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# Synthesis and Characterization of Manganese Pyridazyl Complexes

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SYNTHESIS AND CHARACTERIZATION OF MANGANESE PYRIDAZYL  
COMPLEXES

A Thesis  
Presented to  
The Faculty of the Department of Chemistry  
Western Kentucky University  
Bowling Green, Kentucky

In Partial Fulfillment  
Of the Requirements for the Degree  
Master of Science

By  
Sana Shah

December 2013

SYNTHESIS AND CHARACTERIZATION OF MANGANESE PYRIDAZYL  
COMPLEXES

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# SYNTHESIS AND CHARACTERIZATION OF MANGANESE PYRIDAZYL COMPLEXES

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33 Pages

Directed By: Dr. Chad Snyder, Dr. Bangbo Yan and Dr. Darwin Dahl

Department of Chemistry

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Heterocyclic's and their fused-ring derivatives have been of interest for their use in electronic materials due to their ease of production, synthetic versatility, and low cost compared to traditional inorganic materials like silicon. Pyridazines have been found to be useful in catalysis gas storage, polymeric sensors and biological mimetics. When a transition-metal is fused into a synthesized pyridazine, unique properties such as conductivity and optics are allowed.

In this work, synthesized pyridazine complexes will be analyzed by mass spectroscopy, elemental analysis, nuclear magnetic resonance, imaging, x-ray crystallography, and infrared spectroscopy.

We are interested in synthesizing organometallic pyridazines and manganese pyridazyl complex for polymer research. Off-metal synthesis and characterization of manganese pyridazyl complex required three intermediate steps. The research focuses on the synthesis and characterization of various manganese pyridazyl complexes.

## I. INTRODUCTION

### Pyridazines

Pyridazine is a heteroaromatic organic compound with the molecular formula of  $C_4H_4N_2$ . It contains a six-membered ring with two adjacent nitrogen atoms (Figure 1). Heterocyclic's and their fused-ring derivatives have been of interest for their use in electronic materials due to their ease of production, use of green-chemistry (no harsh industrial chemicals in production), synthetic versatility, ability to function on flexible substrates and low cost. Pyridazines have also been found to have numerous, real world applications like catalysis,<sup>(1)</sup> polymeric sensors<sup>(2)</sup> and biological mimetics.<sup>(3)</sup> It was found that pyridazines can improve the physiochemical properties of drug molecules by increasing their water solubility. Pyridazines are also efficient water oxidation catalysts when compared to dinuclear ruthenium complex and have shown high efficiencies in catalytic water oxidation with turnover numbers up to 700.<sup>(1)</sup>

Pyridazine has no known household usage, but is found in the structures of many medicines around the world. Minaprine and pipofezine are used as antidepressants, while hydralazine and cilazapril are used for the treatment of hypertension. Pyridazine structures are found mainly in research and industry as a building block for most of the complex organic compounds.<sup>(4)</sup>

Our current interest focuses on the potential role of pyridazines in next-generation electronic devices that utilize organics as a semiconducting material. Previous studies have shown that these molecular electronic materials possess several advantages over traditional inorganic semiconducting materials. Our

research focuses on transition metal chemistry of pyridazines, namely, the formation of fused-ring pyridazines complexes to a metal, that is synthesis of 5, 6-fused pyridazines and their organometallic rhenium and manganese complexes. These fused heterocyclic will serve as synthetic models and building blocks for potential organic or organometallic compounding polymers.

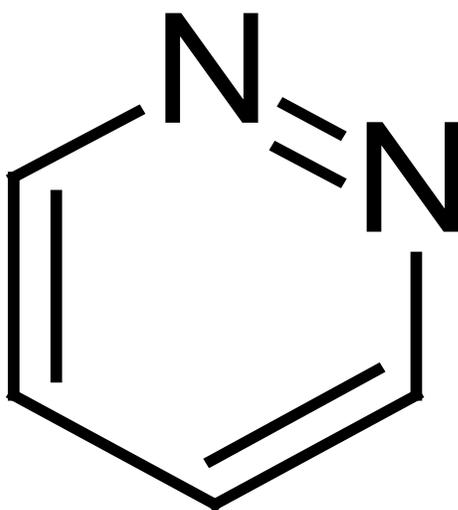


Figure 1: Basic Structure of Pyridazine.

## Organometallic Semiconductors

There are three product categories made using organic semiconductors: organic light emitting diodes (OLEDs), organic solar cells, and organic electronics. There are a number of applications in which organic semiconductors are used, such as the modern day copy machine and laser printers using organic photoconductors.

Organometallic complexes have potential for use as optically active materials in organic photovoltaic (OPV) devices, organic light emitting diodes (OLEDs) and organic light emitting fields effects transistors (OLEFETs).

Organometallic chemistry is the study of chemical compounds containing bonds between carbon and metals (Figure 2). Organic semiconductors are organic materials that have semiconducting properties, which have the electric conductivity that lies between typical metals and insulating compounds. Organometallic semiconductors invention relates to metallic-like organometallic-films which have semiconducting properties.

Organometallic semiconductors have low mobility and low switching speeds compared to silicon wafers. Organic semiconductors are compatible with plastic substances, are flexible and have lower manufacturing temperatures.

Various heterocycles have been incorporated into conducting polymers, resulting in semiconducting properties when doped. Recently, many heterocycle-containing molecules like bis-5'-hexylthiophen-2'-yl-2,6-anthracene, which is a derivative of anthracene, has been shown to behave as an organic thin-film transistor.<sup>(5)</sup> There is a critical challenge in being able to make environmentally

stable organic thin-film transistor's (OTFT's). Since aromatic heterocycles compounds can undergo charge transfer, these compounds have interesting electrical properties.



## Conductive Organometallic Compounds

It is impossible for anyone to get through a day without using more than a dozen synthetic organic polymers. Our clothes are polymers, our food is packaged in polymers, and our appliances and cars contain a number of polymer compounds.

Polymers are macromolecules composed of repeating structural units connected by covalent bonds. A conductive polymer is composed of organic materials that have the ability to conduct electricity. Typically, polymers behave as insulators while metals conduct electricity. Conductive polymers may mimic metallic conductivity and can be used as semiconductors. Biosensors, strain gauges, organic solar cells or organic light-emitting diodes are some of the applications for which conductive polymers have been studied extensively.<sup>(6)</sup>

Polyacetylene (Figure 3a), the simplest conducting polymer, was first synthesized by Natta *et al.* as a black powder and was found to be a semiconductor with the conductivity in the range of  $10^{-11}$  to  $10^{-3}$  S/cm. The range depends upon how the polymer was processed and manipulated. Later, when a polymer chemist, Hideki Shirakawa, an inorganic chemist, Alan MacDiarmid, and a physicist, Alan Heeger, were attempting to synthesize polyacetylene, a thin silvery film was produced as a result of a mistake.<sup>(7)</sup> Shirakawa and coworkers discovered the simplest conducting polymer, polyacetylene with doped halogens, winning them a Nobel Prize in Chemistry in the year 2000.<sup>(8)</sup>

The discovery of polyacetylene, the first highly conducting polymer, in 1977, resulted in huge research efforts on synthesizing conductive organic

materials. Conducting polymer films and coatings have properties such as low densities, high strength, ease of fabrication, design flexibility (can be stretched into thin films), stability, and low cost.<sup>(9)</sup> Even though the performance and stability of organic semiconductors were poor in the beginning, there have been great improvements in synthesis and processing new organic materials suitable for organic semiconductors.<sup>(10)(11)</sup>

Some of the other well known polymers include polyaniline (Figure 3b), polypyrrole (Figure 3c), and polythiophene (Figure 3d). Among the three polymers, polyaniline is considered the most promising polymer due to its simple synthesis, controllable electrical conductivity, and good environmental stability. In efforts of producing conductive polymers that are air-stable, tractable and have low band gaps, polythiophene and polypyrrole have been investigated. Since polythiophene and polypyrrole have lone pair electrons of sulfur and nitrogen atom respectively, the lone pair atoms tend to stabilize the positive charges of the p-doped polymers through resonance.

Poly(*p*-phenylene vinylene) (Figure 3e) is the only polymer that has been successfully processed into a highly ordered crystalline thin film which forms to yield samples with extremely high levels of crystalline. Poly (*p*-phenylene vinylene) is also the first conjugated polymer which was reported in light-emitting diodes.<sup>(12)</sup>

Undoped conjugated polymers can be semiconductors or insulators. Conjugated polymers can be organic semiconductors, in which the semiconducting behavior is associated with the  $\pi$  molecular orbitals delocalized

along the polymer chains. A precursor made with poly(*p*-phenylene vinylene), can be used as the active element in a large-area light-emitting diode. Since poly(*p*-phenylene vinylene) polymer is combined with good structural properties, ease of fabrication and also light emission in the green-yellow part of the spectrum with reasonably high efficiency, the polymer can be useful in the development of large-area light-emitting displays.<sup>(12)</sup>

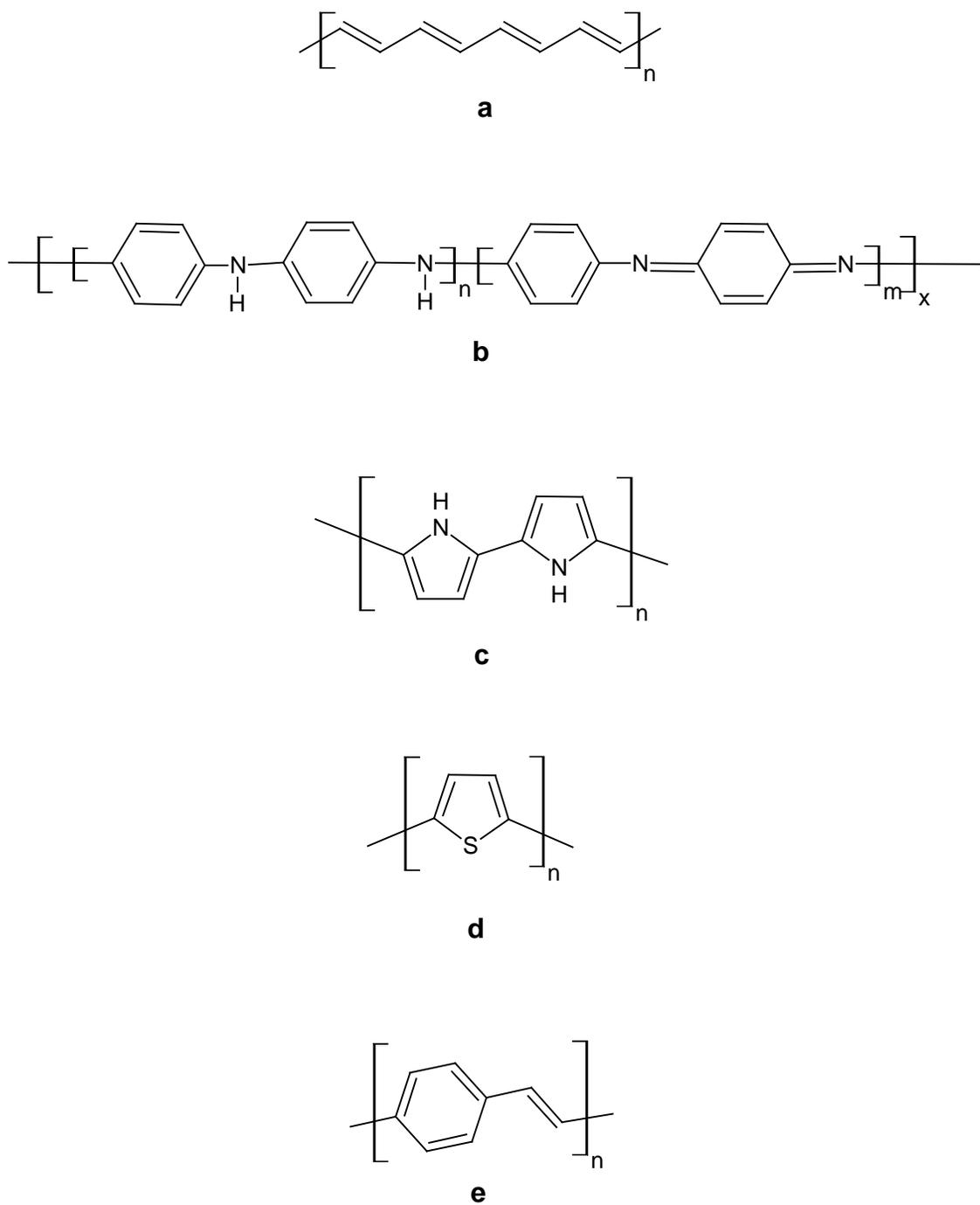


Figure 3: Structure of (a) polyacetylene, (b) polyaniline, (c) polypyrrole, (d) polythiophene, (e) poly[*p*-phenylene vinylene]

## Cymantrene

Cyclopentadienyltricarbonylmanganese, also known as cymantrene (Figure 4), is a 5-membered ring with  $\text{Mn}(\text{CO})_3$  hanging from the ring and has a formula of  $\text{C}_5\text{H}_5\text{-Mn}(\text{CO})_3$ .

Cyclopentadienylmanganese carbonyl's chemistry dates back to 1954 which is shortly after the discovery of ferrocene with the synthesis of mononuclear derivative ( $\eta^5\text{-C}_5\text{H}_5$ ) $\text{Mn}(\text{CO})_3$ , also known as cymantrene.<sup>(13)</sup> In our research we are synthesizing derivatives of cymantrene. The research presented here-in modeled derivatives of cymantrene. However our unique feature was building a pyridazine structure around cymantrene.

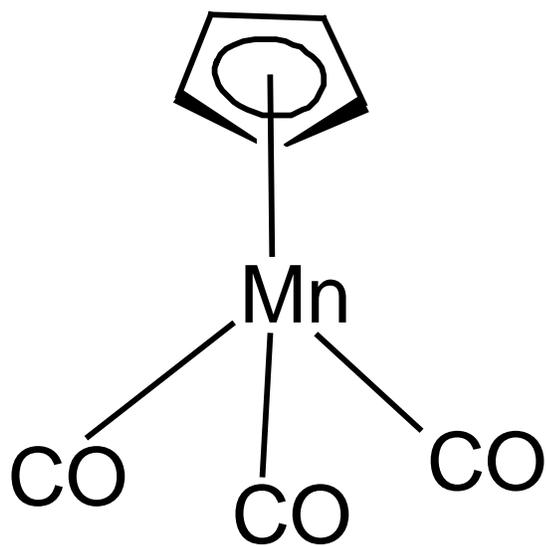


Figure 4: Basic structure of Cymantrene

## II. EXPERIMENTAL PROCEDURE

All reactions were carried out using standard Schlenk techniques under a nitrogen atmosphere unless otherwise noted. NMR solvents  $\text{CDCl}_3$ , acetone- $d_6$ , and DMSO- $d_6$  (Aldrich) were used without further purification.

Dicyclopentadiene, THF, hydrazine hydrate (Aldrich), and thallium (I) ethoxide (Strem) were used without further purification. Fulvenes, 1,2-

$\text{C}_5\text{H}_3(\text{COC}_6\text{H}_4\text{Br})(\text{COHC}_6\text{H}_4\text{Br})$  (**1a**), was prepared according to the literature methods. Ethyl ether and THF were dried over sodium benzophenone ketyl.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL-500 MHz NMR spectrometer at ca. 22 °C and were referenced to residual solvent peaks. All  $^{13}\text{C}$  NMR spectra were listed as decoupled. Infrared spectra were recorded on Spectrum One FT-IR Spectrometer. Electron ionization (EI) mass spectra were recorded at 70 eV on a Varian 500-MS Series LC/MS ion trap at Western Kentucky University's Advanced Materials Institute as well as on a DART SVP MS Thermo Scientific LTQ-XL at Eastern Kentucky University's Department of Chemistry. Melting points were taken on a standard Mel-Temp apparatus. X-ray diffraction data were collected at 90 K on a Nonius KappaCCD diffractometer at the University of Kentucky. Elemental analyses were performed at Western Kentucky University's Advanced Materials Institute and Atlantic Microlabs, Inc in Norcross, GA. Elemental analysis of the thallium salts **3a** afforded carbon and hydrogen values outside the acceptable range than those theoretically calculated. However, we attributed this observation to the presence of thallium impurities commonly present in these types of salts. These traces of inorganic

byproducts did not affect the reactivity of compound **3a** itself and further purification was not attempted.

### Synthesis of 1,2-C<sub>5</sub>H<sub>3</sub>(CO-(5-BrC<sub>6</sub>H<sub>4</sub>)(COH-(5-BrC<sub>6</sub>H<sub>4</sub>)) (**1a**)

In a 250 mL 3-necked round bottom flask, *n*-butyl lithium in hexanes (2.5 M, 13 mL, 0.0325 mol) was added to 50 mL of anhydrous diethyl ether at 0 °C. Freshly cracked cyclopentadiene (2.40 mL, 0.0364 mol) diluted with diethyl ether (10 mL) was then added dropwise to the reaction. A white suspension immediately formed. After stirring for approximately 15 minutes, **1a** (5.19 g, 0.0248 mol) was dissolved into 10 mL of diethyl ether and the solution was added dropwise to the reaction flask, causing a brick red suspension to form. The suspension was allowed to warm to room temperature and was stirred for one hour. The reaction mixture was hydrolyzed with dilute acetic acid (5%) and extracted three times with methylene chloride. The organic layers were collected, dried over MgSO<sub>4</sub>, and filtered, and the volatiles were removed *in vacuo* to yield a red-orange semisolid. Re-crystallization using methylene chloride and pentane afforded **1a** (2.32g,46%) as a red-orange solid. **Mp**: 111–121 °C. **<sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>, ppm)**: δ 6.65 (s, 1H, CHCHCH), 6.84 (s, 2H, CHCHCH), 7.47 (d, 2H, CHCHBr), 8.08 (d, 2H, CHCHBr). **<sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>, ppm)**: δ 115.1 (CHCHCH), 122.4 (CHCHCH), 123.1 (*ipso* Cp), 124.9, 128.4, 139.5, 153.1 (Ar), 167.6 (C=O). **IR (KBr, cm<sup>-1</sup>)**: 1567 (C=O), 3146 (CH), 3435 (OH). **MS(DART-LTQ)**: *m/z* 412.99 (M<sup>+</sup> + H). Analysis Calc. for C<sub>15</sub>H<sub>8</sub>O<sub>4</sub>Br<sub>2</sub>: C, 43.7; H, 1.9. Found: C, 46.1; H, 2.1.

### Synthesis of 1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>BrNH)(CC<sub>6</sub>H<sub>4</sub>BrN) (2a)

1,2-C<sub>5</sub>H<sub>3</sub>(COC<sub>6</sub>H<sub>4</sub>Br)(COHC<sub>6</sub>H<sub>4</sub>Br) (**1a**, 421 mg, 0.970 mmol) was dissolved in methanol (20 mL) in a 25 mL round-bottom flask. An excess of hydrazine hydrate (2.00 mL, 2.06 g, 41.2 mmol) was added to the solution. The solution was stirred 24 hours. To the reaction, water (10 mL) was added and an orange precipitate formed immediately. The aqueous suspension was washed with dichloromethane (3 x 5 mL) and the organic layers were collected, dried (MgSO<sub>4</sub>), and filtered. The volatiles were removed *in vacuo* and the crude product was triturated with cold hexane to give 1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>BrNH)(CC<sub>6</sub>H<sub>4</sub>BrN) (**2b**, 326 mg, 0.762 mmol, 78.6%) as an orange powder. **Mp**: 182–187 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)**: δ 7.04 (d, 2H, <sup>3</sup>J = 3.5 Hz, CHCHCH), 7.54 (t, 1H, <sup>3</sup>J = 3.5 Hz, CHCHCH), 7.67 (d, 1H, <sup>3</sup>J = 8.6 Hz, CHCHCBr), 7.79 (d, 1H, <sup>3</sup>J = 8.6 Hz, CHCHCBr). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm)**: δ 109.3 (CHCHCH), 120.3 (CHCHCH), 124.8 (CCHCH), 130.1, 132.4 (Ph), 133.5 (CN). **IR (KBr, cm<sup>-1</sup>)**: 1591 (CN), 3075 (C–H), 3200 (N–H). **MS**: *m/z* 428 (M<sup>+</sup>), 349 (M<sup>+</sup> – Br). **HRMS**: (M<sup>+</sup>) calcd 427.9348, obsd 427.9348. Anal. Calcd. for C<sub>19</sub>H<sub>12</sub>N<sub>2</sub>Br<sub>2</sub>: C, 53.3; H, 2.83; N, 6.54. Found: C, 53.1; H, 2.88.; N, 6.71

### Synthesis of [TI{1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>BrNH)(CC<sub>6</sub>H<sub>4</sub>BrN)}] (3a)

Thallium (I) ethoxide was added to a solution of 1,2-C<sub>5</sub>H<sub>3</sub>(COC<sub>6</sub>H<sub>4</sub>Br)(COHC<sub>6</sub>H<sub>4</sub>Br) (**2a**, 269 mg, 0.628 mmol) in THF (30 mL). An orange precipitate formed after 5 minutes. The solution was stirred for 24 hours at 22 °C. The precipitate was filtered and washed with cold hexane (3 x 10 mL)

providing [Ti{1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>BrNH)(CC<sub>6</sub>H<sub>4</sub>BrN)}] (**3a**, Quantitative yield, 399 mg, 0.627 mmol) as a yellow solid. **Mp**: 178–195 °C (dec). **<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, ppm)**: δ 6.44 (d, 1H, <sup>3</sup>*J* = 3.4 Hz, CHCHCH), 6.93 (t, 1H, <sup>3</sup>*J* = 3.4 Hz, CHCHCH), 7.66 (d, 1H, <sup>3</sup>*J* = 8.6 Hz, CHCHCBr), 7.99 (d, 1H, <sup>3</sup>*J* = 8.6 Hz, CHCHCBr). **<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, ppm)**: δ 110.0 (CHCHCH), 116.5 (CHCHCH), 127.0 (CCHCH), 131.0, 131.6 (Ph), 155.0 (CN). **IR (KBr, cm<sup>-1</sup>)**: 1591 (CN), 3100 (CH). **MS(EI-pos)**: *m/z* 632 (M<sup>+</sup>), 428 (M<sup>+</sup> – Ti). Anal. Calcd. for C<sub>19</sub>H<sub>13</sub>N<sub>2</sub>Br<sub>2</sub>Ti: C, 36.0; H, 2.07; N, 4.42. Found: C, 29.6; H, 1.74.; N, 2.96

#### **Synthesis of [Mn{1, 2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>OBrCH<sub>3</sub>NH)(CC<sub>6</sub>H<sub>4</sub>OBrCH<sub>3</sub>N)}(CO)<sub>3</sub>] **4a****

To a solution of [Ti{1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>OBrCH<sub>3</sub>NH)(CC<sub>6</sub>H<sub>4</sub>OBrCH<sub>3</sub>N)}] (**3a**, 482 mg, 1.05 mmol) in dry benzene (30 mL) was added [MnBr(CO)<sub>5</sub>] (473 mg, 1.16 mmol). The solution was allowed to reflux for 5 hours. The solution was filtered through a Celite plug using benzene. The solvent was removed under reduced pressure to leave a red semi-solid. The semi-solid was triturated with pentane (2 x 5 mL) to provide a red powder (**4a**, 74.9%). **Mp**: 126–136 °C (dec). **<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, ppm)**: δ 7.66 (d, 1H, <sup>3</sup>*J* = 8.6 Hz, CHCHCBr), 7.99 (d, 1H, <sup>3</sup>*J* = 8.6 Hz, CHCHCBr). **<sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>, ppm)**: δ 107.7 (CHCHCH), 120.4 (CHCHCH), 128.3 (CCHCH), 132.0, 132.2 (Ph). **IR (KBr, cm<sup>-1</sup>)**: 1559 (CN), 3041 (CH), 1933, 2034 (MnCO).

### III. RESULTS AND DISCUSSION

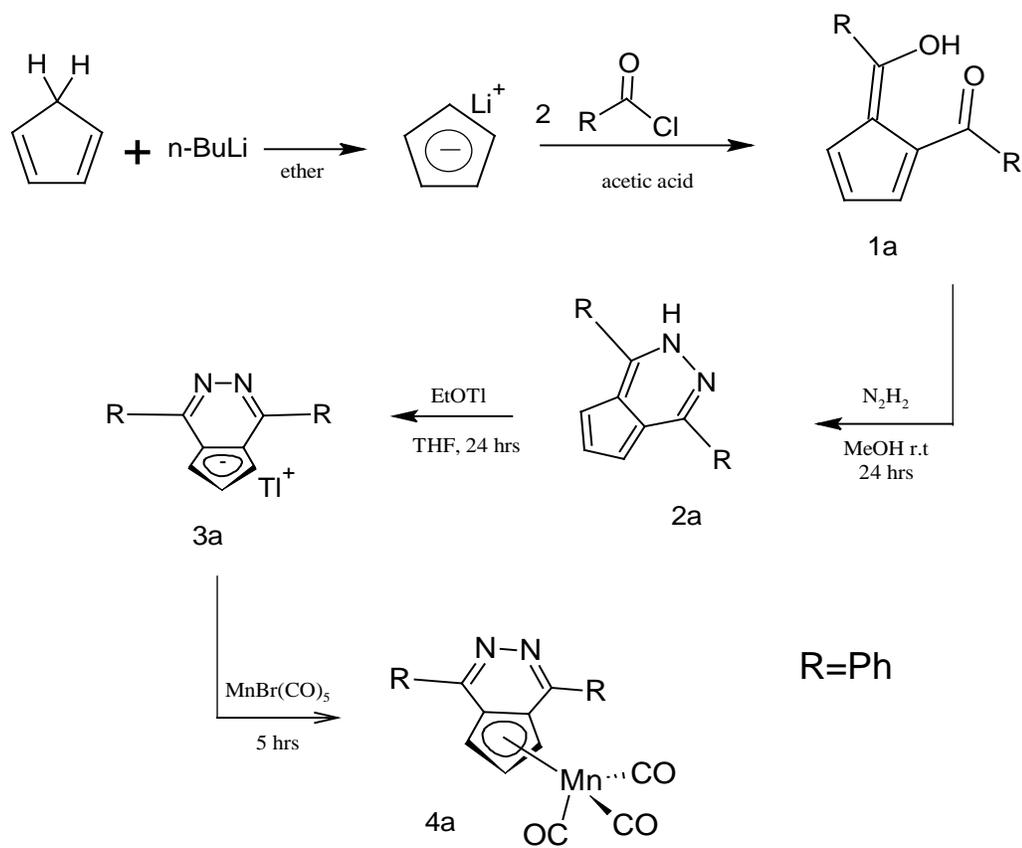
Fulvene **1a** was synthesized by the addition of freshly cracked cyclopentadiene to the solution of cold *n*-butyl lithium in diethyl ether along with 4-chlorobenzol chloride to provide fulvene. The percent yield for fulvene was 74%. IR spectroscopy displayed stretches at  $1567\text{ cm}^{-1}$  (CO) for the fulvene **1a**.  $^{13}\text{C}$  NMR spectroscopy shows a carbonyl at  $\delta$  167.6 (CO) for fulvene **1a**.  $^1\text{H}$  NMR spectroscopy for fulvene **1a** showed the following peaks:  $\delta$  6.65 (s, 1H, CHCHCH), 6.84 (s, 2H, CHCHCH), 7.47 (s, 2H, CHCHBr), 8.08 (s, 2H, CHCHBr), which confirms the fulvene structure (**1a**).

Pyridazine complex **2a** was synthesized by dissolving fulvene **1a** in methanol at room temperature, followed by the addition of hydrazine hydrate, which eventually gave a product with a percent yield of 78.6% for complex **2a**. IR spectroscopy showed stretches at  $1591\text{ cm}^{-1}$  (CN) and  $3075\text{ cm}^{-1}$  (CH) for pyridazine complex **2a**.  $^{13}\text{C}$  NMR spectroscopy has a peak at 133.5 (CN) confirming the formation of a pyridazine complex.  $^1\text{H}$  NMR spectroscopy showed signals for pyridazine complex **2a** at  $\delta$  7.04 (d, 2H,  $^3J = 3.5\text{ Hz}$ , CHCHCH), 7.54 (t, 1H,  $^3J = 3.5\text{ Hz}$ , CHCHCH), 7.67 (d, 1H,  $^3J = 8.6\text{ Hz}$ , CHCHCBr), 7.79 (d, 1H,  $^3J = 8.6\text{ Hz}$ , CHCHCBr).

Thallium salt **3a** was synthesized by the addition of thallium (I) ethoxide to the pyridazine complex **2a** in dry THF. The percent yield for the thallium compound was 99%. IR spectroscopy showed a wave number at  $1591\text{ cm}^{-1}$  (CN) and  $3100\text{ cm}^{-1}$  (CH) for the thallium compound **3a**.  $^{13}\text{C}$  NMR spectroscopy shows the peaks at  $\delta$  110.0 (CHCHCH), 116.5 (CHCHCH), 127.0 (CCHCH),

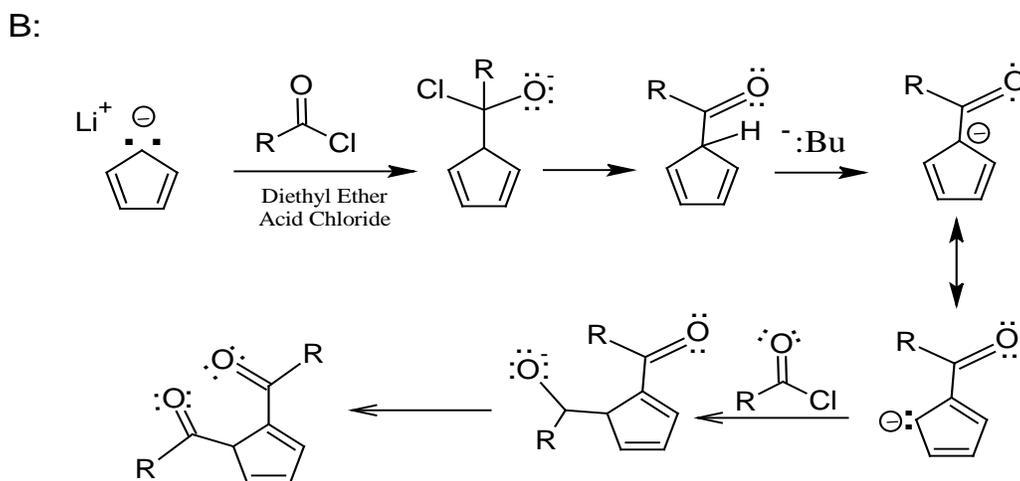
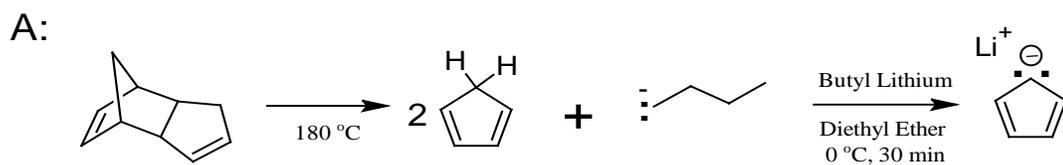
131.0, 131.6 (Ph), 155.0 (CN).  $^1\text{H}$  NMR spectroscopy showed signals for thallium compound **3a** at  $\delta$  6.44 (d, 1H,  $^3J = 3.4$  Hz, CHCHCH), 6.93 (t, 1H,  $^3J = 3.4$  Hz, CHCHCH), 7.66 (d, 1H,  $^3J = 8.6$  Hz, CHCHCBr), 7.99 (d, 1H,  $^3J = 8.6$  Hz, CHCHCBr).

Manganese complex **4a** was synthesized by the addition of manganese pentacarbonyl bromide to thallium salt **3a** in dry benzene. The solution was allowed to reflux for five hours. The percent yield was 75% for manganese complex **4a**. IR spectroscopy showed wave number at  $1559\text{ cm}^{-1}$  (CN) and  $3041\text{ cm}^{-1}$  (CH) for manganese complex **3a**. It also displayed two stretches indication of the manganese tricarbonyl structure; MnCO stretches at  $1933\text{ cm}^{-1}$  and  $2034\text{ cm}^{-1}$ .  $^{13}\text{C}$  NMR spectroscopy showed signals at  $\delta$  107.7 (CHCHCH), 120.4 (CHCHCH), 128.3 (CCHCH), 132.0, 132.2 (Ph) for the manganese complex **4a**.



**Scheme 1-**

Synthetic route for  $[\text{Mn}\{1,2\text{-C}_5\text{H}_3(\text{CC}_6\text{H}_4\text{OBrCH}_3\text{NH})(\text{CC}_6\text{H}_4\text{OBrCH}_3\text{N})\}(\text{CO})_3]$

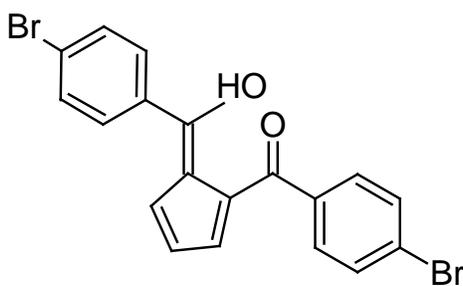


**Scheme 2**

**A.** Retro Diels-Alder Reaction Followed by deprotonation via *n*-butyl lithium  
**B.** 1,2-addition using 4-chlorobenzol chloride.

Selected Data Characterization of Fulvene 1a	
Percent yield	74.0%
Melting Point:	111°C —121°C
IR (KBr, cm <sup>-1</sup> ):	1567 (C=O), 3146 (CH), 3435 (OH).
<sup>1</sup> H NMR (500 MHz, acetone- <i>d</i> <sub>6</sub> , ppm):	δ 6.65 (s, 1H, CHCHCH), δ 6.84 (s, 2H, CHCHCH), δ 7.47 (d, 2H, CHCHBr), δ 8.08 (d, 2H, CHCHBr).
<sup>13</sup> C NMR (125 MHz, acetone- <i>d</i> <sub>6</sub> , ppm):	δ 115.1 (CHCHCH), δ 122.4 (CHCHCH), δ 123.1 ( <i>ipso</i> Cp), δ 124.9, δ 128.4, δ 139.5, δ 153.1 (Ar), δ 167.6 (C=O).

Table 1- Selected Data Characterization of Fulvene (1a).

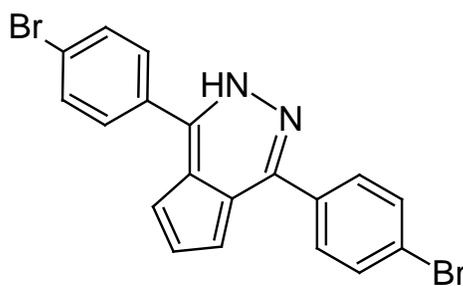


Structure of Fulvene (1a)

Figure 5: Structure of Fulvene.

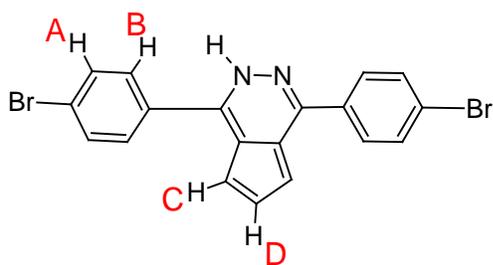
Selected Data Characterization of Pyridazine Compound 2a	
Percent yield	78.6%
Melting Point:	182 °C –187 °C
IR (KBr, cm <sup>-1</sup> ):	1591 (CM), 3075 (C–H), 3200 (N–H).
<sup>1</sup> H NMR (500 MHz, CDCl <sub>3</sub> , ppm):	δ 7.04 (d, 2H, <sup>3</sup> J = 3.5 Hz, CHCHCH), δ 7.54 (t, 1H, <sup>3</sup> J = 3.5 Hz, CHCHCH), δ 7.67 (d, 1H, <sup>3</sup> J = 8.6 Hz, CHCHCBr), δ 7.79 (d, 1H, <sup>3</sup> J = 8.6 Hz, CHCHCBr).
<sup>13</sup> C NMR (125 MHz, CDCl <sub>3</sub> , ppm):	δ 109.3 (CHCHCH), δ 120.3 (CHCHCH), δ 124.8 (CCHCH), δ 130.1, δ 132.4 (Ph), δ 133.5 (CN).

Table 2- Selected Data Characterization of Pyridazine Compound (2a)



Structure of Pyridazine (2a)

Figure 6a: Structure of Pyridazine Complex.



Structure of Pyridazine (**2a**)

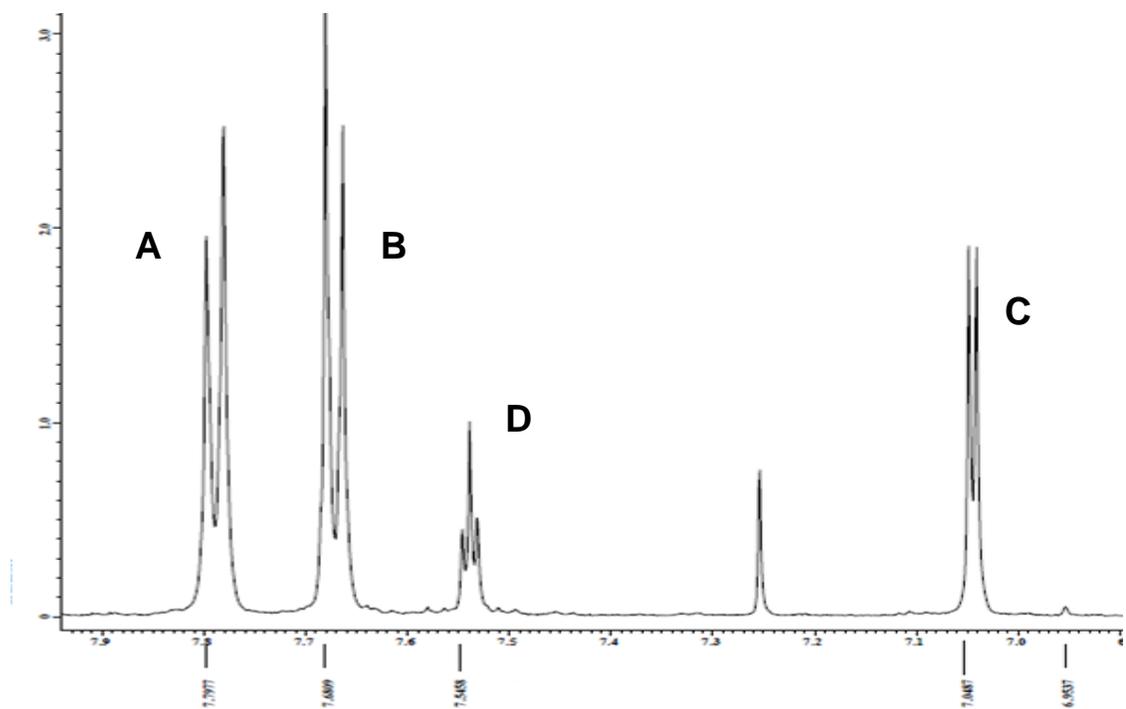


Figure 6b: <sup>1</sup>H NMR Spectroscopy for pyridazine complex.

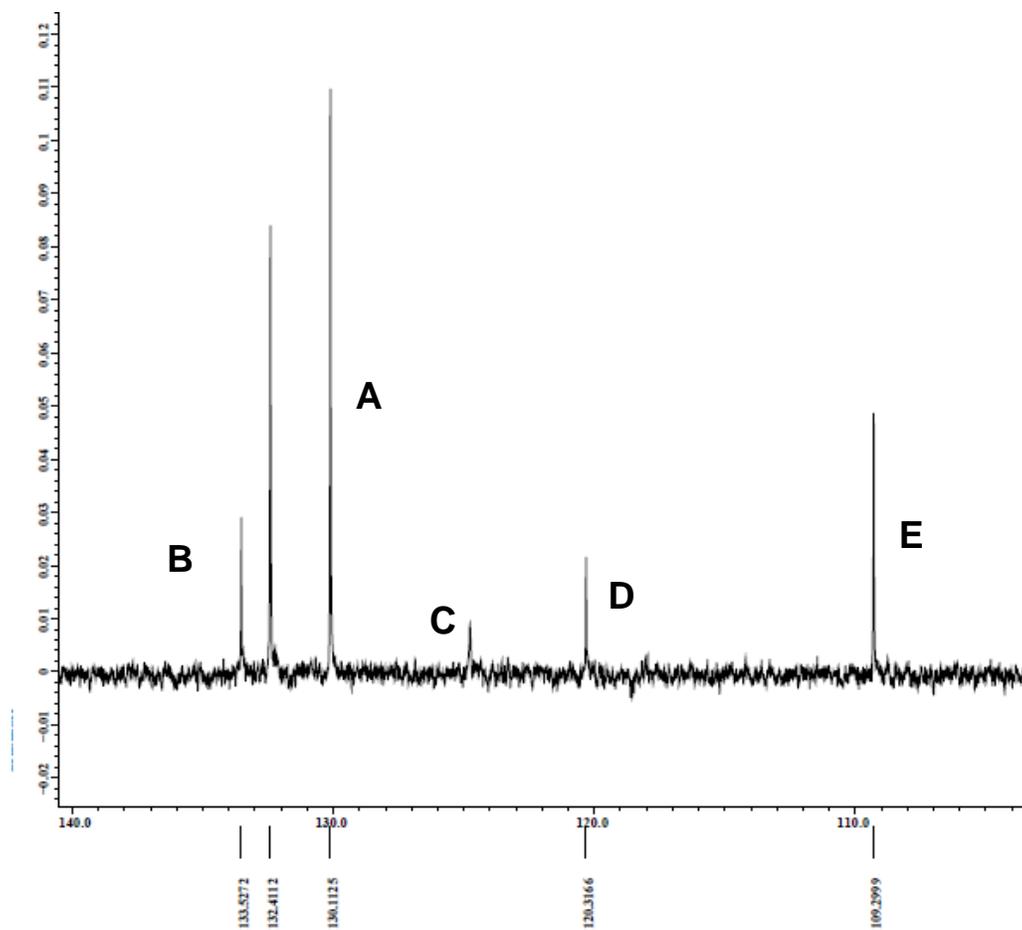
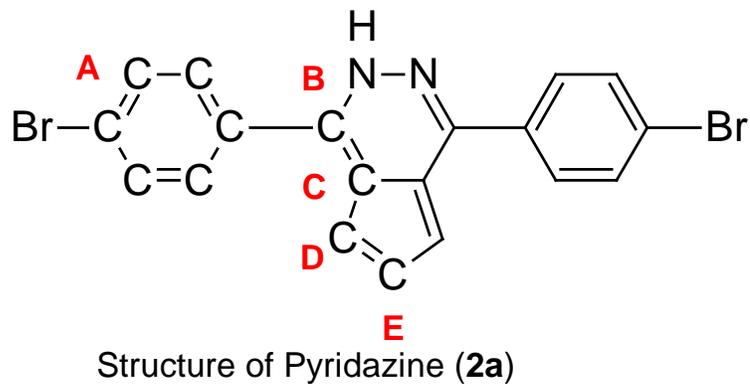


Figure 6c:  $^{13}\text{C}$  NMR Spectroscopy for pyridazine complex.

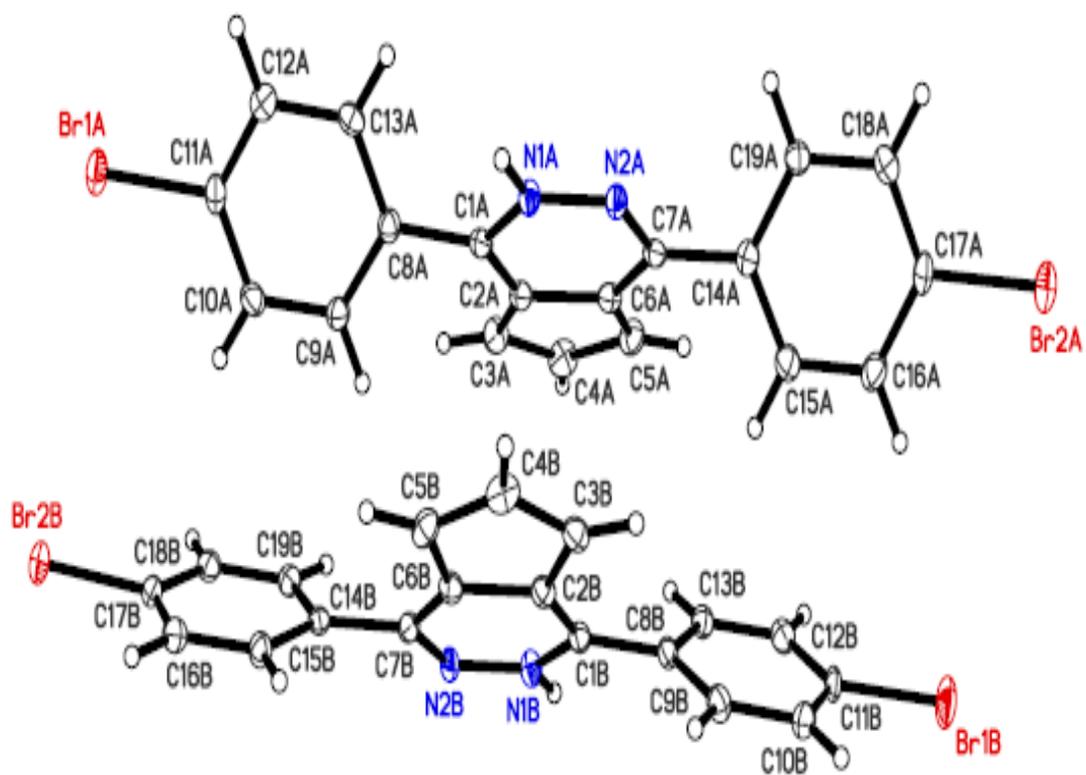
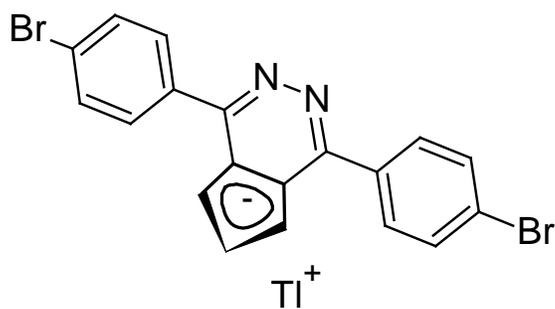


Figure 6d: X-ray crystallography of pyridazine compound (2a).

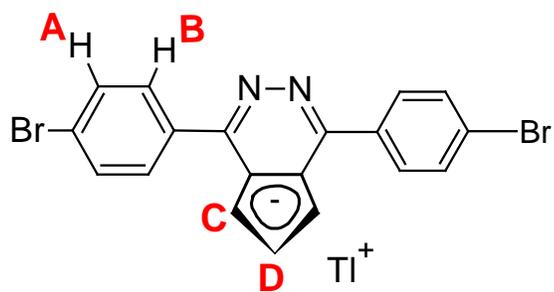
Selected Data Characterization of Thallium Salt 3a	
Percent yield	99%
Melting Point:	178°C-195°C (Dec)
IR (KBr, cm <sup>-1</sup> ):	1591 (CN), 3100 (CH).
<sup>1</sup> H NMR (500 MHz, DMSO- <i>d</i> <sub>6</sub> , ppm):	δ 6.44 (d, 1H, <sup>3</sup> J = 3.4 Hz, CHCHCH), δ 6.93 (t, 1H, <sup>3</sup> J = 3.4 Hz, CHCHCH), δ 7.66 (d, 1H, <sup>3</sup> J = 8.6 Hz, CHCHCBr), δ 7.99 (d, 1H, <sup>3</sup> J = 8.6 Hz, CHCHCBr).
<sup>13</sup> C NMR (125 MHz, DMSO- <i>d</i> <sub>6</sub> , ppm):	δ 110.0 (CHCHCH), δ 116.5 (CHCHCH), δ 127.0 (CCHCH), δ 131.0, δ 131.6 (Ph), δ 155.0 (CN).

Table 3- Selected Data Characterization of Thallium Salt (3a).



Structure of Thallium Salt (3a)

Figure 7a: Structure of Thallium Salt.



Structure of Thallium Salt (**3a**)

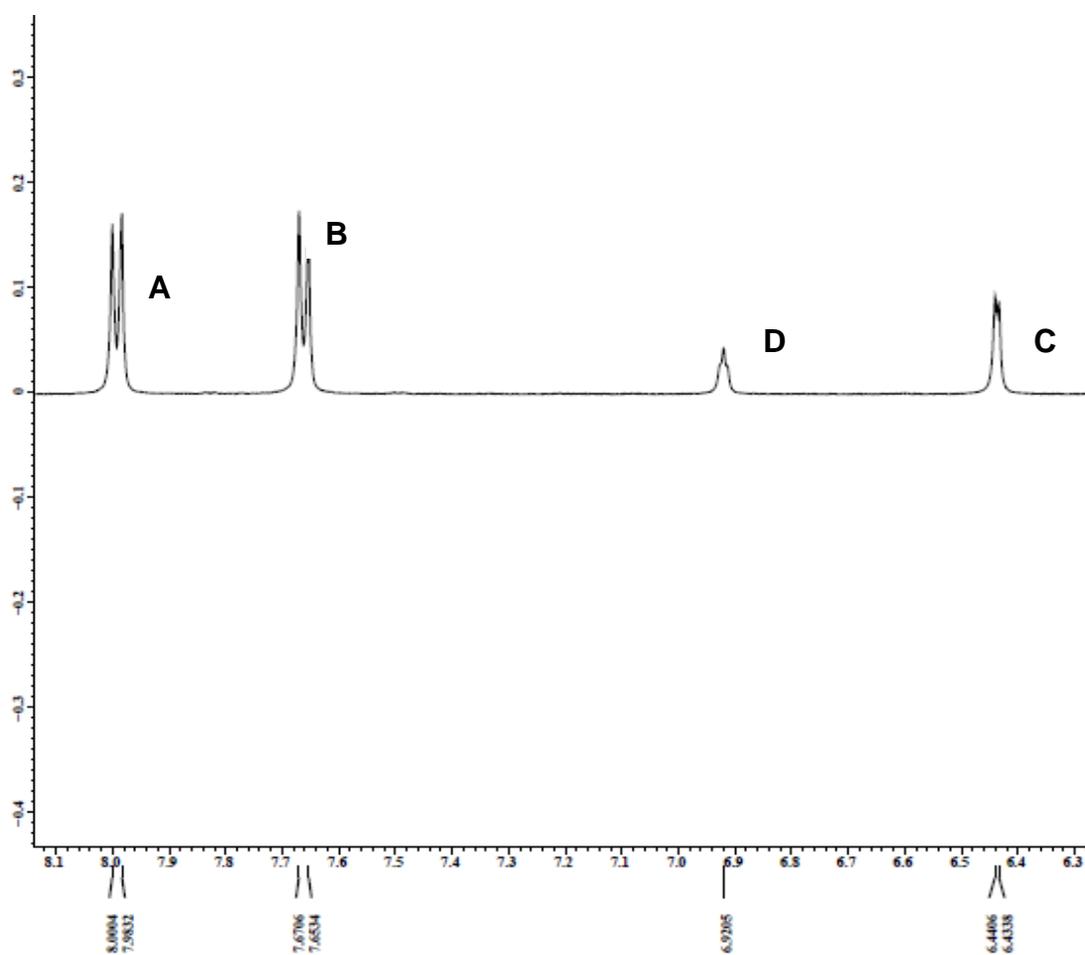
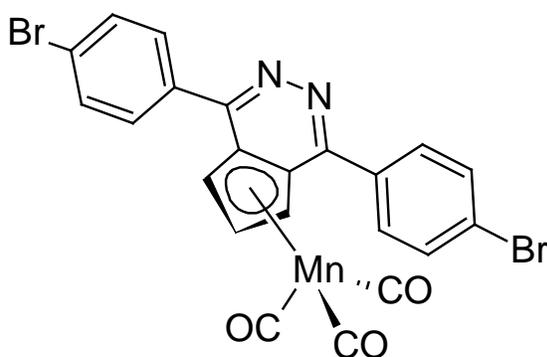


Figure 7b: <sup>1</sup>H NMR Spectroscopy for thallium salt.

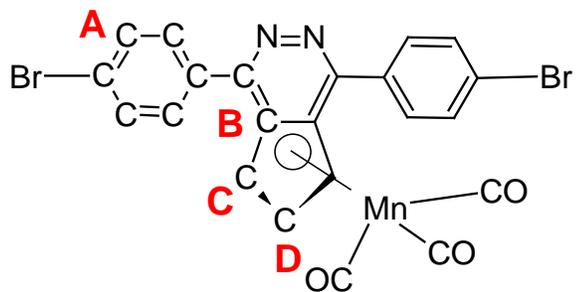
Selected Data Characterization of Manganese Complex 4a	
Percent yield	75%
Melting Point:	126 °C -136°C
IR (KBr, cm <sup>-1</sup> ):	1559 (CN) 3041(CH) 1934, 2027 (MnCO)
<sup>1</sup> H NMR (500 MHz, DMSO- <i>d</i> <sub>6</sub> , ppm):	δ 7.66 (d, 1H, <sup>3</sup> J = 8.6 Hz, CHCHCBr), δ 7.99 (d, 1H, <sup>3</sup> J = 8.6 Hz, CHCHCBr).
<sup>13</sup> C NMR (125 MHz, Acetone- <i>d</i> <sub>6</sub> , ppm):	δ 107.7 (CHCHCH), δ 120.4 (CHCHCH), δ 128.3 (CCHCH), δ 132.0, δ 132.2 (Ph).

Table 4- Selected Data Characterization of Manganese Complex (4a).



Structure of Manganese Complex (4a)

Figure 8a: Structure of Manganese Complex.



Structure of Manganese Complex  
(4a)

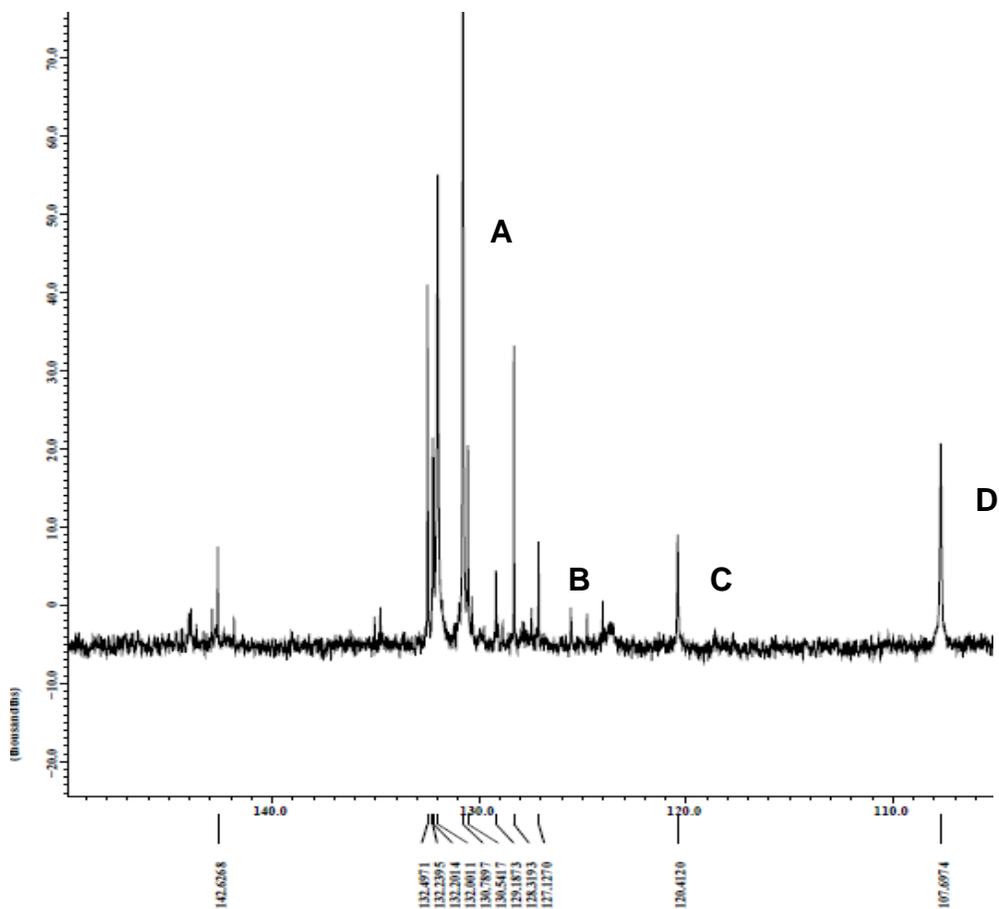
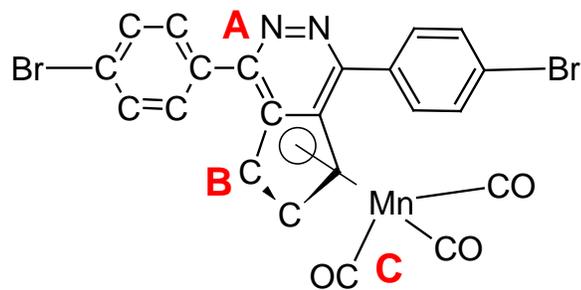


Figure 8b: <sup>13</sup>C NMR Spectroscopy for Manganese Complex.



Structure of Manganese Complex  
(4a)

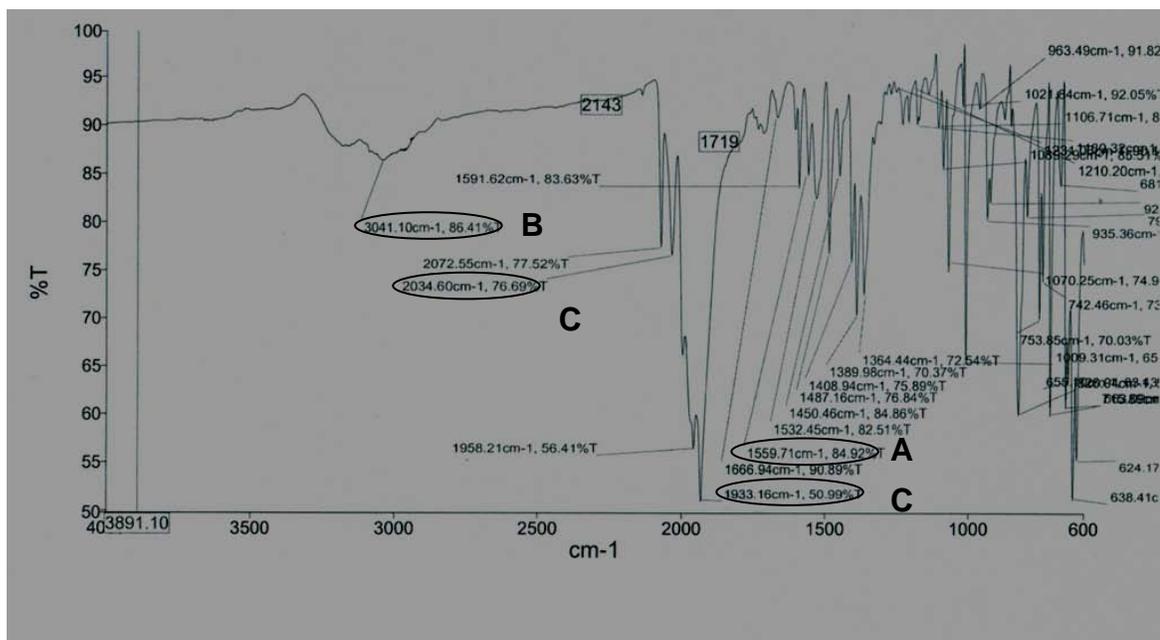


Figure 8c: IR Spectroscopy for Manganese Complex 4a.

#### IV. CONCLUSION

A series of reactions were performed which led to the synthesis of  $[\text{Mn}\{1, 2\text{-C}_5\text{H}_3(\text{CC}_6\text{H}_4\text{OBrCH}_3\text{NH})(\text{CC}_6\text{H}_4\text{OBrCH}_3\text{N})(\text{CO})_3]$ , pyridizayl manganese complex (**4a**).

The yield for the fulvene (**1a**) was 74%. The pyridazine complex's percent yield was at 78.6%. Thallium salt had a percent yield of 99%. Manganese complex yield was 75%.

IR spectroscopy was used to confirm the presence of (CO) at  $1567\text{cm}^{-1}$  for the fulvene compound (**1a**). Carbonyl group in pyridizayl manganese complex (**4a**) was found at  $1933\text{cm}^{-1}$  and  $2034\text{cm}^{-1}$ . The carbonyl group (CO) was always found approximately at  $2000\text{cm}^{-1}$  and  $1900\text{cm}^{-1}$ , which confirms the presence of carbonyl group in the manganese pyridazyl group.

$^{13}\text{C}$  NMR spectroscopy confirmed the presence dicarbonyl and manganese tricarbonyl for compounds **1a-4a**.  $^1\text{H}$  NMR spectroscopy confirmed the presence of cyclopentadiene and its substituent for compounds **1a-4a**.

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