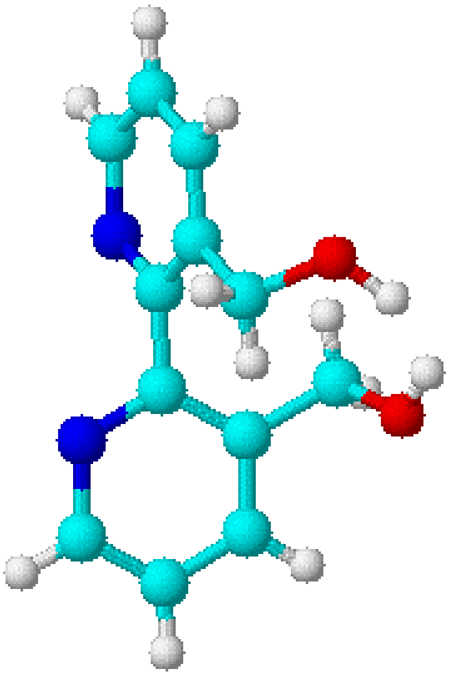

Syntheses and Reactions of Substituted Bipyridines

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Front cover: 3-dimensional structure of substituted bipyridine (2,2'-bipyridyl-3,3'-carbinol) using Advanced Chemistry Development Inc's ACD/3D Viewer.

ACKNOWLEDMENTS

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The study was carried out in the Department of Chemistry at the University of Brunei Darussalam in July – November 2003. Although in my own opinion it was quite a short period of research, during my research I found that the study is very motivating.

I also wish to thank all the staff in the Department of Chemistry. My sincere thanks are also due to my friends and colleagues for all of your support and providing a warm and supporting atmosphere in the Laboratory.

Most importantly I wish to thank my beloved parents and families for their support during my studies.

Hazarry Haji Ali Ahmad

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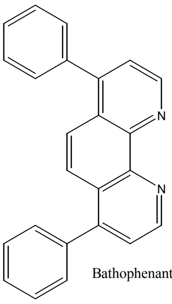
Abstract

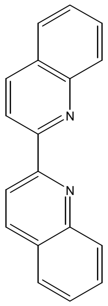
Synthesis of the substituted bipyridine2,2’-bipyridyl-3,3’-dicarbinol, bipyridine was attempted from 1,10-phenantroline. Six different bipyridine ligands (2,2’-biquinoline; 5-nitro-1,10-phenantroline; neocuproin, bathophenantroline and 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline) which cover a wide range of electronic and steric properties were successfully complexed with $Mo(CO)_6$. The properties of the complexes were studied and characterized by infrared and proton nuclear magnetic resonance spectroscopy, and by electronic spectroscopy to study their solvatochromic properties.

List of abbreviations

BPhen	Bathophenantroline
Bpy	Bipyridine
BiQ	2,2’-Biquinoline
DCMB	3,3’-Dicarbomethoxy-2,2’-bipyridine
DDPQxn	6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline
DCMBiQ	4,4’-dicarbomethoxy-2,2’-biquinoline
DMF	Dimethylformamide
EtOH	Ethanol
IR	Infrared
UV	Ultraviolet
MeOH	Methanol
MLCT	Metal to ligand charge transfer
NPhen	5-nitro-1,10-phenantroline
NeoC	Neocuproin
R_f	Refractive index
t-BuOH	tert-Butyl alcohol (2-Methyl-2-propanol)
TLC	Thin-layer chromatography
THF	Tetrahydrofuran
TMNO	Trimethylamine-*N*-oxide



Bathophenantroline



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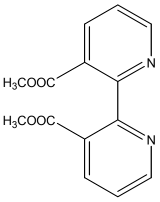

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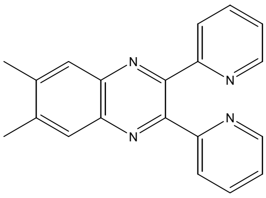

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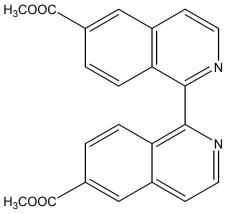

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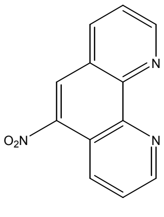
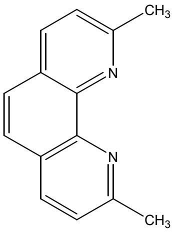


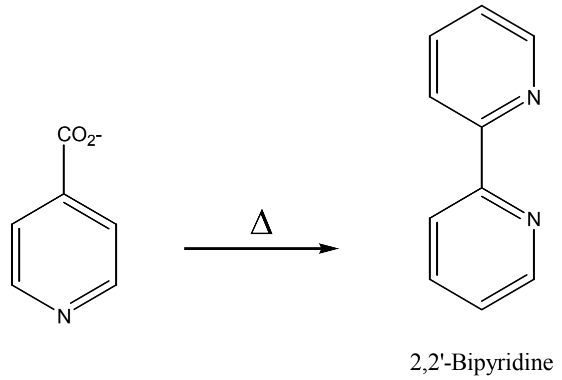
5-Nitro-1,10-phenanthroline



Neocuproin

1. Introduction

Pure 2,2'-bipyridine (Equation 1) was first synthesized in the late 19th century by distillation of copper picolinate. A more convenient synthesis was eventually achieved when Raney-Nickel alloy was used as a catalyst [25]. Since the preparation of the first 2,2'-bipyridine, the derivatives of bipyridine have been widely employed in complexation experiments.



Equation 1. Synthesis of 2,2'-Bipyridine

Transition metals in low oxidation states are able to form complexes with many unsaturated organic ligands. The interactions between the ligands and the metal depend on the orientation of the orbitals with respect to each other. According to their interactions, ligands are classified into three types: σ-donor ligands, π-donor ligands and π-acceptor ligands [2]. So, 2,2'-bipyridine is both a σ-donor and a π-acceptor ligand. The lone electron pair of nitrogen can form a σ-bond with the central atom, while the aromatic system can take part in back-bonding. These will stabilize metal ions, especially transition metal ions in low oxidation states.

In addition, ligands with two or more donor atoms are able to form a chelate ring with metal atoms. The diimine part of the bipyridine delocalizes the electrons in the chelate ring. This ability to coordinate has led to an extremely rich chemistry and constitutes the basis of many important industrial catalytic processes. For example, complexes of methyl substituted bipyridine as catalyst in atom transfer radical polymerization of styrene and acrylates [17].

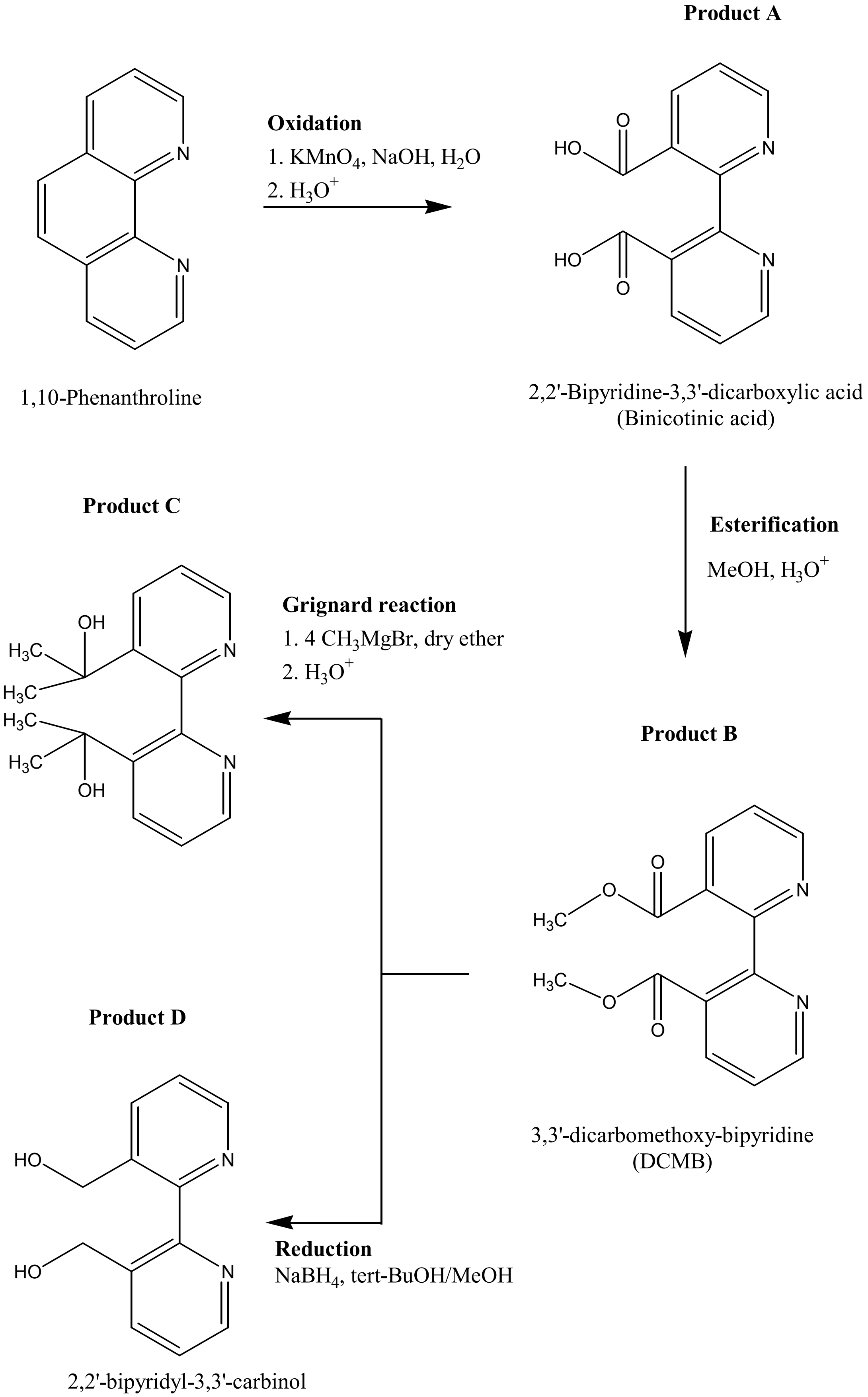
2,2’-Bipyridines are of special interest as complex ligands in coordination and supramolecular chemistry. Their prolonged, luminescent, charge transfer state enables them to be used as sensitizers in photochemistry[5]. Bipyridine complexes are also significant in catalytic studies in the reduction of CO_2 [4] and the hydroformylation of olefins [15].

It is essential in coordination chemistry to understand how ligands are bonded to metal atoms. 2,2’-bipyridine is a versatile chelating agent which binds to most metal ions. The electronic properties of bipyridine can be tailored by varying the substituents on the parent ligand and as a result this will modify the properties of the metal complexes[7].

In one part of this study, alcohol functional groups were aimed to be introduced at position 3,3’ of 2,2’-bipyridine which would change the electronic and steric properties of the bipyridine. The proposed synthesis is shown in Scheme 1. The starting material is phenanthroline. Oxidation of 1,10 phenanthroline yields binicotinic acid (Product A), the carboxylic acid substituents at 3,3’-position of the 2,2’-bipyridine[9]. The next step was to convert the acid into the ester (Product B), 3,3’-

dicarbomethoxy-2,2’-bipyridyl (DCMB). Alcohols can be synthesized from esters with Grignard reagent (Product C) or by reduction with sodium borohydride in mixed solvent[10] (Product D).

Group VIA of the transition metals i.e. $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ were purposely being used in this study as they are neutral and stable metal carbonyls[1] having octahedral coordination. CO can be replaced by an isoelectronic equivalent having two electrons for example H^- and a ligand having a lone pair of electrons such as nitrogen. A study of these hexacarbonyls using infrared and Raman spectra determined the mean dissociation energies for the loss of the first CO in order relative to each other: $Cr(CO)_6 < Mo(CO)_6 > W(CO)_6$ [7]. Hence, generally, we would expect molybdenum hexacarbonyl being more reactive than chromium and tungsten.



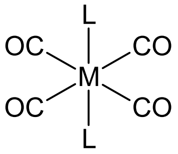
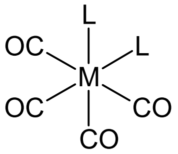
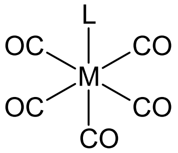
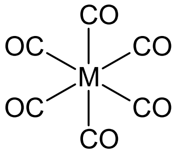
Scheme 1: Proposed synthetic route for the preparation of substituted 3,3'-alcohol functional group of bipyridine ligand.

Infrared spectroscopy

When CO coordinates to a metal center, electron density from a lone-pair on the carbon is donated to the metal, while at the same time the π*-orbitals of the ligand receives electron density from the metal, thereby strengthening the metal-ligand bond. This is known as synergistic bonding[1]. CO is particularly powerful in withdrawing electron density from the metal in this way, i.e. it is a good π-acceptor. Since the C-O stretching frequency is easily observed in the IR spectrum, the position of this band is a sensitive probe for the electron density of the metal center [3] as well as the structural information[6].

The number of infrared bands depends on the molecular symmetry of the metal carbonyl complexes hence its geometry. For a vibration modes to be infrared active there must be a change in the dipole moment of the molecule. Because not all vibrations result in a change in dipole moment, this type of vibration will be invisible in the infrared spectrum[3]. For terminal M-CO, the approximate range for V_{co} in neutral complexes ranges between 1850 – 2120 cm^{-1}. Predicting the number of carbonyl bands of complexes having more than two carbonyls involved the use of Group theory[8]. From the infrared spectrum of metal carbonyl complex, one may be able to decide among several alternatives geometries for a compound. For a complex having octahedral coordination, the number of bands expected for a variety of CO complexes is given in Table 1. Hence by inferring the number of bands in the infrared spectra of the complex can verify whether the reaction has completed.

Table 1: Infrared active carbonyl stretching bands.

Number of Carbonyls	Geometry	CO stretching bands
4		1
4		4
5		3
6		1

* L is a ligand.

Electronic spectroscopy

Solvatochromism refers to changes in electronic absorption spectra with solvent[19]. All ligands may possess a number of molecular orbitals such as σ-, σ*-, π-, π*- and non-bonding. Charge transfer may occur from the filled d-orbitals to the empty ligand orbitals. Absorption due to this process is called a metal-to-ligand charge-transfer bands (MLCT) which can be observed using ultraviolet-visible spectroscopy. Most transition-metal complexes display solvatochromic behavior and usually show significant shifts of absorption band energies with variation in solvent[20].

Previous projects

Some substituted bipyridines of binicotinic acid and DCMB had been successfully synthesized previously. Reduction of DCMB by lithium aluminium hydride to alcohol was unsuccessful[11]. However reduction of DCMB with sodium borohydride in mixed solvents was reported to give a very low yield of diol that was a green solid[12]. Synthesis of alcohol from DCMB failed using Grignard reagent[12]. Table 2 shows the yield of substituted bpy and complexes reported from previous project.

Table 2. Substituted bipyridine and complexes from previous projects.

	Yield (%)	**IR spectral analysis**	**Properties**
Binicotinic acid [b]	71	C=O stretching at 1716 cm^{-1}	White solid
DCMB [b]	85	C=O stretching at 1719 cm^{-1}	White solid
Reduction of DCMB by $LiAlH_4$ [a]	Unsuccessful		
Reaction of DCMB with a Grignard reagent [b]	15	O-H stretching at $3247 cm^{-1}$	Melting point: 156 °C Greenish solid
$Mo(CO)_4(DCMB)$ [b]	90	v_{co}: 4 bands	Red crystal
$W(CO)_4(DCMB)$ [b]	97	v_{co}: 4 bands	Red crystal
$Cr(CO)_4(DCMB)$ [b]	Unsuccessful		

[a] Project report by Norrul Aini Bte Hj. Md. Thani (1997/1998)
[b] Project report by Saidin Lasit (1999)

1.1 Aims of the project

One of the reasons of carrying out this research is concerning the study of physical and chemical properties of metal complexes of substituted bipyridine, which leads to possible application in catalysis. The main task of the project was to illustrate several aspects of the chemistry of metal carbonyl complexes. The primary aims of the study are:

(i) Preparation and characterization of new complexes of substituted bipyridine ligands which cover a wide range of electronic and steric properties.

(ii) To synthesize some metal complexes and to study their properties.

(iii) To study metal binding properties of substituted bpy involved characterization of the substituted bpy using IR, UV and NMR spectroscopy

2. Experimental

2.1 Preparation of substituted bipyridine.

The bipyridine ligands prepared in this project were designed to coordinate with octahedral coordination metal centers where all nitrogen donors can coordinate to metal center. Hopefully, these ligands can be complexed with transition metal carbonyl and their chemical properties and reactions can be studied. Procedures from a previous project[12] were followed. The compounds melting point was recorded. IR spectra of the products were recorded as nujol mulls between potassium bromide discs on a Perkin Elmer FTIR Spectrometer Spectrum 1600.

(i) Synthesis of 2,2'-Bipyridine-3,3'-dicarboxylic acid (Binicotinic acid)

The synthesis of binicotinic acid was reported to produce a high yield (75-80%) by the oxidation of 1,10-phenantroline with alkaline permanganate[9]. Modified procedures were described as follows.

1,10-Phenantroline monohydrate (7.92g; 0.040mol), sodium hydroxide (3.21g; 0.08mol) and potassium permanganate (19.0g; 0.12mol) were dissolved in water (350ml) and boiled in a 500ml conical flask and stirred with a magnetic stirrer for 3 hours. As a precaution, the flask on the hot plate was clamped to avoid the flask from bumping around during boiling. The brown solid manganese dioxide was removed from the solution by vacuum filtration. The yellow filtrate was evaporated on a rotatory evaporator to approximately 150ml. The solution was then acidified with concentrated hydrochloric acid to pH of 2. A small amount of activated charcoal was added to the solution to decolorize the yellow solution and boiled for 5 minutes. The mixture was filtered to remove the charcoal and the colourless filtrate was concentrated on a rotatory evaporator to about 100ml (but not too concentrated to avoid a coloured product being formed). The solution was cooled to room temperature and then cooled in ice. White flakes of binicotinic acid were collected by vacuum filtration and washed repeatedly with cold water followed by 10ml of cold ethanol. The solid was dried in a desiccator over silica gel. [Yield = 37%].

(ii) Synthesis of 3,3'-Dicarbomethoxy-2,2'-bipyridine (DCMB)

Binicotinic acid (3.75g; 0.75mol) was dissolved in methanol (20ml). Carefully, concentrated sulfuric acid (4ml) was added. Some boiling chips were added. The mixture was heated under reflux for 5 hours. The methanol was removed on a rotatory evaporator, water (20 ml) was added and the acidic solution was neutralized with sodium carbonate. The white solid of DCMB was collected by vacuum filtration, washed repeatedly with cold water followed by few drops of cold ethanol. The product was dried in desiccator over silica gel. [Yield = 79%].

(iii) Reaction of DCMB with a Grignard reaction.

All glassware were cleaned and dried. In order to keep out water from entering into the reaction calcium chloride tubes were attached at both openings of the condenser and the addition funnel. The preparation of alcohol from DCMB and a Grignard reagent was as follow.

Magnesium turnings (0.73g; 0.030mol) were weighed into a two-neck 250ml round-bottom flask. A crystal of iodine was added and a magnetic stirring bar was placed in the flask. 10ml of dry ether (ether dried over sodium or once the dry ether was opened the ether was dried over 3A molecular sieve) was added into the flask via the addition funnel and attached with a calcium chloride drying tube. A solution of iodomethane solution was prepared by adding iodomethane (1.84ml; 0.03mol) to dry ether (10ml). The solution was then transferred into the addition funnel.

A few drops of iodomethane solution were added to the contents of the RB flask and stirred. When the reaction started (solution turned chalky) and refluxing started, a further 20ml of dry ether was added in the addition funnel. If no reaction was observed, the flask was immersed in a warm water bath to help to initiate the reaction. The iodomethane solution was added drop wise to maintain a gentle reflux. If the reaction was too vigorous (refluxing very rapidly), the rate was controlled by cooling the reaction flask using an ice bath and if the reaction was too slow (not refluxing) the flask was warmed in a hot water bath. After the addition, the chalky mixture was refluxed for a further 30 minutes on a hot water bath. After refluxing, the mixture was left cool to room temperature.

A solution of DCMB was prepared by adding DCMB (2.02g; 0.0074mol) dissolved in 30ml dry ether in another RB flask with stopper on an ultrasonic water bath for 1 hour. Quickly, the RB flask of the Grignard reagent was replaced with RB flask of DCMB solution. The chalky Grignard reagent was then decanted and rinsed with 10ml of dry ether into the addition funnel leaving behind any unreacted magnesium.

The Grignard reagent was added dropwise to the DCMB solution and the reaction minute was heated and maintained a gentle reflux. After the addition, the orange solution was stirred for a further 30 minutes at room temperature.

Carefully, 5% by volume sulphuric acid (30ml) was added and the mixture was stirred for 30 minutes to dissolve the orange solid. The solution was decanted and rinsed with 10ml water and filtered to a separating funnel leaving behind any insoluble solid. The black-red aqueous layer was evaporated on a rotatory evaporator and the gummy black solid was washed with ethanol and scraped off. The solid was collected by vacuum filtration, washed with small amount of ethanol and dried in a desiccator over silica gel.

Thin-layer chromatography of the product and DCMB dissolved in dichloromethane using silica plates and developed with ethyl acetate were carried out.

(iv) Reduction of Methyl nicotinate by $NaBH_4$

Methyl nicotinate (0.554g; 4.04mmol) and sodium borohydride (0.381g; 10.2mmol) was stirred and dissolved in *t*-BuOH (16ml). Methanol (3.2ml; 0.079mol) stored over 3A molecular sieves was transferred into the addition funnel and added slowly for a period of 1 hour. After the addition, the reaction mixture was refluxed for a further 2 hours followed by cooling to room temperature. Water (10ml) was added to dissolve any solid formed and the yellow solution was further refluxed for 30 minutes. The solution was allowed to cool to room temperature and evaporated on a rotatory evaporator. The solid formed was vacuum filtered, washed with cold water and dried in desiccator over silica gel. [Yield = 56%].

(v) Synthesis of 2,2'-bipyridyl-3,3'-carbinol.

DCMB (0.763g; 2.80mmol) and sodium borohydride (0.321; 8.53mmol) was stirred and dissolved in *t*-BuOH (16ml). Methanol (3.2ml; 0.079mol), stored over 3A molecular sieves was transferred into the addition funnel and added slowly for a period of 2 hours. After the addition, the yellow reaction mixture was refluxed for a further 2 hours followed by cooling to room temperature. Water (10ml) was added to dissolve any solid formed and the yellow solution was further refluxed for 30 minutes. The solution was allowed to cool to room temperature and extracted twice with chloroform (15 ml each). The organic layer was dried over anhydrous magnesium sulphate for 20 minutes. The solution was concentrated on a rotatory evaporator. TLC of the product against DCMB on silica plates and were developed with ethyl acetate.

The unreacted DCMB in the product was separated using column chromatography. Before running the column, crystals formed in the solution were firstly dissolved in minimal amount of methanol. The stationary phase was alumina and ethyl acetate was the eluting solvent. The eluted liquid was collected in sample vials and each fraction collected was spotted separately on a TLC plate alongside with DCMB to determine the identity and composition in each fraction. Sequential fractions that contained a pure component of the product were combined in a RB flask. Solvents (methanol and ethyl acetate) were removed on a rotatory evaporator. The white solid were collected and dried in a desiccator over silica gel. [Yield = 5%].

(vi) Synthesis of 4,4’-dicarbomethoxy2,2’-biquinoline(DCMBiQ)

2,2’-Biquinoline-4,4’-dicarboxylic acid dipotassium salt trihydrate (0.202g; 0.43mmol) was dissolved in absolute methanol (20ml). Carefully, concentrated sulfuric acid (4ml) was added. Some anti-bumping chips were added. The mixture was heated under reflux for 5 hours. The methanol was removed on a rotatory evaporator, water (20 ml) was added and the yellow acidic solution was neutralized with sodium carbonate. The white solid of DCMBiQ was collected by vacuum filtration, washed repeatedly with cold water followed by few drops of cold ethanol. The product was dried in desiccator over silica gel. [Yield = 77%]

2.2 Synthesis of metal complexes

Various substituted bipyridine ligands of biquinoline, 5-nitro-1,10-phenantroline, neocuproin, bathophenantroline and 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline available commercially were reacted with metal carbonyls and their complexes were studied.

As a general rule transition metal organometallic compounds are more air-sensitive in solution then they are in the solid state. All of the following reactions were carried out under dry nitrogen atmosphere (Figure 1) except in the synthesis of (2,2'-biquinoline)tetracabonyltungsten. Precautions however has been taken, where solid products were kept sealed in vials and wrapped with aluminum foils or placed inside film canisters and stored in the desiccator to avoid photodecomposition.

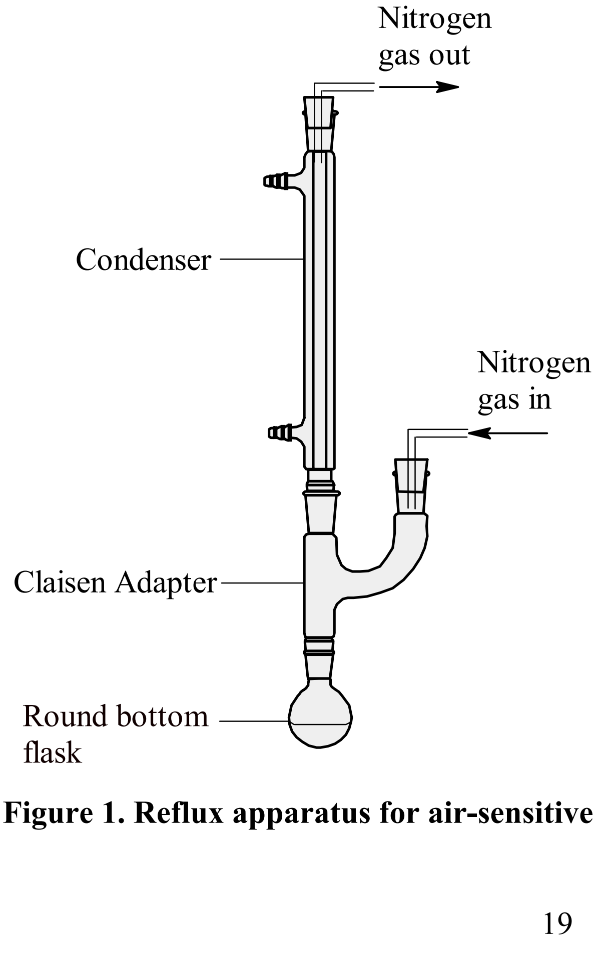


Figure 1. Reflux apparatus for air-sensitive synthesis.

Most of the time, during refluxing, metal hexacarbonyls will tend to sublime from the reaction mixture onto the upper portions of the reaction flask. To avoid incomplete reaction from occurring, the sublimates were brought back into the reaction solution by swirling the reaction mixture in the flask.

The complex melting point was recorded and was uncorrected. The infrared spectra of the complexes in dichloromethane using a solution cell were recorded using a Perkin Elmer FTIR Spectrometer Spectrum 1600. The electronic spectra for all the complexes in carbon tetrachloride, toluene, tetrahydrofuran, acetone and dimethylformamide were recorded in 1 cm silica cuvettes using a Shimadzu UV3100 UV-Vis-NIR recording spectrometer. The substituted bipyridine complexes were also characterized by a 300MHz ^{1}H-NMR spectrometer in solvent $CDCl_3$.

(i) Synthesis of (2,2'-biquinoline)tetracabonylmolybdenum

$Mo(CO)_6$ (0.104g; 0.39 mmol) and ligand BiQ (0.108g; 0.42mmol) in toluene (10ml) were heated under reflux for 3 hours. The dark blue solution was cooled and allowed to crystallize at room temperature overnight. The crystals were filtered, washed with small amount of toluene and petroleum ether and dry in desiccator over silica gel. [Yield = 41%]. Found C=56.92%, H=2.64% and N=5.23% (Calculated for $Mo(CO)_4C_{18}H_{12}N_2$: C=56.91%, H=2.61%, N=6.03%) which was in agreement with the molecule's formula.

(ii) Synthesis of (2,2'-biquinoline)tetracabonyltungsten

$W(CO)_6$ (0.137g; 0.39 mmol) and ligand BiQ (0.112g; 0.43mmol) and $NaBH_4$ were heated under reflux with stirring in absolute ethanol (14ml) for 7 hours. The solid obtained was filtered, washed with ethanol and water (to remove borate salts) and dried in desiccator over silica gel. [Yield = 47%] Found C=68.39%, H=4.06% and N=8.0% (calculated for $W(CO)_4C_{18}H_{12}N_2$: C=47.85%, H=2.19% and N=5.07%).

(iii) Attempted Synthesis of (2,2'-biquinoline)tetracabonylchromium

$Cr(CO)_6$ (0.1003g; 0.46mmol) and trimethylamine-*N*-oxide (0.123g; 1.1mmol) and toluene (10mL) were stirred vigorously for 20 minutes. Solid BiQ (0.119g; 0.46mmol) was added to the mixture. The flask was flushed with nitrogen gas and stoppered. The reaction mixture was stirred at room temperature for 7 days. The purple solid formed were filtered and washed with hexane.

(iv) Synthesis of (neocuproin)tetracarbonylmolybdenum

$Mo(CO)_6$ (0.104g; 0.39mmol) and ligand neocuproin (0.0848g; 0.41mmol) in toluene (10 ml) were refluxed and stirred for 6 hours. The dark red solution was cooled and crystallized in a refrigerator for 3 days. The crystals were filtered and washed with toluene (5ml) and petroleum ether (5ml). The filtrate was concentrated on a rotatory evaporator to recover second crop crystals. [Yield = 79%]. Found C=38.65%, H=2.70% and N=9.87% (calculated for $Mo(CO)_4C_{14}H_{12}N_2$: C=51.94%, H=2.91% and N=6.73%).

(v) Synthesis of (5-nitro-1,10-phenantroline)tetracarbonylmolybdenum

$Mo(CO)_6$ (0.100g; 0.38mmol) and NPhen (0.088g; 0.39mmol) in toluene (10 ml) were refluxed and stirred for 3 hours. The dark red solution was cooled and crystallized in a refrigerator for 2 days. The crystals were filtered and washed with toluene (5ml) and petroleum ether (5ml). The solid was dried in desiccator over silica gel. Solvent in the filtrate was removed on a rotatory evaporator to recover the crystals that stayed in the solvent. [Yield = 46%]. Found C=49.91%, H=22.74% and N=5.66% (calculated for $Mo(CO)_4C_{12}H_7N_3O_2$: C=44.36%, H=1.63% and N=9.70%).

(vi) Attempted synthesis of (5-nitro-1,10-phenantroline)tetracarbonyltungsten

$W(CO)_6$ (0.129g; 0.37mmol) and NPhen (0.0895g; 0.40mmol) in toluene (10 ml) were refluxed and stirred for 6 hours. The dark red solution was cooled and crystallized in a refrigerator overnight. The crystals were filtered and washed with toluene (5ml) and petroleum ether (5ml). The solid was dried in desiccator over silica gel. Solvent in the filtrate was removed on a rotatory evaporator to recover crystals that stayed in the solvent.

(vii) Synthesis of (bathophenantroline)tetracarbonylmolbdenum

$Mo(CO)_6$ (0.100g; 0.38mmol) and BPhen (0.127g; 0.38mmol) in toluene (10ml) were refluxed and stirred for 3 hours. The dark red solution was allowed to cool and crystallize in a refrigerator for overnight. The crystal was filtered with toluene and petroleum ether. The solid was dried in desiccator over silica gel. In order to recover the crystal that dissolved in the solvent, the filtrate was evaporated on a rotatory evaporator. Further crop of the crystal was collected. [Yield = 38%].

(viii) Synthesis of (6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline)tetracarbonyl-molybdenum

$Mo(CO)_6$ (0.1027g; 0.39mmol) and BBPQxn (0.1270g; 0.41mmol) in toluene (10ml) were refluxed and stirred for 4 hours. The purple solution was allowed to cool and crystallize in a refrigerator overnight. The crystals were vacuum filtered and washed with toluene and petroleum ether. The solid was dried in desiccator over silica gel. In order to recover the crystal that dissolved in the solvent, the filtrate was evaporated on a rotatory evaporator. Further crop of the crystal was collected. [Yield = 74%]

(ix) Synthesis of (6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline)bistetracarbonyl-molybdenum

$Mo(CO)_6$ (0.203g; 0.77mmol) and BBPQxn (0.131g; 0.42mmol) in toluene (10ml) were refluxed and stirred for 6 hours. The dark blue solution was allowed to cool and crystallize in a refrigerator overnight. The crystals were vacuum filtered and washed with toluene and petroleum ether. The solid was dried in desiccator over silica gel. In order to recover the crystal that dissolved in the solvent, the filtrate was evaporated on a rotatory evaporator. Further crop of the crystal was collected. [Yield = 43%].

(x) Attempted synthesis of (4,4'-dicarbomethoxy-2,2'-biquinoline)tetracarbonyl-molybdenum

$Mo(CO)_6$ (0.0487g; 0.18mmol) and ligand DCMBiQ (0.0796g; 0.19mmol) in toluene (10ml) were refluxed with stirring for 3 hours. The green solution was allowed cooled and the green solid was filtered by vacuum filtration, washed with toluene followed by petroleum ether.

(xi) Attempted Synthesis of (3,3'-Dicarbomethoxy-2,2'pipridyl)tetracarbonyl-chromium

$Cr(CO)_6$ (0.0857g; 0.18mmol) and ligand DCMB (0.1125g; 0.19mmol) and catalyst sodium borohydride and ethanol (14ml) were refluxed with stirring for 1 hour. The green solution was allowed cooled and the green solid was filtered by vacuum filtration, washed with water to remove borate ions followed by ethanol.

3. Results and Discussions

3.1 Preparation and properties of substituted bipyridine ligands

The IR spectra for the following products can be found in the following figures in Appendix A:

- Figure A1: 1,10-Phenanthroline monohydrate
- Figure A2: Binicotinic acid
- Figure A3: DCMB
- Figure A4: Product of reaction of Grignard reagent with DCMB
- Figure A5: Methyl nicotine
- Figure A6: Reduction of methyl nicotinate by $NaBH_4$
- Figure A7(a): Crude 2,2'-bipyridyl-3,3'-carbinol
- Figure A7(b): Purified 2,2'-bipyridyl-3,3'-carbinol after column chromatography.
- Figure A8: 4,4'-dicarbomethoxy-2,2'-biquinoline

Result and discussion for the preparation of disubtituted bipyridine ligands are described in detail as follows:

(i) Synthesis of 2,2'-bipyridyl-3,3'-dicarboxylic acid (Binicotinic acid)

The proposed oxidation of 1,10-phenantroline is shown in Figure 2 below. Permanganate as an oxidizing agent attacks a double bond through a cyclic five-membered transition state, shown above. Using permanganate for a double bond oxidation is that it is a vigorous oxidizing agent which can further transform the diol initially produced. This ultimately leads to cleavage of the ring at the 3,3' positions and production of the dicarboxylic acid.

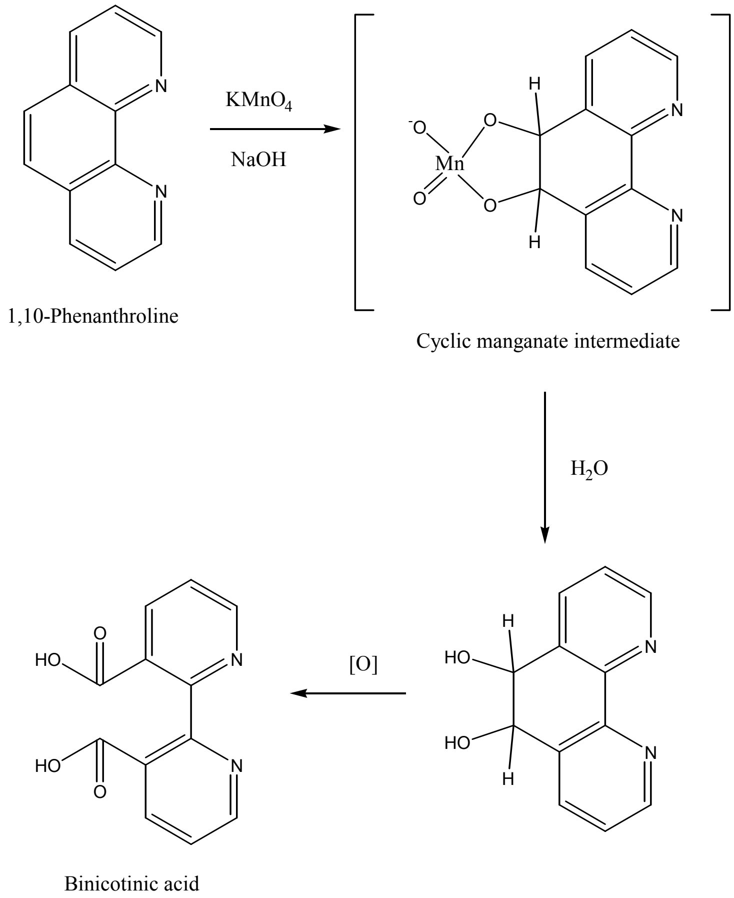


Figure 2. Oxidation of phenanthroline to binicotinic acid.

Experimentally, the oxidation of 1,10 phenantroline monohydarate with potassium permanganate in aqueous sodium hydroxide produced a low yield (37%). It was not in agreement with the reported yield of 75%[14] and as reported in previous project (71%)[12]. The low amount could be due to decomposition of the product when boiling. The product was a white solid. The IR spectrum of the binicotinic acid is shown in Figure A2 (See Appendix).

The production of binicotinic acid was supported by the present of C=O stretching band at 1716 cm^{-1} (lower than saturated C=O stretch due to conjugation[9]), C-O stretch at 1226 cm^{-1}, a small broad O-H stretch at 3481 cm^{-1} and O-H in plane bend at 1434 cm^{-1}. These vibrational frequencies due to the acid were absent in the IR of the original reactant of phenantroline.

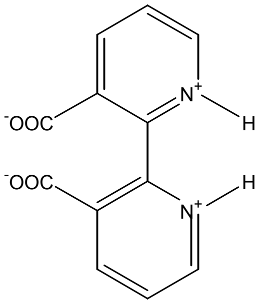


Figure 3. Zwitterion structure of binicotinic acid.

The solid obtained has a melting point from 259°C to 263°C whereupon it decomposed to a black solid. Binicotinic acid is a zwitterion (Figure 3) which explained its high melting point. The melting point was in agreement with reported melting point of binicotinic acid, 262°C[14]. Hence, from these analyses, binicotinic acid was successfully synthesized.

(ii) Synthesis of 3,3'-Dicarbomethoxy-2,2'-bipyridine (DCMB)

Esters can be synthesized by a nucleophilic acyl substitution of a carboxylic acid with an alcohol. The preparation of ester by simply heating a carboxylic acid in an alcoholic solution with a tiny amount of strong acid catalyst is called Fisher esterification. The proposed mechanism of preparation of DCMB is shown in Figure

4. The sulphuric acid protonates the carbonyl-group oxygen atom, thereby making the protonated carboxylic acid more susceptible towards nucleophilic attack by the methanol. In the ester formation reaction, two moles of water are eliminated in the reaction between a binicotinic acid and methanol. In the synthesis, a very large excess of the alcohol was used thus this will favour the equilibrium formation of ester (Le Chatelier's principle). Synthesis of DCMB by esterification of binicotinic acid and methanol was reported to give 86% yield[14]. In this experiment, the esterification produced a satisfactory yield of 79%.

The product obtained was a white flake solid and melted from a white solid to a colourless liquid in a small range of 149 – 151°C which was very close to the literature melting point (152°C). TLC on silica gel plates of the product developed in ethyl acetate revealed there was only one component having average R_f of 0.46. Therefore, the product was pure. The production of DCMB was further supported by its IR spectrum where there was ester band due to the C=O stretching of the aromatic ester at 1718 cm^{-1}; C-C(=O)-O stretching at 1300 cm^{-1}; and O-C-C stretch at 1136 cm^{-1}. The band at 1300 cm^{-1} was absent in the IR spectrum of the starting material of binicotinic acid.

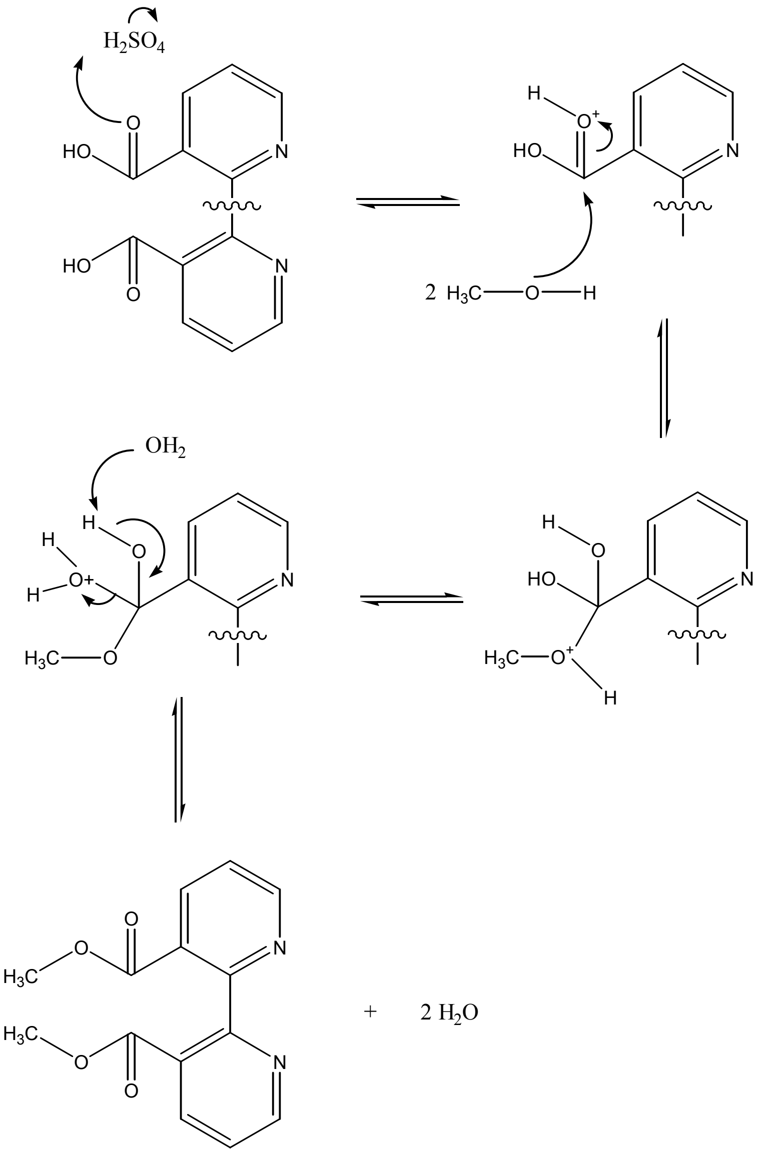


Figure 4. Mechanism of esterification of DCMB.

(iii) Reaction of DCMB with a Grignard reagent.

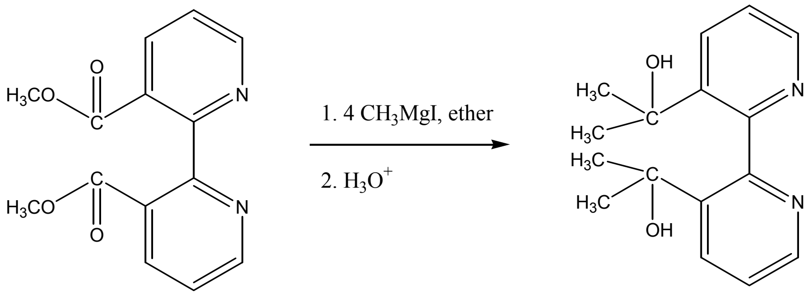
The organomagnesium compounds, Grignard reagents, had been used widely in organic synthesis. One of the applications of this versatile and extraordinary compound is in the production of an alcohol from an ester. The formation of a Grignard reagent is illustrated by the preparation of methylmagnesium iodide (See Equation 2 below). The formation of methylmagnesium iodide resulted in the liberation of heat and can be observed as the reaction mixture turned to a chalky solution.

$$H_3C\text{—}I \quad + \quad Mg \xrightarrow{\text{dry ether}} H_3C\text{—}MgI$$

Iodomethane Methylmagnesium iodide

Equation 2. Formation of a Grignard reagent, methylmagnesium iodide.

DCMB reacts with four equivalents of a Grignard reagent to yield a tertiary alcohol (Equation 3). The reaction occurs by nucleophilic substitution mechanism.



3,3'-Dicarbomethoxy-bipyridine
(DCMB)

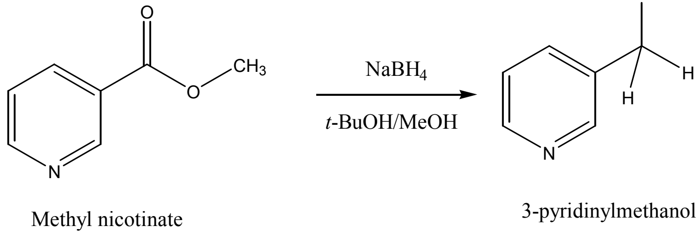
Equation 3. Reaction of DCMB with methylmagnesium iodide.

One of the problems encountered in the experiment was the attempt to dissolve the DCMB in the dry ether as the ester is only partially soluble in ether. Several attempts to dissolve the DCMB in ether were carried out including addition of more ether to the DCMB and using an ultrasonic water bath. These attempts failed and the Grignard reagent had to be transferred to the addition funnel and the DCMB solution to the RB flask. This step may have cause the destruction of the Grignard reagent as this had exposed it to the air and atmospheric water vapour that contains acidic proton will react with a Grignard reagent to give methane. Another difficulty faced in the mixing of the DCMB and the Grignard reagent, as the insoluble DCMB slowed down and eventually stopped the magnetic stirring. This had resulted in a slow reaction and to overcome any possible incomplete reaction the solution was further refluxed for 2 hours. Addition of the Grignard reagent to the DCMB solution resulted in the formation of black gummy solid.

The product was a dark brown solid with a strong pungent smell. IR spectrum of the product showed a medium band at 1718cm^{-1} due to C=O stretching. Therefore, the ester functional group was still present. In addition, TLC of the product on silica gel plates developed in ethyl acetate showed a spot having R_f of 0.46 similar to the starting material (DCMB). Hence, the attempt to produce tertiary alcohol from DCMB and the Grignard reagent was unsuccessful.

(iv) Reduction of methyl nicotinate by $NaBH_4$

Sodium borohydride is a mild reducing agent and can be used in alcoholic solvents. It can readily reduce aldehydes and ketones to primary and secondary alcohol but with esters the process is very slow[28]. A method was adopted using mixed solvent of *t*-BuOH and MeOH and slow addition of methanol to reduce esters to alcohols in high yield[10]. The reduction of methyl nicotinate was reported to yield 78% of 3-pyridinylmethanol (molar ratio $NaBH_4$: ester = 2.5:1). The synthesis was carried out to serve as model and trial for the reduction of DCMB.



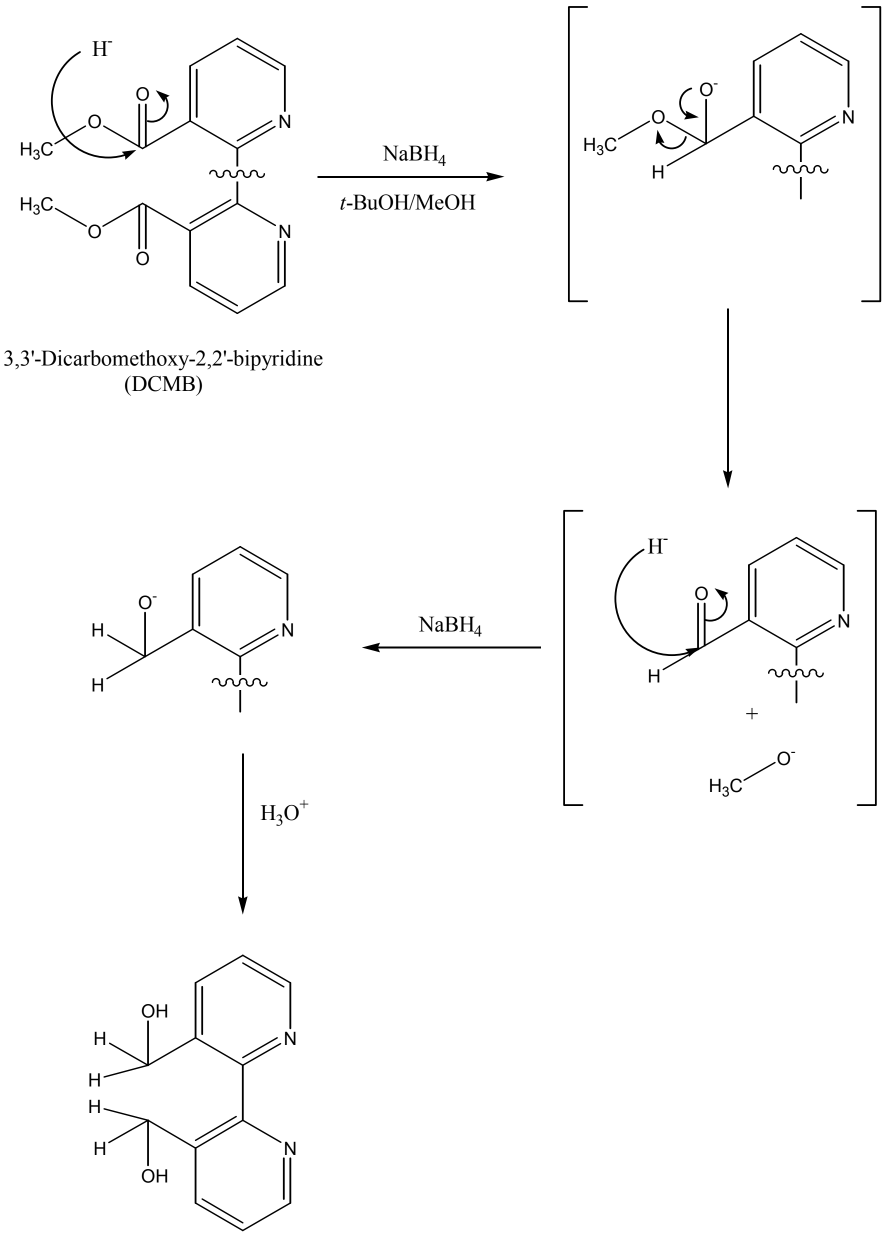
Equation 4. Reduction of methyl nicotinate

Experimentally, reduction of methyl nicotinate with sodium borohydride yield 56% of 3-pyridinylmethanol. This was a lower yield than the reported yield. The reason could be due to the poor quality of sodium borohydride used. In addition, since a tropical environment, the humid condition in the laboratory may have decreased the reducing ability of the borohydride. A suggestion to improve the yield would be to increase the amount of sodium borohydride.

The product obtained from the reduction with sodium borohydride was a white solid. In this experiment, 3-pyridylmethanol was successfully synthesized as this was proven from its IR spectrum. Comparing the IR spectrum of the product and the starting reagent, the ester C=O stretching of methyl nicotine (at 1736 cm^{-1}) was absent in the IR spectra of the product. The presence of a O-H broad band of the product revealed that the alcohol functional group was present. It was concluded at this point that the alcohol could be attempted to be synthesized from reduction of the ester DCMB with sodium borohydride in the presence of a mixed solvent of *t*-BuOH/MeOH.

(v) Synthesis of 2,2'-bipyridyl-3,3'-carbinol

In the mechanism of DCMB reduction (Figure 5), a hydride ion first adds to the carbonyl group, followed by elimination of alkoxide ion to yield an aldehyde. Further reduction of the aldehyde give primary alcohol.



3,3'-Dicarbomethoxy-2,2'-bipyridine
(DCMB)

2,2'-bipyridyl-3,3'-carbinol

Figure 5. Mechanism of reduction of DCMB.

Reduction of DCMB with sodium borohydride (molar ratio $NaBH_4$: DCMB = 3: 1) yield 5% isolated 2,2’-bipyridyl-3,3’-carbinol after purification by column chromatography. Previous project student reported the reduction of DCMB with borohydride produced a 15% yield. The higher yield probably due to the mass of the crude product as purification of the crude product was not carried out previously.

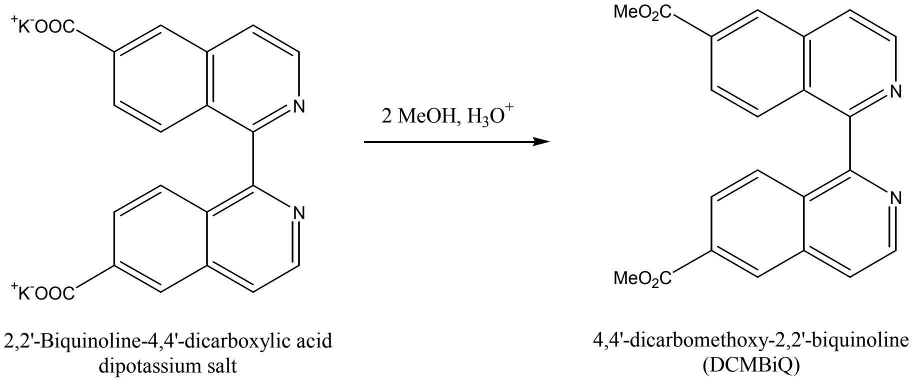
From a silica gel TLC of the crude product developed in ethyl acetate revealed two spots of average R_f 0.11and 0.46. The spot at R_f value of 0.46 due to unreacted ester was larger than the other spot. The different ratio intensity of the spots concluded that there was still a large amount of unreacted DCMB. This is revealed in the IR spectrum of the crude in Figure A7(a) where there is still C=O stretching of a weak intensity at 1736 cm^{-1}. Alcohol being generally more polar than ester is more strongly adsorbed to the silica and therefore migrate through the stationary phase slower than ester. Hence the low R_f of 0.11 was due to the alcohol. The crude product contained mixture of unreacted DCMB and the alcohol. For this reason, column chromatography was carried out to isolate the alcohol.

The IR spectrum in Figure A7(b) of the purified carbinol shows no stretching bands due to the ester carbonyl stretch (1718 cm^{-1}), C-C-O stretch (1300 cm^{-1}) and O-C-C stretch (1136 cm^{-1}) which concluded that reduction of the DCMB with $NaBH_4$ was successfully carried out. A small band at 3252cm^{-1} was due to alcohol O-H stretching. Generally, O-H band was broad but because the functional group was attached to aromatic rings and the structure was quite complex causing the O-H stretching to be less pronounced. The week O-H absorption is also observed in the IR spectra of complex aromatic molecules for example 5-hydroxyisoquinoline and 8-hydroxyquinoxaline[16].

The low yield of the diol could be due to decomposition of the product or DCMB during refluxing. From the column chromatography, the recovered DCMB was 18% relative to the starting amount.

In theory, for every one mole of ester two moles of borohydride is required for a complete reduction. Another attempt to improve the yield of the alcohol was to increase the molar ratio of $NaBH_4$:DCMB to 6:1 because ester DCMB is a diester. Instead, the yield of the carbinol was reduced to 3%. Again the low yield could be due to decomposition of the product while heating. The isolated product was a yellow solid that melted to a colourless liquid at 144°C-147°C. Because of the low yield of the carbinol, the synthesis of metal complexes of carbinol was not carried out.

(vi) Synthesis of 4,4'-dicarbomethoxy-2,2'-biquinoline(DCMBiQ)



Equation 5. Esterification of DCMBiQ

Esterification of 2,2'-Biquinoline-4,4'-dicarboxylic acid dipotassium salt with methanol produce 77% of DCMBiQ (Equation 5). The product was a white solid which sublimed to form needle-like white crystals at 254-260°C and decomposed to a dark brown liquid at 266-272°C. In contrast, the starting material of the salt has a melting point (being a salt) above 300°C. The ester was soluble in chloroform and insoluble in water, vice versa for the starting material of the salt. The IR spectrum of the product showed a C=O stretching at 1732cm^{-1} of the ester. TLC of the product developed in acetyl acetate revealed only one spot with average R_f of 0.71. Hence, production of the ester, DCMBiQ, was successful.

The properties of the disubtituted bipyridines that were prepared in this project are summarized in Table 3 below.

Table 3. Properties of disubtituted bipyridines.

	Literature percentage yield	Experimental percentage yield	Literature melting point	Experimental melting point	Physical property
Binicotinic acid	76%	37%	262°C	259°C -263°C (decompose)	White solid
DCMB	86%	79%	152°C	149°C -151°C	White solid
Reaction of DCMB with a Grignard reagent	-	Unsuccessful	-		Brown
Diol (Reduction with $NaBH_4$)	-	5%	-	144°C -147°C	White solid
DCMBiQ	-	77%	-	266°C -272°C (decompose)	White solid

3.2 Syntheses and properties of metal complexes

The IR spectra of the following complexes in dichloromethane are shown in Appendix B;

- Figure B1: $Mo(CO)_6$
- Figure B2: $W(CO)_6$
- Figure B3: $Cr(CO)_6$
- Figure B4: $Mo(CO)_4$(BiQ)
- Figure B5: $W(CO)_{4(}$BiQ)
- Figure B6: Attempted synthesis of $Cr(CO)_4$(BiQ)
- Figure B7: $Mo(CO)_4$(NeoC)
- Figure B8: $Mo(CO)_4$(NPhen)
- Figure B9: Attempted synthesis of $W(CO)_4$(NPhen)
- Figure B10: $Mo(CO)_4$(BPhen)
- Figure B11: $Mo(CO)_4$(DDPQxn)
- Figure B12: $[Mo(CO)_4]_2$(DDPQxn)
- Figure B13: Attempted synthesis of $Mo(CO)_4$(DCMBiQ)
- Figure B14: Attempted synthesis of $Cr(CO)_4$(DCMB)

In general, several methods have been used to synthesize the complexes. In this project, all of the molybdenum complexes were successfully synthesized by simply refluxing the hexacarbonyl with the ligand in a solvent[22]. Alternatively, if this method failed, synthesis using catalyst sodium borohydride as a catalyst[10] was adopted. When this catalysis do not succeed, TMNO was used instead of borohydride which can induce decarbonylation of the metal carbonyl[24, 26, 27]. The low percentage yield may be due to loss in the product when washing the crystals with toluene as this will cause the solid to be removed as the filtrate. Much of the solid stayed in solution because the complexes are soluble in organic solvents. Discussion on the synthesis and properties of the complexes are explained in detail as follow:

(i) Synthesis of $Mo(CO)_4(BiQ)$

Reacting $Mo(CO)_6$ with BiQ in toluene produce a low yield of dark purple crystals. The crystals have a high melting point above 300°C. The IR spectrum shows four C-O stretching bands.

(ii) Synthesis of $W(CO)_4(BiQ)$

Reaction of tungsten hexacarbonyl with BiQ by refluxing in toluene was unsuccessful. However, using catalyst of sodium borohydride the reaction succeed and produced a low yield. The product was a grey solid and decomposes to a black liquid at 194-198°C. The IR spectrum shows four C-O stretching bands. The CHN values were higher than the calculated composition. This could be due to unreacted BiQ.

(iii) Attempted Synthesis of $Cr(CO)_4(BiQ)$

Refluxing $Cr(CO)_6$ with BiQ in toluene as well as the use of borohydride failed to give the desired product. A green solution formed instead and there was no CO band in the IR spectrum. However, using TMNO in methanol and stirring the reactant mixtures at room temperature for 7 days produced some $Cr(CO)_4(BiQ)$ as the product was purple solid. To support this there was a small band at 1940 cm^{-1} in the IR spectrum. But there was also a strong peak due to unreacted metal hexacarbonyl. Hence, all the three methods adopted were ineffective in producing $Cr(CO)_4(BiQ)$.

(iv) Synthesis of $Mo(CO)_4(NeoC)$

The presence of ortho methyl groups will require a longer time of refluxing as the approaching NeoC will be hindered in chelating with the metal. Though there is a steric effect, the ligand can still bind with the metal atom as revealed by the IR spectrum. The yield was fairly high value. The product was an orange powder that decomposed to a black solid at 186°C. The CHN analysis values were lower than the calculated composition. This could be due to unreacted NeoC present in the complex.

(v) Synthesis of $Mo(CO)_4(NPhen)$

The yield was fairly low and the product was a brown solid and thermally stable. The CHN values were inconsistent with the calculated composition. This could be due to impurities and unreated NPhen present in the complex which will interfere the result.

(vi) Attempted synthesis of W(CO)4(NPhen)

Although unsuccessful, refluxing of $W(CO)_6$ with NPhen in toluene produced some of the wanted product. This was supported as small bands at 2112cm^{-1}, 1960cm^{-1} and 1920 cm^{-1} in the IR spectrum. The solid obtained was mainly unreacted tungsten hexacarbonyl as shown in the IR spectrum as a strong band at 1990 cm^{-1}. A suggestion to complete the reaction is to increase refluxing time.

(vii) Synthesis of Mo(CO)$_4$(BPhen)

The product obtained was an orange solid and it decomposed to black solid at 310-314°C. The yield was fairly low. IR spectrum of the product shows four C-O stretching bands.

(viii) Synthesis of Mo(CO)4(DDPQxn)

The product was a purple solid and in high yield. The solid melted at 197-200°C to a black liquid. The metal complex obtained is a tetra carbonyl as its IR spectrum shows four C-O stretching bands.

(ix) Synthesis of [Mo(CO)$_4$]$_2$(DDPQxn)

The product was a dark purple solid and in low yield. The solid has a melting point lower than Mo(CO)4(DDPQxn). The metal complex obtained is a tetra carbonyl as its IR spectrum shows four C-O stretching bands. This suggested that the DDPQxn is a tetra-dentate ligand of which each of the bipyridyls bind with two metal atoms.

(x) Attempted synthesis of $Mo(CO)_4(DCMBiQ)$

It was observed that refluxing $Mo(CO)_6$ with DCMBiQ in toluene produced a green solution. This was due to complete decarboxylation of the metal hexacarbonyl as accounted for the IR spectrum showed no CO stretching bands.

(xi) Attempted synthesis of $Cr(CO)_4(DCMB)$

It was observed that refluxing $Mo(CO)_6$ with DCMB with catalysts initially produced a red solution but eventually turned to a green solution. Again the green appearance indicate that all the COs have been removed from the metal hexacarbonyl and the IR spectrum shows no CO stretching bands. As with the previous project, the synthesis of Cr(CO)4(DCMB) failed.

From these experiments, $Mo(CO)_6$ can be substituted by the ligands more easily by simply applying heat. On the other hand, substitution of $W(CO)_6$ required more heat and utilized by catalyst. While, $Cr(CO)_6$ is stable and hardly react with the ligands. Therefore, the reactivity (in decreasing order) of the metal hexacarbonyl to undergo substitution reaction are:

$$\mathbf{Mo(CO)_6 > W(CO)_6 > W(CO)_6}$$

The following complexes $Mo(CO)_4(BiQ)$ $W(CO)_4(BiQ)$, $Mo(CO)_4(NeoC)$, $Mo(CO)_4(NPhen)$, $Mo(CO)_4(BPhen)$, $Mo(CO)_4(DDPQxn)$, $[Mo(CO)_4]_2(DDPQxn)$ were successfully produced. The synthesis and the properties of the complexes were summarized in the Table 4.

Table 4. Preparative Data and properties of substituted bpy complexes

Complexes	Substrates	Time of refluxing	Percentage yield	Melting point	Physical properties
$Mo(CO)_4(BiQ)$	$Mo(CO)_6$ + BiQ (1:1) in toluene	3 hours	41%	> 300°C	Dark purple
$W(CO)_4(BiQ)$	$W(CO)_6$ + BiQ (1:1) & $NaBH_4$ in EtOH	7 hours	47%	194-198°C (decompose)	Grey
$Cr(CO)_4(BiQ)$	$Cr(CO)_6$ + BiQ + TMNO (1:1:2) in toluene	7 days*	Unsuccessful	-	Purple
$Mo(CO)_4(NeoC)$	$Mo(CO)_6$ + NeoC (1:1) in toluene	6 hours	79%	186°C (decompose)	Orange
Mo(CO)4(NPhen)	$Mo(CO)_6$ + NPhen (1:1) in toluene	3 hours	46%	> 300°C	Brown
W(CO)4(NPhen)	$W(CO)_6$ + NPhen (1:1) in toluene	6 hours	Unsuccessful	-	Brown
Mo(CO)4(BPhen)	$Mo(CO)_6$ + BiQ (1:1) in toluene	3 hours	38%	310-314°C (decompose)	Orange
Mo(CO)4(DDPQxn)	$Mo(CO)_6$ + BiQ (1:1) in toluene	4 hours	74%	197-200°C	Purple
$[Mo(CO)_4]_2(DDPQxn)$	$Mo(CO)_6$ + BiQ (2:1) in toluene	5 hours	43%	186-190°C	Dark blue
Mo(CO)4(DCMBiQ)	$Mo(CO)_6$ + DCMBiQ (1:1) in toluene	3 hours	Unsuccessful	-	Green
Cr(CO)4(DCMB)	$Cr(CO)_6$ + DCMB (1:1) & $NaBH_4$ in EtOH	1 hour	Unsuccessful	-	Green

* Since there was no refluxing involved, time refers to the stirring of the mixture.

3.3 Interpretation of the IR spectra of the complexes.

Figures B1, B2 and B3 show the infrared spectra for molybdenum, tungsten and chromium hexacarbonyl respectively. For each spectrum, a single peak is observed in the carbonyl stretching region at 1986cm^{-1}, 1984 cm^{-1} and 1980 cm^{-1} respectively. These metal hexacarbonyls are octahedral and therefore belong to the O_h point group which has only the T_{1u} IR active mode of vibration hence only a single peak is observed. From the spectra of the metal hexacarbonyls, we can deduce that chromium hexacarbonyl has a greater electron density on the metal compared to that of tungsten and molybdenum, therefore the greater the back bonding to CO and the lower the energy of the carbonyl stretching vibration.

The IR spectra of the complexes (See Appendix C) in dichloromethane are summarized in Table 5. It is clearly shown that ligands with different substituents attached to the bpy result in a shifting of the C≡O peaks of the metal carbonyl complexes.

Table 5. IR spectroscopic data of substituted bpy complexes.

Complexes	ν(C≡O)^a/ cm^{-1} (intensity)^b			
$Mo(CO)_4(BiQ)$	2017 (sm)	1910 (s)	1876 (m)	1828 (m)
$W(CO)_4(BiQ)$	2009 (sm)	1897 (s)	1860 (m)	1824 (m)
$Mo(CO)_4(NeoC)$	2016 (sm)	1904 (s)	1875 (m)	1824 (m)
Mo(CO)4(NPhen)	2014 (sm)	1905 (s)	1880 (m)	1829 (m)
Mo(CO)4(BPhen)	2013 (sm)	1904 (s)	1878 (m)	1830 (m)
Mo(CO)4(DDPQxn)	2018 (sm)	1912 (s)	1881 (m)	1832 (m)
$[Mo(CO)_4]_2(DDPQxn)$	2015 (sm)	1920 (s)	1884 (m)	1835 (m)

[a] In dichloromethane

[b] (vs)-very strong, (s)-strong, (sh)- sharp, (sm)- sharp medium, (m)-medium, (b)-broad

The four IR bands due to C≡O stretches of the octahedral complexes infer that these metal complexes adopt C_{2v} point group symmetry. The bands are due to two A_1, B_1 and B_2 modes of vibration (See figure 5).

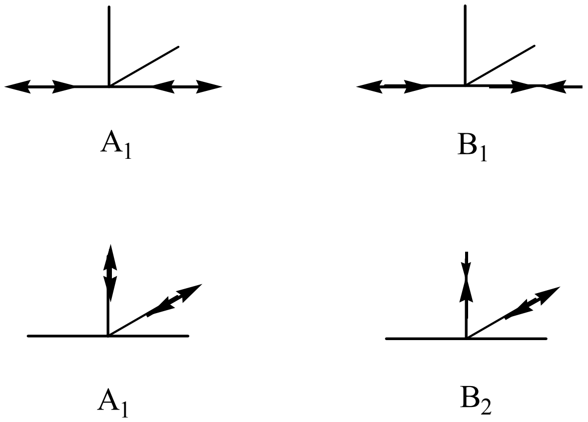


Figure 5. C-O stretching modes of C_{2v} point group complexes.

Hence from the IR spectra we may deduce the gross structure of the complexes as shown in Figure 6 below. The structures give the C_{2v} geometry. The bond angle may not be acceptable and in order to do this a further analysis of the complexes using x-ray diffraction can be employed in order to determine their structures.

From data in Table 5 using only the band that has strong intensity, the order in increasing v_{co} wavenumber of the complexes is:

$W(CO)_4(BiQ) < Mo(CO)_4(NeoC) = Mo(CO)_4(BPhen) < Mo(CO)_4(NPhen) <$

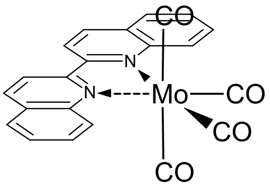
$Mo(CO)_4(BiQ) < Mo(CO)_4(DDPQxn) <[Mo(CO)_4]_2(DDPQxn)$

In the series, the tungsten complex has the lowest wavenumber than the molybdenum complexes. The reason is because the tungsten complex has a greater electron density on the metal compared to that of molybdenum, therefore the greater the back bonding to CO and the lower the energy of the carbonyl stretching vibration. Molybdenum complexes of phenantroline that contained electron-donating substituents (for example methyl and phenyl) have similar frequencies of C-O stretching, but the presence of electron-withdrawing substituents (such as NO_2) increases the carbonyl stretching frequency of the phenanthroline complex because the electrons on the metal will be pulled towards the electron-withdrawing atom and lowers the electron density on the metal atom. This in turn, decreases the back bonding to CO and increases the energy of the carbonyl stretching vibration.

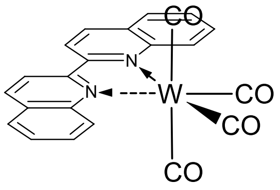
The position of the infrared bands is dependent on the ligand[2]. As the ν_{co} increases, the π acceptor ability of the ligands increases and the σ donor ability decreases. Therefore, the increasing order of π acceptor ability of the substituted bpy ligands is:

CO < BPhen = NeoC < NPhen < BiQ < DDPQxn

From the above series, the strongest π acceptor ability among the substituted bipyridine ligands is DDPQxn, Because of the strong acceptor ability, the molybdenum in the $Mo(CO)_4$(DDPQxn) is the most able to donate electron density to the π^* orbital on the ligand DDPQxn but less able to donate its electron density to the π^* orbital on the CO ligand. This makes the CO ligands in the $Mo(CO)_4$(DDPQxn) have the strongest C-O bonds and the increases the energy stretching bands.



$Mo(CO)_4(BiQ)$



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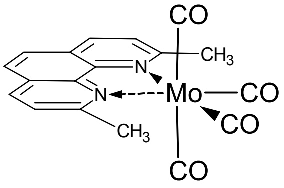

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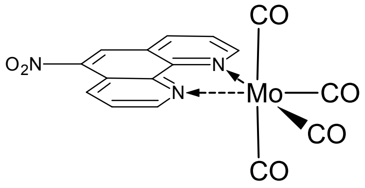

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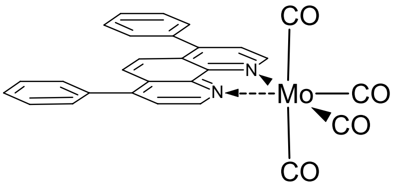

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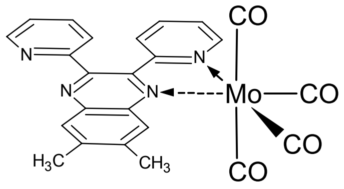
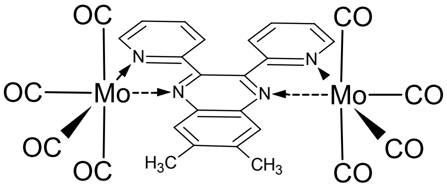


$Mo(CO)_4(DDPQxn)$



$[Mo(CO)_4]_2(DDPQxn)$

Figure 6. Structure of the metal complexes having C_{2v} point group as interpreted from the their infrared spectra.

3.4 Electronic spectroscopy of the complexes

The UV spectra of the following complexes synthesized in various solvents are shown in Appendix C;

- Figure C1: $Mo(CO)_4(BiQ)$
- Figure C2: $W(CO)_4(BiQ)$
- Figure C3: $Mo(CO)_4(NeoC)$
- Figure C4: $Mo(CO)_4(NPhen)$
- Figure C5: $Mo(CO)_4(BPhen)$
- Figure C6: $Mo(CO)_4(DDPQxn)$
- Figure C7: $[Mo(CO)_4]_2(DDPQxn)$

Some of the complexes are insoluble especially in the less polar solvents. Many possessed distinguished colour changes in different solvents. For example, in the case of $[Mo(CO)_4(DDPQxn)]$, the complex appears as a pink solution in acetone, blue in carbon tetrachloride and violet in DMF. All of the complexes show different solvatochromic behavior of the metal-to-ligand charge transfer transition in the visible region. The maximum peak that can be observed at approximately 400 – 700nm is due to metal ligand charge transfer (MLCT). While generally, the peaks with higher energy are due to d→d as well as inter ligand bands. These bands are solvent independent and are not greatly shifted. Notice also that the MLCT of all of the complexes shifted towards the shorter wavelength (blue-shift) as the solvent becomes more polar. The MLCT absorption maxima of the complexes in different solvents were summarized in Table 6 below.

Table 6. Solvent dipole moments & MLCT absorption maxima for $Mo(CO)_4(BiQ)$, $W(CO)_4(BiQ)$, $Mo(CO)_4(NeoC)$, $Mo(CO)_4(NPhen)$, $Mo(CO)_4(BPhen)$, $Mo(CO)_4(DDPQxn)$ and $[Mo(CO)_4]_2(DDPQxn)$ in various solvents.

	Solvents				
	Carbon tetrachloride	**Toluene**	**THF**	**Acetone**	**DMF**
Solvent dipole moment [a]	0	0.37	1.69	3.11	3.82
Complexes	**Maximum peak wavelength (nm)**				
$Mo(CO)_4(BiQ)$	Insoluble (559.3)	Insoluble	549.0	-	536.0
$W(CO)_4(BiQ)$	Insoluble (597.2)	Insoluble	580.0	563.5	558.0
$Mo(CO)_4(NeoC)$	503.5	480.0	454.0	443.0	432.0
Mo(CO)4(NPhen)	Insoluble (494.9)	Insoluble	477.0	463.5	455.0
Mo(CO)4(BPhen)	542.0	530.5	477.5	461.5	447.0
Mo(CO)4(DDPQxn)	601.0	566.0	544.0	529.0	519.5
$[Mo(CO)_4]_2(DDPQxn)$	720.0	676.0	640.0	610.0	585.0

[a] Value from reference 13 and 18.
Number in the brackets are extrapolated value from the Least square plots of E_{MLCT} versus dipole moment.

Using the maximum peak data from Table 7, the energy of MLCT in different solvents was calculated as follow;

$$E_{MLCT} = \frac{h \times c \times N_A}{\lambda},$$

Where h is the Plank's constant, c is the speed of light, N_A is the Avogradro's constant and λ is the wavelength of maximum peak. The solvent parameter used was the dipole moment value shown in Table 6. A graph of EMLCT of the complexes against the dipole moments are plotted and shown in Figure 7. Clearly from the least squares plot, all of the complexes have a good linear correlation coefficient, R^2, except for $Mo(CO)_4(BiQ)$ where only two points set were obtained due to low solubility. From the graph, the MLCT transitions of the complexes are linearly dependent on the solvent used.

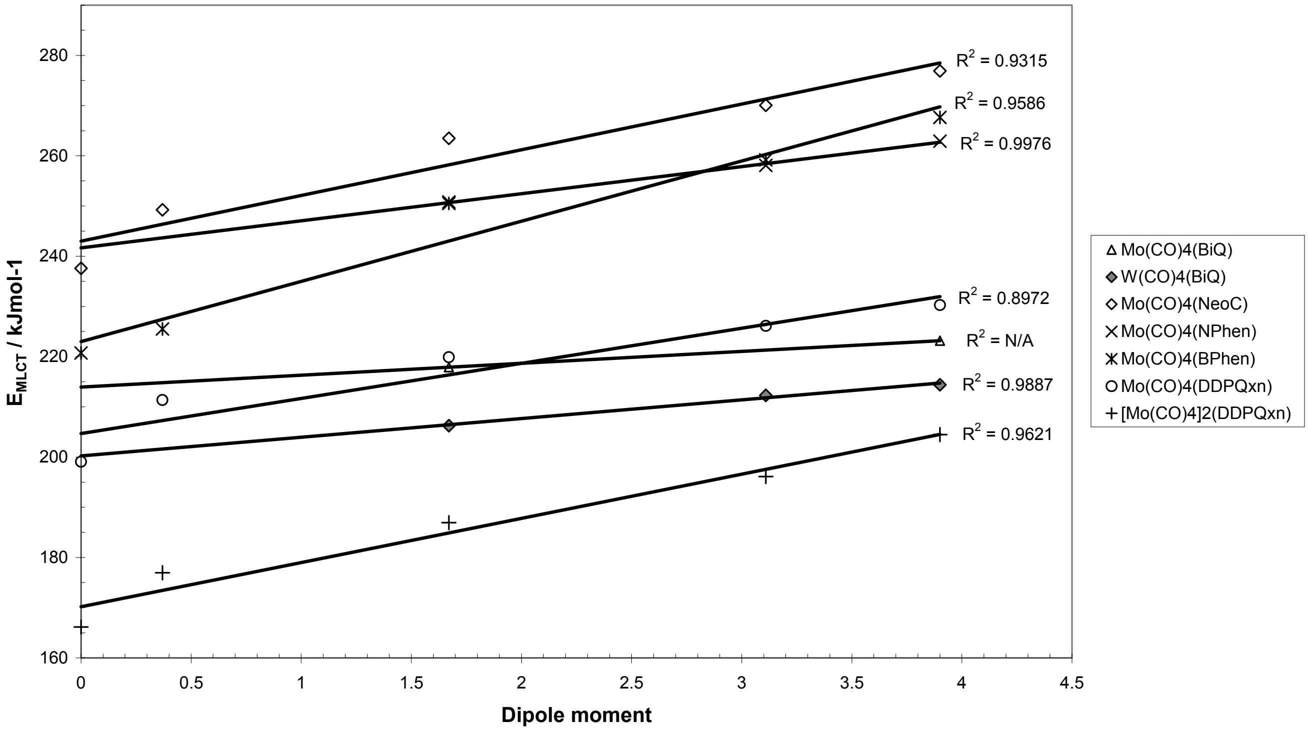


Figure 7. Least square plots of E_{MLCT} vs. dipole moment.

The gradient of the best fit straight line graph of each complex was computed and their E_{MLCT} at 0 dipole moment (which also correspond to the Y-intercept on the graph) were extrapolated. The gradient and the E_{MLCT} at 0 dipole moment values are given in Table 7 below.

Table 7. Gradient and E_{MLCT} at 0 dipole moment of the complexes from the least square plots of E_{MLCT} vs. solvent parameter.

Complexes	Gradient	E_{MLCT} at 0 dipole moment / $kJmol^{-1}$
$Mo(CO)_4(BiQ)$	2.37	213.9
$W(CO)_4(BiQ)$	3.71	200.2
Mo(CO)4(NPhen)	5.39	241.7
Mo(CO)4(DDPQxn)	6.99	204.7
$[Mo(CO)_4]_2(DDPQxn)$	8.80	170.2
$Mo(CO)_4(NeoC)$	9.10	243.0
Mo(CO)4(BPhen)	12.0	223.0

The higher the slope of the line the more sensitivity is the complexes towards solvents. Hence, from the data on Table 7, the order of the metal complexes in increasing sensitivity towards solvent was:

$Mo(CO)_4(BiQ) < W(CO)_4(BiQ) < Mo(CO)_4(NPhen) < Mo(CO)_4(DDPQxn) <$
$[Mo(CO)4]_2(DDPQxn) < Mo(CO)_4(NeoC) < Mo(CO)_4(BPhen)$

The order in decreasing order of energy of MLCT at 0 value of the solvent parameter from Table 7 was:

$Mo(CO)_4(NeoC) > Mo(CO)_4(NPhen) > Mo(CO)_4(BPhen) > Mo(CO)_4(BiQ) >$
$Mo(CO)_4(DDPQxn) > W(CO)4(BiQ) > [Mo(CO)_4]_2(DDPQxn)$

The higher the MLCT energy of the complexes, the more reddish the solution of the complex in a non-polar solvent. The lower the energy will result in a bluish solution when the complex is dissolved in a non-polar solvent.

Speculating from all of the above series of the π acceptor ability of the ligands, complexes sensitivity towards the solvents and E_{MLCT} at 0 value of the solvent parameter, they have no obvious trends and correlation. But, the complexes of $Mo(CO)_4(BPhen)$ and $Mo(CO)_4(NeoC)$ have relatively similar order in all the series.

3.5 Interpretation of H-NMR spectra of complexes.

The ^{1}H-NMR spectra of $Mo(CO)_4(BiQ)$, $W(CO)_4(BiQ)$, $Mo(CO)_4(NeoC)$ and $Mo(CO)_4(NPhen)$ in $CDCl_3$ are shown in Figure D1, D2, D3 and D4 respectively in Appendix D. A proton decoupling spectrum of $W(CO)_4(BiQ)$ is shown in Figure D5. The interpretations on the data of the complexes are summarized in Table 8, 9 and 10 respectively. The ^{1}H-NMR data of the ligand was obtained from SDBS compound information[21].

Table 8. ^{1}H-NMR δ data of BiQ and $Mo(CO)_4(BiQ)$ and $W(CO)_4(BiQ)$

H	BiQ	$Mo(CO)_4(BiQ)$	$W(CO)_4(BiQ)$
A	8.794	9.684 (d)	9.362 (d)
B	8.164	8.681 (d)	8.979 (d)
F	8.073	8.437 (d)	8.704 (d)
C	7.750	8.051 (d)	8.036 (d)
E	7.620	*8.015 (t)	7.959 (t)
D	7.453	7.796 (t)	7.786 (t)

* Superimposed on C

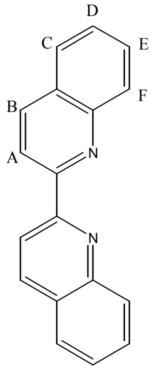


Table 9. ^{1}H-NMR δ data of BiQ and $Mo(CO)_4(NeoC)$

H	NeoC	$Mo(CO)_4(NeoC)$
A	9.091	9.025 (s)
B	8.305	8.863 (dd)
C	7.557	8.805 (dd)
D	2.574	Not provided

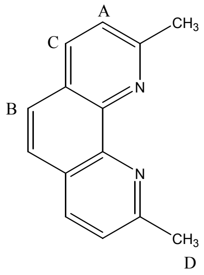
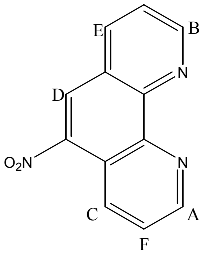


Table 10. ^{1}H-NMR δ data of NPhen and $Mo(CO)_4(NPhen)$

H	NPhen	$Mo(CO)_4(NPhen)$
A	9.337	8.248 (s)
B	9.283	8.219 (s)
C	8.991	7.837 (s)
D	8.655	7.813 (s)
E	8.421	7.731 (dd)
F	7.816	7.689 (s)
G	7.780	7.605 (s)



In all of the spectra, there were impurities present in the complex as there are more peaks than expected. Peaks at around 7.3δ is due to $CDCl_3$. The ^{1}H-NMR spectra of $Mo(CO)_4$(BiQ) and $W(CO)_4$(BiQ) are consistent in terms of the splitting pattern with that of ligand although all the proton shifts for both complexes were at higher field than BiQ. Proton decoupling of $W(CO)_4$(BiQ) analysis showed that proton A is coupled with B and F.

A consistent splitting pattern was also observed for the spectrum of $Mo(CO)_4$(NeoC) compared with NeoC. All the protons of the complex $Mo(CO)_4$(NeoC) are shifted to a higher field than that of NeoC.

The spectrum of $Mo(CO)_4$(NPhen) shows more than 7 peaks between 8.3 to 7.5 ppm. The splitting patterns were inconsistent with the spectrum of the NPhen hence interpretation of the H-NMR of the complex may not be valid. A proton decoupling spectrum should be obtained to further assign the shifts.

One of the problems as can be seen from all spectra is to assign the protons that correspond to their peaks. There are too many peaks in the spectrum and this is possibly due to the complex is a mixture of compounds. One solution is to use 2 dimensional techniques such as a correlation spectroscopy or COSY. Other remedial action would be to purify the complexes.

4. Conclusions

The aims of this project have been accomplished. In this research, the syntheses of binicotinic acid, DCMB were successful and the product from the reduction of DCMB with $NaBH_4$ was isolated although in a very low yield. The DCMB was reduced completely by increasing the amount of $NaBH_4$. Other alternatives should be used to synthesis the dicarbinol to prevent decomposition of the product when heating such as refluxing under low pressure or using a stronger reducing agent such as $LiAlH_4$.

The reaction of DCMB with the Grignard reagent was unsuccessful. Suggestions to improve the synthesis of the alcohol would be to use different and more polar dry ether in order to dissolve the DCMB. The physical and chemical properties of disubstituted bpy will change with different substituents. This can be seen from their diverse melting points and their polarity for example DCMB is less polar than carbinol.

In the synthesis of the metal carbonyl complexes, various methods were employed. A handful of substituted bpy complexes $Mo(CO)_4(BiQ)$ $W(CO)_4(BiQ)$, $Mo(CO)_4(NeoC)$, $Mo(CO)_4(NPhen)$, $Mo(CO)_4(BPhen)$, $Mo(CO)_4(DDPQxn)$, $[Mo(CO)_4]_2(DDPQxn)$ were successfully synthesized. The infrared spectra of the complexes have been assigned and these provide the geometric structure of the complexes. X-ray diffraction should be carried out to determine the bond angle of the complex structure. The order of π acceptor ability of the substituted bpy ligands was also determined. The ^1H-NMR spectra of the metal complexes revealed that the protons were chemically different from that of the ligand.

Some of the complexes have very low solubility especially in less polar solvents. The metal complexes adopt different solution colours in different solvents. From the electronic spectroscopy, the order of the sensitivity of the complexes towards the solvent was determined. The MLCT band of the metal complexes generally show a blue-shift as the solvent becomes more polar.

In the presence of steric effect substituents such as a methyl group, in the case of NeoC, the chelate formation of NeoC with the metal atom was retarded due to the hindrance and required more time to react. The bpy which has substituents of ester functional groups have a decarbonylating property, that is the ability to remove completely the CO from metal carbonyl. Such a property could be useful to study as there might be some application in catalysis.

5. Appendices

- Appendix A: IR Spectra of substituted 2,2’-bipyridines

- Appendix B: IR Spectra of complexes

- Appendix C: Electronic spectra of complexes

- Appendix D: H-NMR spectra of complexes

Figure A1: IR spectrum of 1,10-phenanthroline.

Figure A2: IR spectrum of binicotinic acid

Figure A3: IR spectrum of DCMB

Figure A4: IR spectrum of the product from reaction of DCMB with a Grignard reagent.

Figure A5: IR spectrum of methyl nicotinate

Figure A6: IR spectrum of reduction of methyl nicotinate by $NaBH_4$

Figure A7 (a): IR spectrum of crude 2,2’-bipyridyl-3,3’-carbinol (DCMB:$NaBH_4$=1:3)

Figure A7 (b): IR spectrum of purified 2,2’-bipyridyl-3,3’-carbinol (DCMB:$NaBH_4$=1:3)

Figure A8: IR spectrum of 4,4’-dicarbomethoxy-2,2’-biquinoline

Figure B1: IR spectrum of $Mo(CO)_6$

Figure B2: IR spectrum of $W(CO)_6$

Figure B3: IR spectrum of $Cr(CO)_6$

Figure B4: IR spectrum of $Mo(CO)_4$(BiQ)

Figure B5: IR spectrum of $W(CO)_4(BiQ)$

Figure B6: IR spectrum of the product from attempted synthesis of $Cr(CO)_4(BiQ)$

Figure B7: IR spectrum of $Mo(CO)_4$(NeoC)

Figure B8: IR spectrum of $Mo(CO)_4(NPhen)$

Figure B9: IR spectrum of the product form attempted synthesis of W$(CO)_4$(NPhen)

Figure B10: IR spectrum of $Mo(CO)_4(BPhen)$

Figure B11: IR spectrum of Mo$(CO)_4$(DDPQxn)

Figure B12: IR spectrum of $[Mo(CO)_4]_2(DDPQxn)$

Figure B13: IR spectrum of the product from attempted synthesis of Mo$(CO)_4$(DCMBiQ)

Figure B14: IR spectrum of the product from attempted synthesis of Cr(CO)$_4$(DCMB)

Figure C1: Visible spectra of $Mo(CO)_4(BiQ)$ in various solvents

Figure C2: Visible spectra of $W(CO)_4(BiQ)$ in various solvents

Figure C3: Visible spectra of $Mo(CO)_4(NeoC)$ in various solvents

Figure C4: Visible spectra of $Mo(CO)_4(NPhen)$ in various solvents

Figure C5: Visible spectra of $Mo(CO)_4$(BPhen) in various solvents

Figure C6: Visible spectra of $Mo(CO)_4(DDPQxn)$ in various solvents

Figure C7: Visible spectra of $[Mo(CO)_4]_2(DDPQxn)$ in various solvents

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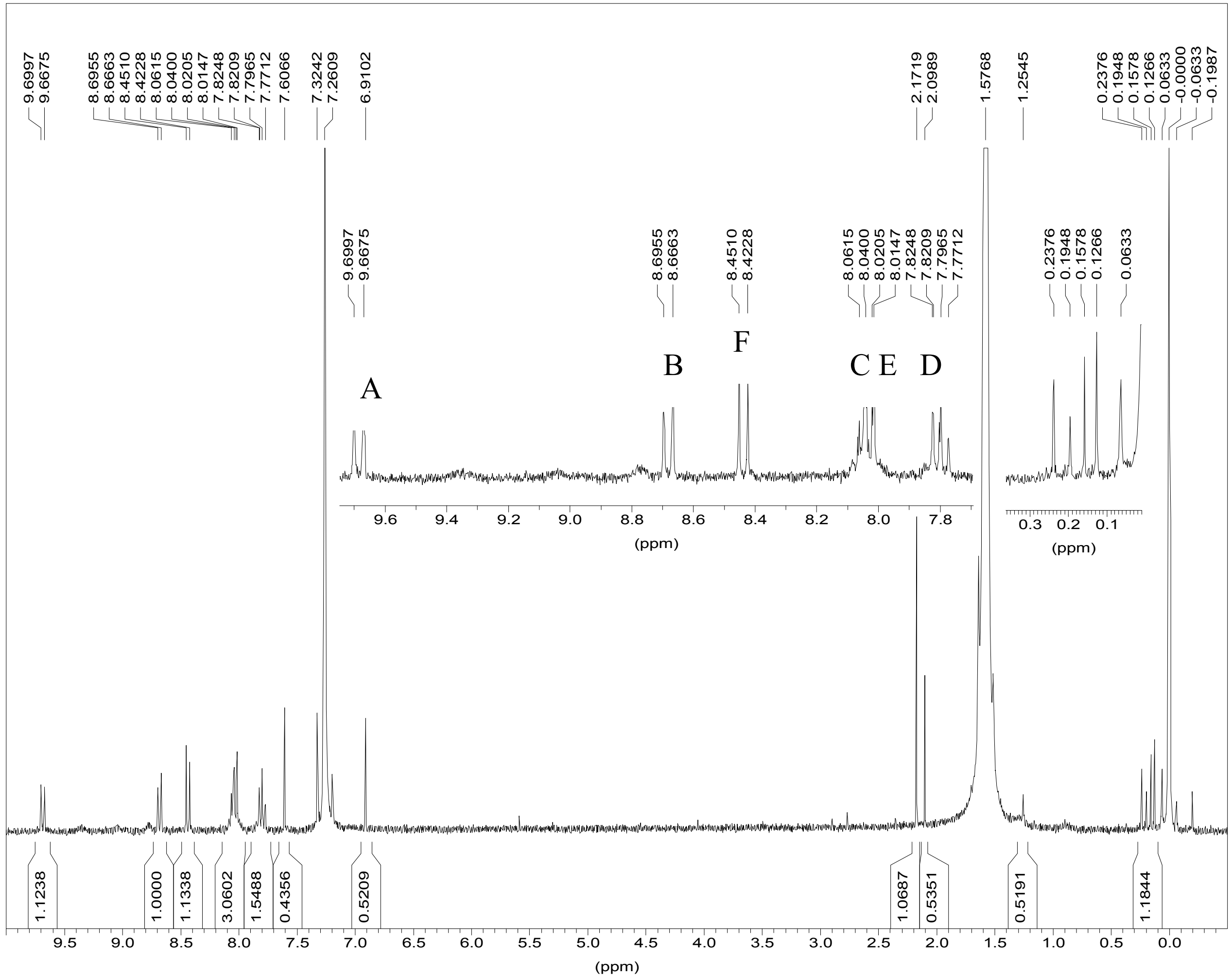
HAZ-1 IN CDCL3



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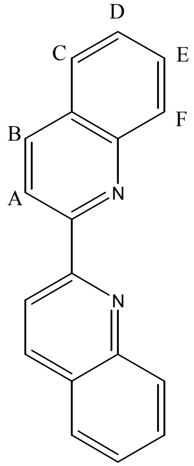

Figure D1: ^{1}H-NMR spectrum of $Mo(CO)_4(BiQ)$

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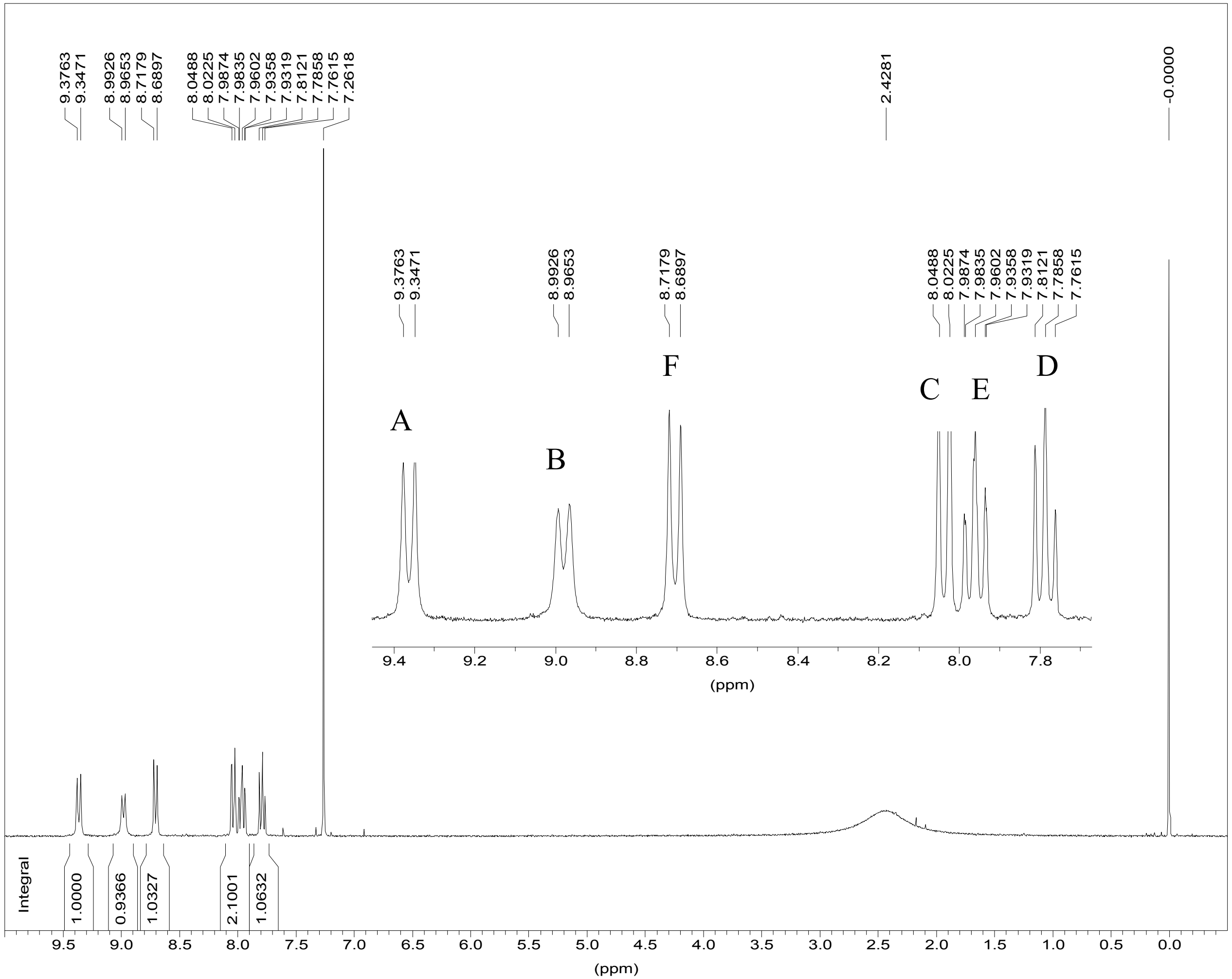
HAZ-2 IN CDCL3



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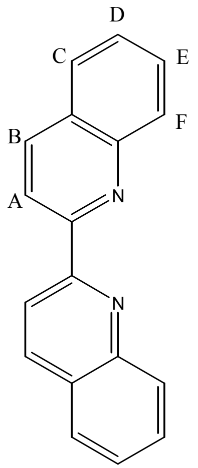


Figure D2: ^{1}H-NMR spectrum of $W(CO)_4(BiQ)$

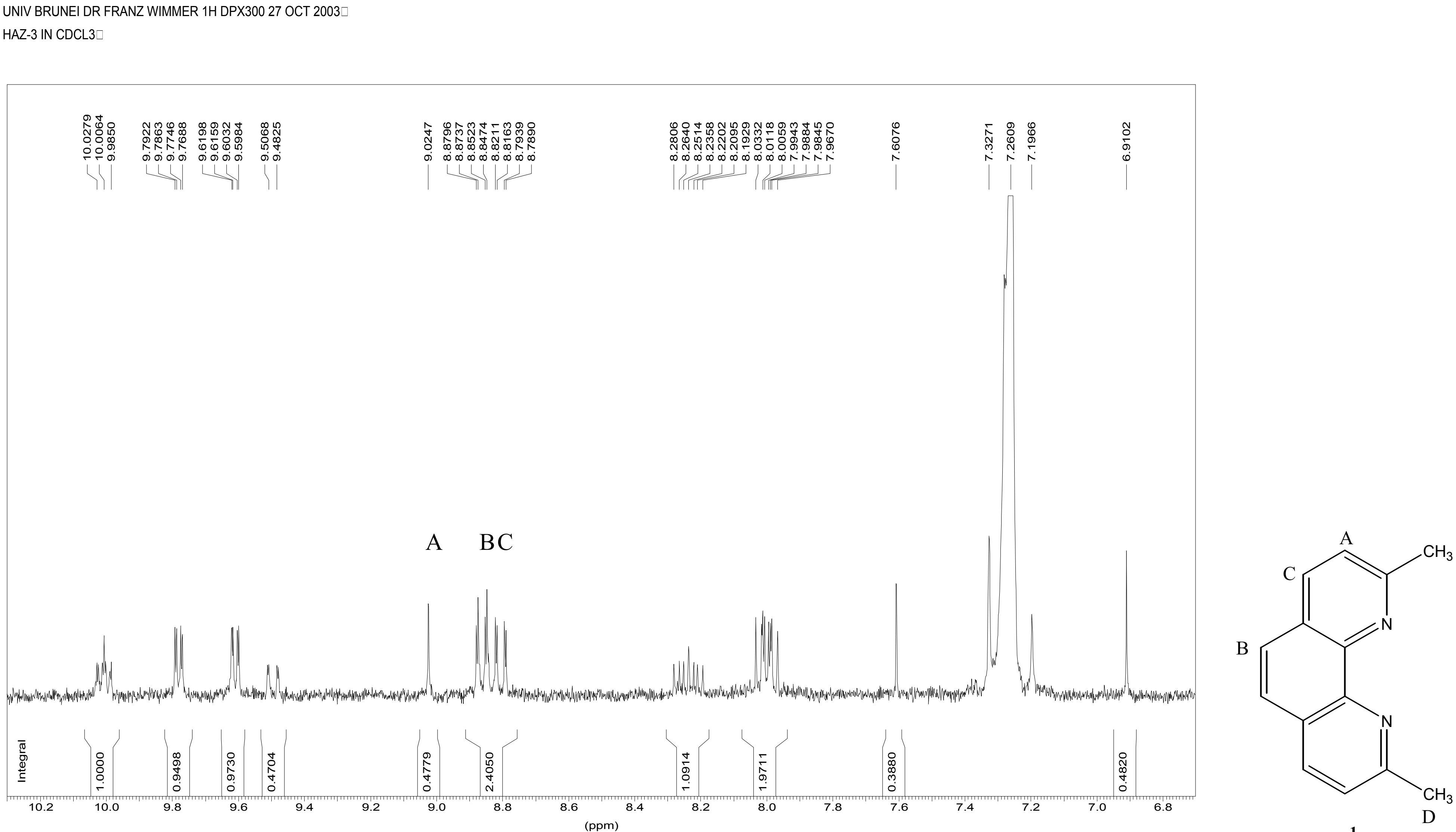
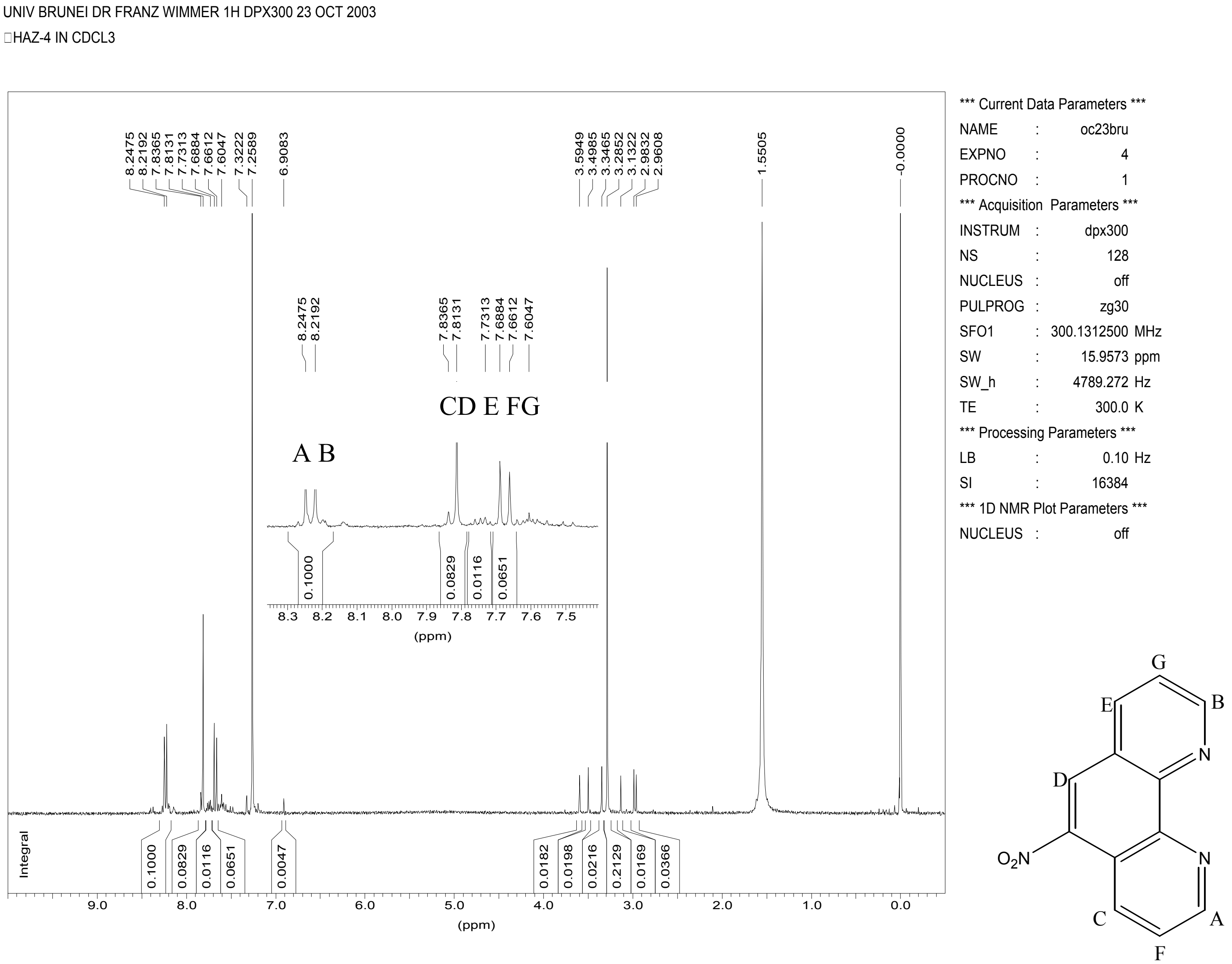


Figure D3: ^{1}H-NMR spectrum of $Mo(CO)_4(NeoC)$



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HAZ-4 IN CDCL3

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SW_h : 4789.272 Hz

TE : 300.0 K

*** Processing Parameters ***

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Figure D4: ^{1}H-NMR spectrum of $Mo(CO)_4(NPhen)$

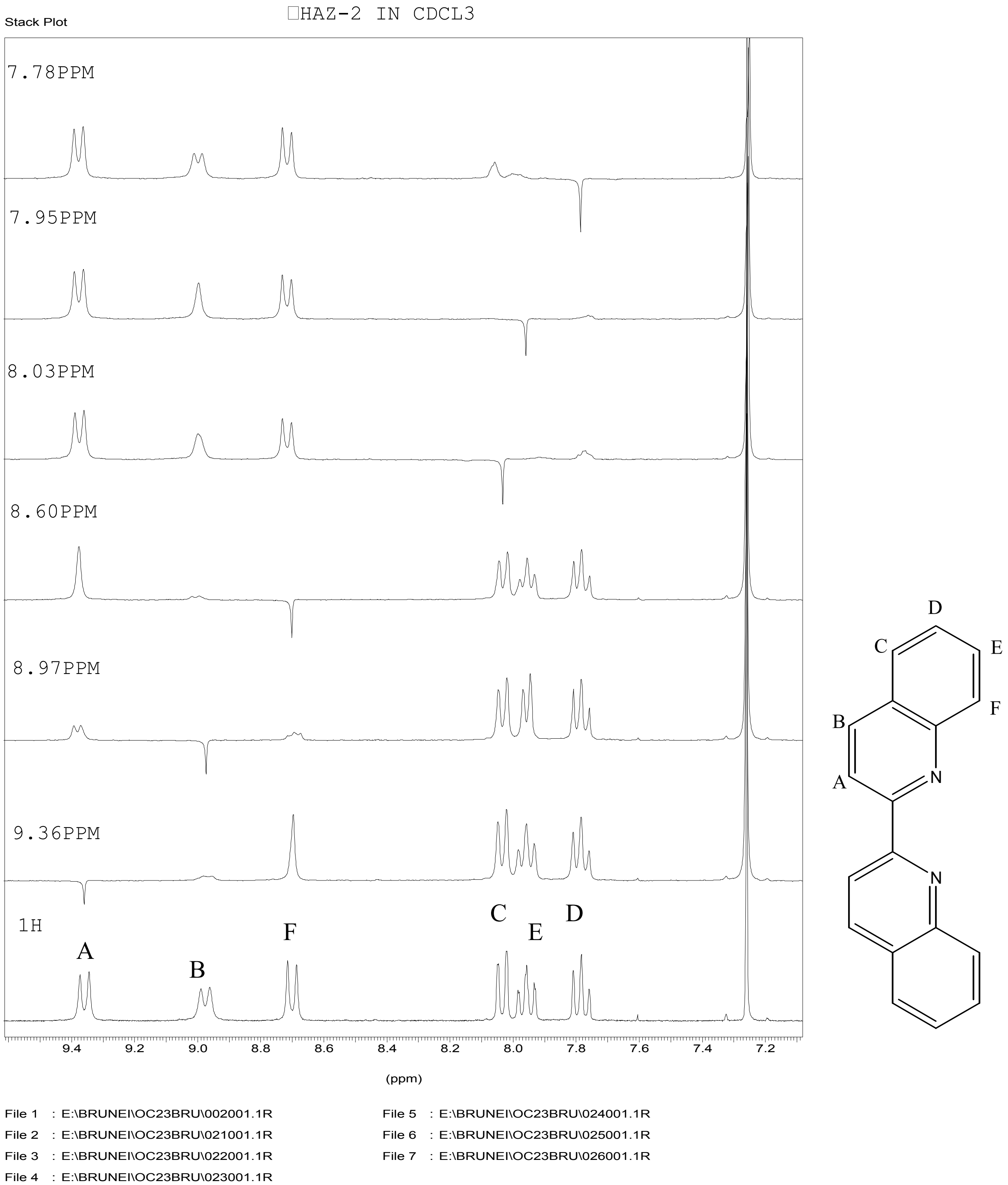

Figure D5: Proton decoupling spectrum of $W(CO)_4(BiQ)$

References

[1] Greenwood, N.N. & Earnshaw, A. (1984). *Chemistry of the elements.* Exeter: A. Wheaton & Co. Ltd.

[2] Spessard, G. O. & Miessler, G.L. (1997). *Organometallic Chemistry*. New Jersey: Prentice-Hall. p 48-137.

[3] Brisdon, A.K. (1998). *Inorganic spectroscopic methods.* New York: Oxford University Press.

[4] Collomb-Dunand-Sauthier M.N., Deronzier, A. & Ziessel, R.(1994). *Electrocatalytic reduction of carbon dioxide with mono(bipyridine)carbonyl-ruthenium complexes in solution or as polymeric thin films*. Inorg Chem 33: 2961-2967.

[5] Denti G, Campagna, S., Sabatino, L., Serroni S., Ciano, M. & Balzani, V. (1990). *Luminescent and redox-reactive building blocks for the design of photochemical molecular devices: mono-, di-, tri-, and tetranuclear ruthenium(II) polypyridine complexes.* Inorg Chem 29: 4750-4758.

[6] Manuta, D.M. & Lees, A.J. *Preparation and reaction of 2,2'-Bipyridinestetracarbonylmolebdenum (0)*. J. Chemical Education. 1987. 64: 637-638.

[7] Tobe, M.L. & Burgess, J. (1999). *Inorganic reaction mechanisms*. New York: Addison Wesly Longman, Inc.

[8] Carter, R.L. (1998). *Molecular symmetry and group theory*. New York: John Wiley & Sons, Inc.

[9] Brian Smith. (1999). *Infrared spectral interpretation: A systematic approach.* New York: CRC Press,

[10] Kenso Soal, Hidekazu Oyamada, Masako Takase & Atushiro Ookawa. (1984). *Practical procedure for the chemoselective reduction of esters by sodium borohydride. Effect of slow addition of methanol.* The chemical society of Japan. 1984. 57: 1948-1953.

[11] Norrul Aini bte Hj. Md. Thani. Synthesis and reactions of substituted bipyridine. Project report 1997/98.

[12] Saidin Lasit. Synthesis. Synthesis and reactions of substituted bipyridine. Project report 1999.

[13] Manuta, D.M. & Lees, A.J. *Solvatochromism of the metal to ligand charge-transfer transitions of zerovalent tungsten carbonyl complexes.* Inorg. Chem. 1986. 25, 3212-3218.

[14] Inglett, G.E. & Smith, G.F. Journal of American Chemical Society. 1950. 72, 842.

[15] Haukka M, Alvila L & Pakkanen TA (1995) *Catalytic activity of ruthenium 2,2'-bipyridine derived catalysts in 1-hexene hydroformylation and 1-heptanal hydrogenation*. JMol Catal 102: 79-92.

[16] Pouchert, C.J. (1985). *The Aldrich library of FT-IR spectra*. Milwaukee: Aldrich Chemical Co.

[17] Huiqi Zhang, Richard Hoogenboom, Martin W.M. Fijten & Schubert. U.S. *Screening and application of ATRP catalysts utilizing an automated synthesizer.* Polymer Preprints 2002, 43(2), 17.

[18] McLellan, A.L. (1963). Tables of experimental dipole moments. San Francisco: W.H. Freeman.

[19] Lever, A. B. P. (1984). *Inorganic Electronic Spectroscopy*, 2nd ed.; Amsterdam: Elsevier.

[20] Gorelskya, S.I. and Levera, A.B.P. *The Electronic Structure and Spectra of [Ru(NH3)4(LL)]2+ (LL = bpy, bpz, bqdi) studied by Density Functional Theory and INDO/S. Charge Transfer Character of Electronic Transitions and their Solvatochromism.* Canadian Journal of Analytical Sciences and Spectroscopy. 2003. Volume 48, No.1.

[21] SDBS compound information. 2003. [Online]. Available: http://www.aist.go.jp/

[22] Stiddard, M.H.B. (1962). 2,2'-bipyridyl derivatives of Group VI Carbonyl ligands. J. Organometallic Chemistry. 4712-4715.

[23] Chatt, J., Leigh, G.J & Thankarajan. Improved preparation of tertiaty phosphine and related substitution products of Group VI metal carbonyls. J. Organometallic Chemistry, 29 (1971) 105-110.

[24] Andy Hor, T.S. & Siti Rohani bte Rus. Subtituted metal carbonyl part VI. Convenient syntheses and chracterizations of group 6 metal tricarbonyls with ligand α-diimine and triethyl phospite. J. Organometllic chemistry. 348 (1988) 343-347.

[25] Billica, H.R. & Adkins, H. (1955). *Organic synthesis collective.* Vol.(3), 176.

[26]Andy Hor, T.S. *Subtituted metal carbonyl part 5. Convenient syntheses of some Group 6 phosphine and pyridine substituted penta- and tetra-carbonyls and isolation of the singly bridging 1,2-Bis(4-pyridyl)ethylene dimeta decarbonyl complexes.* Inorganica Chemica Acta, 143 (1988) 3-5.

[27] Andy Hor, T.S. *Subtituted metal carbonyl part 7. Direct route to Group 6 Tricarbonyl complexes with Tris(2-chloroethyl)phosphite as Ligand.* Inorganica Chemica Acta, 149 (1988) 169-170.

[28] McMurray, J. (2000). *Organic chemistry fifth edition*. Pacific Grove: Brooks/Cole Thomson Learning.