, S. J., & Xu, J. (2018). Influence of catalytic systems in Stille polymerization on the electrochromic performance of diketopyrrolopyrrole-based conjugated polymers. *Materials Chemistry Frontiers*, 2(2), 331–337. <https://doi.org/10.1039/c7qm00377c>
- Newman, S. G., & Lautens, M. (2011). Palladium-catalyzed carboiodination of alkenes: Carbon-carbon bond formation with retention of reactive functionality. *Journal*

- of the American Chemical Society, 133(6), 1778–1780.
<https://doi.org/10.1021/ja110377q>
- Nieves-quinones, Y., Paniak, T. J., Lee, Y. E., Kim, S. M., Tcyrulnikov, S., & Kozlowski, M. C. (2019). *Chromium-Salen Catalyzed Cross-Coupling of Phenols: Mechanism and Origin of the Selectivity*. 141(25), 10016–10032.
<https://doi.org/10.1021/jacs.9b03890>.Chromium-Salen
- Ojha, J. K., Ramesh, G., & Reddy, B. V. (2023). Structure, chemical reactivity, NBO, MEP analysis and thermodynamic parameters of pentamethyl benzene using DFT study. *Chemical Physics Impact*, 7, 100280.
<https://doi.org/10.1016/j.chphi.2023.100280>
- Pal, A., Ghosh, R., Adarsh, N. N., & Sarkar, A. (2010). Pyrazole-tethered phosphine ligands for Pd(0): Useful catalysts for Stille, Kumada and Hiyama cross-coupling reactions. *Tetrahedron*, 66(29), 5451–5458.
<https://doi.org/10.1016/j.tet.2010.05.026>
- Pal, R., & Kumar, P. (2021). Chemical reactivity from a conceptual density functional theory perspective. *Journal of the Indian Chemical Society*, 98, 100008.
<https://doi.org/10.1016/j.jics.2021.100008>
- Perdew, J. P., & Schmidt, K. (2003). Jacob's ladder of density functional approximations for the exchange-correlation energy. *AIP Advances*, 1, 1–20.
<https://doi.org/10.1063/1.1390175>
- Prakash, A., & Adhikari, D. (2011). *Application of Schiff Bases and their Metal Complexes-A Review*. 3(4), 1891–1896.
- Rabelo, R., Toma, L., Julve, M., Lloret, F., Pasán, J., Cangussu, D., Ruiz-García, R., & Cano, J. (2024). How the spin state tunes the slow magnetic relaxation field dependence in spin crossover cobalt(II) complexes. *Dalton Transactions*, 53, 5507–5520. <https://doi.org/10.1039/d4dt00059e>
- Raftani, M., Abram, T., Azaid, A., Kacimi, R., Bennani, M. N., & Bouachrine, M. (2021). Theoretical design of new organic compounds based on diketopyrrolopyrrole and phenyl for organic bulk heterojunction solar cell applications: DFT and TD-DFT study. *Materials Today: Proceedings*, 45, 7334–7343. <https://doi.org/10.1016/j.matpr.2020.12.1228>
- Rai, R., Aubrecht, K. B., Collum, D. B., & H, R. K. O. H. (1995). *Palladium-Catalyzed Stille Couplings of Aryl-, Vinyl-, and Alkyltrichlorostannanes in Aqueous Solution*. 36(18), 3111–3114.

- Reeves, E. K., Bauman, O. R., Mitchem, G. B., & Neufeldt, S. R. (2020). Solvent Effects on the Selectivity of Palladium-Catalyzed Suzuki-Miyaura Couplings. *Israel Journal of Chemistry*, 60(3–4), 406–409. <https://doi.org/10.1002/ijch.201900082>
- Rehman, S. U., Noreen, S., Rashida, M., Ikram, M., Ali, K., Ahmad, I., Arshad, M., & Bukhari, I. H. (2009). Structural Elucidation of Transition Metal Complexes of Modified Diamine along with Bioassay Studies. *The Nucleus*, 46(4), 501–506.
- Rendón-López, V. M., Castro, Á. J. A., Alvarado, M. J. C., Cristóbal, C., Gonzalez, G. G., Montiel, S. G., Serrano, O., & Lopez, J. A. (2019). Ni(II), Pd(II) and Pt(II) complexes with SacNac tridentate ligand. *Polyhedron*, 162, 207–218. <https://doi.org/10.1016/j.poly.2019.01.021>
- Ronson, T. O., Carney, J. R., Whitwood, A. C., Taylor, R. J. K., & Fairlamb, I. J. S. (2015). AsCat and FurCat: New Pd catalysts for selective room-temperature Stille cross-couplings of benzyl chlorides with organostannanes. *Chemical Communications*, 51(16), 3466–3469. <https://doi.org/10.1039/c4cc09810b>
- Rúa-Sueiro, M., Munín-Cruz, P., Bermúdez-Fernández, S., & Vila, J. M. (2022). *Palladium Cyclometallated Compounds: Evaluation of Their Catalytic Activity in Cross-Coupling Reactions*. 10. <https://doi.org/10.3390/eccs2021-11034>
- Russell, J. E. A., Entz, E. D., Joyce, L. M., & Neufeldt, S. R. (2019). Nickel-Catalyzed Stille Cross Coupling of C-O Electrophiles [Research-article]. *ACS Catalysis*, 9(4), 3304–3310. <https://doi.org/10.1021/acscatal.9b00744>
- Sakhare, D. T., Chondhekar, T. K., Shankarwar, S. G., & Shankarwar, A. G. (2015). Synthesis, characterization of some transition metal complexes of bidentate Schiff base and their antifungal and antimicrobial studies. *Pelagia Research Library*, 6(6), 10–16.
- Santos, A. F., Brotto, D. F., Favarin, L. R., Cabeza, N. A., Andrade, G. R., Batistote, M., Cavalheiro, A. A., Neves, A., Rodrigues, D. C., & Anjos, A. (2014). Study of the antimicrobial activity of metal complexes and their ligands through bioassays applied to plant extracts. *Brazilian Journal of Pharmacognosy*, 24, 309–315.
- Sarah, N., Khalili, D., Hidhir, M., Hanim, N., Izzati, I., Hariono, M., & Mikhaylov, A. A. (2024). Synthesis and biological activity of imidazole phenazine derivatives as potential inhibitors for NS2B-NS3 dengue protease. *Heliyon*, 10, e24202. <https://doi.org/10.1016/j.heliyon.2024.e24202>

- Sarwar, A., Bin Shamsuddin, M., & Lingtang, H. (2018). Synthesis, Characterization and Luminescence Studies of Metal-Diimine Complexes. *Modern Chemistry & Applications*, 6(3), 1000262. <https://doi.org/10.4172/2329-6798.1000262>
- Shaikh, T. M., Weng, C., & Hong, F. (2012). Secondary phosphine oxides Versatile ligands in transition metal-catalyzed cross-coupling reactions. *Coordination Chemistry Reviews*, 256, 771–803. <https://doi.org/10.1016/j.ccr.2011.11.007>
- Shang, R., & Liu, L. (2011). Transition metal-catalyzed decarboxylative cross-coupling reactions. *Science China Chemistry*, 54(11), 1670–1687. <https://doi.org/10.1007/s11426-011-4381-0>
- Shimada, N., Nakamura, Y., Ochiai, T., & Makino, K. (2019). Catalytic Activation of Cis-Vicinal Diols by Boronic Acids: Site-Selective Acylation of Carbohydrates. *Organic Letters*. <https://doi.org/10.1021/acs.orglett.9b01231>
- Shukla, B. K., & Yadava, U. (2020). DFT calculations on molecular structure, MEP and HOMO-LUMO study of 3-phenyl-1-(methyl-sulfonyl)-1H-pyrazolo[3,4-d]pyrimidine-4-amine. *Materials Today: Proceedings*, 3056–3060. <https://doi.org/10.1016/j.matpr.2020.10.903>
- Silva, J. K. R. D., Silva, J. R. A., Nascimento, S. B., Luz, S. F. M. D., Meireles, E. N., Alves, C. N., Ramos, A. R., & Maia, J. G. S. (2014). Antifungal activity and computational study of constituents from piper divaricatum essential oil against fusarium infection in black pepper. *Molecules*, 19(11), 17926–17942. <https://doi.org/10.3390/molecules191117926>
- Singh, K., Thakur, R., & Kumar, V. (2016). Co(II), Ni(II), Cu(II), and Zn(II) Complexes Derived from 4-[{3-(4-bromophenyl)-1-phenyl-1H-pyrazol-4-ylmethylene}-amino]-3-mercapto-6-methyl-5-oxo-1,2,4-triazine. *Journal of Basic and Applied Sciences*, 5(1), 21–30. <https://doi.org/10.1016/j.bjbas.2016.02.001>
- Sobola, A. O., Watkins, G. M., & Van Brecht, B. (2014). Synthesis, characterization and antimicrobial activity of copper(II) complexes of some ortho-substituted aniline schiff bases; Crystal structure of Bis(2-methoxy-6-imino)methylphenol copper(II) complex. *South African Journal of Chemistry*, 67, 45–51.
- Soliman, E. A., Khalil, A. A., & Deraz, S. F. (2014). Synthesis, characterization and antibacterial activity of biodegradable films prepared from Schiff bases of zein. *Journal of Food Science Technology*, 51(10), 2425–2434. <https://doi.org/10.1007/s13197-012-0792-y>

- Śpiewak, K., Czerski, G., & Porada, S. (2021a). Effect of K, Na and Ca-based catalysts on the steam gasification reactions of coal. Part I: Type and amount of one-component catalysts. *Chemical Engineering Science*, 229. <https://doi.org/10.1016/j.ces.2020.116024>
- Śpiewak, K., Czerski, G., & Porada, S. (2021b). Effect of K, Na and Ca-based catalysts on the steam gasification reactions of coal. Part II: Composition and amount of multi-component catalysts. *Chemical Engineering Science*, 229. <https://doi.org/10.1016/j.ces.2020.116023>
- Suresh, C. H., Remya, G. S., & Anjalikrishna, P. K. (2022). Molecular electrostatic potential analysis: A powerful tool to interpret and predict chemical reactivity. *WIREs Computational Molecular Science*, 12, 1–31. <https://doi.org/10.1002/wcms.1601>
- Szklarzewicz, J., Jurowska, A., Hodorowicz, M., Kazek, G., & Mordyl, B. (2021). Characterization and antidiabetic activity of salicylhydrazone Schiff base vanadium (IV) and (V) complexes. *Transition Metal Chemistry*, 46, 201–217. <https://doi.org/10.1007/s11243-020-00437-1>
- Thapa, S., Shrestha, B., Gurung, S. K., & Giri, R. (2015). Copper-catalysed cross-coupling: An untapped potential. *Organic and Biomolecular Chemistry*, 13(17), 4816–4827. <https://doi.org/10.1039/c5ob00200a>
- Trevor, A., Matthias, F., Hamlin, T. A., Bickelhaupt, F. M., & Fern, I. (2021). The Pauli Repulsion-Lowering Concept in Catalysis. *Accounts of Chemical Research*, 54, 1972–1981. <https://doi.org/10.1021/acs.accounts.1c00016>
- Tsacheva, I., Todorova, Z., Momekova, D., Momekov, G., & Koseva, N. (2023). Pharmacological Activities of Schiff Bases and Their Derivatives with Low and High Molecular Phosphonates. *Pharmaceuticals*, 16(7), 938. <https://doi.org/10.3390/ph16070938>
- Tsuji, Y., & Fujihara, T. (2012). Carbon dioxide as a carbon source in organic transformation: Carbon–carbon bond forming reactions by transition-metal catalysts. *Chemical Communications*, 48(80), 9956–9964. <https://doi.org/10.1039/c2cc33848c>
- Turaeva, N. (2020). Simple electronic model of enzymatic reactions. *Computational and Theoretical Chemistry*, 1180, 112827. <https://doi.org/10.1016/j.comptc.2020.112827>

- Tyagi, P., Tyagi, M., Agrawal, S., Chandra, S., Ojha, H., & Pathak, M. (2017). Synthesis, characterization of 1,2,4-triazole Schiff base derived 3d-metal complexes: Induces cytotoxicity in HepG2, MCF-7 cell line, BSA binding fluorescence and DFT study. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 171, 246–257. <https://doi.org/10.1016/j.saa.2016.08.008>
- Uivarosi, V. (2013). Metal Complexes of Quinolone Antibiotics and Their Applications: An Update. *Molecules*, 18, 11153–11197. <https://doi.org/10.3390/molecules180911153>
- Uzun, S., Esen, Z., Koç, E., Usta, N. C., & Ceylan, M. (2019). Experimental and density functional theory (MEP, FMO, NLO, Fukui functions) and antibacterial activity studies on 2-amino-4- (4-nitrophenyl) -5,6-dihydrobenzo [h] quinoline-3-carbonitrile. *Journal of Molecular Structure*, 1178, 450–457. <https://doi.org/10.1016/j.molstruc.2018.10.001>
- Verma, P., & Truhlar, D. G. (2020). Status and Challenges of Density Functional Theory. *Trends in Chemistry*, 2(4), 302–318. <https://doi.org/10.1016/j.trechm.2020.02.005>
- Vincent, M., Hartemann, P., & Engels-Deutsch, M. (2016). Antimicrobial applications of copper. *International Journal of Hygiene and Environmental Health*, 219(7), 585–591. <https://doi.org/10.1016/j.ijheh.2016.06.003>
- Vinusha, H. M., Kollur, S. P., Revanasiddappa, H. D., Ramu, R., Shirahatti, P. S., Prasad, M. N. N., Chandrashekar, S., & Begum, M. (2019). Preparation, spectral characterization and biological applications of Schiff base ligand and its transition metal complexes. *Results in Chemistry*. <https://doi.org/10.1016/j.rechem.2019.100012>
- Waiba, S., & Maji, B. (2020). Manganese Catalyzed Acceptorless Dehydrogenative Coupling Reactions. *ChemCatChem*, 12(7), 1891–1902. <https://doi.org/10.1002/cctc.201902180>
- Walther, M., Kipke, W., Renken, R., & Staubitz, A. (2023). Stille vs. Suzuki - cross-coupling for the functionalization of diazocines. *RSC Advances*, 13(23), 15805–15809. <https://doi.org/10.1039/d3ra02988c>
- Wang, D. Y., Kawahata, M., Yang, Z. K., Miyamoto, K., Komagawa, S., Yamaguchi, K., Wang, C., & Uchiyama, M. (2016). Stille coupling via C-N bond cleavage. *Nature Communications*, 7, 1–6. <https://doi.org/10.1038/ncomms12937>

- Wang, X., Wang, Z., Liu, L., Asanuma, Y., & Nishihara, Y. (2019). Nickel-Catalyzed Decarbonylative Stannylation of Acyl Fluorides under Ligand-Free Conditions. *Molecules*, 24(9), 1671. <https://www.mdpi.com/1420-3049/24/9/1671>
- Wei, L., Stogsdill, R. M., & Lingafelter, E. C. (1964). The Crystal Structure of bis-(N-phenylsalicylaldiminato)copper(II). *Acta Cryst.*, 17, 1058–1062. <https://doi.org/10.1107/S0365110X64002663>
- Woznicka, E., Miłos, A., Zapala, L., Pezda, M. K., Szlachta, K. L., & Byczynski, L. (2025). Design and Characterization of Mn(II), Co(II), and Zn(II) Complexes with Chrysin: Spectroscopic, Antibacterial, and Anti-Biofilm Insights. *Processes*, 13, 2468.
- Wu, H., Zhang, S. Q., & Hong, X. (2023). Mechanisms of nickel-catalyzed reductive cross-coupling reactions. *Chemical Synthesis*, 3(4). <https://doi.org/10.20517/cs.2023.20>
- Wu, L., Zhang, X., & Tao, Z. (2012). A Mild and Recyclable Nano-Sized Nickel Catalyst for the Stille reaction in Water. *Catalysis Science and Technology*, 2(4), 707–710. <https://doi.org/10.1039/c2cy00466f>
- Wu, W. Y., Liu, L. J., Chang, F. P., Cheng, Y. L., & Tsai, F. Y. (2016). A Highly Efficient and Reusable Palladium(II)/Cationic 2,2'-Bipyridyl-Catalyzed Stille Coupling in Water. *Molecules*, 21(9). <https://doi.org/10.3390/molecules21091205>
- Xiao, Y., & Cao, C. (2020). Influence of substituents on the structure of Schiff bases Cu(II) complexes. *Journal of Molecular Structure*, 1209. <https://doi.org/10.1016/j.molstruc.2020.127916>
- Xiao, Y., Pu, X., Lu, F., Wang, Y., Xu, Y., Zhang, H., & Liu, Y. (2022). L-cysteine as sustainable and effective sulfur source in the synthesis of diaryl sulfides and heteroarene thiols. *Arabian Journal of Chemistry*, 15(7), 103896. <https://doi.org/10.1016/j.arabjc.2022.103896>
- Xu, L. P., Haines, B. E., Ajitha, M. J., Murakami, K., Itami, K., & Musaev, D. G. (2020). Roles of Base in the Pd-Catalyzed Annulative Chlorophenylene Dimerization. *ACS Catalysis*, 10(5), 3059–3073. <https://doi.org/10.1021/acscatal.9b05328>
- Xue, L., & Lin, Z. (2010). Theoretical aspects of palladium-catalysed carbon-carbon cross-coupling reactions. *Chemical Society Reviews*, 39(5), 1692–1705. <https://doi.org/10.1039/b814973a>

- Yano, H., Nakajima, Y., & Obora, Y. (2013). N,N-Dimethylformamide-stabilized palladium nanoclusters as catalyst for Migita-Kosugi-Stille cross-coupling reactions. *Journal of Organometallic Chemistry*, 745–746, 258–261.
- Yeap, G. Y., Ha, S. T., Ishizawa, N., Suda, K., Boey, P. L., & Mahmood, W. A. K. (2003). Synthesis, Crystal Structure and Spectroscopic Study of Para Substituted 2-hydroxy-3-methoxybenzalideneanilines. *Journal of Molecular Structure*, 658(1–2), 87–99. [https://doi.org/10.1016/S0022-2860\(03\)00453-8](https://doi.org/10.1016/S0022-2860(03)00453-8)
- Yilmaz, M. K. (2018). Palladium(II) complexes with new bidentate phosphine-imine ligands for the Suzuki C–C coupling reactions in supercritical carbon dioxide. *Journal of Supercritical Fluids*, 138, 221–227. <https://doi.org/10.1016/j.supflu.2018.04.022>
- Yu, J., Su, N. Q., & Yang, W. (2022). Describing Chemical Reactivity with Frontier Molecular Orbitals. *Journal of American Chemical Society*, 144, 1383–1394. <https://doi.org/10.1021/jacsau.2c00085>
- Yu, Q., Lin, X., Li, X., & Chen, J. (2020). Photocatalytic Stille Cross-coupling on Gold/g-C₃N₄ Nano-heterojunction. *Chemical Research in Chinese Universities*, 36(6), 1013–1016. <https://doi.org/10.1007/s40242-020-0229-5>
- Yu, Y. (2011). 6-Methoxy-2-[(E)-phenyliminomethyl]-phenol. *Acta Crystallographica Section E: Structure Reports Online*, 67(4), 421–424. <https://doi.org/10.1107/S1600536811009135>
- Zalešny, R., Baranowska-Ączkowska, A., Medveň, M., & Luis, J. M. (2015). Comparison of Property-Oriented Basis Sets for the Computation of Electronic and Nuclear Relaxation Hyperpolarizabilities. *Journal of Chemical Theory and Computation*, 11(9), 4119–4128. <https://doi.org/10.1021/acs.jctc.5b00434>
- Zhang, G., Wang, H., Yang, J., Zhao, Q., Yang, L., Tang, H., Liu, C., Chen, H., Lin, Y., & Pan, F. (2018). Temperature Effect on Co-Based Catalysts in Oxygen Evolution Reaction. *Inorganic Chemistry*, 57(5), 2766–2772. <https://doi.org/10.1021/acs.inorgchem.7b03168>
- Zhang, Y., Teng, H., Chen, J., Xia, R., Zhou, Y., Xie, K., & Chen, Z. (2023). Application of Palladium Single Atoms in C–C Coupling Reactions of Pharmaceutical Synthesis. *Advances in Computer and Engineering Technology Research*, 1(1), 192. <https://doi.org/10.61935/acetr.1.1.2023.p192>
- Zhao, H., Wang, Y., Sha, J., Sheng, S., & Cai, M. (2008). MCM-41-supported bidentate phosphine palladium(0) complex as an efficient catalyst for the heterogeneous

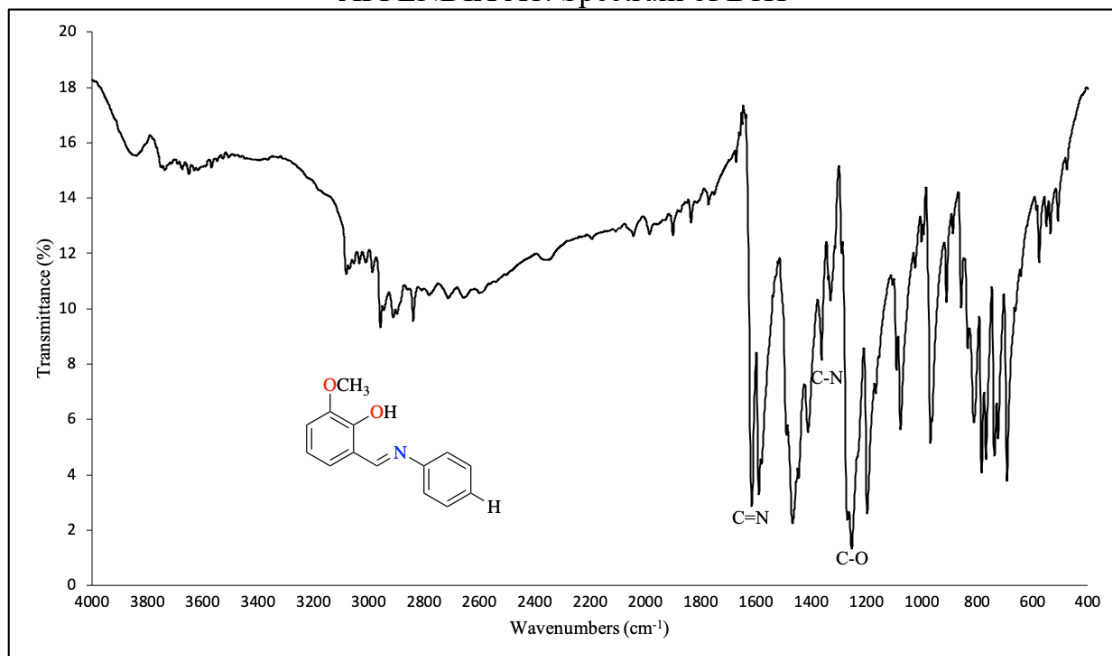
- Stille reaction. *Tetrahedron*, 64(32), 7517–7523.
<https://doi.org/10.1016/j.tet.2008.05.120>
- Zoubi, W. A. (2013). Biological Activities of Schiff Bases and Their Complexes: A Review of Recent Works. *International Journal of Organic Chemistry*, 3, 73–95. <https://doi.org/10.4236/ijoc.2013.33a008>
- Zulu, Z., Nyamoto, G. S., Tshabalala, T. A., & Ojwach, S. O. (2020). Palladium(II) complexes of (pyridyl)imine ligands as catalysts for the methoxycarbonylation of olefins. *Inorganica Chimica Acta*, 501, 119270. <https://doi.org/10.1016/j.ica.2019.119270>

APPENDICES

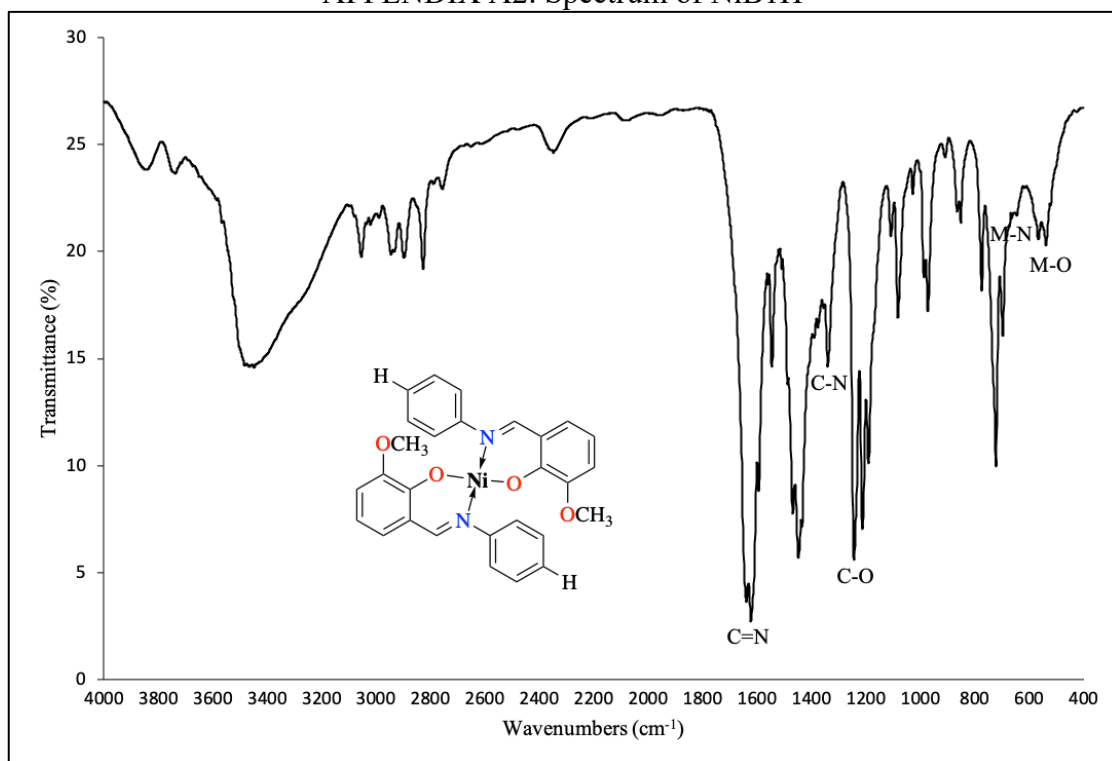
APPENDIX A

FTIR Spectroscopy

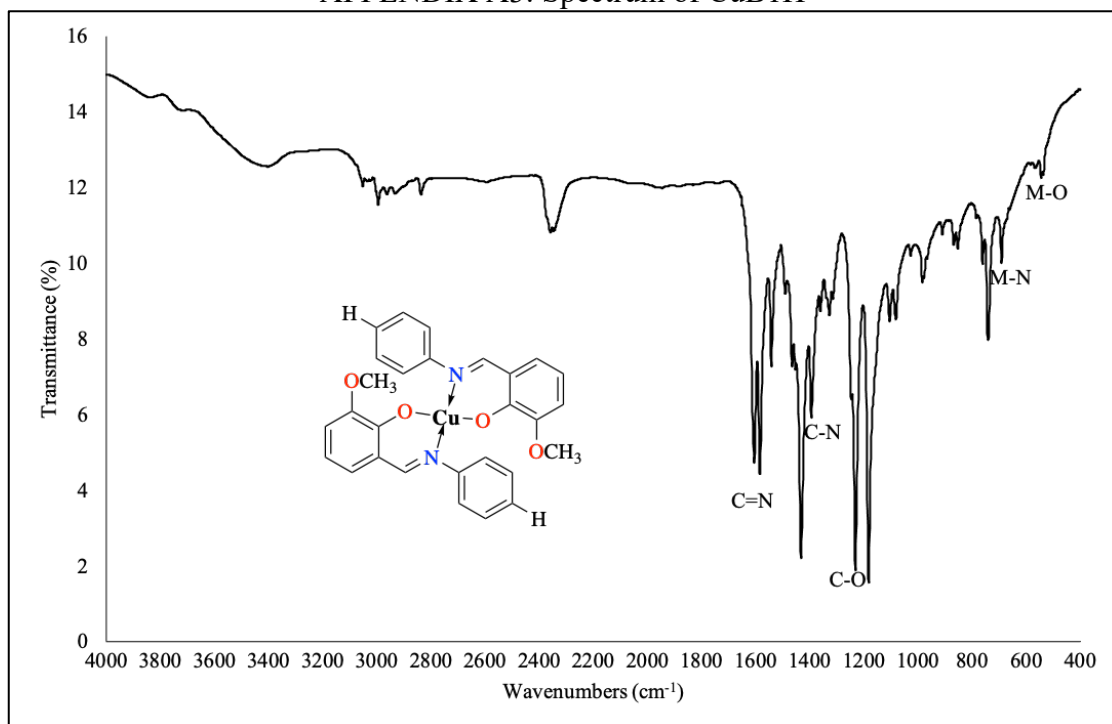
APPENDIX A1: Spectrum of B1H



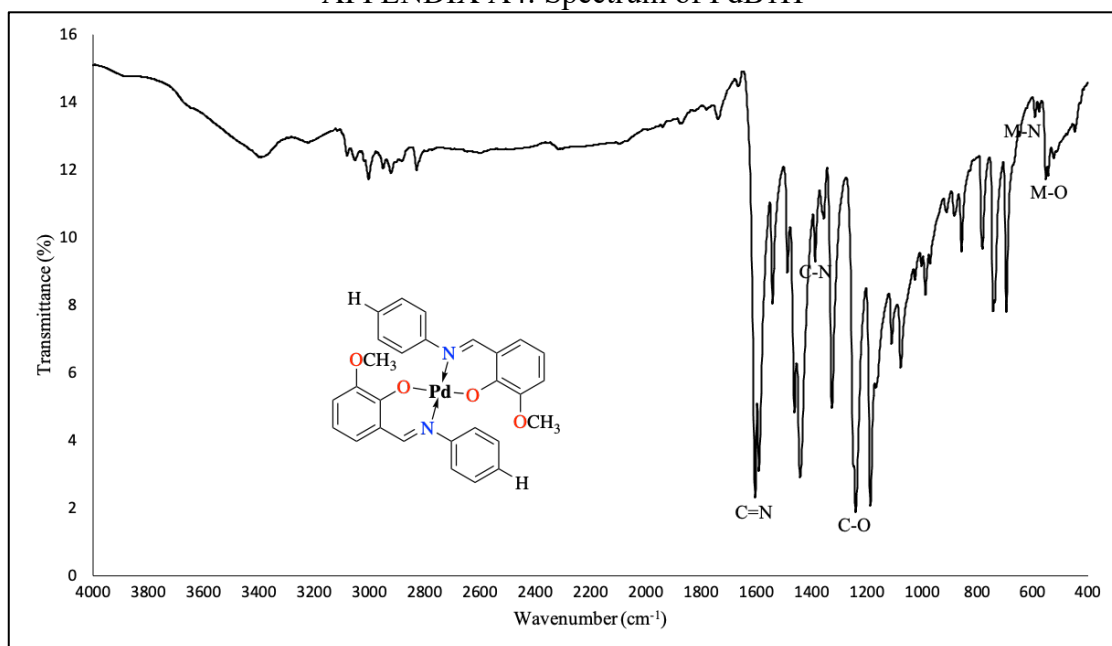
APPENDIX A2: Spectrum of NiB1H



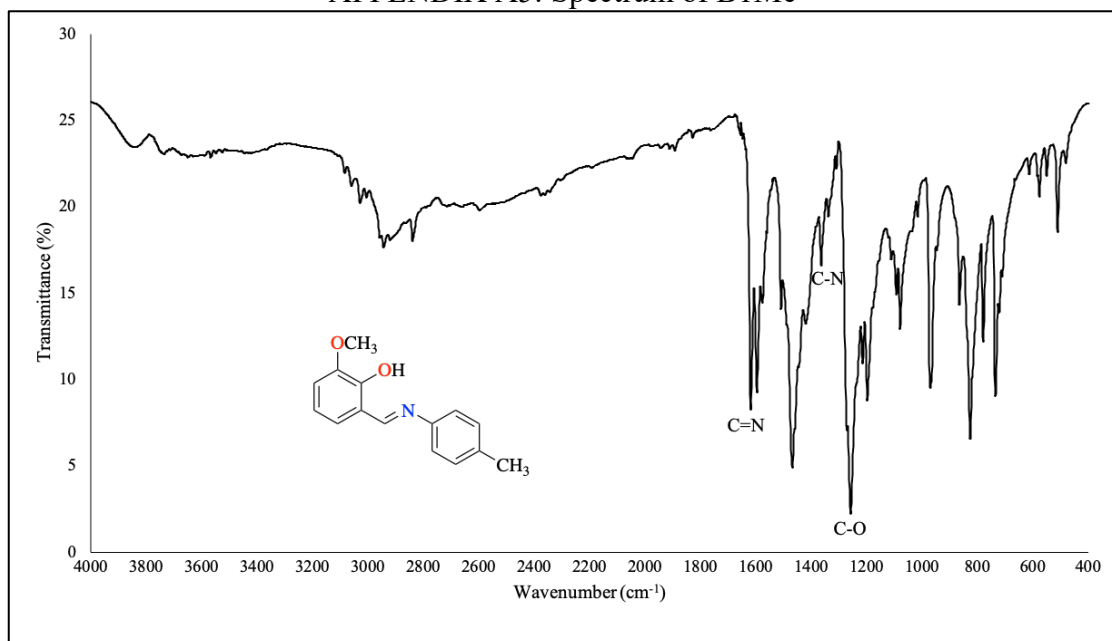
APPENDIX A3: Spectrum of CuB1H



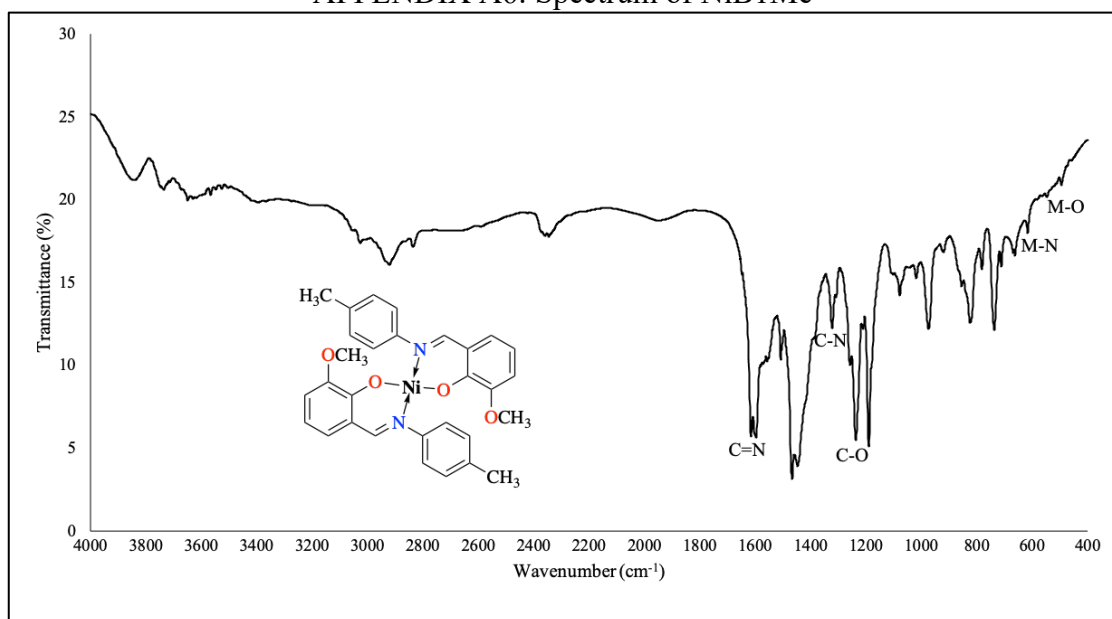
APPENDIX A4: Spectrum of PdB1H



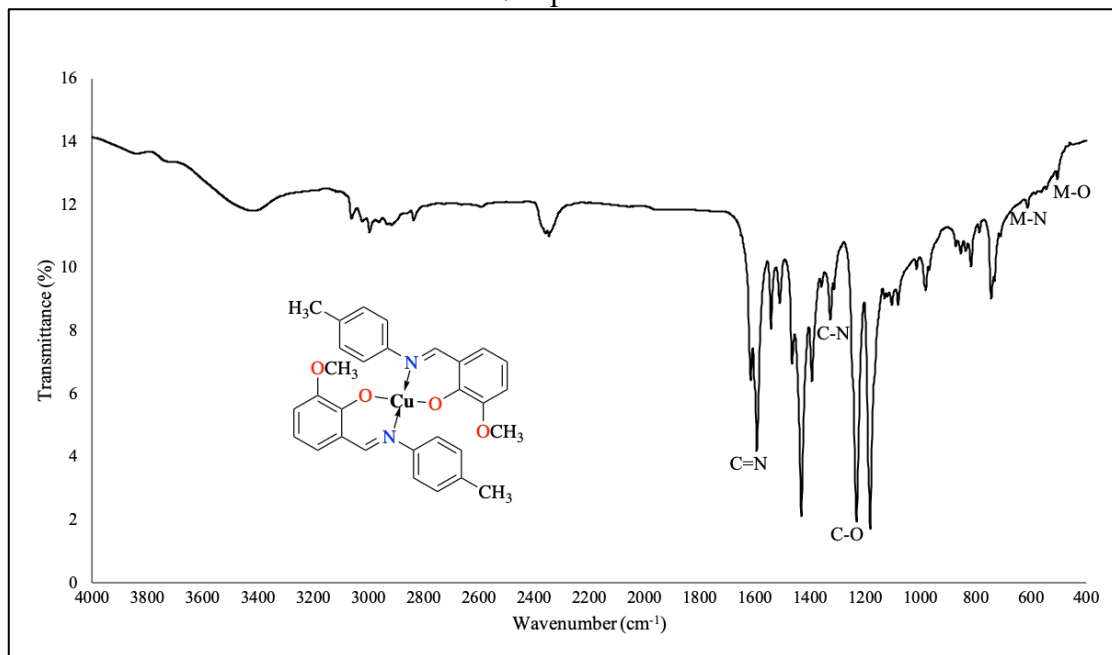
APPENDIX A5: Spectrum of B1Me



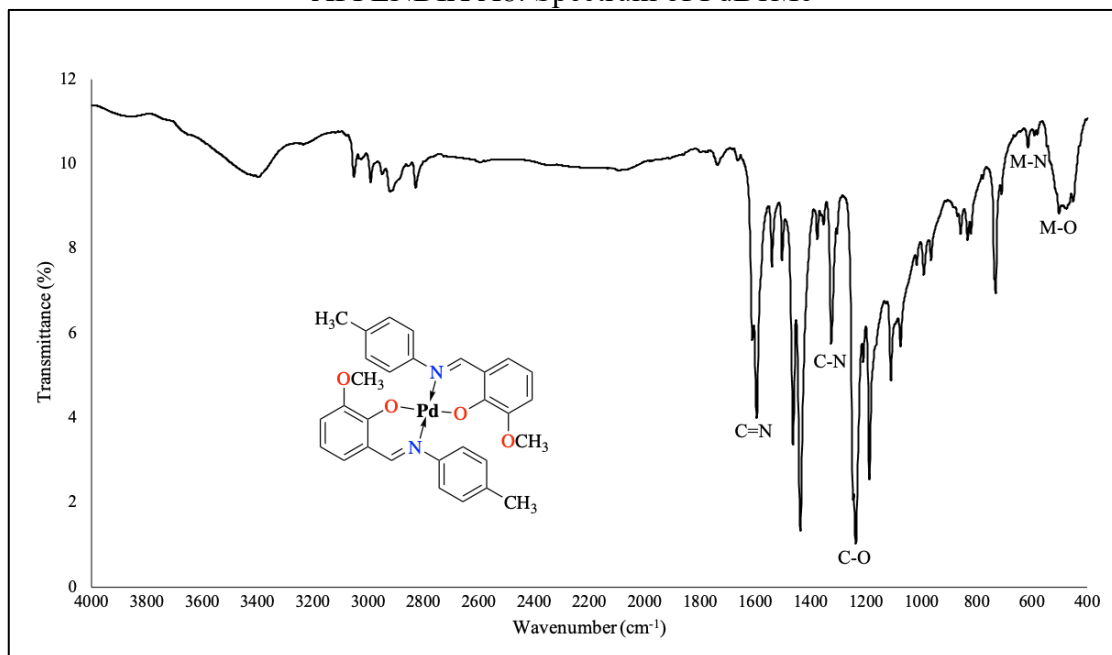
APPENDIX A6: Spectrum of NiB1Me



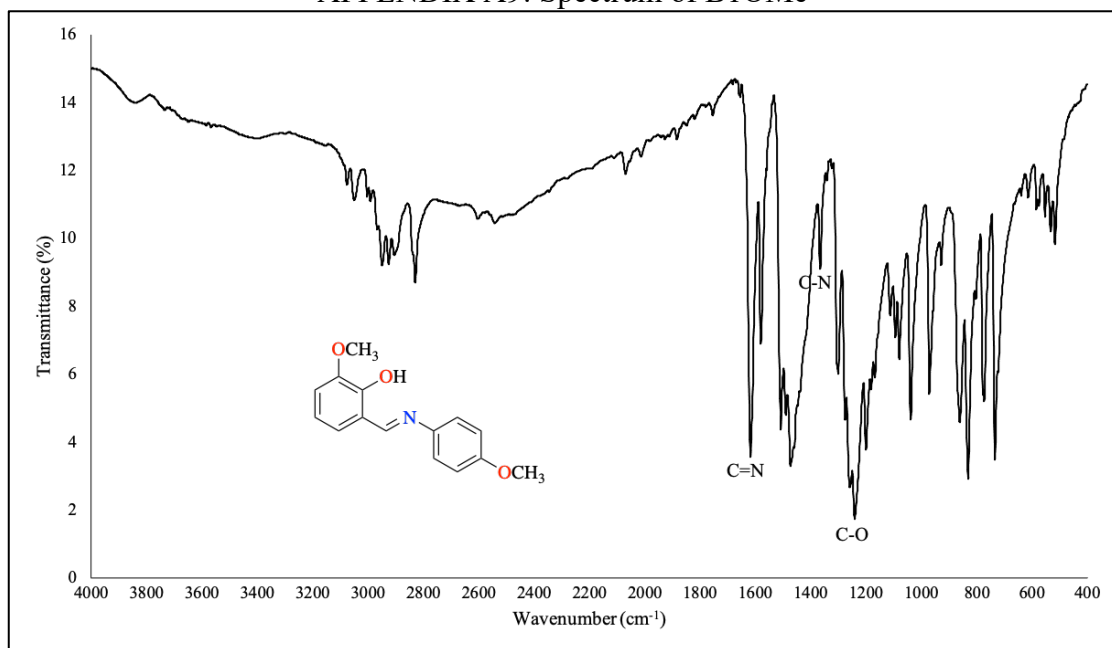
APPENDIX A7: Spectrum of CuB1Me



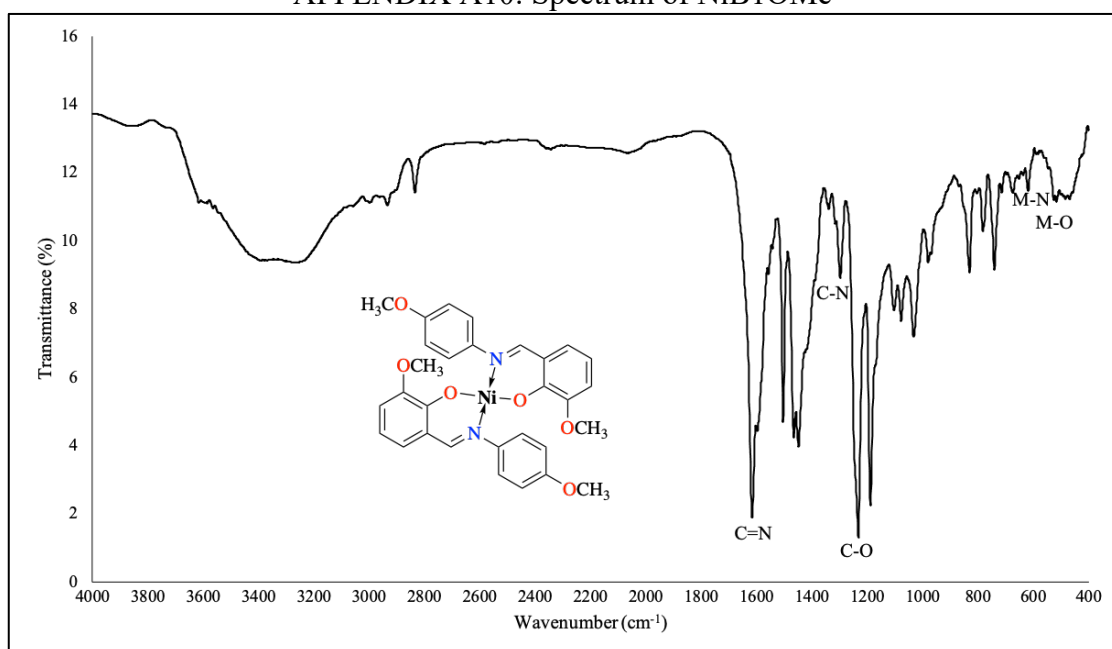
APPENDIX A8: Spectrum of PdB1Me



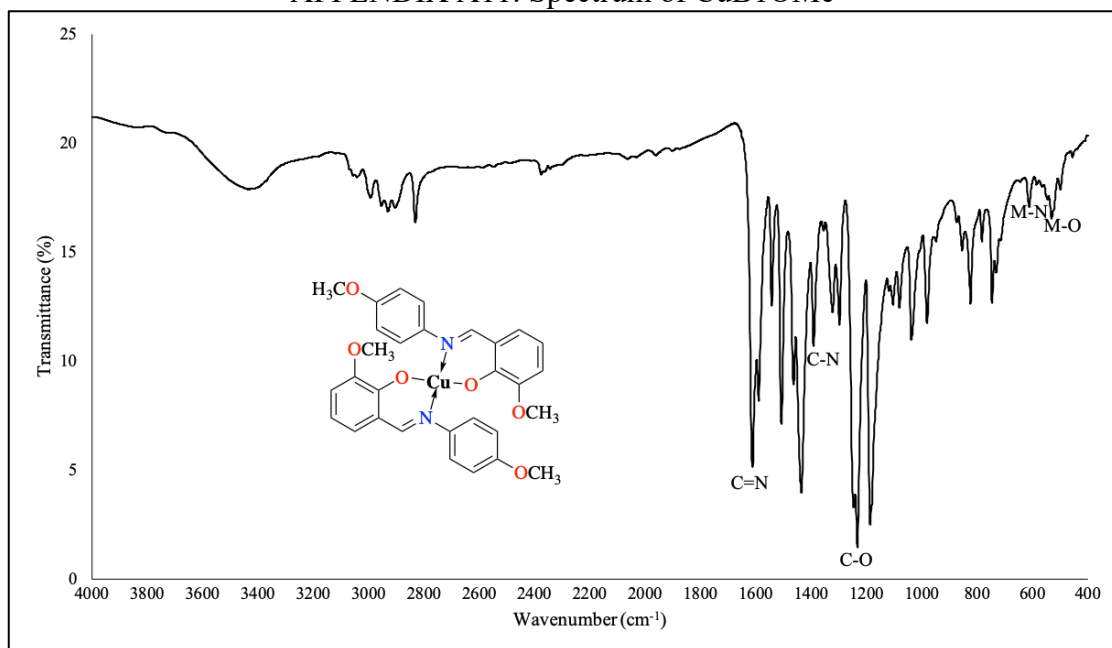
APPENDIX A9: Spectrum of B1OMe



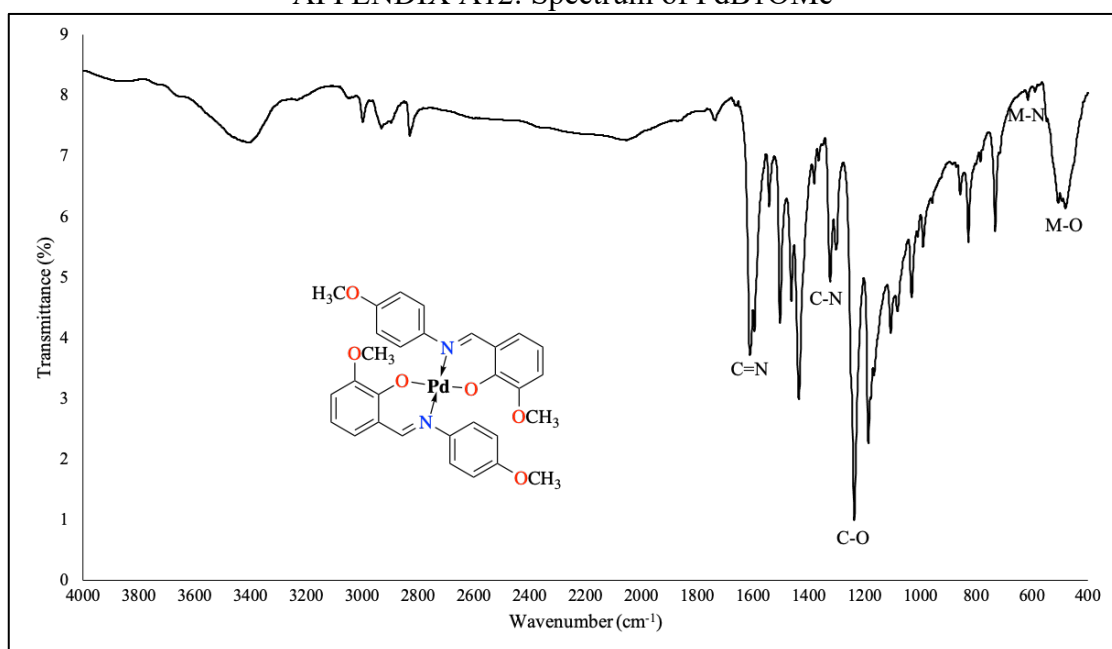
APPENDIX A10: Spectrum of NiB1OMe



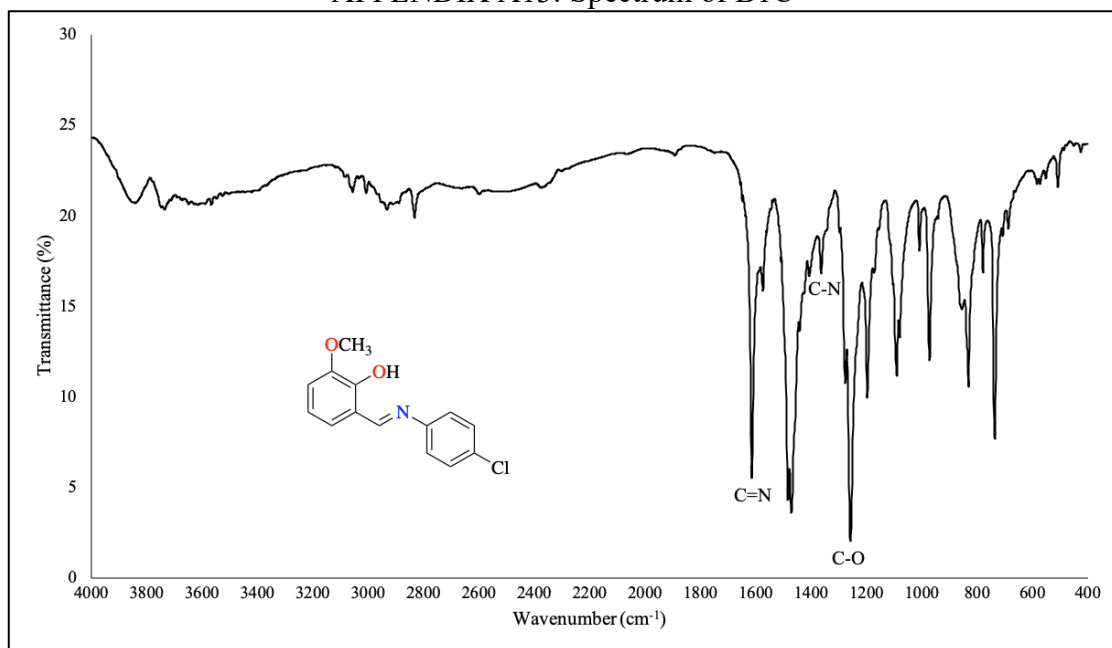
APPENDIX A11: Spectrum of CuB1OMe



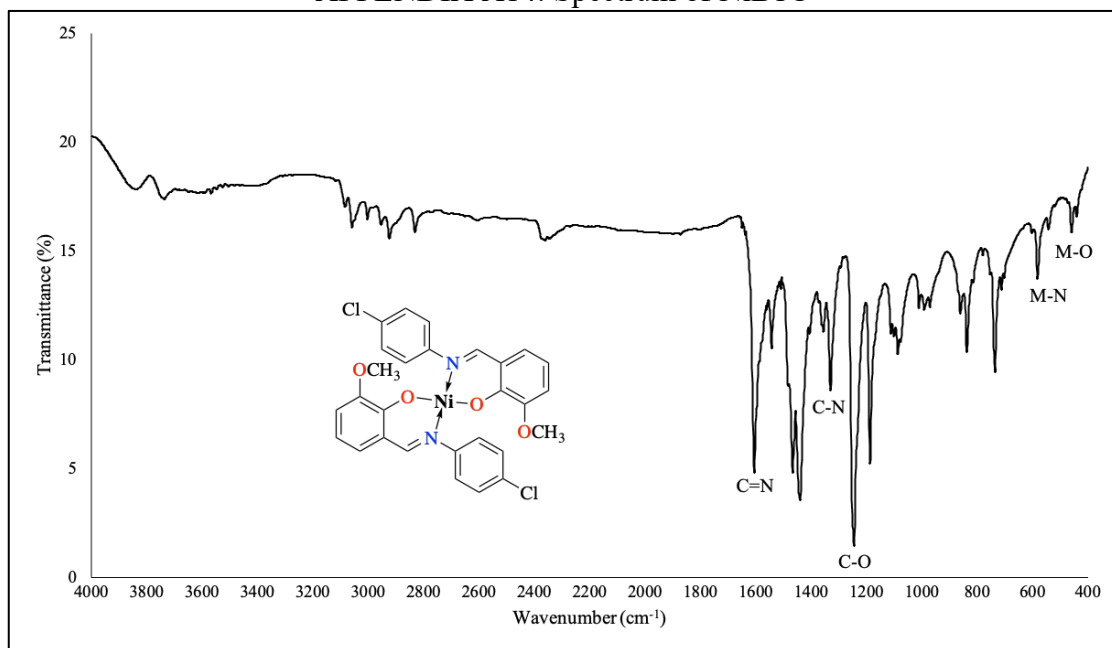
APPENDIX A12: Spectrum of PdB1OMe



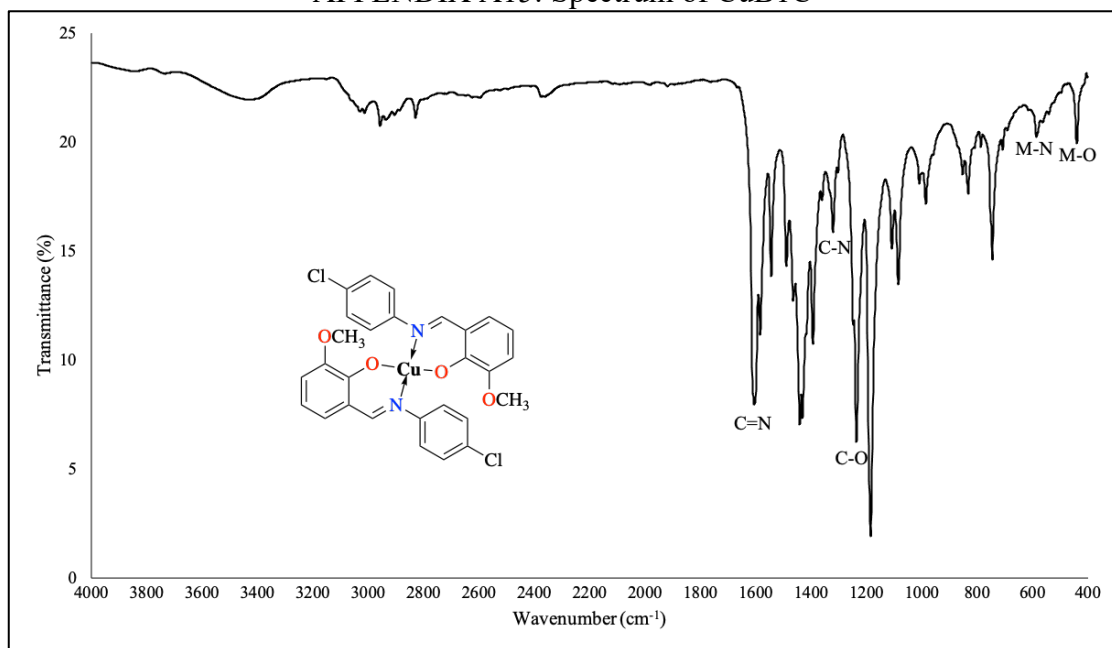
APPENDIX A13: Spectrum of B1C



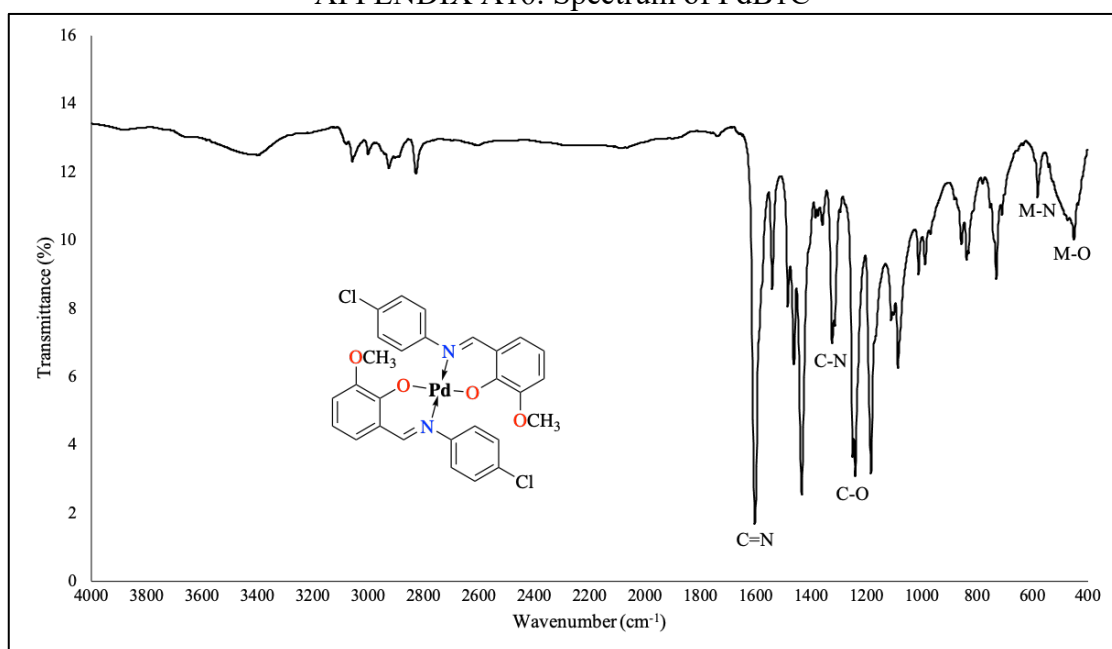
APPENDIX A14: Spectrum of NiB1C



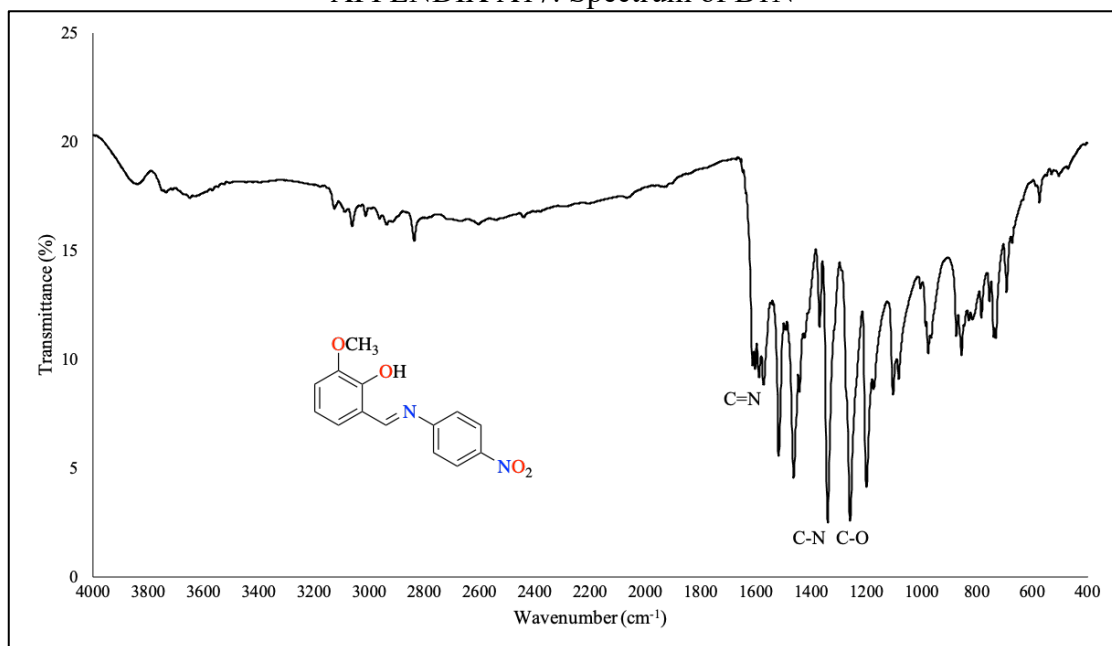
APPENDIX A15: Spectrum of CuB1C



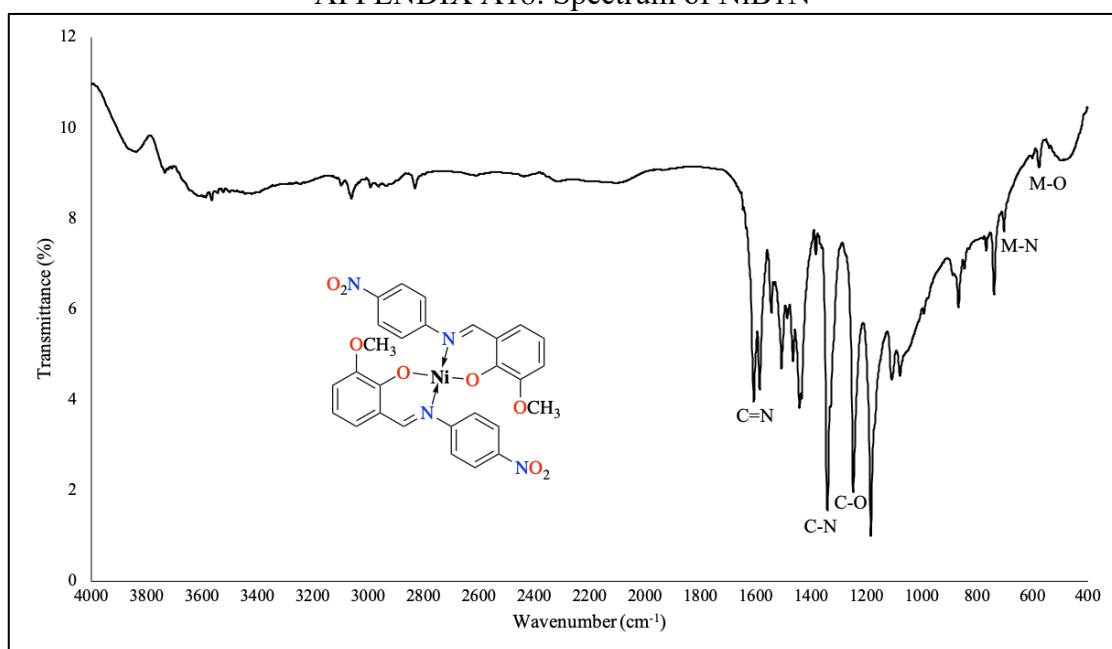
APPENDIX A16: Spectrum of PdB1C



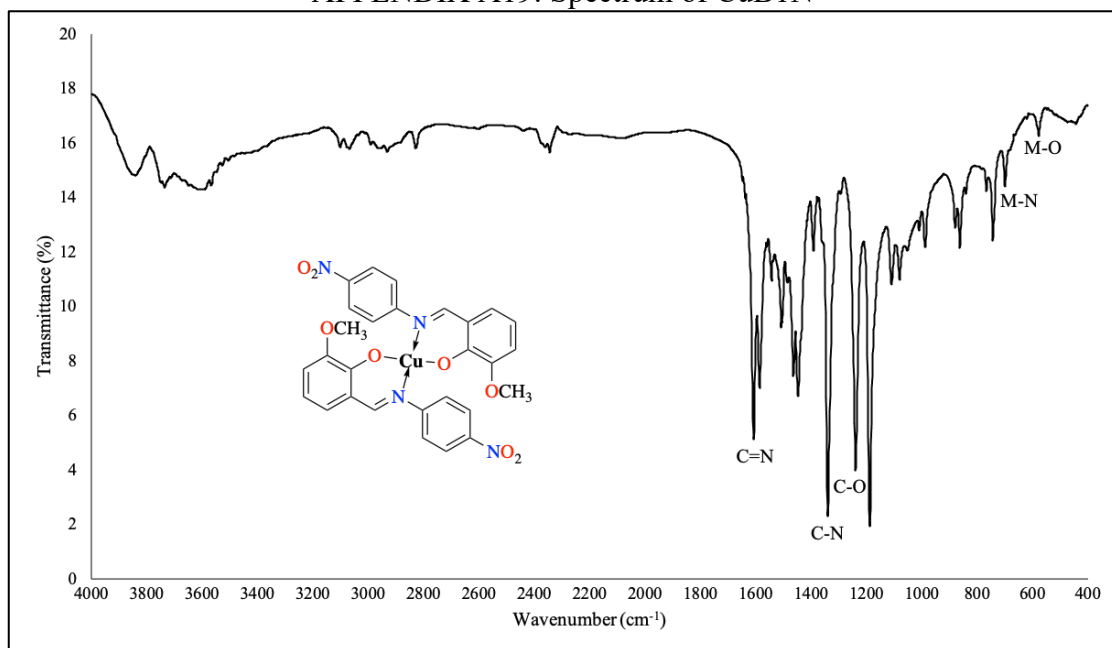
APPENDIX A17: Spectrum of B1N



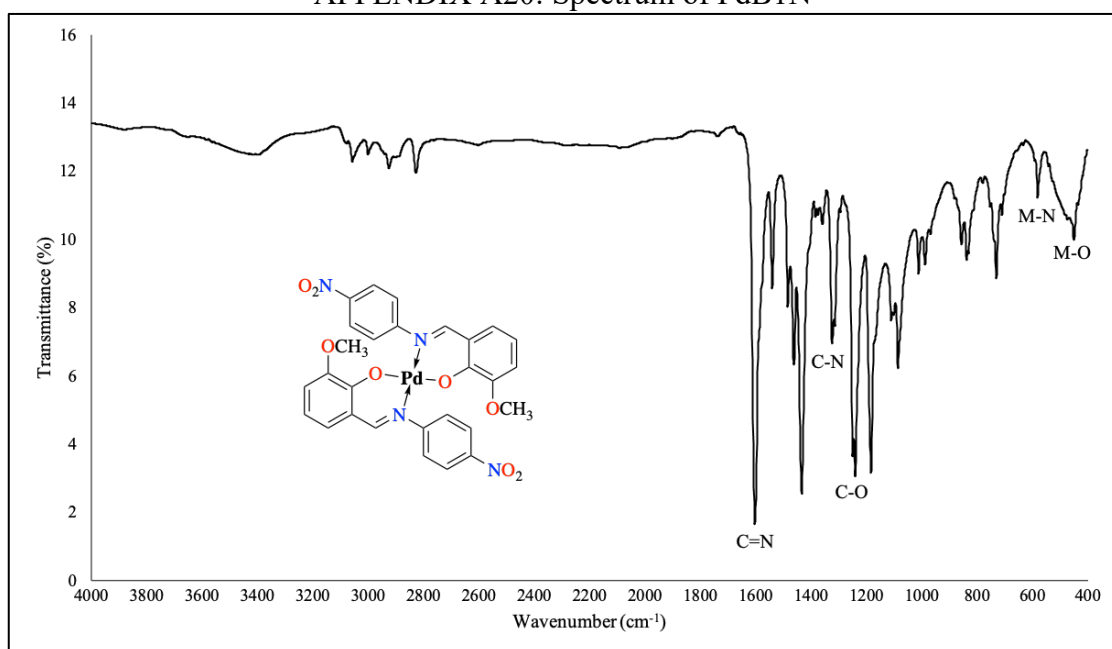
APPENDIX A18: Spectrum of NiB1N



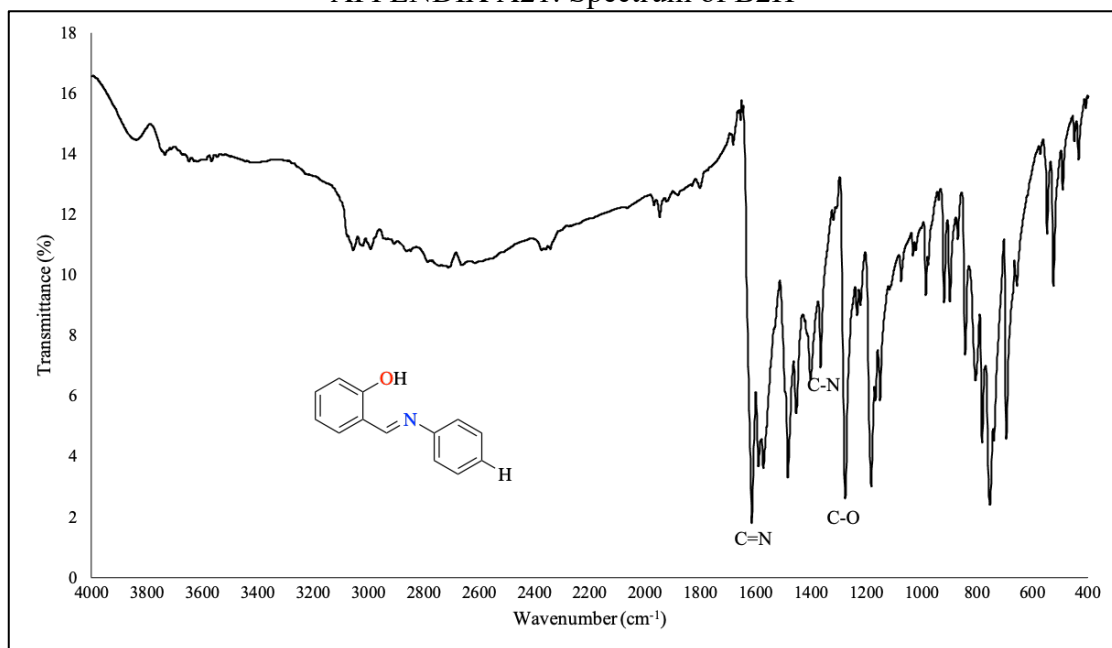
APPENDIX A19: Spectrum of CuB1N



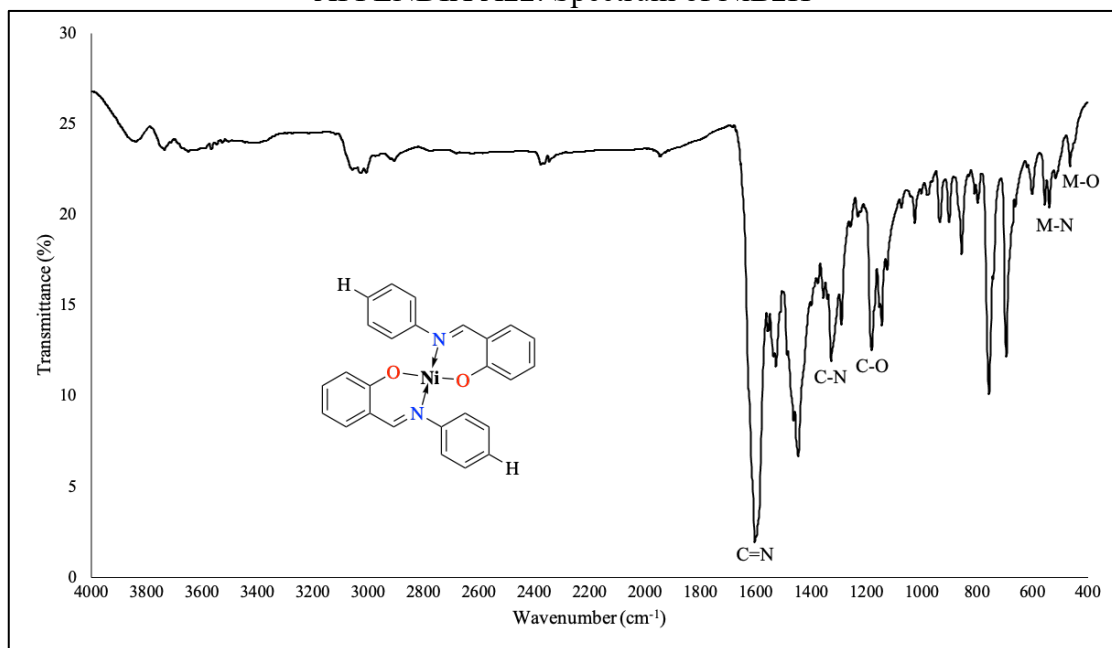
APPENDIX A20: Spectrum of PdB1N



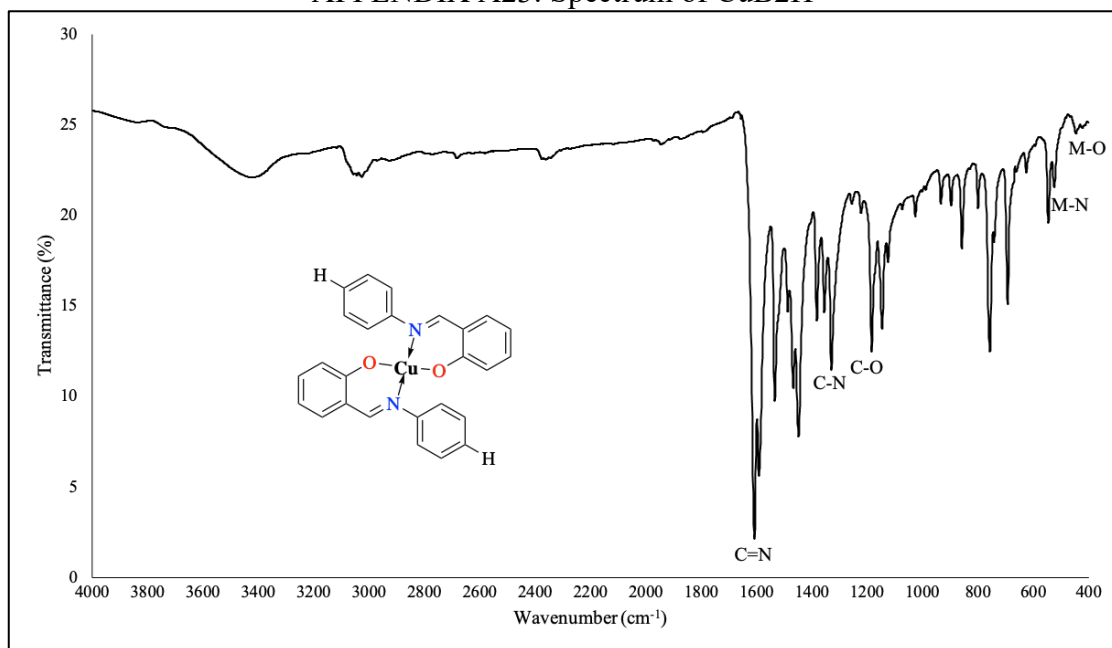
APPENDIX A21: Spectrum of B2H



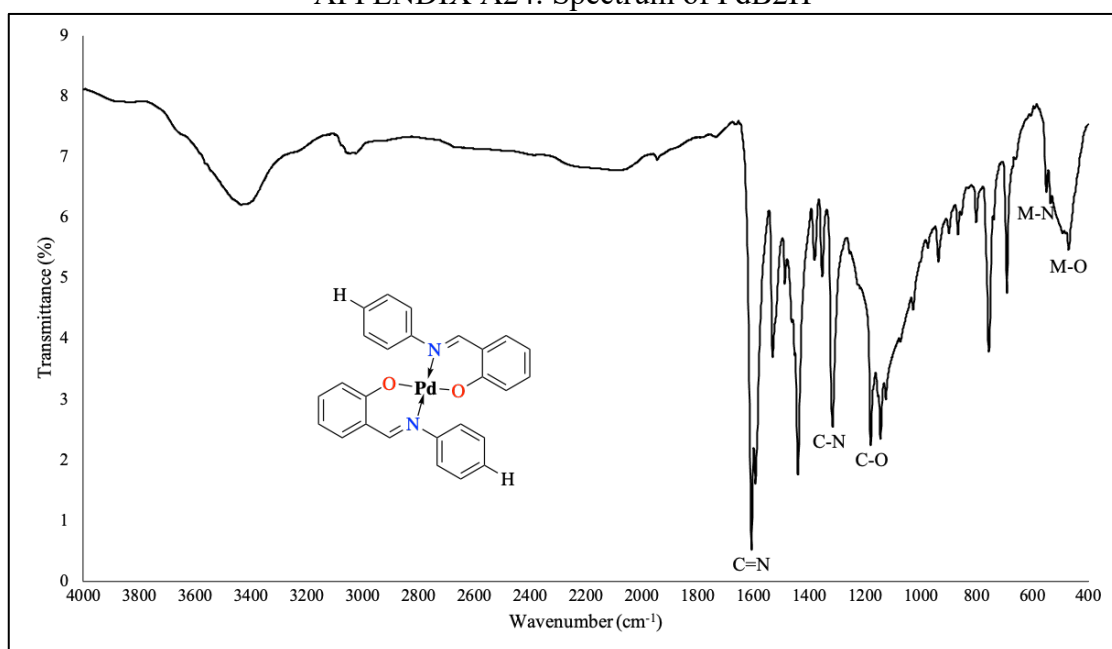
APPENDIX A22: Spectrum of NiB2H



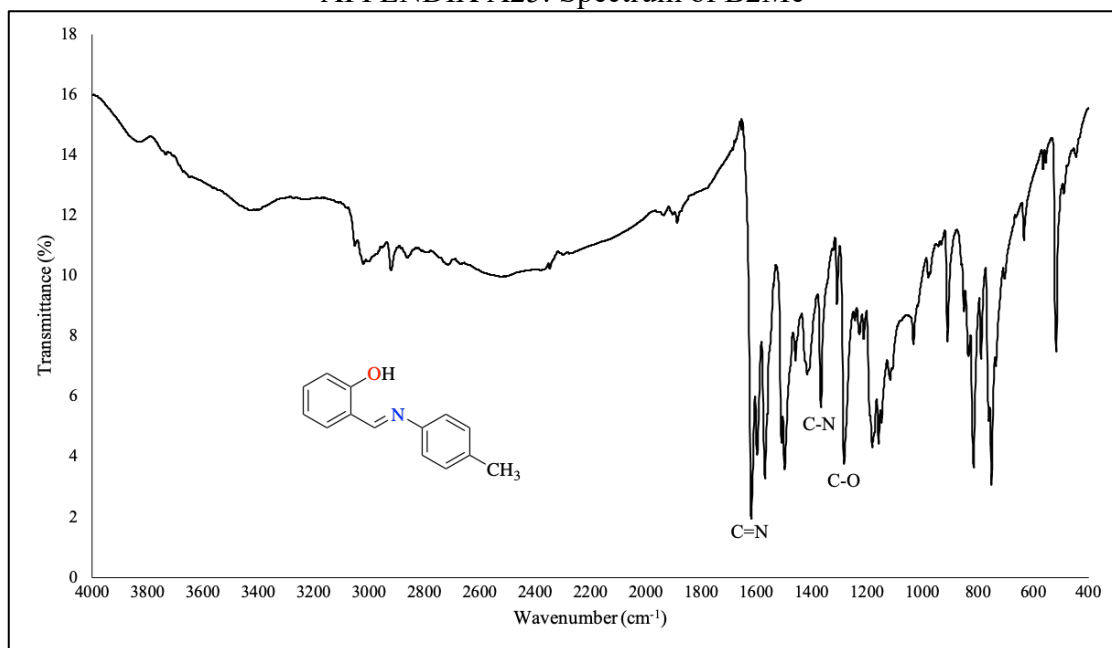
APPENDIX A23: Spectrum of CuB2H



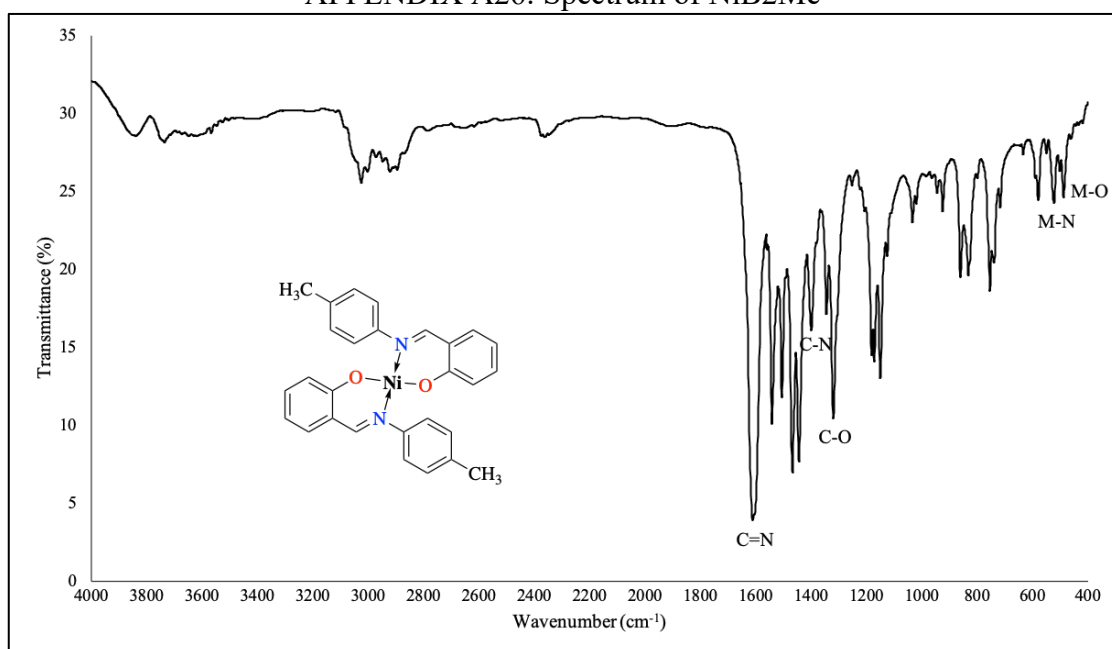
APPENDIX A24: Spectrum of PdB2H



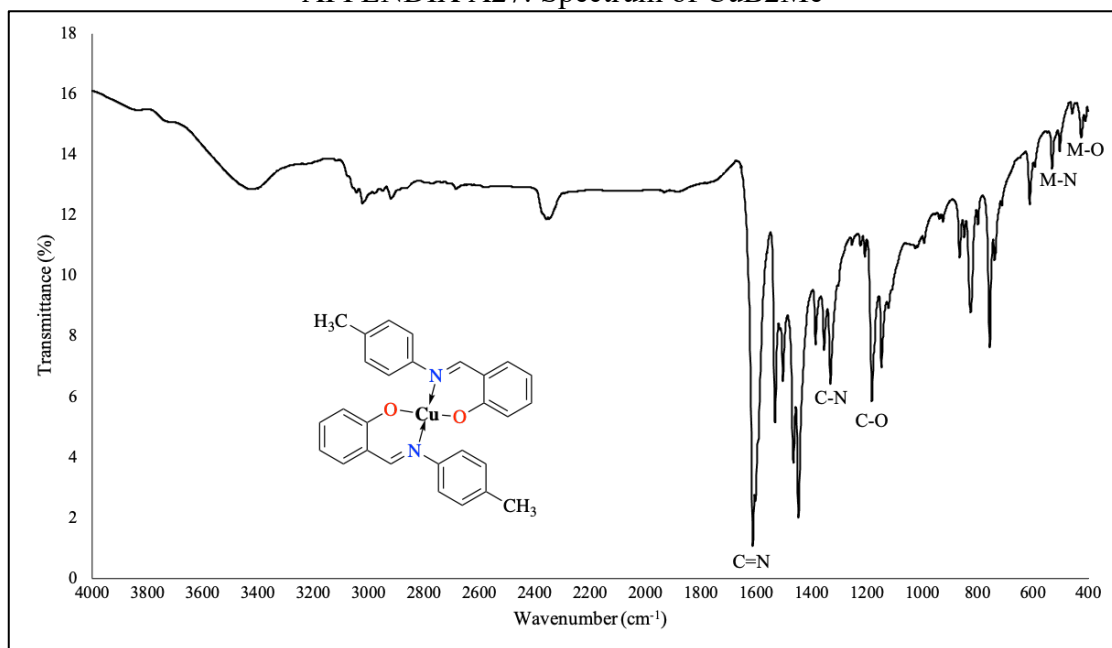
APPENDIX A25: Spectrum of B2Me



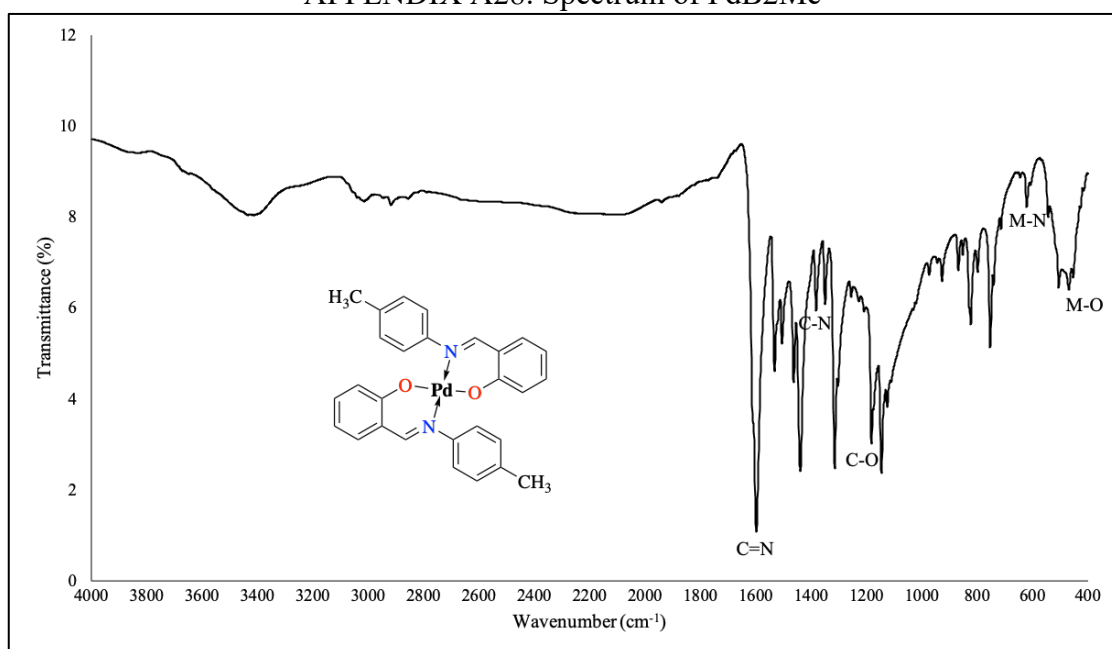
APPENDIX A26: Spectrum of NiB2Me



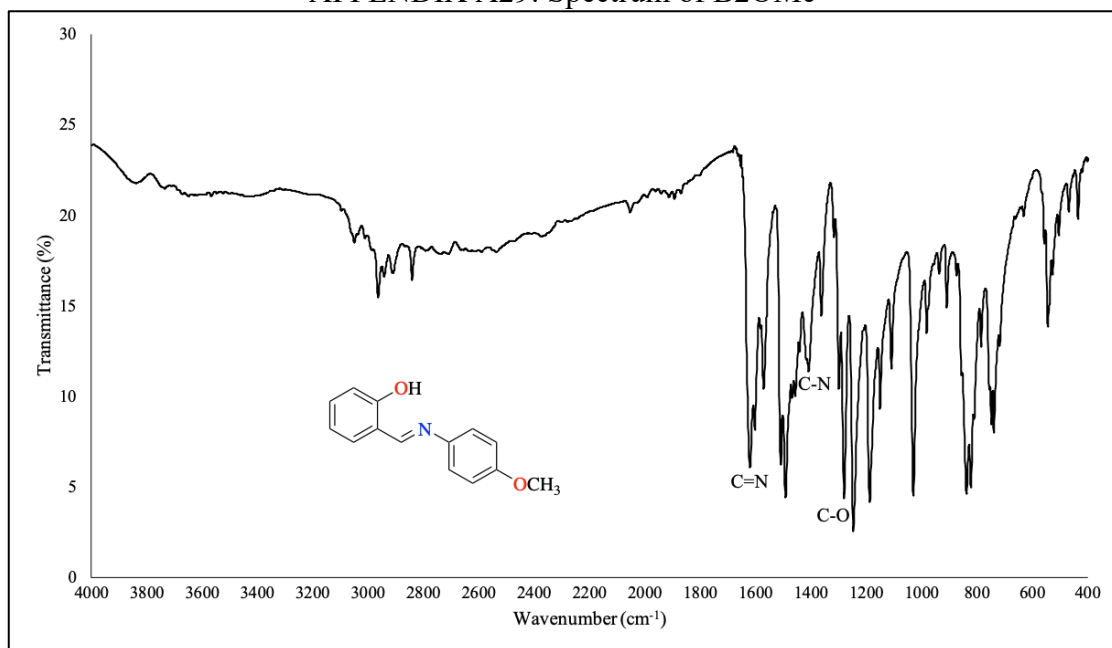
APPENDIX A27: Spectrum of CuB2Me



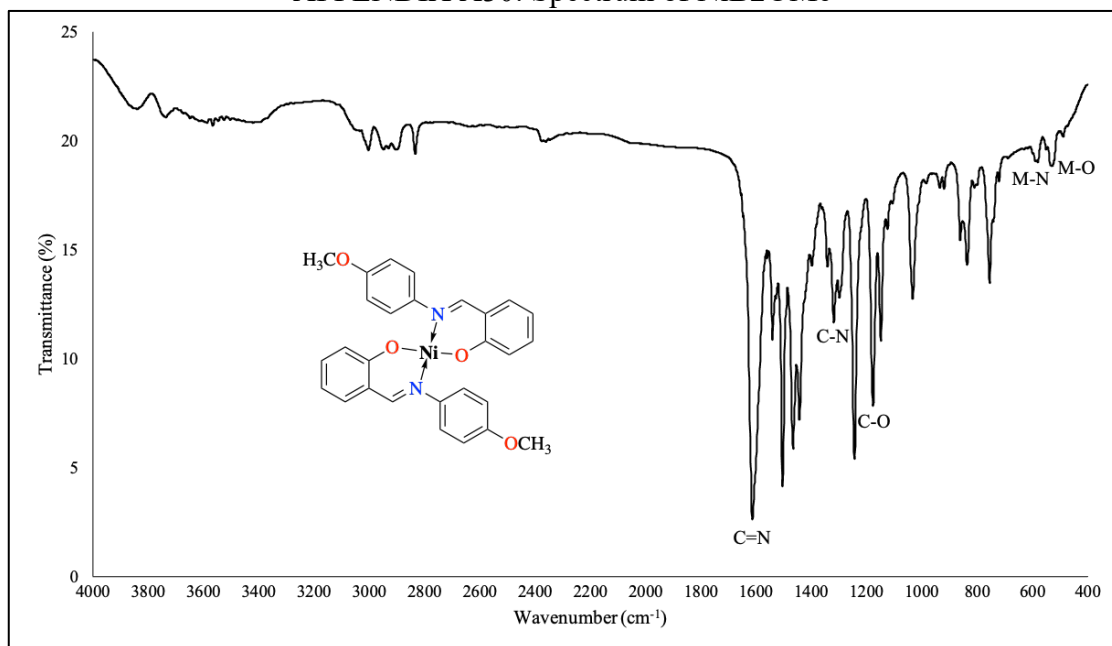
APPENDIX A28: Spectrum of PdB2Me



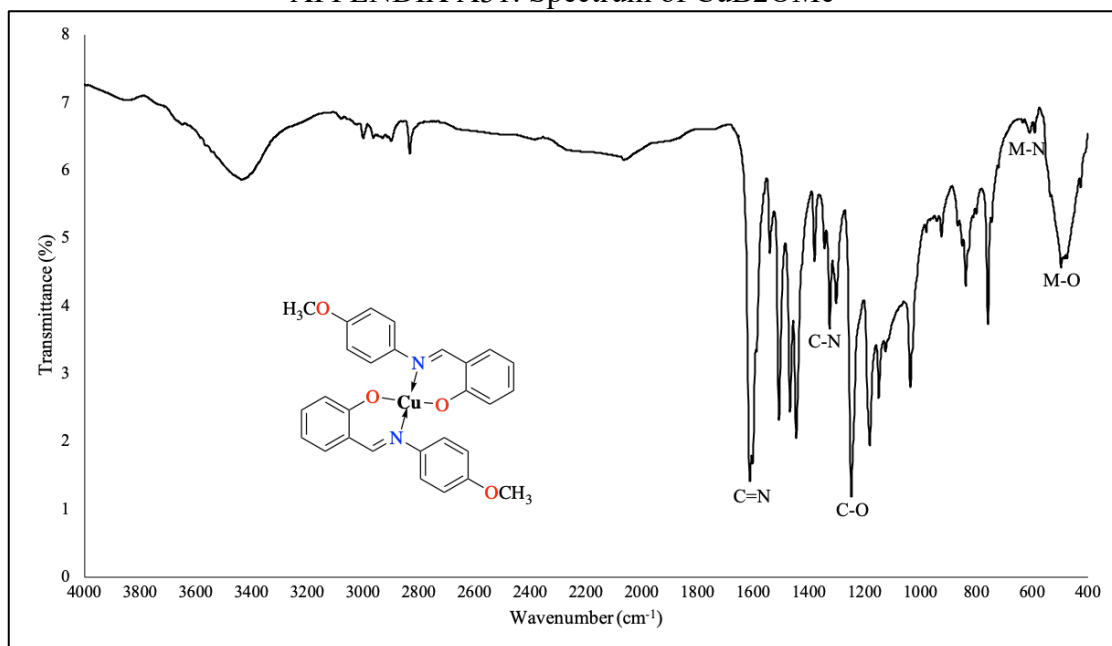
APPENDIX A29: Spectrum of B2OMe



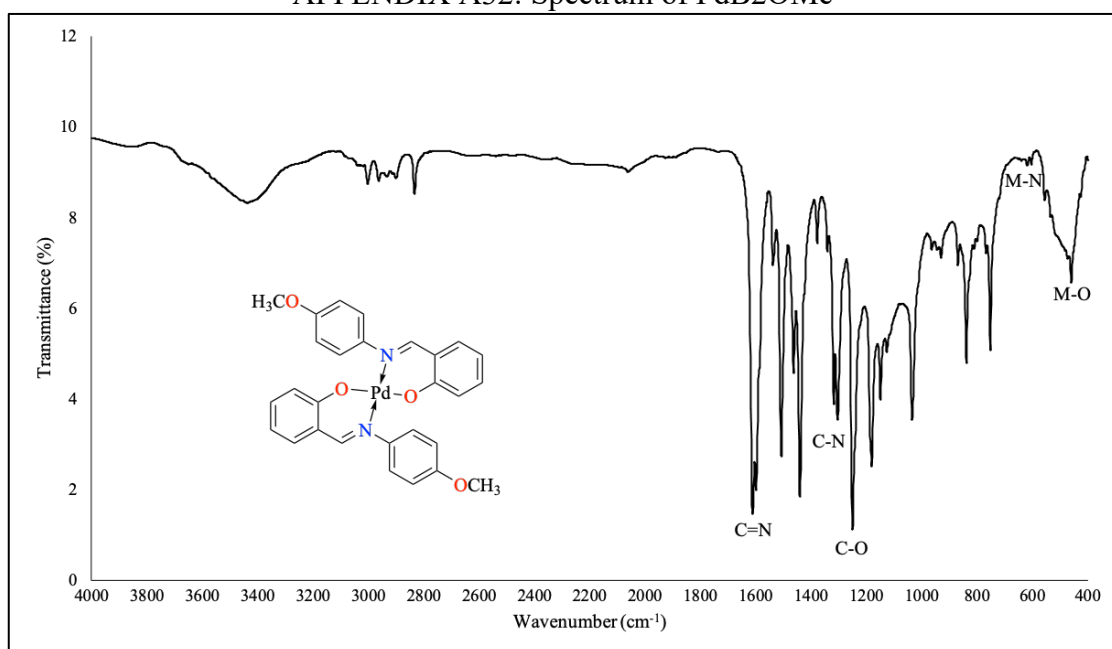
APPENDIX A30: Spectrum of NiB2OMe



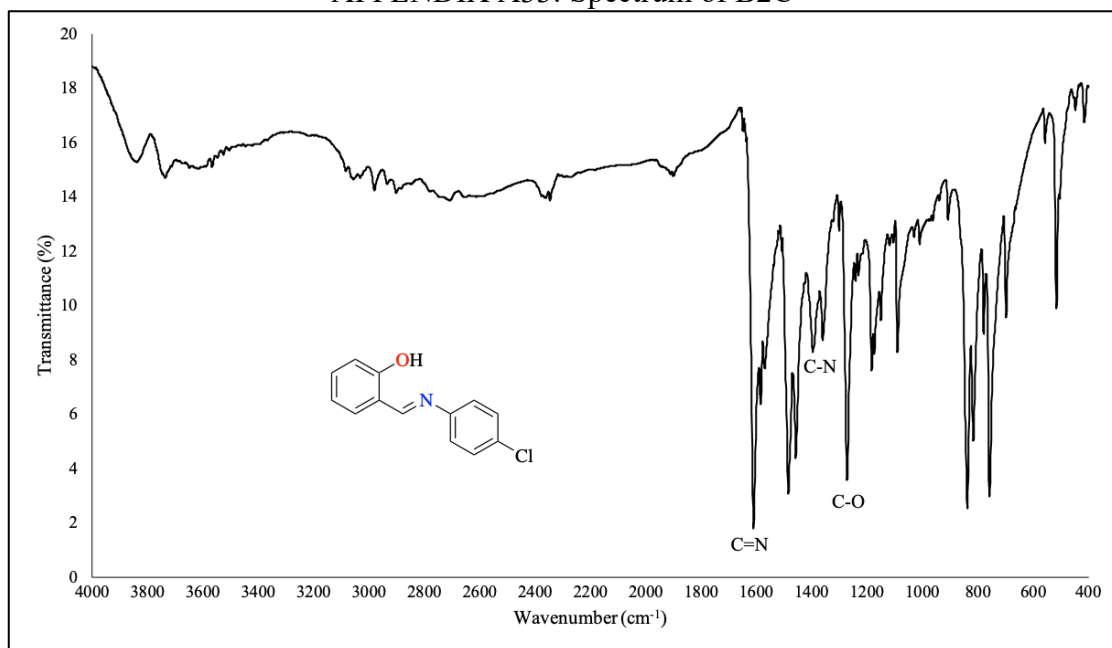
APPENDIX A31: Spectrum of CuB2OMe



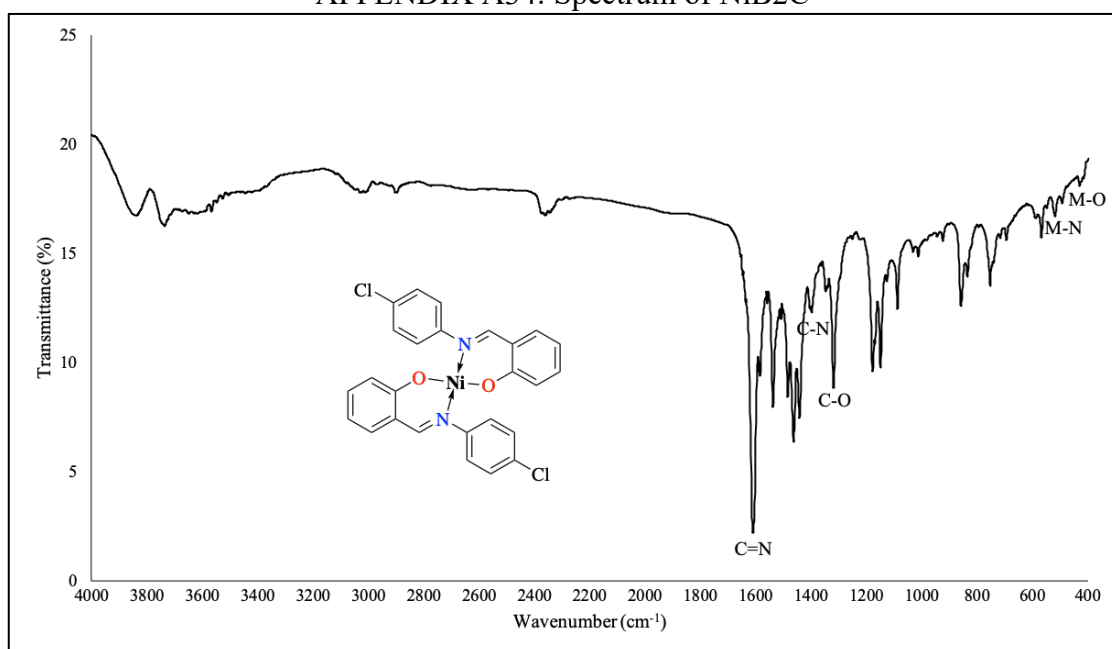
APPENDIX A32: Spectrum of PdB2OMe



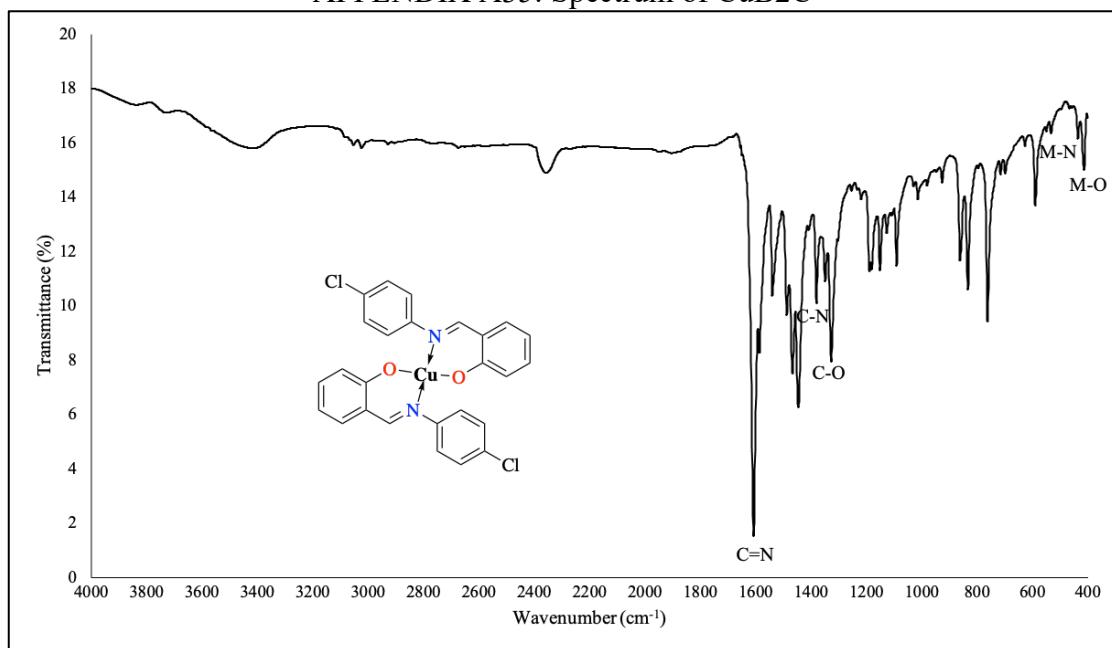
APPENDIX A33: Spectrum of B2C



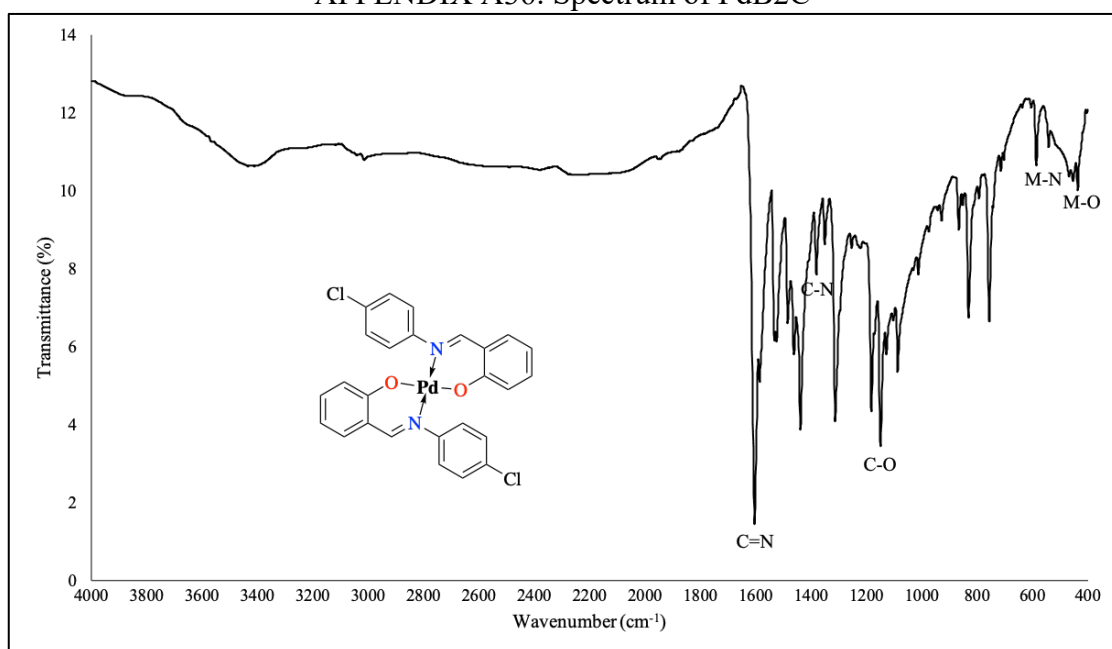
APPENDIX A34: Spectrum of NiB2C



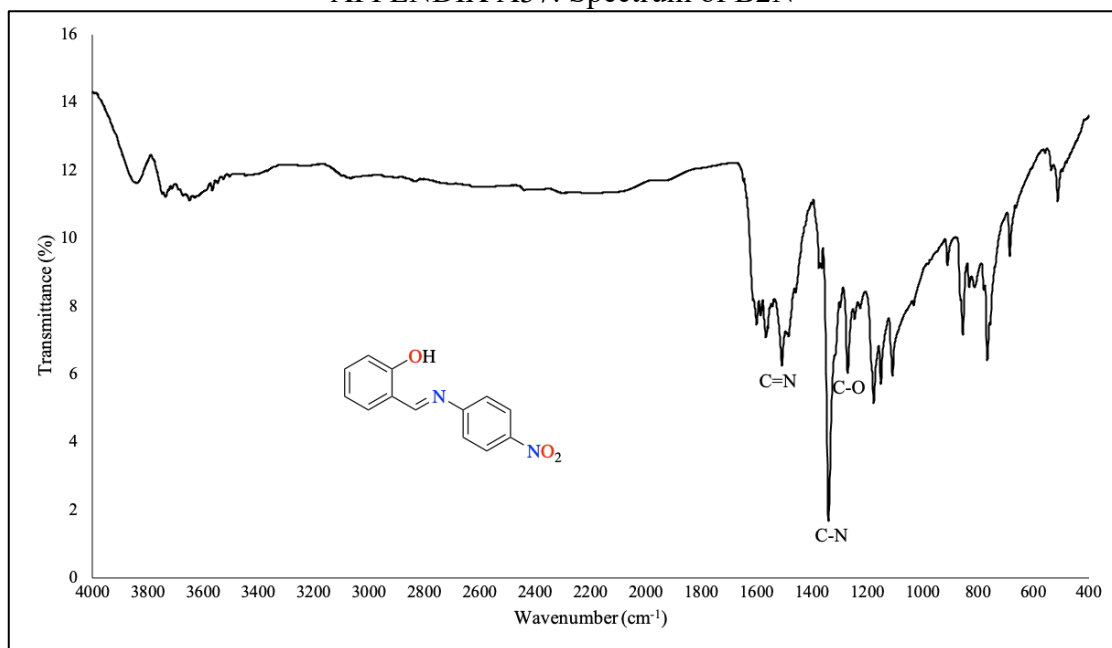
APPENDIX A35: Spectrum of CuB2C



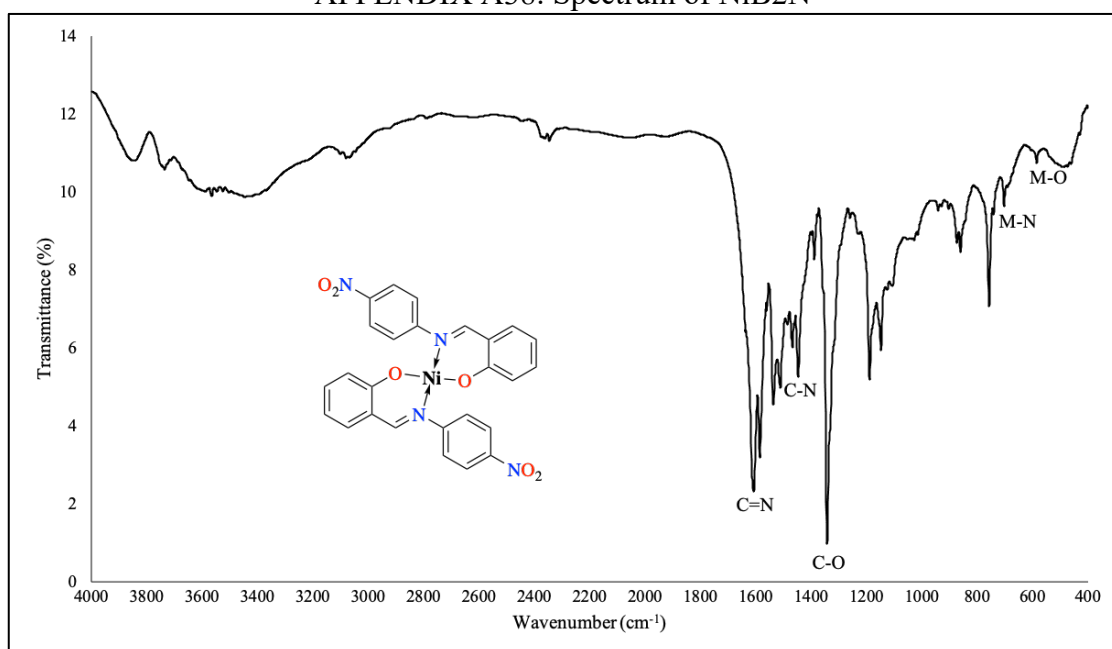
APPENDIX A36: Spectrum of PdB2C



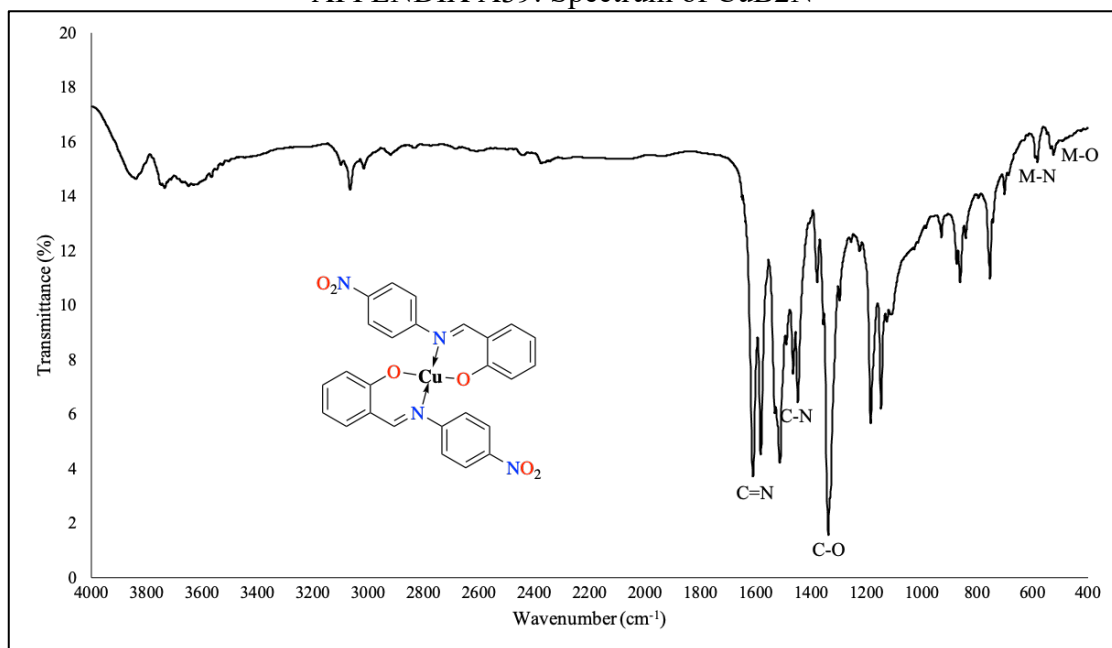
APPENDIX A37: Spectrum of B2N



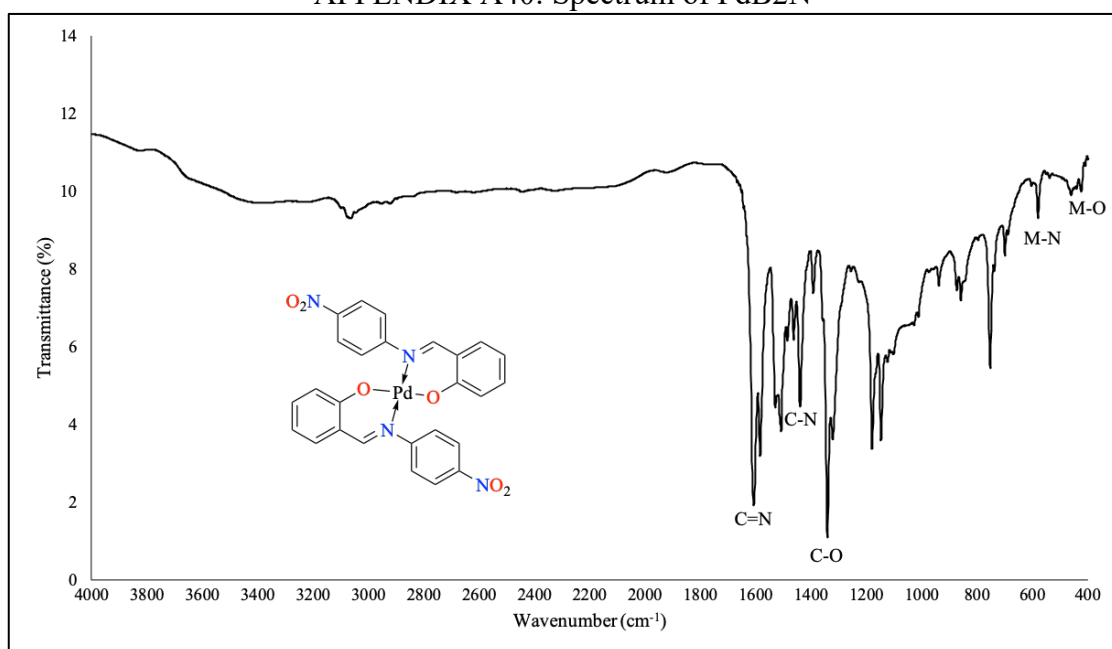
APPENDIX A38: Spectrum of NiB2N



APPENDIX A39: Spectrum of CuB2N



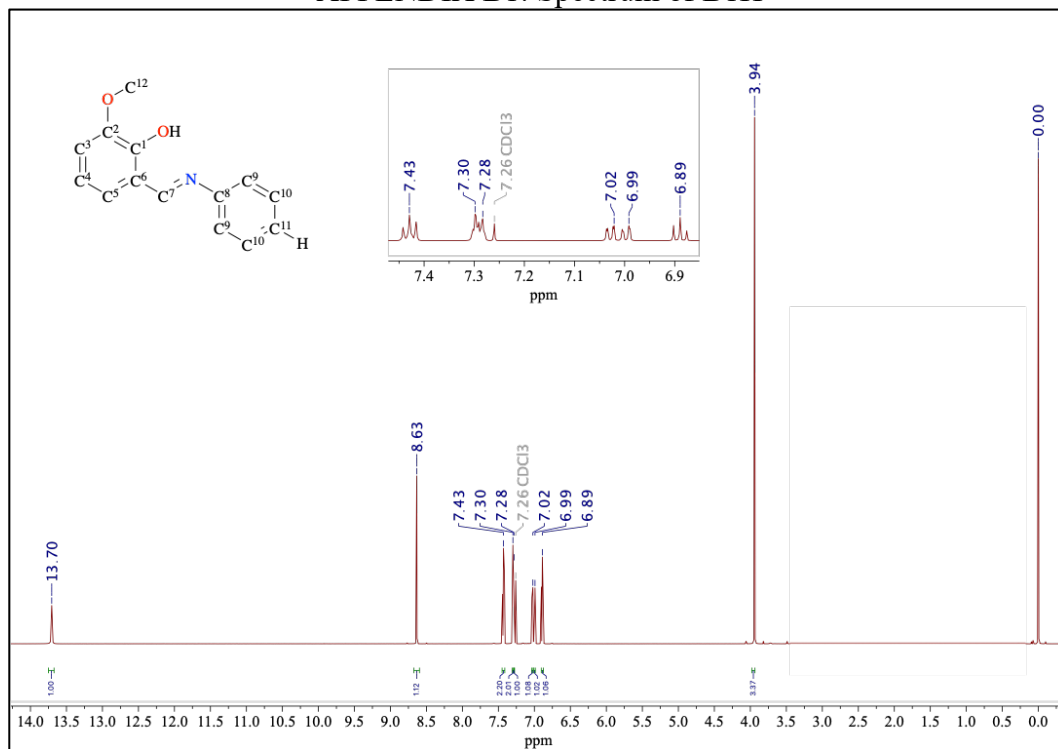
APPENDIX A40: Spectrum of PdB2N



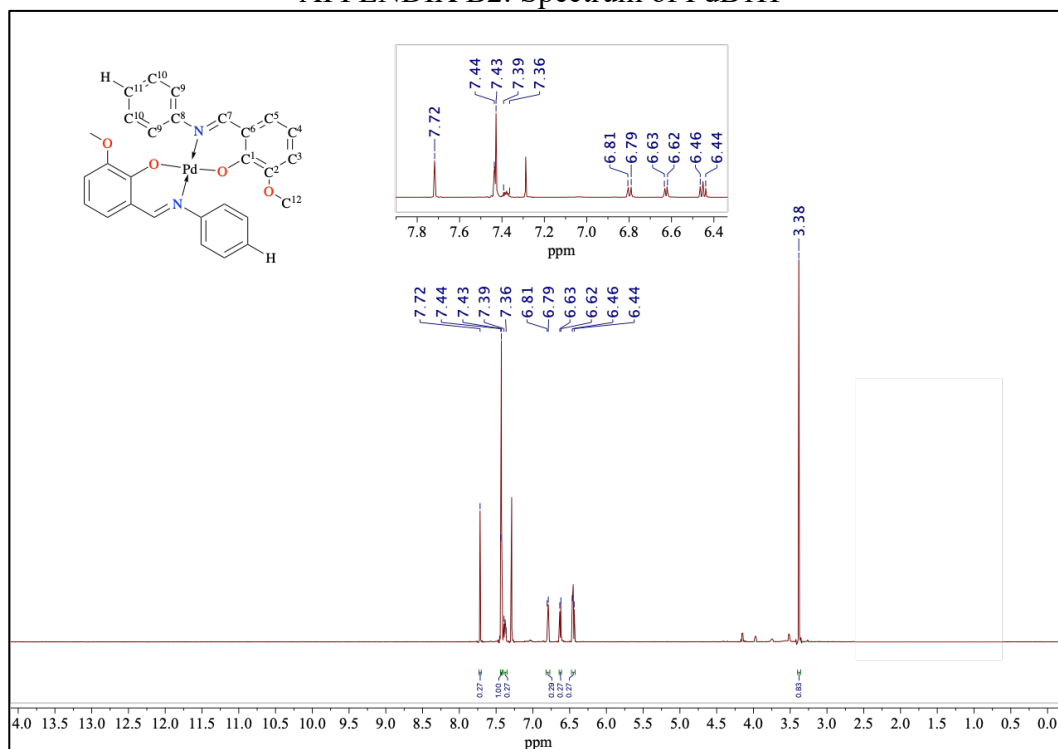
APPENDIX B

^1H NMR Spectroscopy

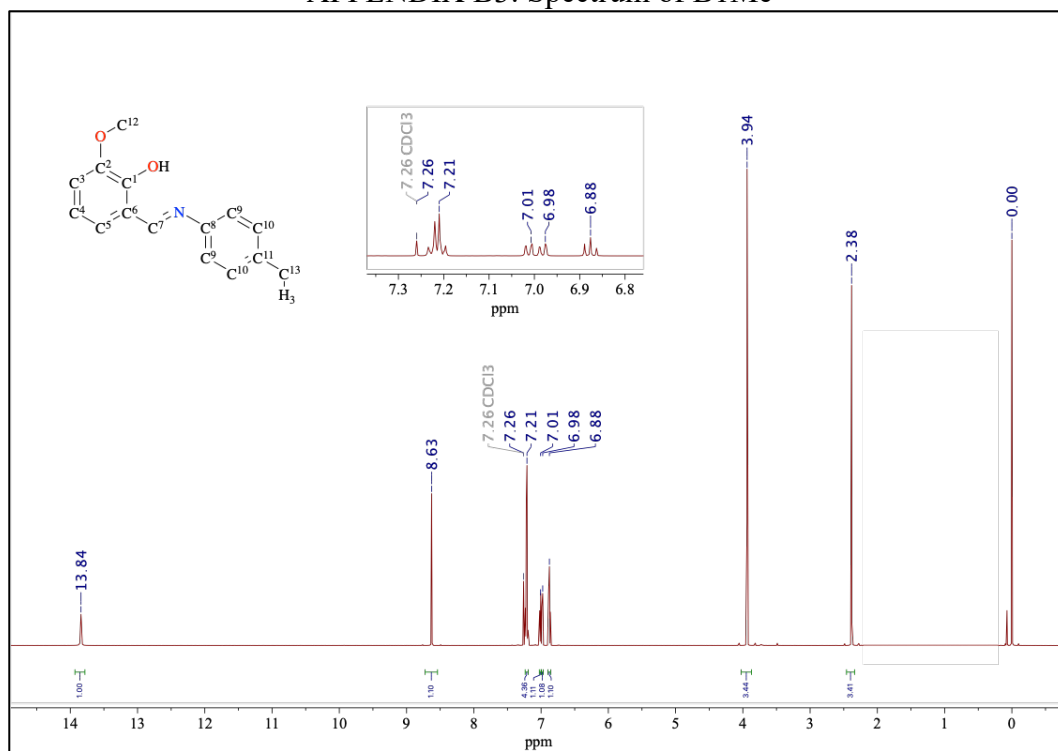
APPENDIX B1: Spectrum of B1H



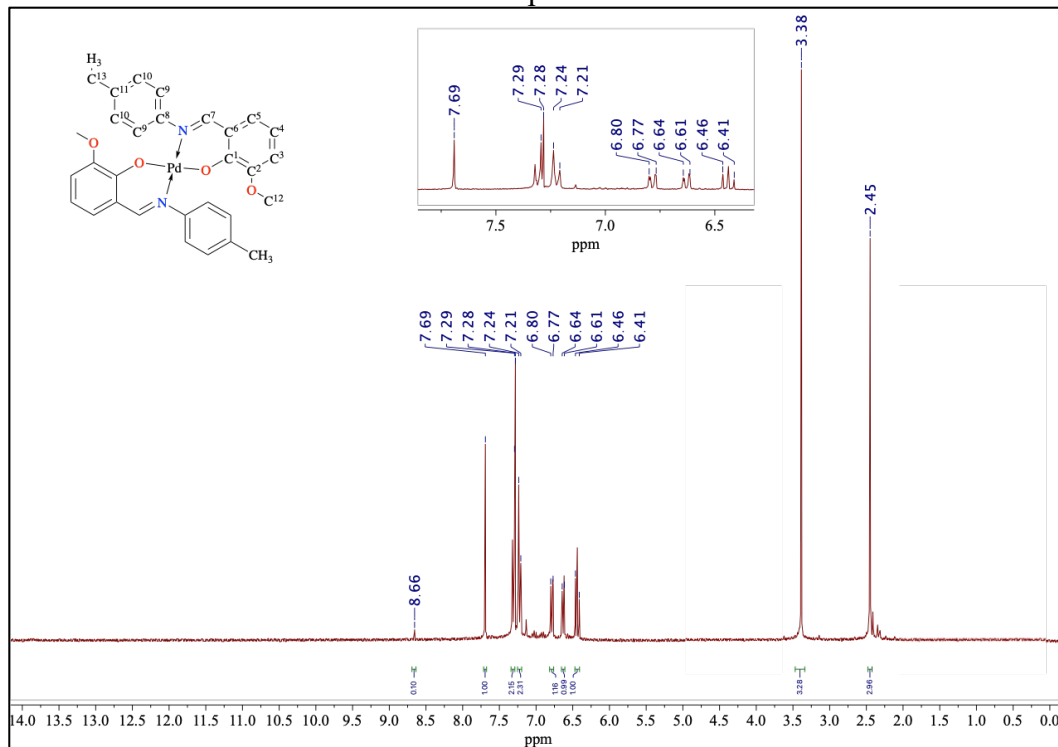
APPENDIX B2: Spectrum of PdB1H



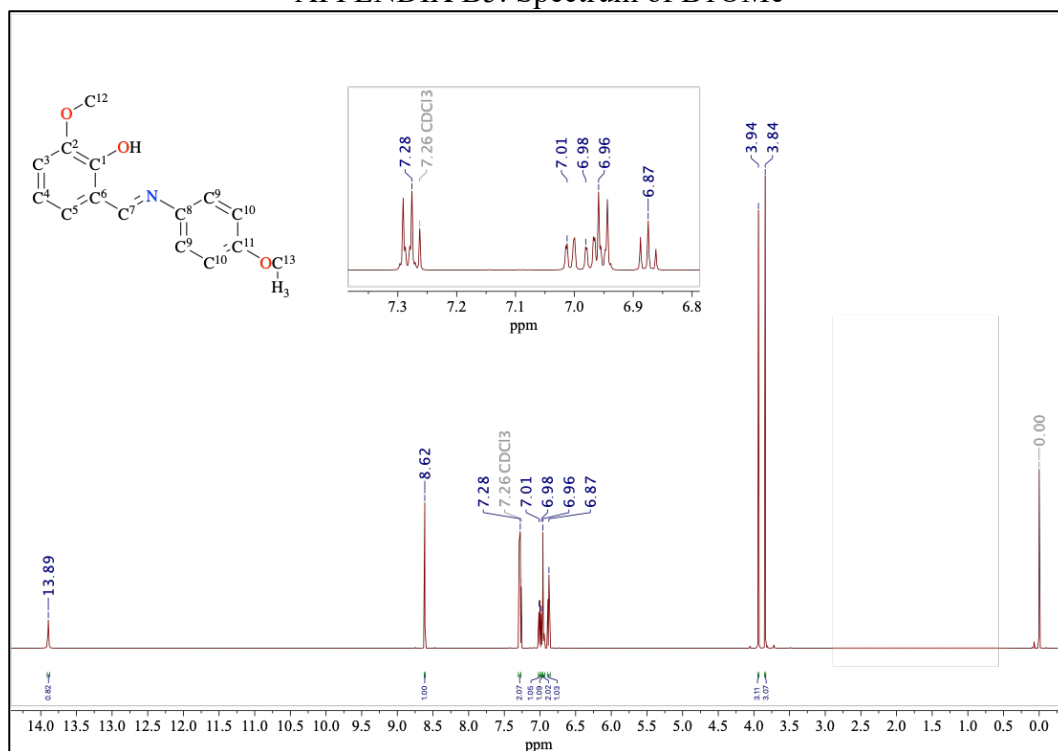
APPENDIX B3: Spectrum of B1Me



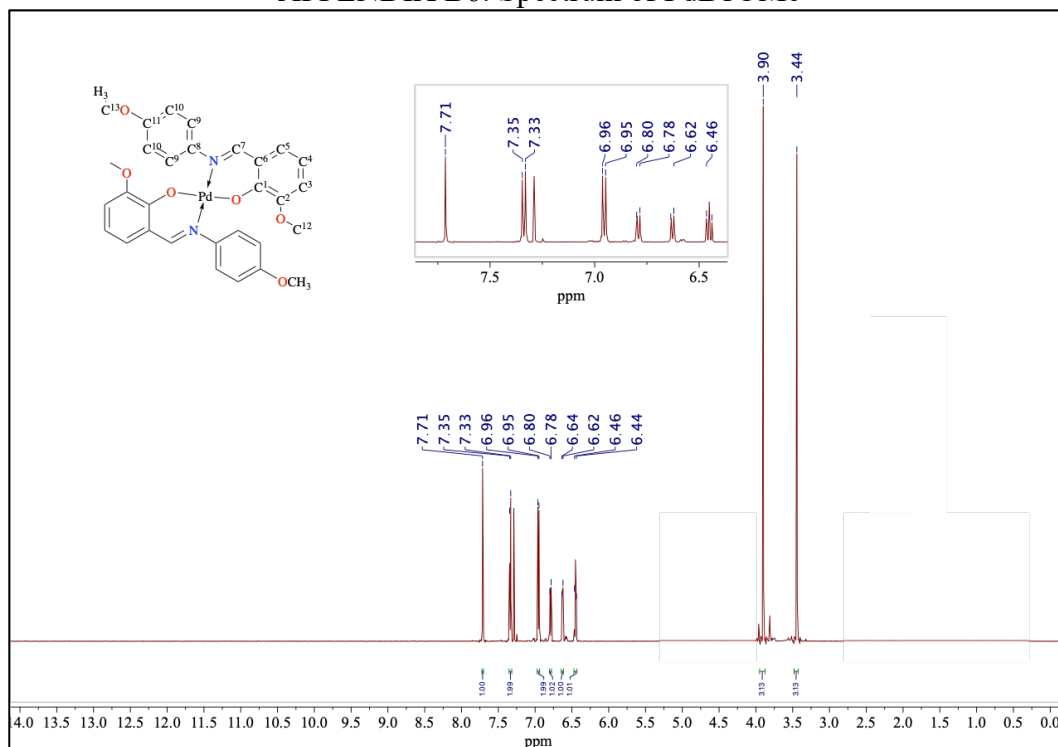
APPENDIX B4: Spectrum of PdB1Me



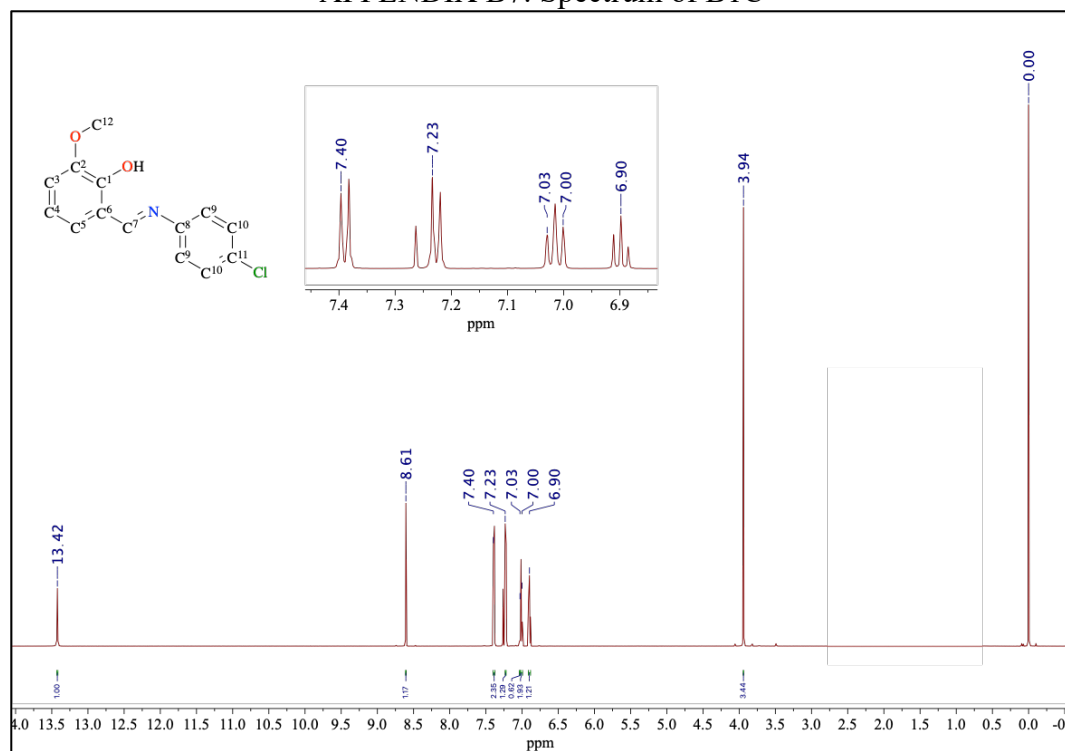
APPENDIX B5: Spectrum of B1OMe



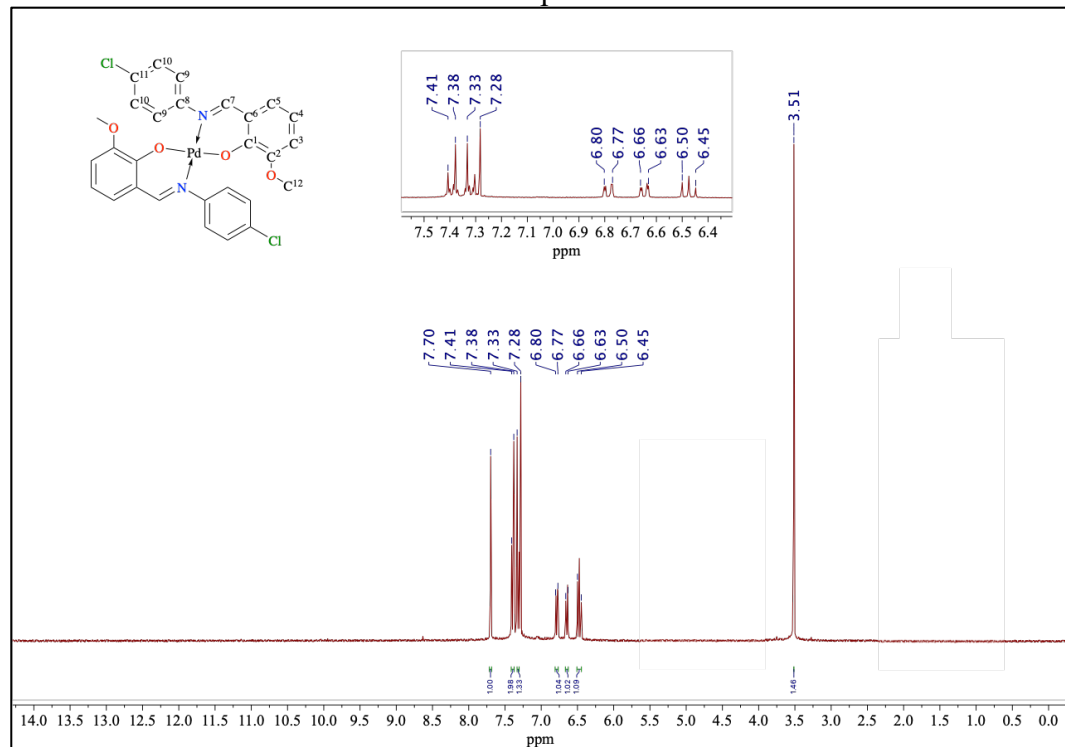
APPENDIX B6: Spectrum of PdB1OMe



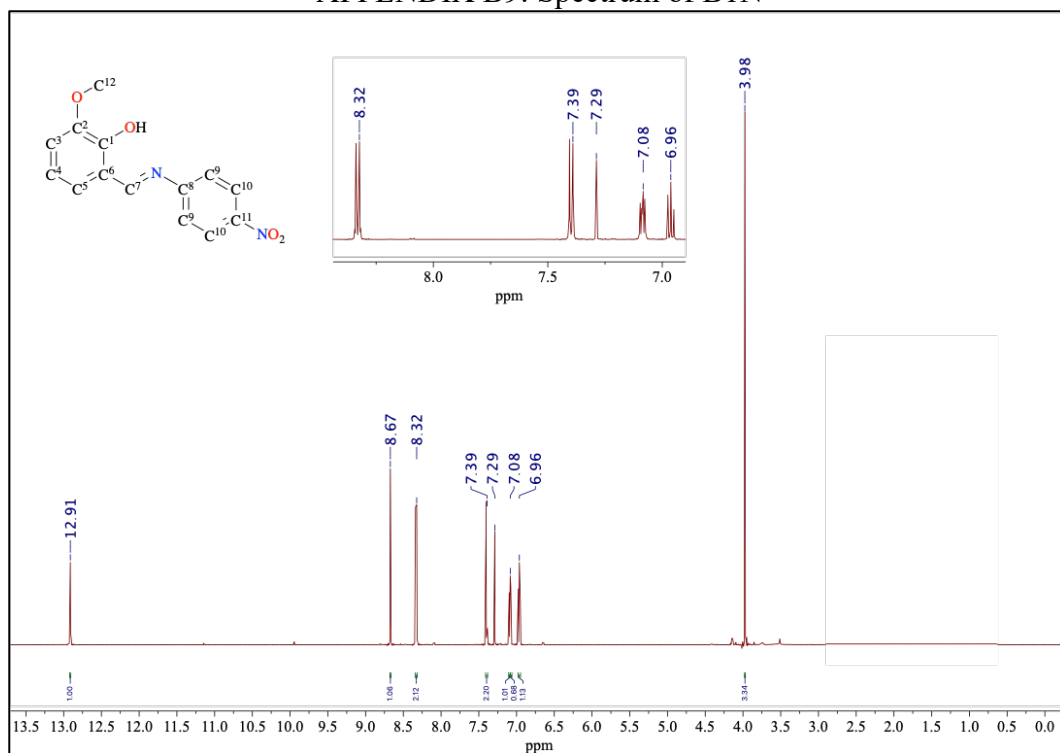
APPENDIX B7: Spectrum of B1C



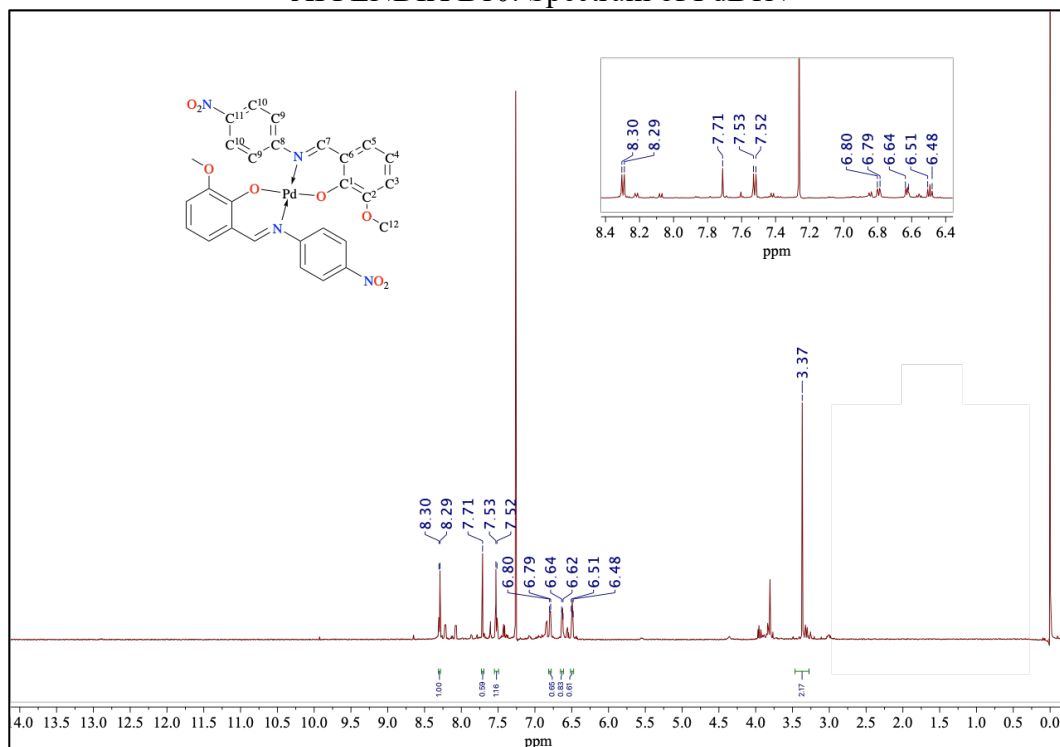
APPENDIX B8: Spectrum of PdB1C



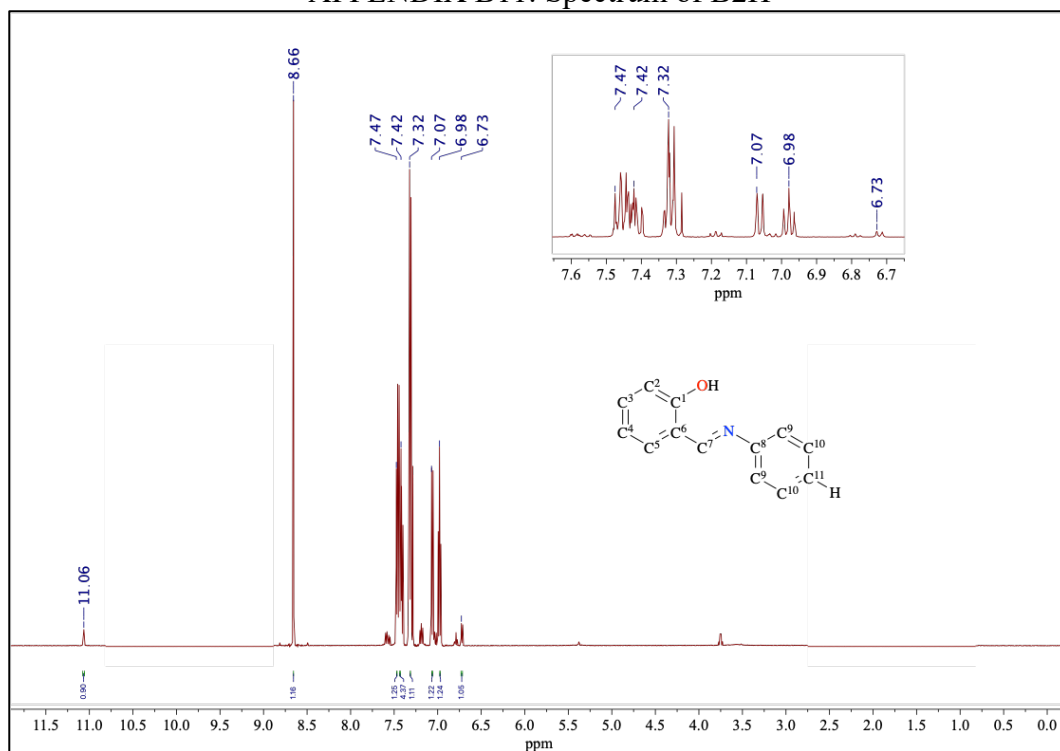
APPENDIX B9: Spectrum of B1N



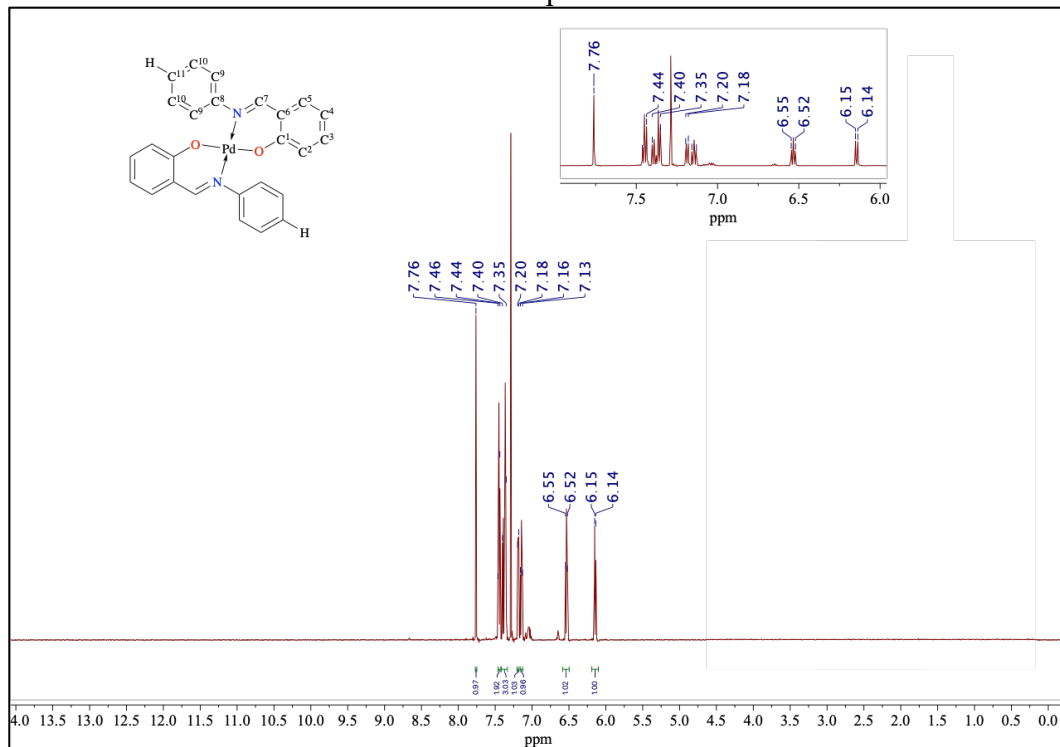
APPENDIX B10: Spectrum of PdB1N



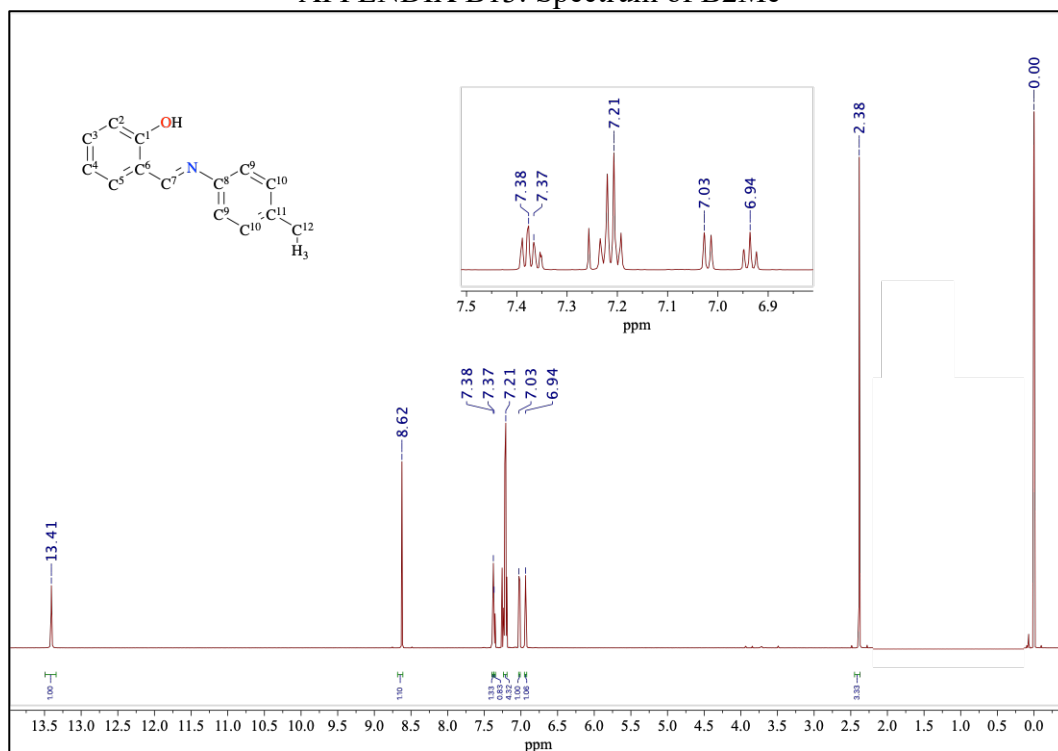
APPENDIX B11: Spectrum of B2H



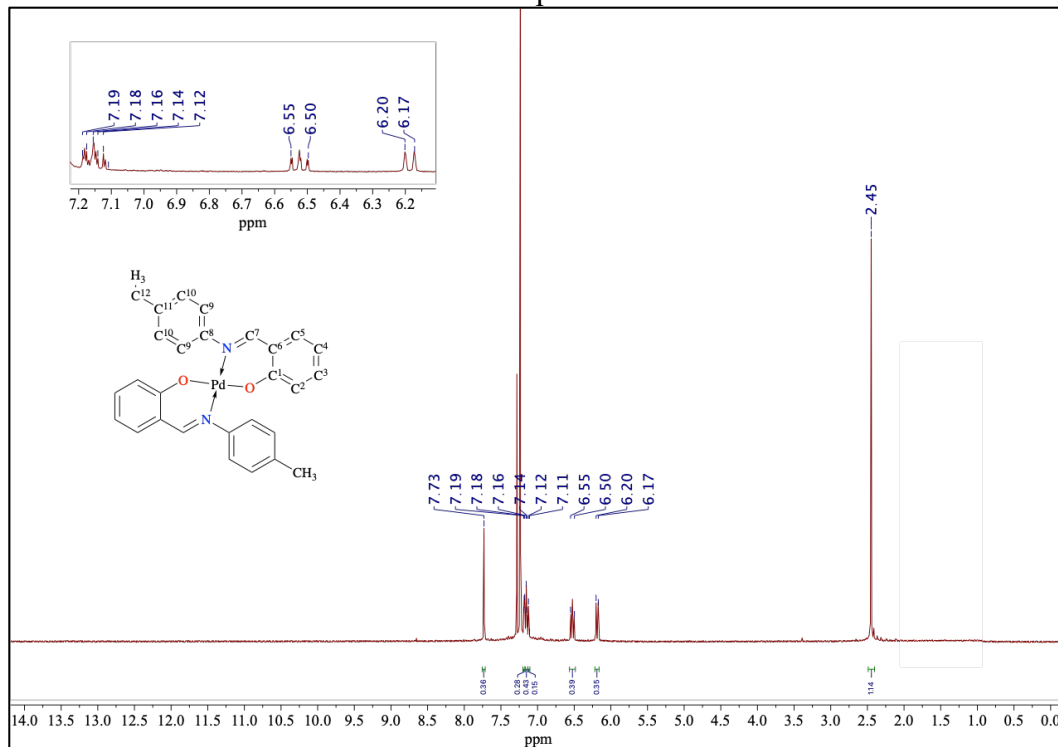
APPENDIX B12: Spectrum of PdB2H



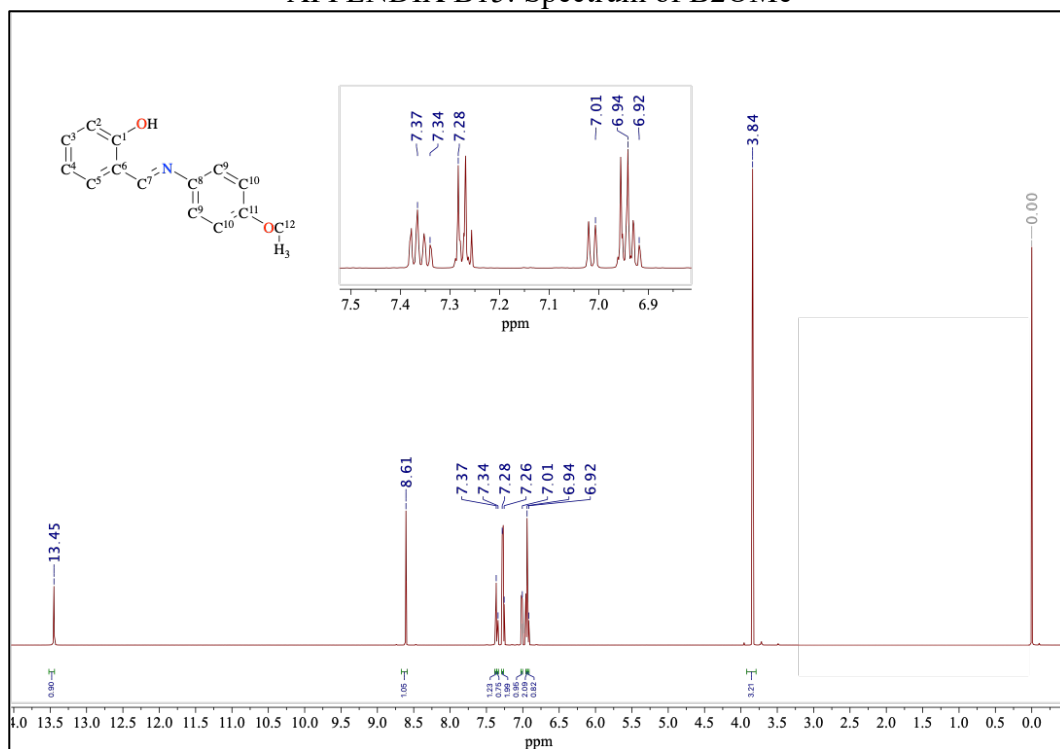
APPENDIX B13: Spectrum of B2Me



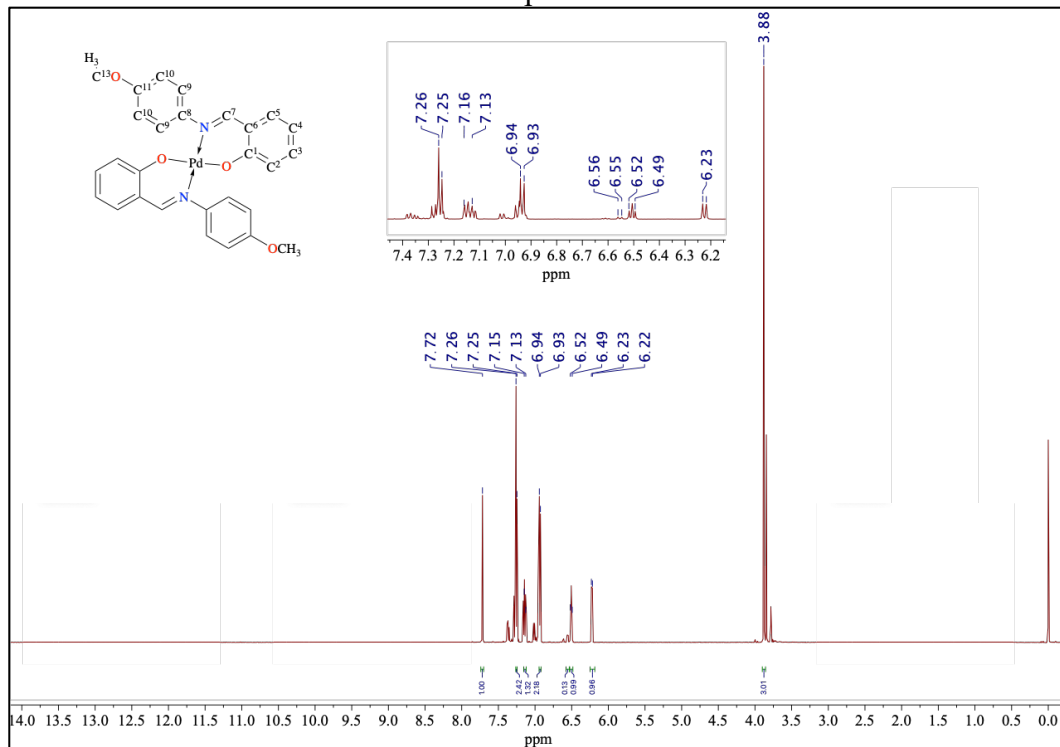
APPENDIX B14: Spectrum of PdB2Me



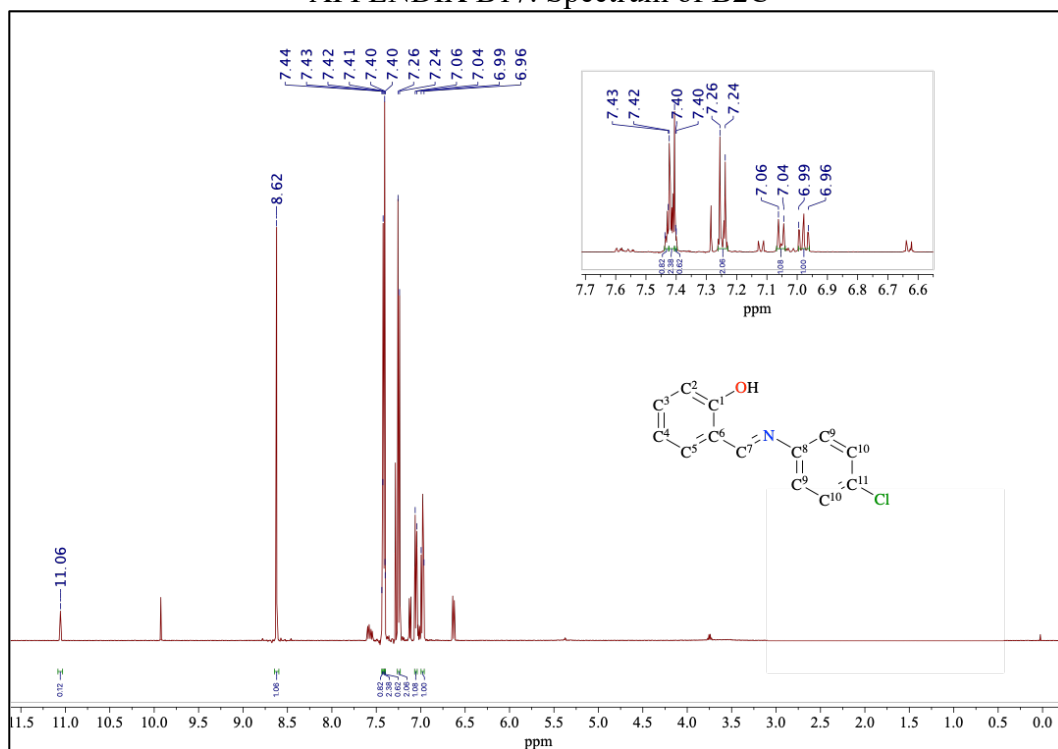
APPENDIX B15: Spectrum of B2OMe



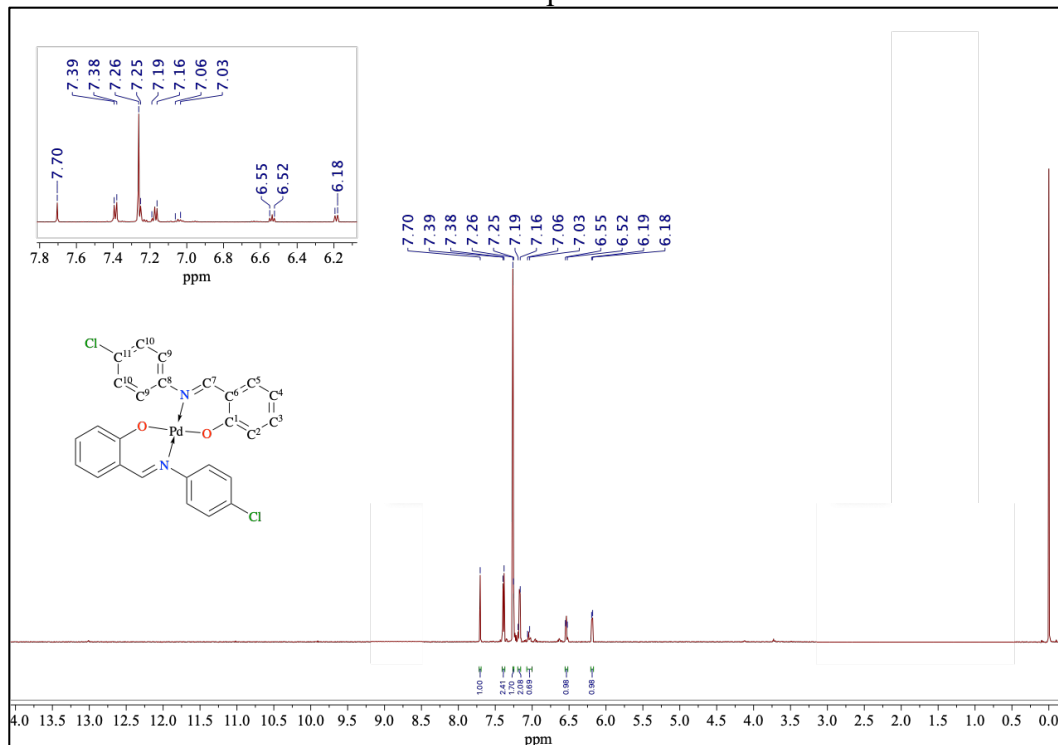
APPENDIX B16: Spectrum of PdB2OMe



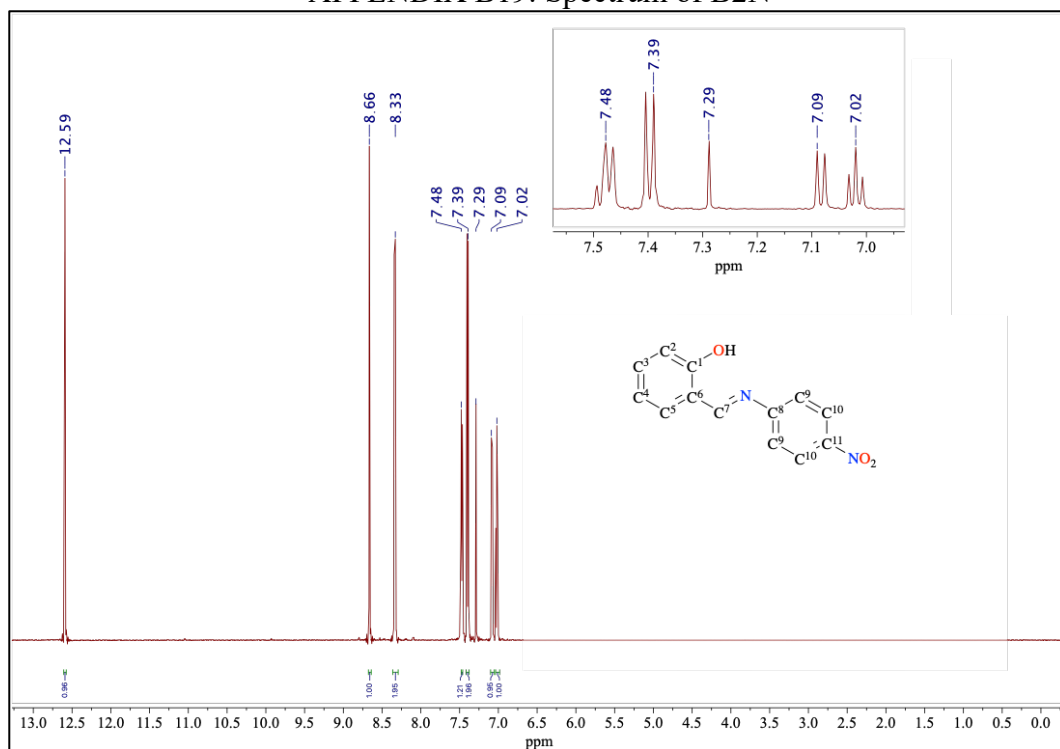
APPENDIX B17: Spectrum of B2C



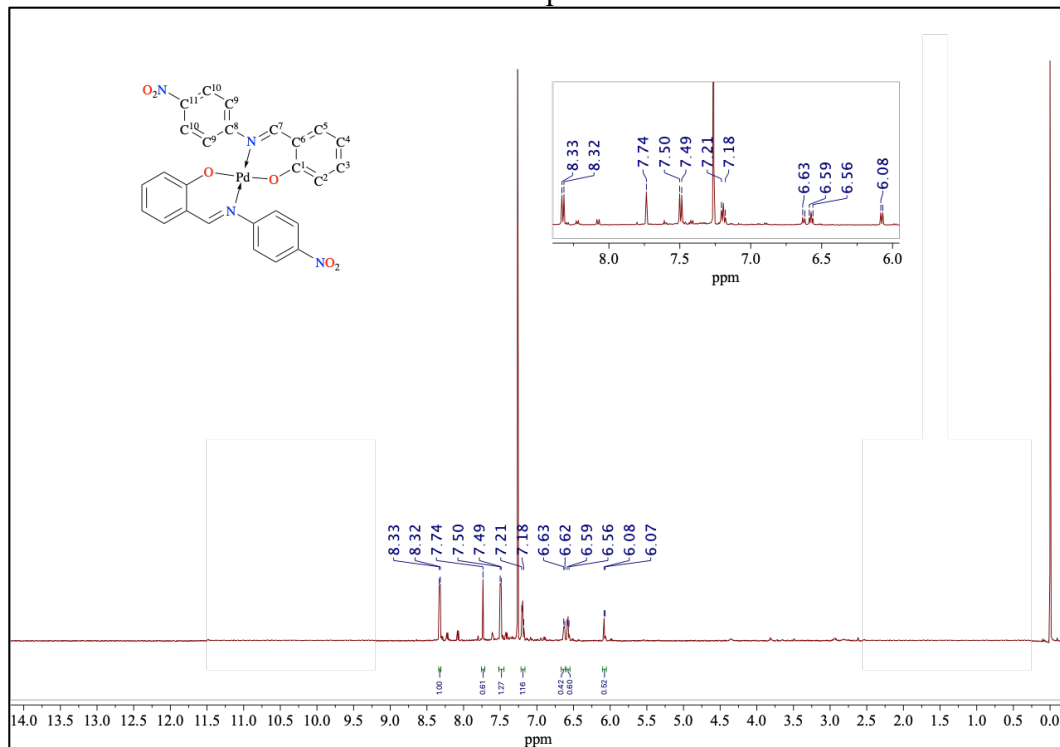
APPENDIX B18: Spectrum of PdB2C



APPENDIX B19: Spectrum of B2N



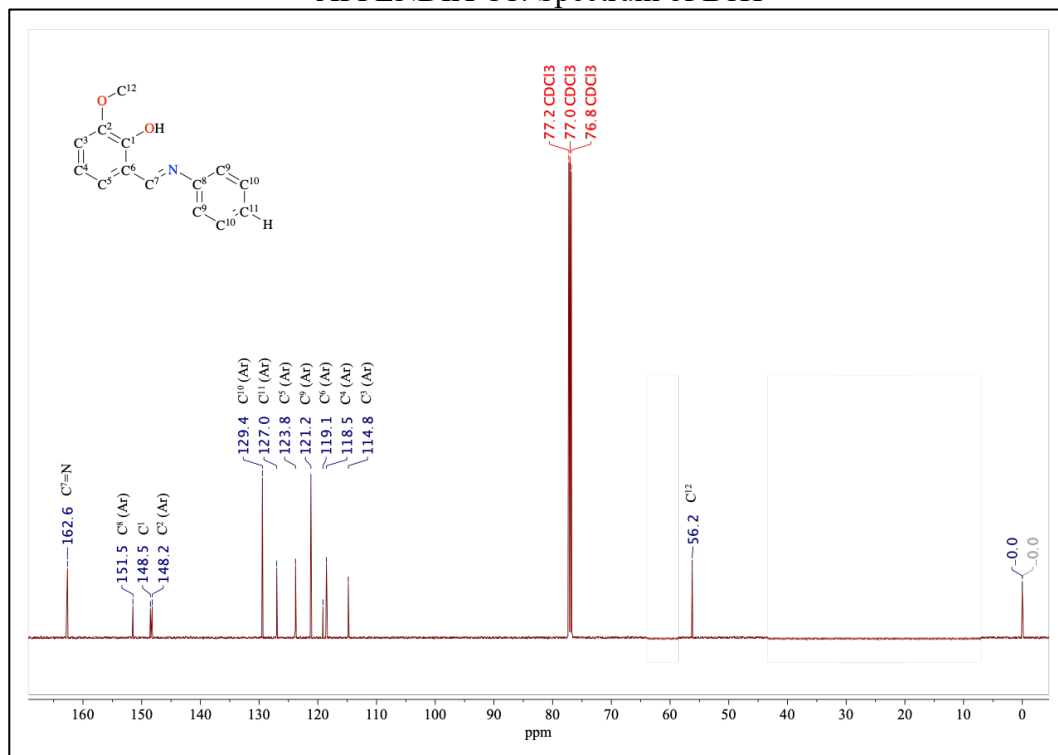
APPENDIX B20: Spectrum of PdB2N



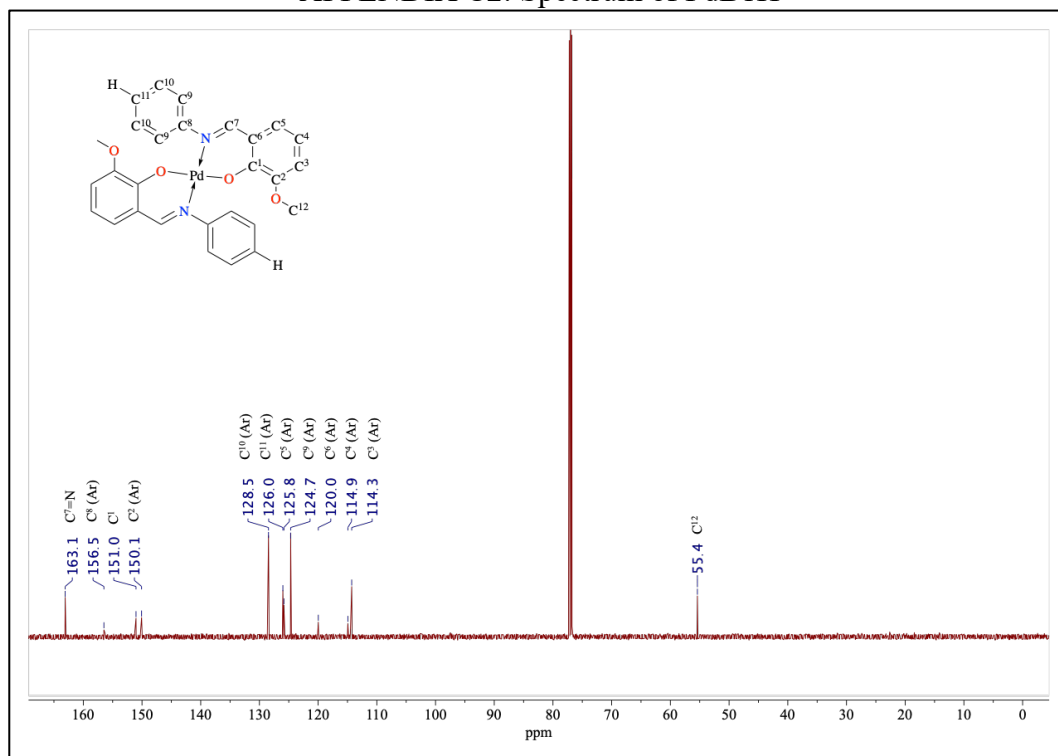
APPENDIX C

^{13}C NMR Spectroscopy

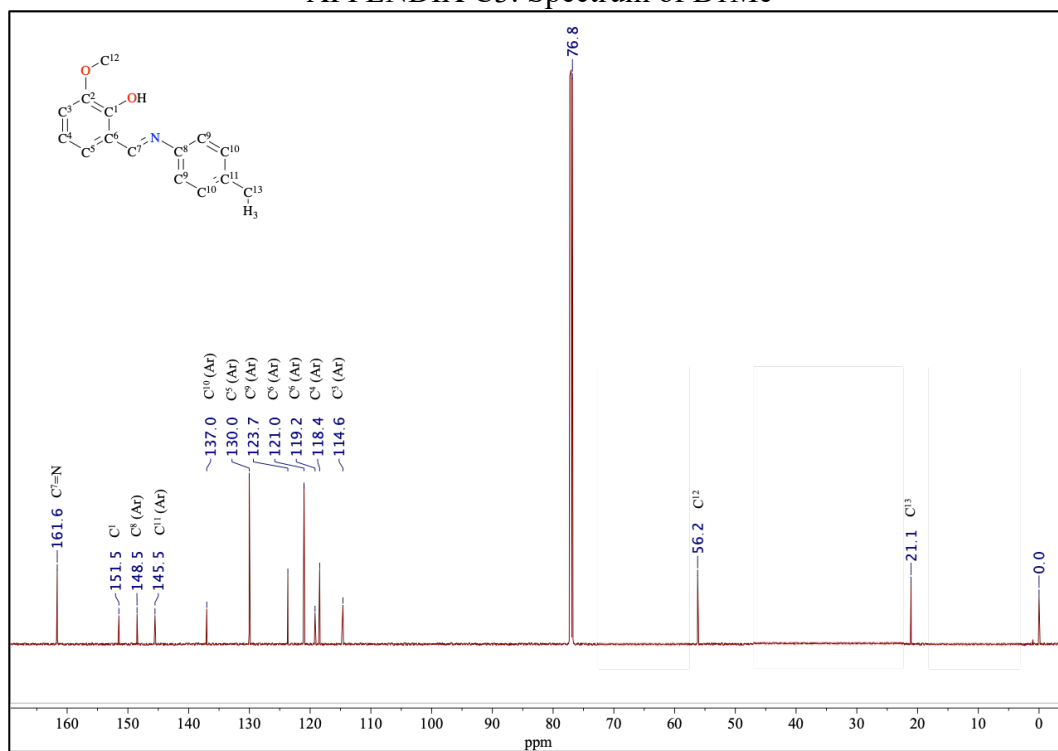
APPENDIX C1: Spectrum of B1H



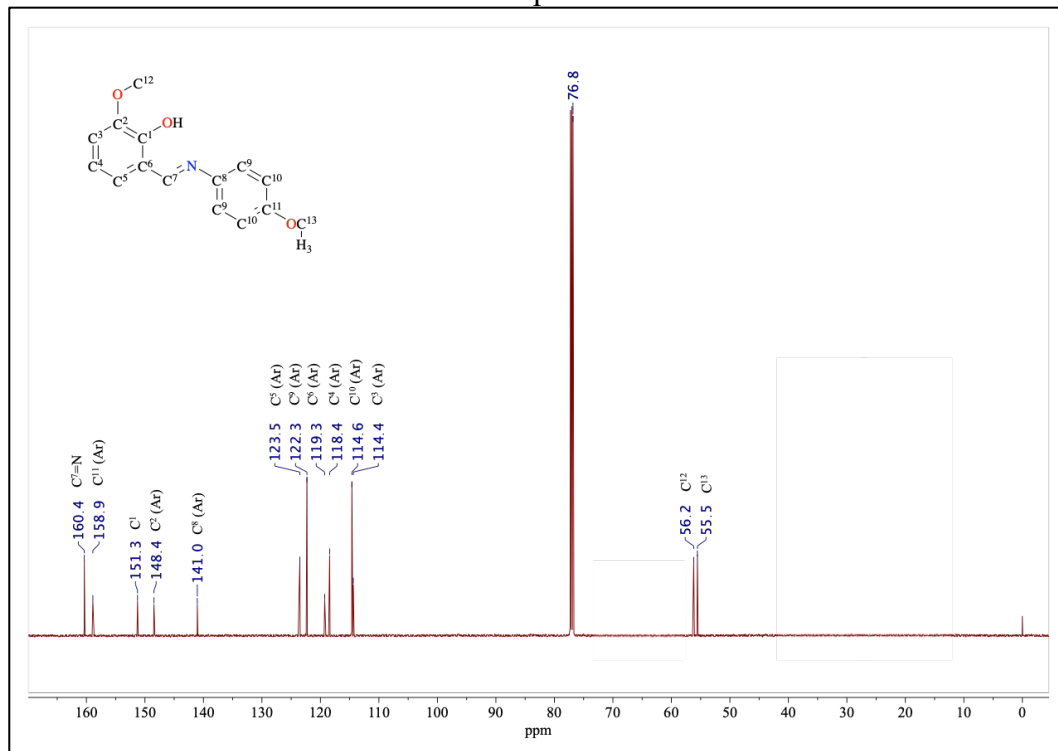
APPENDIX C2: Spectrum of PdB1H



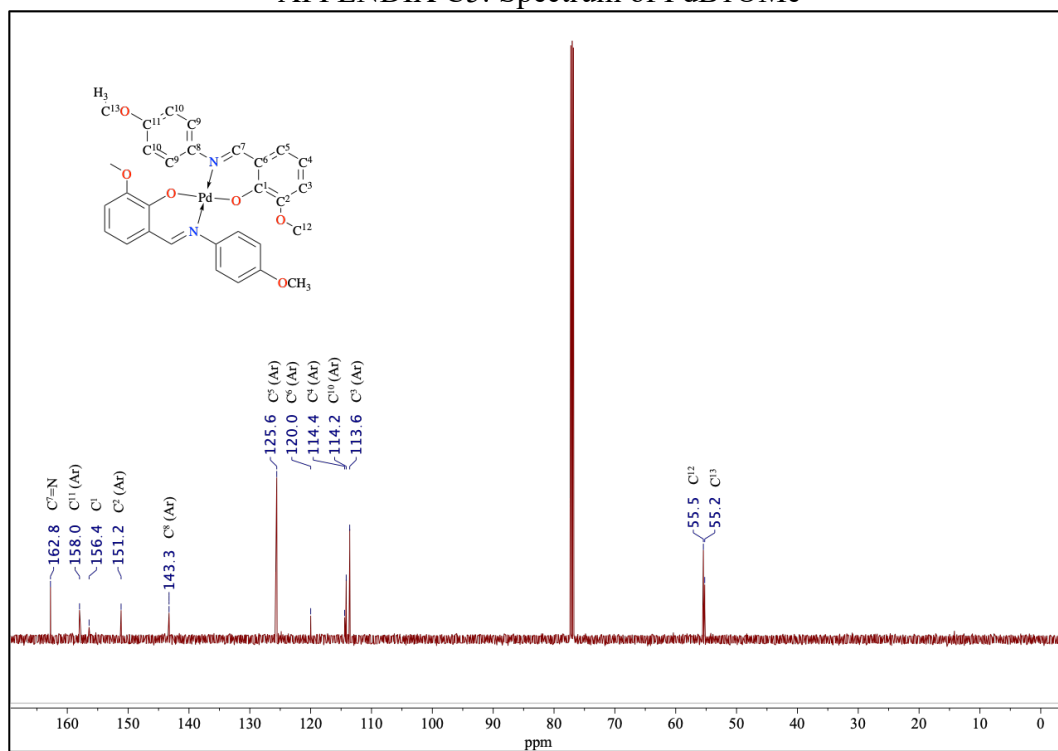
APPENDIX C3: Spectrum of B1Me



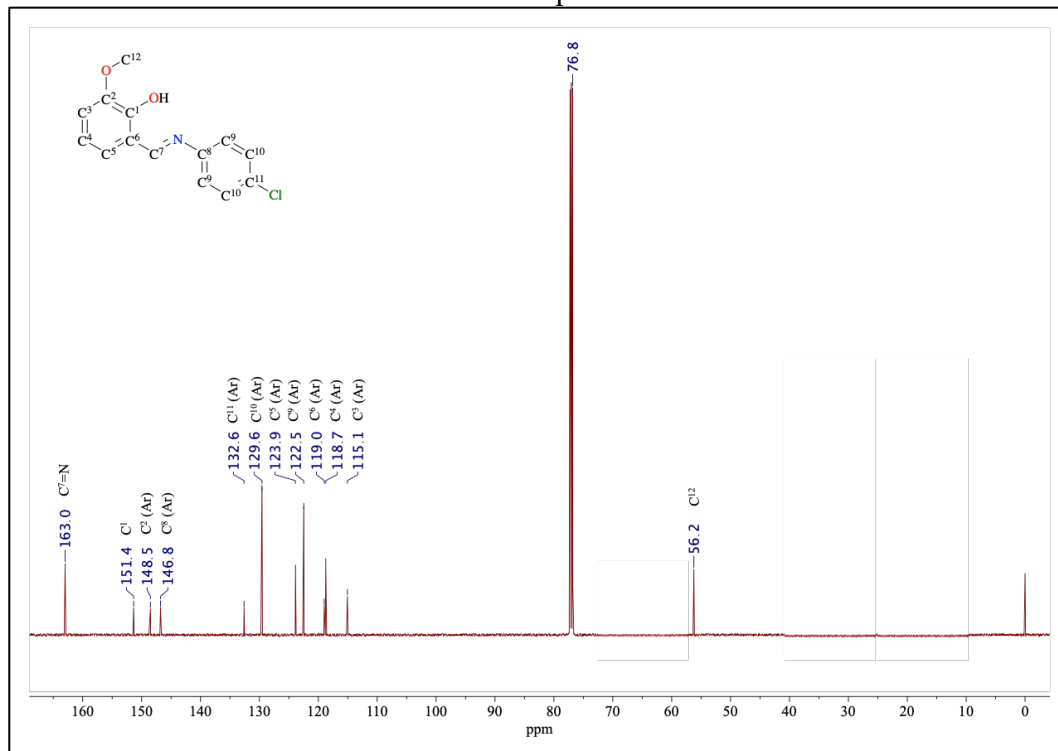
APPENDIX C4: Spectrum of B1OMe



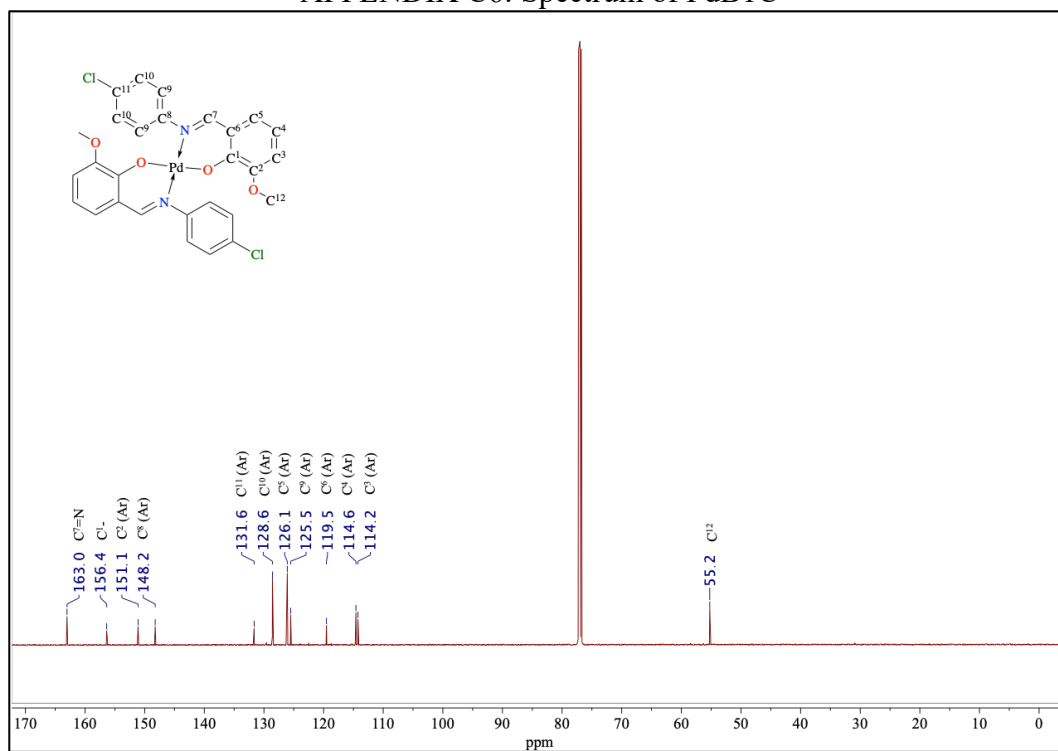
APPENDIX C5: Spectrum of PdBIOMe



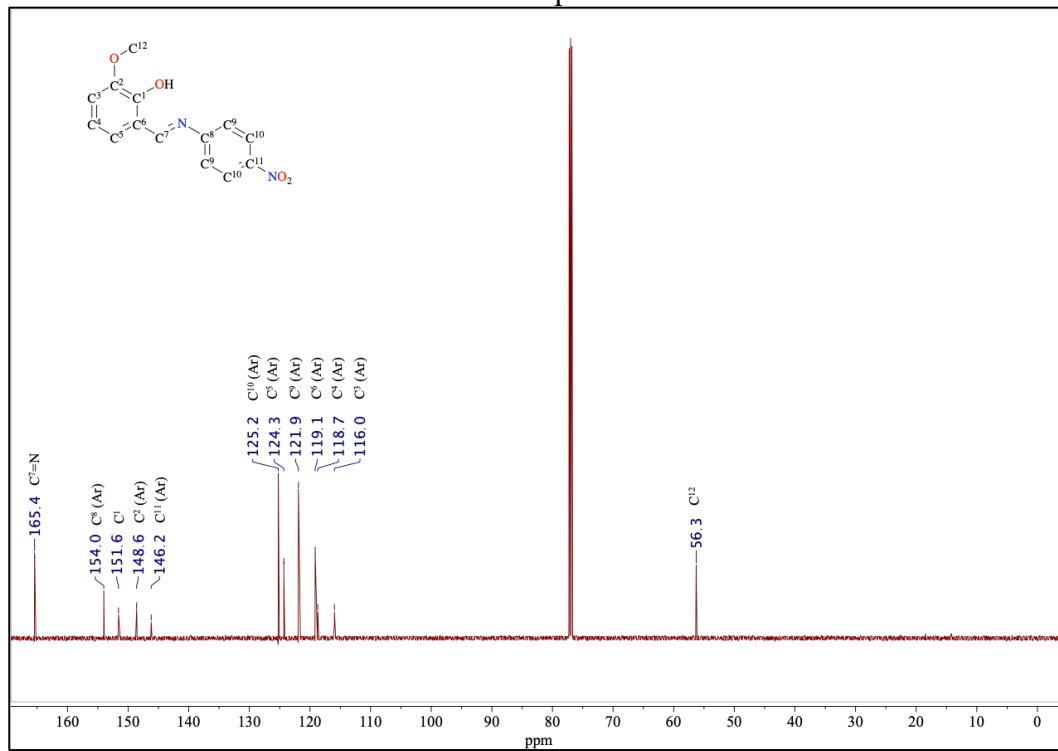
APPENDIX C6: Spectrum of B1C



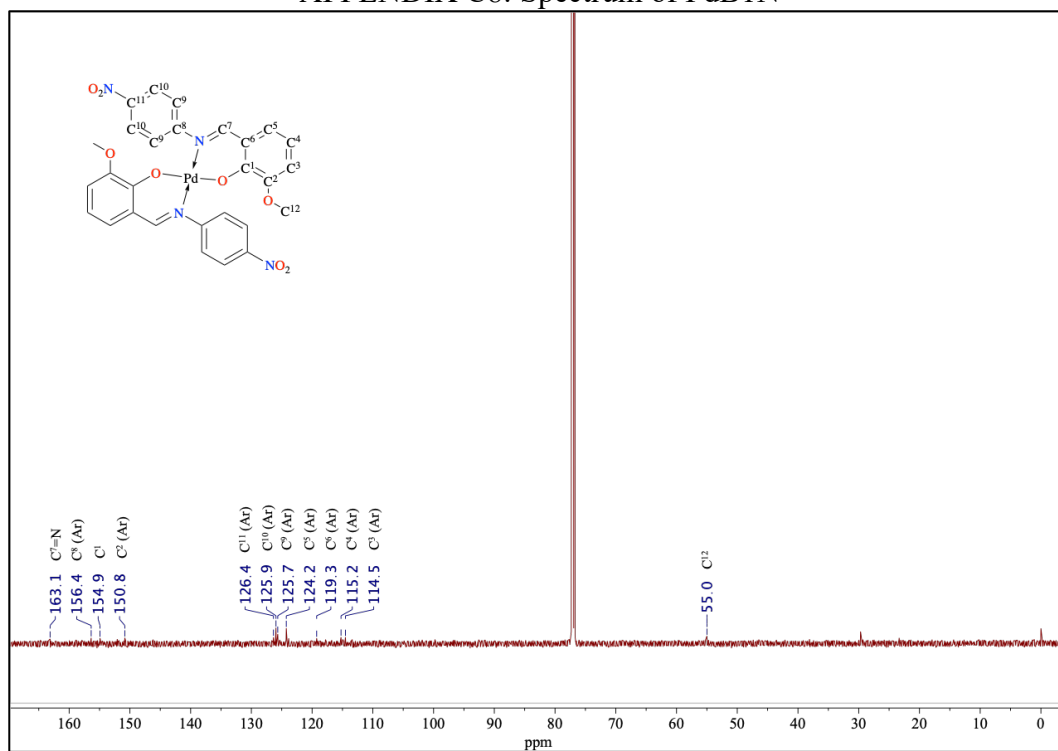
APPENDIX C6: Spectrum of PdB1C



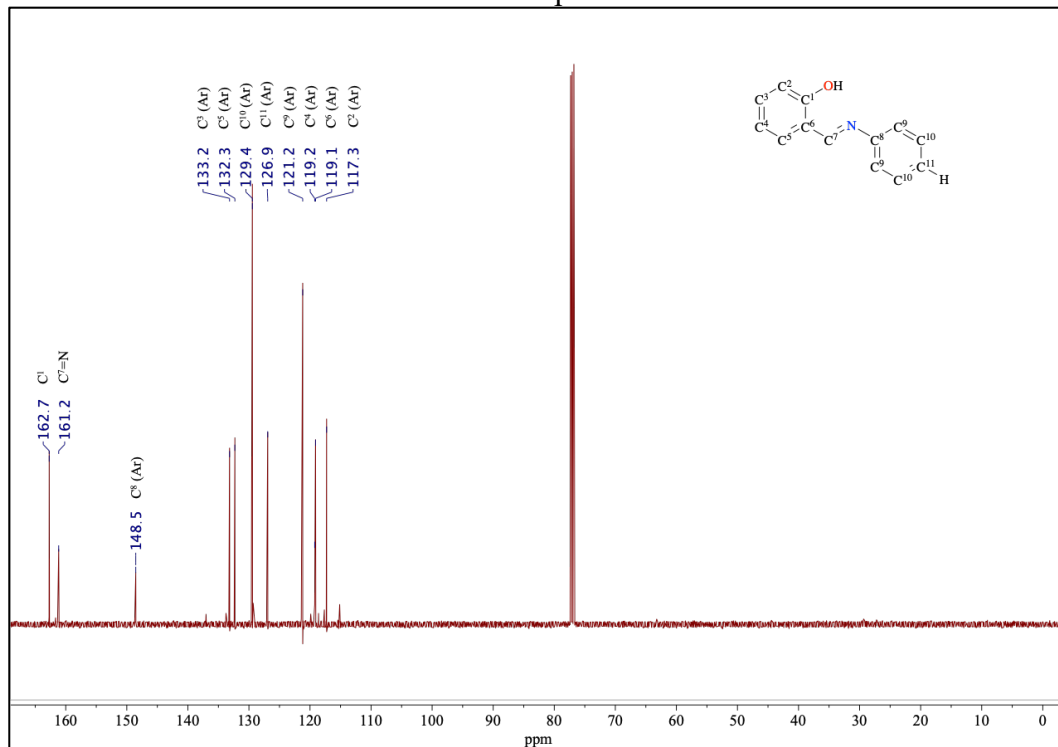
APPENDIX C7: Spectrum of B1N



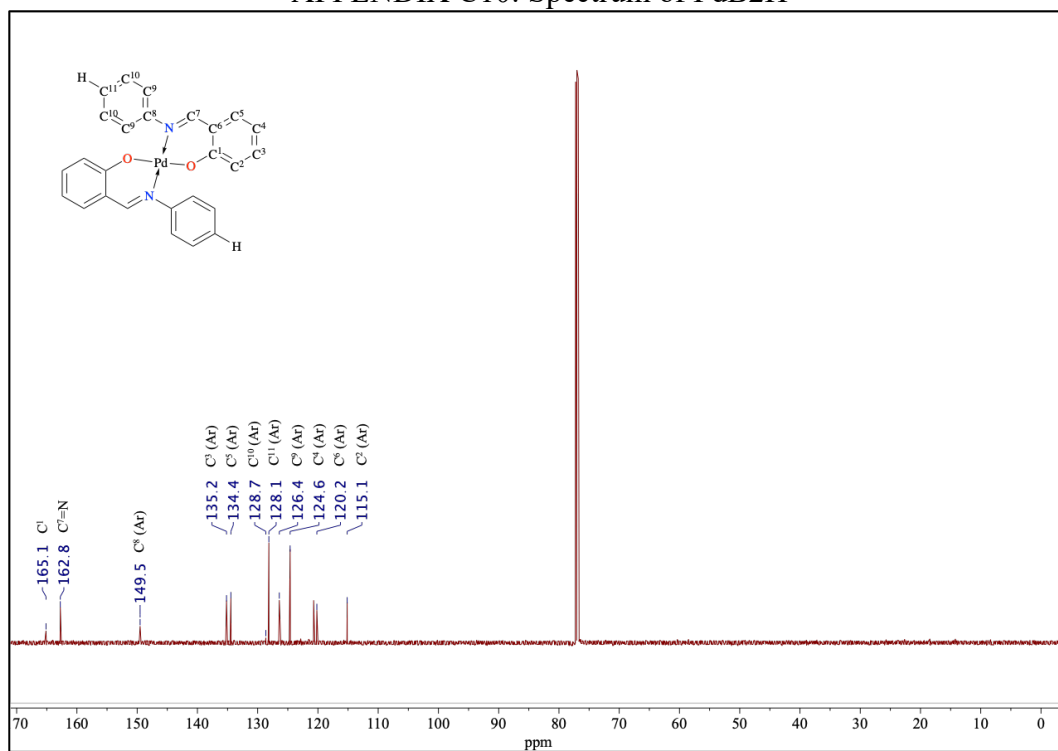
APPENDIX C8: Spectrum of PdB1N



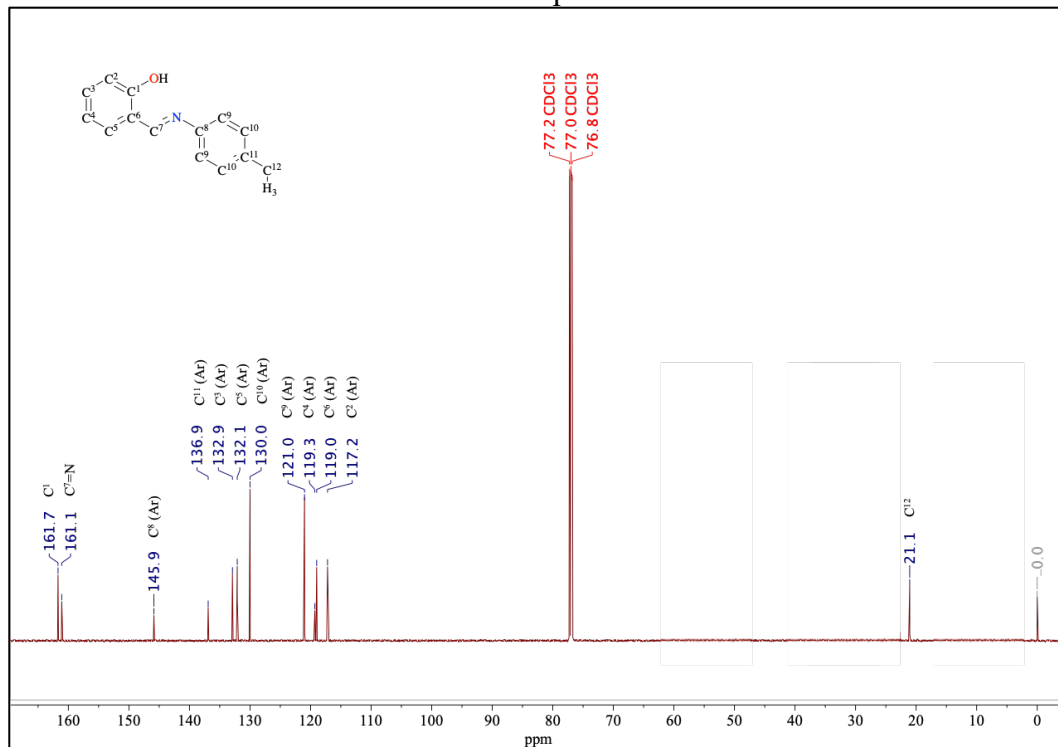
APPENDIX C9: Spectrum of B2H



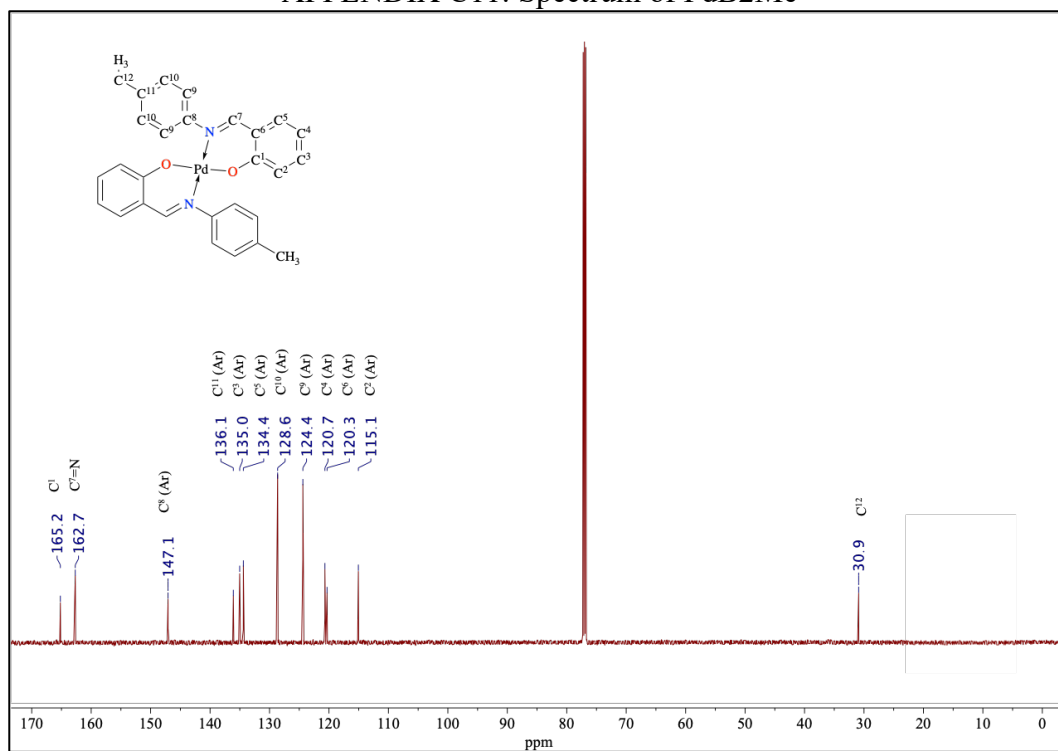
APPENDIX C10: Spectrum of PdB2H



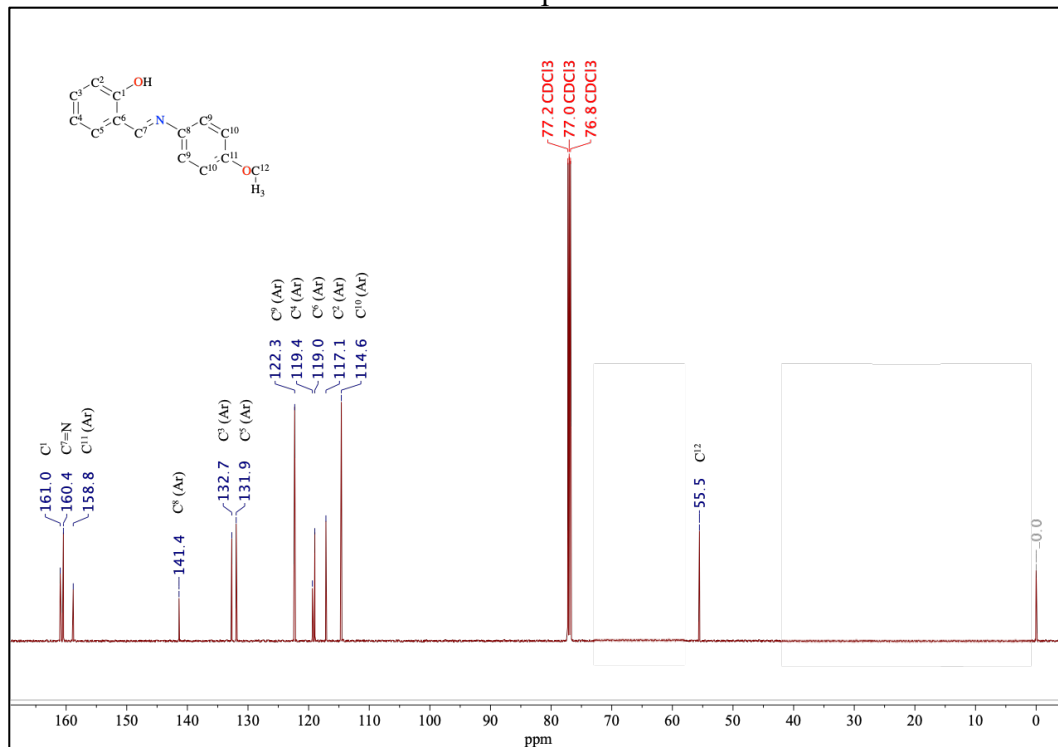
APPENDIX C11: Spectrum of B2Me



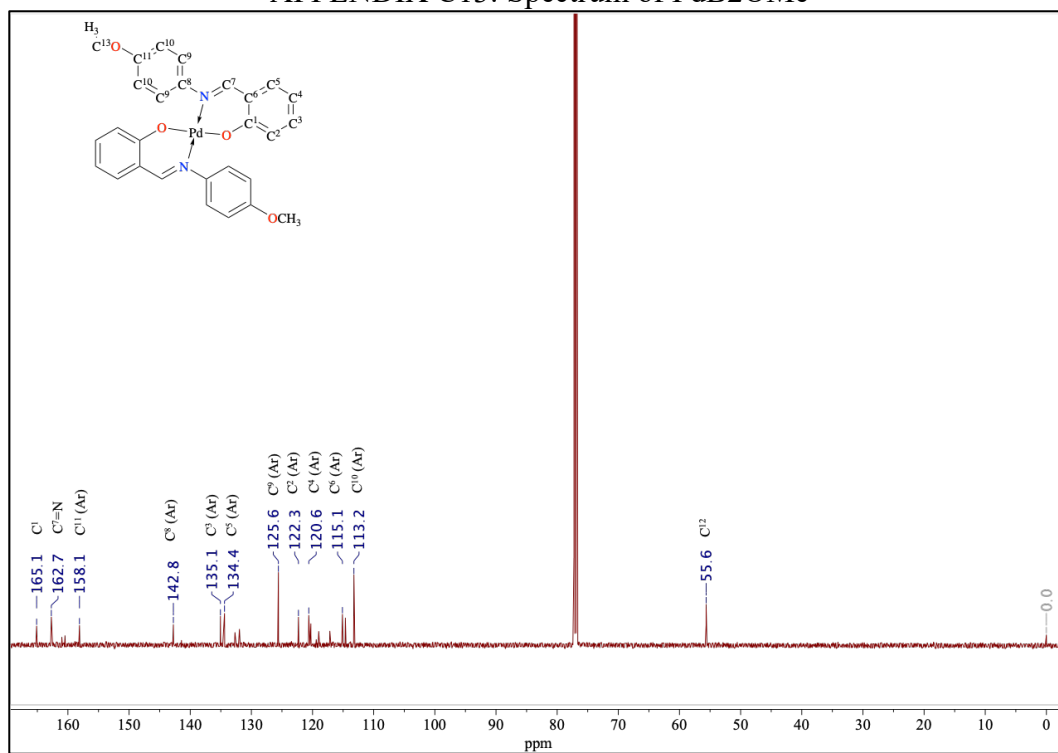
APPENDIX C11: Spectrum of PdB2Me



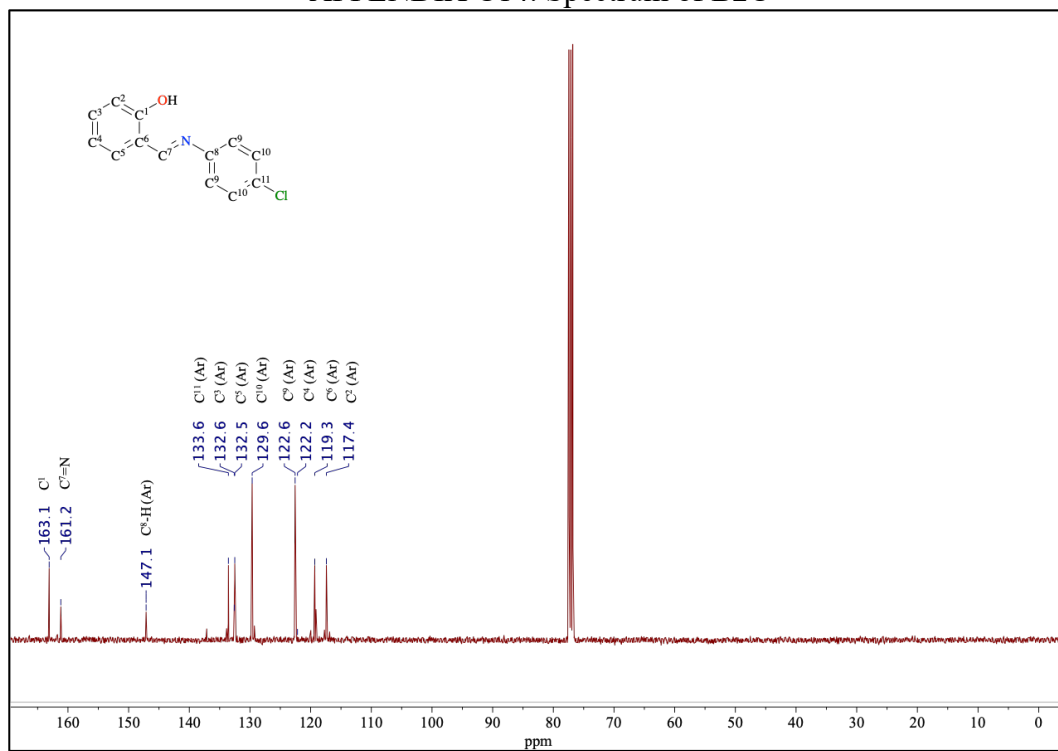
APPENDIX C12: Spectrum of B2OMe



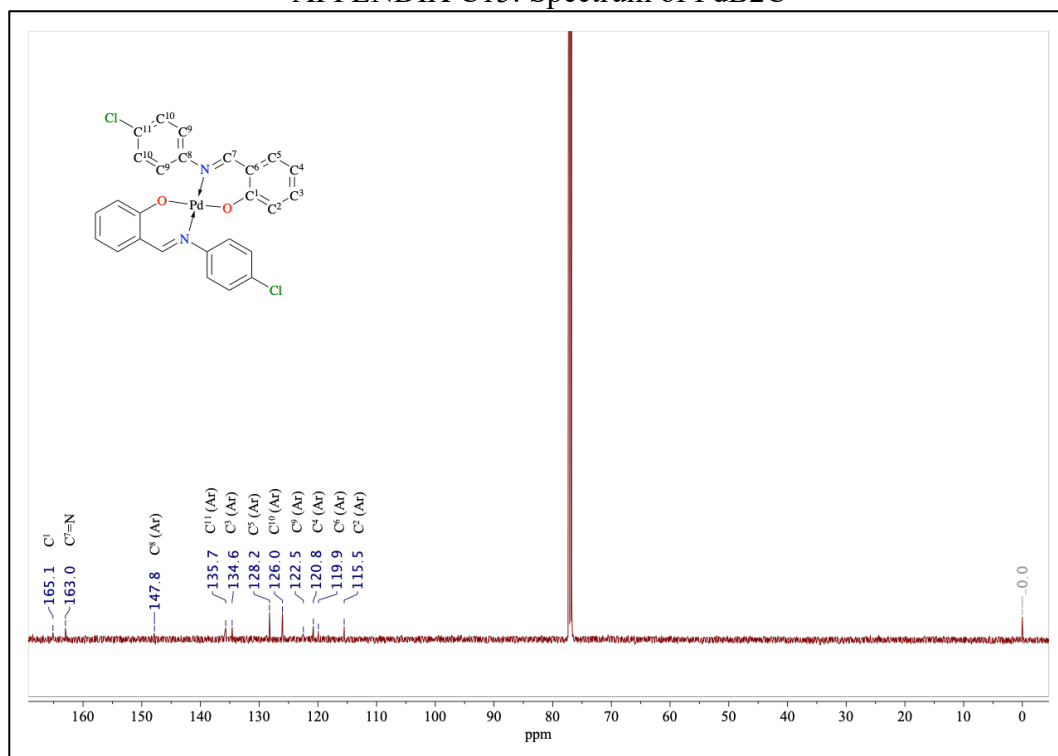
APPENDIX C13: Spectrum of PdB2OMe



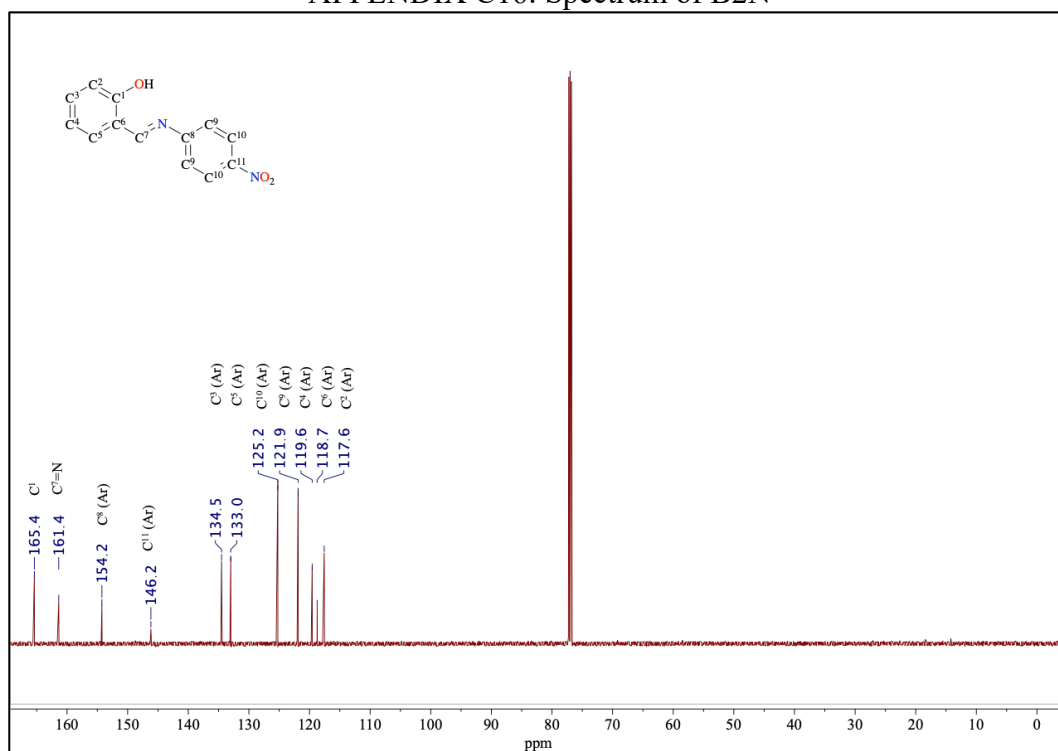
APPENDIX C14: Spectrum of B2C



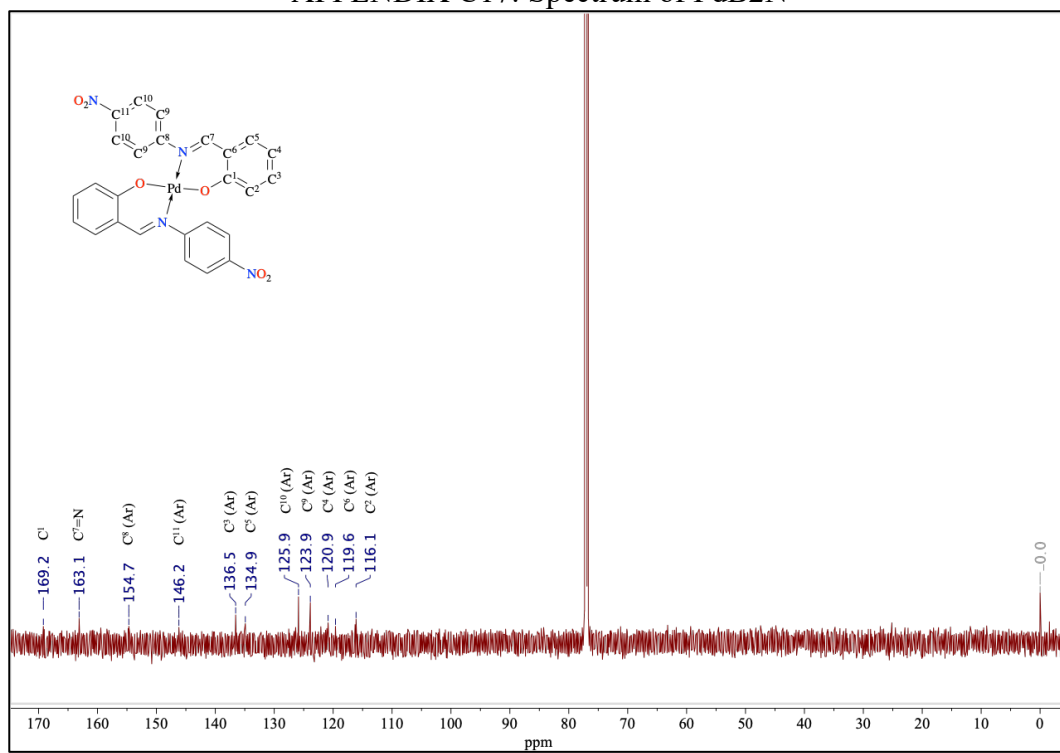
APPENDIX C15: Spectrum of PdB2C



APPENDIX C16: Spectrum of B2N



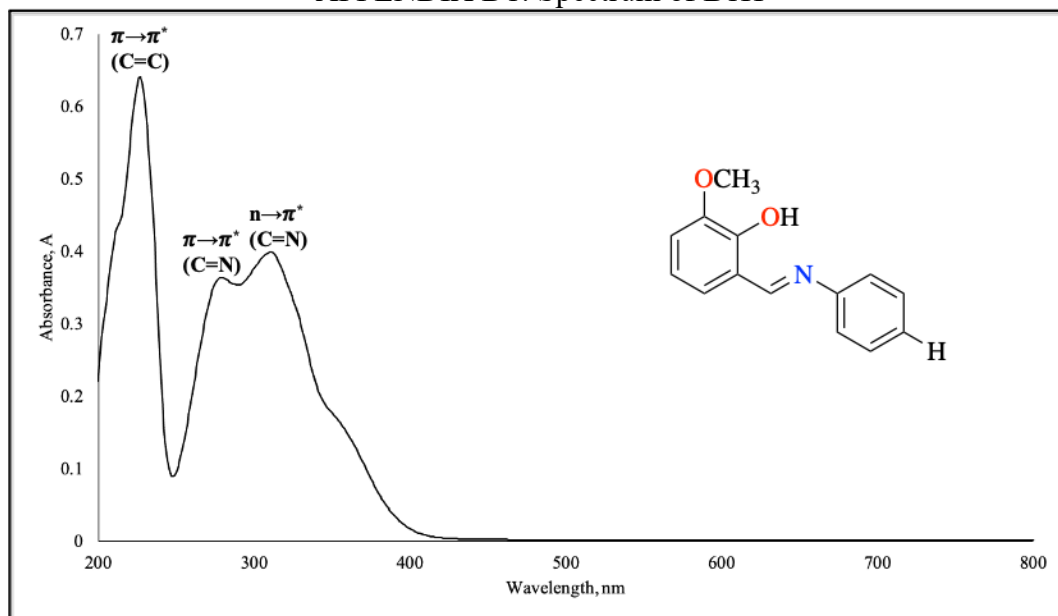
APPENDIX C17: Spectrum of PdB2N



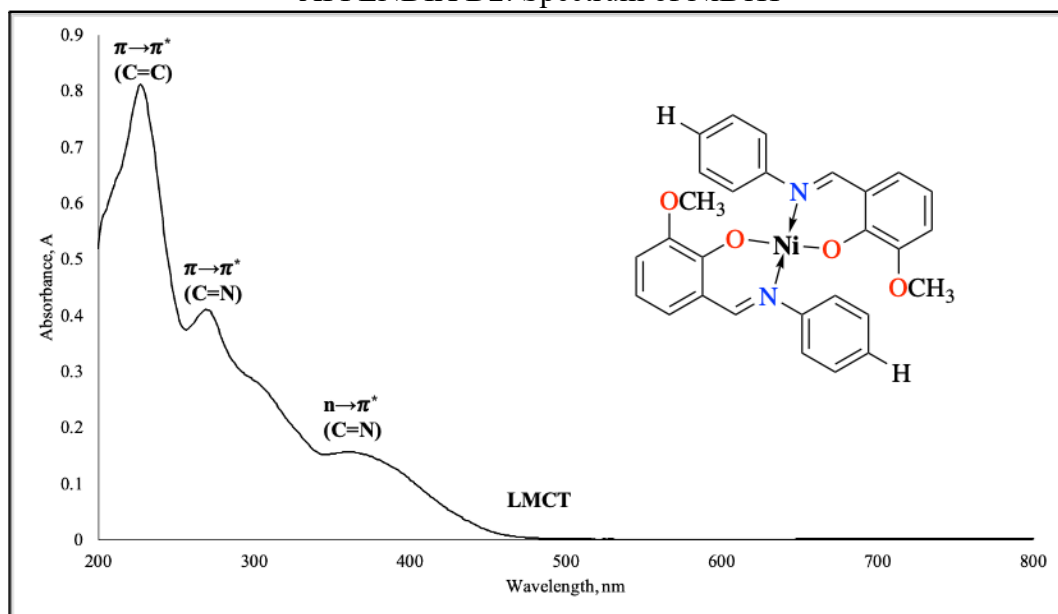
APPENDIX D

UV-Visible Spectroscopy

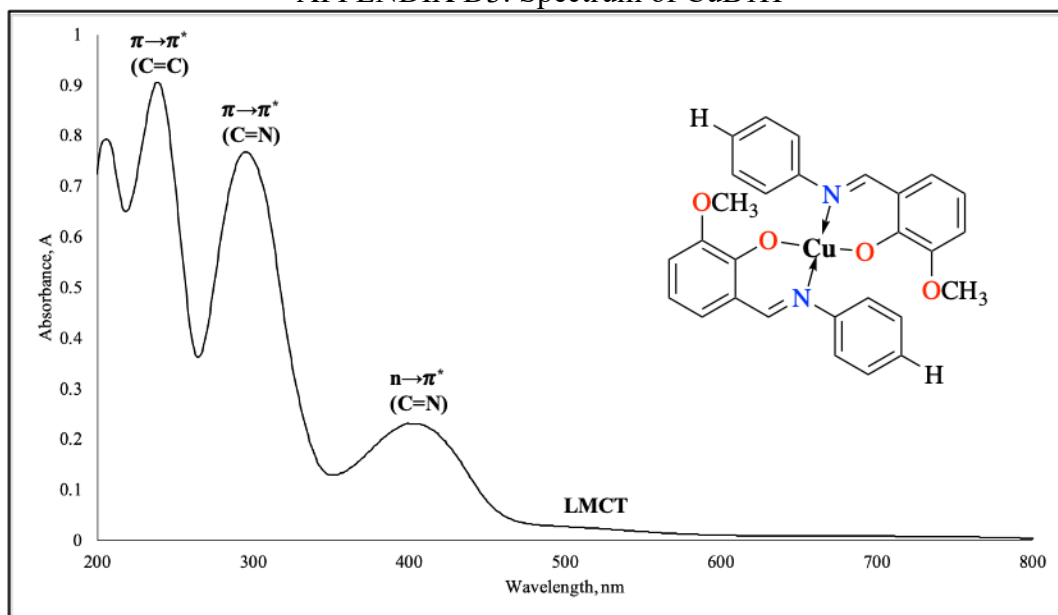
APPENDIX D1: Spectrum of B1H



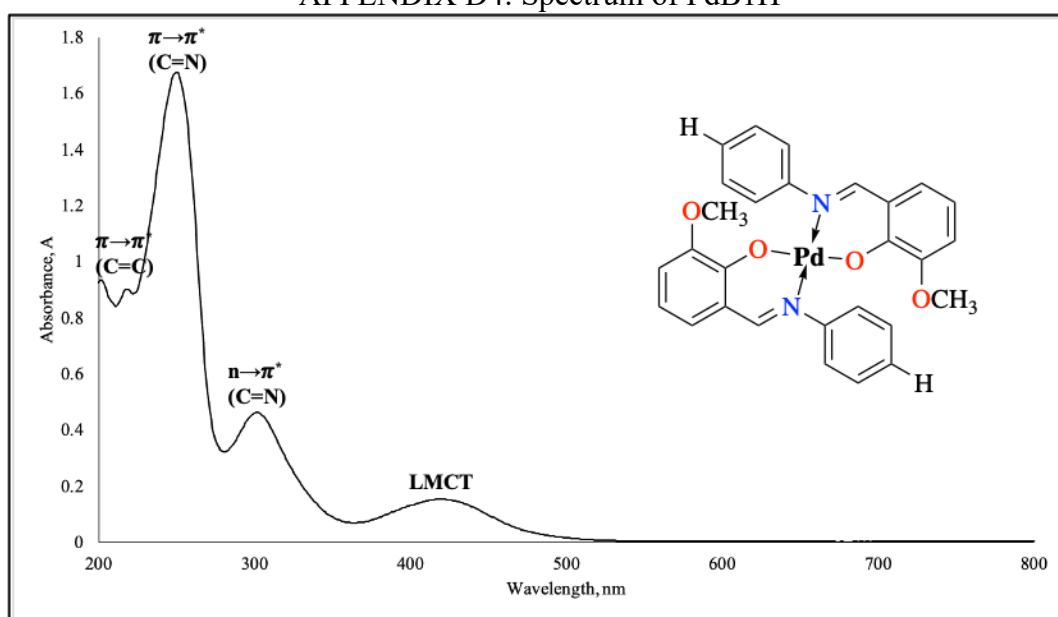
APPENDIX D2: Spectrum of NiB1H



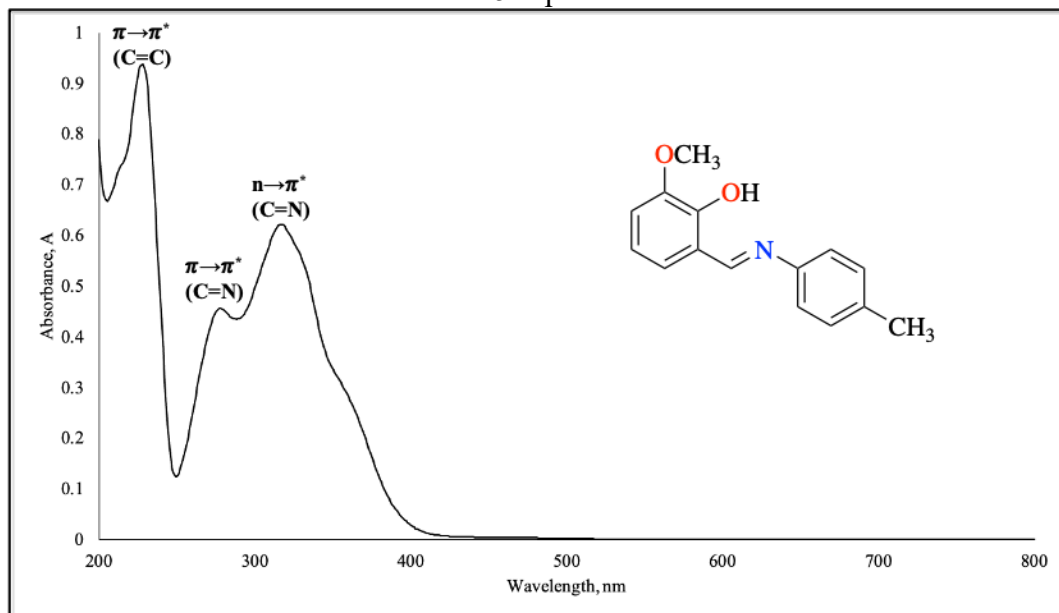
APPENDIX D3: Spectrum of CuB1H



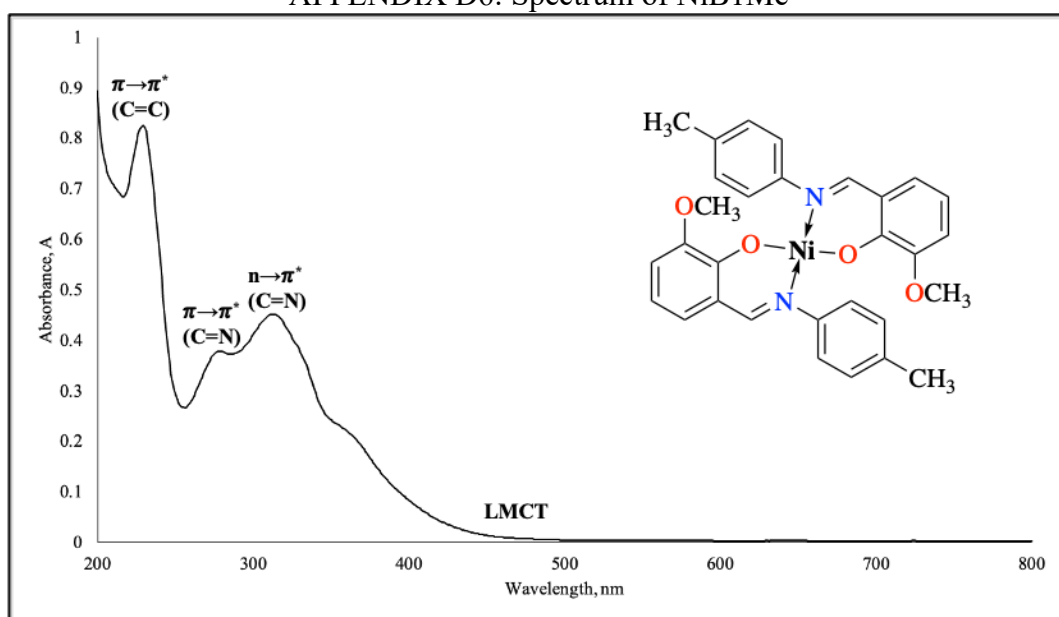
APPENDIX D4: Spectrum of PdB1H



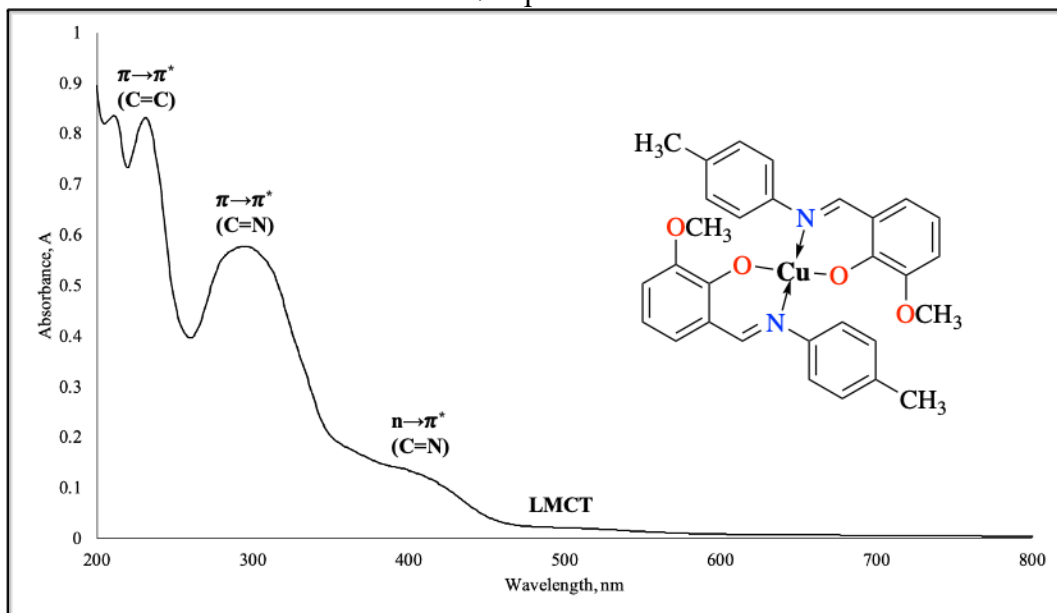
APPENDIX D5: Spectrum of B1Me



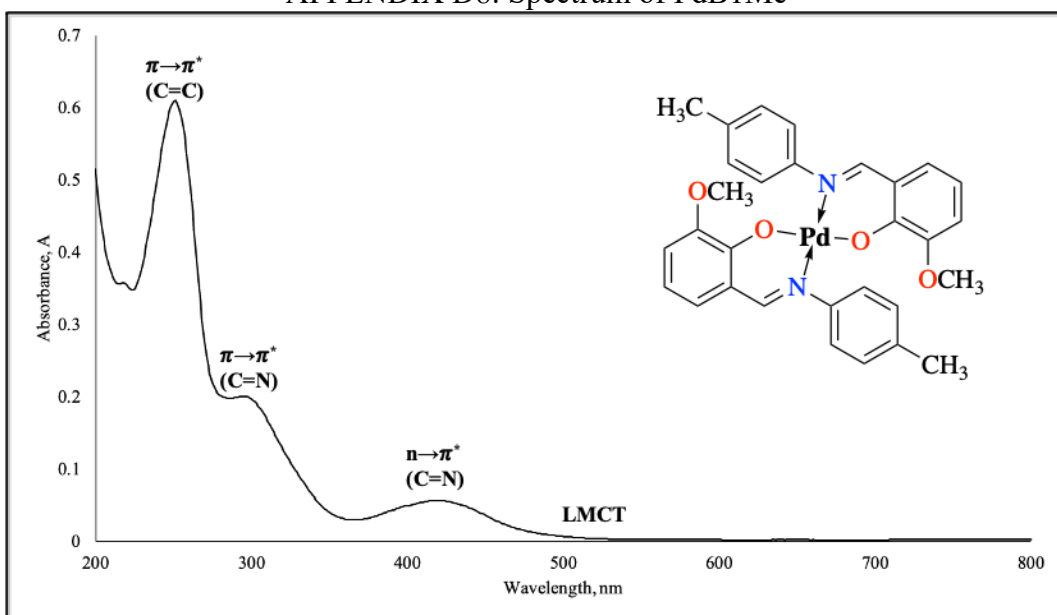
APPENDIX D6: Spectrum of NiB1Me



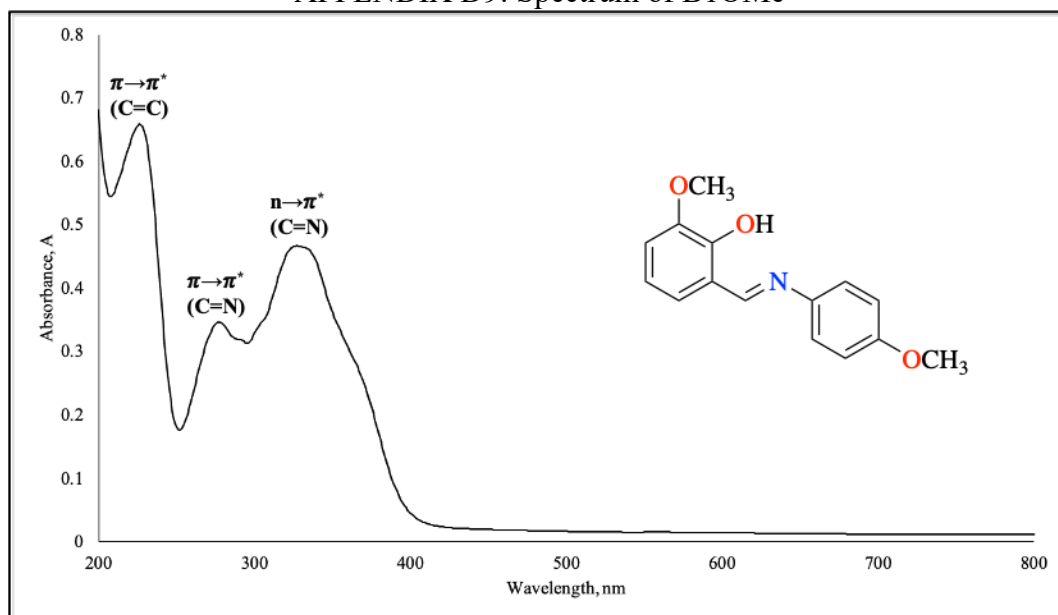
APPENDIX D7: Spectrum of CuB1Me



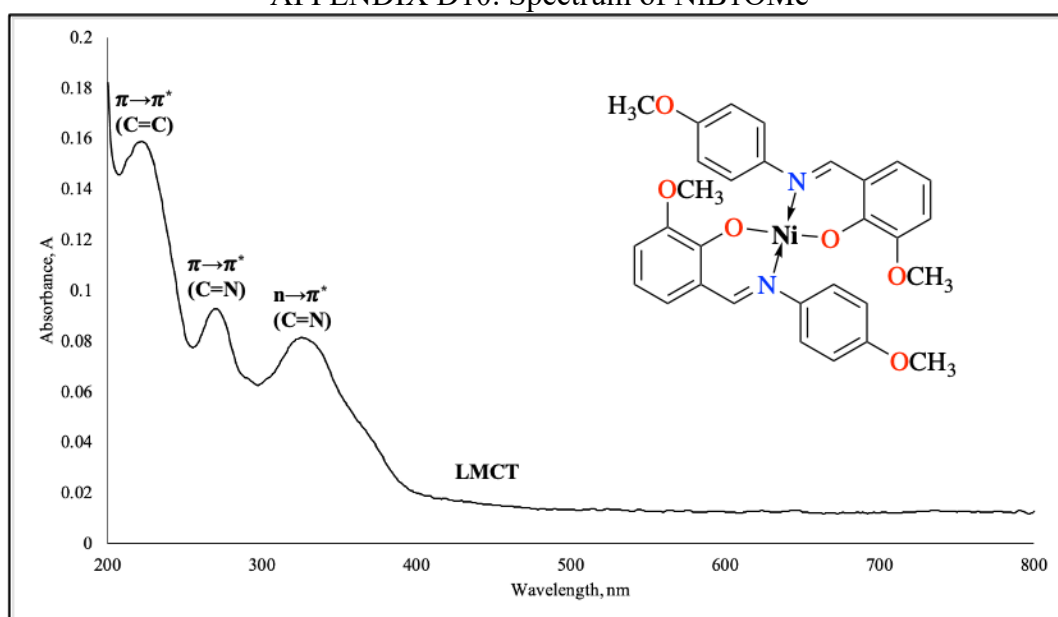
APPENDIX D8: Spectrum of PdB1Me



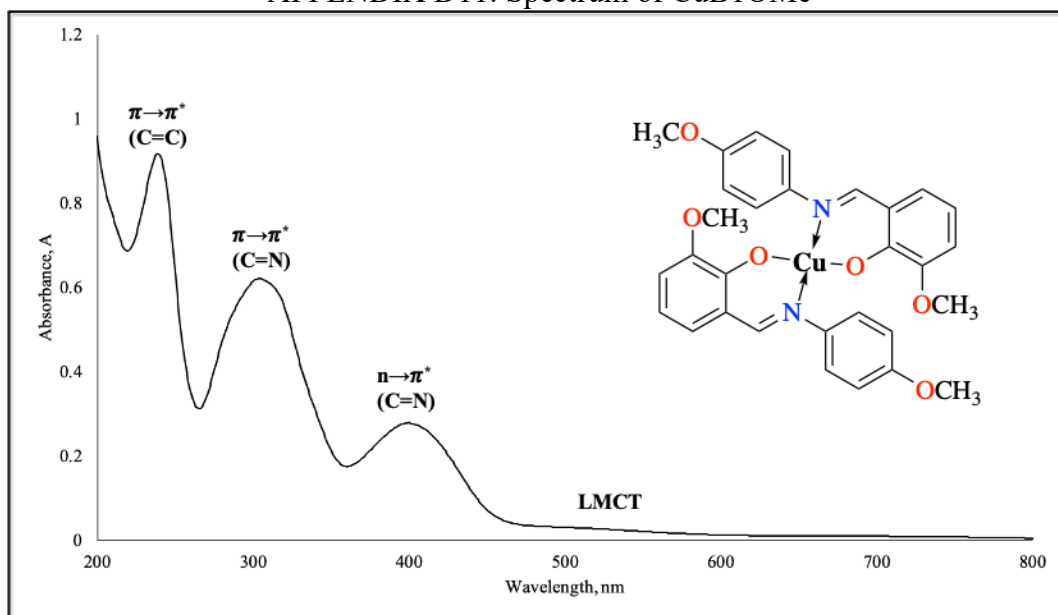
APPENDIX D9: Spectrum of B1OMe



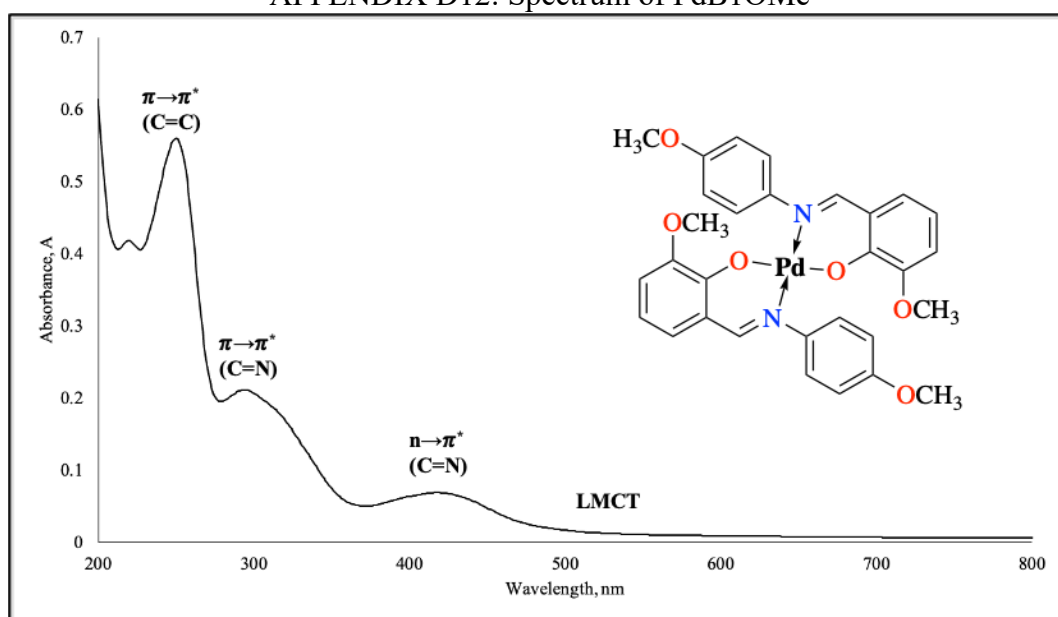
APPENDIX D10: Spectrum of NiB1OMe



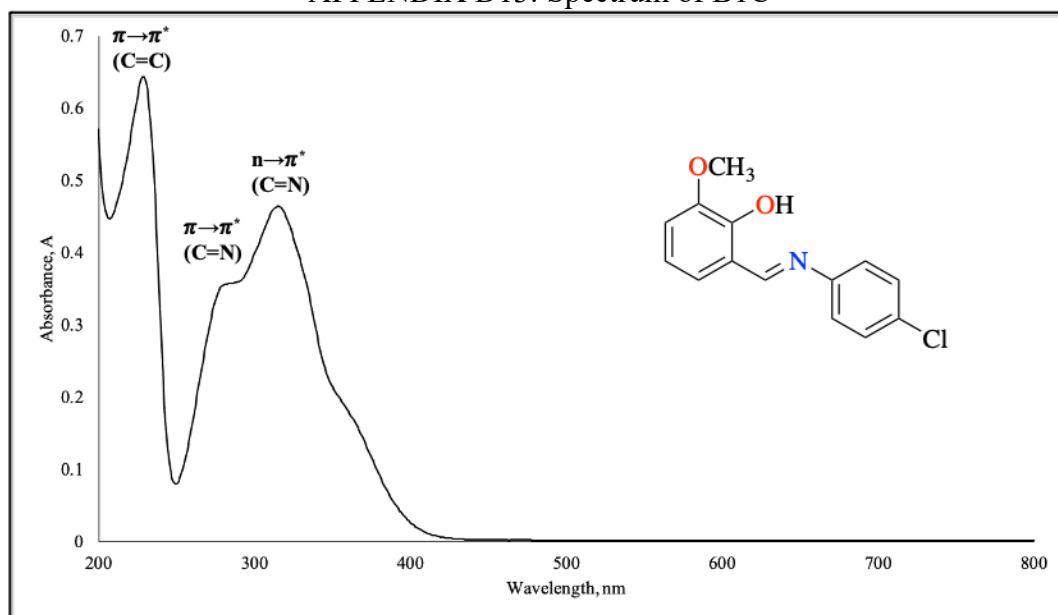
APPENDIX D11: Spectrum of CuB1OMe



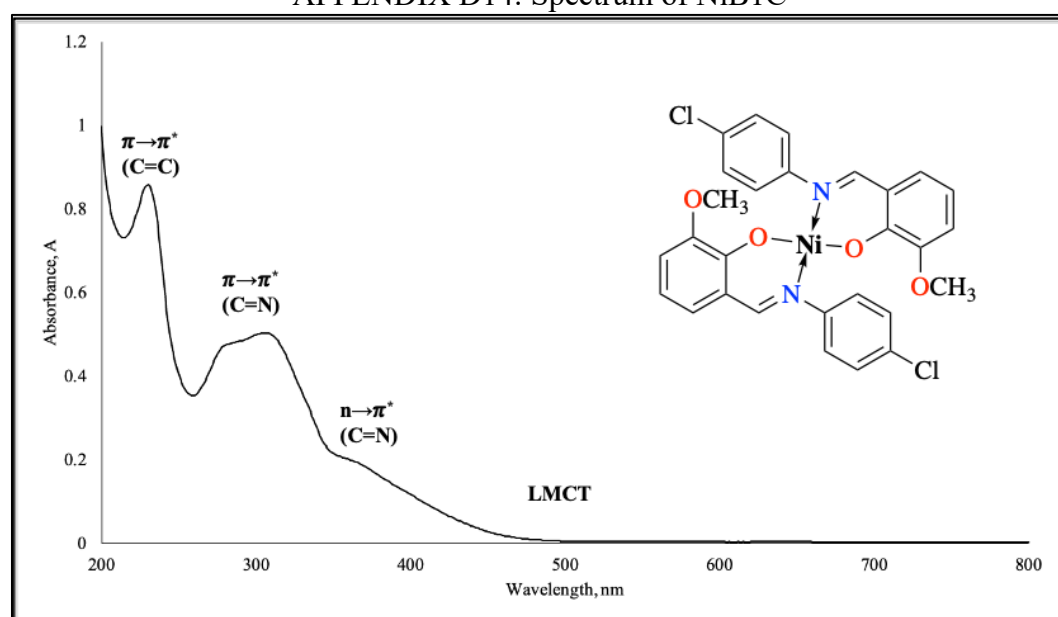
APPENDIX D12: Spectrum of PdB1OMe



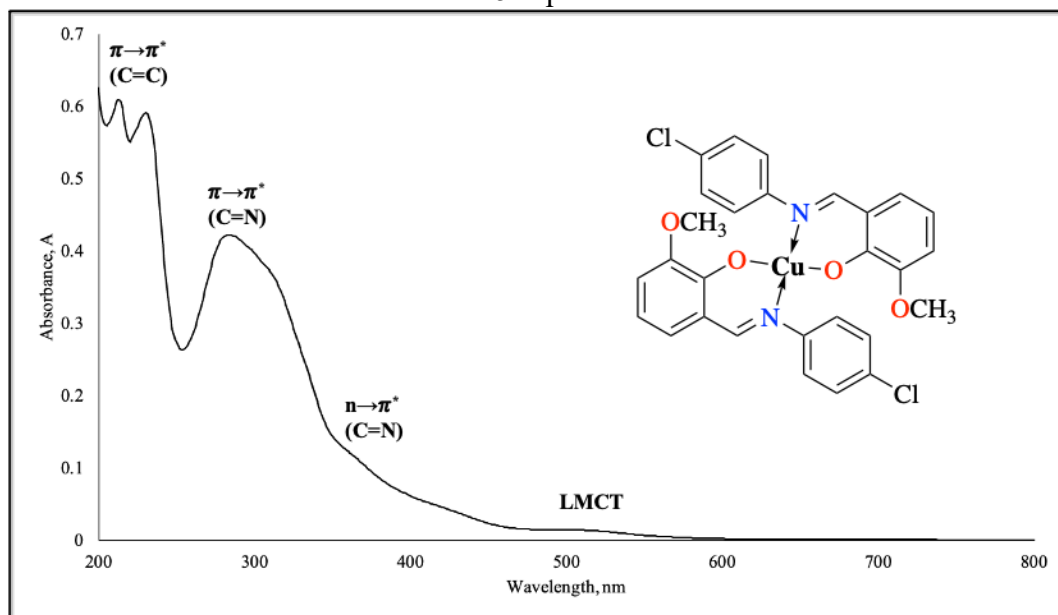
APPENDIX D13: Spectrum of B1C



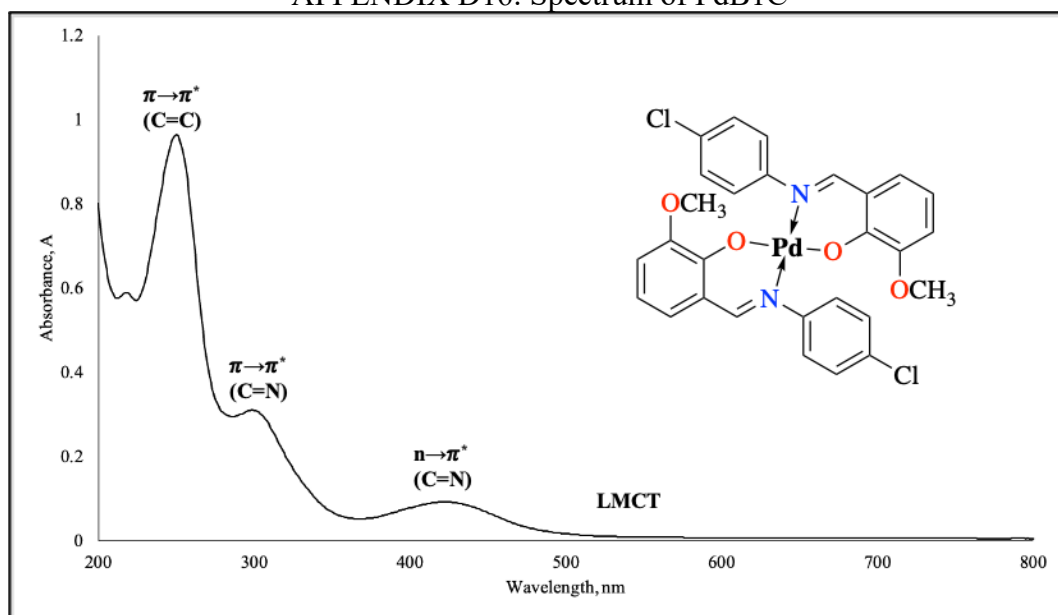
APPENDIX D14: Spectrum of NiB1C



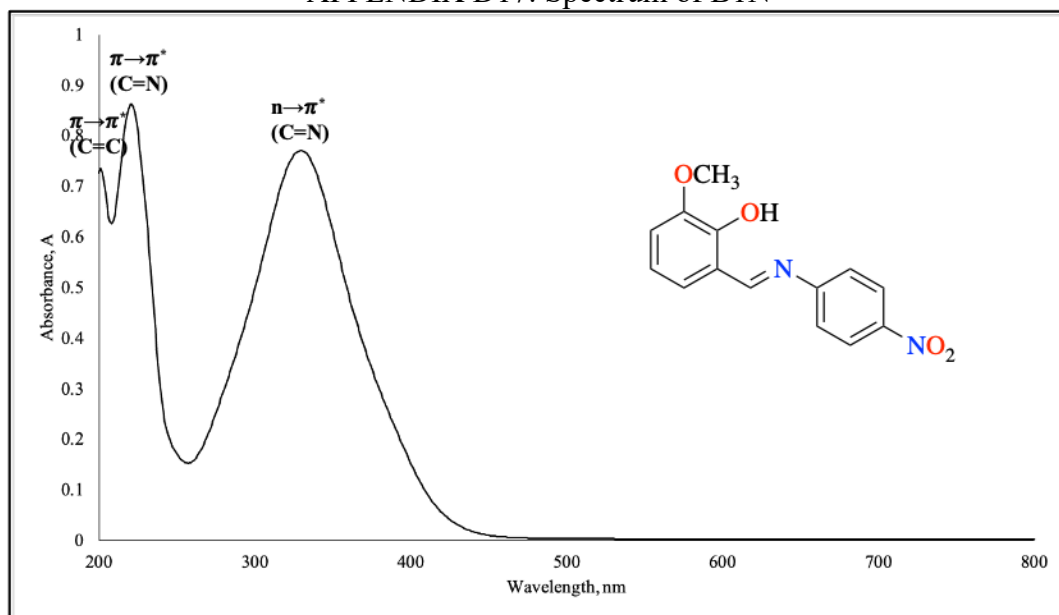
APPENDIX D15: Spectrum of CuB1C



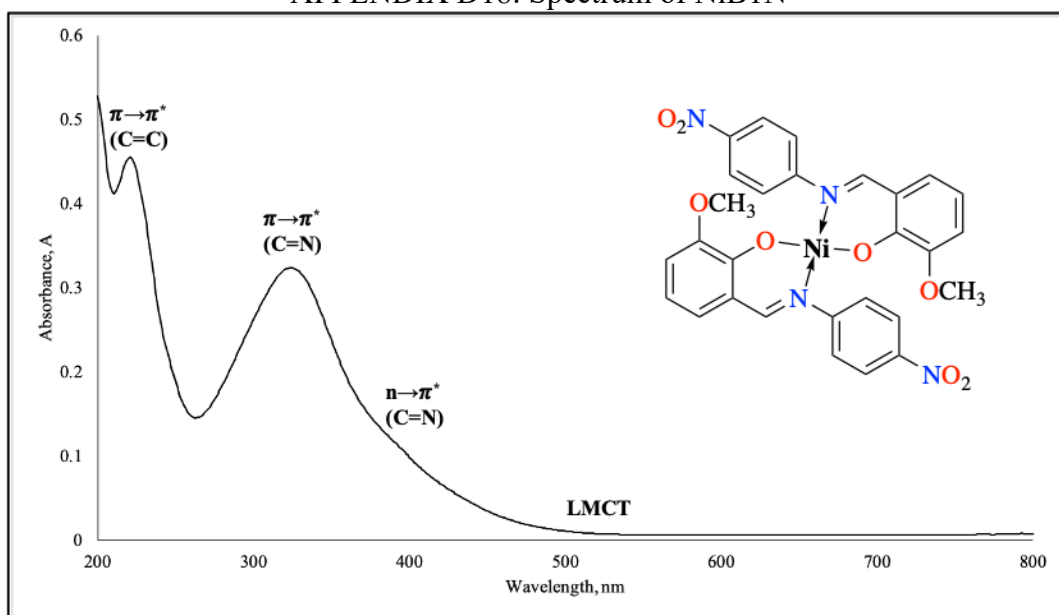
APPENDIX D16: Spectrum of PdB1C



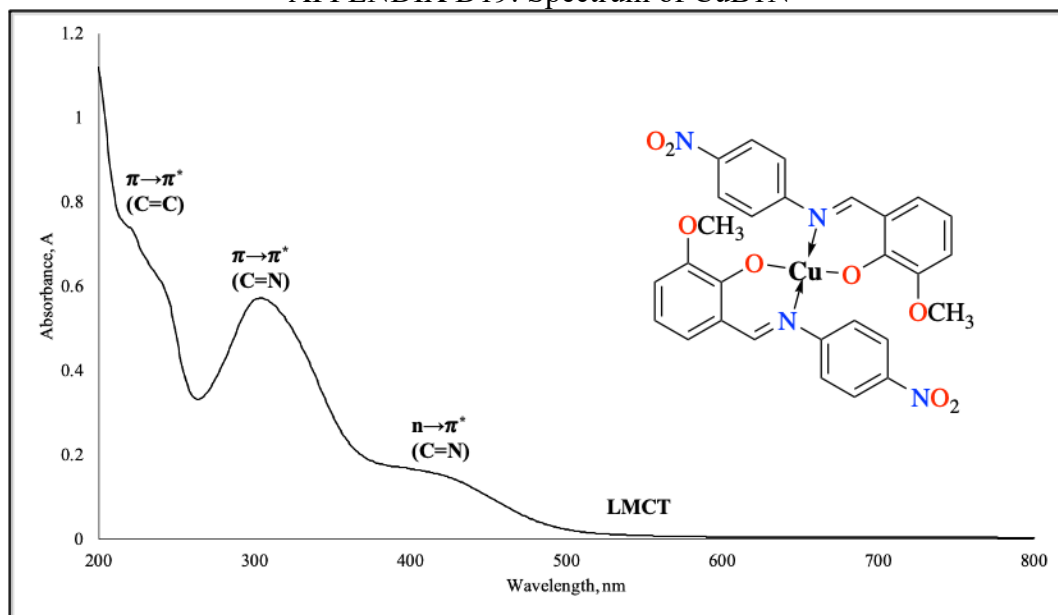
APPENDIX D17: Spectrum of B1N



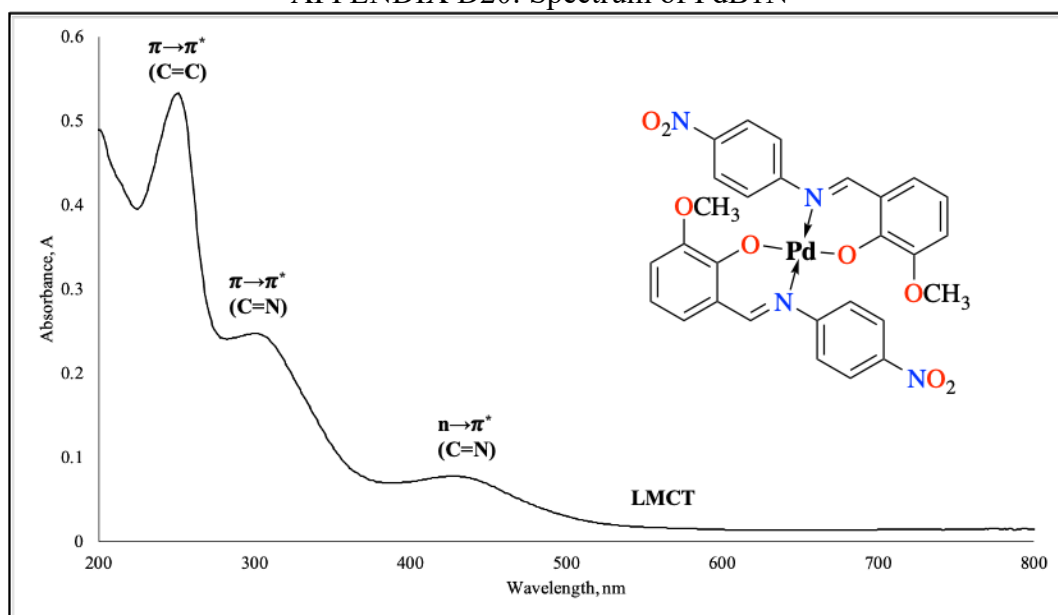
APPENDIX D18: Spectrum of NiB1N



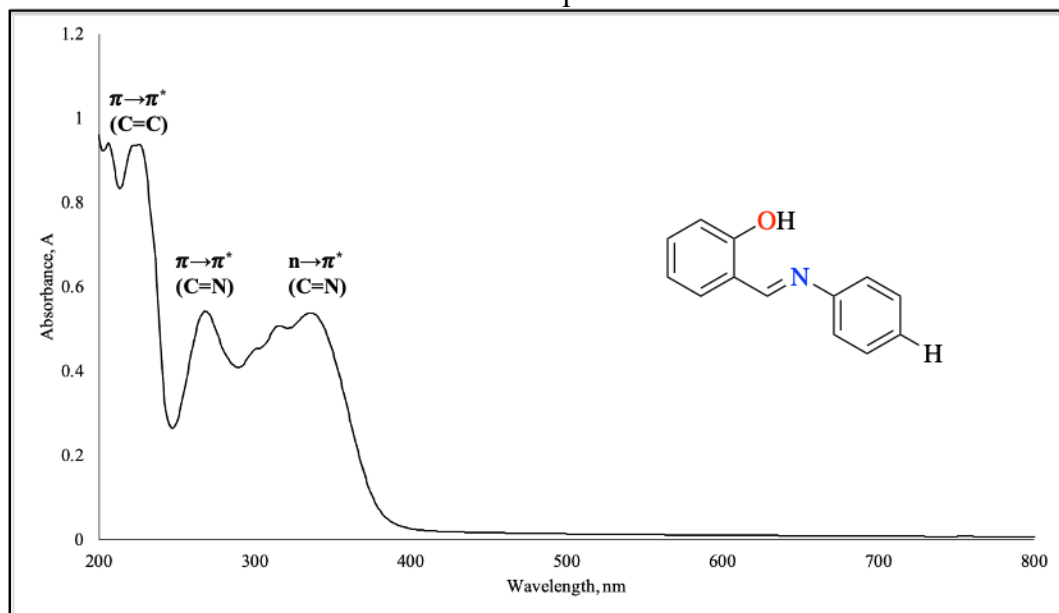
APPENDIX D19: Spectrum of CuB1N



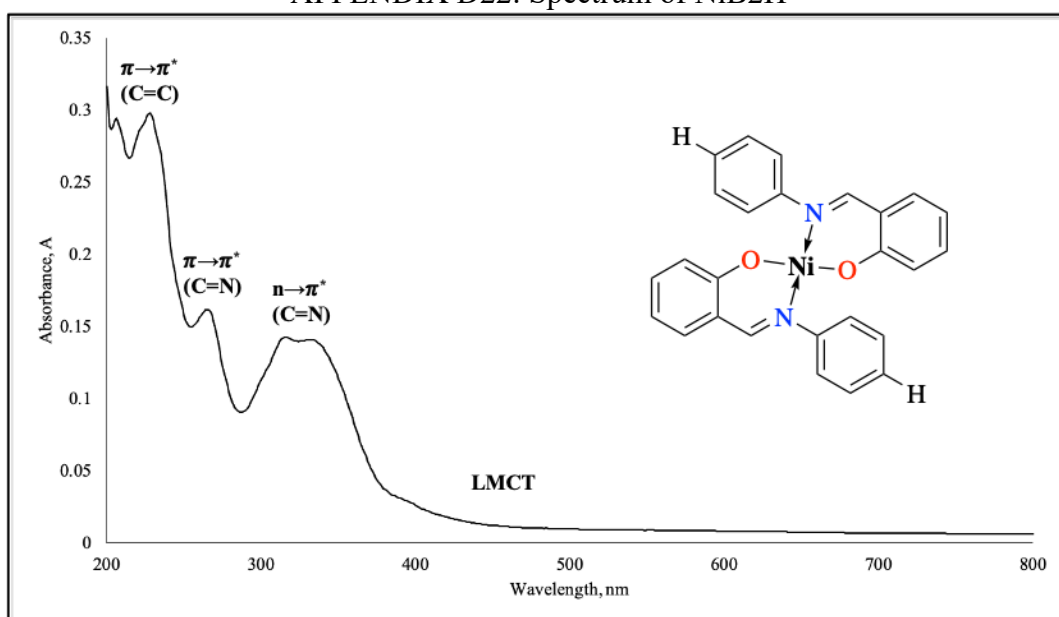
APPENDIX D20: Spectrum of PdB1N



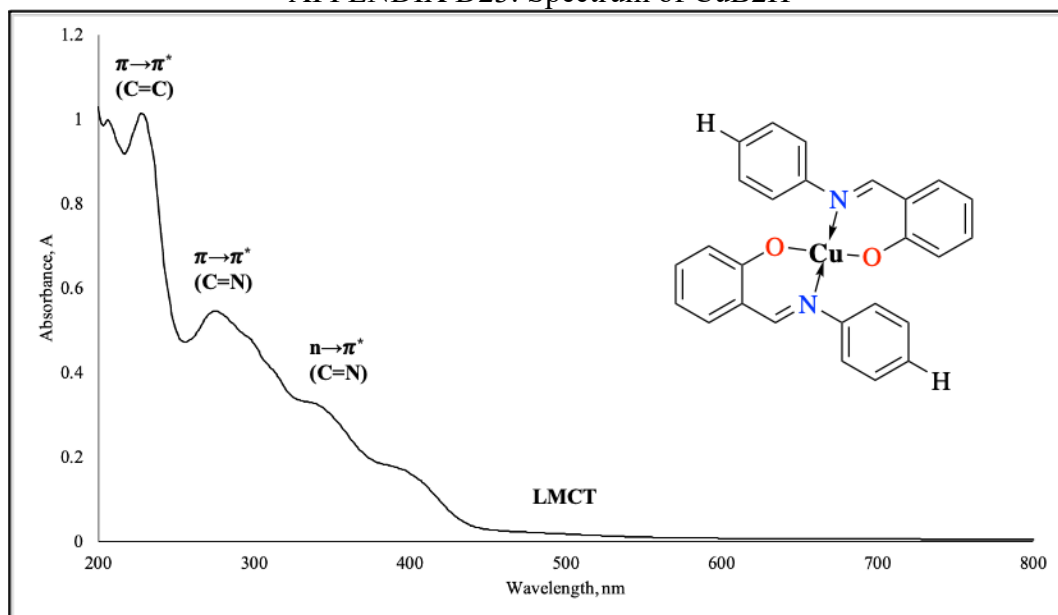
APPENDIX D21: Spectrum of B2H



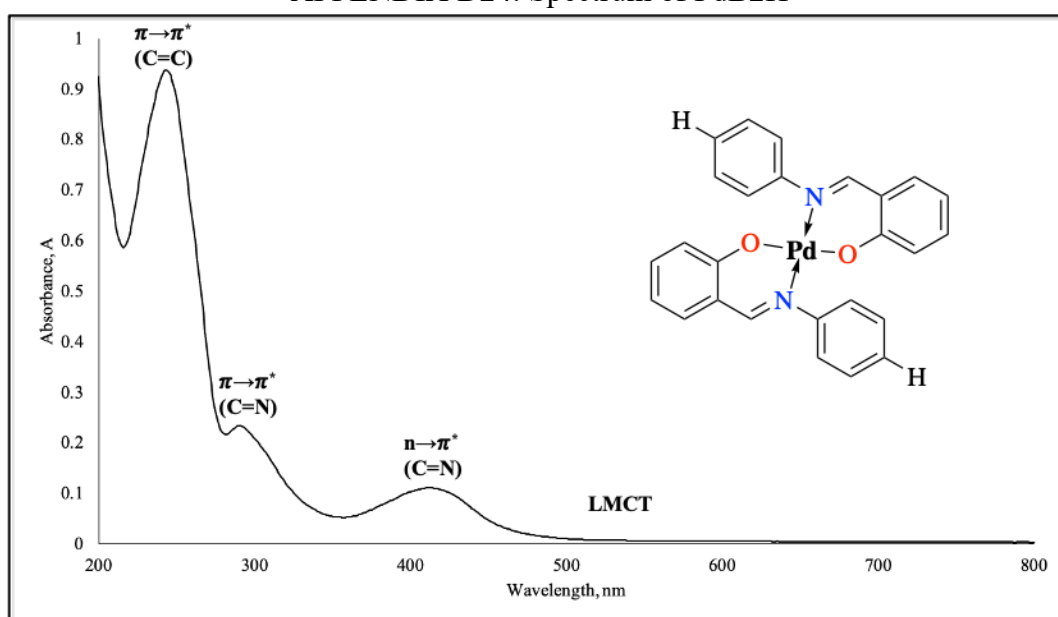
APPENDIX D22: Spectrum of NiB2H



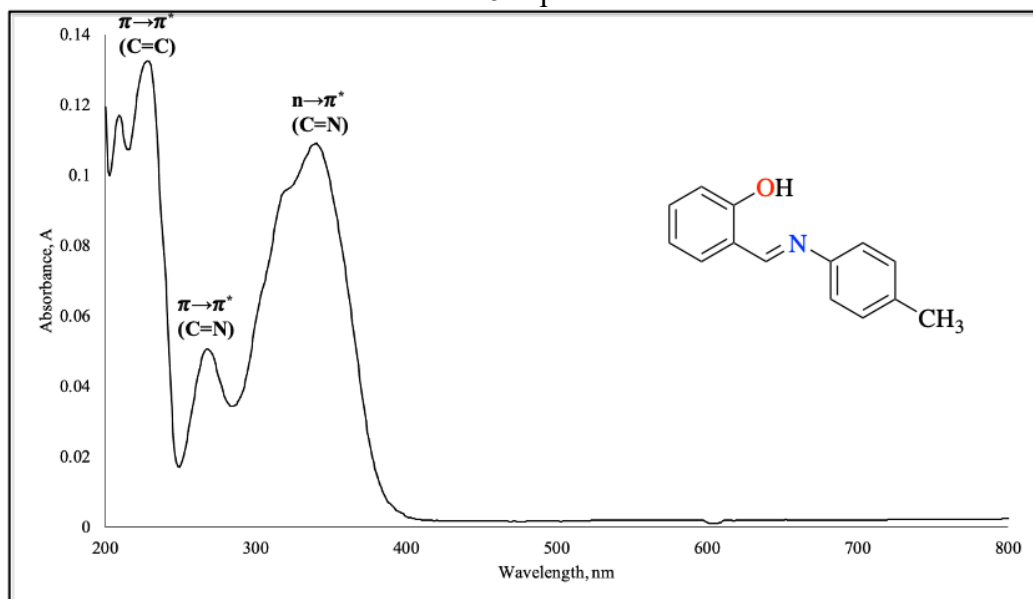
APPENDIX D23: Spectrum of CuB2H



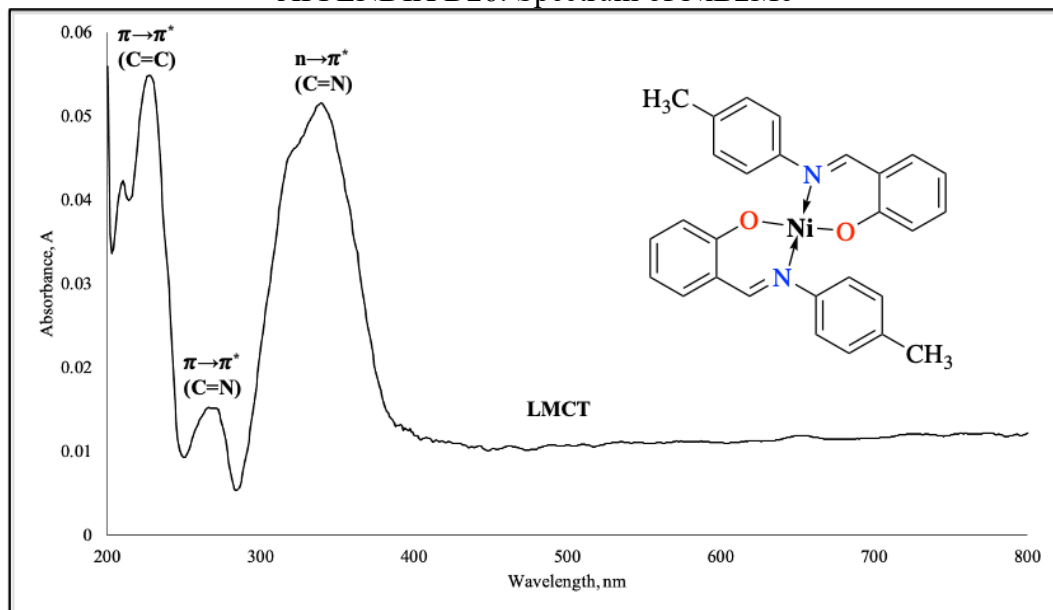
APPENDIX D24: Spectrum of PdB2H



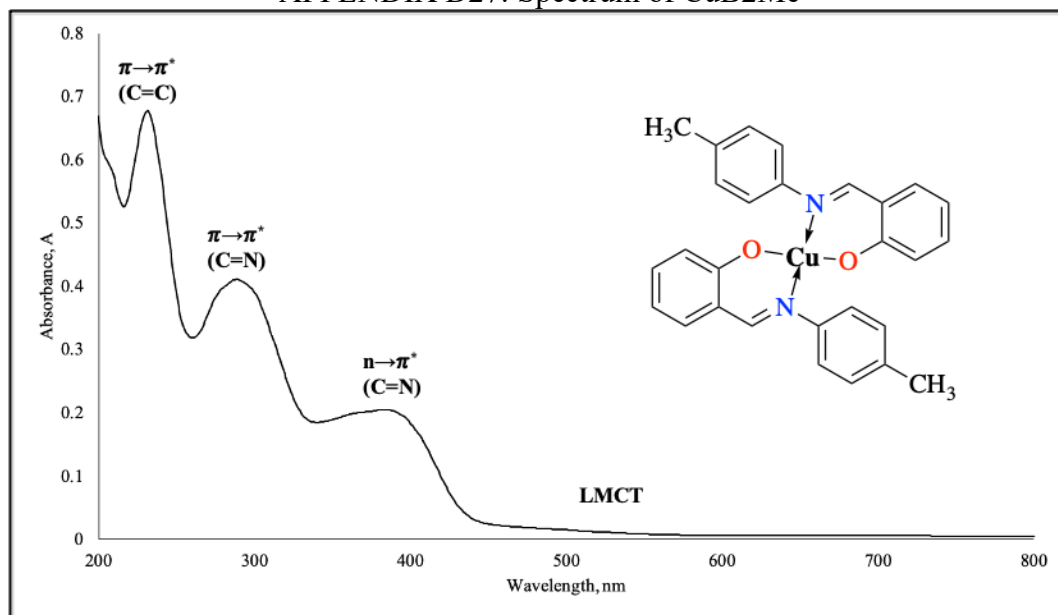
APPENDIX D25: Spectrum of B2Me



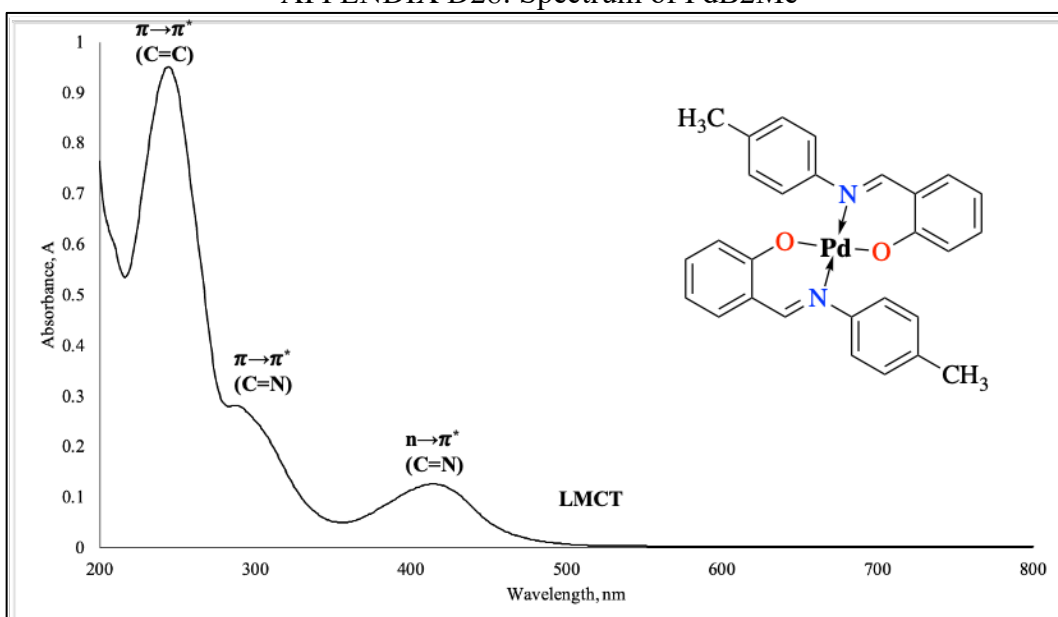
APPENDIX D26: Spectrum of NiB2Me



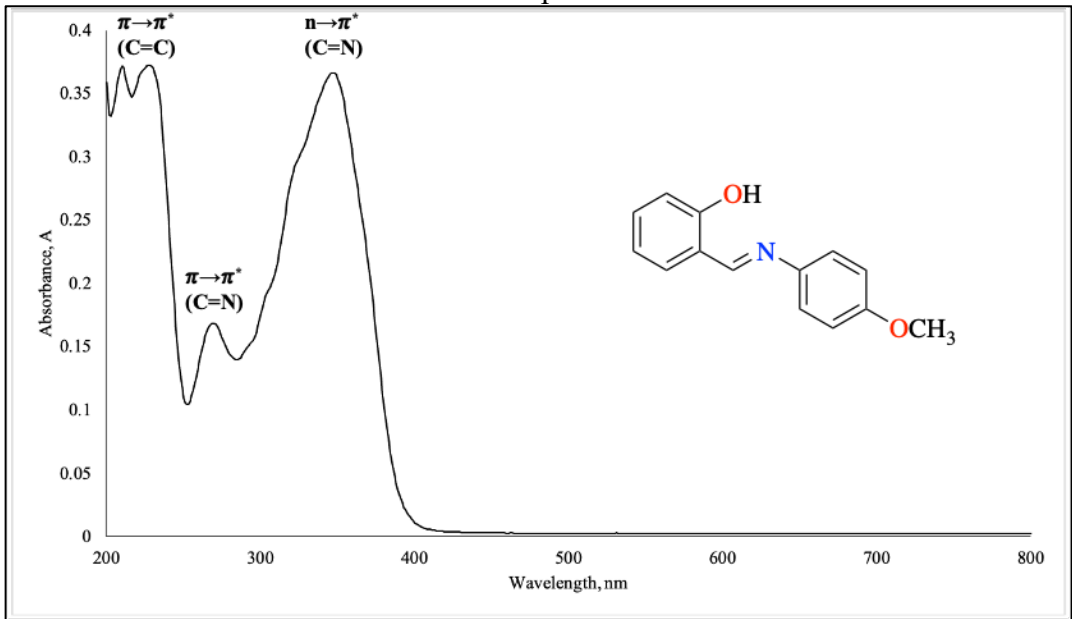
APPENDIX D27: Spectrum of CuB2Me



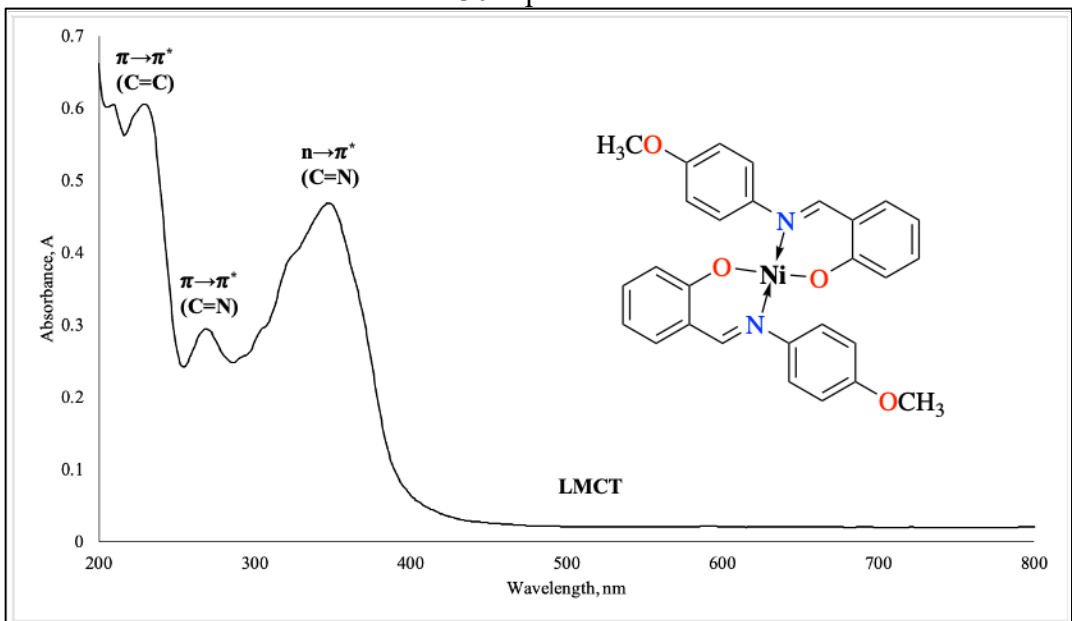
APPENDIX D28: Spectrum of PdB2Me



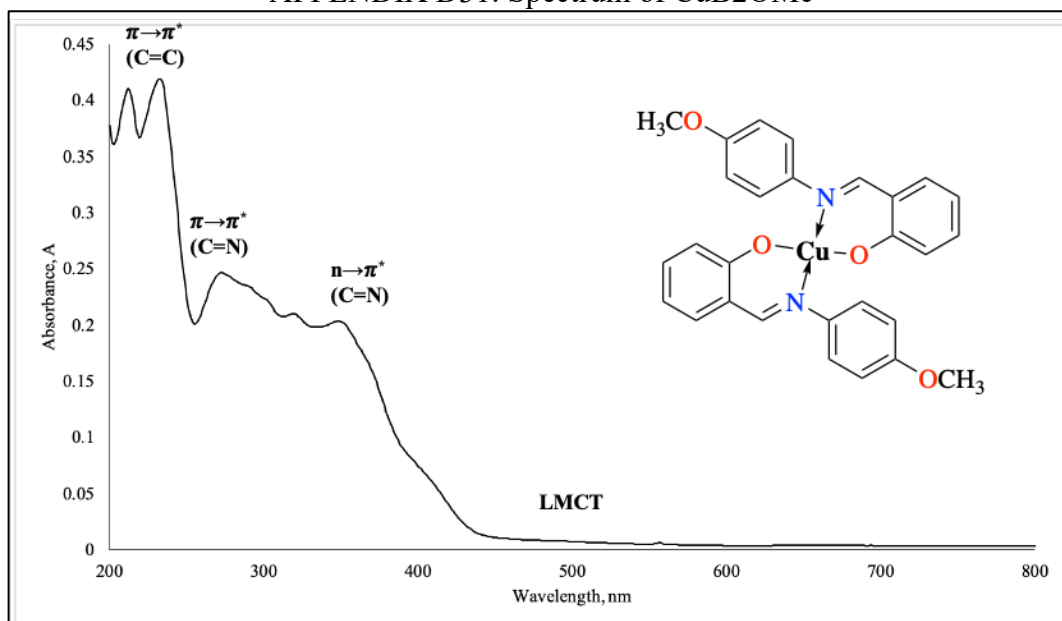
APPENDIX D29: Spectrum of B2OMe



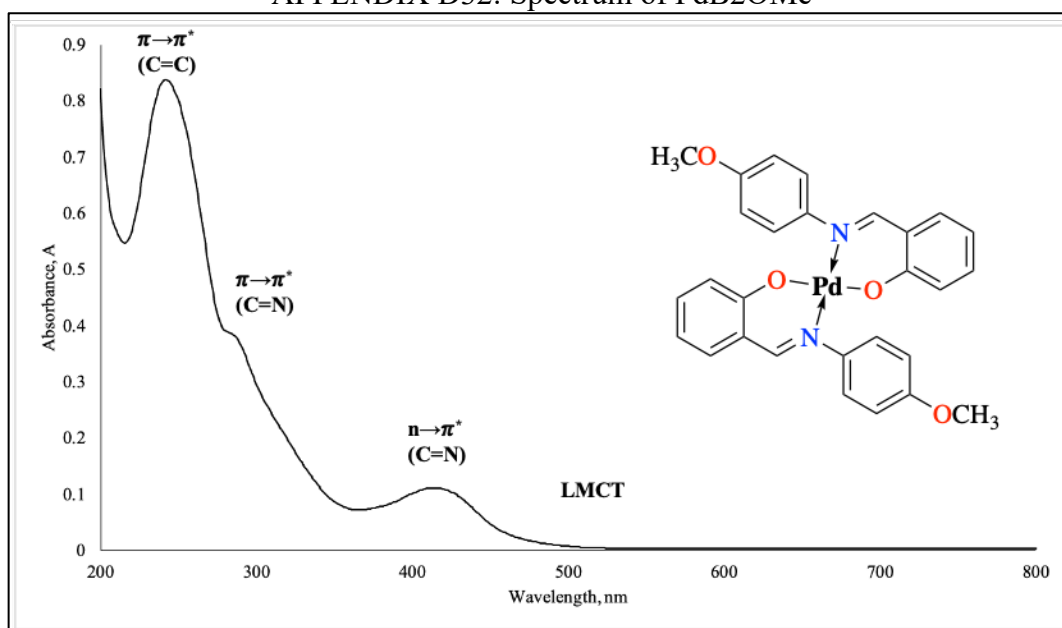
APPENDIX D30: Spectrum of NiB2OMe



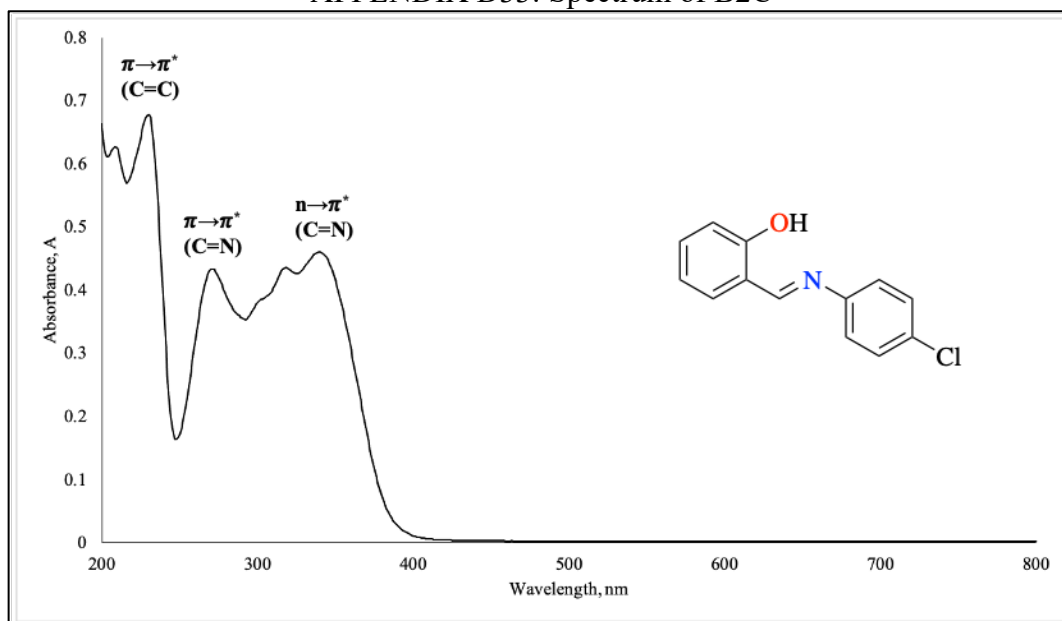
APPENDIX D31: Spectrum of CuB2OMe



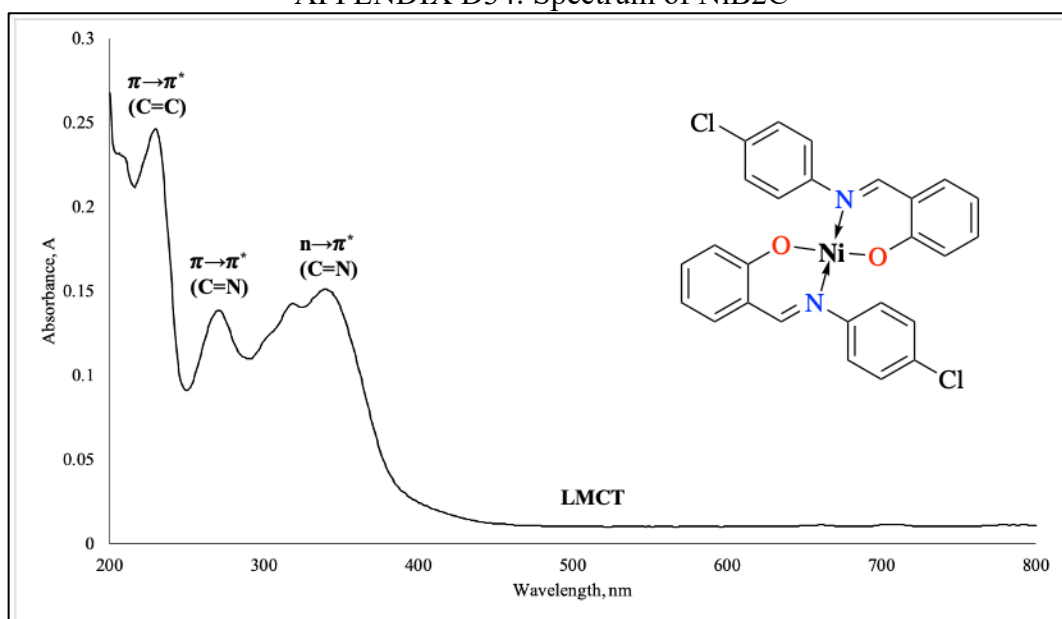
APPENDIX D32: Spectrum of PdB2OMe



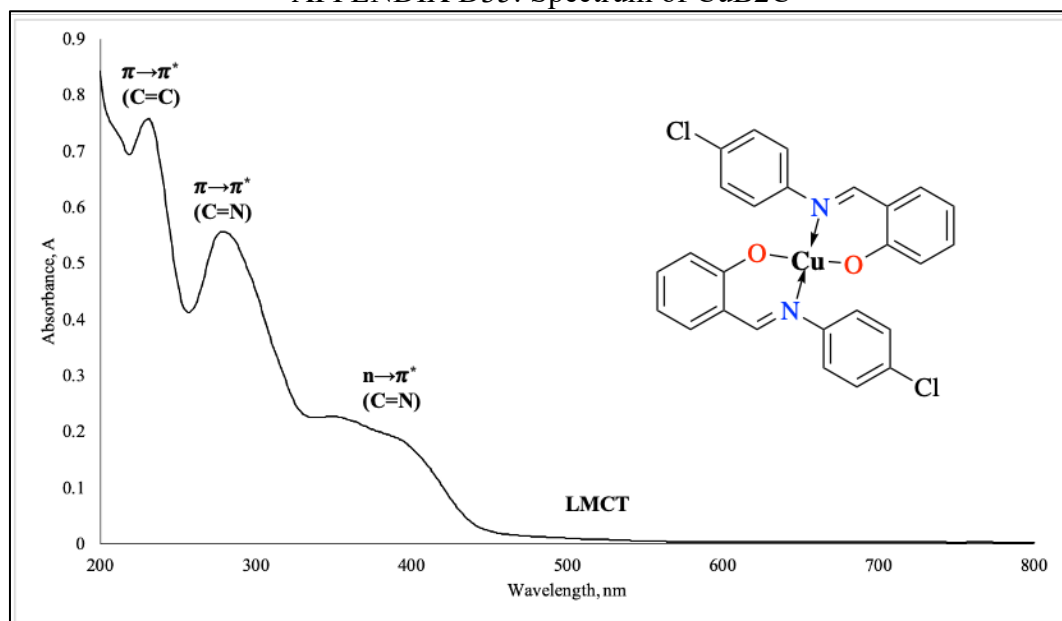
APPENDIX D33: Spectrum of B2C



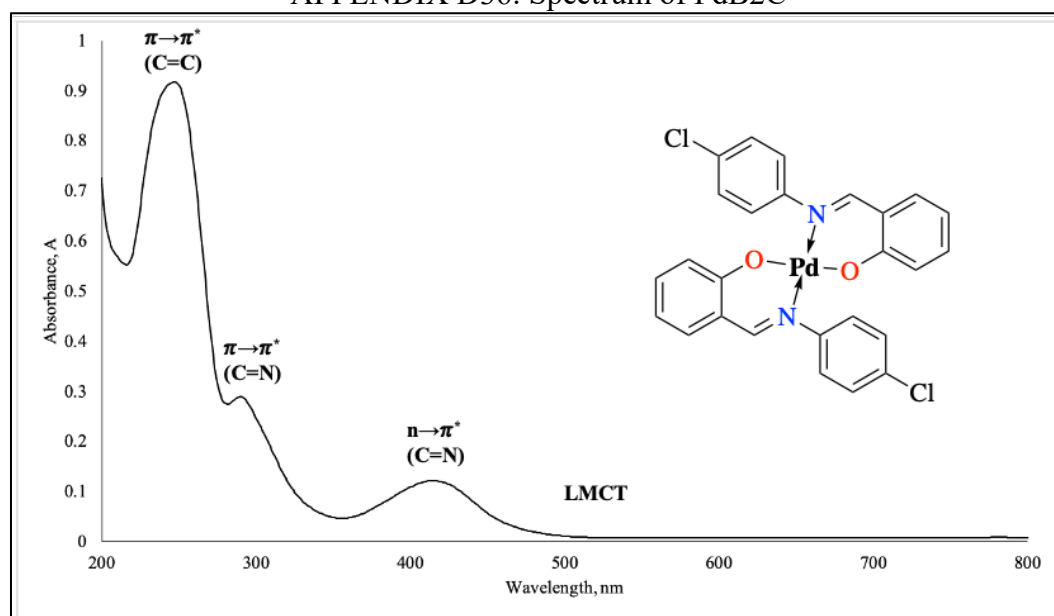
APPENDIX D34: Spectrum of NiB2C



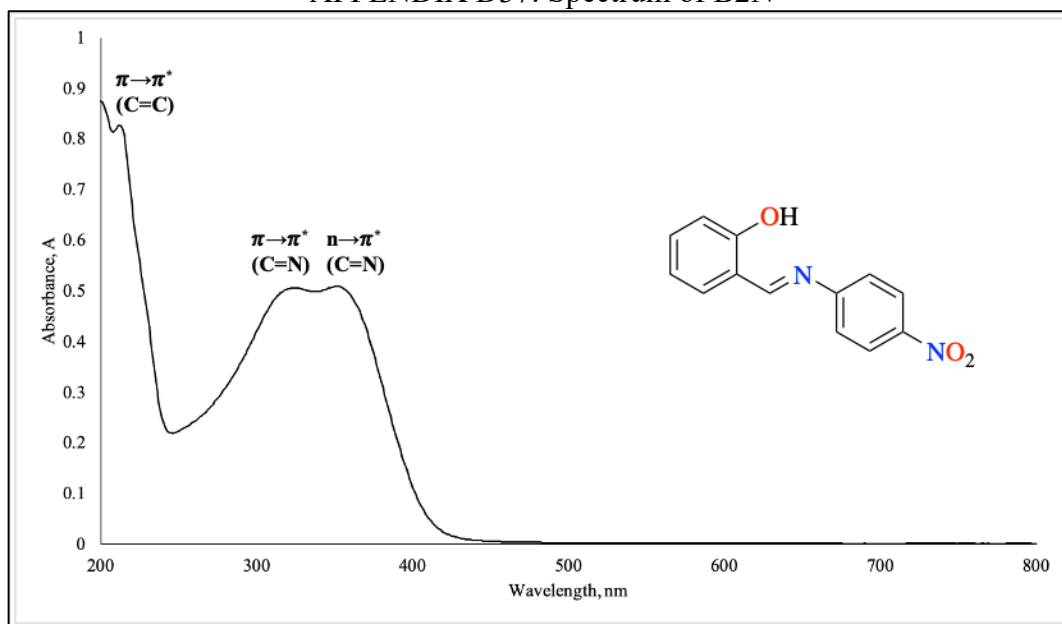
APPENDIX D35: Spectrum of CuB2C



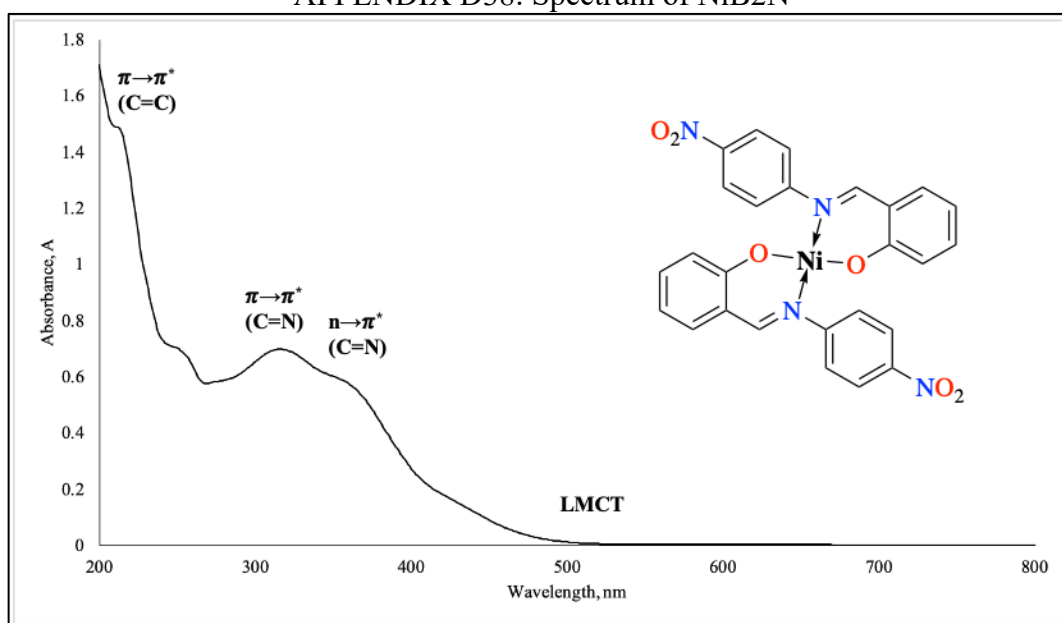
APPENDIX D36: Spectrum of PdB2C



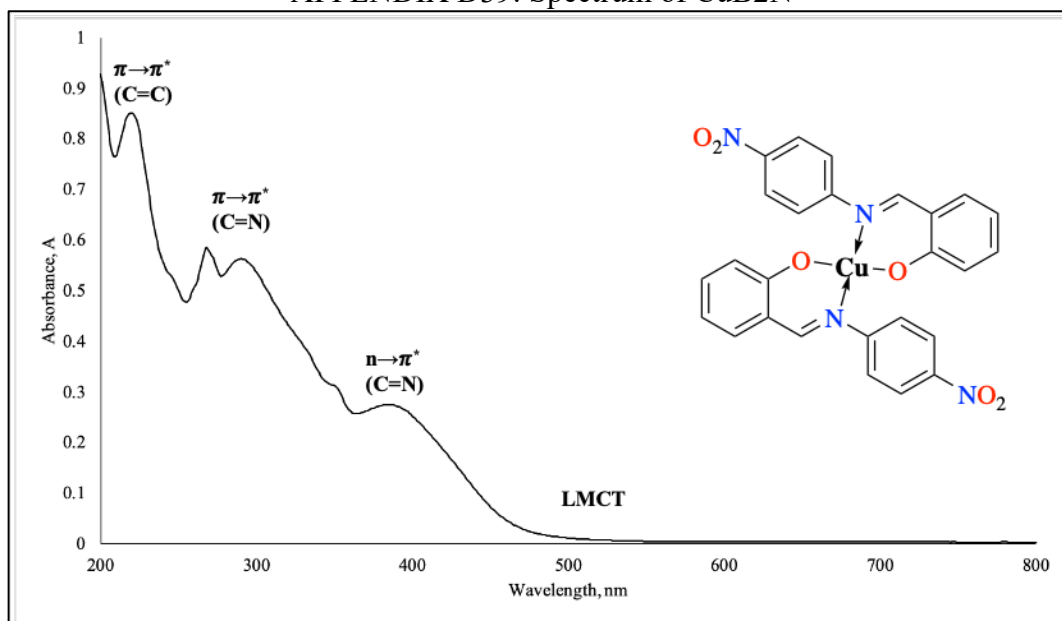
APPENDIX D37: Spectrum of B2N



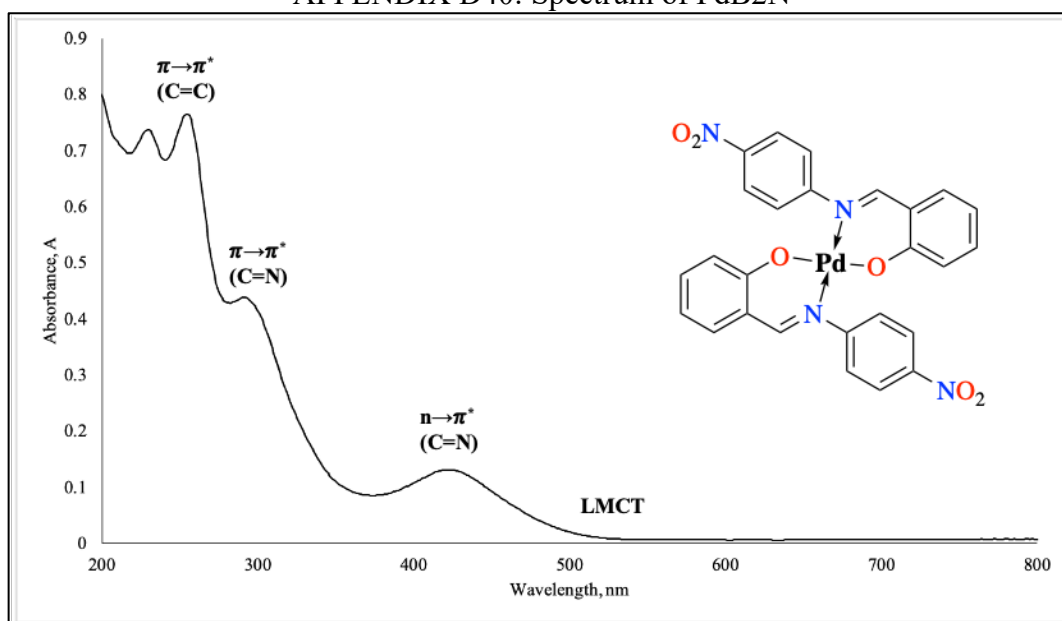
APPENDIX D38: Spectrum of NiB2N



APPENDIX D39: Spectrum of CuB2N



APPENDIX D40: Spectrum of PdB2N



APPENDIX E

Single Crystal X-ray Diffraction

APPENDIX E1: Checkcif report for B1H

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) ovan_an_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: ovan_an_0m_a

Bond precision:	C-C = 0.0028 Å	Wavelength=0.71073	
Cell:	a=6.0879 (2) alpha=90	b=9.1847 (2) beta=90	c=21.0661 (5) gamma=90
Temperature:	299 K		
	Calculated	Reported	
Volume	1177.92 (5)	1177.92 (5)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C14 H13 N O2	C14 H13 N O2	
Sum formula	C14 H13 N O2	C14 H13 N O2	
Mr	227.25	227.25	
Dx, g cm ⁻³	1.281	1.281	
Z	4	4	
Mu (mm ⁻¹)	0.086	0.086	
F000	480.0	480.0	
F000'	480.22		
h,k,lmax	8,12,28	8,12,28	
Nref	2942 [1725]	2933	
Tmin,Tmax	0.968,0.987		
Tmin'	0.958		

Correction method= Not given

Data completeness= 1.70/1.00

Theta(max)= 28.301

R(reflections)= 0.0359(2382)

wR2(reflections)=

0.0943(2933)

S = 1.059

Npar= 159

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level. Click on the hyperlinks for more details of the test.



Alert level C

PLAT193_ALERT_1_C Cell and Diffraction Temperatures Differ by

1 Degree



Alert level G

PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High .	0.300 Report
PLAT850_ALERT_4_G Check Flack Parameter Exact Value 0.00 with s.u.	0.30 Check
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).	3 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600	1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.	1 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by	2 Check

0 **ALERT level A** = Most likely a serious problem - resolve or explain

0 **ALERT level B** = A potentially serious problem, consider carefully

1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

6 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

1 ALERT type 2 Indicator that the structure model may be wrong or deficient

1 ALERT type 3 Indicator that the structure quality may be low

3 ALERT type 4 Improvement, methodology, query or suggestion

1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

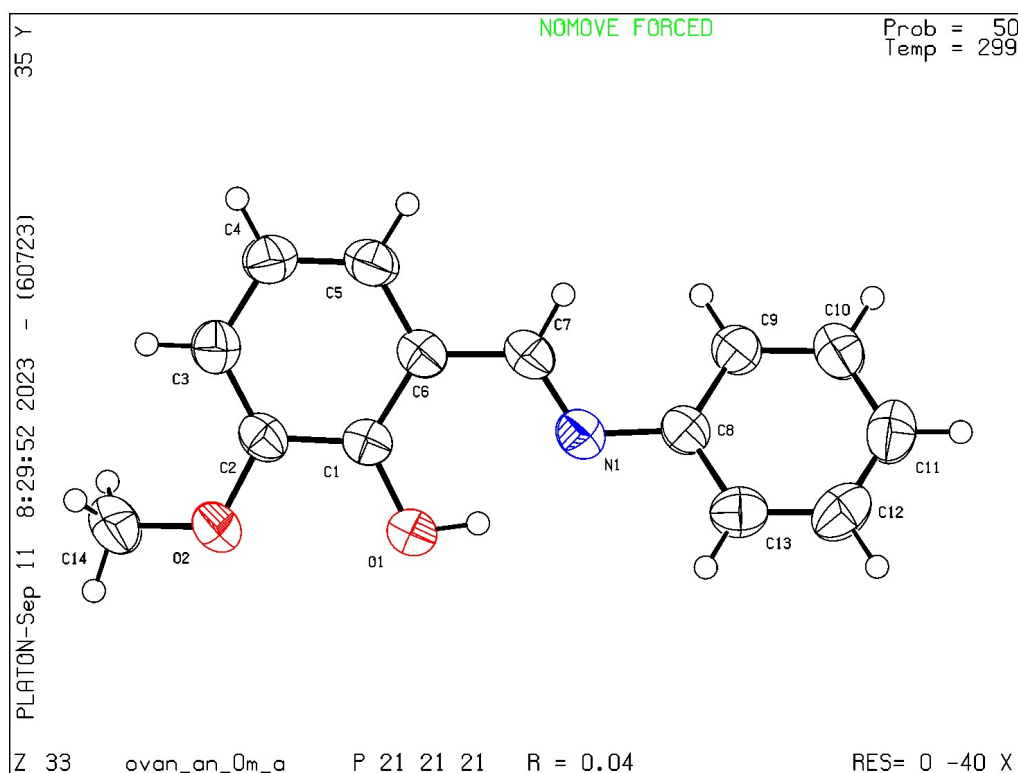
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 06/07/2023; check.def file version of 30/06/2023

Datablock ovan an 0m a - ellipsoid plot



APPENDIX E2: Checkcif report for B1Me
checkCIF/PLATON report

Structure factors have been supplied for datablock(s) ovan4tol_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: ovan4tol_0m

Bond precision:	C-C = 0.0030 Å	Wavelength=0.71073	
Cell:	a=5.9101(14) alpha=90	b=9.235(2) beta=90	c=23.303(6) gamma=90
Temperature:	300 K		
	Calculated	Reported	
Volume	1271.9(5)	1271.9(5)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C15 H15 N O2	C15 H15 N O2	
Sum formula	C15 H15 N O2	C15 H15 N O2	
Mr	241.28	241.28	
Dx, g cm ⁻³	1.260	1.260	
Z	4	4	
Mu (mm ⁻¹)	0.084	0.084	
F000	512.0	512.0	
F000'	512.23		
h, k, lmax	7, 12, 31	7, 12, 30	
Nref	3150[1846]	3145	
Tmin, Tmax	0.973, 0.989		
Tmin'	0.968		

Correction method= Not given

Data completeness= 1.70/1.00

Theta (max)= 28.291

R(reflections)= 0.0392 (2466)

wR2 (reflections)=

0.1110 (3145)

S = 1.014

Npar= 166

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level. Click on the hyperlinks for more details of the test.



Alert level C

STRVA01_ALERT_4_C

Flack parameter is too small

From the CIF: `_refine_ls_abs_structure_Flack` -0.600

From the CIF: `_refine_ls_abs_structure_Flack_su` 0.500



Alert level G

PLAT007_ALERT_5_G	Number of Unrefined Donor-H Atoms	1	Report
PLAT032_ALERT_4_G	Std. Uncertainty on Flack Parameter Value High .	0.500	Report
PLAT883_ALERT_1_G	No Info/Value for <code>_atom_sites_solution_primary</code> .		Please Do !
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).	3	Note
PLAT916_ALERT_2_G	Hooft y and Flack x Parameter Values Differ by .	0.20	Check
PLAT933_ALERT_2_G	Number of HKL-OMIT Records in Embedded .res File	1	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	2	Info
PLAT992_ALERT_5_G	Repd & Actual <code>_reflns_number_gt</code> Values Differ by	2	Check

0 **ALERT level A** = Most likely a serious problem - resolve or explain

0 **ALERT level B** = A potentially serious problem, consider carefully

1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

8 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

3 ALERT type 2 Indicator that the structure model may be wrong or deficient

1 ALERT type 3 Indicator that the structure quality may be low

2 ALERT type 4 Improvement, methodology, query or suggestion

2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing

attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

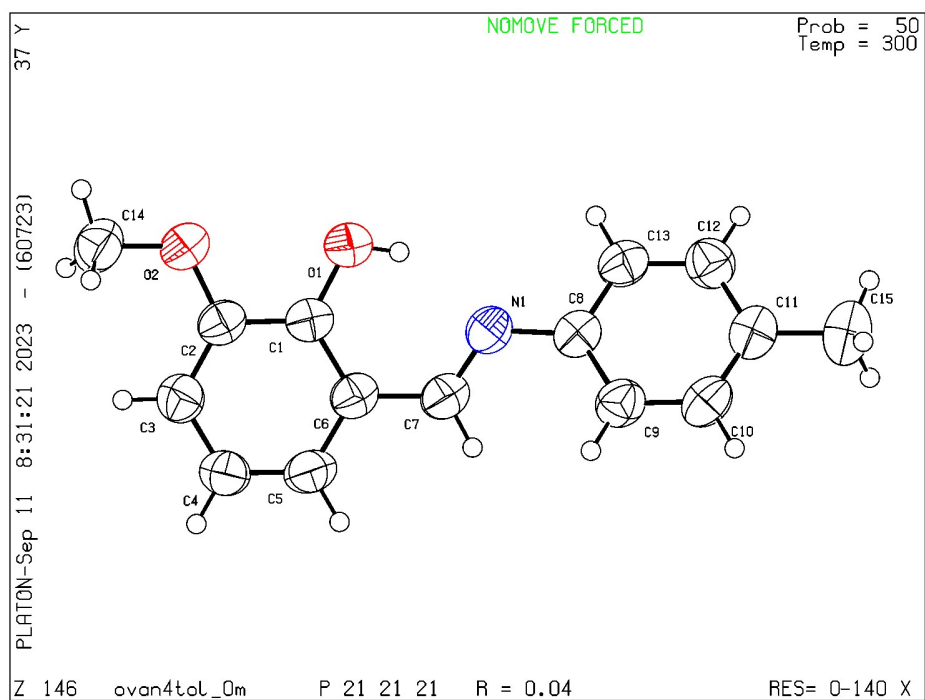
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 06/07/2023; check.def file version of 30/06/2023

Datablock ovan4tol_0m - ellipsoid plot



APPENDIX E3: Checkcif report for B2H

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) b2h_01_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: b2h_01_0m_a

Bond precision:	C-C = 0.0060 Å	Wavelength=0.71073
Cell:	a=6.107(9) alpha=90	b=11.622(19) beta=90
		c=14.46(2) gamma=90
Temperature:	299 K	
	Calculated	Reported
Volume	1026(3)	1026(3)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C13 H11 N O	C13 H11 N O
Sum formula	C13 H11 N O	C13 H11 N O
Mr	197.23	197.23
Dx, g cm ⁻³	1.277	1.276
Z	4	4
Mu (mm ⁻¹)	0.081	0.081
F000	416.0	416.0
F000'	416.17	
h, k, lmax	8, 15, 19	8, 15, 19
Nref	2700[1577]	2645
Tmin, Tmax	0.971, 0.994	
Tmin'	0.965	
Correction method=	Not given	
Data completeness=	1.68/0.98	Theta (max)= 28.855

parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

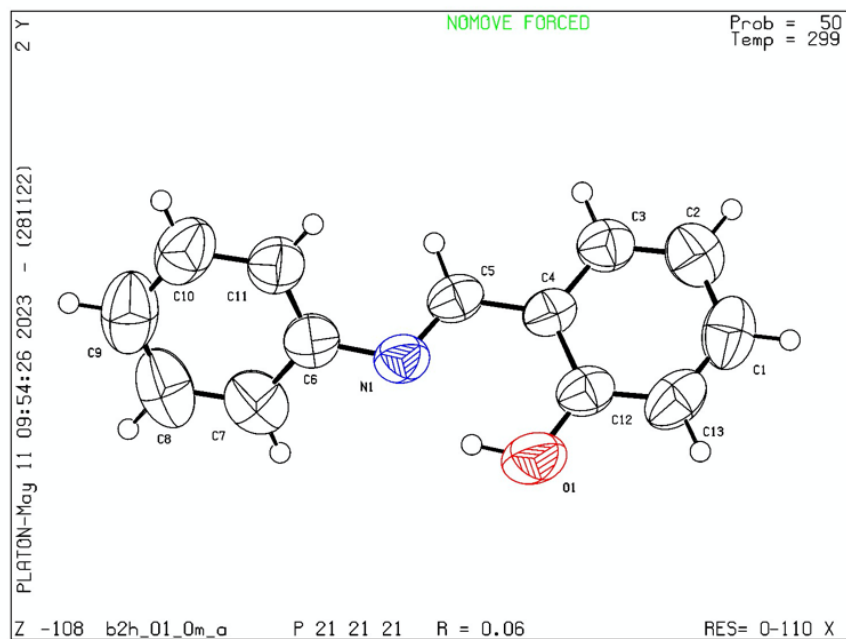
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 28/11/2022; check.def file version of 28/11/2022

Datablock b2h 01 0m a - ellipsoid plot



APPENDIX E4: Checkcif report for B2Me

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) sal4tol_1_0ma_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: sal4tol_1_0ma_a

Bond precision:	C-C = 0.0024 Å	Wavelength=0.71073
Cell:	a=19.3199 (7) alpha=90	b=4.7654 (2) beta=102.141 (1) c=12.2275 (4) gamma=90
Temperature:	301 K	

	Calculated	Reported
Volume	1100.57 (7)	1100.57 (7)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C14 H13 N O	C14 H13 N O
Sum formula	C14 H13 N O	C14 H13 N O
Mr	211.25	211.25
Dx, g cm-3	1.275	1.275
Z	4	4
Mu (mm-1)	0.080	0.080
F000	448.0	448.0
F000'	448.18	
h, k, lmax	25, 6, 16	25, 6, 16
Nref	2753	2749
Tmin, Tmax	0.962, 0.990	
Tmin'	0.961	

Correction method= Not given

Data completeness= 0.999 Theta (max)= 28.307

wR2(reflections)=

R(reflections)= 0.0560(1916)

0.1925(2749)

S = 1.074 Npar= 149

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**. Click on the hyperlinks for more details of the test.



Alert level C

PLAT906_ALERT_3_C Large K Value in the Analysis of Variance	6.492 Check
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .	1 Check
PLAT934_ALERT_3_C Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers ..	1 Check
PLAT939_ALERT_3_C Large Value of Not (SHELXL) Weight Optimized S .	22.93 Check



Alert level G

PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large	0.10 Report
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .	Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).	2 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600	2 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.	9 Info

-
- 0 **ALERT level A** = Most likely a serious problem - resolve or explain
- 0 **ALERT level B** = A potentially serious problem, consider carefully
- 4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
- 5 **ALERT level G** = General information/check it is not something unexpected
-
- 1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
- 2 ALERT type 2 Indicator that the structure model may be wrong or deficient
- 5 ALERT type 3 Indicator that the structure quality may be low
- 1 ALERT type 4 Improvement, methodology, query or suggestion
- 0 ALERT type 5 Informative message, check
-

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

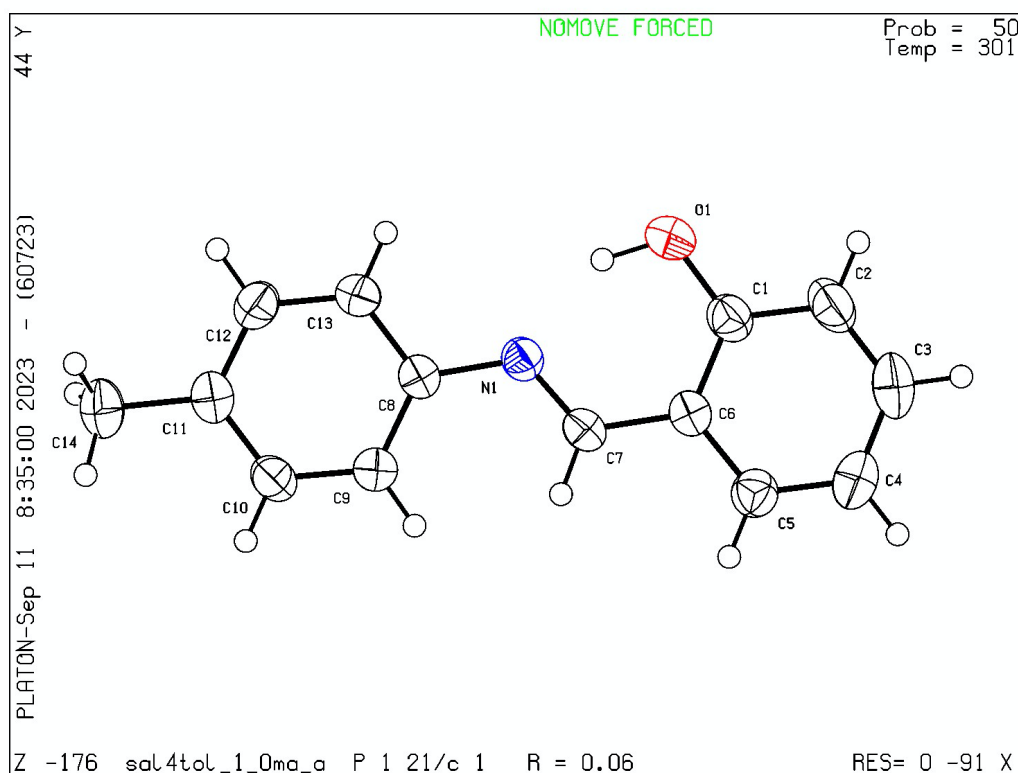
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 06/07/2023; check.def file version of 30/06/2023

Datablock sal4tol 1 0ma a - ellipsoid plot



APPENDIX E5: Checkcif report for CuB1Me

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) cub1me_1_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: cub1me_1_0m_a

Bond precision: C-C = 0.0038 A Wavelength=0.71073

Cell: a=14.1948(10) b=14.2903(12) c=13.8653(10) alpha=90
beta=107.744(2) gamma=90

Temperature: 299 K

	Calculated	Reported
Volume	2678.8(4)	2678.7(4)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C30 H28 Cu N2 O4	C30 H28 Cu N2 O4
Sum formula	C30 H28 Cu N2 O4	C30 H28 Cu N2 O4
Mr	544.09	544.08
Dx, g cm-3	1.349	1.349
Z	4	4
Mu (mm-1)	0.853	0.853
F000	1132.0	1132.0
F000'	1133.70	
h, k, lmax	18, 19, 18	18, 19, 18
Nref	3346	3340
Tmin, Tmax	0.840, 0.910	
Tmin'	0.768	

Correction method= Not given

Data completeness= 0.998

Theta(max)= 28.308

wR2(reflections)=

R(reflections)= 0.0403(2499) 0.1043(3340)

S = 1.088 Npar= 174
 The following ALERTS were generated. Each ALERT has the
 format **test-name_ALERT_alert-type_alert-level**. Click
 on the hyperlinks for more details of the test.

 **Alert level C**

PLAT905_ALERT_3_C Negative K value in the Analysis of Variance ...	-1.324	Report
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min).	5	Note

 **Alert level G**

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...	2	Report
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records	1	Report
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records	1	Report
PLAT300_ALERT_4_G Atom Site Occupancy of C14A Constrained at	0.5	Check
PLAT300_ALERT_4_G Atom Site Occupancy of C14B Constrained at	0.5	Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14A Constrained at	0.5	Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14B Constrained at	0.5	Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14C Constrained at	0.5	Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14D Constrained at	0.5	Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14E Constrained at	0.5	Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14F Constrained at	0.5	Check
PLAT301_ALERT_3_G Main Residue Disorder(Resd 1)	5%	Note
PLAT860_ALERT_3_G Number of Least-Squares Restraints	12	Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .		Please Do !
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600	1	Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File	1	Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.	9	Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
 0 **ALERT level B** = A potentially serious problem, consider carefully
 2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
 17 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 3 ALERT type 2 Indicator that the structure model may be wrong or deficient
 4 ALERT type 3 Indicator that the structure quality may be low 11 ALERT
 type 4 Improvement, methodology, query or suggestion
 0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should

normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

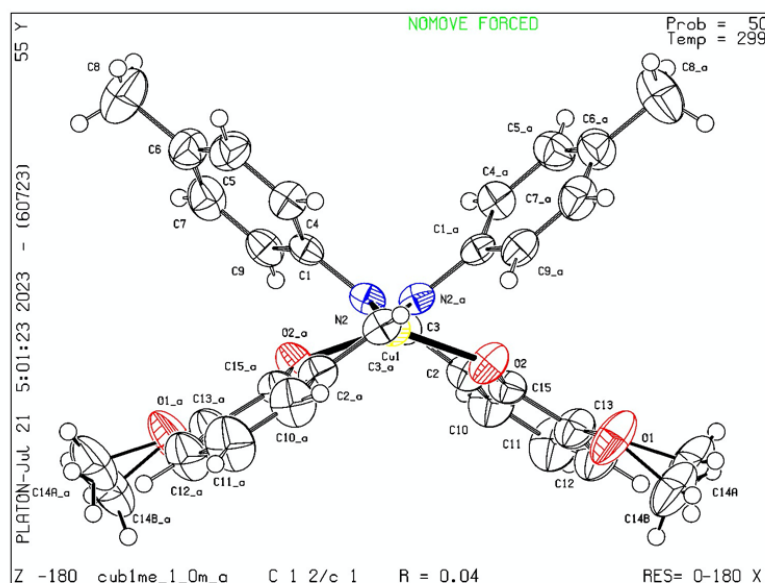
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 06/07/2023; check.def file version of 30/06/2023

Datablock cub1me 1 0m a - ellipsoid plot



APPENDIX E6: Checkcif report for CuB2H

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) cusal_an_1_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: cusal_an_1_0m_a

Bond precision: C-C = 0.0035 A

Wavelength=0.71073

Cell:

a=11.932 (2) b=7.9722 (15) c=12.204 (2) alpha=90
beta=112.216 (8) gamma=90

Temperature: 300 K

	Calculated	Reported
Volume	1074.7 (3)	1074.7 (3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C26 H20 Cu N2 O2	C26 H20 Cu N2 O2
Sum formula	C26 H20 Cu N2 O2	C26 H20 Cu N2 O2
Mr	455.99	455.98
Dx, g cm-3	1.409	1.409
Z	2	2
Mu (mm-1)	1.041	1.041
F000	470.0	470.0
F000'	470.79	
h, k, lmax	15, 10, 16	15, 10, 16
Nref	2697	2593
Tmin, Tmax	0.750, 0.804	
Tmin'	0.695	

Correction method= Not given

Data completeness= 0.961

Theta (max)= 28.381

wR2 (reflections)=

R(reflections)= 0.0314(1950)

0.0829(2593)

S = 1.045 Npar= 142
The following ALERTS were generated. Each ALERT has the
format **test-name_ALERT_alert-type_alert-level**. Click
on the hyperlinks for more details of the test.



Alert level C

RINTA01_ALERT_3_C The value of Rint is greater than 0.12
Rint given 0.134

PLAT193_ALERT_1_C Cell and Diffraction Temperatures Differ by	1 Degree
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance	8.683 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance	2.745 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600	89 Report
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF	9 Note



Alert level G

PLAT019_ALERT_1_G _diffn_measured_fraction_theta_full/*_max < 1.0	0.992 Report
PLAT020_ALERT_3_G The Value of Rint is Greater Than 0.12	0.134 Report
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .	Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).	2 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600	14 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File	7 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.	6 Info

-
- 0 **ALERT level A** = Most likely a serious problem - resolve or explain
 - 0 **ALERT level B** = A potentially serious problem, consider carefully
 - 6 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
 - 7 **ALERT level G** = General information/check it is not something unexpected
-
- 3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 - 2 ALERT type 2 Indicator that the structure model may be wrong or deficient
 - 7 ALERT type 3 Indicator that the structure quality may be low
 - 1 ALERT type 4 Improvement, methodology, query or suggestion
 - 0 ALERT type 5 Informative message, check
-

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing

attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

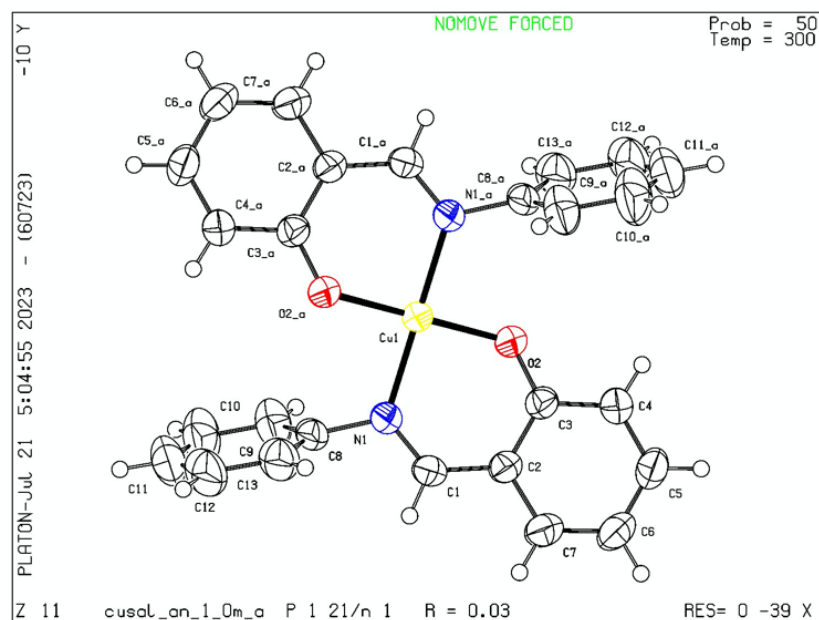
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 06/07/2023; check.def file version of 30/06/2023

Datablock cusal_an_1_0m_a - ellipsoid plot



APPENDIX E7: Checkcif report for CuB2C

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) cusal4cl_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: cusal4cl_0m_a

Bond precision:	C-C = 0.0058 A	Wavelength=0.71073
Cell:	a=9.8226(12) b=11.1394(16) c=10.8118(15) alpha=90 beta=105.414(4) gamma=90	
Temperature:	299 K	

	Calculated	Reported
Volume	1140.5(3)	1140.5(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C26 H18 Cl2 Cu N2 O2	C26 H18 Cl2 Cu N2 O2
Sum formula	C26 H18 Cl2 Cu N2 O2	C26 H18 Cl2 Cu N2 O2
Mr	524.87	524.86
Dx, g cm-3	1.528	1.528
Z	2	2
Mu (mm-1)	1.219	1.219
F000	534.0	534.0
F000'	535.39	
h, k, lmax	13, 14, 14	13, 14, 14
Nref	2873	2844
Tmin, Tmax	0.815, 0.905	
Tmin'	0.592	

Correction method= Not given

Data completeness= 0.990

Theta(max)= 28.442

wR2(reflections)= R(reflections)= 0.0578(1861)
0.1808(2844)

S = 1.174

Npar= 151

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level. Click on the hyperlinks
for more details of the test.



Alert level C

PLAT057_ALERT_3_C	Correction for Absorption Required	RT(exp) ...	1.11	Do !
PLAT241_ALERT_2_C	High 'MainMol' Ueq as Compared to Neighbors of		01	Check
PLAT905_ALERT_3_C	Negative K value in the Analysis of Variance ...		-6.203	Report
PLAT905_ALERT_3_C	Negative K value in the Analysis of Variance ...		-0.621	Report
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L=	0.600	3	Report



Alert level G

PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .			Please Do !
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).		2	Note
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L=	0.600	24	Note
PLAT933_ALERT_2_G	Number of HKL-OMIT Records in Embedded .res File		1	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.		1	Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing

attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

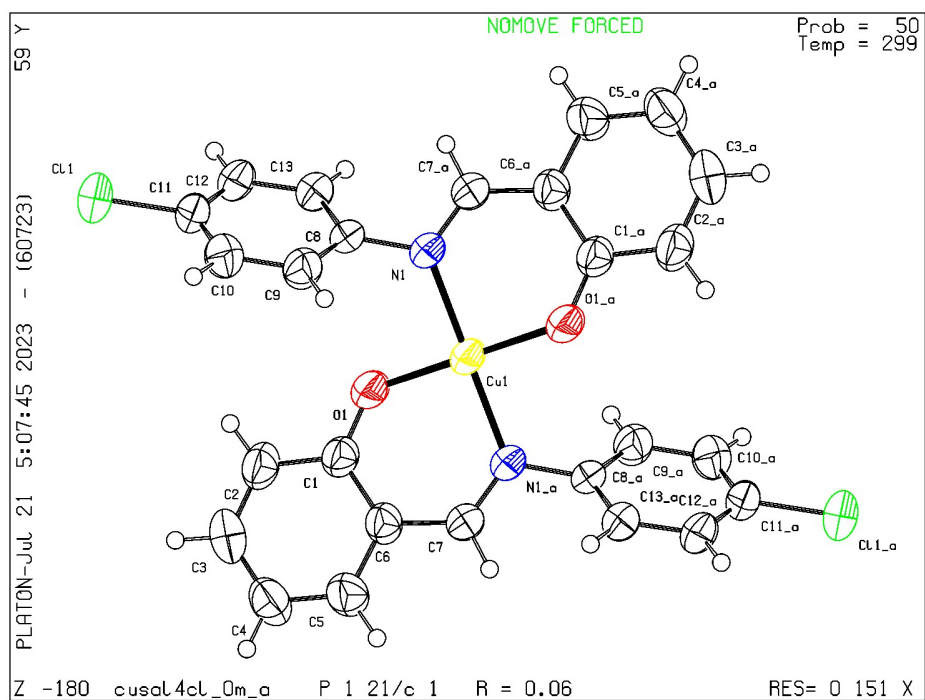
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 06/07/2023; check.def file version of 30/06/2023

Datablock cusal4cl_0m_a - ellipsoid plot



APPENDIX E8: Checkcif report for Pdb1OMe

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) pdb1ome_1_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: pdb1ome_1_0m_a

Bond precision:	C-C = 0.0058 Å	Wavelength=0.71073
Cell:	a=7.123 (3)	b=8.326 (4) c=11.625 (5)
	alpha=98.14 (3)	beta=103.81 (3) gamma=94.38 (3)
Temperature:	299 K	
	Calculated	Reported
Volume	658.4 (5)	658.3 (5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C30 H26 N2 O6 Pd	C30 H26 N2 O6 Pd
Sum formula	C30 H26 N2 O6 Pd	C30 H26 N2 O6 Pd
Mr	616.93	616.93
Dx, g cm ⁻³	1.556	1.556
Z	1	1
Mu (mm ⁻¹)	0.753	0.753
F000	314.0	314.0
F000'	313.14	
h, k, lmax	10, 12, 17	10, 11, 15
Nref	4776	3582
Tmin, Tmax	0.897, 0.956	

Tmin' 0.822

Correction method= Not given

Data completeness= 0.750

Theta(max)= 32.509

R(reflections)= 0.0511(2777)

wR2(reflections)=

0.1198(3582)

S = 1.061

Npar= 180

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**. Click on the hyperlinks for more details of the test.



Alert level C

PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of 02 Check
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min). 5 Note
1 0 0, 0 1 0, 0 -1 1, -1 0 1, 0 0 1,
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 20 Report
0 2 0, 0 -9 1, 0 -3 1, -1 -2 1, 0 -2 1, 1 -2 1,
-2 1 1, -1 2 1, -3 6 1, 1 -4 2, -3 5 2, 5 -8 3,
-5 5 4, 0 6 4, 4 -8 5, 0 5 5, 0 6 5, 6 -5 6,
-6 4 6, -4 6 7,
PLAT975_ALERT_2_C Check Calcd Resid. Dens. 0.97Ang From C4 . 0.84 eA-3
PLAT976_ALERT_2_C Check Calcd Resid. Dens. 0.95Ang From O2 . -0.46 eA-3



Alert level G

PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note) 0.03 Degree
PLAT343_ALERT_2_G Unusual sp? Angle Range in Main Residue for C4 Check
PLAT794_ALERT_5_G Tentative Bond Valency for Pd1 (II) . 2.36 Info
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 1019 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File 5 Note
0 2 0, 0 -3 1, 0 1 0, 1 -4 2, 1 -2 1,
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity 4.9 Low
PLAT952_ALERT_5_G Calculated (ThMax) and CIF-Reported Lmax Differ. 2 Units
PLAT958_ALERT_1_G Calculated (ThMax) and Actual (FCF) Lmax Differ. 2 Units
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value 2.150 Note
Predicted wR2: Based on SigI**2 5.57 or SHELX Weight 11.29
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 2 Info

- 0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
10 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or
missing data 6 ALERT type 2 Indicator that the structure model may
be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low 1
ALERT type 4 Improvement, methodology, query or suggestion
3 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

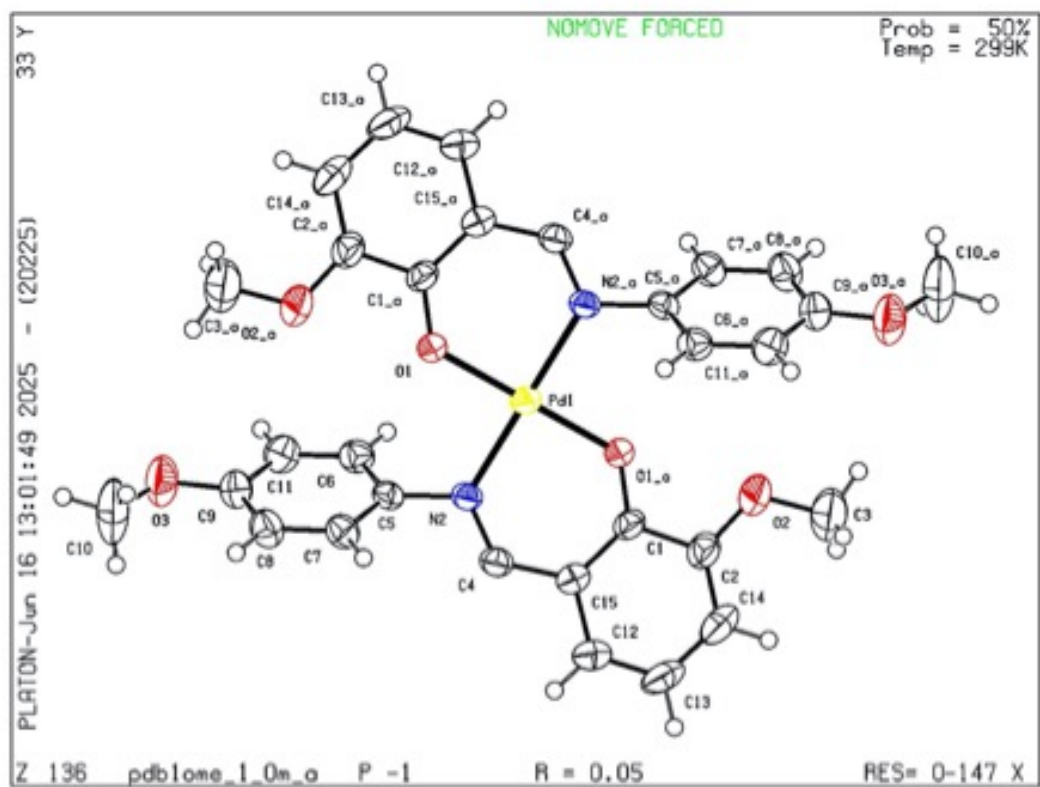
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 02/02/2025; check.def file version of 02/02/2025

Datablock pdb1ome_1_0m_a - ellipsoid plot



APPENDIX E9: Checkcif report for PdB2Me

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) pdb2me_1_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: pdb2me_1_0m_a

Bond precision: C-C = 0.0059 Å

Wavelength=0.71073

Cell:

a=9.941(3) b=10.952(3) c=10.969(3) alpha=90
beta=105.337(8) gamma=90

Temperature: 299 K

	Calculated	Reported
Volume	1151.7(6)	1151.8(5)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C28 H24 N2 O2 Pd	C28 H24 N2 O2 Pd
Sum formula	C28 H24 N2 O2 Pd	C28 H24 N2 O2 Pd
Mr	526.89	526.89
Dx, g cm-3	1.519	1.519
Z	2	2
Mu (mm-1)	0.834	0.834
F000	536.0	536.0
F000'	534.19	
h, k, lmax	13, 14, 14	13, 14, 14
Nref	2882	2867
Tmin, Tmax	0.798, 0.868	
Tmin'	0.798	

Correction method= Not given

Data completeness= 0.995

Theta(max)= 28.311

wR2(reflections)=

R(reflections)= 0.0444(2203) 0.1109(2867)

S = 1.272 Npar= 152

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**. Click on the hyperlinks for more details of the test.



Alert level C

PLAT241_ALERT_2_C	High 'MainMol' Ueq as Compared to Neighbors of	01	Check
PLAT905_ALERT_3_C	Negative K value in the Analysis of Variance ...	-2.814	Report
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.600	4	Report
	1 0 2, 3 0 2, -4 2 2, -1 3 2,		
PLAT934_ALERT_3_C	Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers ..	1	Check
	-2 2 2,		



Alert level G

PLAT794_ALERT_5_G	Tentative Bond Valency for Pd1 (II)	2.36	Info
PLAT883_ALERT_1_G	Absent Datum for _atom_sites_solution_primary ..		Please Do !
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).	4	Note
	1 0 0, 1 1 0, -1 1 1, 0 1 1,		
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	8	Note
PLAT933_ALERT_2_G	Number of HKL-OMIT Records in Embedded .res File	1	Note
	-1 1 1,		
PLAT969_ALERT_5_G	The 'Henn et al.' R-Factor-gap value	5.405	Note
	Predicted wR2: Based on SigI**2 2.05 or SHELX Weight	8.72	
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	0	Info

- 0 **ALERT level A** = Most likely a serious problem - resolve or explain
- 0 **ALERT level B** = A potentially serious problem, consider carefully
- 4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
- 7 **ALERT level G** = General information/check it is not something unexpected
-
- 1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
- 3 ALERT type 2 Indicator that the structure model may be wrong or deficient
- 4 ALERT type 3 Indicator that the structure quality may be low 1 ALERT
- type 4 Improvement, methodology, query or suggestion
- 2 ALERT type 5 Informative message, check
-

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual

parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

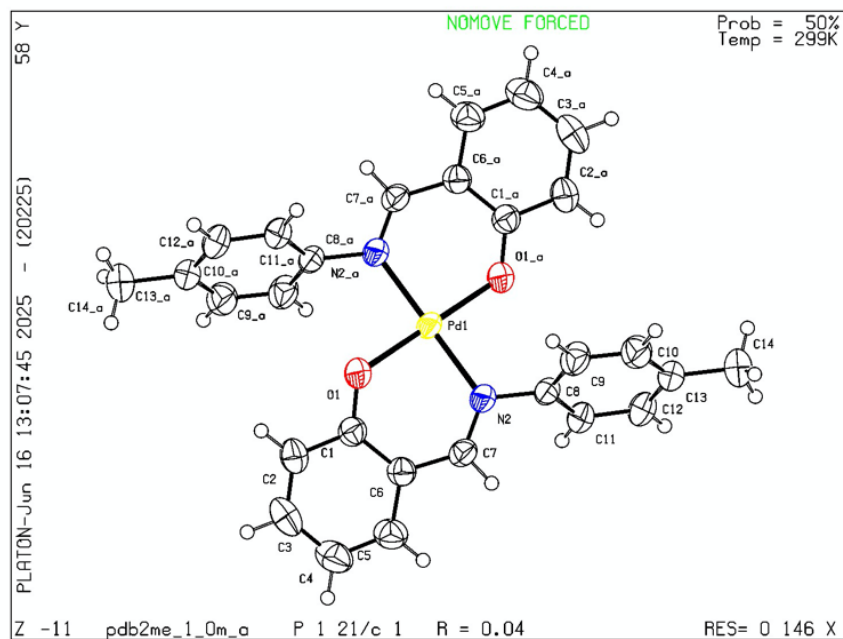
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 02/02/2025; check.def file version of 02/02/2025

Datablock pdb2me 1 0m a - ellipsoid plot



APPENDIX E10: Checkcif report for Pdb2OMe

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) pdb2ome_1_0ma_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: pdb2ome_1_0ma_a

Bond precision: C-C = 0.0030 A

Wavelength=0.71073

Cell:

a=13.396(3) b=11.231(2) c=7.8603(14) alpha=90
beta=97.070(6) gamma=90

Temperature: 300 K

	Calculated	Reported
Volume	1173.6(4)	1173.6(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C28 H24 N2 O4 Pd	C28 H24 N2 O4 Pd
Sum formula	C28 H24 N2 O4 Pd	C28 H24 N2 O4 Pd
Mr	558.89	558.89
Dx, g cm-3	1.582	1.582
Z	2	2
Mu (mm-1)	0.829	0.829
F000	568.0	568.0
F000'	566.23	
h, k, lmax	17, 14, 10	17, 14, 10
Nref	2908	2904
Tmin, Tmax	0.828, 0.876	
Tmin'	0.826	

Correction method= Not given

Data completeness= 0.999

Theta (max)= 28.217

wR2(reflections)=

R(reflections)= 0.0251(2435)

0.0682(2904)

S = 1.122 Npar= 161

The following ALERTS were generated. Each ALERT has the
format **test-name_ALERT_alert-type_alert-level**. Click
on the hyperlinks for more details of the test.



Alert level C

PLAT905_ALERT_3_C Negative K value in the Analysis of Variance ... -0.843 Report



Alert level G

PLAT232_ALERT_2_G	Hirshfeld Test Diff (M-X)	Pd1	--N1	.	6.0 s.u.
PLAT794_ALERT_5_G	Tentative Bond Valency for Pd1		(II)	.	2.25 Info
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary			.	Please Do !
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min)			.	4 Note
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L=	0.600			1 Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.				12 Info

-
- 0 **ALERT level A** = Most likely a serious problem - resolve or explain
- 0 **ALERT level B** = A potentially serious problem, consider carefully
- 1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
- 6 **ALERT level G** = General information/check it is not something unexpected
- 1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
- 2 ALERT type 2 Indicator that the structure model may be wrong or deficient
- 2 ALERT type 3 Indicator that the structure quality may be low
- 1 ALERT type 4 Improvement, methodology, query or suggestion
- 1 ALERT type 5 Informative message, check
-

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

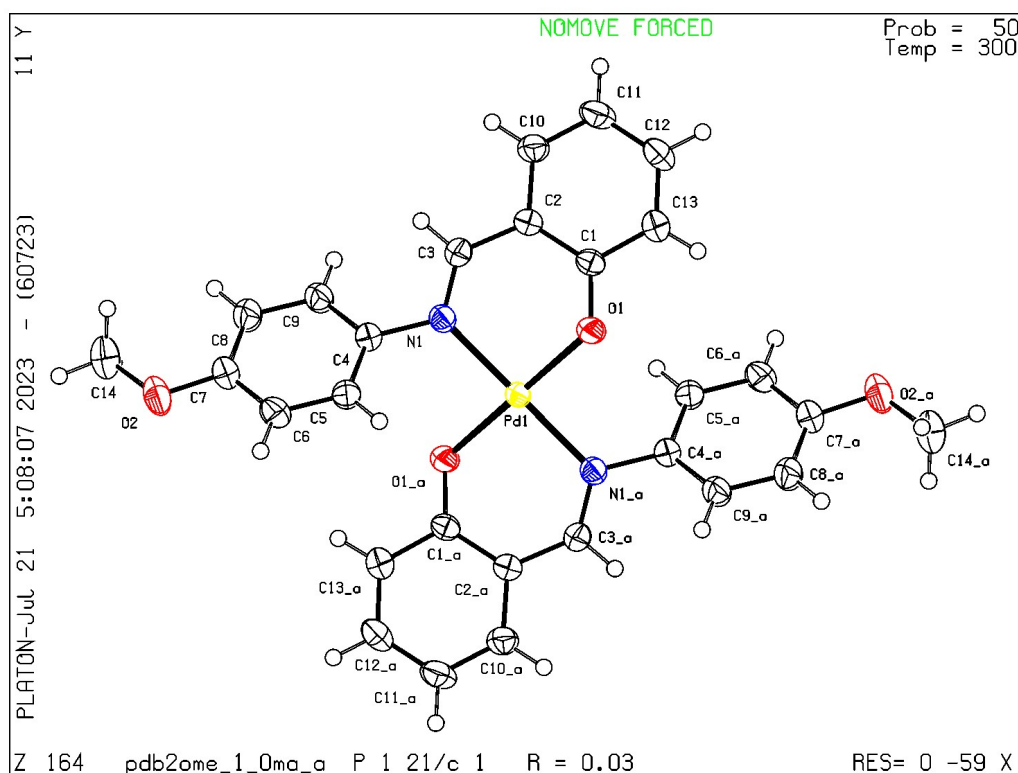
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 06/07/2023; check.def file version of 30/06/2023

Datablock pdb2ome 1 0ma a - ellipsoid plot



APPENDIX E11: Checkcif report for PdB2C

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) pdb2c_2_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: pdb2c_2_0m_a

Bond precision: C-C = 0.0030 A

Wavelength=0.71073

Cell:

a=9.858 (4) b=11.122 (5) c=10.702 (5) alpha=90
beta=104.537 (15) gamma=90

Temperature: 300 K

	Calculated	Reported
Volume	1135.8 (9)	1135.8 (9)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C26 H18 Cl2 N2 O2 Pd	C26 H18 Cl2 N2 O2 Pd
Sum formula	C26 H18 Cl2 N2 O2 Pd	C26 H18 Cl2 N2 O2 Pd
Mr	567.72	567.72
Dx, g cm-3	1.660	1.660
Z	2	2
Mu (mm-1)	1.079	1.079
F000	568.0	568.0
F000'	566.78	
h, k, lmax	13, 14, 14	13, 14, 14
Nref	2802	2793
Tmin, Tmax	0.823, 0.898	
Tmin'	0.764	

Correction method= Not given

Data completeness= 0.997

Theta (max)= 28.229

wR2 (reflections)= R (reflections)= 0.0249 (2224)
0.0659 (2793)

S = 1.109

Npar= 151

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level. Click on the hyperlinks
for more details of the test.



Alert level C

PLAT193_ALERT_1_C Cell and Diffraction Temperatures Differ by 1 Degree



Alert level G

PLAT794_ALERT_5_G Tentative Bond Valency for Pd1 (II) . 2.32 Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta (Min). 4 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 5 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 4 Info

-
- 0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected
- 2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check
-

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

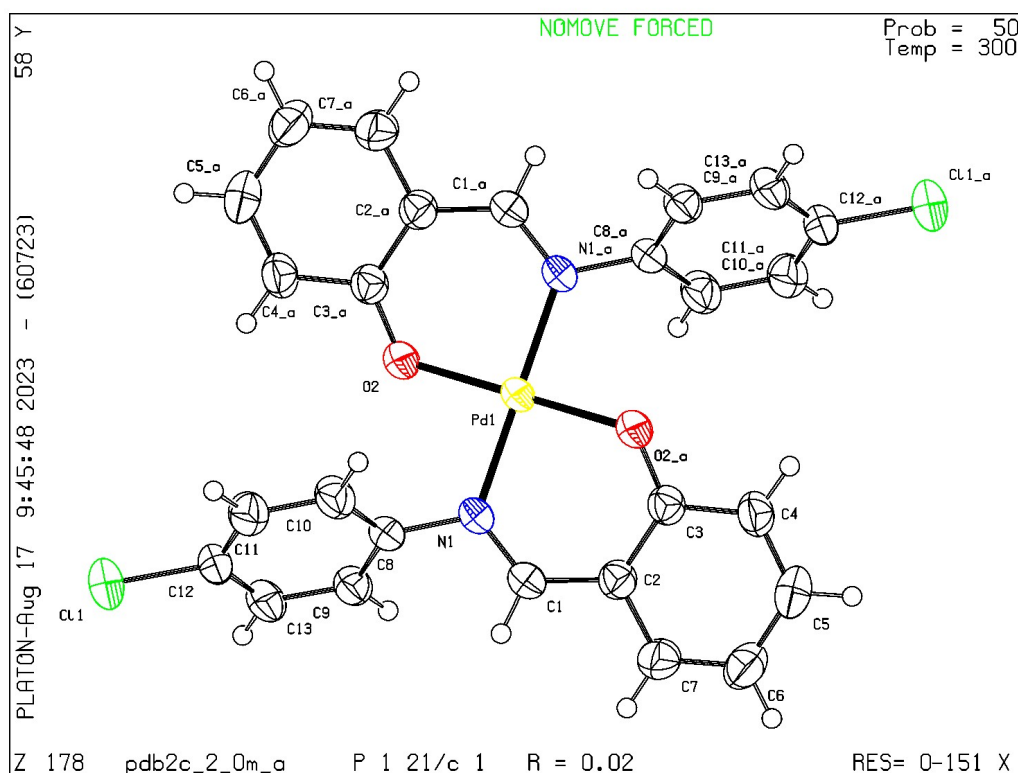
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 06/07/2023; check.def file version of 30/06/2023

Datablock pdb2c 2 0m a - ellipsoid plot



AUTHOR'S PROFILE



Nur Nabihah binti Muzammil received her first-class degree in Bachelor of Science (Hons.) Chemistry from Universiti Teknologi MARA (UiTM), Shah Alam. Building upon her strong foundation in chemical sciences, she continued her academic journey by pursuing a PhD in Inorganic Chemistry, specializing in the synthesis of Schiff base ligands. Her doctoral research focused on the development of these ligands for multiple applications, including their role as catalysts in cross-coupling reactions such as the Stille reaction, as well as their potential antibacterial properties. To complement her experimental work, she incorporated density functional theory (DFT) studies to explore the electronic and structural attributes of the complexes. Throughout her postgraduate research, she has attended few conferences and seminars in domestic and international, reflecting her dedication to advancing knowledge in ligand chemistry and its practical applications in catalysis and inorganic fields

LIST OF PUBLICATIONS

- Muzammil, N. N., Sirat, S. S., Rosli, M. M., Hamali, M. A., Ali, M. T. M., and Tajuddin, A. M. Synthesis, Crystal Structure, and Hirshfeld Surface Analysis of bis{2-[(*E*)-(p-tolylimino)methyl]benzen-1-olato}palladium. *Acta Crystallographica Section E: Structure Reports Online*, 2026. E82.
- Muzammil, N. N., Ali, M. T. M., and Tajuddin, A. M. Synthesis and Characterization of Palladium(II) Schiff Base Complexes Derived From Phenylamines and Their Catalytic Activity For Stille Reaction. *Malaysian Journal of Analytical Sciences*, 2024. 28(2): p. 335-347.

Muzammil, N. N., Bahron, H., and Tajuddin, A. M. A Mini Review on the Effects of Bases, Catalyst Loadings, Temperatures and Solvents in the Stille Cross-Coupling Reaction using Pd(II), Cu(I, II) and Ni(II) Complexes as Homogeneous Catalysts. *Malaysian Journal of Chemistry*, 2023. 25(2): p. 127-137.

LIST OF CONFERENCES

- “Synthesis and Characterization of Palladium(II) Schiff Base and Their Catalytic Activity for Stille Reaction” - The 9th Asian Conference on Coordination Chemistry (ACCC9), 19th to 22nd February 2024. The Berkeley Hotel Pratunam, Bangkok, Thailand
- “Synthesis and Characterization of Palladium(II) Schiff Base Complexes and Their Catalytic Activity for Stille Reaction” - The 35th International Conference of Analytical Sciences (SKAM35), 28th to 30th August 2023. Bayview Hotel, Langkawi