

2007

Multifunctional ligands for supramolecular chemistry

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MULTIFUNCTIONAL LIGANDS FOR SUPRAMOLECULAR CHEMISTRY

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science

in

The Department of Chemistry

by

James Kakoullis
B.S. Eckerd College, 2002
August 2007

I have fought the good fight. I have finished the course. I have kept the faith.

2 Timothy 4:7

Acknowledgments

I thank my parents for all their love and support during these past years that I have attended graduate school. Were it not for them, I would not be at this point. I owe them all that I have accomplished in my life.

I would also like to acknowledge my graduate advisor, under whose supervision this work was conducted. I thank him for this opportunity to demonstrate my abilities and to become a fully realized scientist.

This work would not have developed as it has were it not for the technical expertise and work of Dr. Frank Fronczek with determining crystal structures. Dr. Dale Treleaven has also been a great aid in the area of NMR. Were it not for Dr. Treleaven, I probably would not have attained a tenth of the knowledge of this field.

This research could not have been achieved without our lab's post-doctoral fellows – Dr. Bang-lin Chen, Dr. Chandi Pariya, and Dr. Kalu marakkala Nalin de Silva – and graduate students Sylvester Burton, Christopher Sparrow, Yixun Zhang, Yoseph Marcos, and Jackson Cherutoi.

Table of Contents

Epigraph	ii
Acknowledgments	iii
List of Tables	vi
List of Figures	vii
List of Reaction Schemes	ix
List of Molecules	x
Abstract	xv
Chapter 1 Introduction	1
1.1 Host-Guest Chemistry History: The Organic Period	1
1.2 Host-Guest Chemistry History: The Metal Coordinated Complexes	2
1.3 History of Cu(pyac) ₂	6
1.4 Goal of the Current Research	7
1.5 References	9
Chapter 2 The Attempted Synthesis of a Molecular Square, [Re(CO) ₃ ClCu(pyac) ₂] ₄	11
2.1 Introduction	11
2.2 Experimental Section	13
2.2.1 Materials and Procedures	13
2.2.2 Attempted Direct Synthesis of Molecular Square [Re(CO) ₃ ClCu(pyac) ₂] ₄ , 1.21	14
2.2.3 Attempted Synthesis of Molecular “L” Re(CO) ₃ Cl(Cu(pyac) ₂) ₂ , 1.22	14
2.2.4 Synthesis of Molecular “Corner” Re(CO) ₃ Cl(pyacH) ₂ , 2.2	15
2.2.5 Attempted Synthesis of [Re(CO) ₃ ClCu(pyac) ₂] ₄ , 1.21 with Re(CO) ₃ Cl(pyacH) ₂ , 2.2	15
2.3 Results and Discussion	20
2.3.1 IR Analyses of Direct Synthesis of Molecular Square [Re(CO) ₃ ClCu(pyac) ₂] ₄ , 1.21 and Molecular “L” Re(CO) ₃ Cl(Cu(pyac) ₂) ₂ , 1.22	20
2.3.2 MS Analysis of Direct Synthesis of Molecular Square [Re(CO) ₃ ClCu(pyac) ₂] ₄ , 1.21 and Molecular “L” Re(CO) ₃ Cl(Cu(pyac) ₂) ₂ , 1.22	21
2.3.3 DLS Analysis of Samples Re1a and Re1b	23
2.3.4 IR Analyses of Molecular “Corner” Re(CO) ₃ Cl(pyacH) ₂ , 2.2	23
2.3.5 X-ray Crystallography of Molecular “Corner” Re(CO) ₃ Cl(pyacH) ₂ , 2.2	24
2.4 Conclusions and Future Work	26
2.5 References	27
Chapter 3 The Attempted Synthesis of a Molecular Cube, (Pphac ₃) ₈ (Cu) ₁₂	28
3.1 Introduction	28
3.2 Experimental Section	29
3.2.1 Materials and Procedures	29

3.2.2	Synthesis of Tris(4-formylphenyl)Phosphine 2.2	29
3.2.3	Synthesis of Tris(4-formylphenyl)Phosphine Oxide 3.4	31
3.2.4	Synthesis of Pphac ₃ H ₃ 1.23	32
3.2.5	Synthesis of OPphac ₃ H ₃ , 3.6	32
3.2.6	Attempted Synthesis of (Pphac ₃) ₈ (Cu) ₁₂ 1.24	34
3.3	Results and Discussion	35
3.3.1	X-ray Crystal Structure of Tris(4-formylphenyl)phosphine Oxide 3.4	35
3.3.2	Phosphine Cycle	36
3.4	Conclusions and Future Work	37
3.5	References	39
Chapter 4 Conclusions and Future Work		40
Appendix Spectra.....		42
Vita		99

List of Tables

Table 2.1. Amounts Used and Product Yield for Timed Experiments	16
Table 2.2. Amounts Used for Dilute Experiments.....	18
Table 2.3. IR of CO Stretching Frequencies of Re Samples	22
Table 2.4. X-ray Crystal Parameters of $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$, 2.2	25
Table 3.1. X-ray Crystal Parameters of Tris(4-formylphenyl)phosphine Oxide, 3.4	36

List of Figures

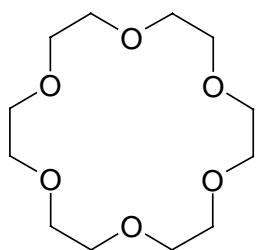
Fig. 1.1.	18-Crown-6	1
Fig. 1.2.	Examples of Cram's Crown Ether Derivative	2
Fig. 1.3.	An Example of Fujita's Molecular Squares	3
Fig. 1.4.	Some Guest Molecules Used by Fujita in his Association Constant Studies	3
Fig. 1.5.	Examples of Hupp's Re Squares	5
Fig. 1.6.	Examples of Stang's Molecular Squares, his Other Polygons, and a Guest	6
Fig. 1.7.	PyacH, 1.19 , and Examples of Pyac Metal Complexes	7
Fig. 1.8.	Target Molecular Square $[\text{Re}(\text{CO})_3\text{ClCu}(\text{pyacH})_2]_4$ 1.21	8
Fig. 1.9.	Target Molecular "L" $\text{Re}(\text{CO})_3\text{Cl}(\text{Cu}(\text{pyac})_2)_2$ 1.22	8
Fig. 1.10.	The Target Molecules Pphac_3H_3 and $(\text{Pphac}_3)_8(\text{Cu})_{12}$	9
Fig. 2.1.	Examples of Hupp's Re Squares	11
Fig. 2.2.	Target Molecular Square $[\text{Re}(\text{CO})_3\text{ClCu}(\text{pyac})_2]_4$ 1.21	12
Fig. 2.3.	Target Molecular "L" $\text{Re}(\text{CO})_3\text{Cl}(\text{Cu}(\text{pyac})_2)_2$, 1.22	13
Fig. 2.4.	Target Molecular "Corner" $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$, 2.2	13
Fig. 2.5.	$\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$ With its Protons Labeled for $^1\text{H-NMR}$	16
Fig. 2.6.	Examples of Re Complexes	21
Fig. 2.7.	X-ray Crystal Structure of $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$, 2.2	24
Fig. 2.8.	X-ray Crystal Structure of $\text{Re}(\text{CO})_3\text{Cl}(\text{py})_2$, 2.3	25
Fig. 3.1.	The Target Molecules Pphac_3H_3 and $(\text{Pphac}_3)_8(\text{Cu})_{12}$	28
Fig. 3.2.	Structure of Tris(4-formylphenyl)phosphine, 3.1 , and Bis(4-formylphenyl)dimethylsilane, 3.2	29
Fig. 3.3.	Tris(4-formylphenyl)phosphine, 3.1 With its Hs Labeled	31
Fig. 3.4.	Tris(4-formylphenyl)phosphine Oxide, 3.4 With its Hs Labeled	32

Fig. 3.5.	Pphac_3H_3 1.27 With its Hs Labeled	33
Fig. 3.6.	Pphac_3H_3 Oxide 3.6 With its Hs Labeled	34
Fig. 3.7.	X-ray Crystal Structure of Tris(4-formylphenyl)phosphine Oxide with THF, 3.4	36
Fig. 3.8.	Triphenylphosphine, 3.7	37
Fig. 3.9.	The Interrelationship Between the Different Phosphines	38
Fig. 3.10.	Target Molecules $\text{OPphac}_3\text{H}_3$ 3.6 and $(\text{OPphac}_3)_8(\text{Cu})_{12}$ 3.8	38
Fig. 4.1.	Target Molecular Square and Cube	40

List of Reaction Schemes

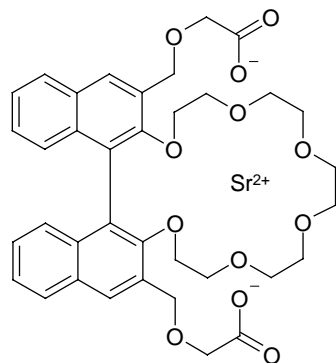
Reaction Scheme 3.1. Synthetic Route to Tris(4-formylphenyl)phosphine, 3.1	30
Reaction Scheme 3.2. Reaction to Synthesize Pphac ₃ H ₃ , 1.23	33

List of Molecules

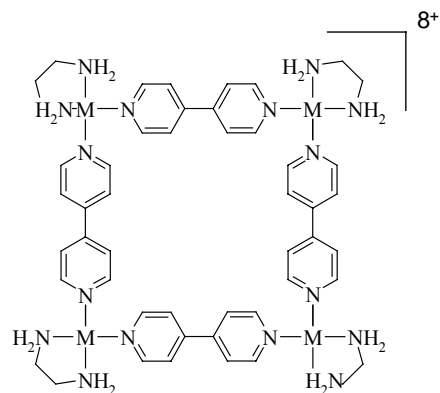


1.1

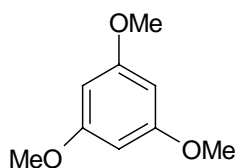
18-crown-6



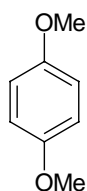
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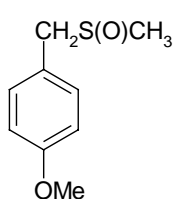
1.3 M = Pt²⁺ or Pd²⁺



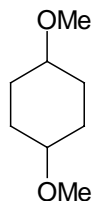
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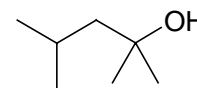
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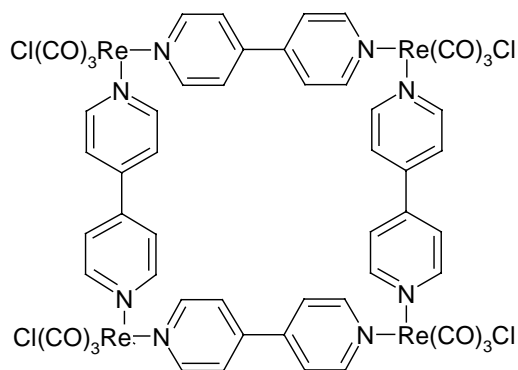
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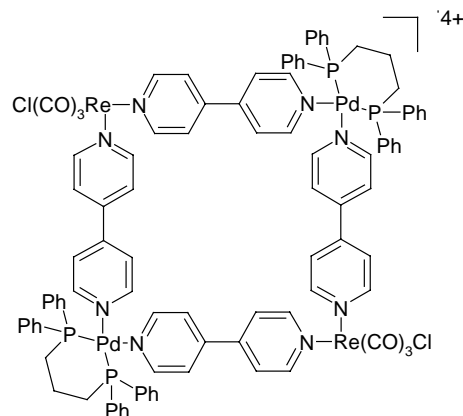
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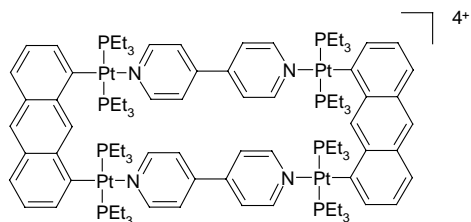
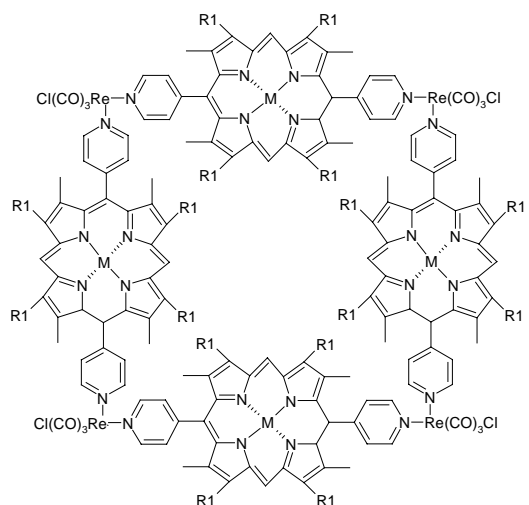
1.8



[Re(CO)₃Cl(4,4'-bpy)]₄ 1.9

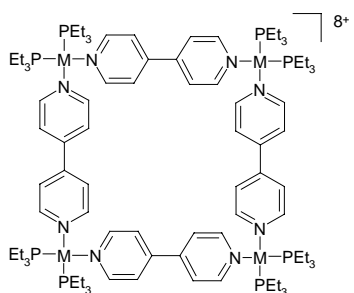


[(Re(CO)₃Cl)₂(Pd(dppp))₂(4,4'-bpy)₄](SO₃CF₃)₄ 1.10

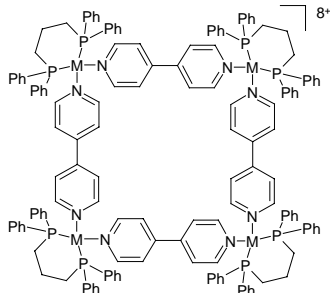


[Re(CO)₃Cl(2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-bis(4-pyridyl)-porphyrin)]₄ **1.11** &

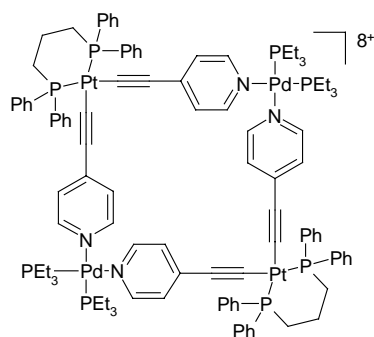
1.12



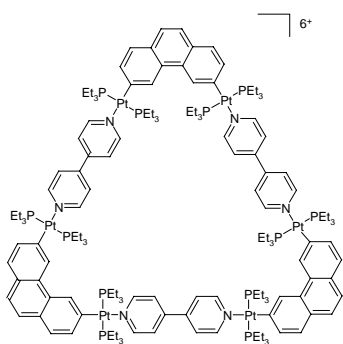
1.13 M= Pt or Pd



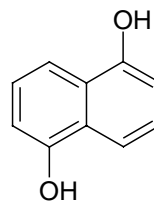
1.14 M = Pt or Pd



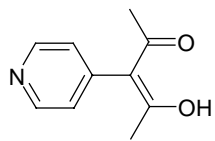
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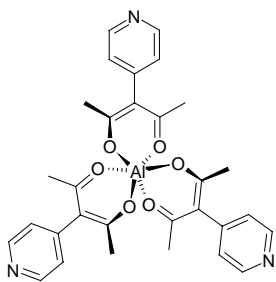
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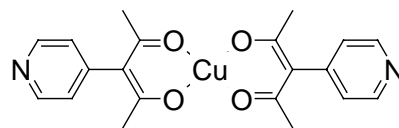
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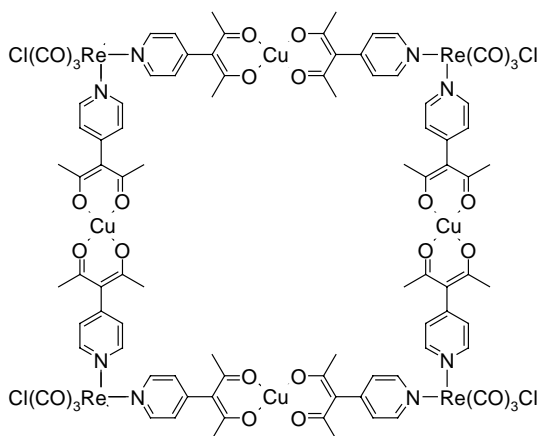
pyacH, **1.18**



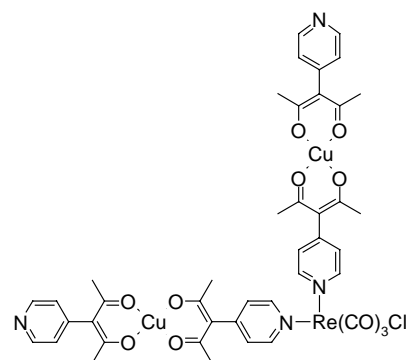
Al(pyac)₃ **1.19**



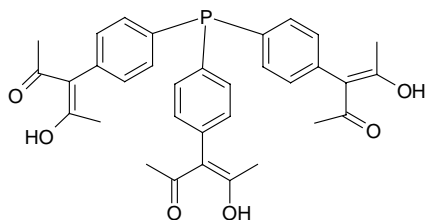
Cu(pyac)₂, **1.20**



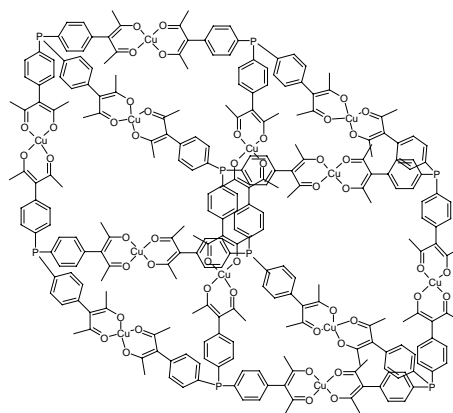
[Re(CO)₃ClCu(pyac)₂]₄ **1.21**



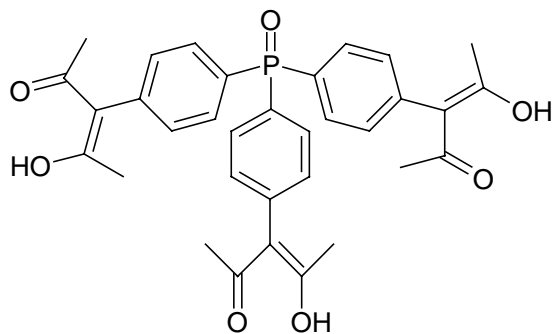
Re(CO)₃Cl(Cu(pyac)₂)₂ **1.22**



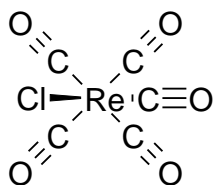
Pphac₃H₃ **1.23**



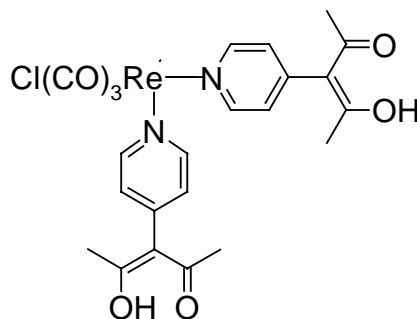
(Pphac₃)₈(Cu)₁₂ **1.24**



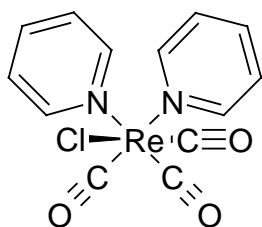
OPphac₃H₃ **1.25**



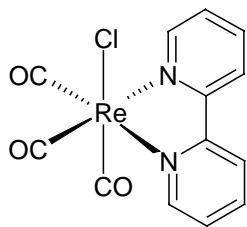
Re(CO)₅Cl, **2.1**



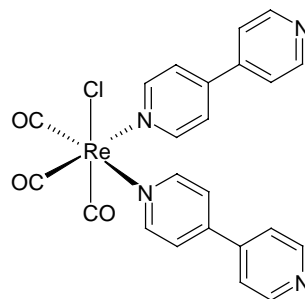
Re(CO)₃Cl(pyacH)₂, **2.2**



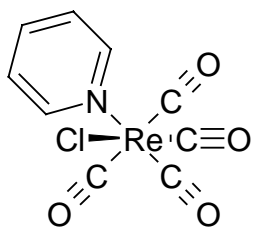
Re(CO)₃Cl(py)₂ **2.3**



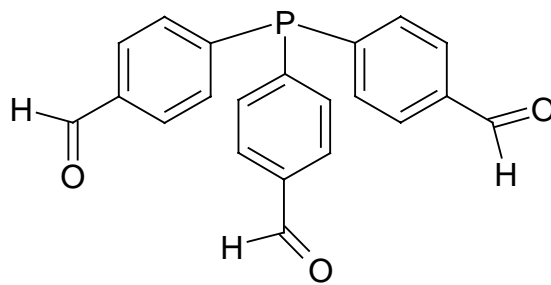
ReCl(CO)₃(2,2'-bpy), **2.4**



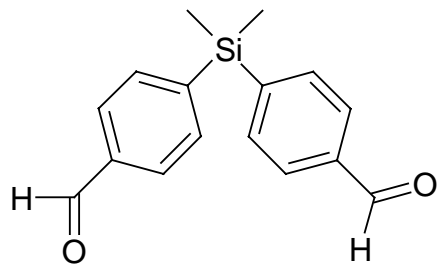
ReCl(CO)₃(4,4'-bpy)₂, **2.5**



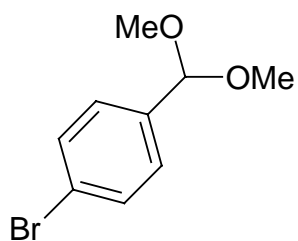
ReCl(CO)₄(pyridine) **2.6**



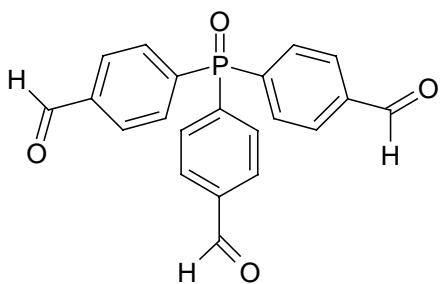
tris(4-formylphenyl)phosphine **3.1**



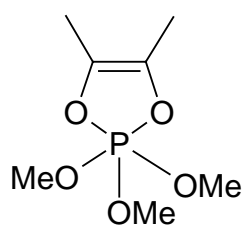
bis(4-formylphenyl)dimethylsilane **3.2**



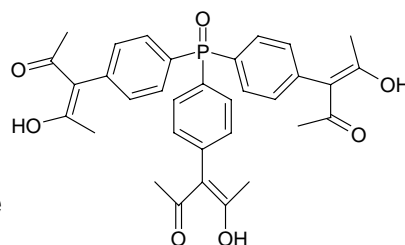
4-bromobenzaldehyde dimethyl acetal **3.3**



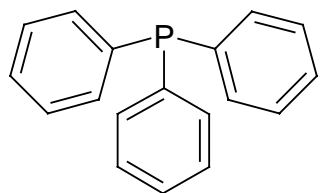
tris(4-formylphenyl)phosphine oxide **3.4**



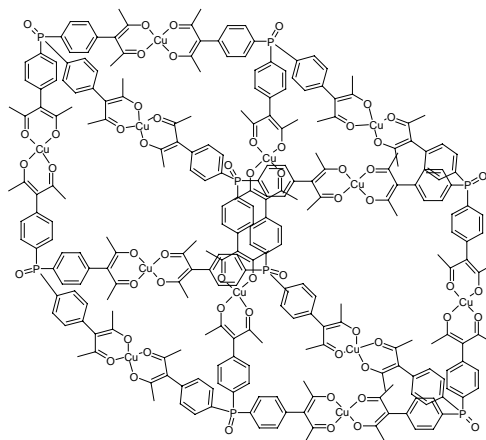
phospholene **3.5**



OPphac₃H₃ **3.6**



Triphenylphosphine **3.7**



(OPphac₃)₈(Cu)₁₂ **3.8**

Abstract

Metal-organic frameworks (MOFs) are the primary focus of the Maverick research group, almost exclusively with the acac moiety. Before such MOFs can be attempted, multifunctional ligands of the appropriate geometry for the desired MOFs first must be synthesized. In this thesis, the synthesis and characterization of two new β -diketone ligands, specifically, $\text{Re}(\text{CO})_3\text{Cl}(\text{PyacH})_2$, **2.2**, Pphac_3H_3 , **1.23**, and its oxide **3.6**, are described. Also in this thesis, attempts to synthesize other new MOFs will be discussed.

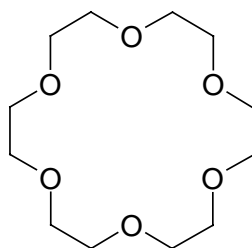
The MOF for which $\text{Re}(\text{CO})_3\text{Cl}(\text{PyacH})_2$, **2.2** was designed was $\text{Re}(\text{CO})_3\text{ClCu}(\text{pyac})_2]_4$, **1.21**, which is predicted to be a square due to the approximate angle of $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$, **2.2**, of 90° . $\text{OPphac}_3\text{H}_3$, **3.6**, was designed for $(\text{OPphac}_3)_8(\text{Cu})_{12}$, **3.8**, which is predicted to be a cube due to the predicted angle of $\text{OPphac}_3\text{H}_3$, **3.6**. Primarily though, the creation of the aforementioned ligands represents the main thrust of this work.

Chapter 1

Introduction

1.1 Host-Guest Chemistry History: The Organic Period

The field of host-guest chemistry began with the development of crown ethers by Pedersen in the 1960s. His major breakthrough was first presented in a paper in 1967 (see Fig. 1.1).^{1,1}



1.1

Fig. 1.1. 18-Crown-6

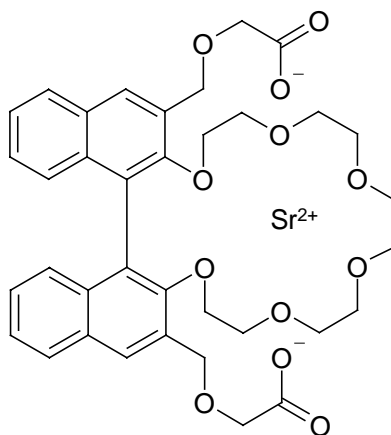
The other great contributor to this field was Cram.^{1,2} He distinguished between hosts and guests by identifying hosts as organic molecules with convergent binding sites and guests as either molecules or ions with divergent binding sites.

This definition, however, does not fit all cases that have emerged since Cram's early work. Most relevant to this researcher in Cram's definition is the concept that one molecule, a guest, goes into a larger molecule, a host. Once inside the host, the guest remains as a result of forces that depend on the interaction between the specific molecules. This host-guest relationship is not necessarily a permanent state, but it should last sufficiently long to be measurable by such means as IR-spectroscopy or NMR.

The work of Pedersen and Cram, together with that of other early researchers in host-guest chemistry, was dominated by the use of crown ethers, crown ether derivatives, and organic

molecules, similar in structure to crown ethers as hosts. This restriction limited the scope of compounds synthesized for use as host-guest systems.

These all-organic host-guest systems did yield good results. A number of Cram's crown ether derivatives were highly selective, being able, for example, to isolate Sr^{2+} from Ba^{2+} , **1.2**. (see Fig. 1.2).^{1,2}



1.2

Fig. 1.2. Examples of Cram's Crown Ether Derivative

1.2 Host-Guest Chemistry History: Metal Coordinated Complexes

The all-organic molecular host days held sway until the mid 1980s, when groups such as those led by Fujita, Hupp, Maverick, and Stang introduced metal-organic frameworks (MOFs). Cram's previous definition of a host-guest system does not fit these newer compounds (see section 1.1); specifically, the newer compounds are not completely organic in nature. Also, these compounds bind to their guests in a different manner than do Cram's molecules.

Fujita was one of the first to make a metal-coordinated host molecule. He created molecules in which metal centers acted as corners and rigid, aromatic ligands acted as rods to connect the centers. Since these molecules are tetramers and due to their shape, they are called

molecular squares. An example of these squares is $[M(en)(4,4'\text{-bpy})]_4^{8+}(\text{NO}_3^-)_8$, **1.3**, where M is either Pt^{2+} or Pd^{2+} (see Fig. 1.3).^{1.3,1.5}

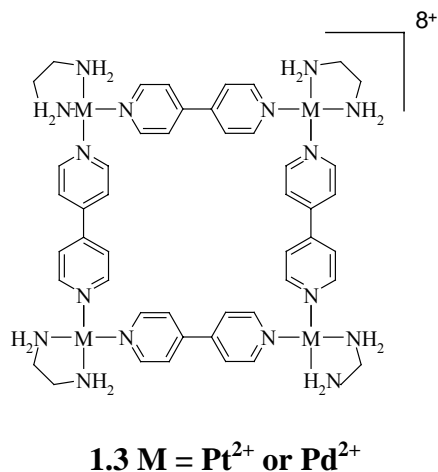


Fig. 1.3. An Example of Fujita's Molecular Squares

Fujita also studied the efficacy of these molecules as hosts and measured the association constants of a number of molecules using NMR. The values of these constants range from 0.3×10^2 to 7.5×10^2 for the compounds below (see Fig. 1.4).

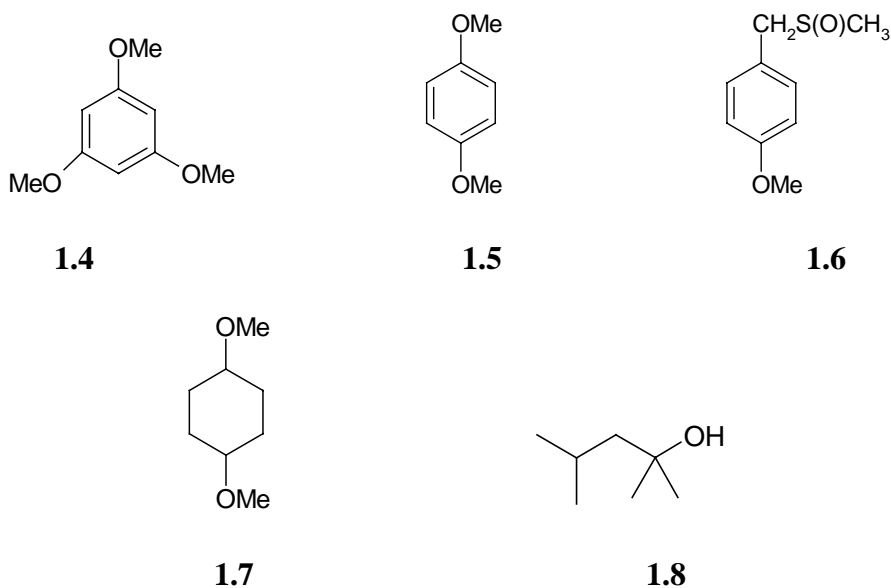


Fig. 1.4. Some Guest Molecules Used by Fujita in his Association Constant Studies

Fujita concluded that the guest interacts with the host's cavity, not with the metal center, and that the interaction is a combination of charge-transfer interactions, i.e. electro-static between the host and the guest and hydrophobic interactions.^{1.6} In Cram's definition and compounds, there were set binding sites. In Fujita's compounds, the entire cavity acts as a "binding site" as a result of hydrophobics.

Hupp has also done work in the area of creating molecular squares for use as hosts. In contrast to Fujita's squares, Hupp uses metal centers that are luminescent, namely Re. Some examples of Hupp's squares are $[\text{Re}(\text{CO})_3\text{Cl}(4,4'\text{-bpy})]_4$, **1.9**, $[(\text{Re}(\text{CO})_3\text{Cl})_2(\text{Pd}(\text{dppp}))_2(4,4'\text{-bpy})_4](\text{SO}_3\text{CF}_3)_4$, **1.10**, and $[\text{Re}(\text{CO})_3\text{Cl}(2,8,12,18\text{-tetrabutyl-3,7,13,17-tetramethyl-5,15-bis(4-pyridyl)-porphyrin})]_4$, **1.11** (see Fig. 1.5).^{1.7,1.10} The choice of a luminescent metal center was made with the intent that these properties of these squares could be harnessed to detect the presence or absence of a guest in the host. Hupp not only postulated this model, but also went on to study the squares' luminescent properties with guests. With Re square **1.10** when tetraethylammonium perchlorate was added, the emission spectrum was enhanced by the perchlorate anion's binding interaction in the tetracationic cavity.^{1.7} In square **1.11**, the luminescence was due to the porphyrin and not the Re center; it was found that in the Zn version there was a red shift when pyridine was added, signifying an interaction with the Zn center in the porphyrin.^{1.10}

Stang has also contributed much to this field by making not only molecular squares, but also other shapes (see Fig. 1.6).^{1.11-1.15} He has also done host-guest studies with some of these squares, specifically, **1.14** and **1.15**. With **1.14**, the guest molecule was 1,5-dihydroxynaphthalene **1.17**; and when the two interacted, the guest went inside the host, causing a shift in the NMR of the host (see Fig. 1.6).^{1.12} Molecular square **1.15** was studied with Ag^+ as the guest. It was

confirmed via IR spectroscopy that a host-guest complexation interaction did occur between the two molecules.^{1,13}

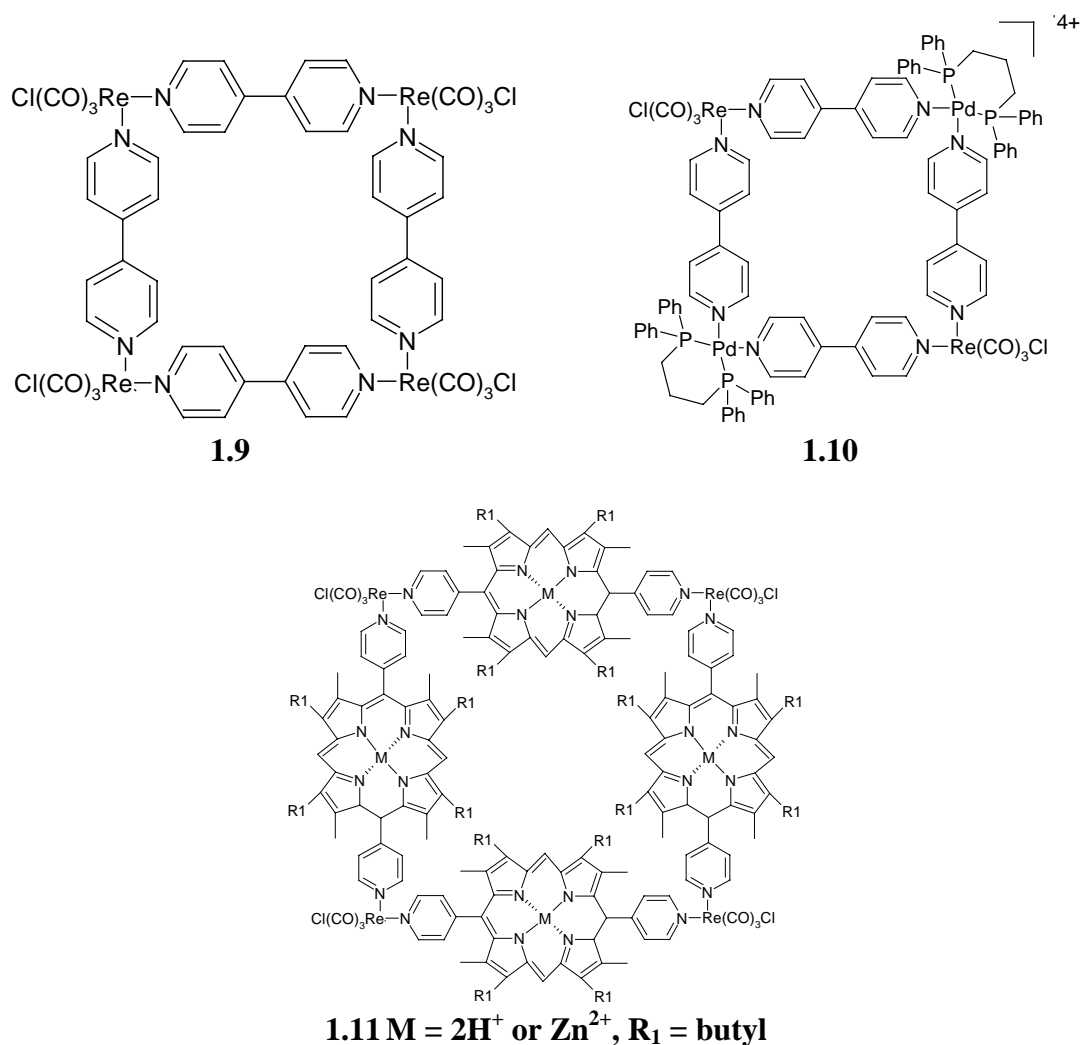
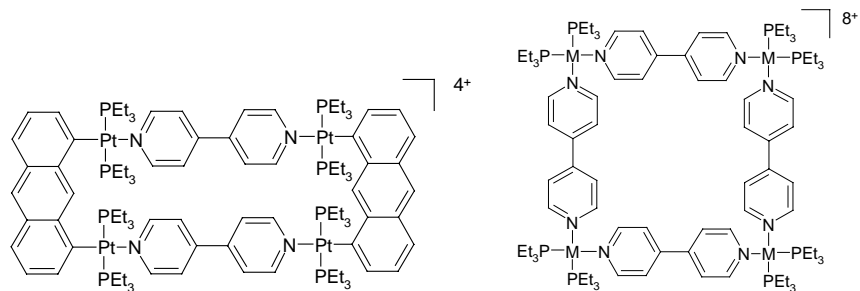


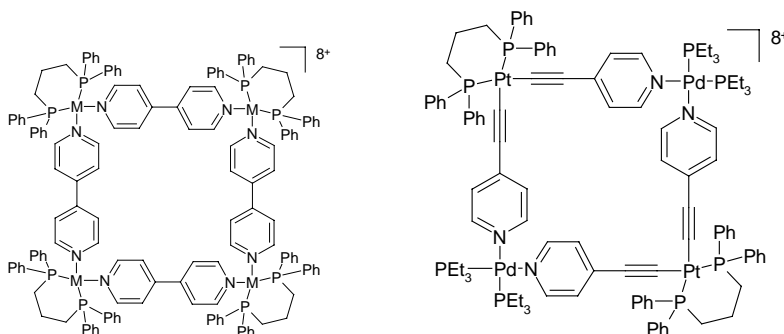
Fig. 1.5. Examples of Hupp's Re Squares

Another important influence on the work of this researcher is that of the Long group. Even though Long did not do host-guest chemistry, he has contributed to this researcher's work through his work on two- and three-dimensional complexes. He has made not only molecular squares, but also three-dimensional cubes. However, the Long group has not yet done research to determine whether these potential hosts do interact with guests.^{1.15-1.18}



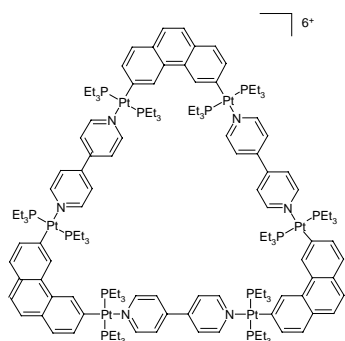
1.12

1.13 M= Pt or Pd

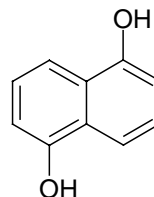


1.14 M = Pt or Pd

1.15



1.16



1.17

Fig. 1.6. Examples of Stang's Molecular Squares, his Other Polygons, and a Guest

1.3 History of Cu(pyac)₂

PyacH, **1.18** first appeared in the literature via a Japanese patent.^{1.19} A metal pyacH complex, specifically Al(pyac)₃, **1.19**, seems to have been used as a guest molecule for the first time by Sanders.^{1.20} Cu(pyac)₂, **1.20** was first synthesized by Turner (see Fig. 1.7).^{1.21}

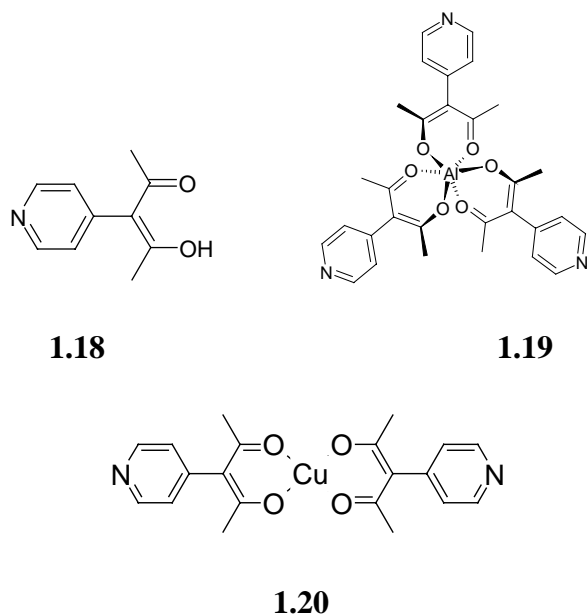


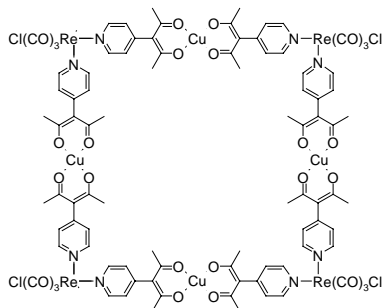
Fig. 1.7. PyacH, **1.19**, and Examples of Pyac Metal Complexes

The use of $\text{Cu}(\text{pyac})_2$ **1.20** to make two-dimensional arrays and complexes was developed by the Maverick research group.^{1,22} Our group thought that a ligand such as $\text{Cu}(\text{pyac})_2$ **1.20** could be used in place of (4,4'-bpy) to make a molecular square. Since the Cu is coordinatively unsaturated, guests could interact with it in the same manner as the pyridine did with Hupp's **1.11**. Also from the Maverick group, Chen has prepared 1- and 2-dimensional porous extended solids from $\text{Cu}(\text{pyac})_2$ **1.20** and Cd salts.^{1,22}

1.4 Goal of the Current Research

The general goal of this research was to attempt to synthesize new MOFs to be used as hosts in host-guest chemistry. This goal was pursued by attempting to synthesize a Re molecular square.

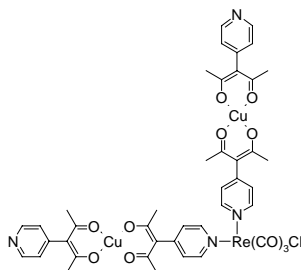
Our group has used $\text{Cu}(\text{pyac})_2$, **1.20** since 2002. One goal of the present research was to make a new molecular square, using Re as the corner and $\text{Cu}(\text{pyac})_2$ **1.20** as the rod to create the structure **1.21** (see Fig. 1.8).



1.21

Fig. 1.8. Target Molecular Square $[\text{Re}(\text{CO})_3\text{ClCu}(\text{pyacH})_2]_4$ **1.21**

Another specific goal of this research was to make a new molecular "L," using Re as the corner and $\text{Cu}(\text{pyac})_2$, **1.20** as the rod to create the structure **1.22** (see Fig. 1.9).

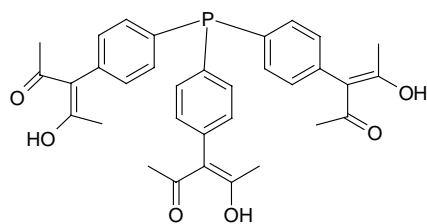


1.22

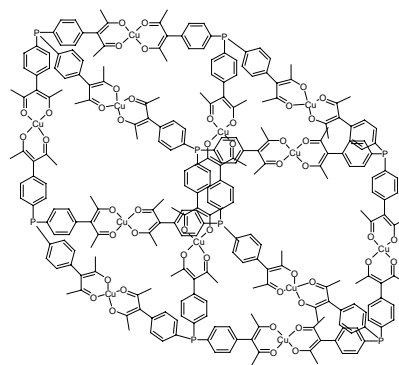
Fig. 1.9. Target Molecular "L" $\text{Re}(\text{CO})_3\text{Cl}(\text{Cu}(\text{pyac})_2)_2$ **1.22**

Making this molecule was attempted as a possible intermediate step in the preparation of the square and as an alternative to a direct synthesis of the square. Re was selected because of Hupp's extensive work with hosts such as **1.9-1.11**.

Another goal of the Maverick research group is to develop a three-dimensional host. Our group decided to focus on a cube. This researcher came up with the idea of using a phosphine ligand as the corner and a metal as the rod. The ligand that was eventually developed was Pphac_3H_3 , **1.23**, which, it was theorized, would form a cube $(\text{Pphac}_3)_8(\text{Cu})_{12}$, **1.24**, when reacted with Cu (see Fig. 1.10).



1.23



1.24

Fig. 1.10. The Target Molecules Pphac₃H₃ and (Pphac₃)₈(Cu)₁₂

Our group hoped that including a moiety similar to Cu(pyac)₂ **1.20** and in the design of the cube itself would result in its properties being retained by the cube. The property we most wanted to retain was the ability to bond to a guest.

In chapter 2 of this paper, there will be a discussion of the attempted creation of the Re square [Re(CO)₃ClCu(Pyac)₂]₄ **1.21** which, though not succeeding, did culminate in the new molecule Re(CO)₃Cl(PyacH)₂ **2.2**. In chapter 3 of this paper, there will be a discussion of the attempted creation (Pphac₃)₈(Cu)₁₂ **1.24**. While this molecule was not made, two new β-diketones were made Pphac₃H₃ **1.23** and OPphac₃H₃, **3.6**. In chapter 4, these results will be summarized.

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Chapter 2

The Attempted Synthesis of a Molecular Square, $[\text{Re}(\text{CO})_3\text{ClCu}(\text{pyac})_2]_4$

2.1 Introduction

The general goal of this research was to attempt to synthesize new MOFs to be used as hosts in host-guest chemistry. This goal was pursued by attempting to synthesize a Re molecular square. Such squares had been previously prepared by the Hupp group. Some examples of Hupp's squares are $[\text{Re}(\text{CO})_3\text{Cl}(4,4'\text{-bpy})]_4$ **1.9**, $[(\text{Re}(\text{CO})_3\text{Cl})_2(\text{Pd}(\text{dppp}))_2(4,4'\text{-bpy})_4](\text{SO}_3\text{CF}_3)_4$ **1.10** and $[\text{Re}(\text{CO})_3\text{Cl}(2,8,12,18\text{-tetrabutyl-3,7,13,17-tetramethyl-5,15-bis(4-pyridyl)-porphyrin})]_4$ **1.11** (see Fig. 2.1).^{2.1,2.2}

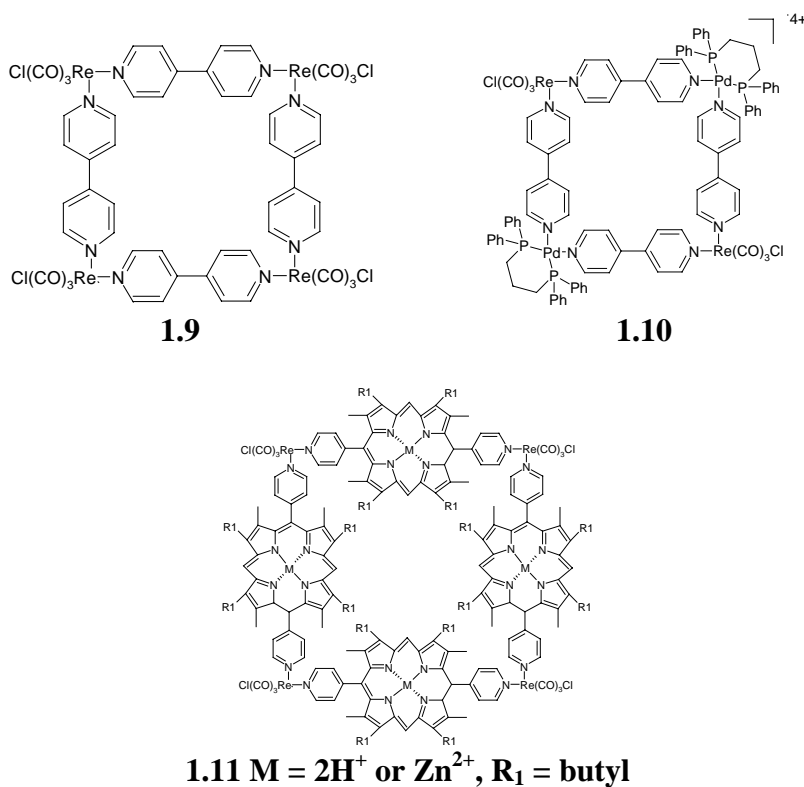
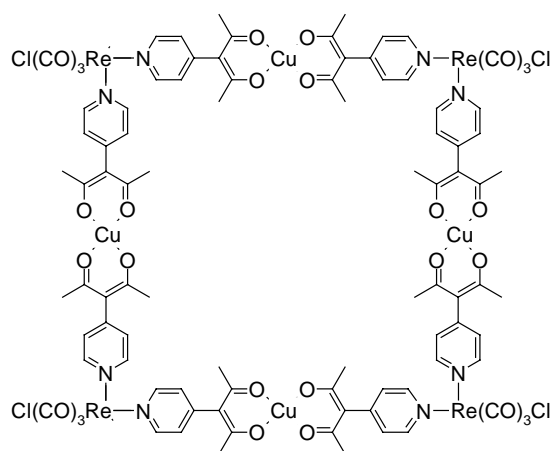


Fig. 2.1. Examples of Hupp's Re Squares

The choice of a luminescent metal center was made with the intent that the properties of these squares could be harnessed to detect the presence or absence of a guest in the host. Hupp not

only postulated this, but also went on to study the squares' luminescent properties with guests. With Re square **1.10**, when tetraethylammonium perchlorate was added, the emission spectrum was enhanced by the perchlorate anion's binding interaction in the tetracationic cavity.^{2.2}

Since 2002, our group, in remaking $[\text{Re}(\text{CO})_3\text{Cl}(4,4'\text{-bpy})]_4$ **1.9**, used $\text{Cu}(\text{pyac})_2$ **1.20** rather than using $(4,4'\text{-bpy})$ as the ligand/rod unit in the square. One present goal, then, is to make a new molecular square, using Re as the corner and $\text{Cu}(\text{pyac})_2$ **1.20** as the rod to create the structure **1.21** (see Fig. 2.2).

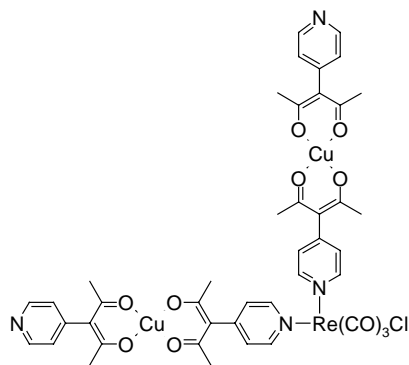


1.21

Fig. 2.2. Target Molecular Square $[\text{Re}(\text{CO})_3\text{ClCu}(\text{pyac})_2]_4$ **1.21**

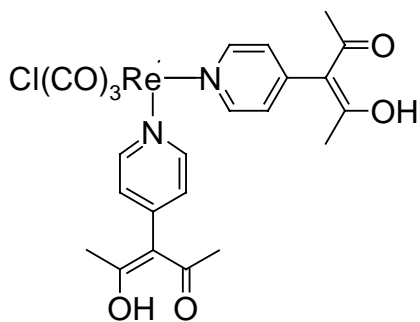
To achieve this goal, three schemes were attempted. The first was direct reaction of $\text{Re}(\text{CO})_5\text{Cl}$, **2.1**, with $\text{Cu}(\text{pyac})_2$ **1.20** to make the square. Another scheme was to make a new molecular "L" using Re as the corner and $\text{Cu}(\text{pyac})_2$ **1.20** as the rod to create the structure **1.22** (see Fig. 2.3). Making this molecule was attempted as a possible intermediate step in the preparation of the square and as an alternative to a direct synthesis of the square.

The third scheme was to make a corner by reacting Re and pyacH. In this scheme to make a corner, Re would serve as the center and pyacH **1.18** as the rod to create the structure, **2.2** (see Fig. 2.4).



1.22

Fig. 2.3. Target Molecular “L” $\text{Re}(\text{CO})_3\text{Cl}(\text{Cu}(\text{pyac})_2)_2$, **1.22**



2.2

Fig. 2.4. Target Molecular “Corner” $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$, **2.2**

2.2 Experimental Section

2.2.1 Materials and Procedures

All reagents were used as received and without further purification unless mentioned.

These materials were of reagent grade or better.

The ^1H -NMR spectra were recorded on a Bruker DPX-250 spectrometer. The IR spectra were recorded on a Bruker Tensor 27. Elemental analyses were performed by MHW Laboratories in Phoenix, Arizona. Mass spectrometer analyses were performed by the facilities at LSU. The dynamic light scattering experiments were conducted by the Russo group. The instrument used was custom built (see section 3.3). The X-ray crystallography was performed by

Dr. Fronczek, using the Nonius Kappa CCD area-detector instrument equipped with a Mo K α source. All spectra are in the Appendix.

2.2.2. Attempted Direct Synthesis of Molecular Square [Re(CO)₃ClCu(pyac)₂]₄, **1.21**

This compound was prepared following the procedure used by Hupp for [Re(CO)₃Cl(4,4'-bpy)]₄ **1.9**.^{2,3} A sample of Re(CO)₅Cl **2.1** (0.1008 g, 2.79 x 10⁻⁴ mol) was combined with Cu(pyac)₂ **1.20** (0.1170 g, 2.81 x 10⁻⁴ mol) in a round bottom flask. To this flask, a solution of 100 mL of 75% tetrahydrofuran as well as 25% toluene was added, dissolving the solids. The reason for using the tetrahydrofuran and toluene solution was that this was the solvent system used by Hupp to synthesize [Re(CO)₃Cl(4,4'-bpy)]₄ **1.9**. The solution was stirred while refluxing for 48 h under a flowing stream of N₂. From this reaction sample, Re1 (0.0874 g) was recovered by filtering out the solid and washing it with octane. A Soxhlet extraction with acetone was run on this sample and yielded sample Re1a (0.0204 g, 23% of Re1), which was soluble in acetone, and sample Re1b (0.0677 g, 77% of Re1), which was insoluble in acetone.

Anal Calcd For [Re(CO)₃ClCu(pyac)₂]₄ (**1.21**) sample Re1a C₉₂H₈₈N₈O₂₈Re₄Cl₄Cu₄:

C, 38.17; H, 3.06; N, 3.87; Found C, 28.28; H, 2.31; N, 2.06. Anal Calcd For

[Re(CO)₃ClCu(Pyac)₂]₄ (**1.21**) sample Re1b C₉₂H₈₈N₈O₂₈Re₄Cl₄Cu₄:

C, 38.17; H, 3.06; N, 3.87; Found C, 29.30; H, 3.13; N, 3.13.

2.2.3 Attempted Synthesis of Molecular "L" Re(CO)₃Cl(Cu(pyac)₂)₂, **1.22**

This compound was also prepared, using the procedure followed by Hupp for [Re(CO)₃Cl(4,4'-bpy)]₄ **1.9**,^{2,3} but with an excess of Cu(pyac)₂, **1.20**. A sample of Re(CO)₅Cl, **2.1** (0.0396 g, 1.09 x 10⁻⁴ mol) was combined with Cu(pyac)₂, **1.20** (0.2505 g, 6.023 x 10⁻⁴ mol) in a round bottom flask. To this flask, a solution of 500 mL of 75% tetrahydrofuran and 25% toluene was also added, dissolving the solids. The solution was stirred while refluxing for 48 h

under a stream of N₂. From this reaction, sample Re2 (0.0694 g) was recovered. This was done by filtering the solution through a glass frit and collecting the solid on the glass frit. The solid was then washed with octane and then dried. Anal Calcd For Re(CO)₃Cl(Cu(pyac)₂)₂ (**1.22**) sample Re2 C₄₃H₄₄N₄O₁₁ReClCu₂: C, 45.24; H, 3.88; N, 4.91; Found C, 35.55; H, 3.37; N, 4.00.

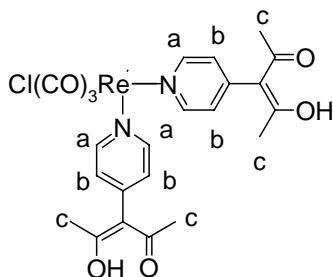
2.2.4. Synthesis of Molecular “Corner” Re(CO)₃Cl(pyacH)₂, **2.2**

This compound was prepared in a similar manner to the procedure followed by Trovati for Re(CO)₃Cl(py)₂, **2.3**,^{2,4} but with pyacH **1.18**. A sample of Re(CO)₅Cl **2.1** (0.0812 g, 2.24 x 10⁻⁴ mol) was combined with pyacH **1.18** (0.1048 g, 5.91 x 10⁻⁴ mol) in a round bottom flask. To this flask, 100 mL of CHCl₃ was added, dissolving the solids. The solution was stirred while refluxing for 72 h under a stream of N₂. At the beginning of the reaction the solution was yellow; at the end it was almost colorless. The solution concentrated down to about 10 mL; then the solution was added to pentane to precipitate out a white, flocculent solid. This was collected on the glass frit. The solid was then washed with pentane and then dried. From this reaction (0.1346 g) was recovered. This was a 91% yield. The material, once dried, was an off-white. The ¹H-NMR of Re(CO)₃Cl(pyacH)₂, **1.22**, (250 MHz, Acetone-d₆) is as follows: ¹H-NMR: 17.08 (s, 1H), 8.84 (d, 2H, J = 6.24, Ha), 7.54 (d, 2H, J = 6.35, Hb), 1.95 (s, 6H, Hc) (note for reference the ¹H-NMR of PyacH **1.18** in Acetone-d₆ is 8.61, 7.30, 1.88) (see Fig. 2.5 for the molecule's Hs labeled; see Spectrum 10 for spectra). Anal. Calcd. For Re(CO)₃Cl(pyacH)₂ (**2.2**), C₂₃H₂₂ClN₂O₇Re: C, 41.85; H, 3.36; N 4.24. Found C, 41.59; H, 3.51; N, 4.15.

2.2.5. Attempted Synthesis of [Re(CO)₃ClCu(pyac)₂]₄, **1.21** ith Re(CO)₃Cl(pyacH)₂, **2.2**

A number of experiments were set up in an attempt to synthesize the target molecule [Re(CO)₃ClCu(pyac)₂]₄, **1.21**. This experiment can be divided into four different types: timed reactions, dilute reactions, concentrated reactions, and growing crystals on templates.

The first set of reactions can be described as timed reactions. Four reactions were set up in which $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$, **2.2**, was reacted with Cu^{2+} over varying time periods. These time periods were 3 h, 4 h, 6 h, and 8 h. The general procedure used is discussed below. Table 2.1 shows the amounts used and product yield.



2.2

Fig. 2.5. $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$ With its Protons Labeled for $^1\text{H-NMR}$

Table 2.1. Amounts Used and Product Yield for Timed Experiments

Samples	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	$\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$, 2.2	yield
3 h	0.0748 g 3.00×10^{-4} mol	0.0992 g 1.50×10^{-4} mol	0.0087 g
4 h	0.0750 g 3.02×10^{-4} mol	0.0995 g 1.51×10^{-4} mol	0.0197 g
6 h	0.0758 g 3.05×10^{-4} mol	0.1004 g 1.52×10^{-4} mol	0.0103 g
8 h	0.0760 g 3.06×10^{-4} mol	0.1003g 1.52×10^{-4} mol	0.0337 g

A sample of $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$, **2.2** was dissolved in 100 mL of CHCl_3 . To this 100 mL of $\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$ solution was added so the desired square would form. The $\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$ was prepared from $\text{Cu}(\text{SO}_4) \cdot 5\text{H}_2\text{O}$ that was dissolved in H_2O . Then NH_4OH was added to the solution to create $\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$. This mixture was stirred for the appropriate time. At the conclusion of the stirring, the two phases were separated. The organic phase was washed with

water and dried over Na₂SO₄. The solvent was then evaporated, leaving a forest-green colored compound. This compound was triturated with MeOH and then filtered. The solid was tested if soluble in CH₂Cl₂ and the compounds were not soluble.

Anal Calcd For [Re(CO)₃ClCu(pyac)₂]₄ (**1.21**) sample 3 h C₉₂H₈₈N₈O₂₈Re₄Cl₄Cu₄: C, 38.17; H, 3.06; N, 3.87; Found C, 41.87; H, 3.88; N, 3.83.

Anal Calcd For [Re(CO)₃ClCu(pyac)₂]₄ (**1.21**) sample 4 h C₉₂H₈₈N₈O₂₈Re₄Cl₄Cu₄: C, 38.17; H, 3.06; N, 3.87; Found C, 41.20; H, 4.18; N, 3.47.

Anal Calcd For [Re(CO)₃ClCu(pyac)₂]₄ (**1.21**) sample 6 h C₉₂H₈₈N₈O₂₈Re₄Cl₄Cu₄: C, 38.17; H, 3.06; N, 3.87; Found C, 38.55; H, 3.19; N, 4.22.

Anal Calcd For [Re(CO)₃ClCu(pyac)₂]₄ (**1.21**) sample 8 h C₉₂H₈₈N₈O₂₈Re₄Cl₄Cu₄: C, 38.17; H, 3.06; N, 3.87; Found C, 38.00; H, 2.21; N, 4.00.

The next series of reactions can be described as dilute reactions. In this series not only Cu salts were used but other salts such as Al, Zn, Fe, and Ni. The Cu reaction is different from other reactions. In the Cu reaction Re(CO)₃Cl(pyacH)₂, **2.2** was dissolved in 50 mL MeOH. The Cu(OAc)₂·H₂O was then dissolved in 20 mL of H₂O. The solutions were combined while stirring, and a precipitate formed. The precipitate was filtered out and washed with MeOH and water. The filtrate was then placed in test tubes so that crystals could grow. The solid was sent off for elemental analysis.

The other reactions were conducted as follows. The metal salt was dissolved in a solution of 100 mL of MeOH/H₂O with NaHCO₃. This solution was slowly added to the Re(CO)₃Cl(pyacH)₂, **2.2**, dissolved in MeOH while stirring. This addition was done over approximately 1 h. This approach was an attempt to maximize filtrate. The reason for the difference, specifically using a higher dilution than with the copper reaction, was to have more

filtrate from which to grow crystals. Some of the solution was then placed in test tubes so that crystals could grow. The remainder was put in a beaker and the solvent was evaporated, leaving a solid that was washed with MeOH and water. The solid was filtered out and sent for elemental analysis. No crystals grew from any of the experiments. The procedures used are discussed below. Another elemental analysis was taken. This time the solid was dissolved in CHCl_3 . The soluble portion was sent for analysis and the insoluble portion was not sent. These results are listed below. See the elemental analysis.

Table 2.2. Amounts Used for Dilute Experiments

	M	$\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$	NaHCO_3
$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	0.0283 g 1.41×10^{-4} mol	0.0970 g 1.47×10^{-4} mol	None
$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	0.0064 g 2.92×10^{-5} mol	0.0204 g 3.09×10^{-5} mol	0.0049 g 5.83×10^{-5} mol
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.0056 g 1.49×10^{-5} mol	0.0200 g 3.03×10^{-5} mol	0.0050 g 5.95×10^{-5} mol
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.0185 g 4.58×10^{-5} mol	0.0201 g 3.04×10^{-5} mol	0.0053 g 6.31×10^{-5} mol
$\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$	0.0071 g 2.85×10^{-5} mol	0.0207 g 3.14×10^{-5} mol	0.0052 g 6.19×10^{-5} mol

Anal Calcd For $[\text{Re}(\text{CO})_3\text{ClCu}(\text{pyac})_2]_4$ (**1.21**) sample Cu $\text{C}_{92}\text{H}_{88}\text{N}_8\text{O}_{28}\text{Re}_4\text{Cl}_4\text{Cu}_4$: C, 38.17; H, 3.06; N, 3.87; Found C, 38.42; H, 2.30; N, 4.00.

Anal Calcd For $[\text{Re}(\text{CO})_3\text{ClCu}(\text{pyac})_2]_4$ (**1.21**) sample Cu $\text{C}_{92}\text{H}_{88}\text{N}_8\text{O}_{28}\text{Re}_4\text{Cl}_4\text{Cu}_4$: C, 38.17; H, 3.06; N, 3.87; Found C, 41.14; H, 4.09; N, 2.24.

Anal Calcd For $[\text{Re}(\text{CO})_3\text{Cl}(\text{pyac})_2]_3\text{Al}_2$ sample Al $\text{H}_{60}\text{C}_{69}\text{N}_6\text{O}_{21}\text{Al}_2\text{Cl}_3\text{Re}_3$: C, 40.86; H, 2.98; N, 4.14; Found C, 43.19; H, 4.11; N, 4.17.

Anal Calcd For $[\text{Re}(\text{CO})_3\text{ClNi}(\text{pyac})_2]_4$ sample Ni $\text{C}_{92}\text{H}_{80}\text{N}_8\text{O}_{28}\text{Cl}_4\text{Re}_4\text{Ni}_4$: C, 38.54; H, 2.81; N, 3.91; Found C, 41.81; H, 3.87; N, 4.19.

Anal Calcd For $[\text{Re}(\text{CO})_3\text{Cl}(\text{pyac})_2]_3\text{Fe}_2$ sample Fe $\text{H}_{60}\text{C}_{69}\text{N}_6\text{O}_{21}\text{Cl}_3\text{Fe}_2\text{Re}_3$: C, 39.73; H, 2.90; N, 4.03; Found C, 58.43; H, 6.38; N, 1.22.

Anal Calcd For $[\text{Re}(\text{CO})_3\text{ClZn}(\text{pyac})_2]_4$ sample Zn $\text{C}_{92}\text{H}_{80}\text{N}_8\text{O}_{28}\text{Cl}_4\text{Re}_4\text{Zn}_4$: C, 38.18; H, 2.79; N, 3.87; Found C, 23.92; H, 1.89; N, 2.38.

The next series of reactions can be described as concentrated reactions. In these, there is an excess of Cu^{2+} reacting with $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$ **2.2** under concentrated conditions. The procedures used for these reactions are given below. In one experiment, a sample of $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$, **2.2**, (0.0200 g, 3.03×10^{-5} mol) was dissolved in 10 mL of CHCl_3 , to which $\text{Cu}(\text{NH}_3)_4^{2+}$ (aq) was added so the desired square would form. The $\text{Cu}(\text{NH}_3)_4^{2+}$ (aq) was prepared from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.0387 g, 1.55×10^{-4} mol) that was dissolved in H_2O . Then NH_4OH was added to the solution to create $\text{Cu}(\text{NH}_3)_4^{2+}$ (aq). This mixture was stirred for 17 h. At the conclusion of the stirring, the two phases were separated and the organic phase was washed with water. It was then dried over Na_2SO_4 . The solvent was evaporated off, leaving a forest green colored compound. This compound was triturated with MeOH and then filtered. This compound was not soluble in CH_2Cl_2 . It was designated Cu2 and sent off for elemental analysis. Anal Calcd For $[\text{Re}(\text{CO})_3\text{ClCu}(\text{pyac})_2]_4$ (**1.21**) sample Cu2 $\text{C}_{92}\text{H}_{88}\text{N}_8\text{O}_{28}\text{Re}_4\text{Cl}_4\text{Cu}_4$: C, 38.17; H, 3.06; N, 3.87; Found C, 38.42; H, 2.30; N, 4.00.

Another reaction was done with both $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$ **2.2** (0.0198 g, 3.00×10^{-5} mol) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.0274 g, 1.37×10^{-4} mol) dissolved in MeOH. The solution was evaporated, leaving a solid. The solid was triturated with MeOH, and then the solid was filtered. This compound was not soluble in CH_2Cl_2 .

The reaction was done again, but under more concentrated conditions. A total of (0.0207 g, 3.14×10^{-5} mol) of $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$ **2.2** and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.0280 g, 1.40×10^{-4} mol)

were dissolved in 8 mL MeOH and 2 mL H₂O and stirred for 12 h. The solution was evaporated, leaving a solid. The solid was triturated with MeOH and the solid was filtered out. A portion of this compound was soluble in CH₂Cl₂. The sample could be dried and then redissolved in CH₂Cl₂. This portion was used to set up layering experiments in an attempt to grow crystals with hexane over the Re/Cu complex in CH₂Cl₂. None of these layering experiments yielded any crystals. This reaction was run again with (0.0200 g, 3.03 x 10⁻⁵ mol) of Re(CO)₃Cl(pyacH)₂, **2.2**, and Cu(OAc)₂·H₂O (0.0279 g, 1.40 x 10⁻⁴ mol). A total of 0.0066 g was collected and sent off for elemental analysis and designated Cu3. Anal Calcd For [Re(CO)₃ClCu(pyac)₂]₄ (**1.21**) sample Cu₂ C₉₂H₈₈N₈O₂₈Re₄Cl₄Cu₄: C, 38.17; H, 3.06; N, 3.87; Found C, 34.38; H, 3.44; N, 1.19.

The final set of reactions can be described as attempting to grow crystals on templates. Groups of layering experiments were performed to grow [Re(CO)₃ClCu(pyac)₂]₄ **1.21** directly, but in these reactions guests were also introduced as templates so the complex could form around them. Several series of these were done with the guests 1,2-di(4-pyridyl)ethylene, 1,2-bis(4-pyridyl)ethane and Cu(pyac)₂ **1.20**. In these layering experiments, Re(CO)₃Cl(pyacH)₂ **2.2** was dissolved in CHCl₃ and Cu(OAc)₂·H₂O in MeOH. There was an intermediate middle layer with MeOH/CHCl₃. The guest was with the Re, the Cu, or the middle layer. In the case of Cu(pyac)₂ **1.20** the Re was dissolved in THF and the Cu(pyac)₂ **1.20** was always with the Re layer. None of the thirty layering experiments yielded any crystals.

2.3 Results and Discussion

2.3.1 IR Analyses of Direct Synthesis of Molecular Square [Re(CO)₃ClCu(pyac)₂]₄, **1.21** and Molecular “L” Re(CO)₃Cl(Cu(pyac)₂)₂, **1.22**

In this experiment, the samples Re1, Re1a, and Re1b (from Sect. 2.2.2), and Re2 (from Sect. 2.2.3), and Re(CO)₅Cl had thin film IR's taken. The CO stretching frequencies of Re1,

Re1a, Re1b, Re2 along with $\text{Re}(\text{CO})_5\text{Cl}$ **2.1** were measured (see Table 2.3). For the spectra of $\text{Re}(\text{CO})_5\text{Cl}$ **2.1** Re1, Re1a, Re1b, and Re2 (see Appendix, Spectrum 1-5).

The ν_{CO} values for samples Re1, Re1a, Re1b, and Re2 agreed with those values in the literature for $\text{ReCl}(\text{CO})_3(2,2'\text{-bpy})$, **2.4**, and $\text{ReCl}(\text{CO})_3(4,4'\text{-bpy})_2$, **2.5**, (see Fig. 2.6).^{2,5} However, these values do not match those of $\text{ReCl}(\text{CO})_4(\text{pyridine})$, **2.6**, which are 2111, 2009, 1934 cm^{-1} .^{2,6} From these data, it seems that $\text{Re}(\text{CO})_5\text{Cl}$ **2.1**, the starting material, did react to form $\text{Re}(\text{CO})_3\text{ClX}_2$ in the case of samples Re1, Re1a, Re1b, and Re2.

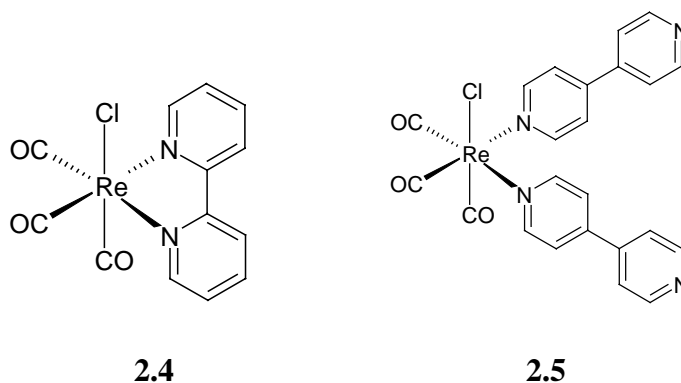


Fig. 2.6. Examples of Re Complexes

2.3.2 MS Analysis of Direct Synthesis of Molecular Square $[\text{Re}(\text{CO})_3\text{ClCu}(\text{pyac})_2]_4$, **1.21** and Molecular “L” $\text{Re}(\text{CO})_3\text{Cl}(\text{Cu}(\text{pyac})_2)_2$, **1.22**

Different MS techniques were used to characterize the different samples in this research. For the samples Re1a, Re1b, and Re2, MALDI-MS was used. By doing this experiment, one is able to determine if a molecule of the correct molecular weight is present. Although this alone doesn't confirm that the desired compound was made, it is another piece of evidence. In addition, MS and their fragmentation patterns are distinguishing characteristics of a compound.

The MALDI -MS was taken as an attempt to characterize samples Re1a and Re1b. If the samples are the correct compound, the molecular weight should be 2886.48 (see Appendix,

Spectrum 6a-c and 7a-c, respectively labeled as James 4588 with Dithranol and James 4589 with Dithranol).

The MALDI-MS was also taken as an attempt to characterize sample Re2. If the sample is the correct compound, the molecular weight should be 1137.57 (see Appendix, Spectrum 8 labeled as James 4590 with Dithranol).

Table 2.3. IR of CO Stretching Frequencies of Re Samples

Sample	ν_{CO}
Re1	2026
	----- 1896
Re1a	2026
	----- 1894
Re1b	2020
	----- 1888
Re2	2022
	1913
	1889
Re(CO) ₅ Cl	2022
	1949
[Re(CO) ₃ Cl(4,4'-bpy)] ₄ 1.9 ^{2,6}	2024 ¹
	1923
	1893
ReCl(CO) ₃ (2,2'-bpy), 2.4 ^{2,5}	2024 ²
	1921
	1899
ReCl(CO) ₃ (4,4'-bpy) ₂ , 2.5 ^{2,5}	2027 ³
	1926
	1891

In Spectrum 6a-c and Spectrum 7a-c, the parent ion was not shown to be present, and neither were any fragments, such as Re(CO)₃Cl(Cu(Pyac)₂)₂, **1.22**, (1137.57 FW); (Re(CO)₃Cl)₂(Cu(pyac)₂)₃ (1859.20 FW); (Re(CO)₃Cl)₃(Cu(pyac)₂)₃ (2164.89 FW); (Re(CO)₃Cl)₂(Cu(pyac)₂)₂ (1443.26 FW). In Spectrum 8a-d, the parent ion was not shown to be

¹FT-IR measurements taken in a solution in Acetone.

² FT-IR measurements taken in a solution in CH₂Cl₂.

³ Ibid.

present and neither were any fragments such as $\text{Re}(\text{CO})_3\text{Cl}(\text{Cu}(\text{pyac})_2)$ (721.62 FW). One conclusion that can be drawn is that the target molecules did not exist in the first place.

2.3.3 DLS Analysis of Samples Re1a and Re1b

A series of dynamic light scattering (DLS) experiments was carried out on samples Re1a and Re1b. The instrument used was one that had been custom built by the Russo group with a laser radiation of 6328 Å and an ALV-5000 digital autocorrelator.^{2,8} These experiments were done in an attempt to measure the molecular size of the samples. The attempted square has dimensions of 2 nm x 2 nm. Since the instrument's minimum detection size is 20 nm, it could tell if some type of polymer had been made if the sample was over 20 nm. Although it can detect particles below this limit (because it can tell the difference between a blank and a sample that is below its threshold), it cannot determine their size.

The samples Re1a and Re1b were dissolved in acetone and DMSO respectively, and the solutions were filtered through a 45-micrometer filter that was fitted on a syringe. The sample Re1a was measured twice over a period of 5 minutes. The first measurement gave a value of 40 nm, and the second gave a value of 100 nm. The sample Re1b was measured once, giving a value of 600 nm. The changing results for sample Re1a clearly show that the sample is aggregating, so no determination of size could be made. The result for sample Re1b is beyond the range for a normal polymer and is most likely also a result of aggregation of the sample. Therefore, no conclusions on the size of the molecules of the samples measured could be drawn from this method.^{2,9}

2.3.4 IR Analyses of Molecular “Corner” $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$, 2.2

An IR was taken of the sample prepared in section 2.1.21. The wavenumbers of the ν_{CO} stretching were 2020, 1908, and 1877 (see Appendix, Spectrum 9). These values match the

values of the compounds $[\text{Re}(\text{CO})_3\text{Cl}(4,4'\text{-bpy})_4]$ **2.5** 2024, 1923, 1893, $\text{ReCl}(\text{CO})_3(2,2'\text{-bpy})$ **2.4** $\text{ReCl}(\text{CO})_3(4,4'\text{-bpy})_2$ **2.5** and not the values of $\text{ReCl}(\text{CO})_4(\text{pyridine})$ **2.6** which are 2111, 2009, 1934 cm^{-1} .^{2,6} From these data, it seems that $\text{Re}(\text{CO})_5\text{Cl}$ **2.1** the starting material, did react to form $\text{Re}(\text{CO})_3\text{ClX}_2$ in this reaction.

2.3.5 X-ray Crystallography of Molecular “Corner” $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$, **2.2**

A sample of $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$ **2.2** was dissolved in CHCl_3 and hexane layered on top of this. Over 15 days, white needle-like crystals grew. An X-ray crystal structure was taken. This experiment revealed the desired compound in a 1:1 ratio with CHCl_3 (see Fig. 2.7 and Table 2.4). For the CIF File, see CIF 2.1. in Appendix.

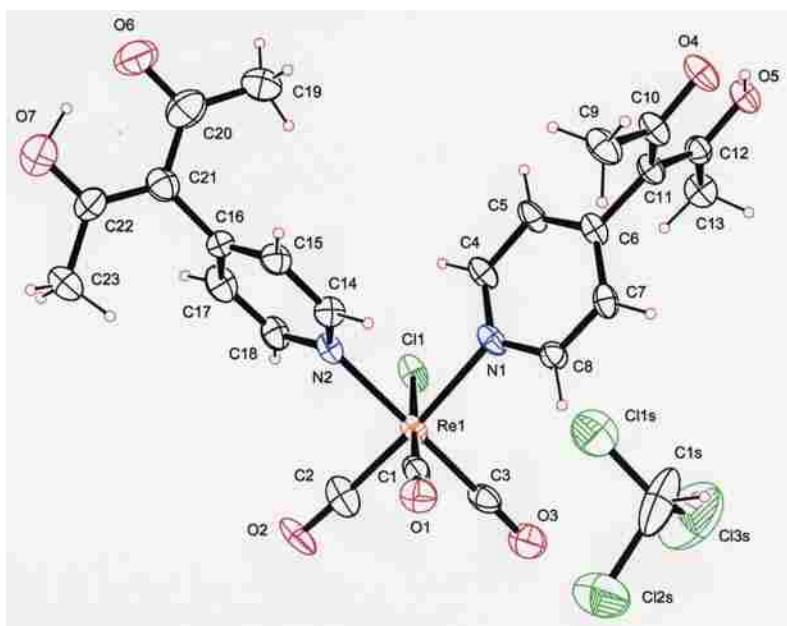


Fig. 2.7. X-ray Crystal Structure of $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$, **2.2**

The N1-Re1-N2 angle is 84.1° ; this angle is almost exactly the same as the as N1-Re1-N2 in $\text{Re}(\text{CO})_3\text{Cl}(\text{py})_2$, **2.3** which is 84.2° (see Fig. 2.8). Another compound that is very similar to the synthesized compound, $\text{ReCl}(\text{CO})_3(4,4'\text{-bpy})_2$, **2.5** has an N1-Re1-N2 angle of 87.0° .^{2,2} This is larger than the angle found in $\text{Re}(\text{CO})_3\text{Cl}(\text{py})_2$ **2.3** or $\text{Re}(\text{CO})_3\text{Cl}(\text{PyacH})_2$ **2.2**. The former compound was prepared as stated in the literature.^{2,11} Crystals were grown by dissolving

the substance in CH_2Cl_2 and allowing the solvent to evaporate. In $\text{ReCl}(\text{CO})_3(4,4'\text{-bpy})_2$ **2.5** the Re-N1 distance is 2.211 Å, while in $\text{Re}(\text{CO})_3\text{Cl}(\text{py})_2$ **2.3** the Re-N1 is 2.218 Å. In $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$ **2.2**, the Re-N1 and Re-N2 distance are 2.237 and 2.202 Å, respectively.^{2,10} It seems then, all of these compounds have approximately the same Re-N distance of 2.2 Å.

The other issue to note is that since the angle is so close to 90° , there is a strong possibility that when $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$ **2.2** is reacted with Cu(II) a tetramer or square would form, i.e. $[\text{Re}(\text{CO})_3\text{ClCu}(\text{pyac})_2]_4$ **1.21**.

Table 2.4. X-ray Crystal Parameters of $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$, **2.2**

Compound	$\text{Re}(\text{CO})_3\text{Cl}(\text{PyacH})_2$ 2.2
Crystal system	Monoclinic
Space group	$P2_1/c$
a(Å)	10.889 (4)
b(Å)	11.607 (4)
c(Å)	24.306 (10)
α (°)	90.0
β (°)	102.477 (14)
γ (°)	90.0
V(Å ³)	2999 (2)
Z	4
R	0.058

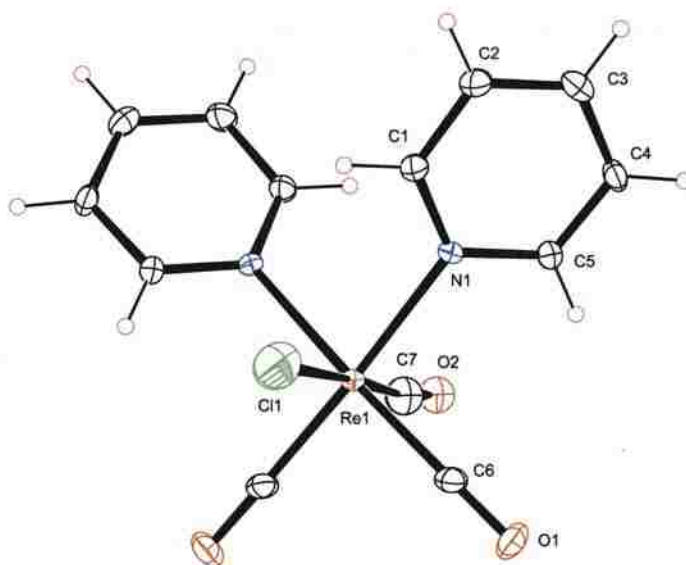


Fig. 2.8. X-ray Crystal Structure of $\text{Re}(\text{CO})_3\text{Cl}(\text{py})_2$, **2.3**

2.4 Conclusions and Future Work

From the research conducted, it can not be concluded that $[\text{Re}(\text{CO})_3\text{Cl}(\text{Cu}(\text{pyac}))_2]_4$ **1.21** or $\text{Re}(\text{CO})_3\text{Cl}(\text{Cu}(\text{pyac})_2)_2$ **1.22** were synthesized. This is because even though the IR evidence does show that CO stretching frequency is that of a tricarbonyl (see section 2.3.1), the MS data does not show the parent ion or any fragment (see section 2.3.2) and the elemental analysis of the compounds do not match that of the predicted.

Also, no MOFs were made from $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$ **2.2** using other metals such as Al, Zn, Ni, and Fe based on their elemental analysis.

On the positive side, $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$ **2.2** was prepared based on its elemental analysis, IR (see section 2.3.4), and crystal structure (see section 2.3.5)

The reason why the direct route did not work for $[\text{Re}(\text{CO})_3\text{Cl}(\text{Cu}(\text{pyac}))_2]_4$ **1.21** may be that the inherent weakness of $\text{Cu}(\text{pyac})_2$ **1.20**. When compared to (4,4'-bpy) in its analogous role in $[\text{Re}(\text{CO})_3\text{Cl}(4,4'\text{-bpy})]_4$ **1.9**, $\text{Cu}(\text{pyac})_2$ **1.20** is far less soluble than (4,4'-bpy) and has an affinity to form complexes with itself. This could have led to the formation of a polymeric product.

It is clear that although $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$ **2.2** was synthesized, no MOFs were created. There is no clear electronic or steric reason for $[\text{Re}(\text{CO})_3\text{Cl}(\text{Cu}(\text{pyac}))_2]_4$ **1.21** not to form, or any other targeted metal complexes. There is also a good chance that $[\text{Re}(\text{CO})_3\text{Cl}(\text{Cu}(\text{pyac}))_2]_4$ **1.21** would be more soluble, or at least as soluble as $\text{Cu}(\text{pyac})_2$ **1.20**. This is because of the CO groups and Cl on the Re. Also the squares would probably not cling to each other in the same manner as $\text{Cu}(\text{pyac})_2$ **1.20**. The inability of this experimental group series to succeed in forming metal complexes may come from a lack of appropriate conditions for necessary reactions, rather than from any absence of chemical theory or the application thereof. In future applications, the

researcher will seek to purify $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$ **2.2**, which will lead to an improved $^1\text{H-NMR}$ of this compound. This work will be written up and submitted to the journal *Acta Crystallographica Section E*.

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Chapter 3

The Attempted Synthesis of a Molecular Cube, $(\text{Pphac}_3)_8(\text{Cu})_{12}$

3.1 Introduction

The general goal of this research was to synthesize new MOFs to be used as hosts in host-guest chemistry. The specific goal of the Maverick research group is to develop a three-dimensional host. Our group decided to focus on a cube. This researcher came up with the idea of using a phosphine ligand as the corner, and a metal as the rod. The ligand that was eventually developed was Pphac_3H_3 **1.23** which, it was theorized, would form a cube $(\text{Pphac}_3)_8(\text{Cu})_{12}$ **1.24** when reacted with Cu (see Fig. 3.1). Our group hoped that including a moiety similar to $\text{Cu}(\text{pyac})_2$ **1.20**, in the design of the cube, would result in its properties being retained by the cube. The property that we most wanted to retain was the ability to bond to a guest. Our group has used $\text{Cu}(\text{pyac})_2$ **1.20** since 2002.

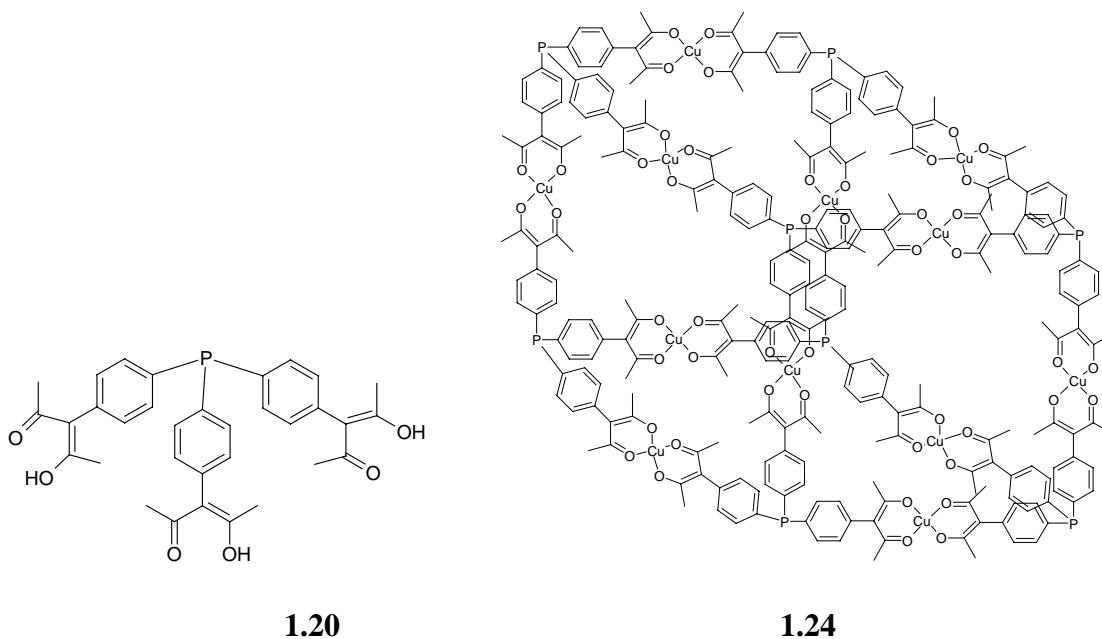


Fig. 3.1. The Target Molecules Pphac_3H_3 and $(\text{Pphac}_3)_8(\text{Cu})_{12}$

3.2 Experimental Section

3.2.1 Materials and Procedures

All reagents were used as received without further purification unless mentioned. These materials were of reagent grade or better.

The $^1\text{H-NMR}$ spectra were recorded on a Bruker DPX-250 spectrometer. Elemental analyses were performed by MHW Laboratories in Phoenix, Arizona. Mass spectrometer analyses were performed by the facilities at LSU. The X-ray crystallography was performed by Dr. Fronczek using the Nonius KappaCCD area-detector instrument equipped with a Mo $K\alpha$ source. All spectra are in the Appendix.

3.2.2 Synthesis of Tris(4-formylphenyl)Phosphine **2.2**

To prepare this compound, the precursor tris(4-formylphenyl)phosphine **3.1** was made first. This compound was prepared following and combining the elements of the procedures for the synthesis of tris(4-formylphenyl)phosphine, **3.1**^{3.1}, and bis(4-formylphenyl)dimethylsilane, **3.2**^{3.2}, (see Fig. 3.2).

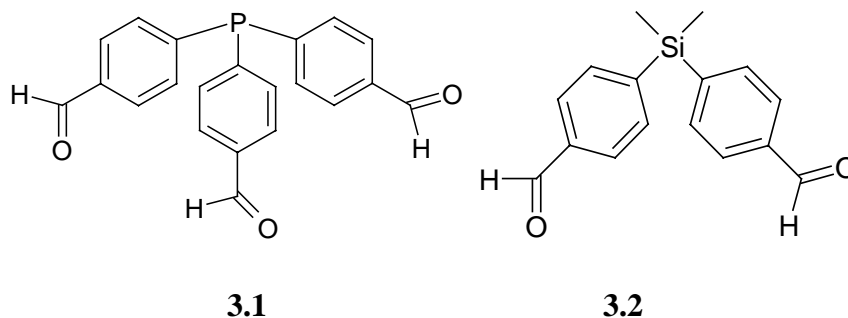
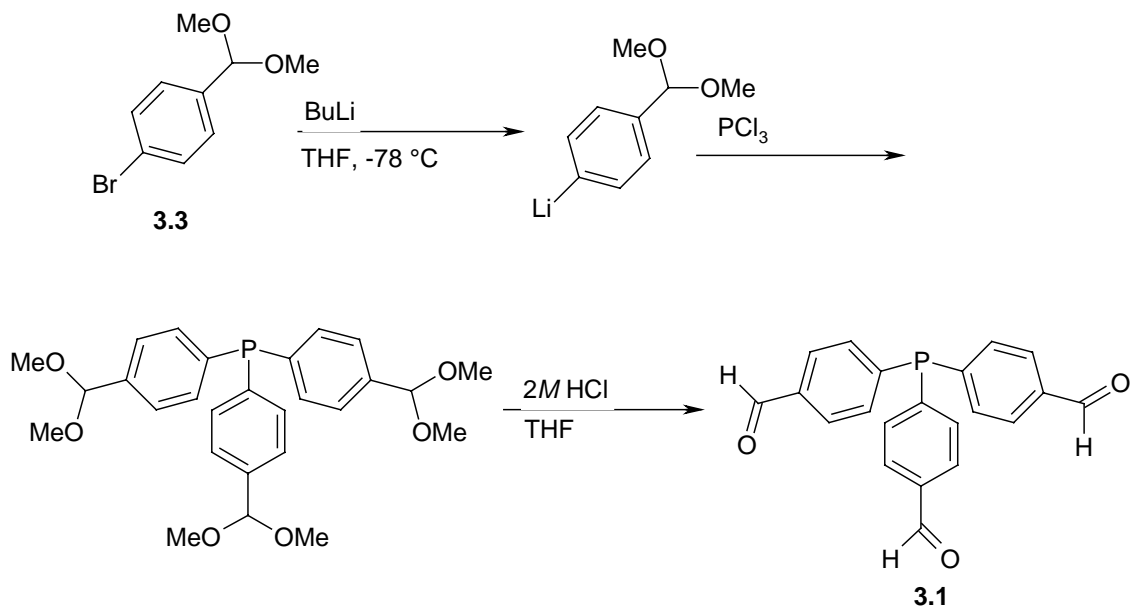


Fig. 3.2. Structure of Tris(4-formylphenyl)phosphine **3.1** and Bis(4-formylphenyl)dimethylsilane **3.2**.

A sample of 4-bromobenzaldehyde dimethyl acetal **3.3** (5 mL, 2.99×10^{-2} mol) was combined with 40 mL dry THF in an inert atmosphere in a round bottom flask. The solution was brought to $-78\text{ }^\circ\text{C}$ under streaming N_2 , and *n*-butyllithium/hexanes 1.6 M (19.8 mL, 3.17×10^{-2}

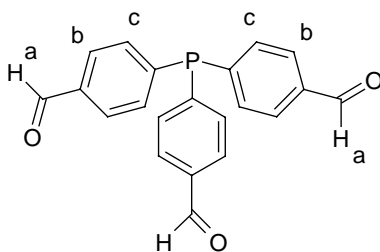
mol) was added over approximately 1 h while stirring. The solution initially turned from colorless to light yellow, then to milky white. After 2 h, at $-78\text{ }^{\circ}\text{C}$, PCl_3 (0.80 mL , $9.17 \times 10^{-3}\text{ mol}$) was added over a period of 15 minutes. When the PCl_3 was added, the solution turned orange-red. The solution was kept at $-78\text{ }^{\circ}\text{C}$ for another 1 h. (see Reaction Scheme 3.1).

Reaction Scheme 3.1. Synthetic Route to Tris(4-formylphenyl)phosphine, **3.1**



Then the solution was allowed to come to room temperature over 1 h. The solvent was evaporated, leaving the crude acetal. The crude acetal was dissolved in a mixture of dichloromethane and water. The solution was then washed: first with concentrated NaHCO_3 and then with brine. The organic phase was dried over Na_2SO_4 . The organic phase was then evaporated, leaving a residue (5.24 g). The sample was stored under N_2 in a freezer until the next day. The next day, the crude material was dissolved in 50 mL THF and $50\text{ mL } 2\text{ M HCl}$. The solution was stirred under reflux conditions for 1 h under a stream of N_2 . To the solution, 50 mL of water and 50 mL of ethyl acetate were added. The organic phase was then washed, first with concentrated NaHCO_3 and then with brine, dried over Na_2SO_4 and evaporated, leaving a residue (3.97g). This residue, which is the crude tris(4-formylphenyl)phosphine **3.1**, was dissolved in

25% CHCl₃/ 75% Ethyle acetate and applied to a silica gel column with 25% CHCl₃/ 75% Ethyle acetate as the mobile phase. The column was run as a flash column. This process yielded a pure tris(4-formylphenyl)phosphine **3.1** sample of 1.51 g. This is a percent yield of 44 %. The ¹H-NMR of tris(4-formylphenyl)phosphine **2.2** (250 MHz, CDCl₃) is as follows: 10.0 (s, 3H, Ha), 7.89 (d, 6H, *J* = 7.5, Hb), 7.50 (t, 6H, *J* = 7.5, Hc). ³¹P{¹H}NMR: -4.2 (see Fig. 3.3, and Spectrum 11, Spectrum 15,16). GC/MS: 346 (M⁺)



3.1

Fig. 3.3. Tris(4-formylphenyl)phosphine, **3.1** With its Hs Labeled

3.2.3. Synthesis of Tris(4-formylphenyl)Phosphine Oxide **3.4**

To prepare this compound, the precursor tris(4-formylphenyl)phosphine **3.1** was made first. This residue, which is the crude tris(4-formylphenyl)phosphine **3.1**, was dissolved in 25% CHCl₃/ 75% Ethyl acetate and applied to a silica gel column with 25% CHCl₃/ 75% Ethyl acetate as the mobile phase. The column was run as a flash column. This process yielded a pure tris(4-formylphenyl)phosphine oxide **3.4** sample of 1.92g. This is a percent yield of 56%. Its melting point was 128-130 °C. The ¹H-NMR of tris(4-formylphenyl)phosphine oxide **3.4** (250 MHz, CDCl₃) is as follows: ¹H-NMR: 10.1 (s, 3H, Ha), 8.03 (m, 6H, Hb), 7.91 (m, 6H, Hc). ³¹P{¹H}NMR: 26.9. A GC/MS of this compound showed peaks attributable to the parent ion (m/z 362 (M⁺) and 361((M-H)⁺)). (see Fig. 3.4, and Spectrum 12-14.)

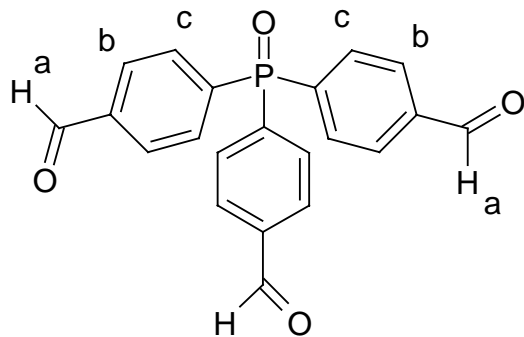


Fig. 3.4. Tris(4-formylphenyl)phosphine Oxide, **3.4** With its Hs Labeled

3.2.4. Synthesis of Pphac₃H₃ **1.23**

Samples of tris(4-formylphenyl)phosphine, **3.1** (0.65 g, 1.88×10^{-3} mol) and phospholene, **3.5** (1.30 g, 6.19×10^{-3} mol) were combined with 2-4 mL dry CH₂Cl₂ in an inert atmosphere. The stoichiometry of this reaction is 1 tris(4-formylphenyl)phosphine **3.1**: 3.3 phospholene **3.5**. The phospholene was synthesized, following procedures used by Ramirez et al.^{3.3} The solution was stirred for 24 h. Then 50 mL of MeOH was added to the solution, which was refluxed for 3 h under a stream of N₂. This produced the crude Pphac₃H₃ **1.23** (see Reaction Scheme 3.2).^{3.3-3.5} The solvent was evaporated and the residue dissolved in hot MeOH. H₂O was added until the solution became opaque. Over time Pphac₃H₃ **1.23** precipitated as a white solid. This reaction yielded 0.386 g (6.94×10^{-4} mol), which is a yield of approximately 37%. The ¹H-NMR (250 MHz, CDCl₃) is as follows: 16.69 ppm (s, 1, Ha), 7.28 ppm (m, 2, Hd), 7.16 ppm (m, 2, He), 1.92 ppm (s, 6, Hb). The ³¹P-NMR (300 MHz, CDCl₃) is as follows: -7.80 ppm (see Fig. 3.5, and Spectrum 17, 18).

3.2.5. Synthesis of OPphac₃H₃, **3.6**

A sample of Pphac₃H₃ **1.23** (0.015 g, 2.69×10^{-5} mol) was dissolved in 2 mL CH₂Cl₂. To this solution, 0.06 mL 0.8 M of NaClO (aq) (i.e. commercial chlorine bleach) was added and stirred for 5 minutes. This was done to quickly and completely convert Pphac₃H₃ **1.23** to

Reaction Scheme 3.2. Reaction to Synthesize Pphac₃H₃, 1.23

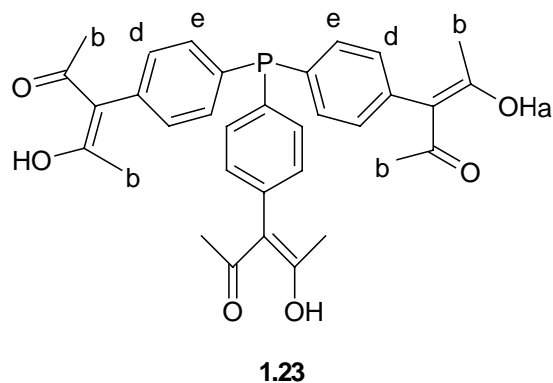
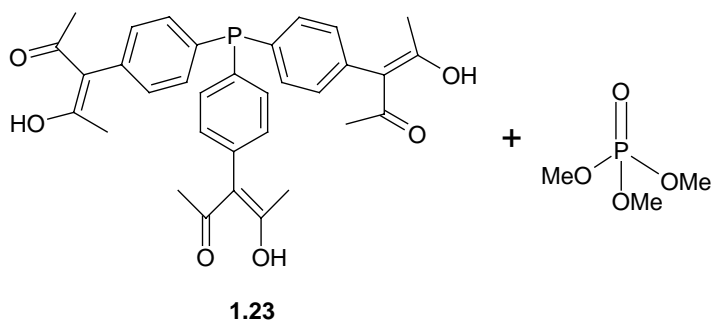
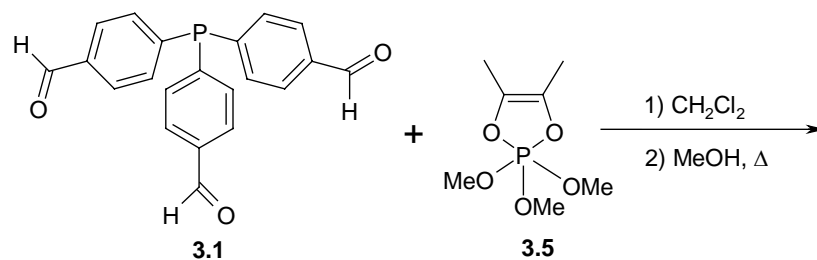
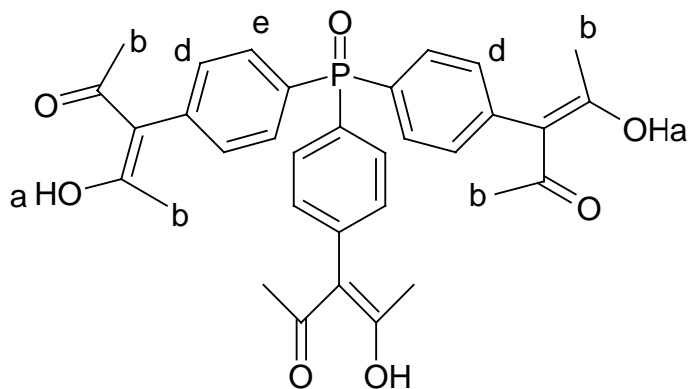


Fig. 3.5. Pphac₃H₃ 1.27 With its Hs Labeled

OPphac₃H₃ 3.6. This reaction produced 0.014 g (2.44×10^{-5} mol) a yield of 91%. The ¹H-NMR (250 MHz, CDCl₃) is as follows: 16.74 ppm (s, 1, Ha), 7.65 ppm (m, 2, Hd), 7.32 ppm (m, 2, He), 2.21 ppm (s, 6, Hb). The ³¹P-NMR (300 MHz, CDCl₃) is as follows: 28.52 ppm (see Fig. 3.6, and Spectrum 19, Spectrum 20).



3.6

Fig. 3.6. Pphac₃H₃ Oxide **3.6** With its Hs Labeled

3.2.6 Attempted Synthesis of (Pphac₃)₈(Cu)₁₂ **1.24**

The purified Pphac₃H₃ **1.23** (2.14 g, 3.84 mmol) was dissolved in 100 mL of CHCl₃. The resulting solution then had Cu(NH₃)₄²⁺ (aq) added. Then the organic phase of CHCl₃ was washed with water. The solvent was evaporated off, leaving a forest green powder (P1). The sample was triturated with MeOH at room temperature and the mixture was filtered, leaving a solid (P2) and a filtrate (P3). The solid was a light green while the filtrate was aqua blue. The filtrate had the MeOH evaporated off, leaving a solid. The original sample before trituration was labeled as P1. The filtered solid was labeled P2; it was only soluble in hot pyridine. The MeOH solution, once dried, was labeled P3; it was soluble in CH₂Cl₂, CHCl₃, and MeOH. The total amount of P1 was (1.65 g). The total amount of P2 was (1.12 g, 67% of P1) and P3 was (0.53 g, 33% of P1).

Layering experiments were set up with the sample P3 dissolved in MeOH using H₂O, hexane, EtOAc, and ether in an attempt to grow crystals. The solvents H₂O, hexane, EtOAc, and ether were used, because when a drop of P3 in MeOH was added to them, a precipitate formed. A total of 26 layering experiments was set up. Also, some P3 in MeOH was allowed to evaporate in an attempt to grow crystals. No crystals grew from these attempts, nor did a precipitate form.

Anal. Calcd. For (Pphac₃)₈(Cu)₁₂ (**1.24**) sample P2 C₂₆₄H₂₆₄Cu₁₂O₄₈P₈: C, 60.08; H, 4.66; Found C, 36.88; H, 4.53.

Anal. Calcd. For (Pphac₃)₈(Cu)₁₂ (**1.24**) sample P3 C₂₆₄H₂₆₄Cu₁₂O₄₈P₈: C, 60.08; H, 4.66; Found C, 58.34; H, 5.09.

Anal. Calcd. For (Pphac₃)₈(Cu)₁₂·2CHCl₃ sample P3 C₂₆₆H₂₆₆Cu₁₂O₄₈P₈Cl₆: C, 58.83; H, 4.49; Found C, 58.34; H, 5.09.

Anal. Calcd. For (Pphac₃)₈(Cu)₁₂ (**1.24**) sample P3 C₂₆₄H₂₆₄Cu₁₂O₄₈P₈: C, 60.08; H, 4.66; Cu, 14.62; P, 4.75; Found C, 59.34; H, 5.20; Cu, 3.70; P, 4.68. (This sample was prepared without adding any CHCl₃ to the P3 after the trituration with MeOH, to reduce the chances that the compound would be a solvate.)

3.3. Results and Discussion.

3.3.1. X-ray Crystal Structure of Tris(4-formylphenyl)phosphine Oxide **3.4**

The crystal structure was also determined for the tris(4-formylphenyl)phosphine oxide, **3.4**, this crystal was prepared by dissolving the oxide in THF, then allowing the solvent to evaporate over a week (see Fig. 3.7 and Table 3.1). For the CIF File, see CIF 3.1. in Appendix. The C8-P1-C1 angle of the molecule is 106°. Tris(4-formylphenyl)phosphine oxide **3.4** is less likely to form a β-diketone through a reaction with phospholene **3.5**. This is because the oxygen is electron withdrawing, which is inhibiting to the point that the reaction does not go to completion and stops at an intermediate step.^{3.3-3.6} This was also observed when

tris(4-formylphenyl)phosphine oxide **3.4** was treated with phospholene **3.5** and only a miniscule enol peak was detected. The C-P-C angle for tris(4-formylphenyl) phosphine **2.2** is probably close to that of triphenylphosphine, **3.3**, which is 103 ° (see Fig. 3.8)^{3.6}. The other

possible platonic solid that Pphac₃H₃ **1.23** could form with Cu(II) is a dodecahedron. The size of such dodecahedron would be 5 nm.

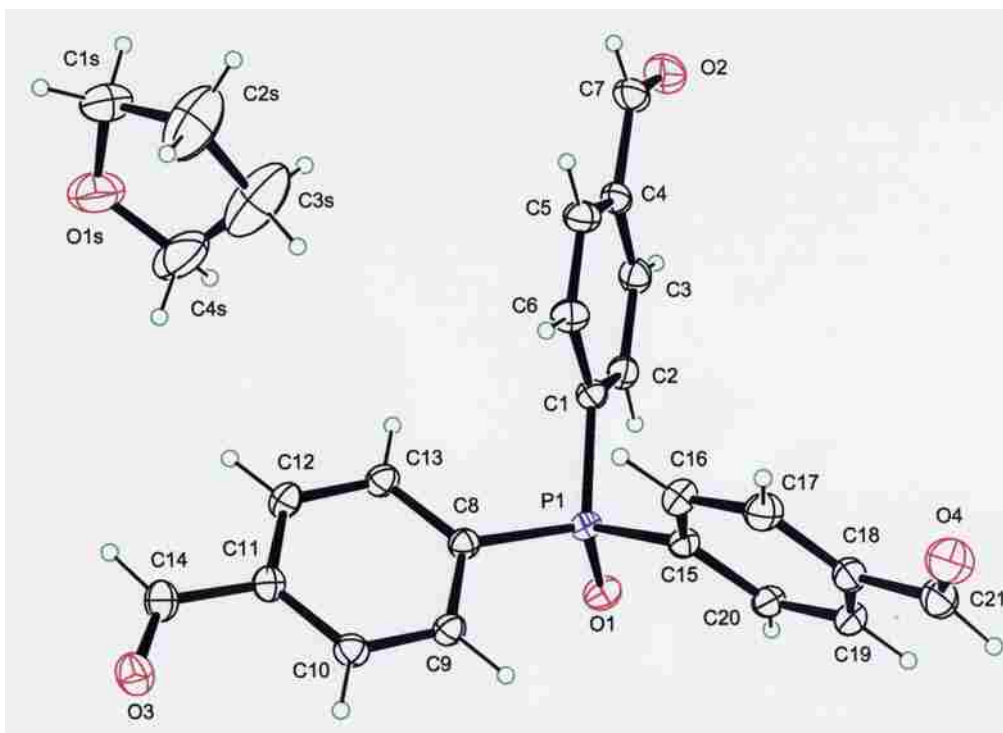


Fig. 3.7. X-ray Crystal Structure of Tris(4-formylphenyl)phosphine Oxide with THF, **3.4**

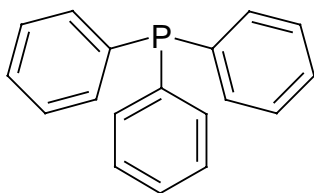
Table 3.1 X-ray Crystal Parameters of Tris(4-formylphenyl)phosphine Oxide, **3.4**

Compound	OP(C ₆ H ₄ -4-CHO) ₃ ·C ₄ H ₈ O
Crystal system	Monoclinic
Space group	<i>C2/c</i>
a(Å)	21.371 (3)
b(Å)	13.474 (2)
c(Å)	13.436 (2)
α(°)	90.0
β(°)	99.018 (9)
γ(°)	90.0
V(Å ³)	3821.1 (10)
Z	8
R	0.042

3.3.2. Phosphine Cycle

After working with the different phosphine compounds, the interrelationships among them came to light. The tris(4-formylphenyl)phosphine **3.1** can be treated with phospholene to

form the acac Pphac_3H_3 **1.23**. Tris(4-formylphenyl)phosphine **3.1** though, is O_2 sensitive. If left out in open atmosphere, it will convert to tris(4-formylphenyl)phosphine oxide **3.4** in approximately 48 hours. This oxidation can be prevented by keeping tris(4-formylphenyl)phosphine **3.1** in an inert atmosphere. Tris(4-formylphenyl)phosphine oxide **3.1**, when treated with phospholene, doesn't form any appreciable Pphac_3H_3 oxide, **3.6**. Pphac_3H_3 **1.23** is also O_2 sensitive; therefore, if left out in open atmosphere, Pphac_3H_3 **1.23** will convert to $\text{OPphac}_3\text{H}_3$ **3.6** in less than 10 hours. These relationships can be seen in Fig. 3.9



3.7

Fig. 3.8. Triphenylphosphine **3.7**

3.4 Conclusions and Future Work.

From the research conducted $(\text{Pphac}_3)_8(\text{Cu})_{12}$ **1.24**, was not synthesized. It is clear though, that Pphac_3H_3 **1.23** and $\text{OPphac}_3\text{H}_3$ **3.6** were synthesized.

The primary reason why the MOFs was not created was because the ligands Pphac_3H_3 **1.23** and $\text{OPphac}_3\text{H}_3$ **3.6** took far longer to create than was initially anticipated. This was due to the fact that the synthesizing of the underlying molecule tris(4-formylphenyl)phosphine **3.1**, was in the literature, yet not well understood. In other words, the literature procedure was never reproduced. Additionally, in the literature and when asking the authors directly, the compound sensitivity of tris(4-formylphenyl)phosphine **3.1** to O_2 remained unknown. This all led to spending far more time than anticipated in creating a new path to the molecule, but the process led to the creation of the new molecule tris(4-formylphenyl)phosphine oxide **3.4**, as well as

targets, Pphac₃H₃ **1.23** and OPphac₃H₃ **3.6**. With this established synthesis of OPphac₃H₃ **3.6**, future research can be conducted and will most probably synthesize (OPphac₃)₈(Cu)₁₂ **3.8**. (see figure 3.10) or if not such a complex molecule, at least a simpler metal complex.

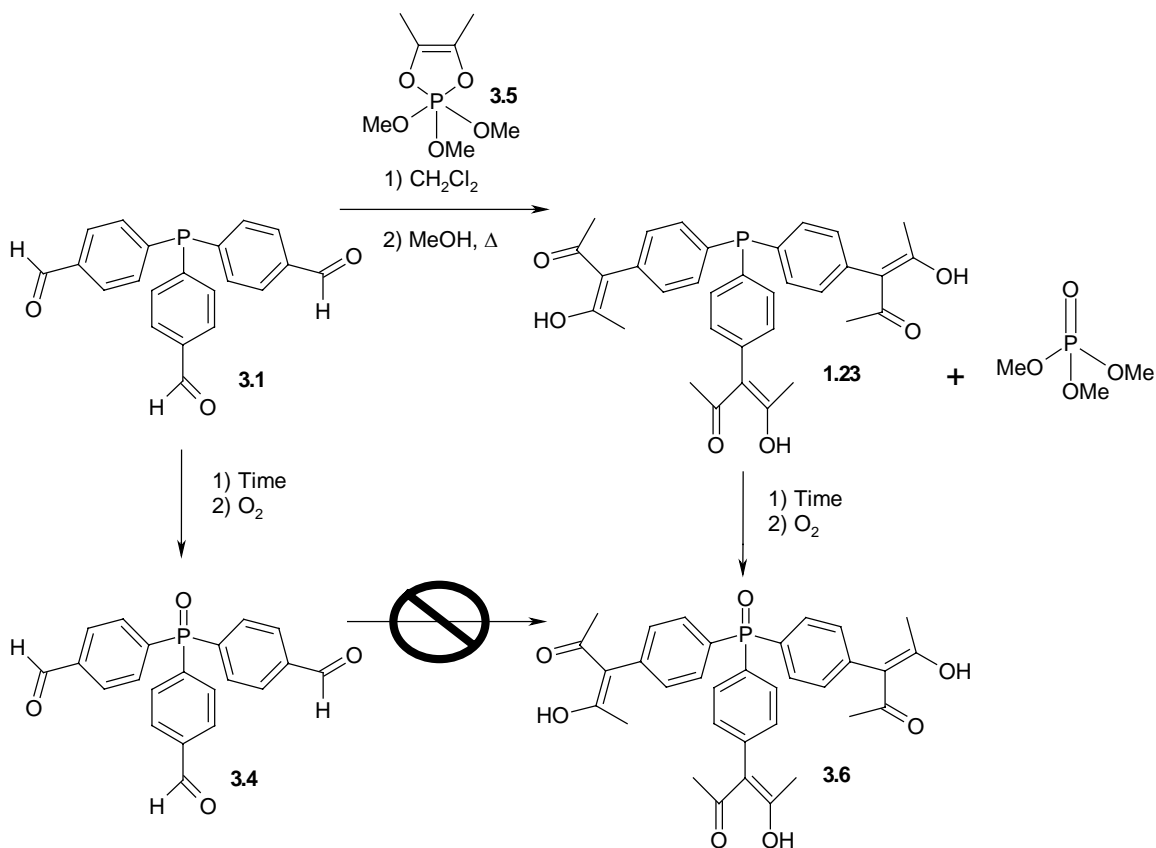


Fig. 3.9. The Interrelationship Between the Different Phosphines

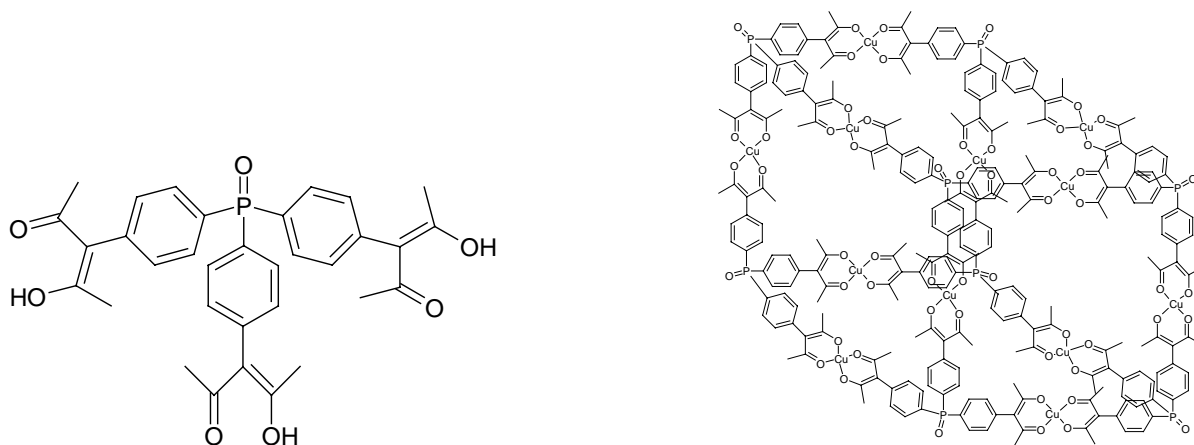


Figure 3.10. Target Molecules OPphac₃H₃ **3.6** and (OPphac₃)₈(Cu)₁₂ **3.8**.

This research will continue to obtain an elemental analysis of the discussed molecules and MS for Pphac₃H₃ **1.23** and OPphac₃H₃ **3.6**. Also, attempts will be made to obtain crystal structures of those molecules that have none. This will be done in preparation of submitting this work to the journal *Tetrahedron*.

3.5 References

- 3.1 Bartlett, P. A.; Bauer, B.; Singer, S. J. *J. Am. Chem. Soc.* **1978**, *100*, 5085-5089.
- 3.2 Kumagai, T.; Itsuno, S. *Tetrahedron: Asymmetry*. **2001**, *12*, 2509-2516.
- 3.3 Ramirez, F.; Ramanathan, N.; Desai, N. B. *J. Am. Chem. Soc.*, **1962**, *84*, 1317-1318.
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- 3.5 Ramirez, F.; Bhatia, S. B.; Patwardhan, A. V.; Smith, C. P. *J. Org. Chem.*, **1967**, *32*, 3547-3553.
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Chapter 4

Conclusions and Future Work

The goal of this research was to synthesize new MOFs. This goal was pursued by attempting to synthesize a Re molecular square $[\text{Re}(\text{CO})_3\text{ClCu}(\text{Pyac})_2]_4$ **1.21** and a phosphine cube $(\text{Pphac}_3)_8(\text{Cu})_{12}$ **1.24** (see Fig. 4.1).

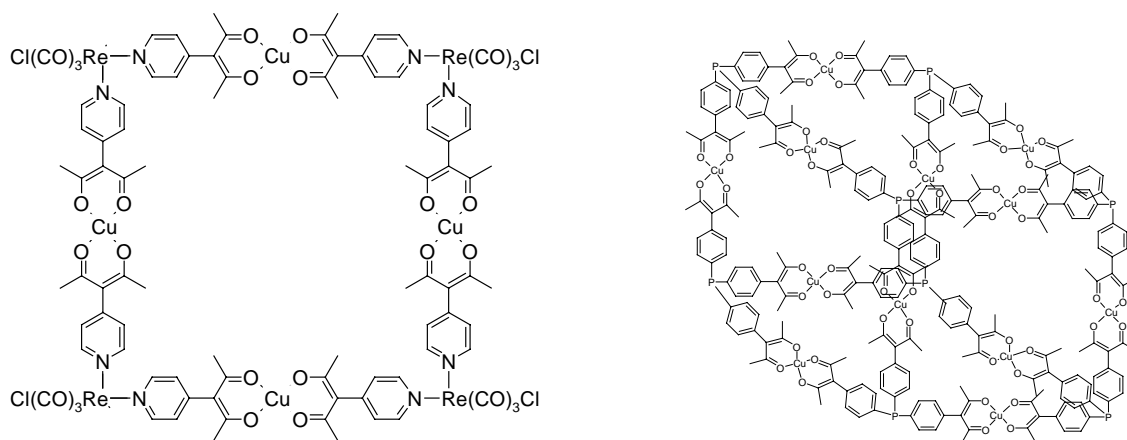


Fig. 4.1 Target Molecular Square and Cube

These target molecules were not achieved. Possible precursor molecules to synthesize this molecule were synthesized.

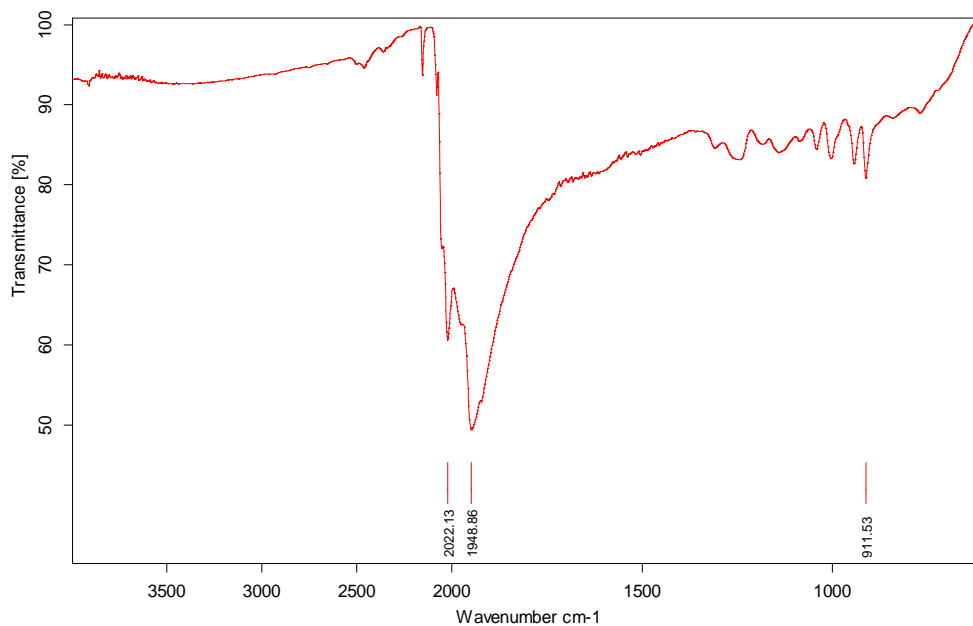
In the case of the Re research $\text{Re}(\text{CO})_3\text{Cl}(\text{PyacH})_2$ **2.2** was made the target MOF $[\text{Re}(\text{CO})_3\text{Cl}(\text{Cu}(\text{Pyac}))_2]_4$ **1.21** was not. To make this Re square two approaches were applied a direct synthesis and a second making $\text{Re}(\text{CO})_3\text{Cl}(\text{PyacH})_2$ **2.2** then reacting it with a metal. This is why it was created. The reason why direct synthesis did not work as it had in the creation of $[\text{Re}(\text{CO})_3\text{Cl}(4,4'\text{-bpy})]_4$ **1.9** can be probably accounted for by the differences between the two rods i.e. (4,4'-bpy) and $\text{Cu}(\text{Pyac})_2$ **1.20**. This approach took up most of the researchers time before working on the second approach. The reason for the failure of the second approach is most probably due to not finding the right conditions and since the ground work here has been laid a future research should be able to find the right conditions and create the target MOF.

In the area of the phosphine research it can not be concluded that the MOF $(\text{Pphac}_3)_8(\text{Cu})_{12}$ **1.24** was made. The positive conclusions that can be drawn though are that Pphac_3H_3 **1.23** and $\text{OPphac}_3\text{H}_3$ **3.6** were made. The reason for not synthesizing $(\text{Pphac}_3)_8(\text{Cu})$ **1.24** was that too much time was expended on preparing the precursor compound. This was due to the fact the literature used to make this compound may not have included all the information needed to prepare tris(4-formylphenyl)phosphine 3.1. This then forced the researcher to develop a new way to make the target molecule.

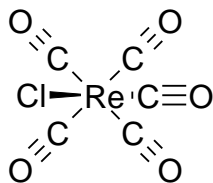
With more time then since the ground work has been laid, future research can take the new molecules Pphac_3H_3 **1.23** and $\text{OPphac}_3\text{H}_3$ **3.6** and create if not MOFs at least simple metal complexes.

Appendix Spectra

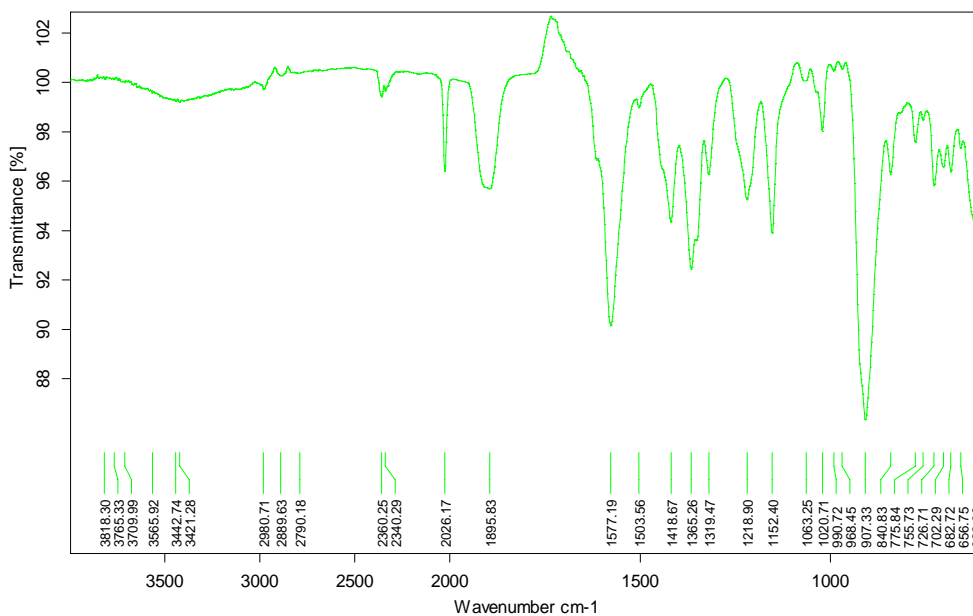
Spectrum 1. IR spectrum (thin film) of $\text{Re}(\text{CO})_5\text{Cl}$ 2.6



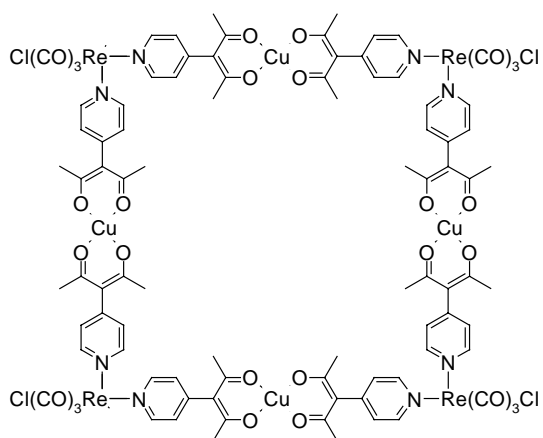
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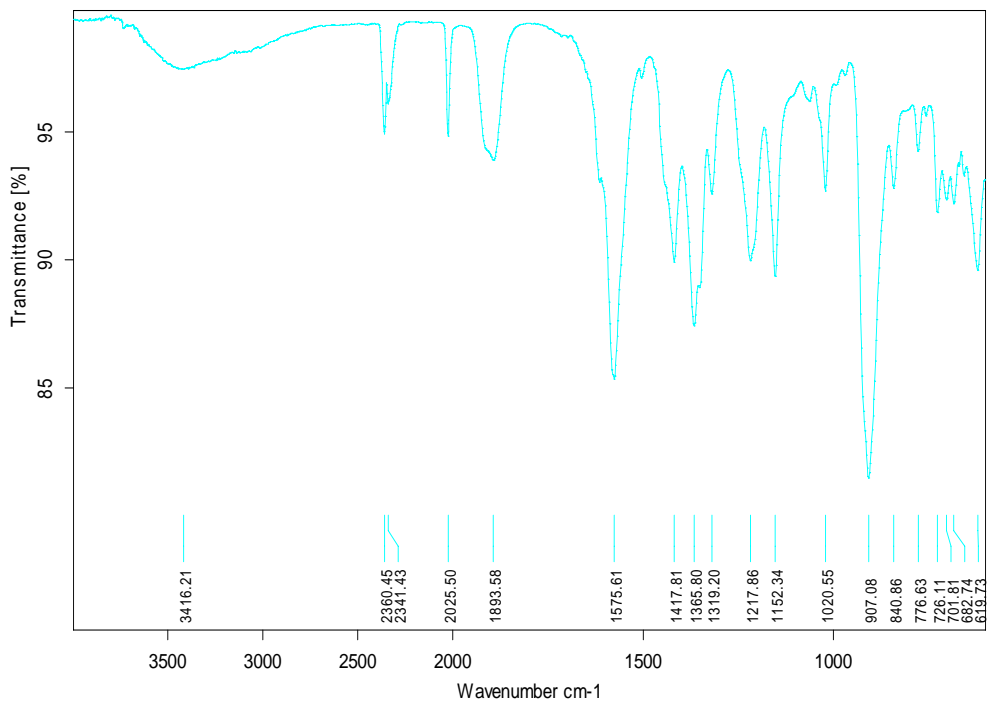
Spectrum 2. IR spectrum (thin film) of possible “molecular square” product Re1



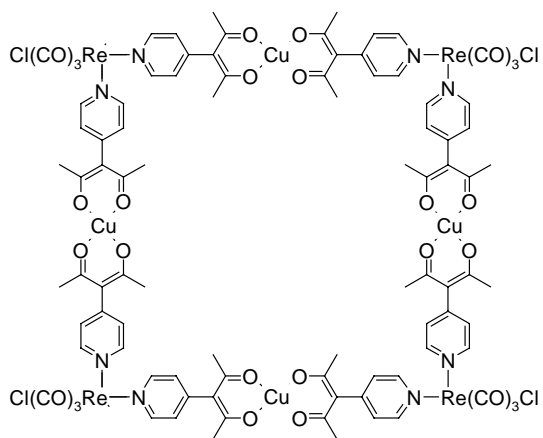
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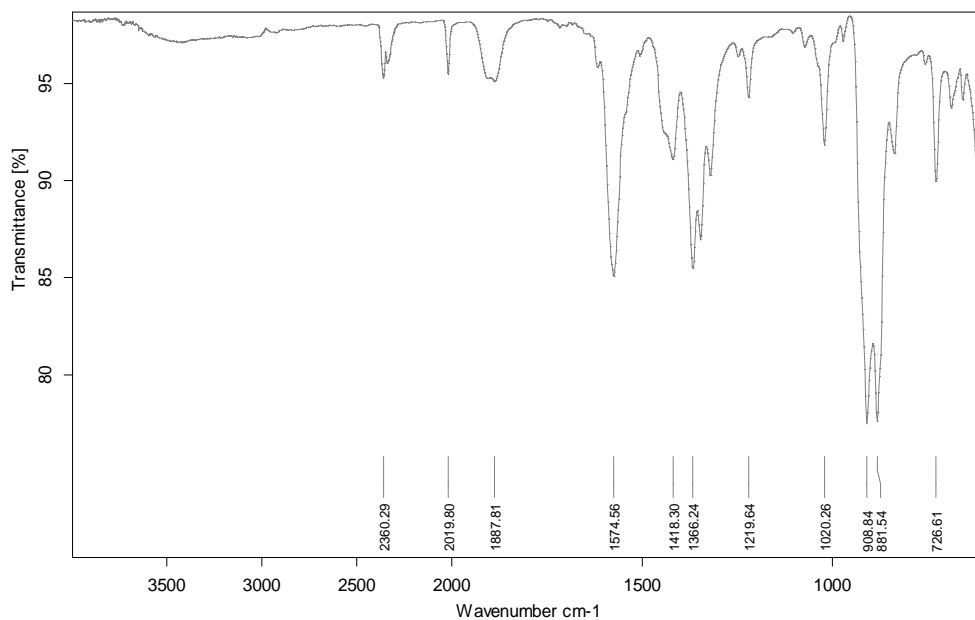
Spectrum 3. IR spectrum (thin film) of Re1a, possible “molecular square” product



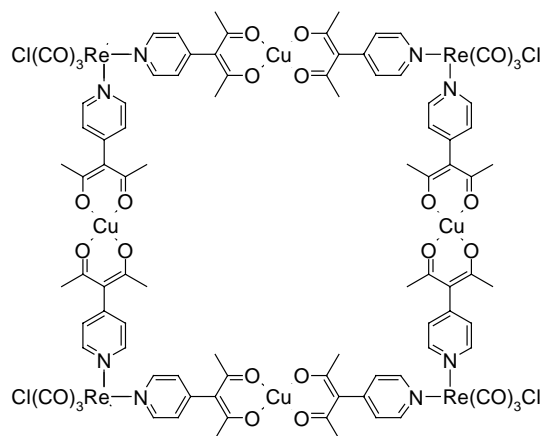
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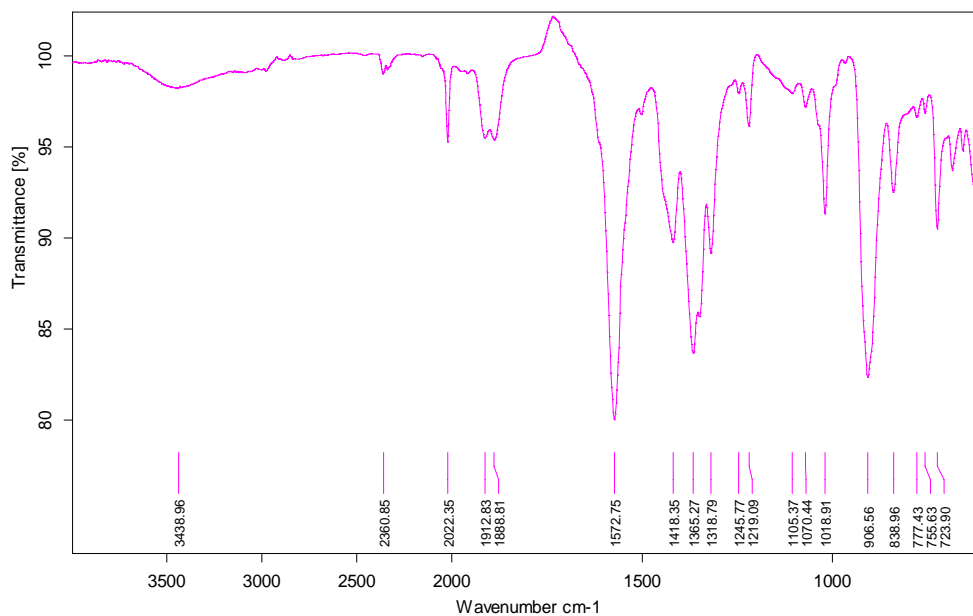
Spectrum 4. IR spectrum (thin film) of possible “molecular square” product Re1b



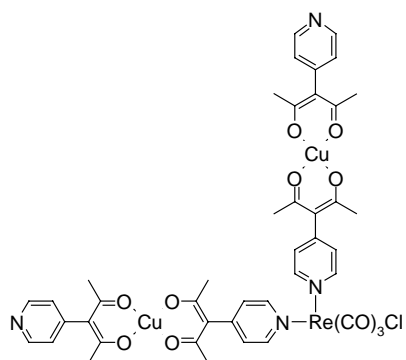
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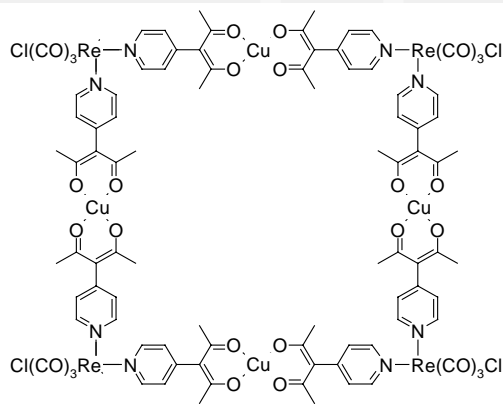
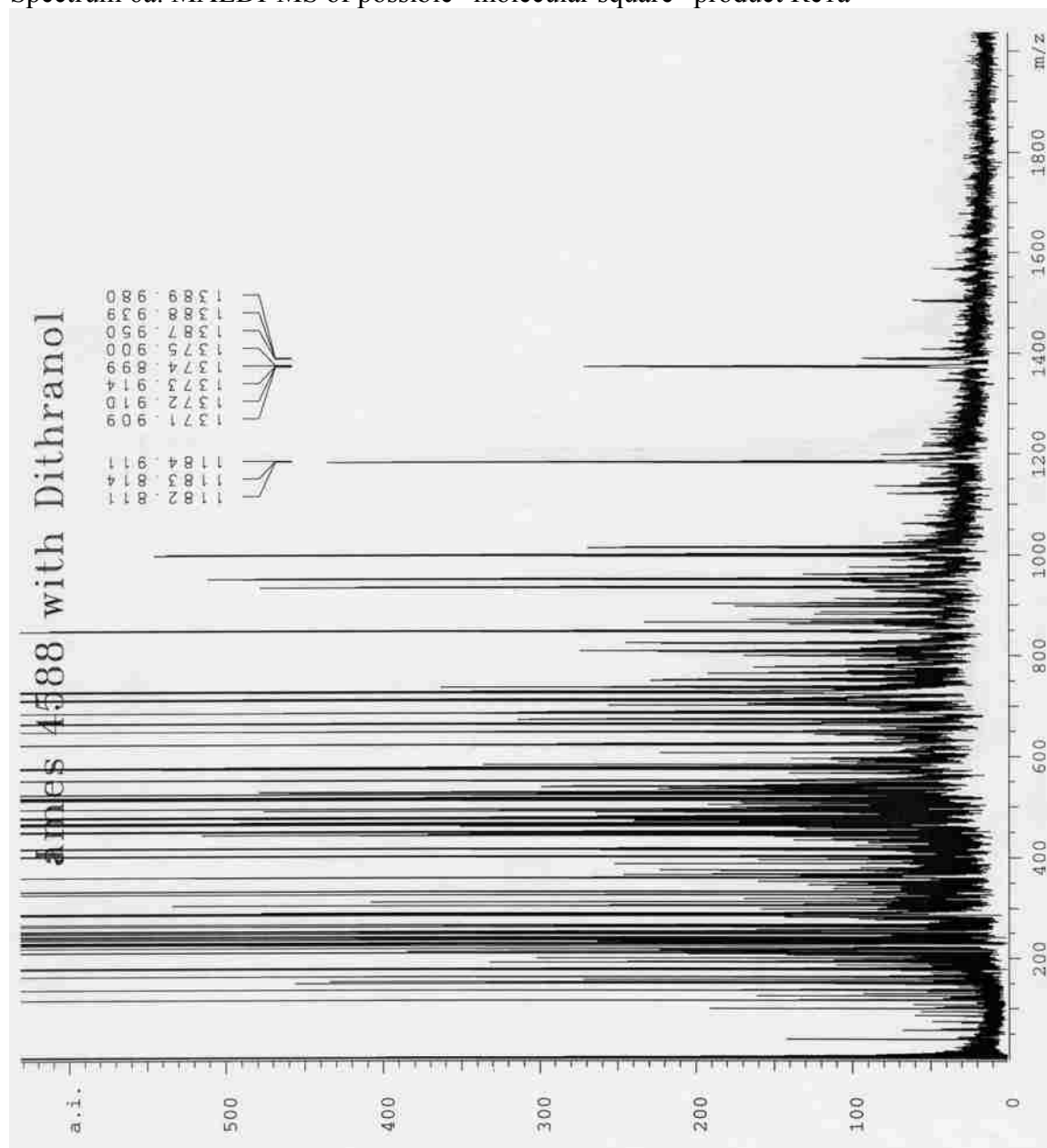
Spectrum 5. IR spectrum (thin film) of possible "L" product Re2



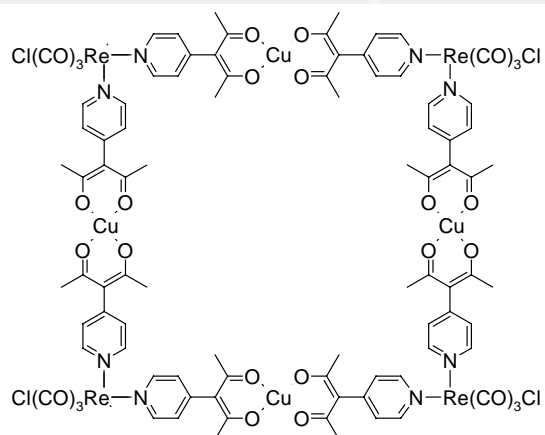
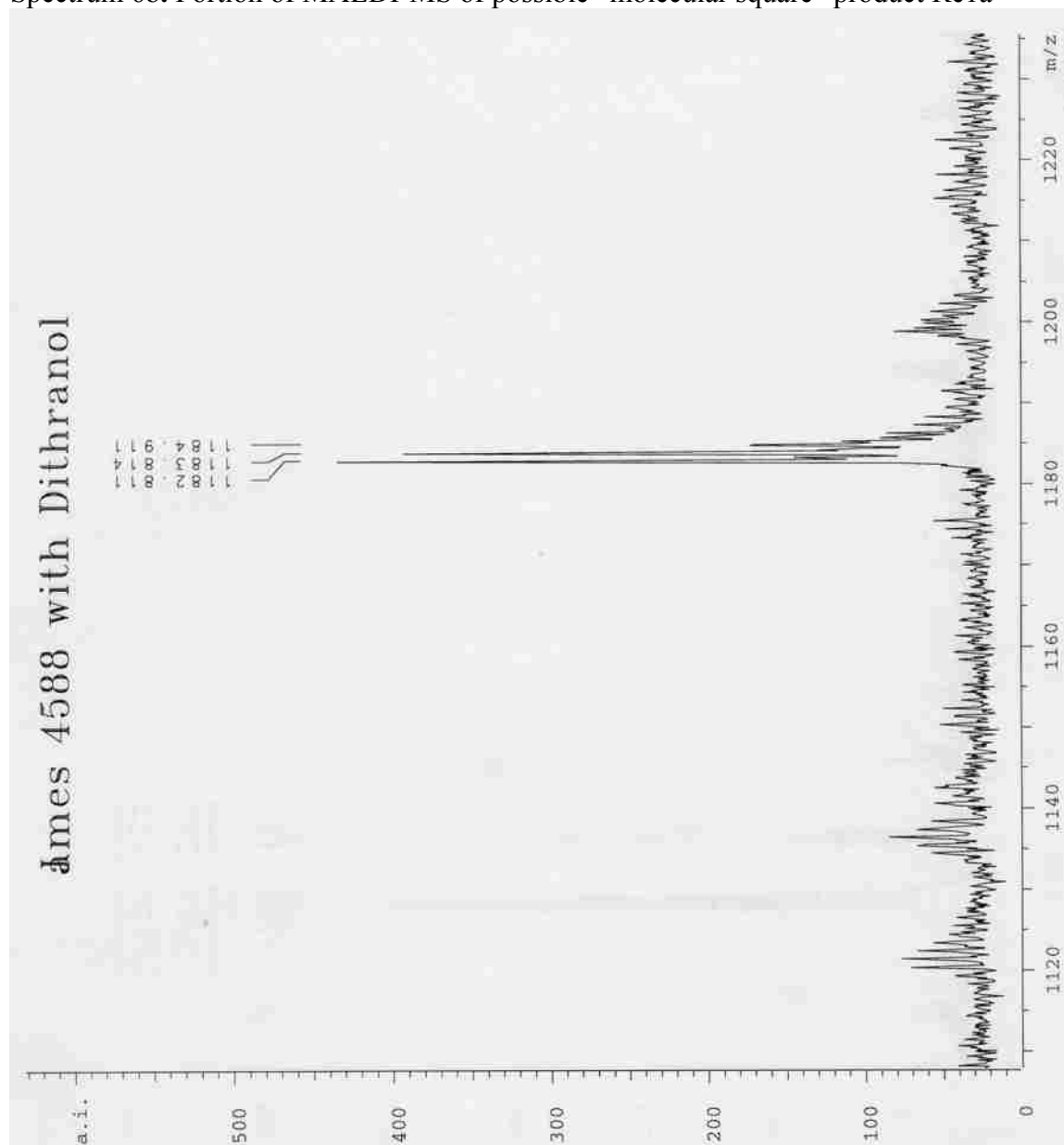
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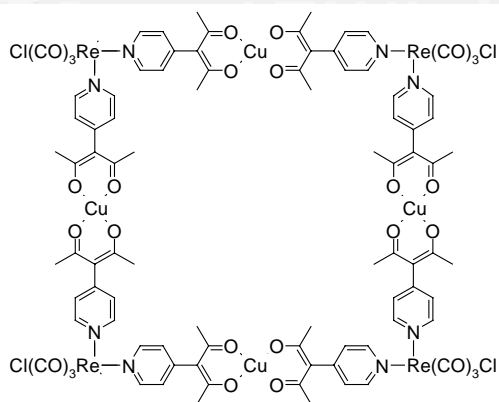
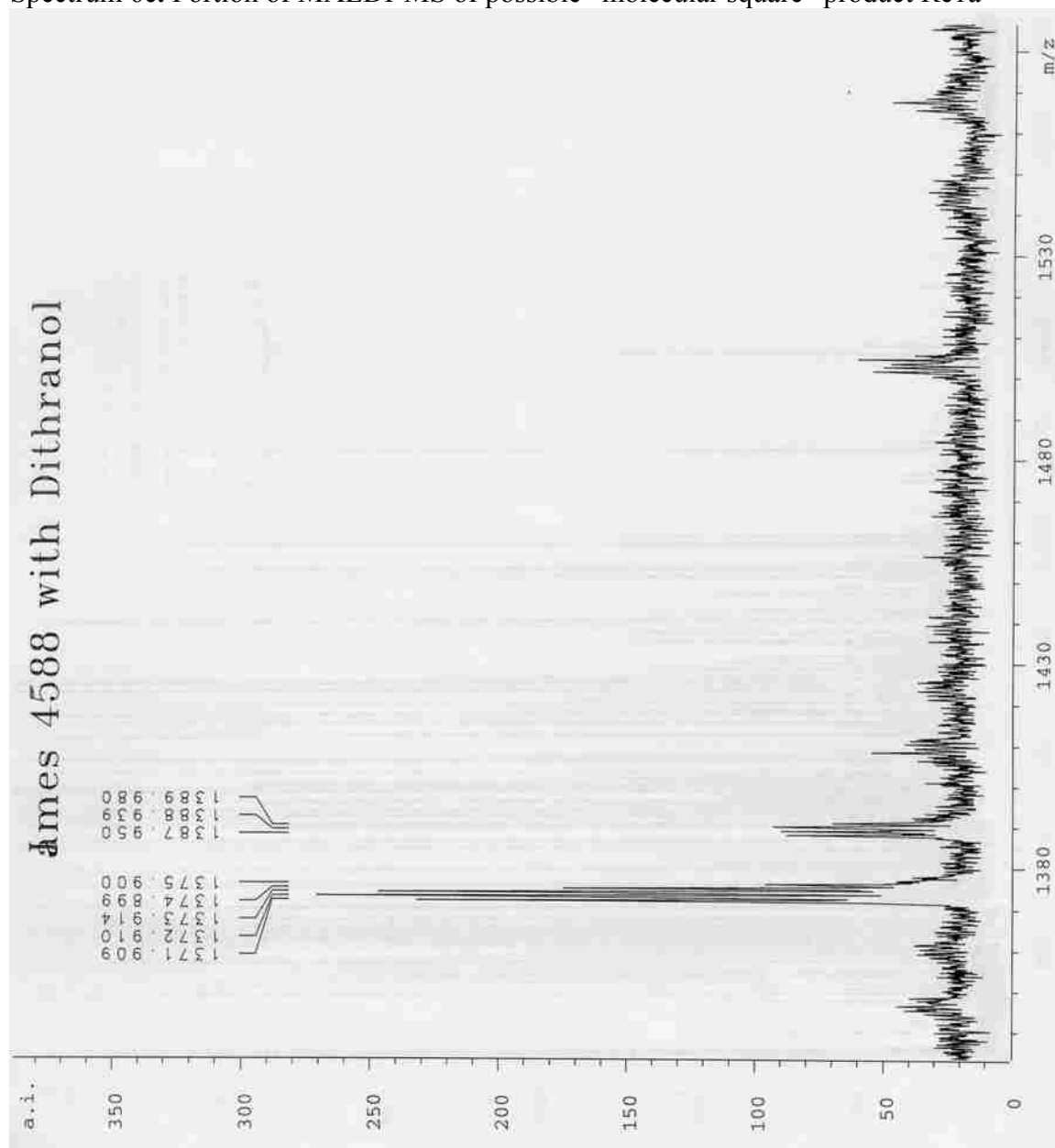
Spectrum 6a. MALDI-MS of possible “molecular square” product Re1a



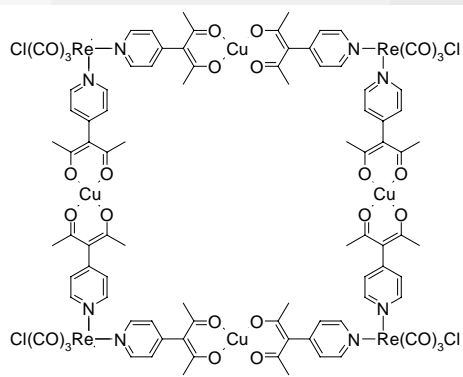
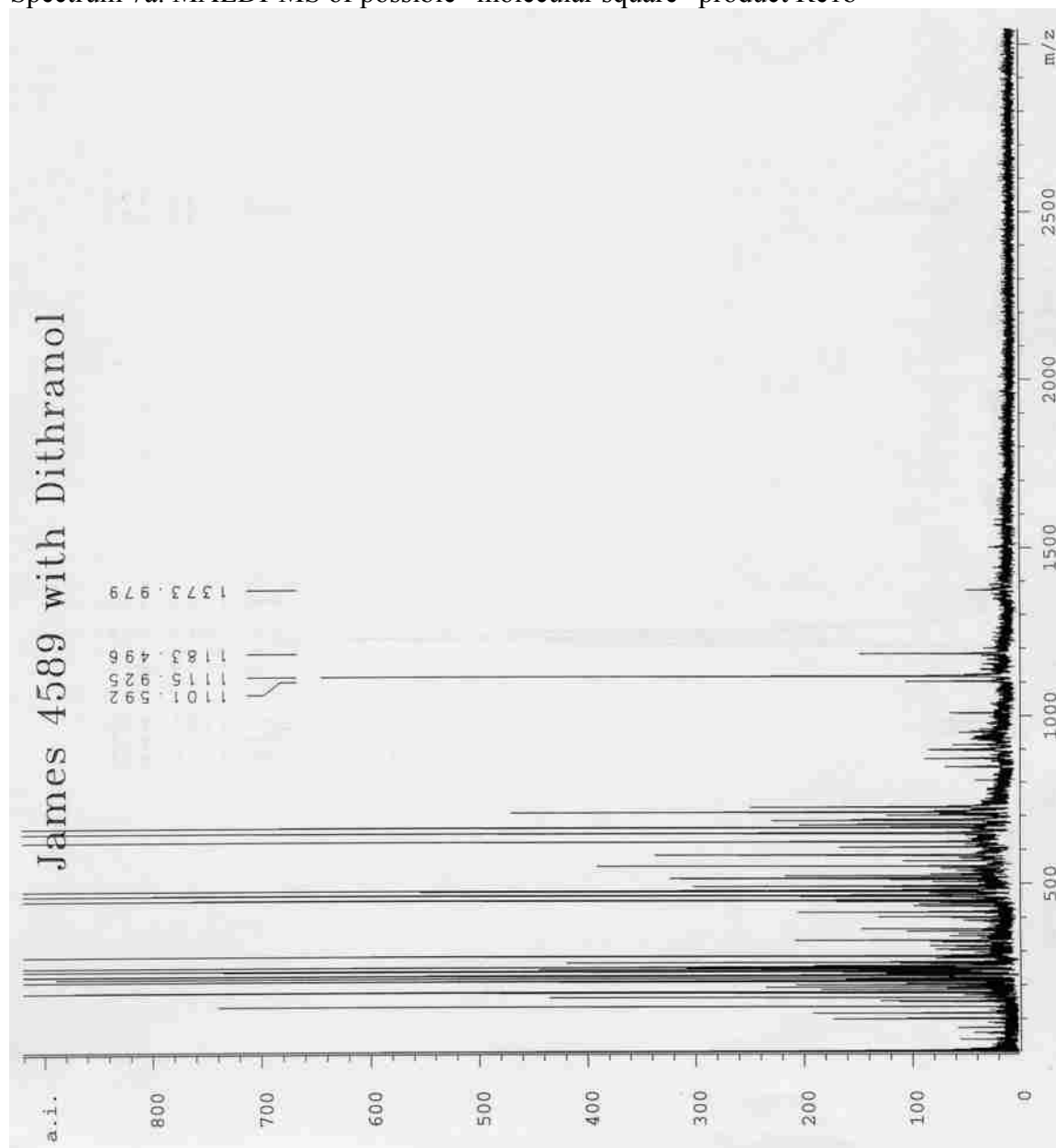
Spectrum 6b. Portion of MALDI-MS of possible “molecular square” product Re1a



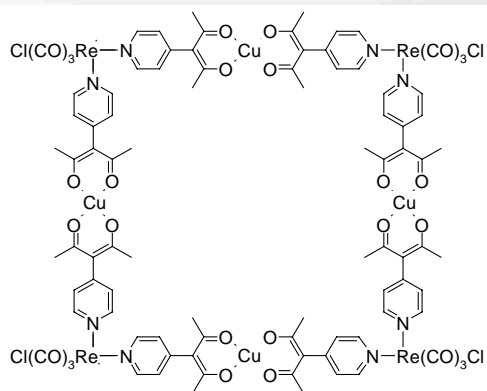
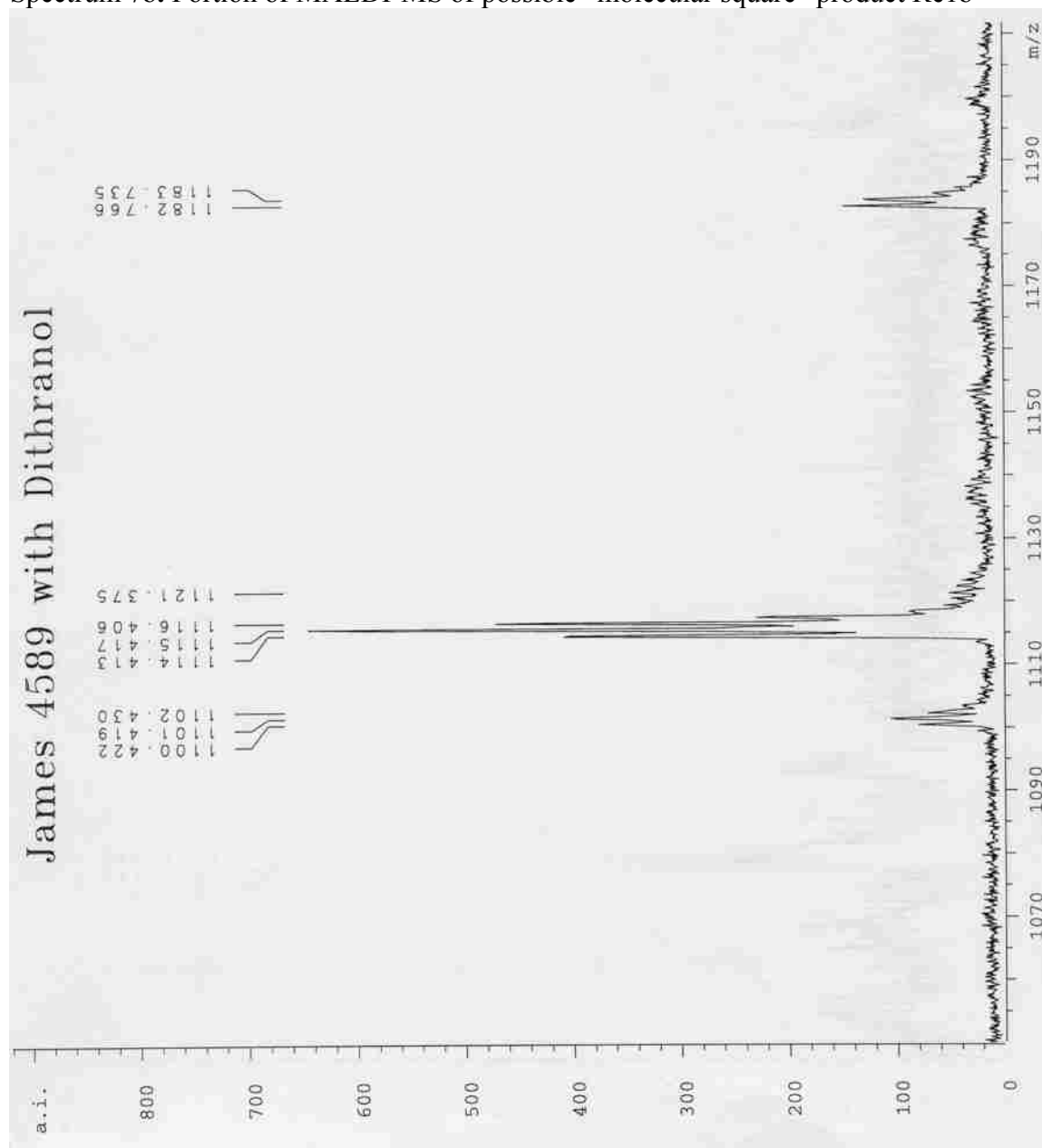
Spectrum 6c. Portion of MALDI-MS of possible “molecular square” product Re1a



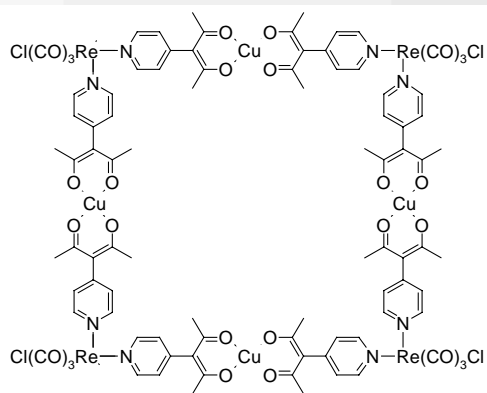
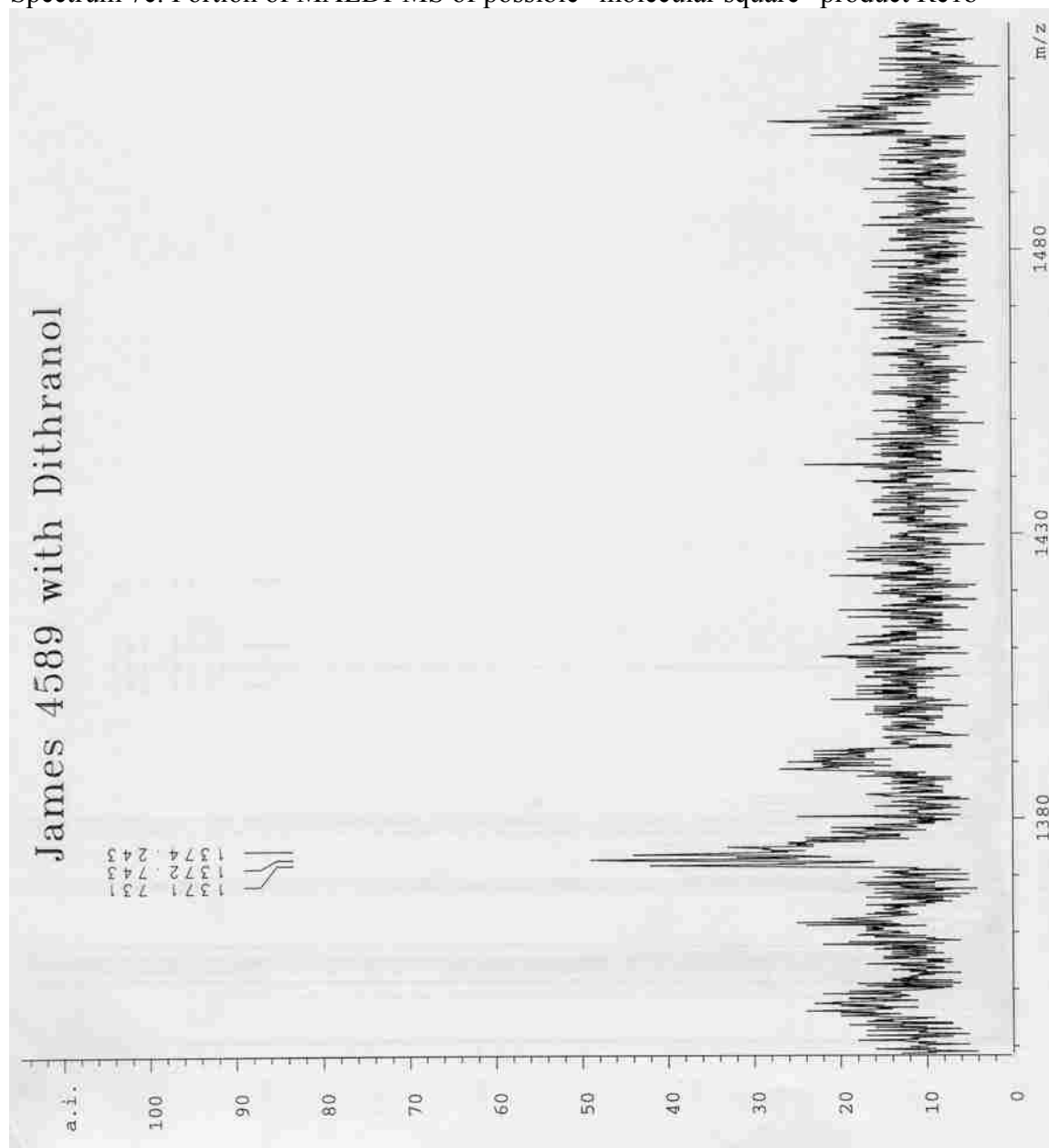
Spectrum 7a. MALDI-MS of possible “molecular square” product Re1b



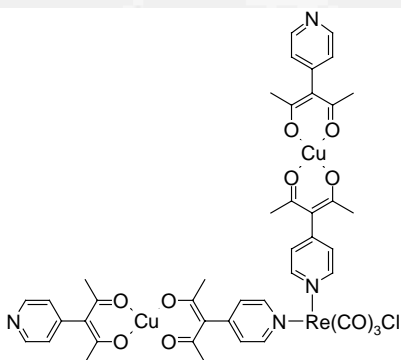
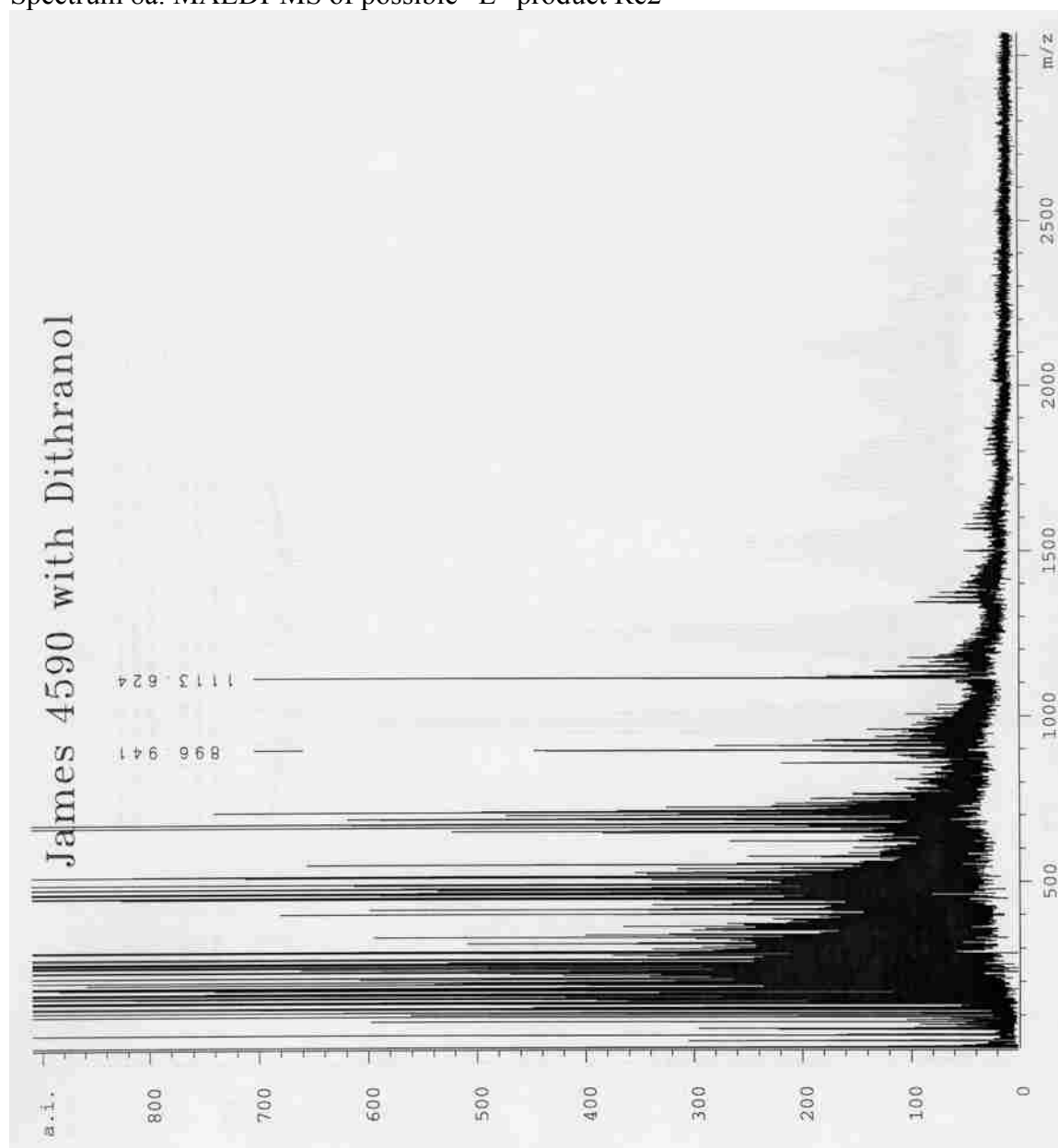
Spectrum 7b. Portion of MALDI-MS of possible “molecular square” product Re1b



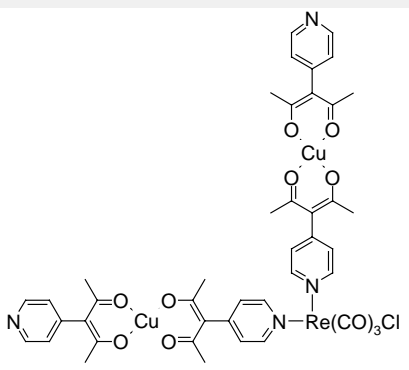
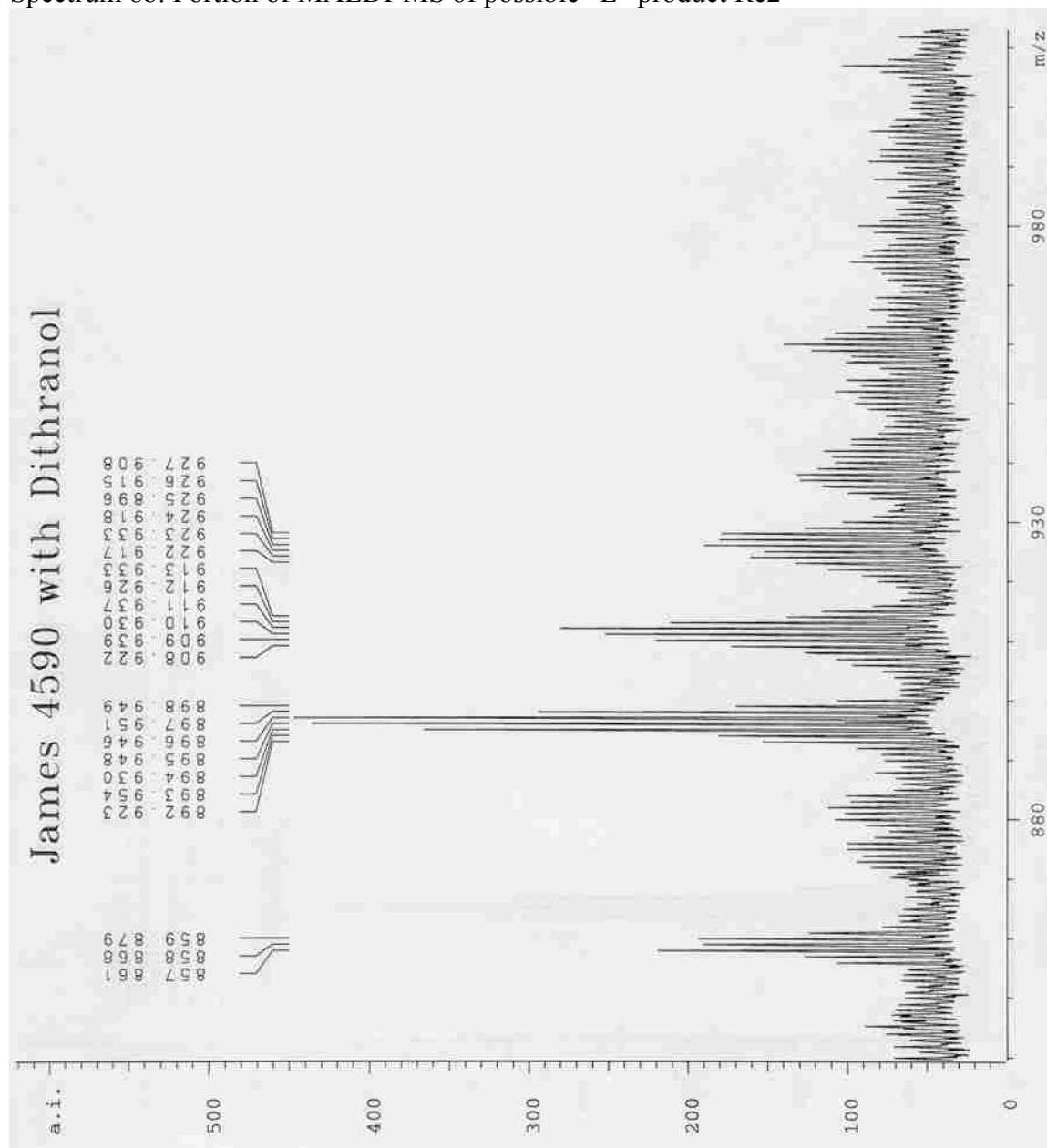
Spectrum 7c. Portion of MALDI-MS of possible “molecular square” product Re1b



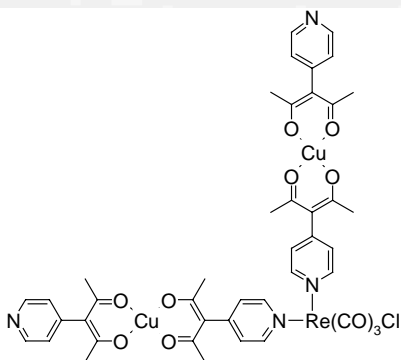
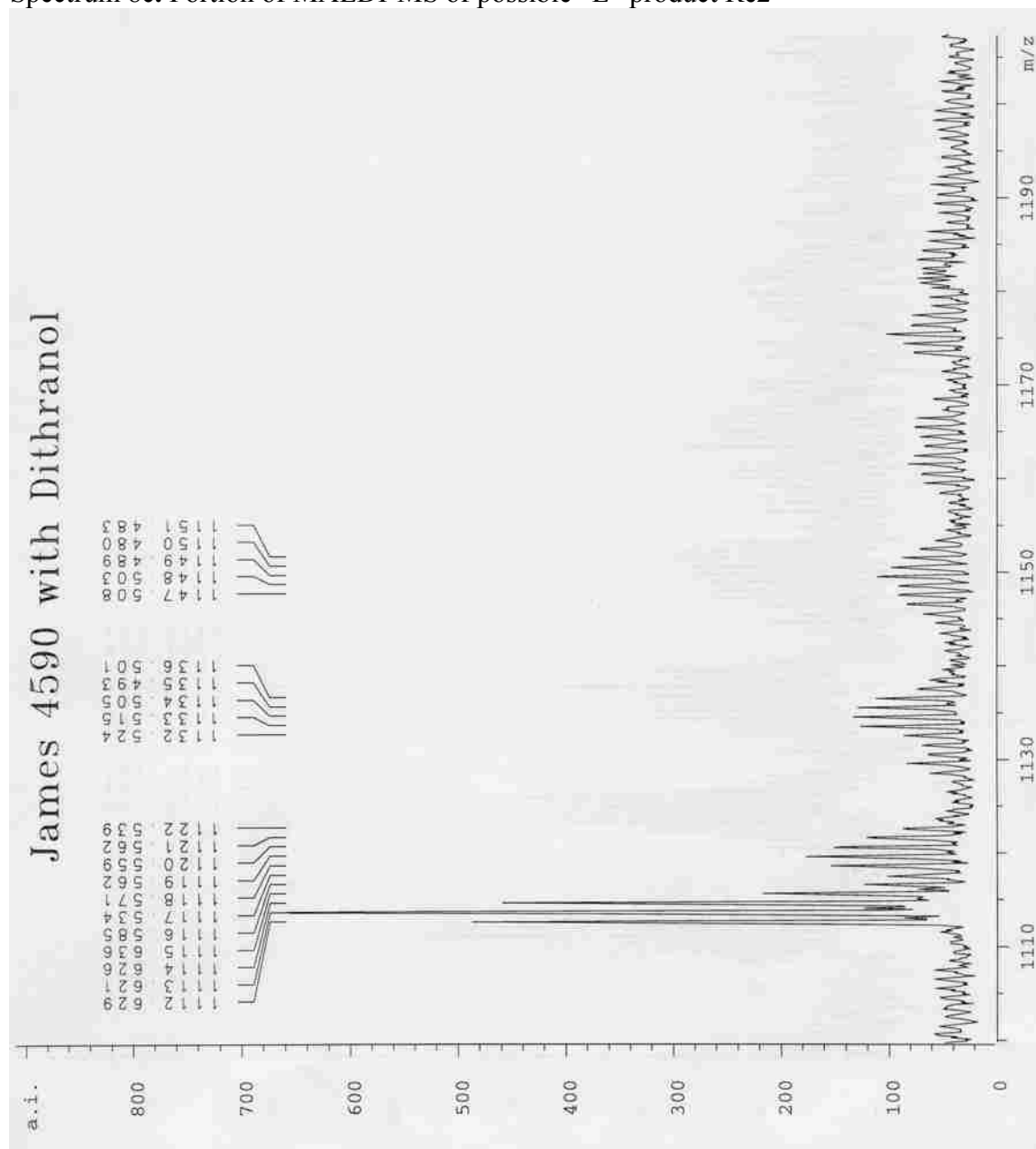
Spectrum 8a. MALDI-MS of possible "L" product Re2



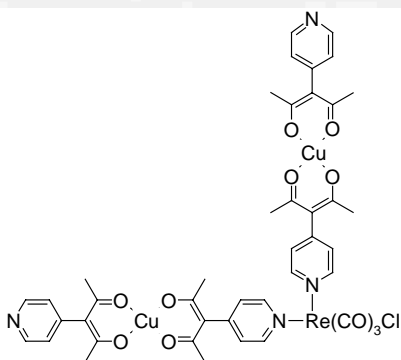
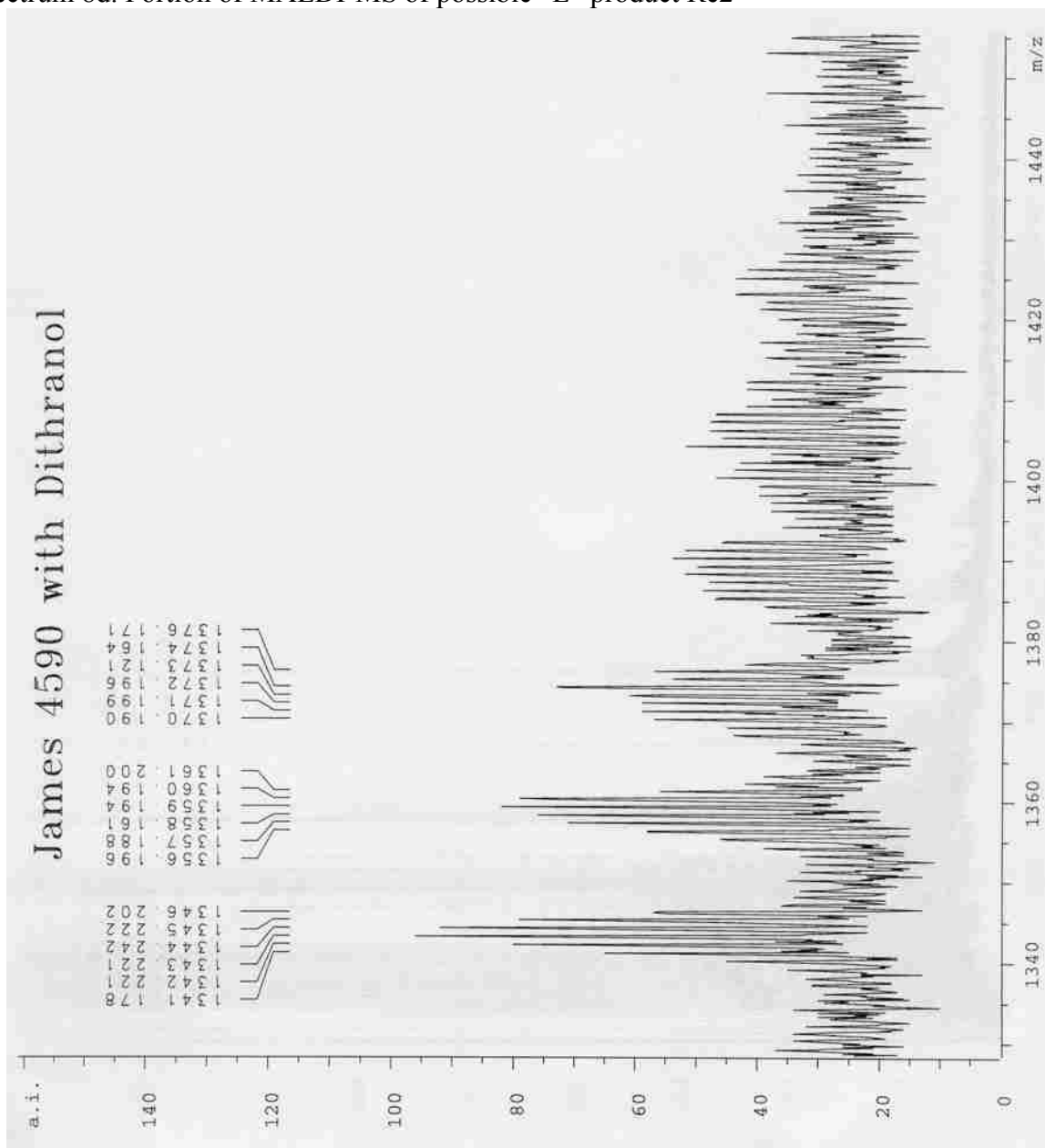
Spectrum 8b. Portion of MALDI-MS of possible "L" product Re2



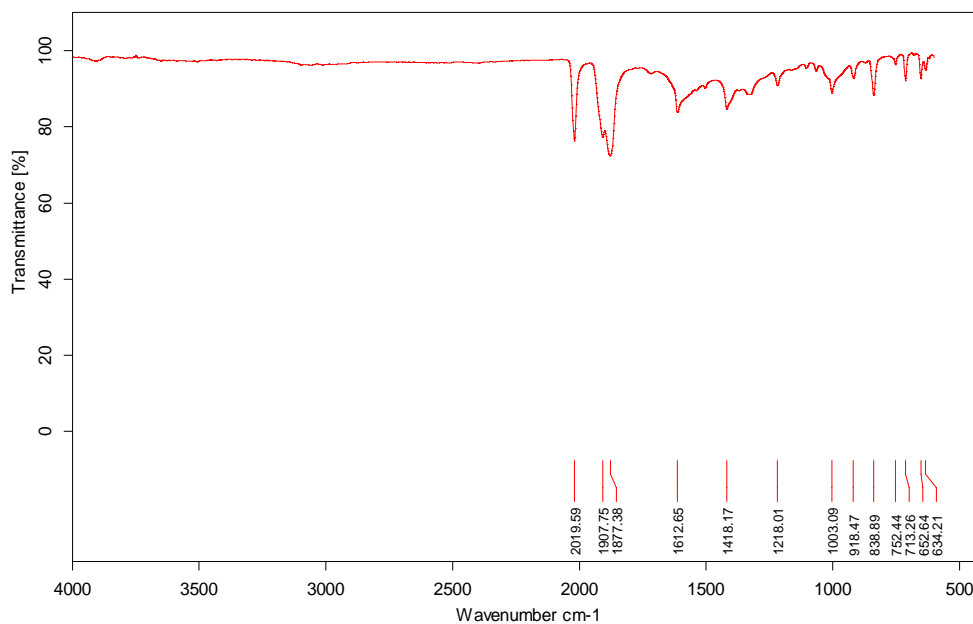
Spectrum 8c. Portion of MALDI-MS of possible “L” product Re2



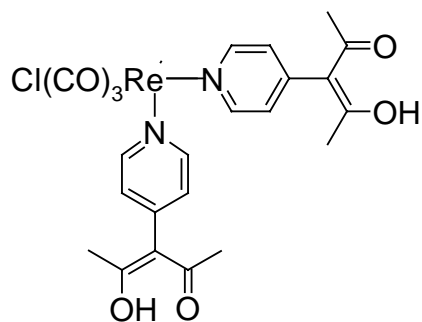
Spectrum 8d. Portion of MALDI-MS of possible "L" product Re2



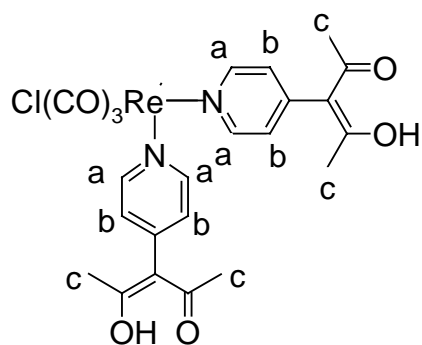
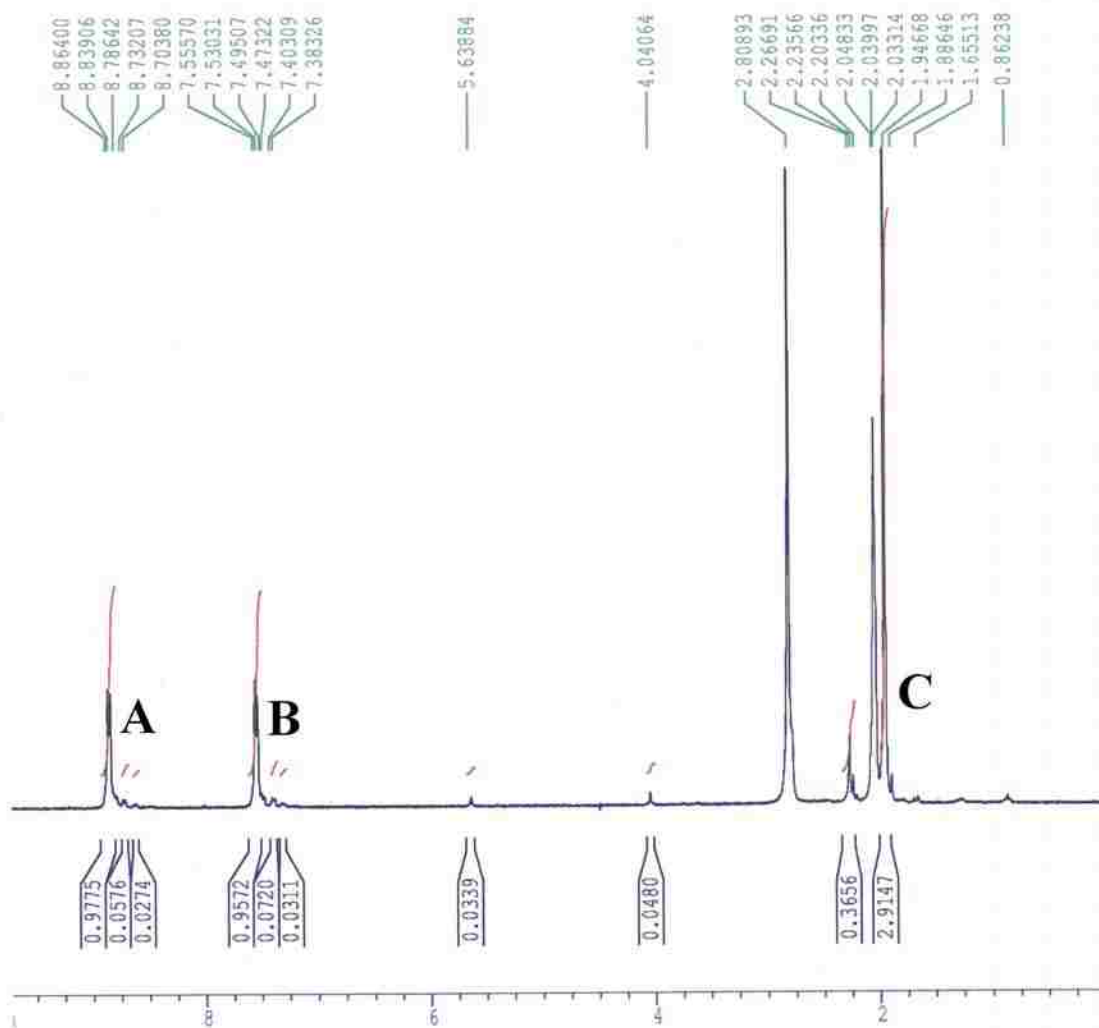
Spectrum 9. IR spectrum (thin film) of $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$



D:\Kakoullis\nRe.0	nRe	solid	20/04/2006
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Spectrum 10. $^1\text{H-NMR}$ of $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$ **2.2** (NS 64 in Acetone- d_6)



CIF 2.1. CIF File of $\text{Re}(\text{CO})_3\text{Cl}(\text{pyacH})_2$, 2.2
data_Kakoullis8

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F2 > 2sigma(F2) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on F2 are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
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Cl1	Cl	0.4886(3)	0.81552(19)	0.31775(9)	0.0452(6)	Uani	1	1	d . . .		
O1	O	0.2549(7)	0.3933(6)	0.2683(3)	0.0484(18)	Uani	1	1	d . . .		
O2	O	0.3017(8)	0.6311(5)	0.4118(3)	0.056(2)	Uani	1	1	d . . .		
O3	O	0.1247(8)	0.7359(7)	0.2449(3)	0.068(2)	Uani	1	1	d . . .		
O4	O	0.6907(7)	0.5455(5)	0.0010(3)	0.0473(18)	Uani	1	1	d . . .		
O5	O	0.6508(7)	0.7541(6)	-0.0046(3)	0.0433(17)	Uani	1	1	d . . .		
H5O	H	0.672(10)	0.664(9)	-0.018(4)	0.065	Uiso	1	1	d . . .		
O6	O	1.1297(8)	0.3703(7)	0.4053(4)	0.073(2)	Uani	1	1	d . . .		
O7	O	1.0437(9)	0.2884(8)	0.4836(3)	0.074(2)	Uani	1	1	d . . .		
H7O	H	1.102(14)	0.338(12)	0.463(6)	0.111	Uiso	1	1	d . . .		
N1	N	0.4579(8)	0.6302(6)	0.2197(3)	0.0355(18)	Uani	1	1	d . . .		
N2	N	0.5625(7)	0.5502(6)	0.3366(3)	0.0340(18)	Uani	1	1	d . . .		
C1	C	0.3013(10)	0.4786(10)	0.2791(4)	0.043(3)	Uani	1	1	d . . .		
C2	C	0.3286(12)	0.6298(7)	0.3675(4)	0.051(3)	Uani	1	1	d . . .		
C3	C	0.2215(11)	0.6978(8)	0.2652(4)	0.046(3)	Uani	1	1	d . . .		
C4	C	0.5719(10)	0.6674(7)	0.2197(4)	0.036(2)	Uani	1	1	d . . .		
H4	H	0.6231	0.6932	0.2543	0.044	Uiso	1	1	calc R . . .		
C5	C	0.6212(10)	0.6707(8)	0.1712(4)	0.039(2)	Uani	1	1	d . . .		
H5	H	0.7044	0.6975	0.1732	0.046	Uiso	1	1	calc R . . .		
C6	C	0.5483(9)	0.6350(7)	0.1206(3)	0.033(2)	Uani	1	1	d . . .		
C7	C	0.4262(10)	0.6003(7)	0.1203(3)	0.035(2)	Uani	1	1	d . . .		
H7	H	0.3719	0.5780	0.0859	0.042	Uiso	1	1	calc R . . .		

C8 C 0.3833(9) 0.5982(7) 0.1699(3) 0.034(2) Uani 1 1 d . . .
 H8 H 0.2996 0.5738 0.1690 0.041 Uiso 1 1 calc R . . .
 C9 C 0.6380(11) 0.4245(8) 0.0714(4) 0.048(3) Uani 1 1 d . . .
 H9A H 0.6502 0.3650 0.0445 0.072 Uiso 1 1 calc R . . .
 H9B H 0.5561 0.4135 0.0812 0.072 Uiso 1 1 calc R . . .
 H9C H 0.7048 0.4186 0.1055 0.072 Uiso 1 1 calc R . . .
 C10 C 0.6423(10) 0.5410(8) 0.0455(4) 0.040(2) Uani 1 1 d . . .
 C11 C 0.5980(9) 0.6418(7) 0.0673(3) 0.033(2) Uani 1 1 d . . .
 C12 C 0.6035(9) 0.7476(7) 0.0401(3) 0.034(2) Uani 1 1 d . . .
 C13 C 0.5524(10) 0.8569(7) 0.0582(4) 0.045(2) Uani 1 1 d . . .
 H13A H 0.6192 0.9150 0.0658 0.067 Uiso 1 1 calc R . . .
 H13B H 0.5210 0.8431 0.0925 0.067 Uiso 1 1 calc R . . .
 H13C H 0.4835 0.8845 0.0282 0.067 Uiso 1 1 calc R . . .
 C14 C 0.6049(9) 0.4565(7) 0.3144(4) 0.034(2) Uani 1 1 d . . .
 H14 H 0.5546 0.4239 0.2812 0.041 Uiso 1 1 calc R . . .
 C15 C 0.7192(10) 0.4050(8) 0.3379(4) 0.039(2) Uani 1 1 d . . .
 H15 H 0.7464 0.3399 0.3201 0.046 Uiso 1 1 calc R . . .
 C16 C 0.7928(9) 0.4468(9) 0.3863(4) 0.040(2) Uani 1 1 d . . .
 C17 C 0.7474(11) 0.5455(8) 0.4109(4) 0.046(3) Uani 1 1 d . . .
 H17 H 0.7949 0.5781 0.4447 0.055 Uiso 1 1 calc R . . .
 C18 C 0.6338(10) 0.5924(8) 0.3848(4) 0.040(2) Uani 1 1 d . . .
 H18 H 0.6040 0.6578 0.4015 0.047 Uiso 1 1 calc R . . .
 C19 C 1.0096(12) 0.4825(12) 0.3309(5) 0.083(4) Uani 1 1 d . . .
 H19A H 1.0853 0.5294 0.3332 0.124 Uiso 1 1 calc R . . .
 H19B H 0.9357 0.5328 0.3257 0.124 Uiso 1 1 calc R . . .
 H19C H 1.0005 0.4293 0.2990 0.124 Uiso 1 1 calc R . . .
 C20 C 1.0203(12) 0.4164(11) 0.3833(5) 0.064(3) Uani 1 1 d . . .
 C21 C 0.9210(11) 0.3978(8) 0.4121(4) 0.045(3) Uani 1 1 d . . .
 C22 C 0.9372(11) 0.3346(11) 0.4607(5) 0.059(3) Uani 1 1 d . . .
 C23 C 0.8322(13) 0.3104(16) 0.4899(5) 0.102(5) Uani 1 1 d . . .
 H23A H 0.8365 0.2298 0.5022 0.153 Uiso 1 1 calc R . . .
 H23B H 0.7514 0.3245 0.4638 0.153 Uiso 1 1 calc R . . .
 H23C H 0.8399 0.3609 0.5227 0.153 Uiso 1 1 calc R . . .
 Cl1S Cl 0.2166(4) 0.3560(3) 0.11919(15) 0.0815(10) Uani 1 1 d . . .
 Cl2S Cl -0.0285(5) 0.3272(5) 0.1385(2) 0.1329(18) Uani 1 1 d . . .
 Cl3S Cl 0.0342(6) 0.5336(5) 0.0859(3) 0.170(2) Uani 1 1 d . . .
 C1S C 0.0705(17) 0.3922(13) 0.0883(6) 0.113(7) Uani 1 1 d . . .
 H1S H 0.0461 0.3569 0.0499 0.135 Uiso 1 1 calc R . . .

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Cl1 0.075(2) 0.0287(12) 0.0353(12) 0.0000(9) 0.0183(12) 0.0014(12)
O1 0.051(5) 0.039(4) 0.057(4) 0.002(3) 0.016(4) -0.001(4)
O2 0.095(7) 0.042(4) 0.048(4) 0.011(3) 0.051(4) 0.012(4)
O3 0.064(6) 0.065(5) 0.081(6) 0.033(4) 0.030(5) 0.024(5)
O4 0.073(6) 0.039(4) 0.038(3) -0.005(3) 0.030(4) -0.001(3)
O5 0.057(5) 0.041(4) 0.036(3) 0.008(3) 0.019(3) -0.003(3)
O6 0.045(6) 0.083(6) 0.093(6) 0.007(5) 0.014(5) 0.005(5)
O7 0.066(7) 0.088(7) 0.064(5) 0.008(4) 0.007(5) 0.012(5)
N1 0.054(5) 0.025(4) 0.034(4) 0.005(3) 0.023(4) 0.005(4)
N2 0.047(5) 0.031(4) 0.026(4) 0.000(3) 0.012(3) -0.003(4)
C1 0.046(7) 0.054(7) 0.036(5) 0.018(5) 0.021(5) 0.022(5)
C2 0.090(9) 0.020(5) 0.048(6) 0.001(4) 0.028(6) 0.015(5)
C3 0.052(8) 0.038(6) 0.057(6) 0.019(5) 0.029(6) 0.010(5)
C4 0.055(7) 0.029(5) 0.030(5) -0.004(4) 0.019(5) -0.006(4)
C5 0.051(7) 0.035(5) 0.033(5) 0.005(4) 0.016(5) -0.016(4)
C6 0.050(6) 0.023(4) 0.027(4) -0.002(3) 0.012(4) -0.005(4)
C7 0.052(7) 0.028(5) 0.025(4) -0.001(3) 0.007(4) 0.004(4)
C8 0.036(6) 0.037(5) 0.029(4) -0.003(4) 0.009(4) -0.004(4)
C9 0.071(8) 0.039(5) 0.043(6) -0.004(4) 0.029(5) 0.009(5)
C10 0.055(7) 0.039(5) 0.030(5) -0.003(4) 0.017(5) -0.003(5)
C11 0.046(6) 0.027(5) 0.028(4) -0.002(3) 0.013(4) -0.002(4)
C12 0.037(6) 0.035(5) 0.031(5) 0.002(4) 0.008(4) -0.004(4)
C13 0.057(7) 0.031(5) 0.048(6) -0.002(4) 0.015(5) -0.001(5)
C14 0.040(6) 0.028(5) 0.035(5) -0.010(4) 0.009(4) 0.000(4)
C15 0.044(7) 0.041(5) 0.032(5) -0.010(4) 0.012(4) 0.000(4)
C16 0.030(6) 0.056(6) 0.035(5) 0.007(4) 0.008(4) 0.006(5)
C17 0.068(8) 0.038(6) 0.034(5) -0.010(4) 0.014(5) -0.006(5)
C18 0.055(7) 0.033(5) 0.033(5) -0.002(4) 0.015(5) 0.005(5)
C19 0.052(9) 0.122(12) 0.080(9) 0.028(8) 0.025(7) -0.011(8)
C20 0.049(9) 0.061(7) 0.076(8) -0.004(6) 0.001(7) -0.006(6)
C21 0.054(7) 0.044(6) 0.041(6) -0.005(4) 0.016(5) 0.003(5)
C22 0.042(8) 0.082(8) 0.050(7) 0.010(6) 0.006(5) 0.017(6)
C23 0.060(10) 0.192(16) 0.060(8) 0.049(10) 0.026(7) 0.003(10)
Cl1S 0.096(3) 0.073(2) 0.078(2) -0.0085(17) 0.027(2) -0.0042(19)
Cl2S 0.102(4) 0.188(5) 0.118(4) 0.011(4) 0.044(3) -0.034(4)
Cl3S 0.131(5) 0.118(4) 0.236(7) 0.037(4) -0.018(5) 0.015(4)
Cl4S 0.120(15) 0.099(12) 0.084(10) -0.032(9) -0.053(10) 0.041(10)

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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only

used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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O6 H7O 1.55(14). ?

O7 C22 1.290(13). ?

O7 H7O 1.06(15). ?

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C8 N1 Re1 119.5(6) .. ?
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H9A C9 H9C 109.5 .. ?
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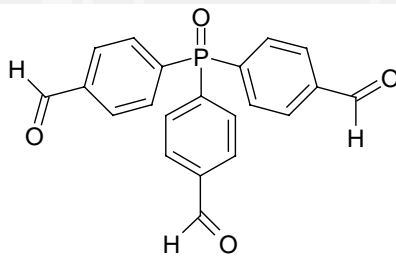
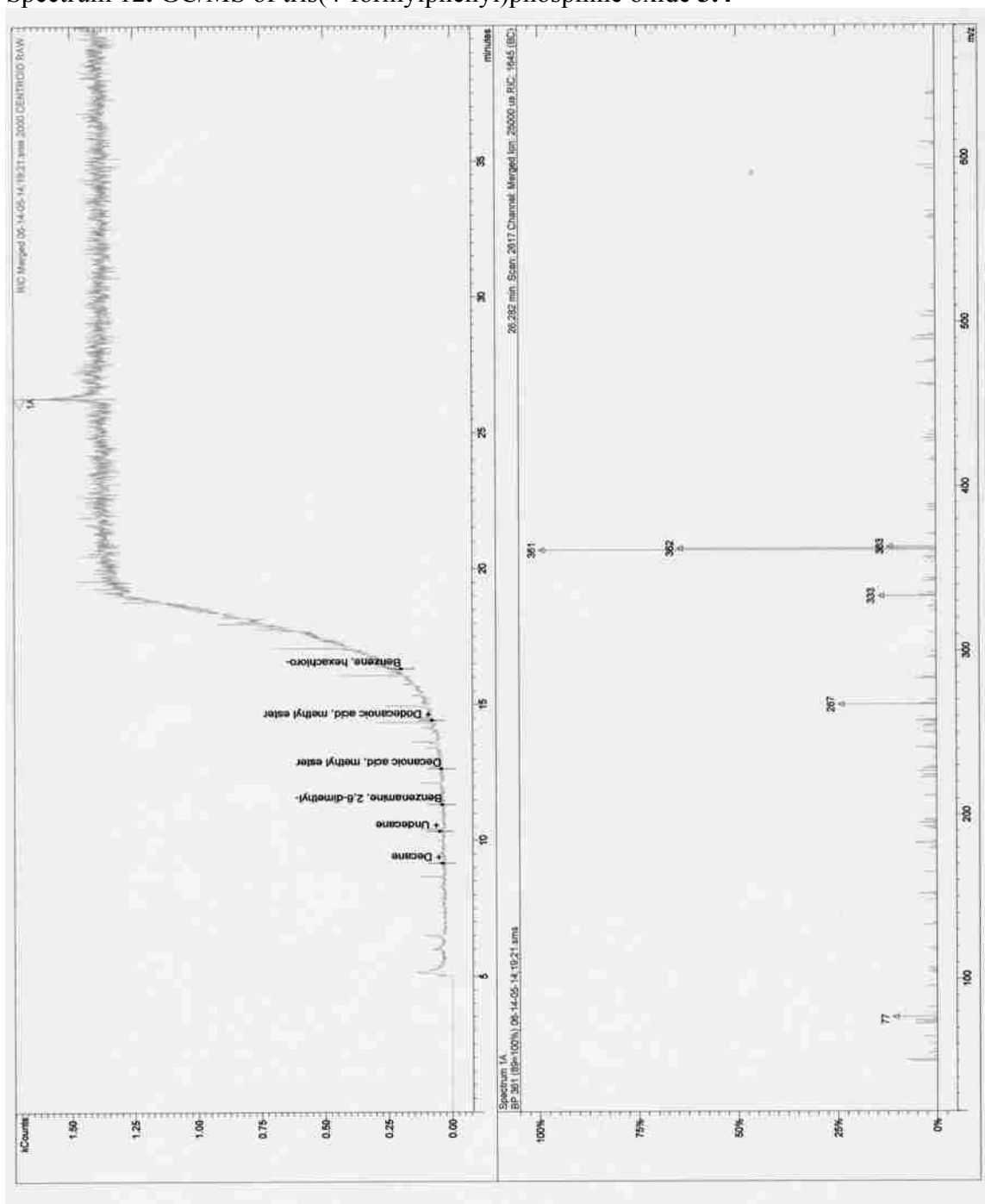
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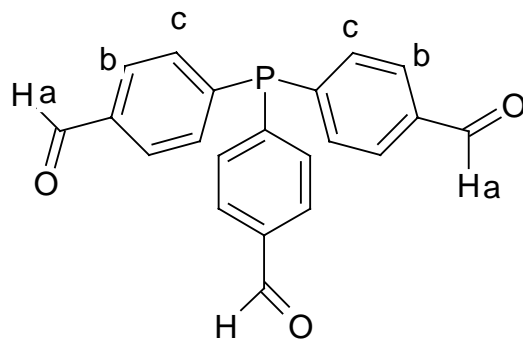
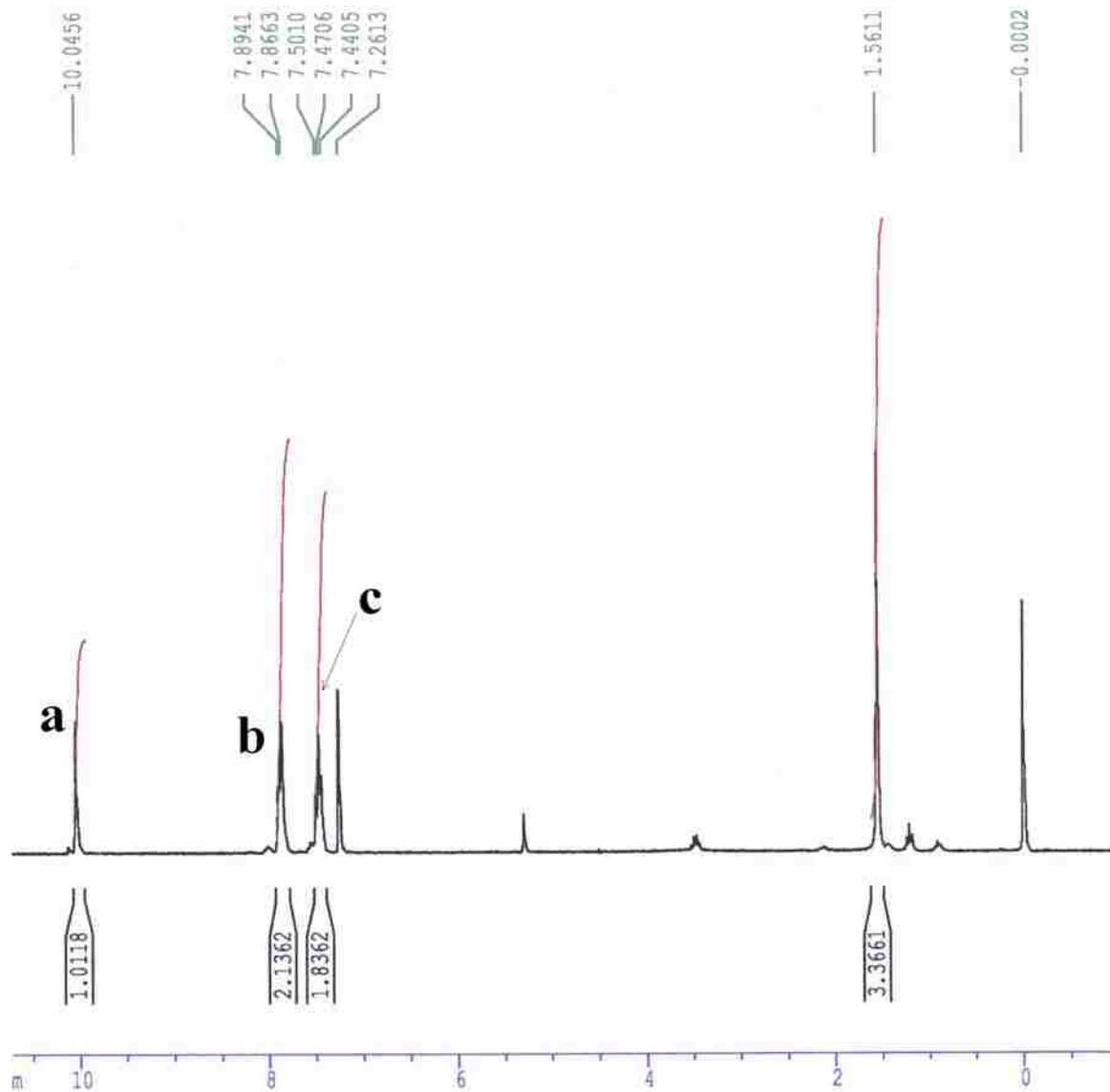
Spectrum 11. GC/MS of tris(4-formylphenyl)phosphine **3.1**



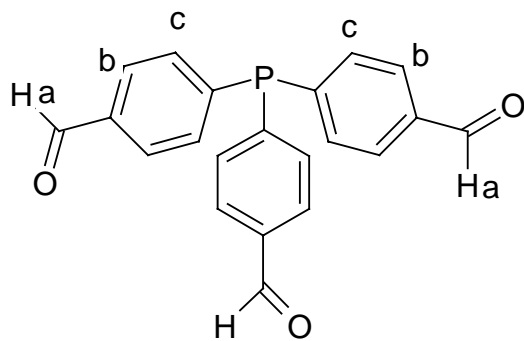
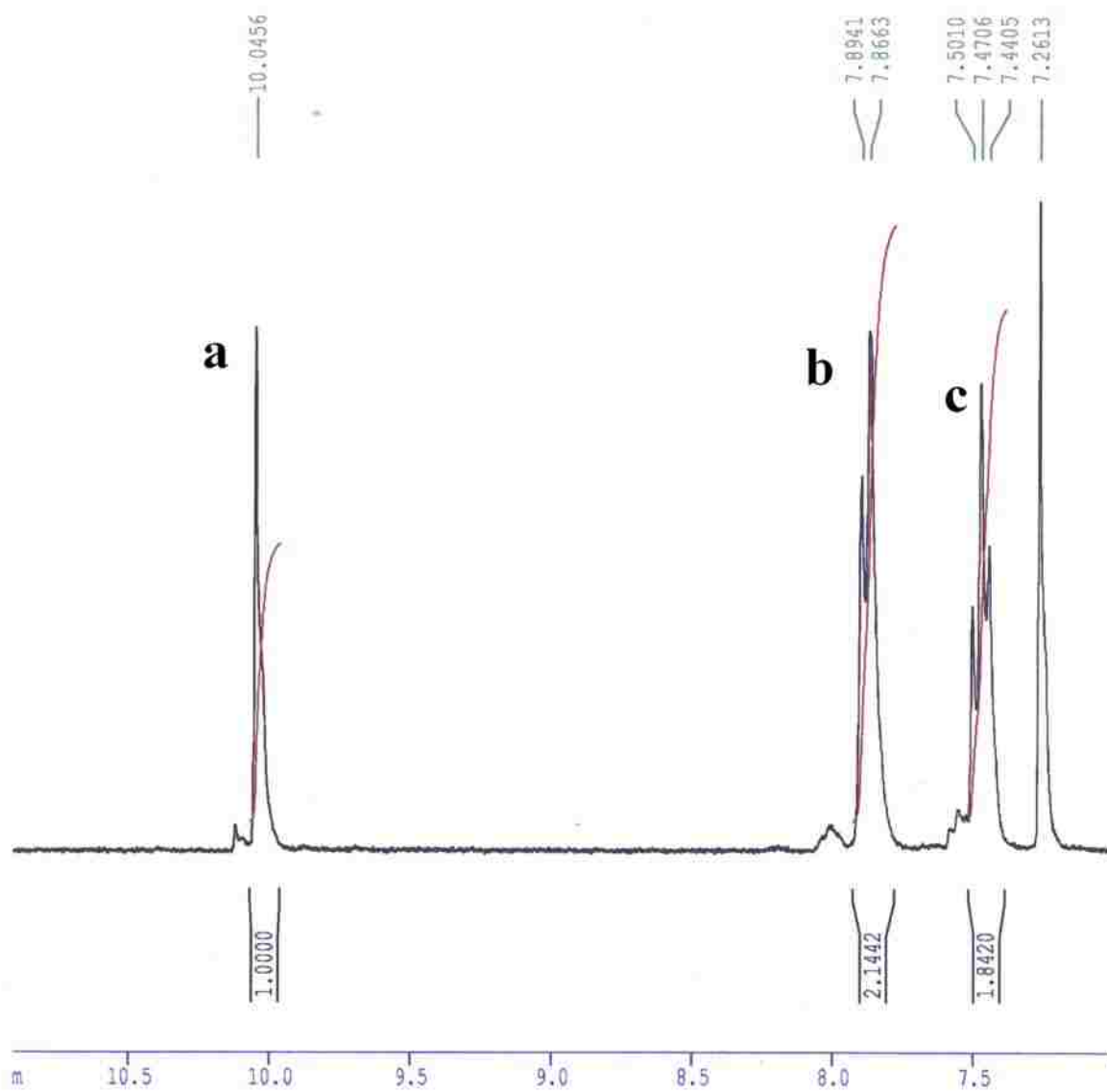
Spectrum 12. GC/MS of tris(4-formylphenyl)phosphine oxide **3.4**



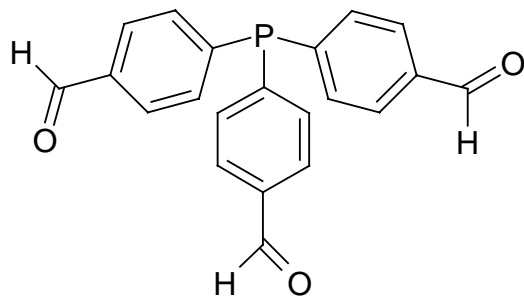
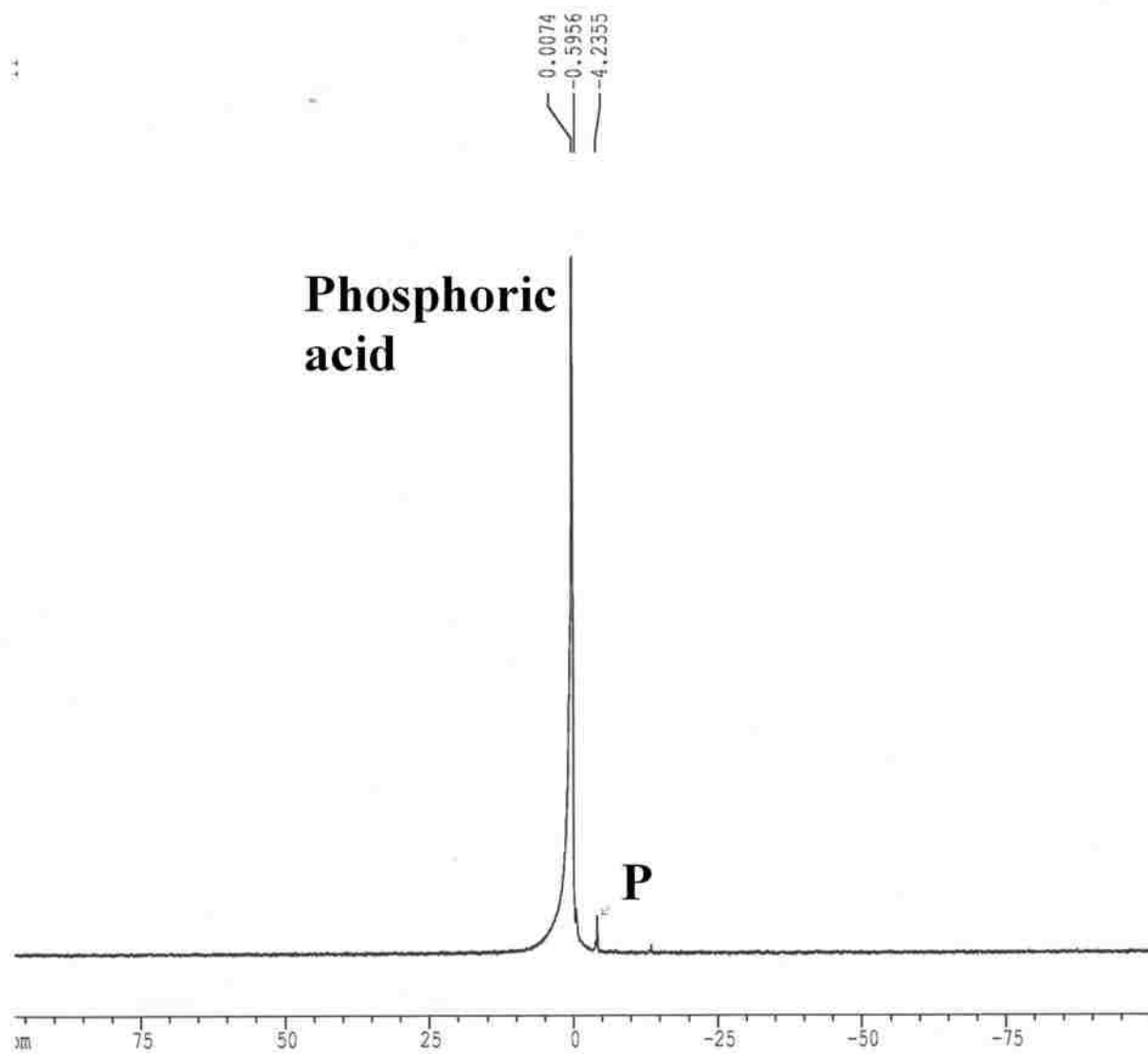
Spectrum 13a. $^1\text{H-NMR}$ of tris(4-formylphenyl)phosphine **3.1** (NS 128 in CDCl_3)



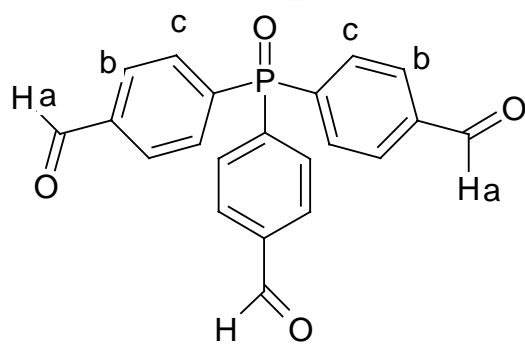
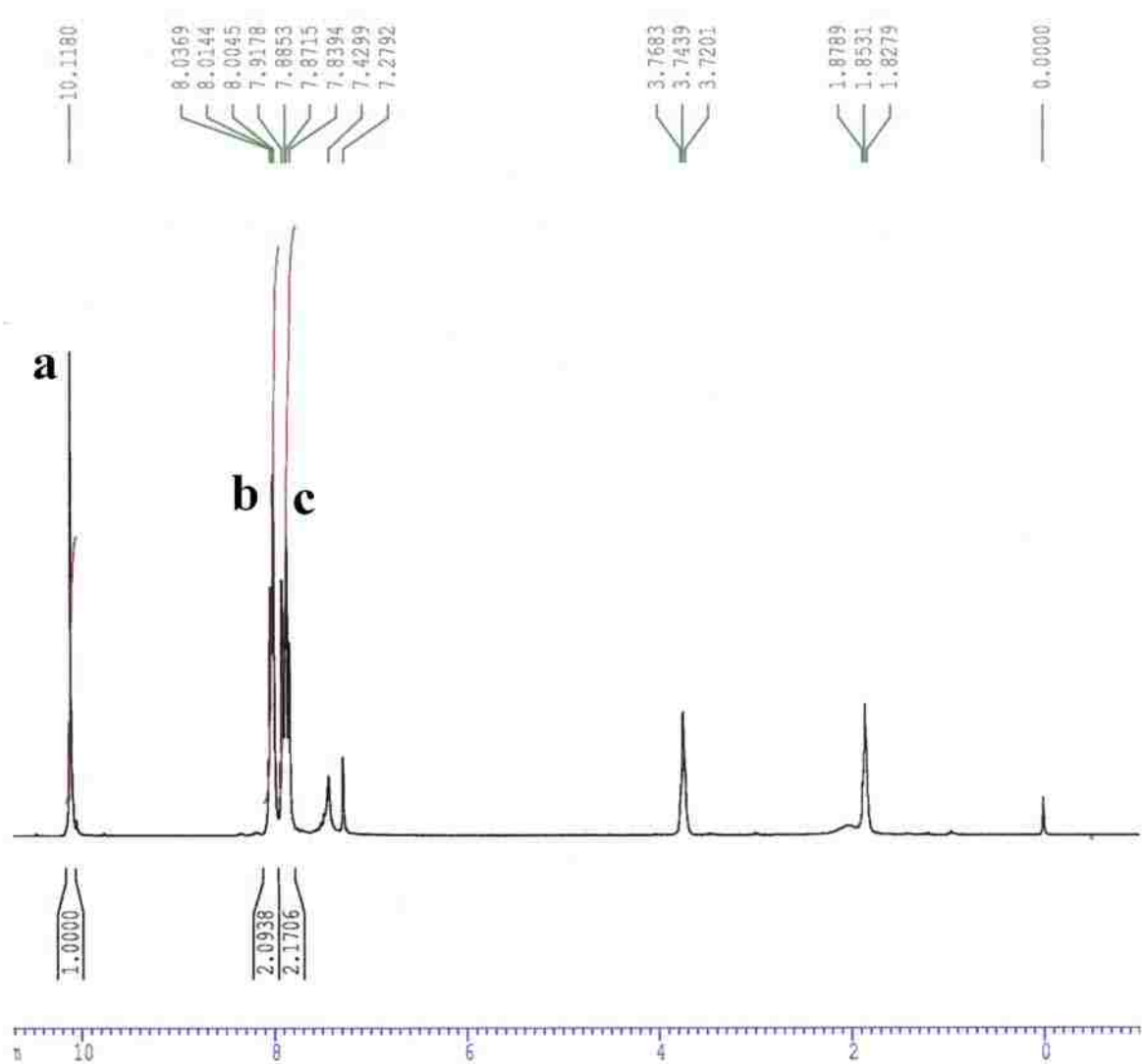
Spectrum 13b. Portion of $^1\text{H-NMR}$ of tris(4-formylphenyl)phosphine **3.1** (NS 128 in CDCl_3)



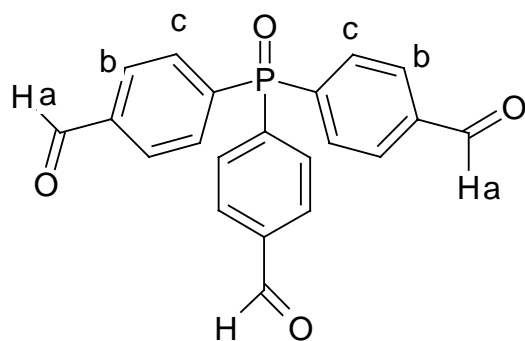
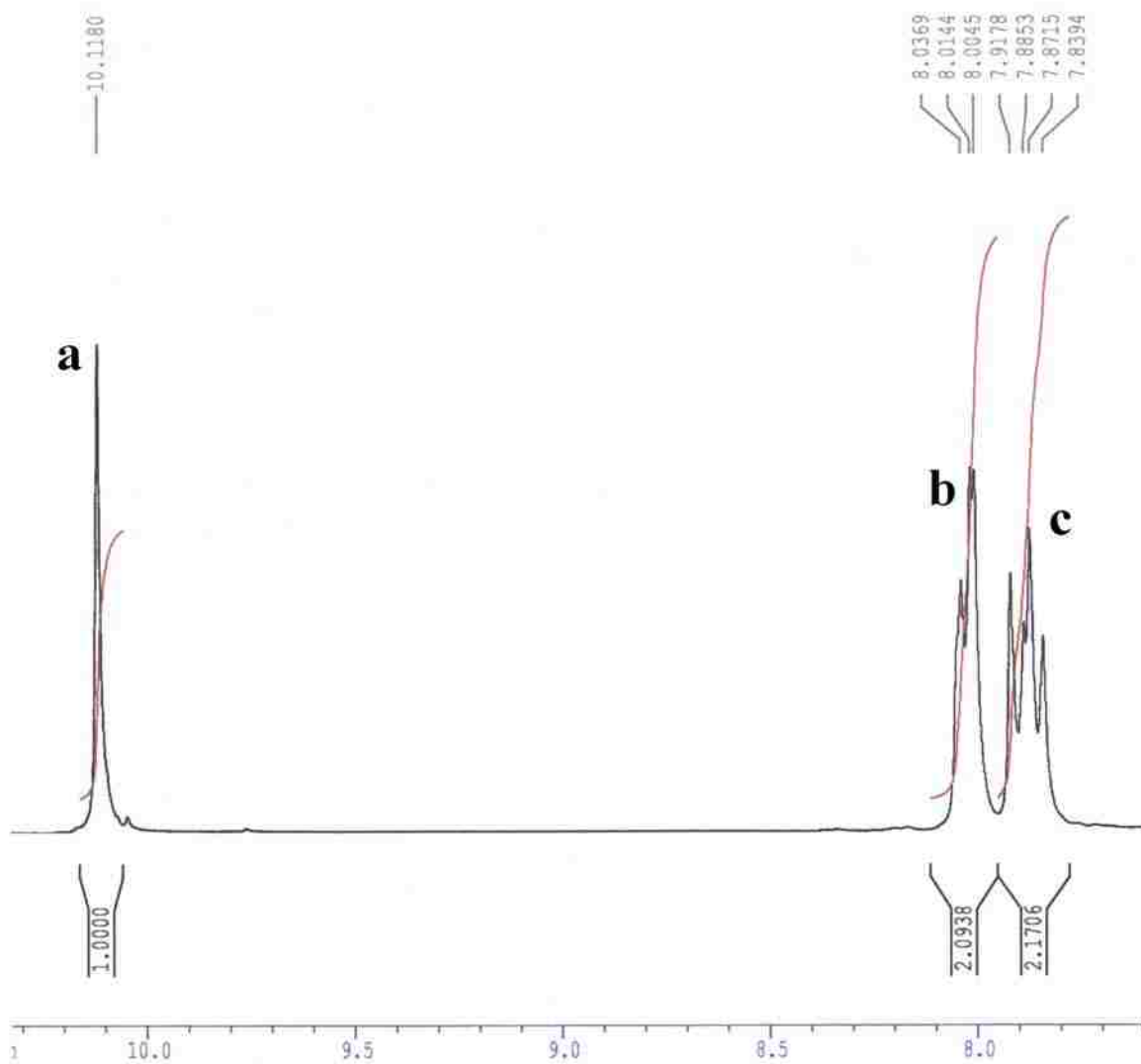
Spectrum 14. ^{31}P -NMR of tris(4-formylphenyl)phosphine **3.1** (NS 1000 in CDCl_3)



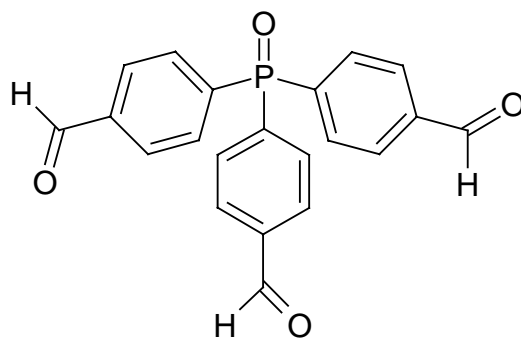
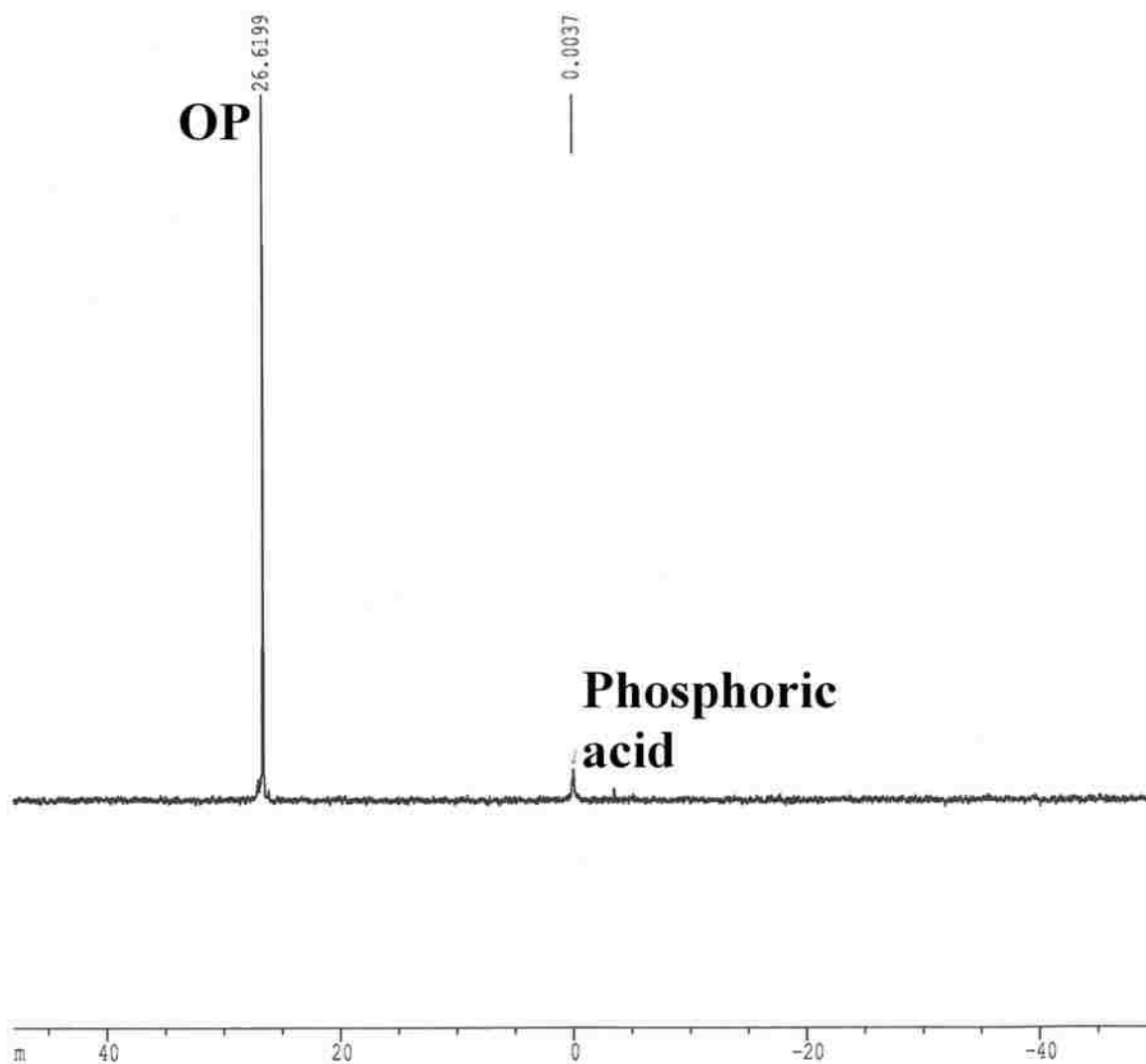
Spectrum 15a. $^1\text{H-NMR}$ of tris(4-formylphenyl)phosphine oxide **3.4** (NS 64 in CDCl_3)



Spectrum 15b. Portion of $^1\text{H-NMR}$ of tris(4-formylphenyl)phosphine oxide **3.4** (NS 64 in CDCl_3)



Spectrum 16. ^{31}P -NMR of tris(4-formylphenyl)phosphine oxide **3.4** (NS 1000 in CDCl_3)



CIF3.1. CIF File of tris(4-formylphenyl)phosphine oxide 3.4
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on F, with F set to zero for negative F2. The threshold expression of
F2 > 2sigma(F2) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on F2 are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
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O1 O 0.27730(4) 0.35710(6) 0.23209(6) 0.02304(16) Uani 1 1 d . . .
O2 O 0.58557(5) 0.58191(7) 0.41717(7) 0.0341(2) Uani 1 1 d . . .
O3 O 0.21889(4) -0.06198(6) 0.57196(7) 0.02736(18) Uani 1 1 d . . .
O4 O 0.42853(5) -0.02731(8) -0.07657(8) 0.0385(2) Uani 1 1 d . . .
C1 C 0.40140(5) 0.34656(8) 0.32453(7) 0.01777(18) Uani 1 1 d . . .
C2 C 0.40518(5) 0.44958(8) 0.31497(8) 0.02015(19) Uani 1 1 d . . .
H2 H 0.3691 0.4861 0.2848 0.024 Uiso 1 1 calc R . .
C3 C 0.46164(5) 0.49869(8) 0.34949(8) 0.0224(2) Uani 1 1 d . . .
H3 H 0.4643 0.5687 0.3425 0.027 Uiso 1 1 calc R . .
C4 C 0.51435(5) 0.44465(8) 0.39446(8) 0.02102(19) Uani 1 1 d . . .
C5 C 0.51021(5) 0.34239(9) 0.40684(8) 0.0227(2) Uani 1 1 d . . .
H5 H 0.5459 0.3063 0.4393 0.027 Uiso 1 1 calc R . .
C6 C 0.45398(5) 0.29303(8) 0.37179(8) 0.0217(2) Uani 1 1 d . . .
H6 H 0.4512 0.2232 0.3798 0.026 Uiso 1 1 calc R . .
C7 C 0.57583(6) 0.49462(10) 0.42927(9) 0.0268(2) Uani 1 1 d . . .
H7 H 0.6096 0.4556 0.4632 0.032 Uiso 1 1 calc R . .
C8 C 0.30889(5) 0.20142(7) 0.36429(7) 0.01710(17) Uani 1 1 d . . .
C9 C 0.26866(5) 0.12078(8) 0.33428(8) 0.01918(19) Uani 1 1 d . . .
H9 H 0.2543 0.1092 0.2647 0.023 Uiso 1 1 calc R . .
C10 C 0.24976(5) 0.05794(8) 0.40579(8) 0.01975(19) Uani 1 1 d . . .
H10 H 0.2230 0.0029 0.3855 0.024 Uiso 1 1 calc R . .
C11 C 0.27051(5) 0.07641(8) 0.50828(8) 0.01879(18) Uani 1 1 d . . .

C12 C 0.30915(5) 0.15758(8) 0.53806(8) 0.0211(2) Uani 1 1 d . . .
 H12 H 0.3223 0.1703 0.6078 0.025 Uiso 1 1 calc R . .
 C13 C 0.32874(5) 0.22025(8) 0.46671(8) 0.01944(18) Uani 1 1 d . . .
 H13 H 0.3554 0.2753 0.4873 0.023 Uiso 1 1 calc R . .
 C14 C 0.25276(5) 0.01018(8) 0.58758(8) 0.0222(2) Uani 1 1 d . . .
 H14 H 0.2692 0.0255 0.6557 0.027 Uiso 1 1 calc R . .
 C15 C 0.35007(5) 0.21019(7) 0.16835(7) 0.01758(18) Uani 1 1 d . . .
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 C17 C 0.40635(6) 0.07555(9) 0.10328(9) 0.0244(2) Uani 1 1 d . . .
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 C18 C 0.38019(5) 0.10291(9) 0.00515(8) 0.0234(2) Uani 1 1 d . . .
 C19 C 0.34019(5) 0.18443(9) -0.01138(8) 0.0236(2) Uani 1 1 d . . .
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 C21 C 0.39321(6) 0.04313(10) -0.08199(9) 0.0303(3) Uani 1 1 d . . .
 H21 H 0.3722 0.0616 -0.1469 0.036 Uiso 1 1 calc R . .
 O1S O 0.45041(11) 0.23429(19) 0.84831(19) 0.0494(6) Uani 0.50 1 d P A -1
 C1S C 0.51269(14) 0.1940(3) 0.8648(3) 0.0386(6) Uani 0.50 1 d P A -1
 H11S H 0.5170 0.1448 0.9202 0.058 Uiso 0.50 1 calc PR A -1
 H12S H 0.5443 0.2473 0.8831 0.058 Uiso 0.50 1 calc PR A -1
 C2S C 0.5231(3) 0.1445(4) 0.7670(3) 0.0762(15) Uani 0.50 1 d P A -1
 H21S H 0.5678 0.1498 0.7565 0.114 Uiso 0.50 1 calc PR A -1
 H22S H 0.5104 0.0738 0.7652 0.114 Uiso 0.50 1 calc PR A -1
 C3S C 0.4797(3) 0.2050(3) 0.6906(4) 0.0720(16) Uani 0.50 1 d P A -1
 H31S H 0.5012 0.2656 0.6715 0.108 Uiso 0.50 1 calc PR A -1
 H32S H 0.4648 0.1657 0.6292 0.108 Uiso 0.50 1 calc PR A -1
 C4S C 0.4278(2) 0.2296(4) 0.7434(3) 0.0701(14) Uani 0.50 1 d P A -1
 H41S H 0.4094 0.2944 0.7196 0.105 Uiso 0.50 1 calc PR A -1
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 O2 0.0340(5) 0.0338(5) 0.0348(5) -0.0057(4) 0.0062(4) -0.0149(4)
 O3 0.0300(4) 0.0246(4) 0.0285(4) 0.0020(3) 0.0075(3) -0.0029(3)
 O4 0.0330(5) 0.0477(6) 0.0363(5) -0.0206(4) 0.0103(4) -0.0048(4)
 C1 0.0174(4) 0.0189(4) 0.0169(4) -0.0020(3) 0.0024(3) -0.0015(3)

C2 0.0220(5) 0.0203(4) 0.0182(4) 0.0007(4) 0.0032(3) -0.0007(4)
 C3 0.0260(5) 0.0209(5) 0.0209(4) -0.0006(4) 0.0050(4) -0.0049(4)
 C4 0.0196(5) 0.0259(5) 0.0183(4) -0.0043(4) 0.0052(3) -0.0045(4)
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 C6 0.0201(5) 0.0197(5) 0.0249(5) -0.0024(4) 0.0015(4) 0.0004(4)
 C7 0.0223(5) 0.0335(6) 0.0253(5) -0.0076(5) 0.0059(4) -0.0075(4)
 C8 0.0164(4) 0.0176(4) 0.0172(4) -0.0003(3) 0.0021(3) 0.0005(3)
 C9 0.0196(5) 0.0209(4) 0.0166(4) -0.0033(3) 0.0014(3) -0.0014(4)
 C10 0.0193(4) 0.0190(4) 0.0210(4) -0.0027(4) 0.0035(3) -0.0022(4)
 C11 0.0202(4) 0.0177(4) 0.0190(4) -0.0010(3) 0.0049(3) 0.0018(3)
 C12 0.0251(5) 0.0215(5) 0.0162(4) -0.0019(3) 0.0017(4) -0.0001(4)
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 C15 0.0177(4) 0.0187(4) 0.0159(4) -0.0008(3) 0.0012(3) -0.0024(3)
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 C18 0.0229(5) 0.0287(5) 0.0192(4) -0.0064(4) 0.0053(4) -0.0076(4)
 C19 0.0231(5) 0.0311(5) 0.0160(4) -0.0004(4) 0.0009(4) -0.0066(4)
 C20 0.0197(4) 0.0230(5) 0.0177(4) 0.0013(4) -0.0001(3) -0.0028(4)
 C21 0.0289(6) 0.0398(7) 0.0235(5) -0.0111(5) 0.0086(4) -0.0105(5)
 O1S 0.0330(11) 0.0568(14) 0.0539(14) 0.0064(11) -0.0072(10) -0.0007(10)
 C1S 0.0297(13) 0.0431(17) 0.0399(16) -0.0067(14) -0.0043(12) -0.0004(11)
 C2S 0.107(5) 0.078(3) 0.039(2) -0.008(2) 0.001(2) 0.021(3)
 C3S 0.128(5) 0.0307(17) 0.046(2) 0.0030(17) -0.022(3) -0.003(2)
 C4S 0.070(3) 0.078(3) 0.050(2) 0.036(2) -0.0275(19) -0.030(2)

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All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.

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 P1 C8 1.8050(10) . ?
 P1 C1 1.8083(11) . ?
 P1 C15 1.8129(10) . ?

O2 C7 1.2099(16) . ?
O3 C14 1.2107(14) . ?
O4 C21 1.2078(17) . ?
C1 C2 1.3975(15) . ?
C1 C6 1.4009(15) . ?
C2 C3 1.3905(15) . ?
C2 H2 0.9500 . ?
C3 C4 1.3968(16) . ?
C3 H3 0.9500 . ?
C4 C5 1.3924(16) . ?
C4 C7 1.4851(15) . ?
C5 C6 1.3895(15) . ?
C5 H5 0.9500 . ?
C6 H6 0.9500 . ?
C7 H7 0.9500 . ?
C8 C13 1.3981(14) . ?
C8 C9 1.4049(14) . ?
C9 C10 1.3873(15) . ?
C9 H9 0.9500 . ?
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C12 C13 1.3904(15) . ?
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C15 C20 1.3963(14) . ?
C15 C16 1.4050(15) . ?
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C16 H16 0.9500 . ?
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C19 C20 1.3944(15) . ?
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O1S C1S 1.422(4) . ?
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C1S H12S 0.9900 . ?
C2S C3S 1.510(6) . ?
C2S H21S 0.9900 . ?

C2S H22S 0.9900 . ?
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C6 C1 P1 121.87(8) . . ?
C3 C2 C1 120.11(10) . . ?
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C2 C3 C4 119.68(10) . . ?
C2 C3 H3 120.2 . . ?
C4 C3 H3 120.2 . . ?
C5 C4 C3 120.36(10) . . ?
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C6 C5 C4 120.07(10) . . ?
C6 C5 H5 120.0 . . ?
C4 C5 H5 120.0 . . ?
C5 C6 C1 119.79(10) . . ?
C5 C6 H6 120.1 . . ?
C1 C6 H6 120.1 . . ?
O2 C7 C4 124.11(12) . . ?
O2 C7 H7 117.9 . . ?
C4 C7 H7 117.9 . . ?
C13 C8 C9 120.03(9) . . ?
C13 C8 P1 120.75(8) . . ?
C9 C8 P1 119.01(7) . . ?
C10 C9 C8 120.31(9) . . ?

C10 C9 H9 119.8 .. ?
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C12 C13 H13 120.3 .. ?
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C18 C19 H19 120.0 .. ?
C20 C19 H19 120.0 .. ?
C19 C20 C15 119.93(10) .. ?
C19 C20 H20 120.0 .. ?
C15 C20 H20 120.0 .. ?
O4 C21 C18 124.90(12) .. ?
O4 C21 H21 117.6 .. ?
C18 C21 H21 117.6 .. ?
C4S O1S C1S 107.6(3) .. ?
O1S C1S C2S 107.0(3) .. ?
O1S C1S H11S 110.3 .. ?
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O1S C1S H12S 110.3 .. ?
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H11S C1S H12S 108.6 .. ?
C3S C2S C1S 101.2(4) .. ?

C3S C2S H21S 111.5 .. ?
C1S C2S H21S 111.5 .. ?
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C1S C2S H22S 111.5 .. ?
H21S C2S H22S 109.4 .. ?
C4S C3S C2S 103.1(4) .. ?
C4S C3S H31S 111.2 .. ?
C2S C3S H31S 111.2 .. ?
C4S C3S H32S 111.2 .. ?
C2S C3S H32S 111.2 .. ?
H31S C3S H32S 109.1 .. ?
O1S C4S C3S 109.3(3) .. ?
O1S C4S H41S 109.8 .. ?
C3S C4S H41S 109.8 .. ?
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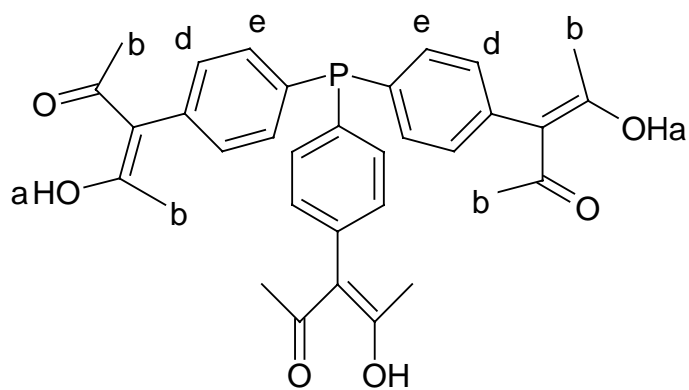
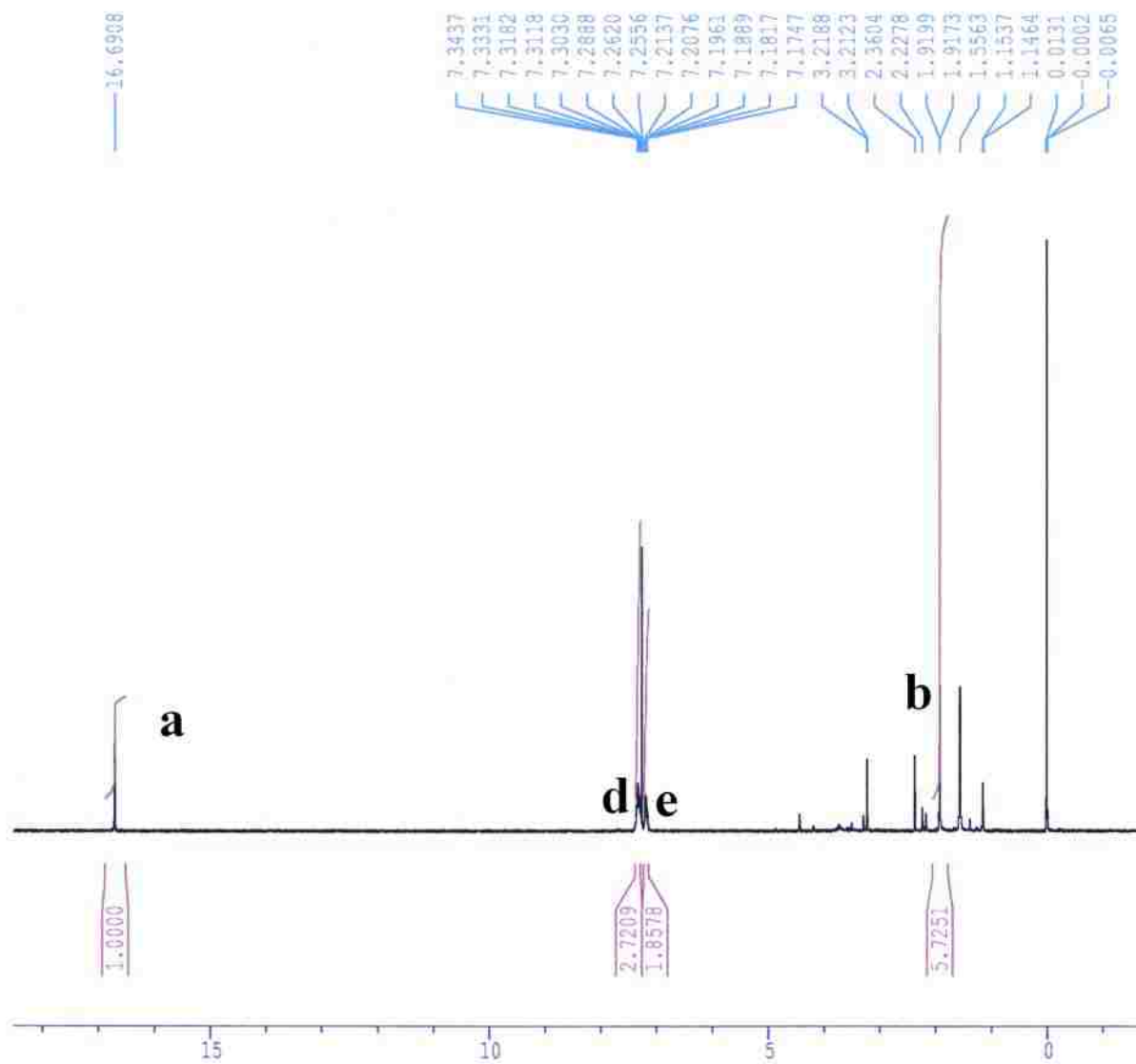
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C5 C4 C7 O2 175.74(11) ?

C3 C4 C7 O2 -3.83(17) ?
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 C15 P1 C8 C9 -46.53(9) ?
 C13 C8 C9 C10 -1.68(16) ?
 P1 C8 C9 C10 -176.43(8) ?
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 C1 P1 C15 C16 66.79(10) ?
 C20 C15 C16 C17 0.10(16) ?
 P1 C15 C16 C17 -178.04(8) ?
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 P1 C15 C20 C19 179.73(8) ?
 C19 C18 C21 O4 177.78(12) ?
 C17 C18 C21 O4 -4.24(19) ?
 C4S O1S C1S C2S -11.3(4) ?
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 C1S C2S C3S C4S -33.6(5) ?
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 C2S C3S C4S O1S 29.0(5) ?

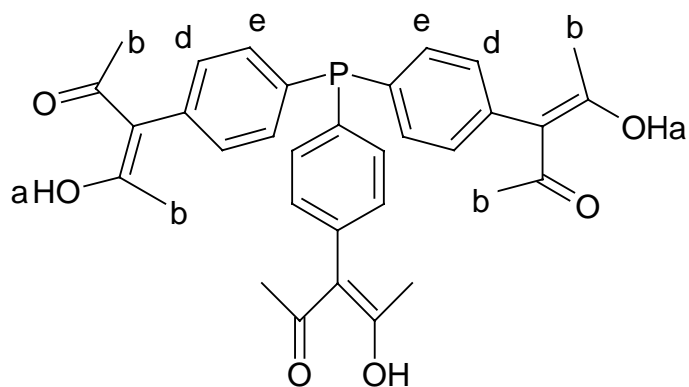
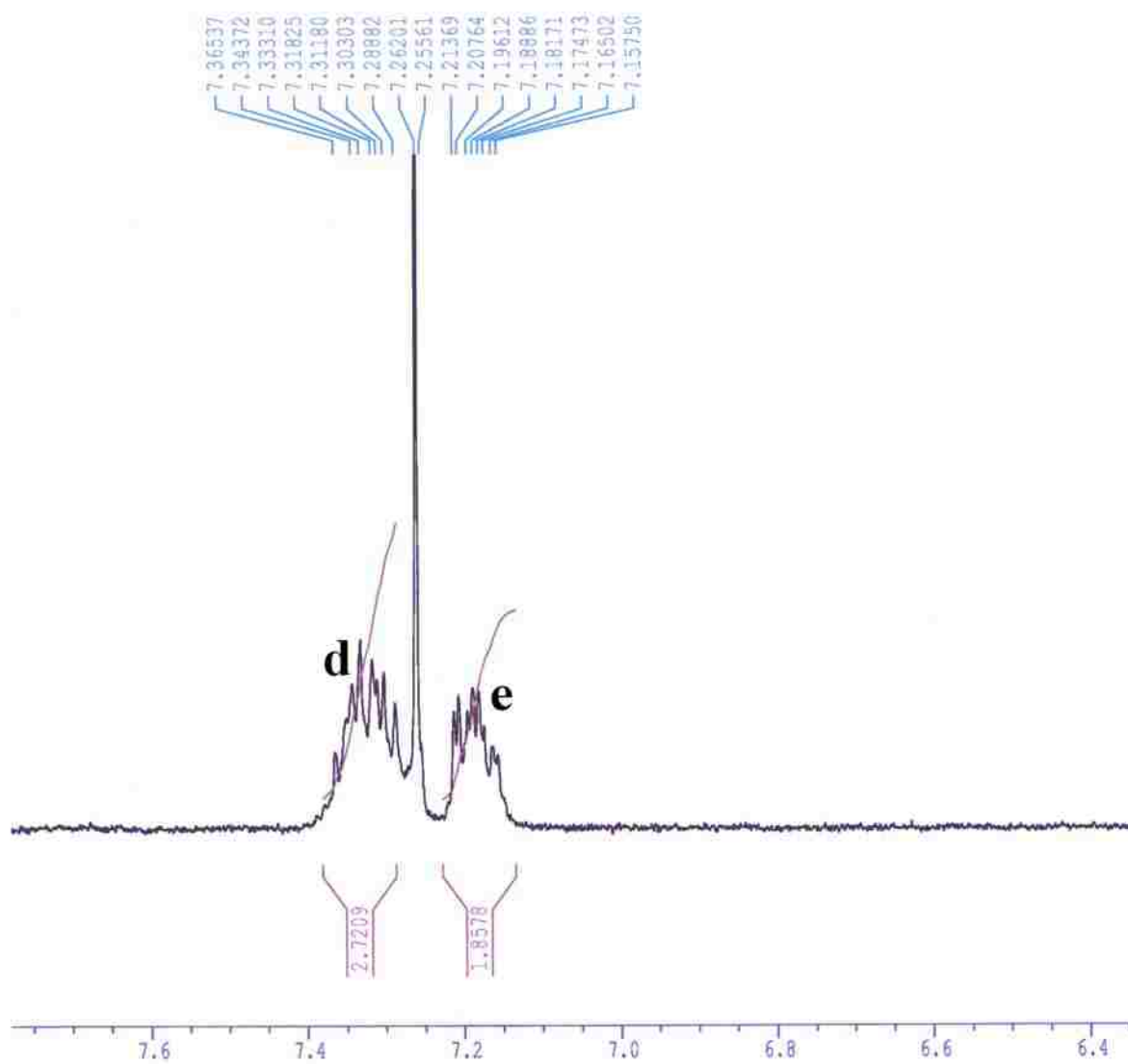
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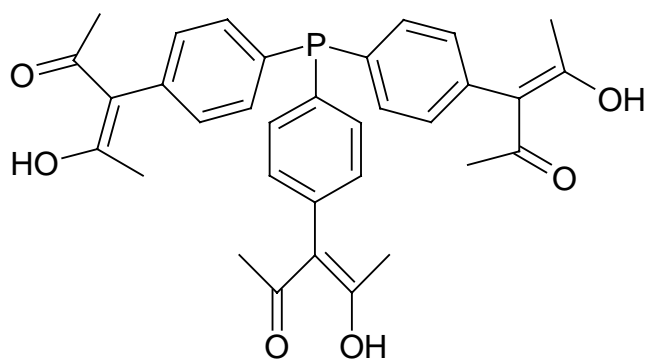
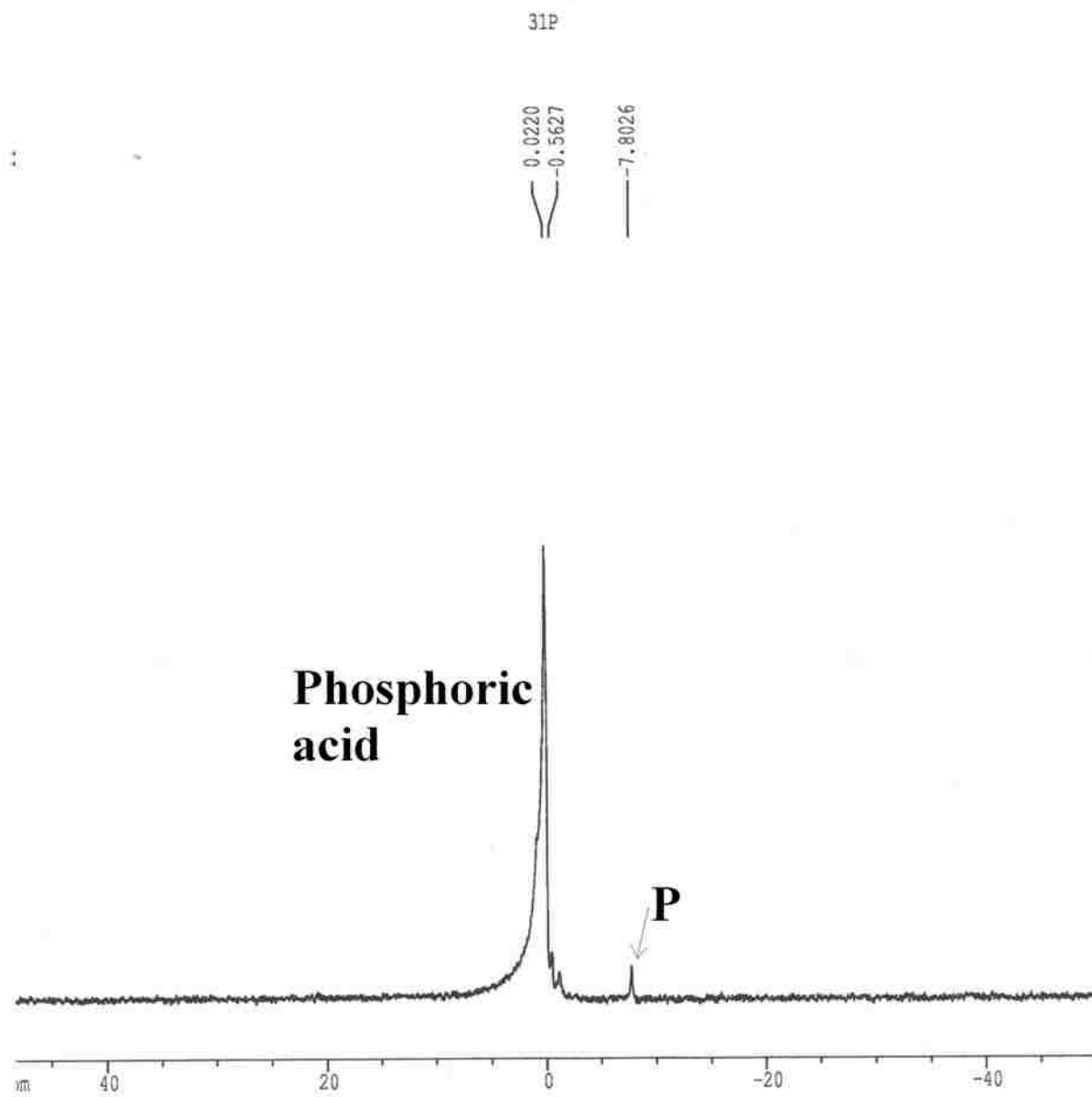
Spectrum 17a. $^1\text{H-NMR}$ of Pphac_3H_3 , **1.23** (NS 64 in CDCl_3)



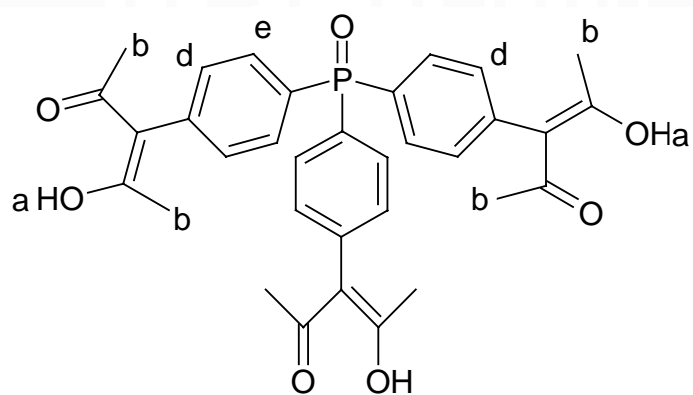
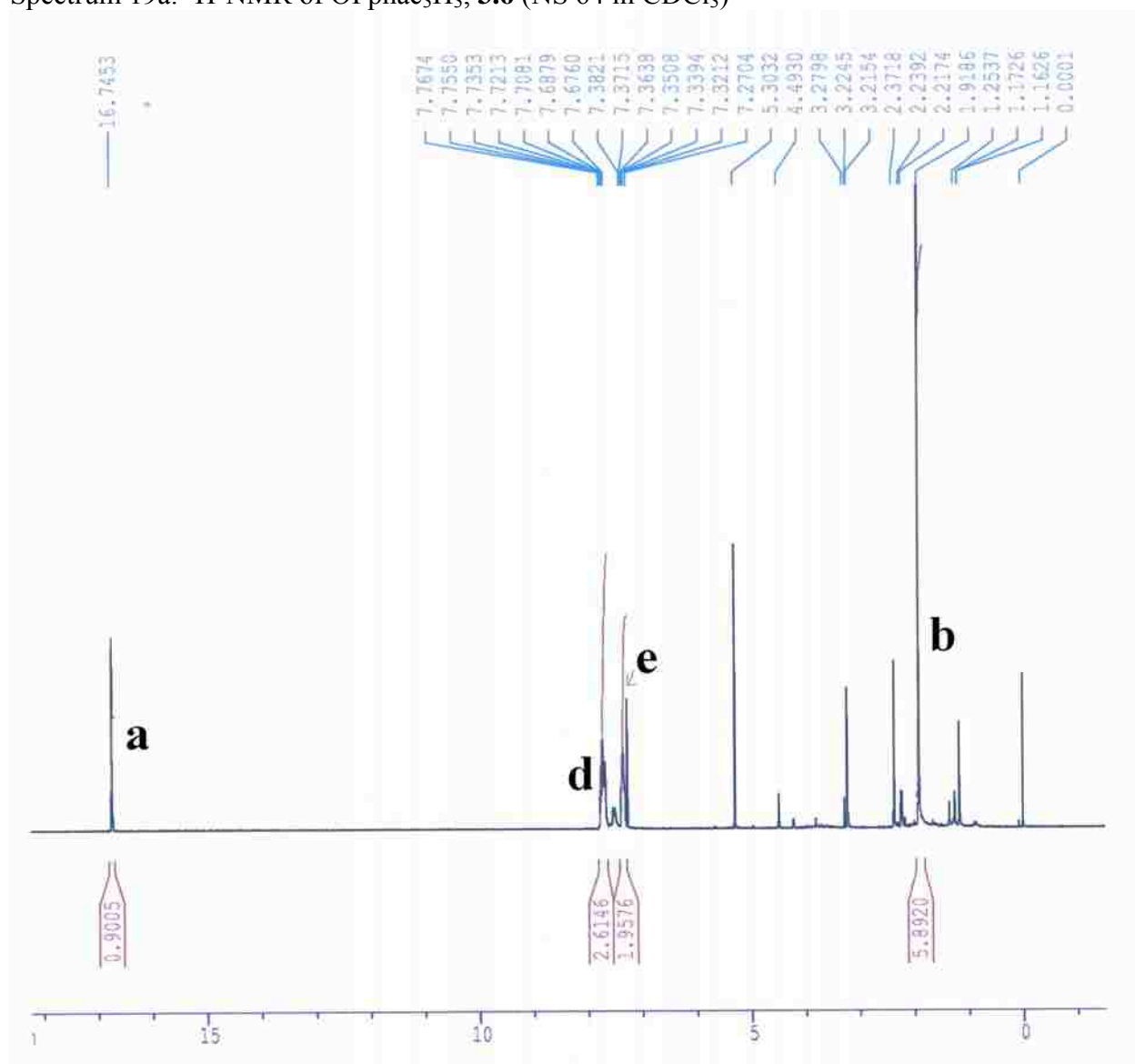
Spectrum 17b. Portion of $^1\text{H-NMR}$ of Pphac_3H_3 , **1.23** (NS 64 in CDCl_3)



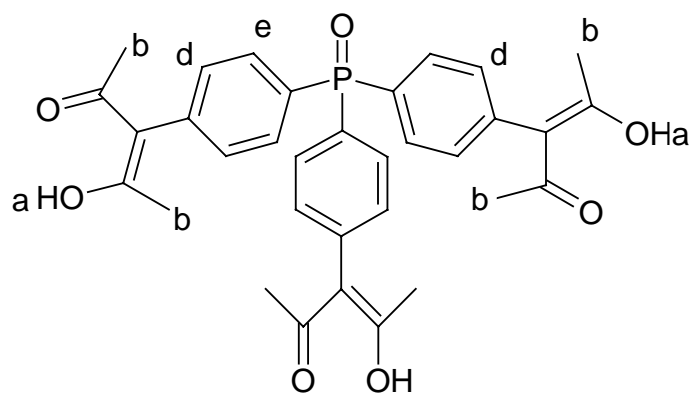
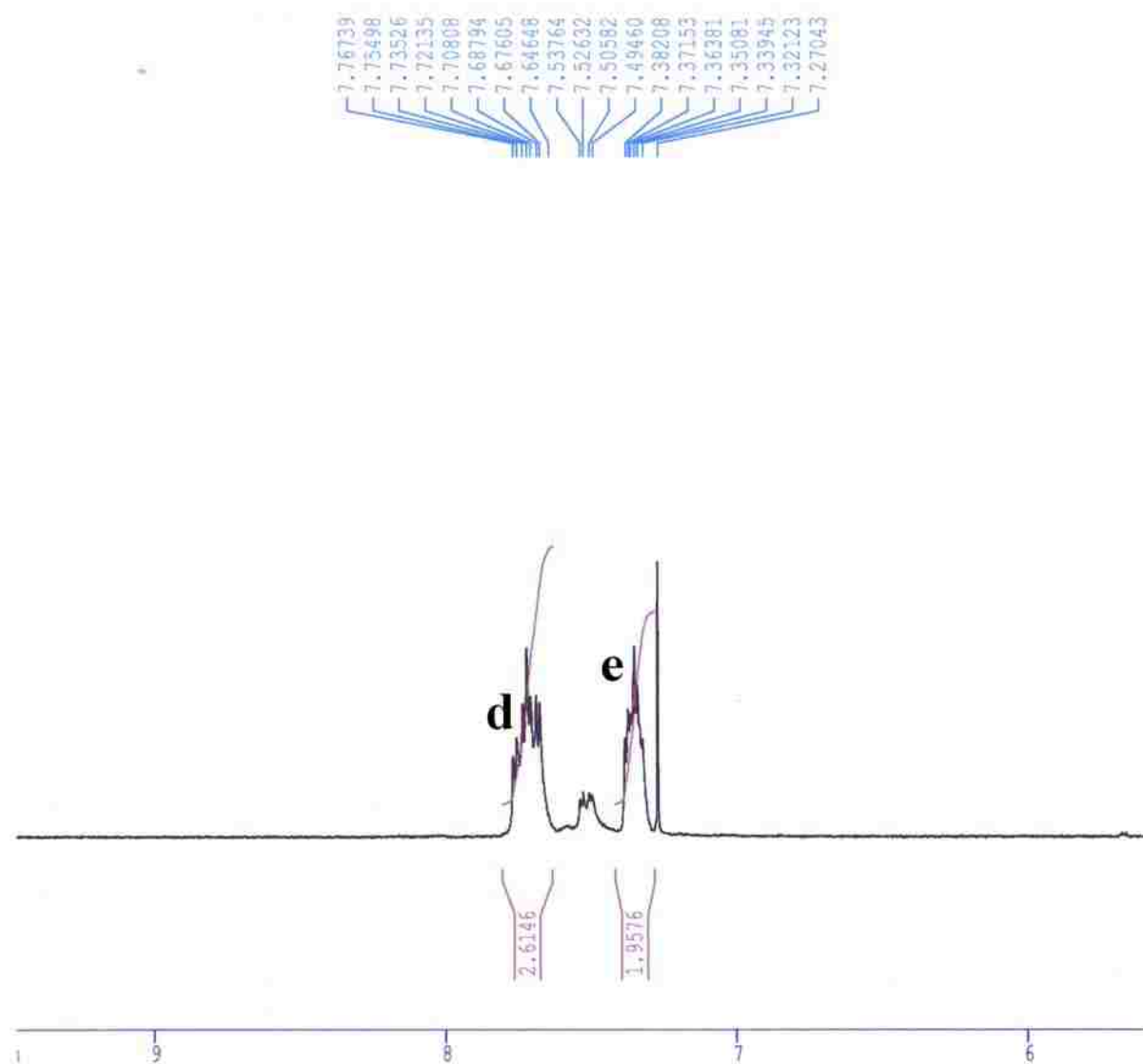
Spectrum 18. ^{31}P -NMR of Pphac $_3\text{H}_3$, **1.23** (NS 250 in CDCl_3)



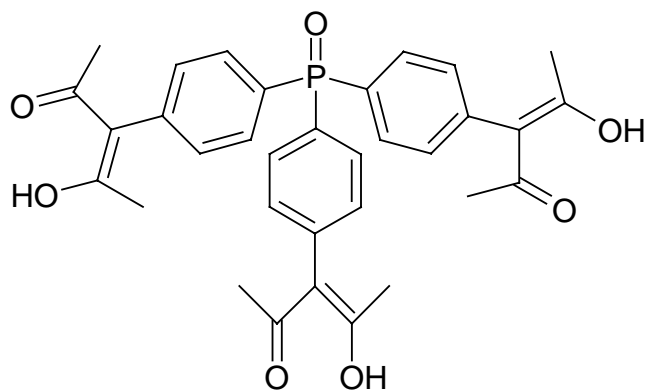
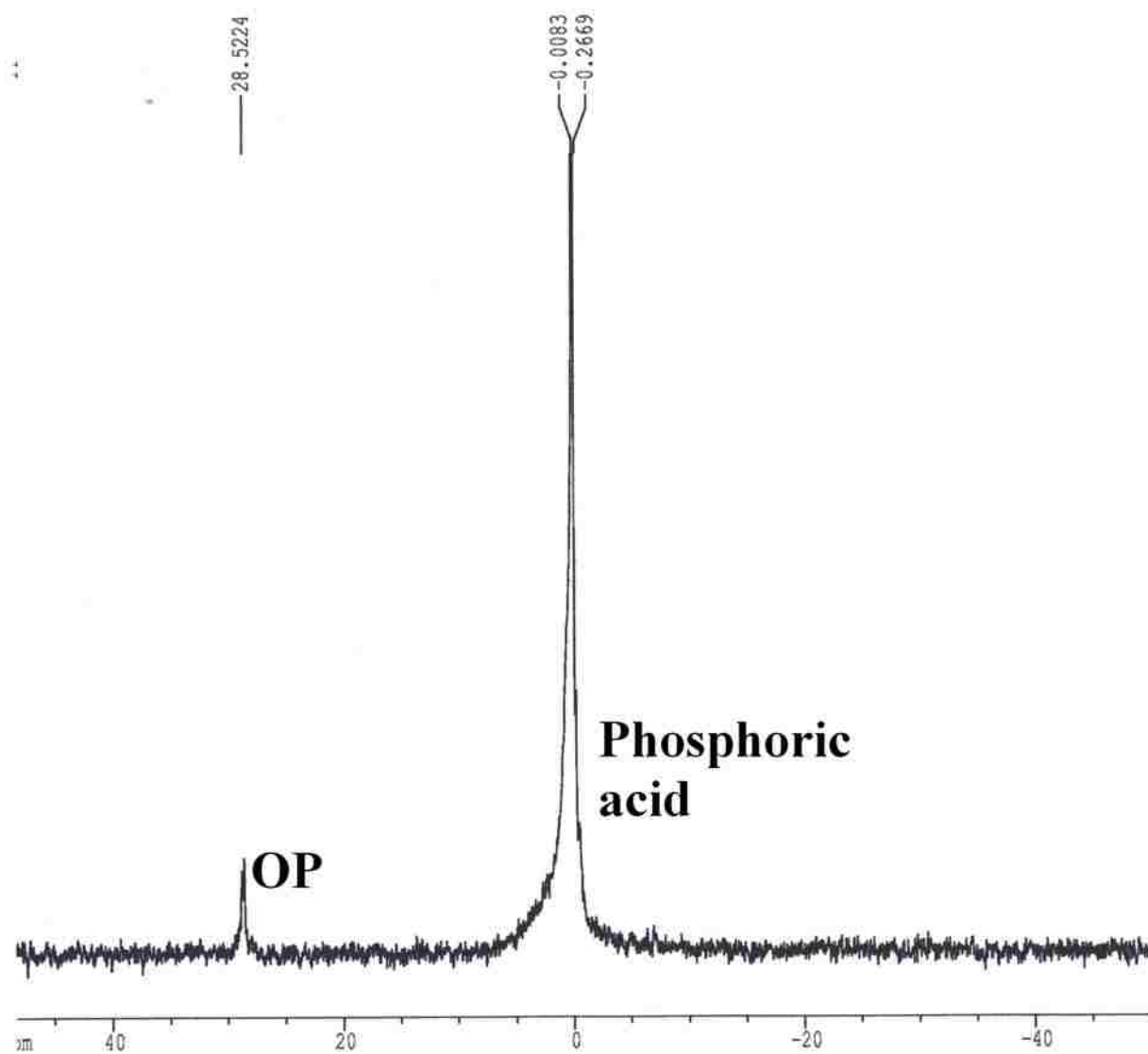
Spectrum 19a. $^1\text{H-NMR}$ of OPphac $_3\text{H}_3$, **3.6** (NS 64 in CDCl_3)



Spectrum 19b. Portion of $^1\text{H-NMR}$ of OPphac $_3\text{H}_3$, **3.6** (NS 64 in CDCl_3)



Spectrum 20. ^{31}P -NMR of OPphac₃H₃, **3.6** (NS 250 in CDCl₃)



Vita

James Kakoullis, Jr. was born in Kingston, New York, on January 16, 1980. He graduated from Pinellas Park High School in Largo, Florida, in June 1998. After graduating from Eckerd College, St. Petersburg, Florida, in May of 2002 with a Bachelor of Science, ACS certified degree in chemistry and with a concentration in biochemistry, Kakoullis began graduate work at Louisiana State University, Baton Rouge, Louisiana, under the direction of Andrew W. Maverick. James Kakoullis is currently a candidate for the degree of Master of Science in the Department of Chemistry, and will be graduating in August, 2007.