

PREPARATION AND CHARACTERIZATION OF POSS/DICYCLOPENTADIENE
NANOHYBRIDS

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วิทยานิพนธ์นี้ศึกษาการสังเคราะห์สารออกตะโบรโมฟีนิลซิลเซสควิออกเซน (Br_8OPS) ด้วยสารไดไซโคลเพนตะไดอินด้วยปฏิกิริยาเฮ็ค (Heck Reaction) สารที่สังเคราะห์ได้เป็นสารที่มีขนาดระดับนาโนเมตร สาร Br_8OPS ในงานวิจัยนี้สังเคราะห์ตามวิธีของเลน แนวนุ่มที่ได้ผลิตภัณฑ์ตามวัตถุประสงค์ที่ตั้งไว้คือได้สาร ออกตะโบรโมฟีนิลเซสควิออกเซน (DCPD_8OPS) ขึ้นอยู่กับปริมาณสารไดไซโคลเพนตะไดอิน (DCPD) ที่เติมเข้าไปในปฏิกิริยา, ชนิดของตัวเร่งปฏิกิริยา, เวลาและอุณหภูมิในการทำการทดลอง ผลการวิเคราะห์ตรวจสอบหมู่ฟังก์ชันที่ทดสอบด้วยเครื่อง FTIR เกิดจุดยอดที่ค่า $1000\text{-}1150\text{ cm}^{-1}$, $1620\text{-}1680\text{ cm}^{-1}$ และ $3010\text{-}3100\text{ cm}^{-1}$ เป็นค่าที่บอกถึงหมู่ฟังก์ชัน O-Si-O, C=C และ C-H ตามลำดับ ซึ่งเป็นจุดยอดที่เกิดขึ้นในสารผลิตภัณฑ์ แต่อย่างไรก็ตามยังมีจุดยอดที่ค่า 500 cm^{-1} เป็นจุดที่แสดงถึงหมู่ฟังก์ชันของ C-Br จากผลนี้ชี้ให้เห็นว่าปฏิกิริยาเกิดไม่สมบูรณ์ จากผล NMR ที่ตำแหน่ง 5-6 ppm เป็นตำแหน่งที่จุดยอดแสดงให้เห็นถึงการจับกันระหว่างสาร DCPD จับกับวงฟีนิลของพอส คือพันธะของ -C-H- (เกิดจุดยอด 4 จุด) และสุดท้ายที่ตำแหน่ง 1-3.5 ppm เป็นตำแหน่งที่จุดยอดแสดงตำแหน่งโปรตอนของสาร DCPD ซึ่งประกอบด้วยพันธะ C=CH-, -CH₂- และ -CH- ผลการวิเคราะห์ด้วยเครื่อง MALDI-TOF จุดยอดที่ 1779.41 m/z แสดงถึงโครงสร้างของการจับตัวของ DCPD กับวงฟีนิลเป็นจำนวน 5 โมเลกุล เป็นตำแหน่งที่มีจุดยอดที่สูงที่สุดเมื่อเปรียบเทียบกับจุดยอดตำแหน่งอื่นๆ และ จุดยอดที่ 1699, 1857, 1935 และ 2173 m/z แสดงตำแหน่งของโครงสร้าง DCPD_4OPS , DCPD_6OPS , DCPD_7OPS and DCPD_8OPS ตามลำดับ เมื่อสังเคราะห์ได้สาร DCPD_8OPS ซึ่งมีคุณสมบัติทางด้านความร้อนดีและมีคุณสมบัติเชิงกลที่มีความเสถียรที่สูง ทำให้สาร DCPD_8OPS มีลักษณะโปร่งใสเป็นสารเริ่มต้นที่มีความแปลกใหม่ในขนาดอนุภาคระดับนาโนเมตรต่อไป

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In this study, Octabromophenylsilsesquioxane (Br_8OPS) nanocomposite was prepared following Laine's method. The reaction of Br_8OPS and dicyclopentadiene (DCPD) was investigated in order to produce new nanocomposites by Heck reactions. As the synthesis proceeded, high peaks depend on loading of DCPD, types of catalyst, time and temperature of reaction. Characteristic absorption bands of all condition are appearance of the important absorption band at $1000\text{-}1150\text{ cm}^{-1}$, $1620\text{-}1680\text{ cm}^{-1}$ and $3010\text{-}3100\text{ cm}^{-1}$ due to the formation of the O-Si-O, C=C and C-H group respectively. Furthermore phenyl group is partially formed by DCPD because FTIR spectrum of all samples showed Br group at 500 cm^{-1} wavenumber. The peaks at 5-6 ppm of NMR is approximately one group, indicating DCPD attached with phenyl ring in which there are three protons (3+1, 4 peaks) in this environment (-CH-). Finally, the alkene protons show several peaks in this area (1-3.5 ppm), as expected C=CH-, -CH₂- and -CH-. From MALDI-TOF results, based on the intensity spectrum of all samples only DCPD₅OPS peak at 1779.41 m/z is higher than other peaks. The peaks at 1699, 1857, 1935 and 2173 m/z are very weak and are assigned to structures DCPD₄OPS, DCPD₆OPS, DCPD₇OPS and DCPD₈OPS respectively. The products are in formable state with good thermal and mechanical stability and could be used as the starting materials for the formation of transparent nanocomposite systems.

Department: Chemical Engineering Student's Signature:

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CHAPTER I

INTRODUCTION

1.1 General Introduction

Recent technological breakthroughs and the desire for new functions generate an enormous demand for novel materials. Many of the well-established materials, such as metals, ceramics or plastics cannot fulfill all technological desires for the various new applications. Scientists and engineers realized early on that mixtures of materials can show superior properties compared with their pure counterparts. Most of the resulting materials show improved mechanical and thermal properties. Inorganic–organic hybrids can be applied in many branches of materials chemistry because they are simple to process and are amenable to design on the molecular scale [1].

The structural building blocks in these materials which are incorporated into the matrix are predominantly inorganic in nature and show a size range from the lower micrometer to the millimeter range and therefore their heterogeneous composition is quite often visible to the eye. Soon it became evident that decreasing the size of the inorganic units to the same level as the organic building blocks could lead to more homogeneous materials that allow further fine tuning of materials' properties on the molecular and nanoscale level, generating novel materials that either show characteristics in between the two original phases or even new properties [2].

Polyhedral oligomeric silsesquioxane (POSS), which is a class of nanofillers, has attracted widespread interest as precursor to new hybrid inorganic/organic nanocomposites because it shows well-defined rigid cage structures coupled with high symmetry and nanometer size. The empirical formulas involve POSS are $(R\text{SiO}_{1.5})_n$ where R can be epoxy, alkyl, alkylene, aryl, arylene group and hydrogen [3].

One derivative of poly(bromo-octaphenylsilsesquioxane), $\text{Br}_{5,3}\text{OPS}$, has been extensively developed for nanoconstruction applications using catalytic coupling reactions [4]. Br_8OPS was synthesized from octa-phenylsilsesquioxane (OPS) through bromination reaction in dichloromethane medium under nitrogen atmosphere. Theoretically, DCPD can be transformed to cyclopentadiene (CPD) at high temperature and CPD is reversible to DCPD at room temperature. In accordance with the recently successful development of new derivative - Br_8OPS [5], the investigation of reaction of Br_8OPS with dicyclopentadiene (DCPD) is performed to produce new nanohybrid and transparent smart materials. Nanohybrid was synthesized by using Heck reaction.

The Heck reaction couples aryl or unsaturated halides with alkenes in the presence of a strong base and a palladium catalyst to form substituted alkenes. Especially, palladium-catalyzed arylation has proven to be one of the most powerful means to form carbon-carbon bonds in organic synthesis [6]. Bromophenylsilsesquioxane (Br_8OPS), has an octahedral structure that represents a very useful nanoconstruction site. Dicyclopentadiene is a suitable substrate for multiple arylations with aryl bromides in palladium-catalyzed reaction. The strong base is destroyed the cage of POSS thus we have to use weak base in this reaction.

In this respect we became interested in the synthesis of octadicyclopentadiene substituted in Br₈OPS. Thus, various palladium catalysts under appropriate conditions will be investigated to obtain the optimal parameters for synthesis. Because DCPD can be transformed to be CPD while heating and vice versa while cooling, we expect that the new nanohybrid will be used as thermoformable material which exhibits high strength as ceramic but can be thermoformed at low temperature (around 100 °C).

1.2 Objectives

To synthesize Octaphenyldicyclopentadiene silsesquioxane derivative from Br₈OPS and study their chemical properties

1.3 Scopes of the research

1.3.1 Vary the conditions for synthesis of Octadicyclopentadienephenyl silsesquioxane (DCPD₈OPS). The following parameters are studied:

- a. Various time for synthesized reaction i.e. 3 and 7 days
- b. Various temperature for synthesized reaction i.e. 40, 60, and 80 °C
- c. Various catalyst for synthesized reaction i.e. Bis(tri-tert-butylphosphine) palladium(0), tris(dibenzylidenacetone) dipalladium(0) and palladium(II) acetate

1.3.2 Compare chemical properties of nanocomposites from each condition. The following properties are studied:

- a. Functional group of DCPD₈OPS
 - Fourier Transform Infrared Spectroscopy (FTIR)
- b. Interaction of molecule DCPD₈OPS
 - Nuclear Magnetic resonance (NMR)
- c. Molecular weight of DCPD₈OPS
 - Matrix-Assisted Laser-Desorption/Time-of-Flight Spectrometry (MALDI-TOF)

CHAPTER II

THEORY

2.1 The development of hybrid materials

Although we do not know the original birth of hybrid materials exactly it is clear that the mixing of organic and inorganic components was carried out in ancient world. At that time the production of bright and colorful paints was the driving force to consistently try novel mixtures of dyes or inorganic pigments and other inorganic and organic components to form paints that were used thousands of years ago. Therefore, hybrid materials or even nanotechnology is not an invention of the last decade but was developed long time ago. However, it was only at the end of the 20th and the beginning of the 21st century that it was realized by scientists, in particular because of the availability of novel physico–chemical characterization methods, the field of nanoscience opened many perspectives for approaches to new materials. The combination of different analytical techniques gives rise to novel insights into hybrid materials and makes it clear that bottom up strategies from the molecular level towards materials' design will lead to novel properties in this class of materials [1].

Apart from the use of inorganic materials as fillers for organic polymers, such as rubber, it was a long time before much scientific activity was devoted to mixtures of inorganic and organic materials. One process changed this situation: the sol–gel process. This process, which will be discussed in more detail later on, was developed in the 1930s using silicon alkoxides as precursors from which silica was produced. In fact this process is similar to an organic polymerization starting from molecular precursors resulting in a bulk material. Contrary to many other procedures used in the

production of inorganic materials this is one of the first processes where ambient conditions were applied to produce ceramics. The control over the preparation of multicomponent systems by a mild reaction method also led to industrial interest in that process. In particular the silicon based sol-gel process was one of the major driving forces which has become the broad field of inorganic-organic hybrid materials. The reason for the special role of silicon was its good processability and the stability of the Si—C bond during the formation of a silica network which allowed the production of organic-modified inorganic networks in one step [1].

2.1.1 Advantages of Combining Inorganic and Organic Species in One Material

The most obvious advantage of inorganic-organic hybrids is that they can favorably combine the often dissimilar properties of organic and inorganic components in one material (Table 2.1). Because of the many possible combinations of components this field is very creative, since it provides the opportunity to invent an almost unlimited set of new materials with a large spectrum of known and as yet unknown properties. Another driving force in the area of hybrid materials is the possibility to create multifunctional materials [2].

2.1.2 Building Block

In recent years many building blocks have been synthesized and used for the preparation of hybrid materials. Chemists can design these compounds on a molecular scale with highly sophisticated methods and the resulting systems are used for the formation of functional hybrid materials. Many future applications, in particular in nanotechnology, focus on a bottom-up approach in which complex structures are hierarchically formed by these small building blocks. This idea is also one of the driving forces of the building block approach in hybrid materials. Representative

examples of such well-defined building blocks are modified inorganic clusters or nanoparticles with attached reactive organic groups (Figure. 2.1) [2].

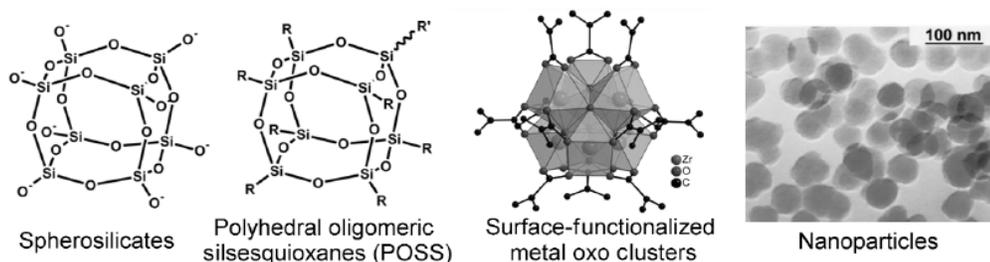


Figure 2.1 Typical well-defined molecular building blocks used in the formation of hybrid materials [2].

Table 2.1 Comparison of general properties of typical inorganic and organic materials [1]

<i>Properties</i>	<i>Organics (polymers)</i>	<i>Inorganics (SiO₂, transition metal oxides (TMO))</i>
Nature of bonds	covalent [C—C], van der Waals, H-bonding	ionic or iono-covalent [M—O]
T_g	low (–120 °C to 200 °C)	high (>>200 °C)
Thermal stability	low (<350 °C–450 °C)	high (>>100 °C)
Density	0.9–1.2	2.0–4.0
Refractive index	1.2–1.6	1.15–2.7
Mechanical properties	elasticity plasticity rubbery (depending on T_g)	hardness strength fragility
Hydrophobicity	hydrophilic	hydrophilic
Permeability	hydrophobic ±permeable to gases	low permeability to gases
Electronic properties	insulating to conductive redox properties	insulating to semiconductors (SiO ₂ , TMO) redox properties (TMO) magnetic properties
Processability	high (molding, casting, film formation, control of viscosity)	low for powders high for sol–gel coatings

2.2 Polyhedral Oligomeric Silsesquioxane (POSS)

POSS technology is derived from a continually evolving class of compounds closely related to silicones through both composition and a shared system of nomenclature. POSS chemical technology has two unique features; i.e. the hybrid composition and the large molecules of POSS. The chemical composition is a hybrid, intermediate ($\text{RSiO}_{1.5}$) between that of silica (SiO_2) and silicone (R_2SiO). In addition, POSS molecules are physically large with respect to polymer dimensions and nearly equivalent in size to most polymer segments and coils as illustrated in Figure 2.2 [7].

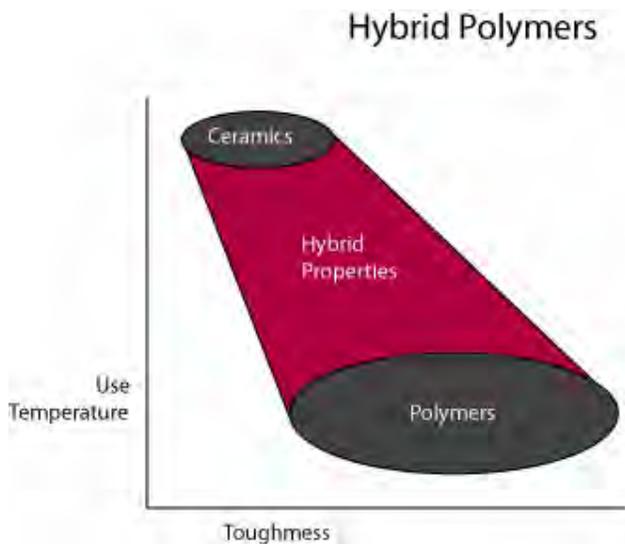


Figure 2.2 Polymer with oxidation resistance, toughness and processability [7].

Polyhedral oligomeric silsesquioxane (POSS) molecules consist of core silica cage with organic-inorganic hybrid composition and their formulas are $(\text{RSiO}_{1.5})_n$ where R can be epoxy, alkyl, alkylene, aryl, arylene group and hydrogen and n can be 8, 10, 12, respectively [6]. The structures of POSS depend on the method of their preparation, experimental factors, including product solubilities, initial monomer

concentration, nature and stability of the solvent, temperature, pH, the amount of free water available, and the type of catalyst (acid or base) used to facilitate condensation.

The general structures of POSS are T_8^R , T_{10}^R , T_{12}^R as illustrated in Figure 2.3 [8]

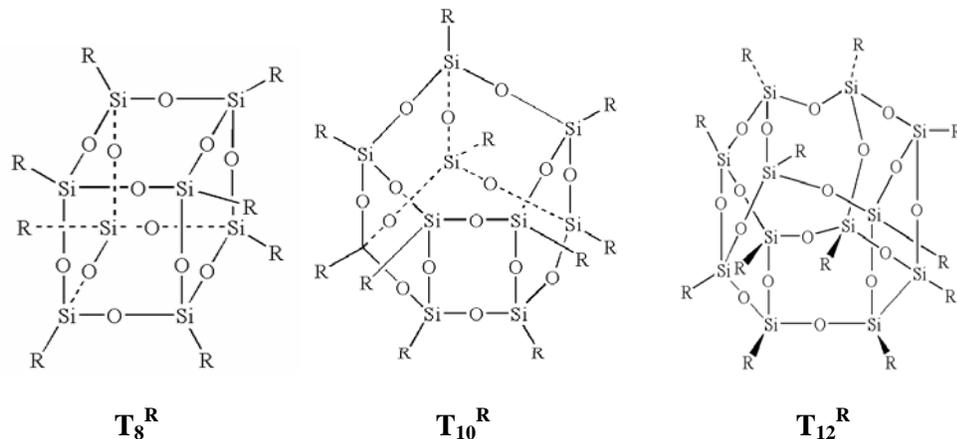


Figure 2.3 Diagram showing the fully condensed and prismatic POSS structures, T_8^R , T_{10}^R , T_{12}^R , followed the hydrolysis process [8].

POSS molecule contains covalent bonded reactive functional groups which are suitable for polymerization or grafting. They also have one or more functional groups on vertex cage of them as shown in Figures 2.4 and 2.5. The results of adding POSS cage structure into polymeric network are the improvement in polymer's properties, increase thermal and mechanical properties, enhancement oxidation resistance and surface hardening. These enhancements result in improved mechanical properties as well as reductions in flammability [6]. The T_8 structure has been suggested as a model for silica surfaces.

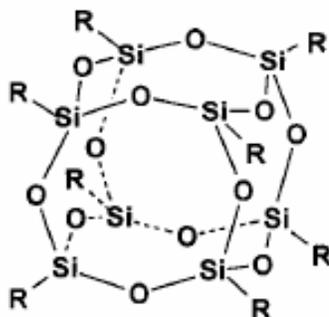


Figure 2.4 Schematic illustration of polyhedral oligomeric silsesquioxane (POSS) functional molecules [6].

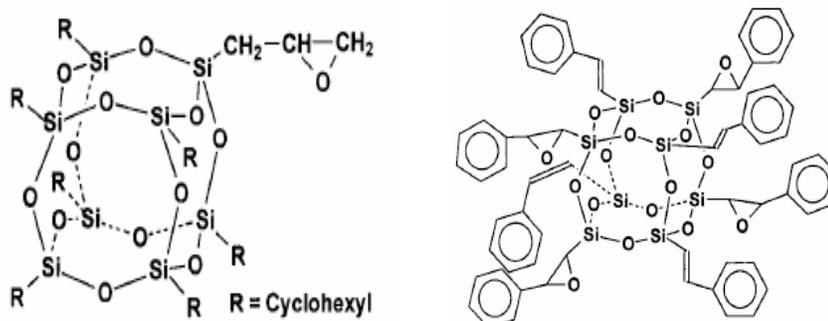


Figure 2.5 Schematic illustrations of polyhedral oligomeric silsesquioxane (POSS) multifunctional molecules [6].

As shown in Figures 2.3, POSS frameworks may be prepared by using trifunctional organosilicon monomers as illustrated in Figure 2.6 [6].

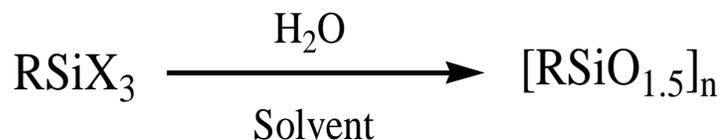


Figure 2.6 Diagram showing how POSS frameworks may be prepared by using trifunctional organosilicon monomers

As illustrated in Figure 2.7, the size of POSS cage is comparable to dimensions of linear polymer. Enhancement in the physical and mechanical properties of POSS incorporating polymer segments results from POSS's ability to control the motion of polymer chains while still maintaining the process. This is a direct result of POSS nano size related to polymer dimension [8].

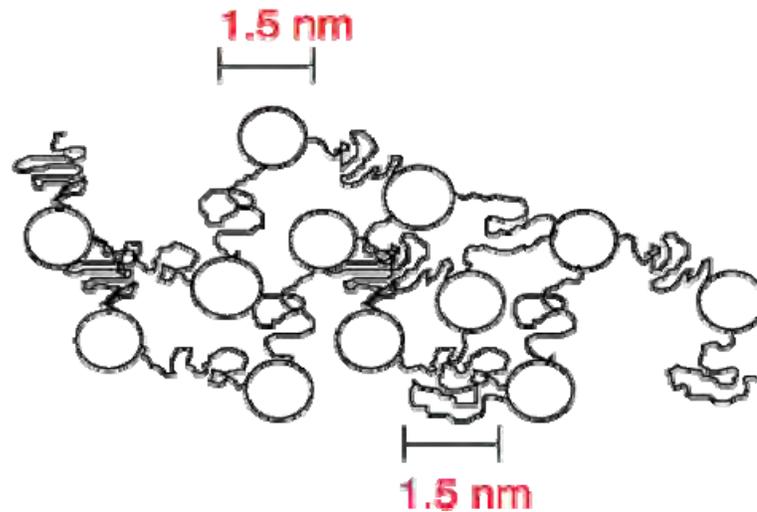


Figure 2.7 Diagram showing the size of the pendant POSS cage - i.e. 1.5 nm [8].

Polymer nanocomposites are polymers filled with particles having at least one dimension in the nanometer range and have attracted tremendous attention from researchers in the field of polymer science during the recent years. Compared to neat polymers, properties enhancements of POSS can exhibit substantially improved:

- Increased T_g
- Reduced Flammability
- Reduced Heat Evolution
- Low Density
- Disposal as Silica

- Extended Temperature Range
- Low Thermal Conductivity
- Thermoplastic or Curable
- Enhanced Blend Miscibility
- Altered Mechanical properties
- Reduced Viscosity

2.3 Rice Husk Ash (RHA)

Husk is byproduct from rice milling generates. Husk surrounds the paddy grain. During milling of paddy about 78% and 22% are weight received as rice and husk, respectively. This husk is used as fuel for power generation in small electricity plant in Thailand. In the rice mills husk is used to generate steam for the parboiling process. This husk contains about 75% organic volatile. In addition 25% of the weight of this husk is converted into ash during the firing process, which is known as rice husk ash (RHA). This RHA contains around 85% to 90% amorphous silica [9]. Color of RHA depends on heat temperature, in which high and low temperature of heat often show RHA in white and black, respectively. The chemical components of RHA are shown in Table 2.2. RHA is an excellent insulator, having low thermal conductivity, high melting point, low bulk density and high porosity [10].

Table 2.2 Chemical constituents of RHA [10]

Compositions	Quantity (%)
SiO ₂	86.9 – 97.3
K ₂ O	0.58 – 2.5
Na ₂ O	0.0 – 1.75
CaO	0.2 – 1.5
MgO	0.12 – 0.96
Fe ₂ O ₃	0.0 – 0.54
P ₂ O ₅	0.2 – 2.85
SO ₃	0.10 – 1.13
Cl ₂	0.0 – 0.42

2.4 Dicyclopentadiene

Dicyclopentadiene, abbreviated as DCPD, is the chemical compound with the formula of C₁₀H₁₂. The structure of DCPD is shown in Figure 2.8. At room temperature, it is a white crystalline solid with a camphor-like odor. Its energy density is 10,975 Wh/l. Dicyclopentadiene is coproduced in large quantities in the steam cracking of naphtha and gas oils to ethylene [11].

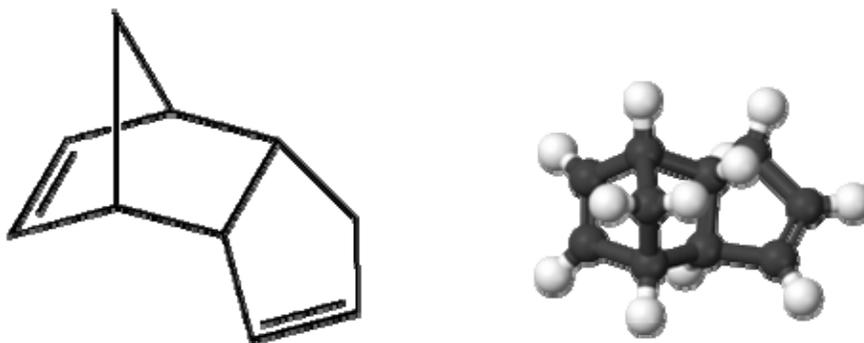


Figure 2.8 Structure of Dicyclopentadiene [11]

When heated above 100 °C, dicyclopentadiene undergoes a retro-Diels-Alder reaction to yield cyclopentadiene (CPD), which is an important compound in both organic and inorganic chemistry. The reaction is reversible and at room temperature cyclopentadiene slowly dimerizes to reform dicyclopentadiene [11]. The mechanism of DCPD transforming to CPD is shown in Figure 2.9. The major use of DCPD is resins, particularly unsaturated polyester resins. It is also used in inks, adhesives, and paints.

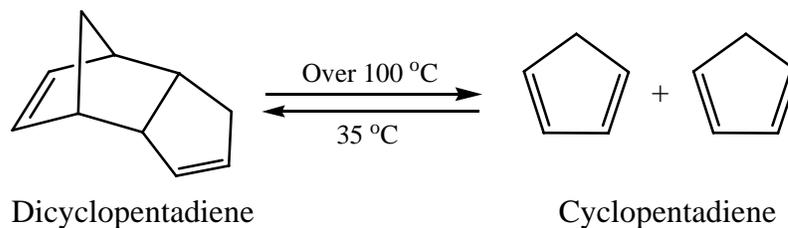


Figure 2.9 Mechanism of DCPD transforming to CPD

2.5 Heck reaction

The Heck reaction (also called the Mizoroki-Heck reaction) is the chemical reaction of an unsaturated halide (or triflate) with an alkene and a strong base and palladium catalyst to form a substituted alkene. Figure 2.10 shows mechanism of Heck reactions [12]. Halide ion is halogen atom bearing a negative charge. The halide anions are fluoride (F^-), chloride (Cl^-), bromide (Br^-), iodide (I^-) and astatide (At^-). Such ions are presented in all ionic halide salts. It is named after the American chemist Richard F. Heck. DCPD₈OPS can be synthesized by Heck reaction. Figure 2.11 shows mechanism of Heck reaction in this research.

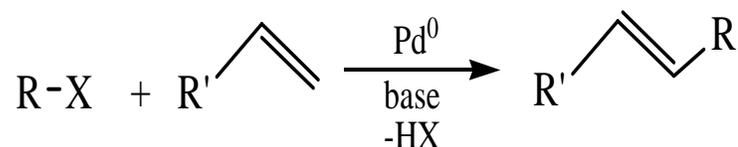


Figure 2.10 Mechanism of Heck reactions [12]

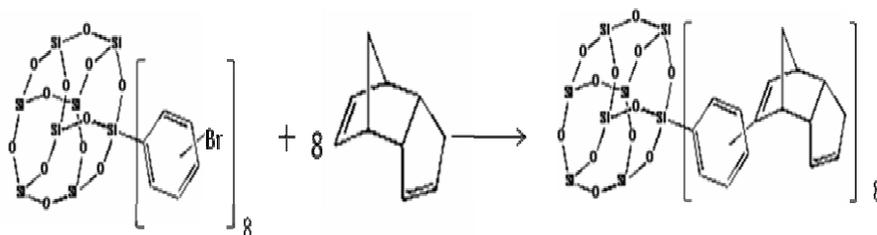


Figure 2.11 Mechanism of Octadicyclopentadienylphenyl silsesquioxane

The reaction is performed in the presence of an organopalladium catalyst. The halide or triflate is an aryl, benzyl, or vinyl compound and the alkene contains at least one proton and is often electron-deficient such as acrylate ester or an acrylonitrile. The catalyst can be tetrakis(triphenylphosphine)palladium(0), palladium chloride or palladium(II) acetate. The ligand is triphenylphosphine or BINAP. The base is triethylamine, potassium carbonate or sodium acetate.

This coupling reaction is stereoselective with a propensity for trans coupling as the palladium halide group and the bulky organic residue move away from each other in the reaction sequence in a rotation step. The Heck reaction is applied industrially in the production of naproxen and the sunscreen component octylmethoxycinnamate. As illustrated in Figure 2.12, the naproxen synthesis includes a coupling between a brominated naphthalene compounds with ethylene [12].

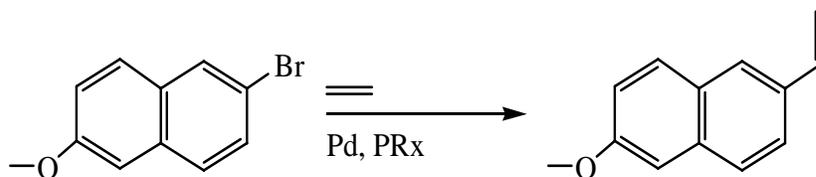


Figure 2.12 Mechanism reaction of brominated naphthalene compound with ethylene [12]

Reaction mechanism cycle

The Figure 2.13 shows mechanism cycle of Heck reaction. For instance, palladium (II) acetate is reduced by triphenylphosphine to di(triphenylphosphine) palladium(0) and triphenylphosphine is oxidized to triphenylphosphine oxide in step I. Step II is an oxidative addition in which palladium inserts itself in the aryl to bromide bond. In step III, palladium forms a π complex with the alkene and in step IV the alkene inserts itself in the palladium - carbon bond in a syn addition step. Step V is a torsional strain relieving rotation and step 6 is a Beta-hydride elimination step with the formation of a new palladium - alkene π complex. This complex is destroyed in step VII. The palladium (0) compound is regenerated by reductive elimination of the palladium (II) compound by potassium carbonate in the final step VIII [12].

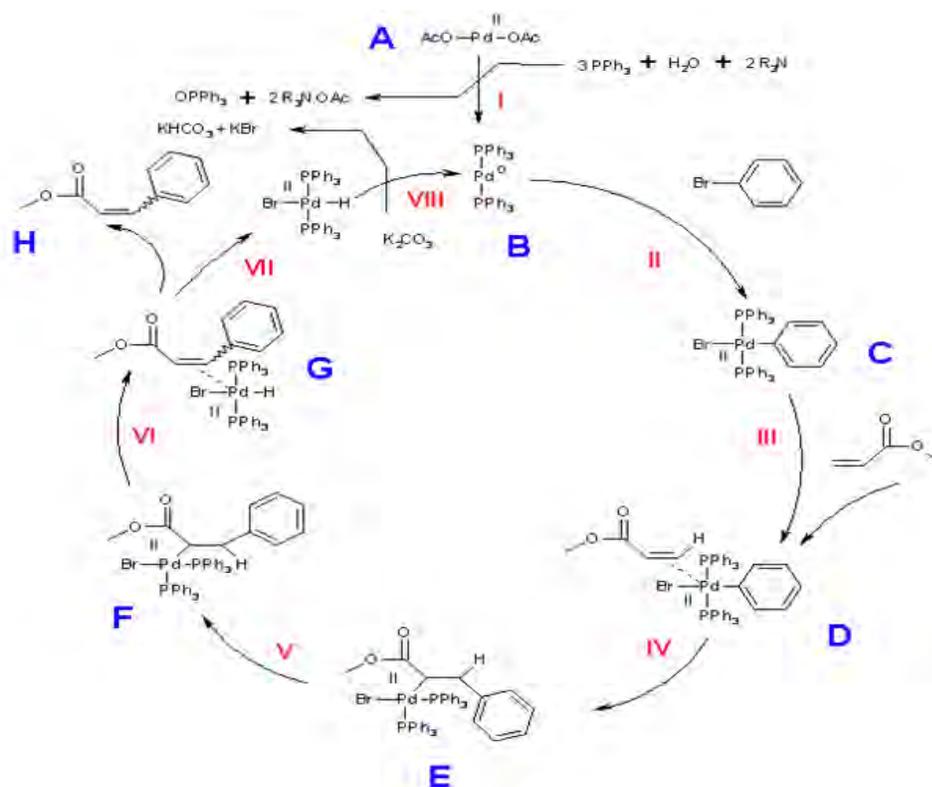


Figure 2.13 Mechanism cycle of aryl halide with alkene [12]

2.6 Octabromophenyl silsesquioxane (Br₈OPS)

Octaphenylsilsesquioxane (OPS) is a cubic, highly insoluble molecule. Figure 2.14 shows the structure of OPS. Functionalizing OPS with bromine would make it so that the molecule could be used to make a variety of new materials. The Br would be added to the phenyl rings that are attached to each Si at the corner of cage [13]. The mechanism of this reaction is shown in figure 2.15.

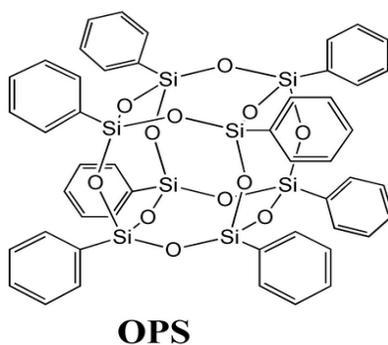


Figure 2.14 Structure of Octaphenylsilsesquioxane [13]

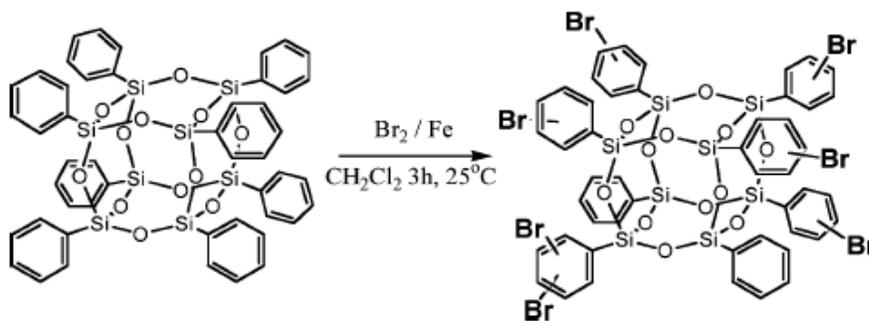


Figure 2.15 Mechanism of Octabromophenyl silsesquioxane formation [4]

For the Br₈OPS reaction, MALDI-TOF analysis of the reaction product showed peaks at 1693, 1773 and 1853 m/z. The 1773 m/z peak is the largest and indicates Br₈OPS. The other peaks are both less than 30% and indicate Br₇OPS and Br₉OPS. The average of the reaction is Br_{8.1} OPS. Figure 2.16 shows MALDI-TOF data for this reaction [13].

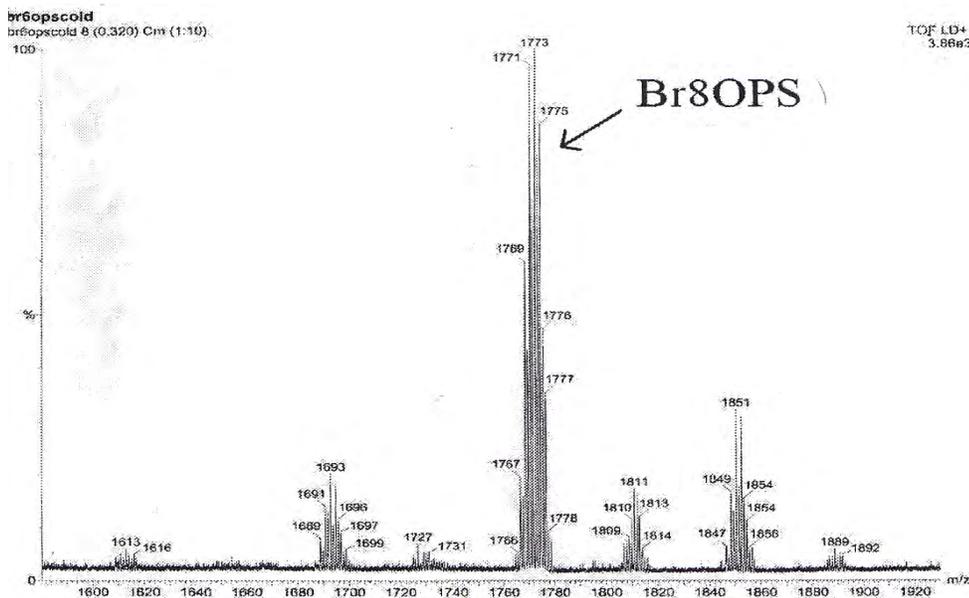


Figure 2.16 MALDI-TOF data of Br₈OPS [13]

CHAPTER III

LITERATURE REVIEWS

This chapter presents the literature reviews of the previous works related to this research. The developments of organic-inorganic nanocomposites' properties have attracted much research interest in recent years. The inorganic nanophases are polyhedral oligomeric silsesquioxanes (POSS). Typical cage of POSS are referred to as T_8 , T_{10} and T_{12} cages. Most of researchers are interested in T_8 cage and various functional groups of POSS [3-5, 15-16]. The main materials for synthesizing POSS are silica. The burning of husk in air always leads to the formation of silica. POSS can be synthesized from rice husk ash which is a product from combustions.

The work can be classified into two parts. The first part concerns the functionalizing cubic silsesquioxanes with bromine while the other part concerns types of reaction to synthesize Br_8OPS with new chemicals. Both parts are shown as follows.

3.1 Functionalizing cubic silsesquioxanes with bromine

Octaphenylsilsesquioxane (OPS) can be functionalized by adding bromine to phenyl rings. Br_8OPS can be made by combining Br_2 with OPS in the presence of solvent, while $Br_{16}OPS$ and $Br_{24}OPS$ can be synthesized by using a Lewis catalyst like Fe or $FeBr_3$ to complete the reaction. High concentration of bromine can be added to OPS to make a functional molecule, thus Br_8OPS can be made without a catalyst. Br was found to substitute at the 2 and 5 positions on each phenyl ring [13]. The new materials can be created and studied by substituting Br.

3.2 Types of reaction to substitute Bromine with new materials

Once the details of the bromination process were completely worked, it became possible to explore the use of Br_xOPS compounds as nanoconstruction sites using a wide variety of catalytic coupling reaction including Heck, Suzuki, and Sonogashira method, which can often be effected at room temperature. $\text{Br}_{5,3}\text{OPS}$ was used to ensure that the products were primarily para-substituted [4]. The synthesis of Br_xOPS derivatives is shown in the Figure 3.1. Reactions i, iii and iv have been optimized for conversion, as reported in the Table 3.1.

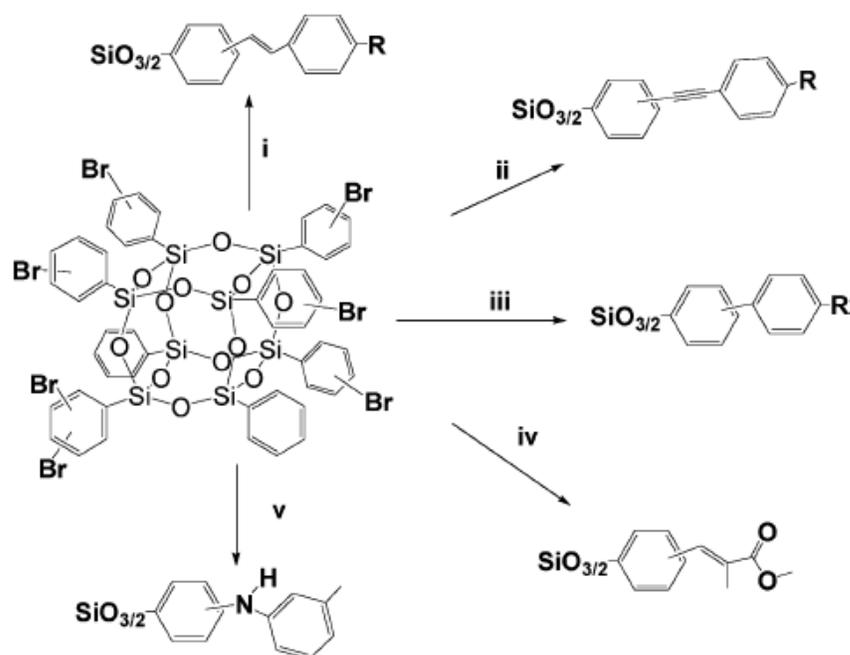
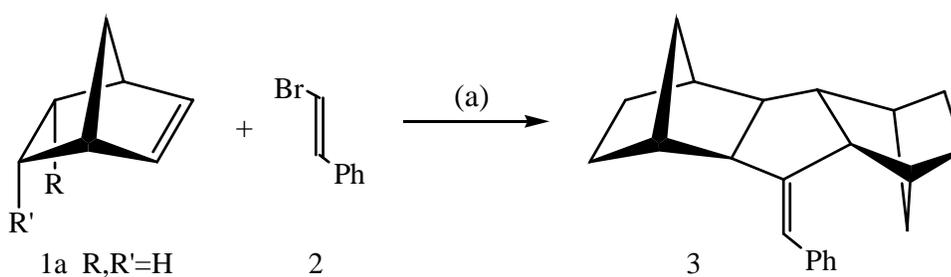


Figure 3.1 Synthesis of Br_xOPS Derivatives [4]

Table 3.1 Data for Br_{5,3}OPS Derivatives [4]

Compound	% conversion
1. Reaction i	99
2. Reaction ii	51
3. Reaction iii	99
4. Reaction iv	99
5. Reaction v	63

Karsten et al, studies on palladium-catalyzed sequential coupling process of various aryl halides to bicyclohept-2-ene systems. The palladium-catalyzed coupling of β -bromostyrene(2) to norbornene (1a) has been reported to produce dinorbornenestyrene (3) (79% yield based on converted 2) when Pd(pPh_3)₄ is used as the catalyst, potassium acetate (KOAc) as the base and anisole as the solvent as illustrated in the Figure 3.2 [17].

**Figure 3.2 Palladium-Catalyzed reactions of β -bromostyrene with norbornene**

[17]

A new type of triaryl phosphine-functionalized imidazolium (salts) was prepared. Using 1 mol% of Pd(dba)₂ and 1 mol% of 2,6-diisopropylphenyl phosphine-functionalized imidazolium (6c) in the presence of 2 equiv of K₂CO₃ in DMAc. Ai-E Wang et al, studied the Heck reaction of 4-bromotoluene with styrene using in situ generated palladium complexes of phosphine-functionalized NHC ligands. The results are summarized in Table 3.2. Arylation of styrene with 4-bromotoluene at 140°C gave 100% conversion and offered 96% yield of the coupling product (Entry 1) [5]. A variety of styrene derivatives with phenyl ring was tested, and 100% conversions with good to excellent yield were obtained within 12 h.

Table 3.2 Heck reactions of 4-bromotoluene with styrene derivatives^a [5]

Entry	Olefin	Product	Yield (%) ^b
1			96
2			96
3			93
4			91
5			91
6			74 ^c
7			99
9		Polymer	—
10		Polymer	—

^a Performed with 1.5 equiv olefin, L/Pd=1, 2.0 equiv base, 0.5 M, 140 °C, 12 h.

^b Isolated yield.

^c Polymer was observed.

Triethanolamine was found to be an efficient and reusable base and reaction medium for phosphane-free palladium-catalyzed Heck reactions. The olefination of iodo- and bromoarenes generated the corresponding products in good to excellent yields in the presence of catalytic amounts of palladium acetate in triethanolamine without any additives, as shown in Table 3.3 [18].

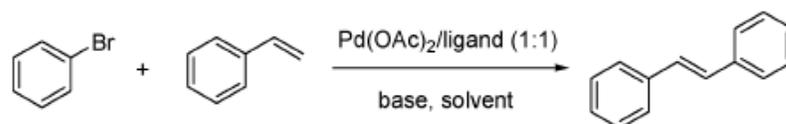
Table 3.3 Effect of palladium source on the Heck reaction.^[a] [18]

$$\text{PhBr} + \text{PhCH}=\text{CH}_2 \xrightarrow[\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3]{\text{Palladium source}} \text{Ph}-\text{CH}=\text{CH}-\text{Ph}$$

Entry	Palladium source (amount)	Yield [%] ^[b]
1	palladium powder (micron, 1 mol-%)	n.r. ^[c]
2	[Pd ₂ (dba) ₃] (1 mol-%)	n.r. ^[c]
3	[Pd(PPh ₃) ₂]Cl ₂ (1 mol-%)	trace
4	[Pd(CH ₃ CN) ₂]Cl ₂ (1 mol-%)	75
5	Pd on activated carbon (1 mol-%)	50
6	PdCl ₂ (1 mol-%)	98
7	[Pd(OAc) ₂] (1 mol-%)	99

[a] Styrene (104 mg, 1.00 mmol), bromobenzene (157 mg, 1.00 mmol), palladium source (0.01 mmol) and triethanolamine (2.0 mL) at 100 °C for 10 h. [b] Isolated yields. [c] n.r. = no reaction.

The use of (*N,N*-dimethyl)-β-alanine (**2**) in Heck reaction between bromobenzene and styrene was studied and compared its performance with *N,N*-dimethylglycine (**1**) and 4-(*N,N*-dimethylamino)butanoic acid (**3**) [19]. In this study, the ratio between Pd and ligan was set to 1:1 (Pd/ligan). The yield for Pd/**1** (81%) and Pd/**3** (70%) were also determined to be lower than that of Pd/**2** (99%) under the same conditions as showed in Table 3.4. The *N*-Methylpyrrolidone (NMP) was concluded as best solvent.

Table 3.4 Heck reaction between Bromobenzene and Styrene^a [19]

entry	Pd (mol %)	ligand	base	<i>T</i> (°C)	time (h)	solvent	yield ^b (%)
1	1	2	K ₂ CO ₃	130	10	DMF	86
2	1	2	K ₂ CO ₃	130	10	DMA	83
3	1	2	K ₂ CO ₃	130	10	DMSO	38
4	1	2	K ₂ CO ₃	130	10	NMP	99
5	0.1	2	K ₂ CO ₃	130	10	NMP	99
6	0.01	2	K ₂ CO ₃	130	20	NMP	96
7	0.1		K ₂ CO ₃	130	10	NMP	42
8	0.1	1	K ₂ CO ₃	130	10	NMP	81
9	0.1	3	K ₂ CO ₃	130	10	NMP	70

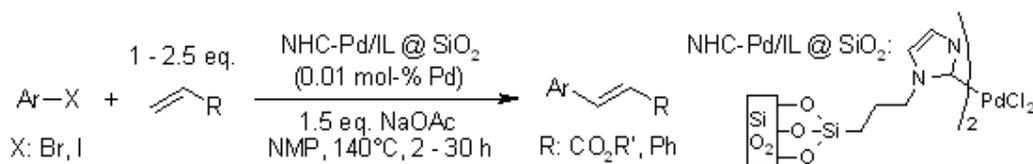
^a Reaction conditions: bromobenzene (0.5 mmol), styrene (0.75 mmol), base (1 mmol), solvent (1 mL), under Ar. ^b GC yields.

Recent Literature

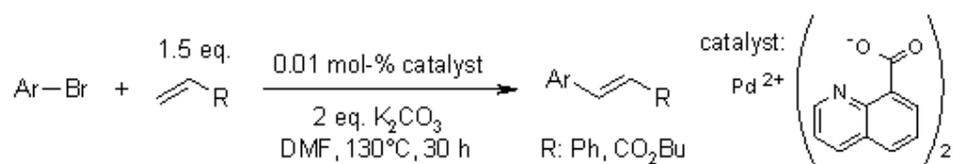
1. New N-Heterocyclic Carbene Palladium Complex/Ionic Liquid Matrix

Immobilized on Silica: Application as Recoverable Catalyst for the Heck Reaction

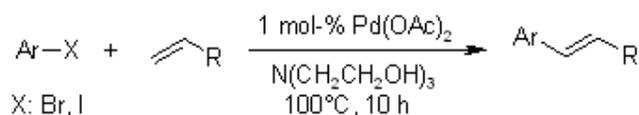
[20]



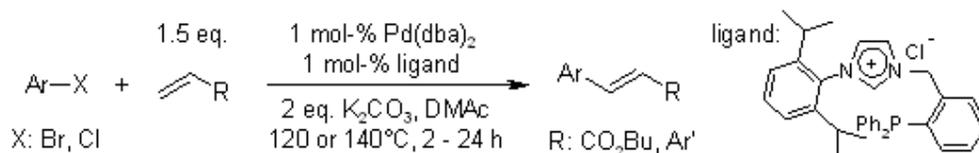
2. Pd (quinoline-8-carboxylate)₂ as a Low-Priced, Phosphine-Free Catalyst for Heck and Suzuki Reactions [20]



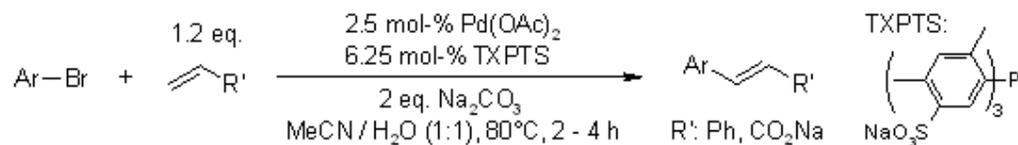
3. Triethanolamine as an Efficient and Reusable Base, Ligand and Reaction Medium for Phosphane-Free Palladium-Catalyzed Heck Reactions [20]



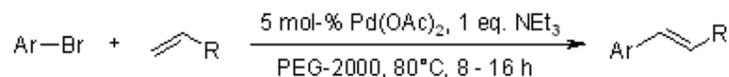
4. Triaryl phosphine-functionalized *N*-heterocyclic carbene ligands for Heck reaction [20]



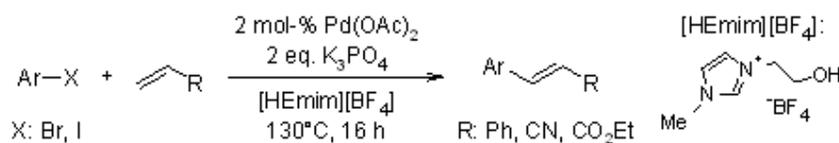
5. Efficient Aqueous-Phase Heck and Suzuki Couplings of Aryl Bromides Using Tri(4,6-dimethyl-3-sulfonatophenyl)phosphine Trisodium Salt (TXPTS) [20]



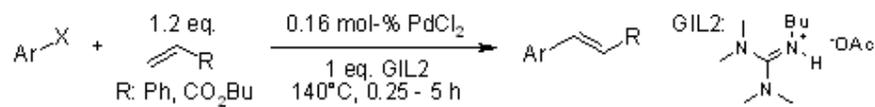
6. Poly (ethylene glycol) (PEG) as a Reusable Solvent Medium for Organic Synthesis. Application in the Heck Reaction [20]



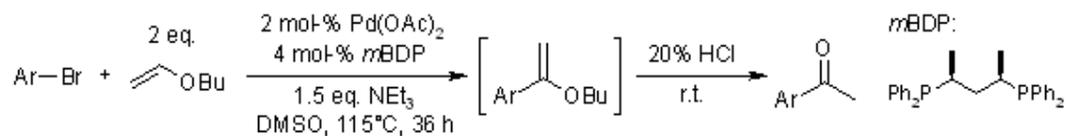
7. Functionalized Ionic Liquid as an Efficient and Recyclable Reaction Medium for Phosphine-Free Palladium-Catalyzed Heck Reaction [20]



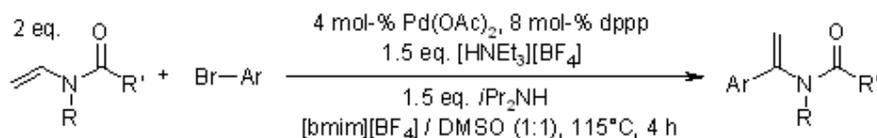
8. Bronsted Guanidine Acid-Base Ionic Liquids: Novel Reaction Media for the Palladium-Catalyzed Heck Reaction [20]



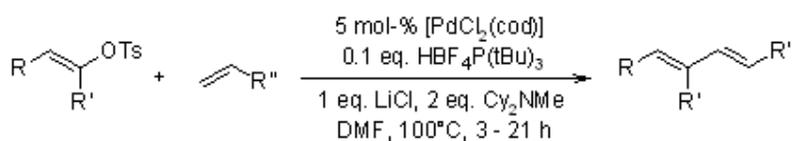
9. Pd-*m*BDPP-Catalyzed Regioselective Internal Arylation of Electron-Rich Olefins by Aryl Halides [20]



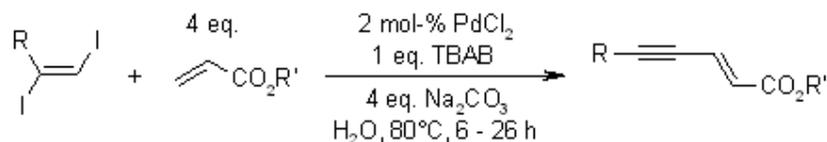
10. The Heck Reaction of Electron-Rich Olefins with Regiocontrol by Hydrogen-Bond Donors [20]



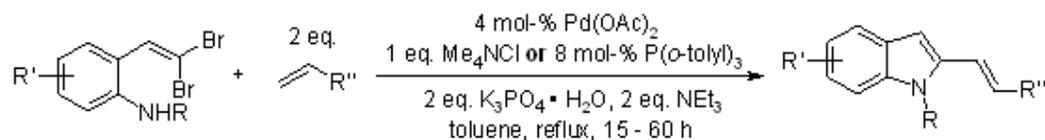
11. Heck Coupling with Nonactivated Alkenyl Tosylates and Phosphates: Examples of Effective 1,2-Migrations of the Alkenyl Palladium(II) Intermediates [20]



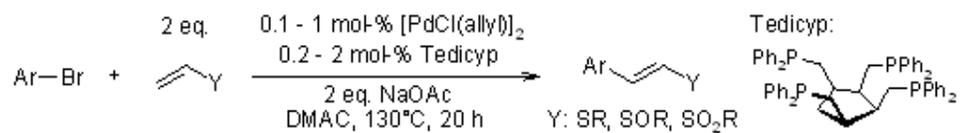
12. A New Route to the Synthesis of (*E*)- and (*Z*)-2-Alkene-4-ynoates and Nitriles from *vic*-Diiodo-(*E*)-alkenes Catalyzed by Pd(0) Nanoparticles in Water [20]



13. Synthesis of 2-Vinyl Indoles and Derivatives via a Pd-Catalyzed Tandem Coupling Reaction [20]



14. Heck Vinylations Using Vinyl Sulfide, Vinyl Sulfoxide, Vinyl Sulfone, or Vinyl Sulfonate Derivatives and Aryl Bromides Catalyzed by a Palladium Complex Derived from a Tetraphosphine [20]



CHAPTER IV

EXPERIMENTAL

In this chapter, the experimental procedures in this study were divided into six parts. The flow diagram of research methodology is shown in Figure 4.1.

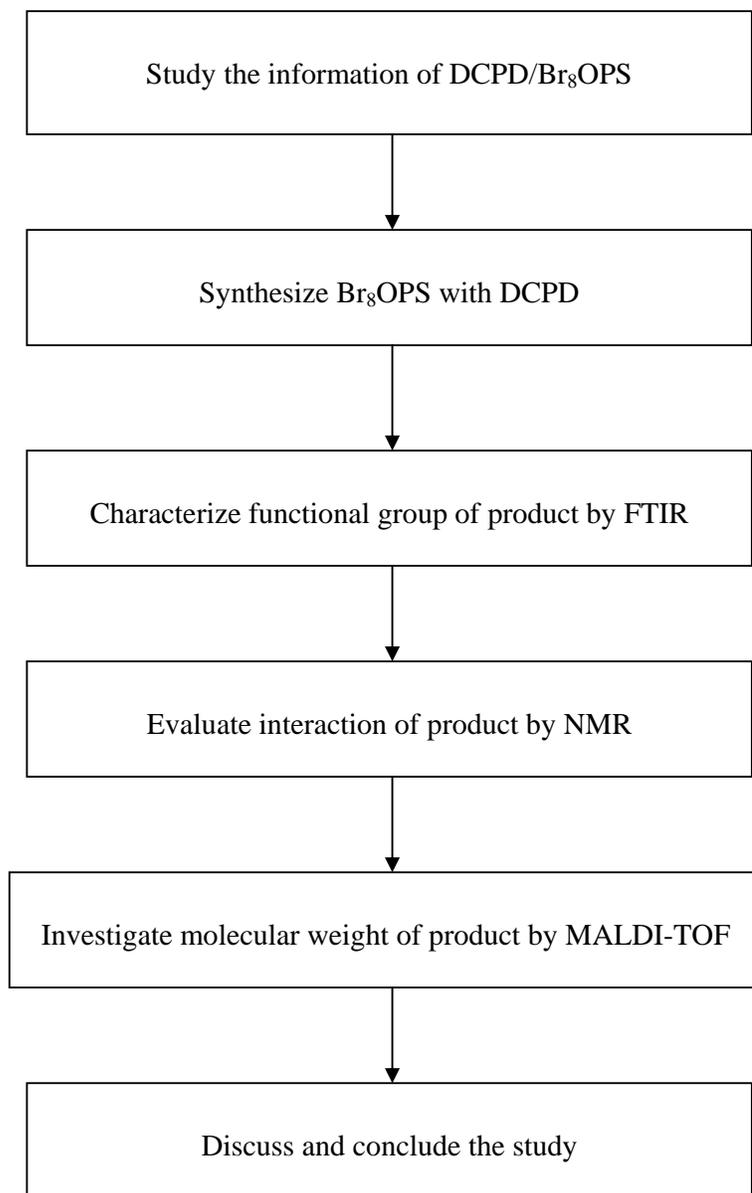


Figure 4.1 Flow diagram of methodology.

4.1 Materials

Octabromophenyl silsesquioxane was produced following Laine group's methods [13]. Catalyst that were used for increasing rate of reaction in this research were Bis-(tri-tert-butylphosphine) palladium (0) (98%), tris(dibenzylidenacetone)di-palladium (99.9%)(0) and palladium acetate (98%) which were provided by Stream Chemical. Dicyclopentadiene (DCPD) (95%) was purchased from Sigma-Aldrich. The property of DCPD was appeared in Table 4.1. Base that was used in this reaction was dicyclohexylmethylamine (99%) purchased from Sigma-Aldrich. Dioxane, methanol and THF used in this study were purchased from Sigma-Aldrich.

Table 4.1 Normal properties of DCPD [11]

Properties	DCPD
1. Molar mass (g/mol)	132.20
2. Density (g/cm ³)	0.98
3. Melting point (°C)	32.5
4. Boiling point (°C)	170
5. Flash point (°C)	32

4.2 Synthesis Section

4.2.1 The synthesis of Br₈OPS derivatives from OPS

Octaphenylsilsesquioxanes can be functionalized by adding bromine to phenyl rings.

The steps of synthesis are shown as follows:

1. A dry ice bath containing ethanol and ethylene glycol was cooled to -40°C. 50 mL dichloromethane and 13 mL (3.0 mol) Br₂ were added into a dried 100 mL Schlenk flask (under N₂). Once cooled, 20.0 g (0.02mol) of OPS were added and magnetically stirred for 48 h.

2. The reaction was then worked up by quenching the Br₂ with water and NaHSO₃ solution and then removed the aqueous layer.

3. The solution was then washed with water for several times to neutralize the pH and the aqueous layer was once again removed. The material was then precipitated in methanol and filtered.

4.2.2 The synthesis of Br₈OPS and DCPD with Heck reaction

The various types of catalysts, time and temperature that were explained in the synthesis section were used to study the effect of them on the yield of new materials. All of conditions were shown in the Table 4.2. The steps of synthesis were shown as follows:

Coupling catalyst

1. A dry Schlenk flask 50 ml (under Ar), Br₈OPS 0.5 g (2.4 mmol-Br), Bis(tri-tert-butylphosphine) palladium(0) 31 mg (0.073 mmol) and tris(dibenzylidenacetone) dipalladium(0) 29 mg (0.037 mmol) was added in 13 ml of dioxane in a dry Schlenk flask 50 ml (under N₂).

2. After that dicyclohexylmethylamine 0.74 ml (4.1 mmol) was then added, followed by dicyclopentadiene 0.33 ml (2.4 mmol).

3. The mixture was stirred at 60°C for 72 h. This solution was cooled to room temperature and was then precipitated into 100 ml of methanol and the solid was filtered off. The solid was redissolved in THF and then reprecipitated in 100 ml methanol to further purify the material. The solution was filtered again and the solid was dried in a vacuum for 3 h.

Palladium (II) acetate

1. Br₈OPS 0.5 g (2.4 mmol-Br), palladium(II) acetate 0.01 mg (0.125 mmol) was added in dioxane 13 ml in a dry Schlenk flask (under N₂).

2. After that dicyclohexylmethylamine 0.74 ml (4.1 mmol) was then added, followed by dicyclopentadiene 0.33 ml (2.4 mmol). The mixture was stirred at 60°C for 72 h.

3. This solution was then filtered and precipitated into 100 ml of methanol. After that it was filtered and the solid was redissolved in THF. The solution was then reprecipitated in 100 ml methanol. The solution was filtered again and dried in vacuum for 3 h.

Table 4.2: Conditions of reaction

Entry	Br ₈ OPS (g)	DCPD (ml)	Pd(P(tbut) ₃) ₂ (g)	Pd ₂ (dba) ₃ (g)	NCy ₂ Me (ml)	Pd(OAc) ₂ (g)	Time (Day)	Temp (°C)
1	0.5	2	-	-	0.75	0.01	7	80
2	0.5	1	0.031	0.029	0.75	-	3	40
3	0.5	1	0.031	0.029	0.75	-	3	60
4	0.5	1	0.031	0.029	0.75	-	3	80
5	0.5	0.33	0.031	0.029	0.75	-	7	80
6	0.5	1	0.031	0.029	0.75	-	7	80
7	0.5	1	0.062	0.058	0.75	-	7	80
8	0.5	2	0.093	0.087	1.5	-	7	80

4.3 Specimen characterization

4.3.1 Functional group of samples

Fourier transform infrared spectrometry (FTIR) is the most useful technique to identify chemicals that are either organic or inorganic substance. It can be utilized to analyze materials containing some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses [21]. FTIR can be used to support data of Heck reaction between the O-Si-O groups of POSS and H-C=C-H function of DCPD.

Fourier transform infrared spectra of all samples under various conditions were acquired by using a Spectrum GX FT-IR spectrometer from Perkin Elmer with an IR accessory. Optical grade potassium bromide (KBr, International Crystal Laboratories, Garfield, NJ) was used as a background material. Cured sample (5 mg) and KBr crystal (500 mg) were ground together using an alumina mortar and pestle. The ground powder was packed into a sample holder and leveled off with a glass plate to give a smooth surface. The holder was placed in the sample chamber, and the spectrum was recorded under air purge. At least 100 scans were averaged for each spectrum.

4.3.2 Interaction of samples

NMR spectroscopy is the study of the interaction of electromagnetic radiation with matter. Nuclear magnetic resonance (NMR) spectroscopy is the use of the NMR phenomenon to study physical, chemical, and biological properties of matter. NMR spectroscopy is routinely used by chemists to study chemical structure using simple one-dimensional techniques. Solid state NMR spectroscopy is used to determine the molecular structure of solids [22].

All ^1H and ^{13}C NMR measurement were performed in CDCl_3 and recorded on Varian INOVA 400 MHz spectrometer. ^1H NMR spectra were collected at 400.0 MHz using a 600 Hz spectral width, a relaxation delay of 3.5 s, 30K data point, a pulse width of 38° , and CHCl_3 (7.27 ppm) was used as the internal reference.

4.3.3 Elemental composition of samples

Matrix-assisted laser desorption/ionization (MALDI) is a soft ionization technique used in mass spectrometry, allowing the analysis of bio-molecules (biopolymers such as proteins, peptides and sugars) and large organic molecules (such as polymers, dendrimers and other macromolecules), which tend to be fragile and fragment when ionized by more conventional ionization methods. It is most similar in character to electrospray ionization both in relative softness and the ions produced (although it causes many fewer multiply charged ions). The ionization is triggered by a laser beam (normally a nitrogen laser) [23]. A matrix is used to protect the bio-molecule from being destroyed by direct laser beam and to facilitate vaporization and ionization.

MALDI-TOF was performed on a MicromassTofSpec-2E equipped with a 337 nm nitrogen laser in positive-ion reflection mode using poly(ethylene glycol) as the calibration standard, dithranol as the matrix, and AgNO_3 as the ion source. Samples were prepared by mixing solution of five parts dithranol (10 mg/mL in THF), five parts sample (1 mg/mL in THF) and one part AgNO_3 (10 mg/mL in water) and blotting the mixture on the target plate.

CHAPTER V

RESULTS AND DISCUSSION

After obtaining eight products, DCPD₈OPS was characterized by FTIR, NMR and MALDI-TOF as shown below:

5.1 Percent Yield

The predicted yield is determined by the masses used in a reaction and the mole ratios in the balanced equation. This predicted yield is the ideal. It is not always possible to get this amount of product. Reactions are not always simple. There often are competing reactions. In chemistry, yield, also referred to as chemical yield and reaction yield, is the amount of product obtained in a chemical reaction [24]. The absolute yield can be given as the weight in grams or in moles (molar yield). The fractional yield or relative yield or percentage yield, which served to measure the effectiveness of a synthetic procedure, is calculated by dividing the amount of the obtained product in moles by the theoretical yield in moles [25]. After this reaction finished, white powder was produced.

Percent Yield of all condition was shown in Table 5.1. In this research, octaphenyldicyclopentadiene silsesquioxane was prepared by Heck reaction at fixed weight 0.5 grams of octabromophenyl silsesquioxane (Br₈OPS). From this table, the percent yield by weights ratio of white powder nanocomposite increased continuously by 56 percent at 6 times of DCPD content when compared with other DCPD loadings. In other words, the percent yield of coupling catalyst (Entry 8) was better than that of palladium (II) acetate (Entry 1) at the same materials loading, time and temperature. The same trends were also observed in coupling catalyst loading of entry 7 compared

with entry 6, the percent yield at high content of catalyst was better than at low content as 40 % and 44% respectively. Moreover, percent yield increased gradually with increasing time and temperature at the same materials content as entry 6 compared with entry 4 and entry 4 compared with entry 2 respectively. The percent yield of entry 6 was triple of that of entry 4 when reaction time was extended from 3 to 7 days. In addition the percent yield of entry 4 was double of that of entry 2 when the temperature was increased from 40 to 80 °C in these reactions. However, the yields for these types of reaction are typically very poor and hydrolysis process for the production of discrete silsesquioxane cages is not trivial [4]. Percent yield of DCPD₈OPS was also calculated by equation as summarized in appendix B. Moreover, weigh of all entries after vacuum was summarized in table C.1 (appendix C)

Table 5.1 Percent Yield of all reactions

Name	Compound (mole ratio)	Time (day)	Temperature (°C)	Yielding (%)
Entry1	1:6:3:2 ^a	7	80	20
Entry2	1:3:1:1:1 ^b	3	40	8
Entry3	1:3:1:1:1 ^b	3	60	12
Entry4	1:3:1:1:1 ^b	3	80	14
Entry5	1:1:1:1:1 ^b	7	80	37
Entry6	1:3:1:1:1 ^b	7	80	40
Entry7	1:3:2:2:1 ^b	7	80	44
Entry8	1:6:3:3:2 ^b	7	80	56

^a Br₈OPS : DCPD : Pd (II) acetate : NCy₂Me

^b Br₈OPS : DCPD : Pd(P(tbut)₃)₂ : Pd₂(dba)₃ : NCy₂Me

5.2 DCPD₈OPS Characterizations

5.2.1 Fourier Transform Infrared Spectroscopic Investigation

The basic structure of polyhedral oligomeric silsesquioxane (POSS) and alkenes was studied by FT-IR spectroscopic technique. The important functional groups of Br₈OPS reacted with DCPD are O-Si-O, C-Br and C=C-H which were the characteristics of Br₈OPS/DCPD from the Heck reaction. In general, the absorption band around 500 cm⁻¹ was assigned to the C-Br of Aryl halide structure while several O-Si-O bands of POSS cage were located at a wavenumber range of 1000-1150 cm⁻¹. In addition, the observed DCPD band C=C, =C-H was observed at 1620-1680 cm⁻¹, 3010-3100 cm⁻¹[26] respectively. The FT-IR result of DCPD is shown in Figure 5.1.

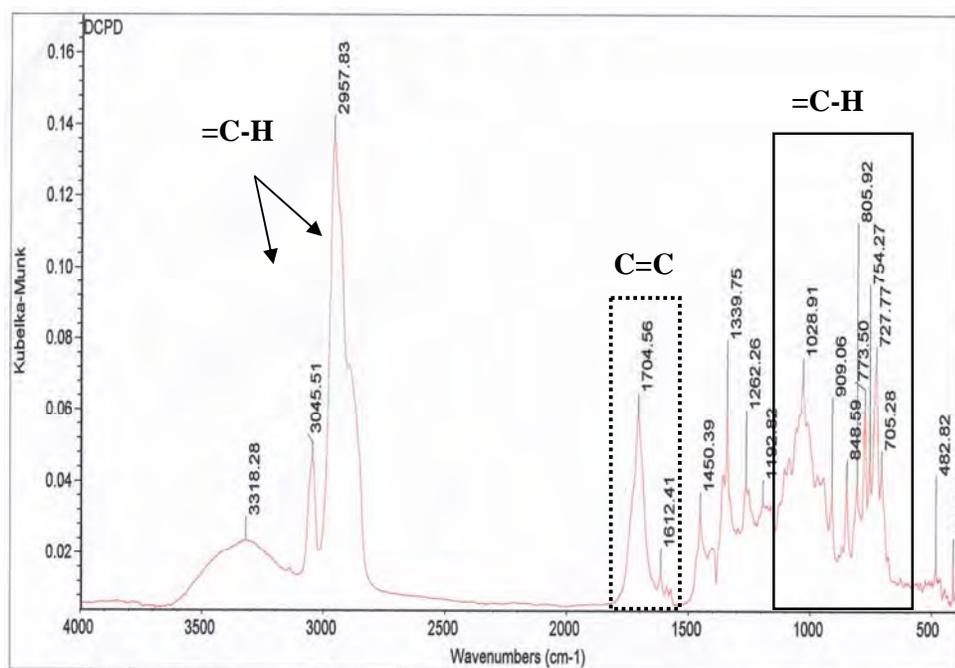


Figure 5.1 FT-IR diagram of DCPD

Figure 5.2 shows the FT-IR spectra of Br₈OPS before its reaction with DCPD formation. In this study, the Br₈OPS was obtained from OPS via bromination with Br₂/Fe in dichloromethane starting materials for 2 days at -40°C under nitrogen atmosphere. The result in this figure indicated the appearance of the absorption band at 500 cm⁻¹ due to the formation of the C-Br group.

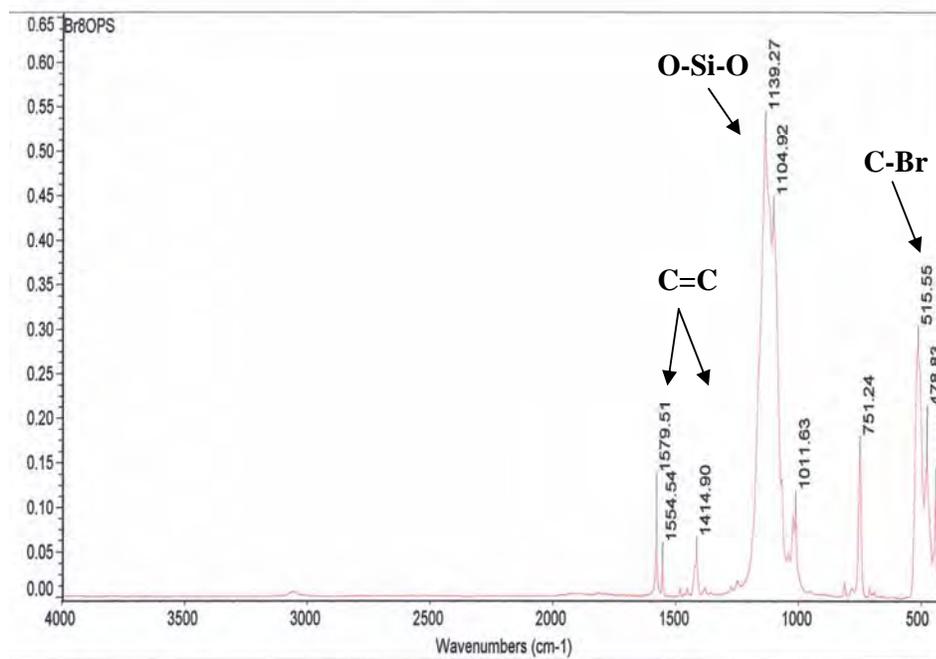


Figure 5.2 FT-IR diagram of Br₈OPS

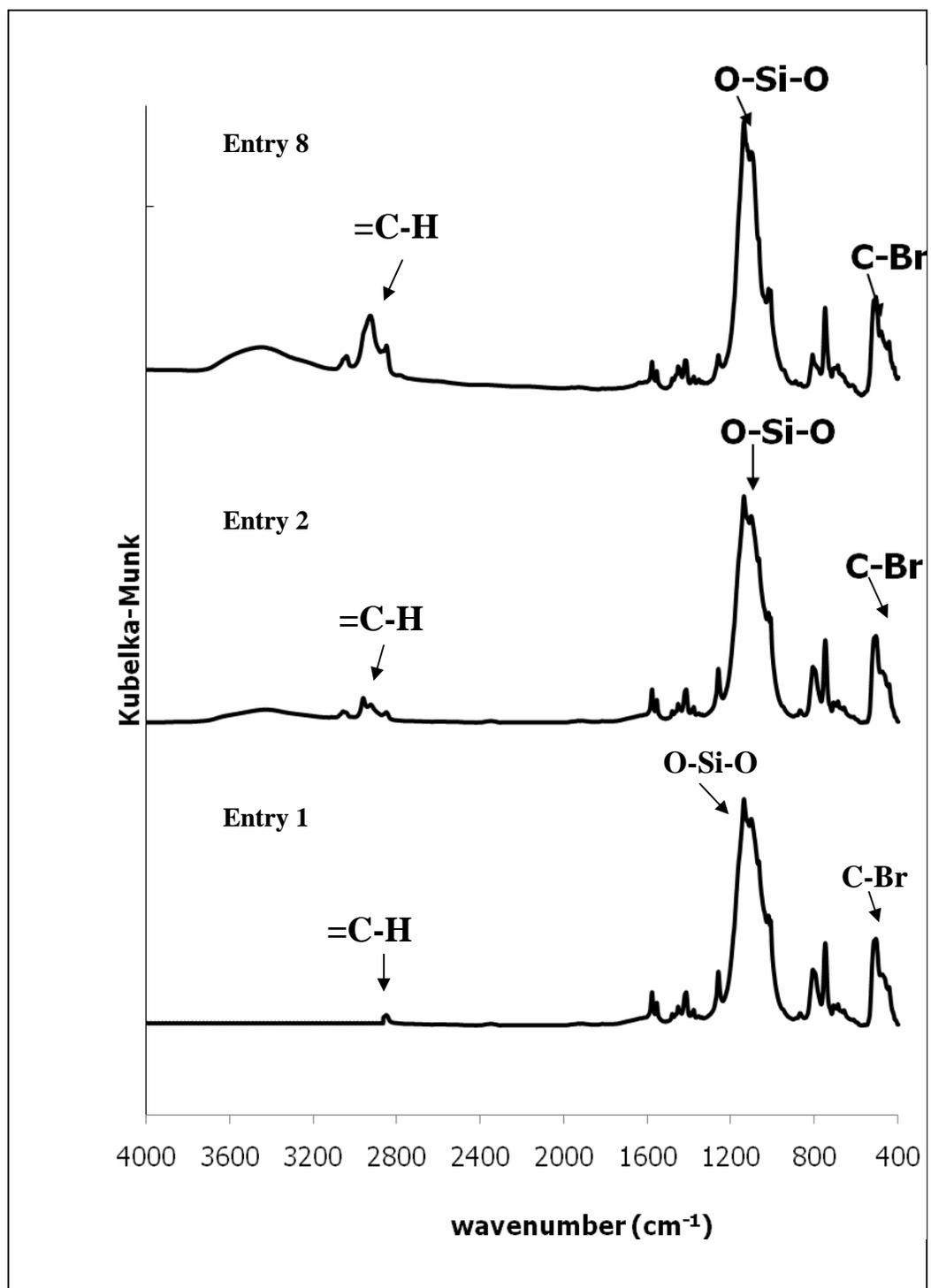


Figure 5.3 FT-IR diagram of the DCPD₈OPS

FT-IR spectra of DCPD₈OPS were shown in Figure 5.3. Characteristic absorption bands of all condition are the appearance of the important absorption band at 1000-1150 cm⁻¹, 1620-1680 cm⁻¹ and 3010-3100 cm⁻¹ due to the formation of the O-Si-O, C=C and C-H group respectively. The band tended to increase to maximum after the mixture reacted completely. When an excess of DCPD and coupling catalyst was loaded at 80 °C, the peaks are distinct as seen in entry 8. However, when palladium (II) acetate was added, the reaction does not proceed because palladium acetate cannot undergo a reaction between the carbon of the phenyl ring and bromine; therefore, no peak at 3010-3100 cm⁻¹ was observed for entry 1. The coupling catalyst is an oxidative addition in which palladium inserts itself in the aryl to bromide bond [12]. As the synthesise process proceeded, a height of peaks depends on loading of DCPD, types of catalyst, time and temperature. The limited temperature of this reaction is 80 °C because the cage structure of POSS can be broken at higher temperature than 80 °C as shown in Figure 5.4. In addition this reaction strong base can destroy cage of POSS. Thus, we must use weak base for this experiment. However, phenyl group is partially formed by DCPD because FTIR of all sample showed Br group at 500 cm⁻¹ wavenumber. FT-IR diagram of other entries are shown in appendix F.

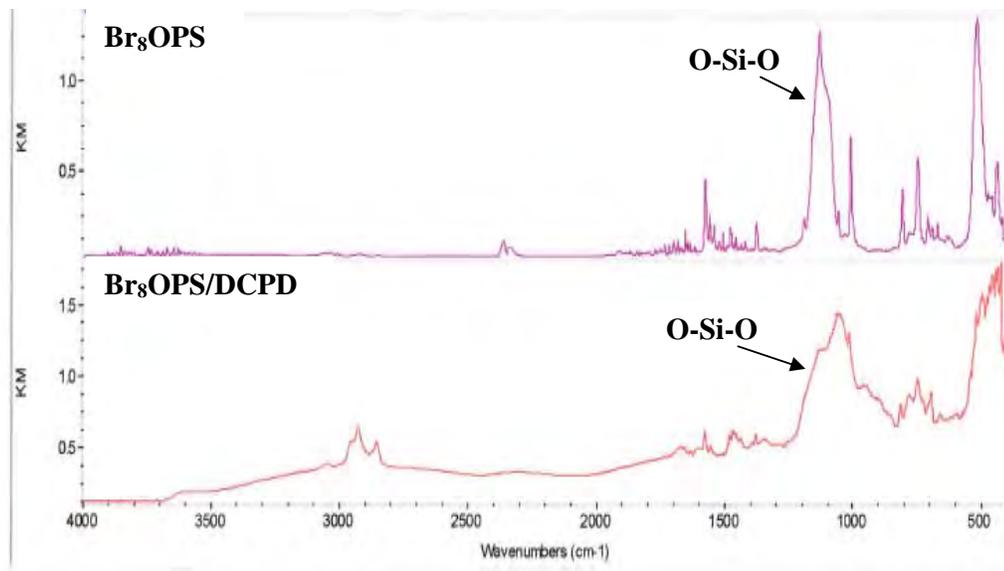


Figure 5.4 FT-IR diagram of the DCPD₈OPS at 100 °C

5.2.2 Nuclear Magnetic Resonance

For all products, characterized by ¹H NMR to confirm about proton peaks of interaction between phenyl ring with alkene groups. Proton Nuclear Magnetic Resonance (¹H NMR) Spectroscopy is a powerful method used in the determination of the structure of unknown organic compounds. The ¹H NMR spectrum of an organic compound provides information concerning [27]:

- the number of different types of hydrogens presented in the molecule
- the relative number's of the different types of hydrogens
- the electronic environment of the different types of hydrogens

The splitting pattern of a given nucleus (or set of equivalent nuclei) can be predicted by the n+1 rule, where n is the number of neighboring spin-coupled nuclei with the same (or very similar) place. If there are 2 neighboring, spin-coupled nuclei the observed signal is a triplet (2+1=3) [28].

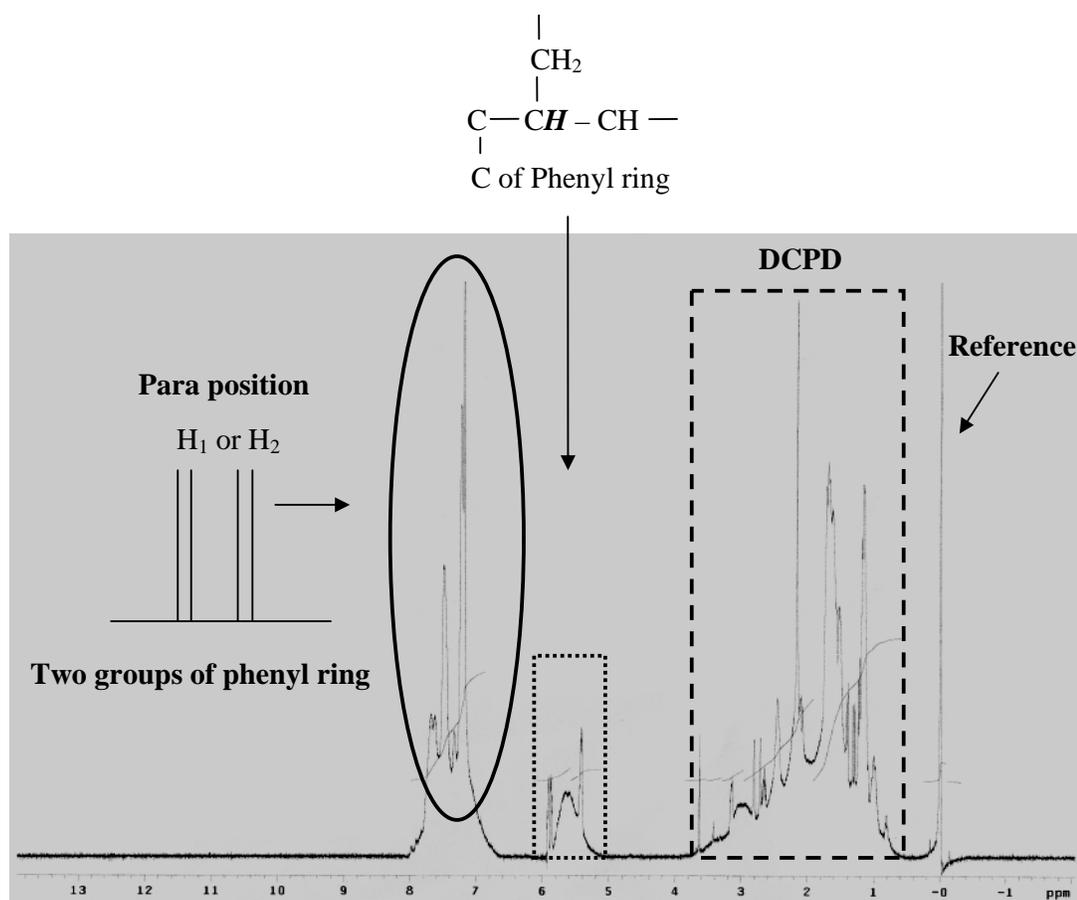
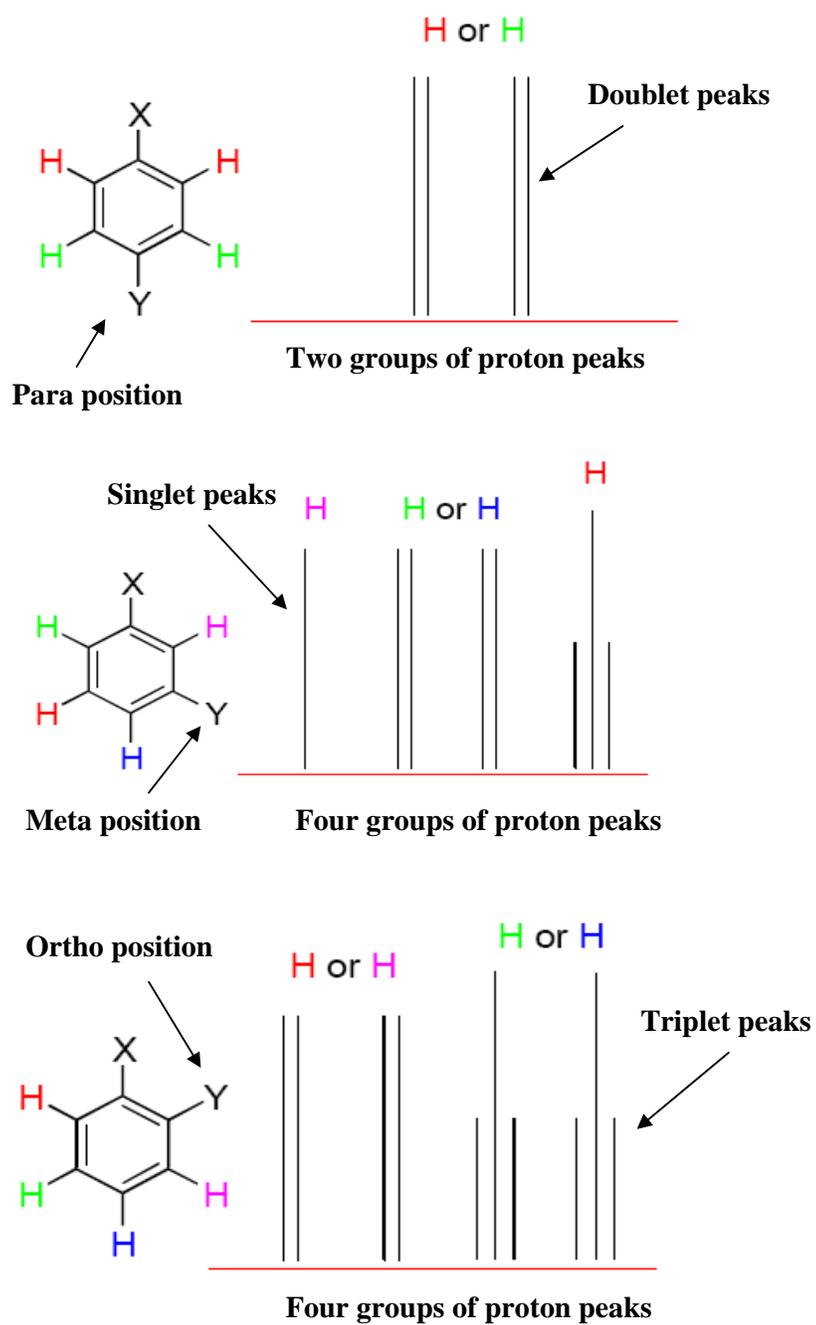


Figure 5.5 NMR diagram of Entry 8

The spectrum in the Figure 5.5 shows several interesting things: firstly, there are four cluster of peaks. The single peak at 0 ppm is the TMS reference peak. Tetramethylsilane, usually referred to as TMS, meets all these characteristics, and has become the reference compound of choice for proton and carbon NMR [28]. These NMR peaks correspond to the protons in the phenyl ring, proton at the interaction between carbon bonds of phenyl ring with carbon bond of alkene groups and the alkene groups, going from left to right in the range of 7-8, 5-6, 1-3.5 ppm. The area under these peaks corresponds to the number of protons in the same environment.

The position that DCPD substituted in aromatic ring can be para-DCPD, because Br₂OPS reactant which was synthesized following Laine's method ensure that the products were primarily para-substituted and reduce the potential to form unwanted (for the current purposes) disubstituted phenyl rings [4]. A group of proton peaks at 7-8 ppm indicated -C-H bond of aromatic or phenyl ring. These phenyl rings have four proton peaks. We can observe two groups of proton peaks in which group has two proton peaks at 7-8 ppm as shown in Figure 5.5. One, two and three proton peaks are called singlet, doublet and triplet peaks respectively. If DCPD substituted at meta or ortho position, the chemical shift at 7-8 ppm were also observed four groups of peaks as singlet, doublet and triplet peak. Types of proton peak can be appeared at 7-8 ppm, when carbon bond of DCPD phenyl ring substituted in carbon bond of aromatic ring as shown in Figure 5.6 [29].



X= Si of POSS, Y= Carbon of DCPD

Figure 5.6 Types of proton peaks of phenyl ring at 7-8 ppm [22]

We found one of group that approximately showed peaks at 5-6 ppm, indicating that DCPD can be attached to phenyl ring. There are three protons (3+1, 4 peaks) in this environment (-CH-) as shown in Figure 5.5. If proton peaks at 5-6 ppm disappeared in the case of entry 1, it means that DCPD disubstituted in phenyl ring as shown in Figure 5.7. Finally, the alkene protons have several peaks in this area (1-3.5 ppm), as expected C=CH-, -CH₂- and -CH-. It was very difficult to separate proton peaks of alkene group. When we increase the period of reaction time and increase the temperature of this reaction to 7 days and 80 °C respectively, it affected the increasing of area, indicating the higher quality of proton than that with other conditions. Comparison of different condition was shown in Figure 5.8. Moreover, the NMR diagram of all products was summarized in appendix G.

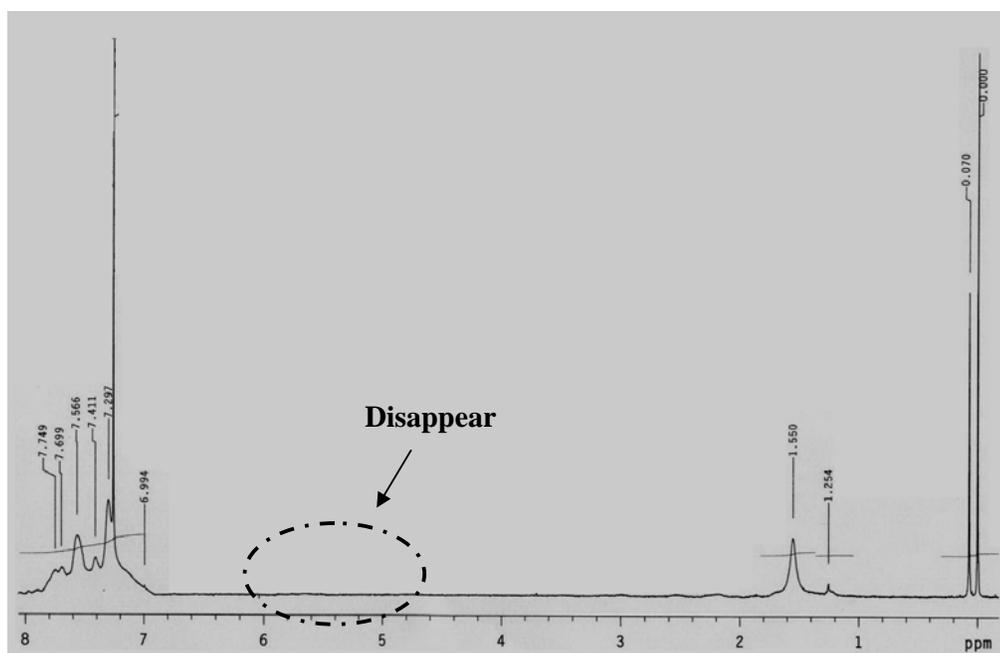


Figure 5.7 NMR diagram of Entry 1

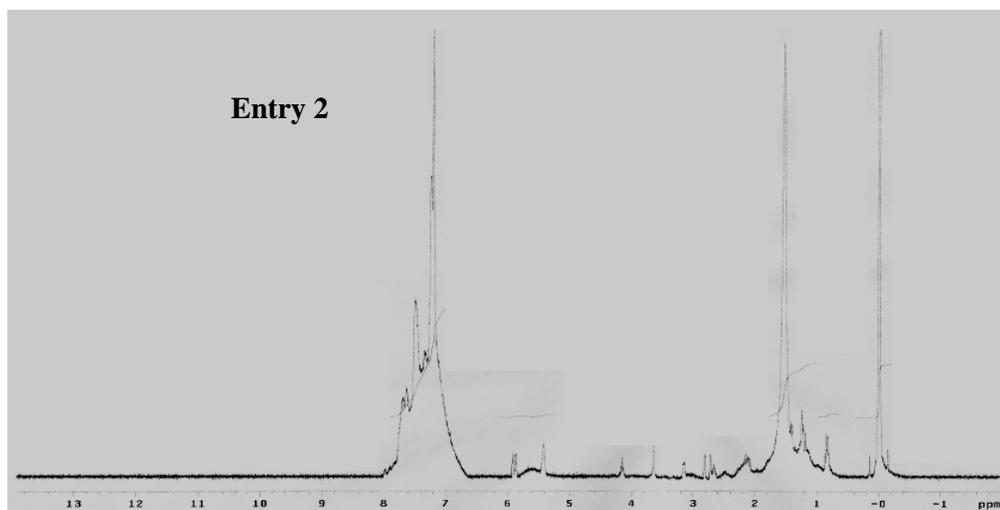
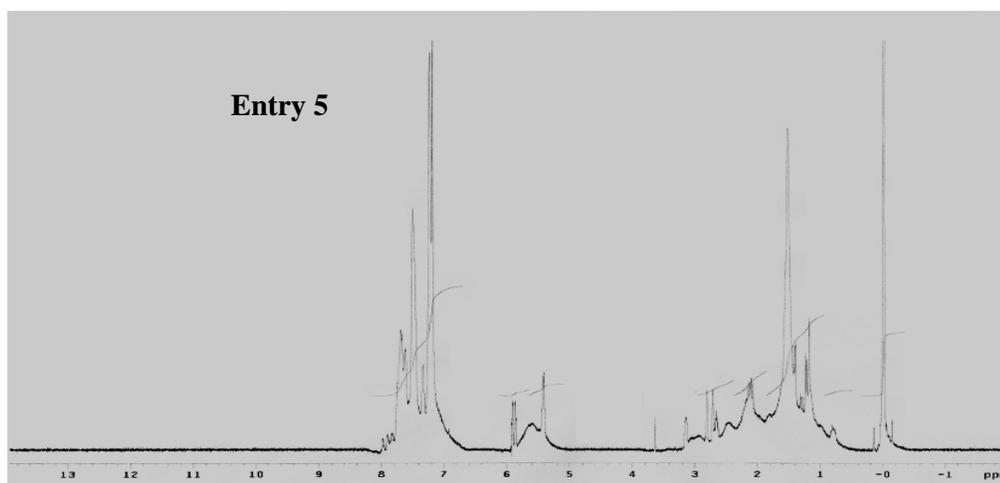
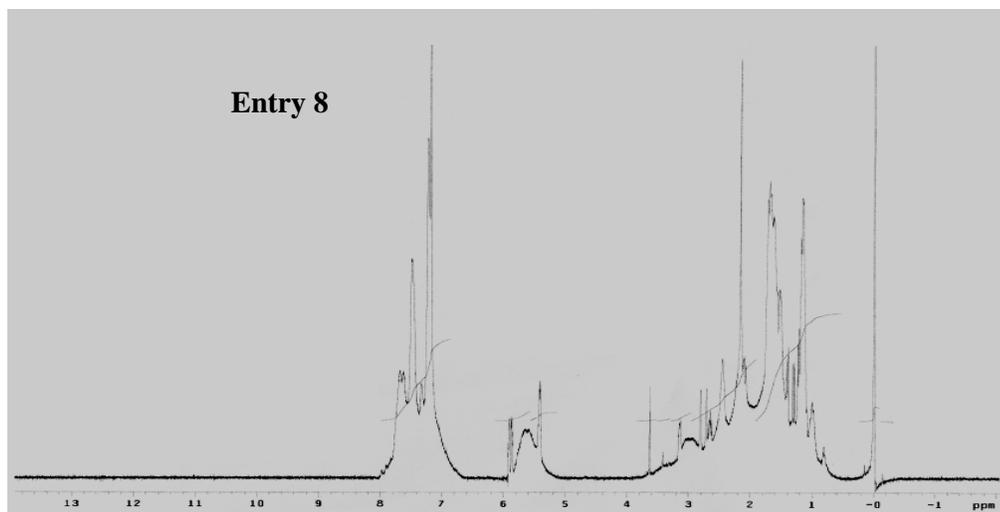


Figure 5.8 NMR diagram of hybrids at difference conditions

5.2.3 Matrix-assisted laser desorption/ionization

Traditionally, mass-spectrometry techniques based on magnetic and electrical fields, time-of-flight, ion trap and ion cyclotron resonance, are the most commonly used techniques to separate ions by their mass over charge ratio. Until recently, the most common ionization technique was electron ionization. This technique is based on the electron irradiation of vaporized sample molecules, resulting in ionized molecules and fragments. Since polymers are not volatile and fragmentation of ionized polymers should be avoided, this technique is not suitable to obtain structural information of complex mixtures of polymer molecules. A more appropriate choice would be a mass spectrometry technique that place charged polymer molecules in the gas phase without degrading the polymer sample. Matrix is very important for characterized by MALDI-TOF. The organic solvent allows hydrophobic molecules to dissolve into the solution, while the water allows for water-soluble (hydrophilic) molecules to do the same. The matrix suitable for this case is dithranol because these samples are non-polar materials. The MALDI-TOF-MS raw data spectra of dithranol matrix are shown in Figure 5.9 [30].

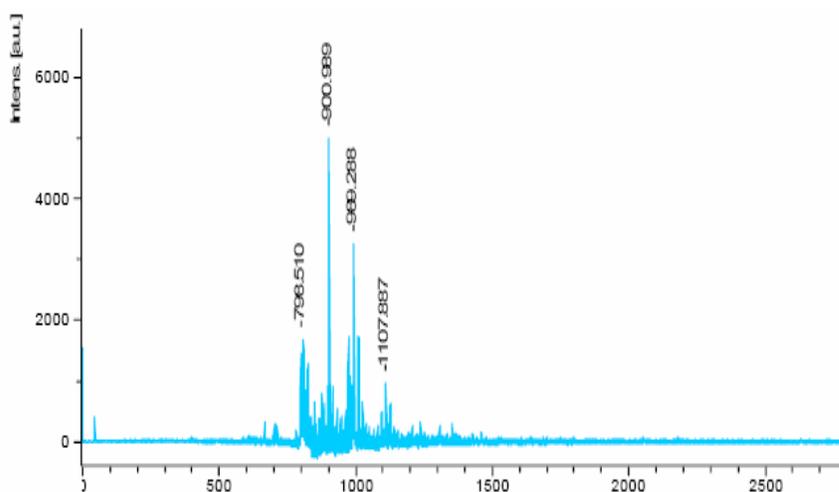


Figure 5.9 MALDI-TOF-MS raw data spectra of dithranol

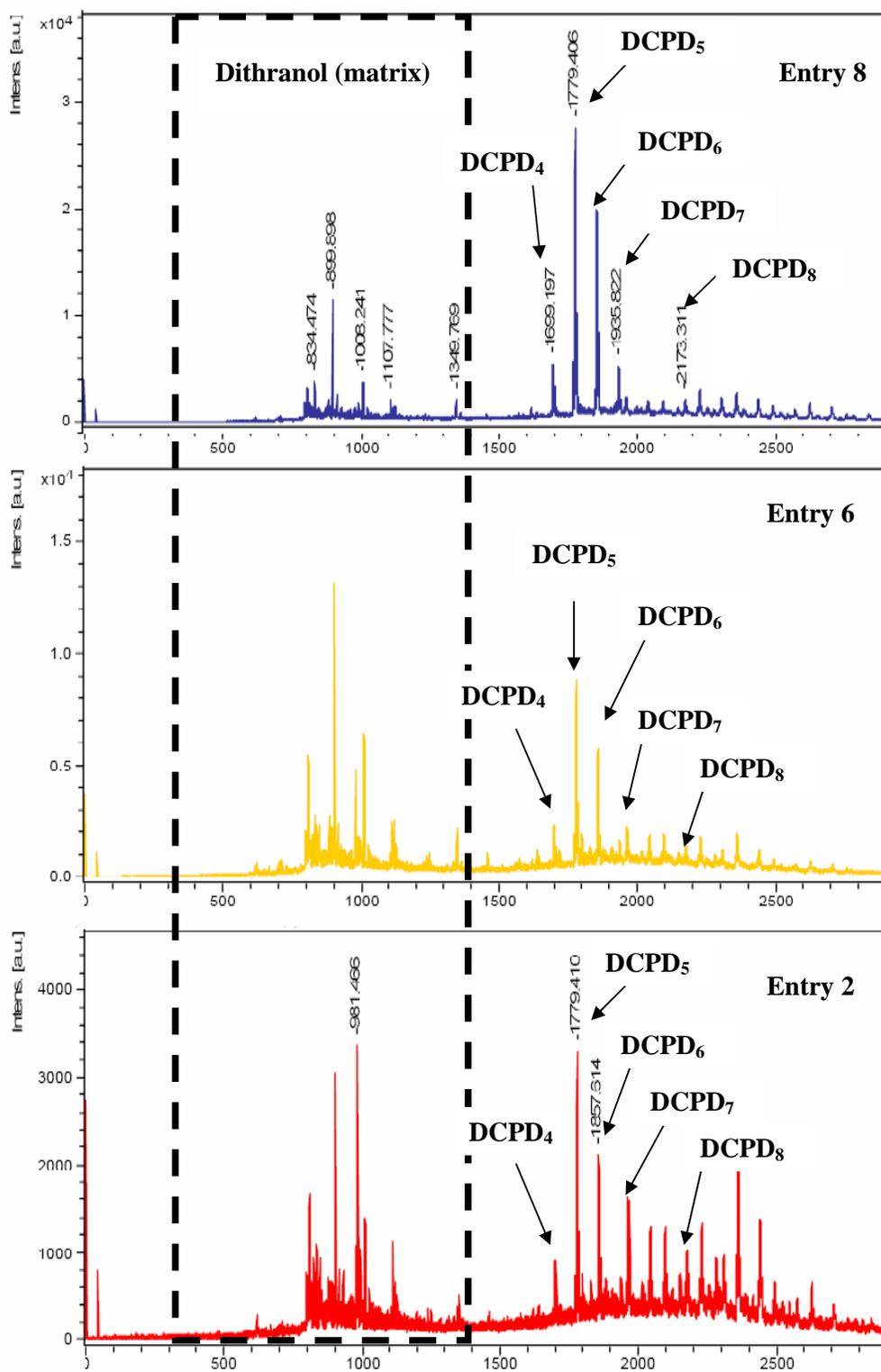


Figure 5.10 MALDI-TOF-MS diagrams of hybrids at different conditions

Figure 5.10 shows DCPD₅OPS pattern of the peak at 1779.41 m/z is compared with the patterns of peaks at 1699, 1857, 1935 and 2173 m/z as DCPD₄OPS, DCPD₆OPS, DCPD₇OPS and DCPD₈OPS respectively. The peak at 0-1500 m/z is assigned to dithranol matrix. Based on the intensity spectrum of all samples DCPD₅OPS peak at 1779.41 m/z is higher than other peaks as shown in Table 5.2. A general observation is that the height of every peak increased with time and temperature of experiment as entry 2 compared with that of entry 6. The last situation in which an observed DCPD loading can be effected on intensity of peaks as entry 6 compared with that of entry 8. The low intensity of the observed DCPD₈OPS peak exhibited that the reaction did not proceed completely. However, we know that increase temperature leads to a significant increase in the intensity of the peaks but there is the upper limit of reaction temperature at 80 °C due to the destroyed cage of POSS.

Table 5.2 Intensity of MALDI-TOF diagrams of hybrids

	Conditions	DCPD₄	DCPD₅	DCPD₆	DCPD₇	DCPD₈
Entry 2	DCPD = 1 ml 3 days (40 °C)	900	3,100	2,100	1,800	800
Entry 6	DCPD = 1 ml 7 days (80 °C)	2,000	8,000	5,500	2,000	1,000
Entry 8	DCPD = 2 ml 7 days (80 °C)	6,000	28,000	20,000	5,000	2,000

Table 5.2 indicated spectrum of the high DCPD loading sample (Entry 8) whose intensity at 2173 m/z is 2,000. In addition, the DCPD₈OPS peak of entry 8 is much higher than that of entry 6. Furthermore the DCPD₅OPS peak of entry 8 shows nine times higher intensity that of entry 2. The DCPD₃OPS peak at 1621 m/z does not occur in any entries indicated the disappearance of DCPD₃OPS in the product. The peaks at 1699, 1857, 1935 and 2173 m/z are very weak and are assigned to structures DCPD₄OPS, DCPD₆OPS, DCPD₇OPS and DCPD₈OPS respectively in all entries. In summary, structures DCPD₄OPS, DCPD₅OPS, DCPD₆OPS and DCPD₇OPS are the relevant because if reaction occurred completely these peaks would disappear at 1600-2,000 m/z. Moreover, peak of DCPD₈OPS shows very low intensity indicating that reaction is partial complete. Note that a maximum of peak intensity is formed after added high DCPD loading and ran for 7 days at 80 °C.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Br₃OPS was mixed with DCPD in dioxane by Heck reaction at different DCPD loading, types of catalyst, time and temperature. The DCPD₈OPS structure such as functional groups and the interaction between carbon bonds of DCPD with carbon bonds of phenyl ring were investigated.

From percent yield results, it indicated that coupling catalyst was better than palladium (II) acetate and high content of coupling catalyst was better than at low content at the same condition. Moreover, percent yield increased gradually with increasing time and temperature at the same materials content.

From FT-IR results, when an excess of DCPD and coupling catalyst is loaded at high temperature and long reaction time as 80 °C and 7 days the peaks are distinct. However, when palladium (II) acetate was added, the reaction did not proceed because functional group of DCPD at 2800-3600 cm⁻¹ was not observed. FTIR of all samples showed Br group at 500 cm⁻¹ wavenumber that indicated partially substituted of DCPD in phenyl ring.

From NMR results, when we increase the period of reaction time and increase the temperature of the reaction, it increased area, indicating the higher quality of proton than that of other condition. Palladium (II) acetate cannot be used as catalyst to synthesize DCPD₈OPS because the NMR peaks were disappears at 5-6 ppm.

From MALDI-TOF results, based on the intensity spectrum of all samples only DCPD₅OPS peak at 1779.41 m/z is higher than other peaks. The peaks at 1699, 1857, 1935 and 2173 m/z are very weak and are assigned to structures DCPD₄OPS, DCPD₆OPS, DCPD₇OPS and DCPD₈OPS respectively. In summary, structures DCPD₄OPS, DCPD₅OPS, DCPD₆OPS and DCPD₇OPS are the relevant because if reaction completely these peaks are disappear at 1600-2,000 m/z.

6.2 Recommendations

1. Selective types of catalyst on Br₈OPS/DCPD by Heck reaction should be investigated.
2. The mechanism for different behaviors of palladium catalyst supported on Heck reaction and DCPD loading should be investigated.
3. Selective increase the period of reaction time of this reaction should be investigated.

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APPENDIX A

Determination of Materials Loading

Material loading that was added into the Heck reaction was calculated as shown below.



Molecular weight of Br₈OPS (C₄₈H₃₂Si₈O₁₂Br₈) = 1,664 g/mol

Molecular weight of DCPD (C₁₀H₁₂) = 132 g/mol

For example, preparation of material by using 0.5 g of Br₈OPS

$$n = M / \text{Mw}$$

where n = mole molecule (mol)

M = mass (g)

Mw = molecular weight (g/mol)

$$\begin{aligned} \text{Mole of Br}_8\text{OPS} &= 0.5 \text{ (g)} / 1,664 \text{ (g/mol)} \\ &= 0.3 \text{ mmol} \end{aligned}$$

From mechanism we used 1 mol of Br₈OPS react with 8 mol of DCPD, thus loading of DCPD was calculated as shown below.

$$\begin{aligned} \text{Mole of DCPD} &= \frac{0.3 \text{ (mmol)} \times 8 \text{ (mol)}}{1 \text{ (mol)}} \\ &= 2.4 \text{ mmol} \end{aligned}$$

$$M = n \times M_w$$

$$\begin{aligned}\text{Mass of DCPD} &= 2.4 \text{ (mmol)} \times 132 \text{ (g/mol)} \\ &= 0.32 \text{ g}\end{aligned}$$

When density of DCPD is $0.98 \text{ (g/cm}^3\text{)}$

$$D = M / V$$

Where $D = \text{density (g/cm}^3\text{)}$

$M = \text{mass (g)}$

$V = \text{volume (cm}^3\text{)}$

$$\begin{aligned}\text{Volume of DCPD} &= 0.32 \text{ (g)} / 0.98 \text{ (g/cm}^3\text{)} \\ &= 0.33 \text{ cm}^3\end{aligned}$$

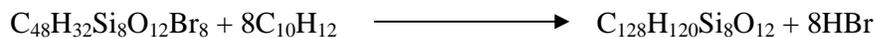
APPENDIX B

Yield Calculation

The percent yield of product in Br₈OPS/DCPD reactions was calculated by percent yield equation as shown below.

$$\text{Percent yield} = 100 \times \left[\frac{\text{Actual mass of product}}{\text{Predicted mass of product}} \right]$$

For example (Entry 3), the reaction started with 0.5 grams (0.3mmol) of Br₈OPS. What is the predicted yield and the percent yield if only 0.075 grams of DCPD₈OPS are produced?



From mechanism predicted mass of product are calculated as shown below.

$$\text{Predicted mass of product} = n \times \text{Mw}$$

$$\text{When } n = 0.3 \text{ mmol} = 0.0003 \text{ mol}$$

$$\text{Mw} = 2,072 \text{ (g/mol)}$$

$$\text{Predicted mass of product} = 0.0003 \times 2,072 = 0.62 \text{ g}$$

$$\text{Percent yield} = 100 \times [0.075 / 0.62] = 12\%$$

Answer: The percent yield is 12 %.

APPENDIX C**Quantity of product****Table C.1 Weigh of all products**

Name	Quantity (g)
Entry1	0.124
Entry2	0.050
Entry3	0.074
Entry4	0.087
Entry5	0.229
Entry6	0.248
Entry7	0.273
Entry8	0.347

APPENDIX D

Fourier transforms infrared spectrometry (FTIR)

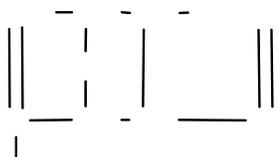
Characterization

Table D.1 Characteristic IR absorption frequencies of functional groups

Functional group	Characteristic Absorption (cm ⁻¹)
POSS	
O-Si-O	1000-1200
Alkene	
=C-H	3010-3100
=C-H	675-1000
C=C	1620-1680
Alkyl halide	
C-Br	500-600
Aromatic	
C-H	300-3100
C=C	1400-1600

APPENDIX E
Nuclear Magnetic Resonance Spectra
Characterization

Table E.1 Approximate Chemical Shift of Protons

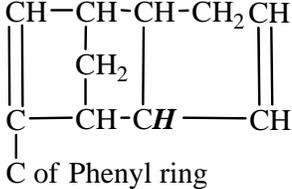
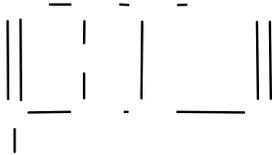
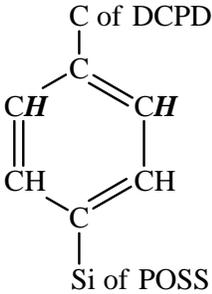
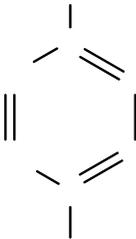
Proton	Chemical shifts (ppm)
<p>Case 1 (1H, 2 peaks)</p> 	1-3 ppm
<p>Case 2 (4H, 5 peaks)</p> $ \begin{array}{ccccccc} \text{CH} & - & \text{CH} & - & \text{CH} & - & \text{CH}_2 & \text{CH} \\ & & & & & & & \\ & & \text{CH}_2 & & & & & \\ \text{C} & - & \text{CH} & - & \text{CH} & - & \text{CH} \\ & & & & & & & \\ \text{C of Phenyl ring} & & & & & & & \end{array} $	1-3 ppm
<p>Case 3 (2H, 3 peaks)</p> $ \begin{array}{ccccccc} \text{CH} & - & \text{CH} & - & \text{CH} & - & \text{CH}_2 & \text{CH} \\ & & & & & & & \\ & & \text{CH}_2 & & & & & \\ \text{C} & - & \text{CH} & - & \text{CH} & - & \text{CH} \\ & & & & & & & \\ \text{C of Phenyl ring} & & & & & & & \end{array} $	1-3 ppm

CH CH CH CH₂CH

CH₂

C CH CH CH

C of Phenyl ring

Proton	Chemical shifts (ppm)
<p>Case 4 (3H, 4 peaks)</p>  <p>C of Phenyl ring</p>	1-3 ppm
<p>Case 5 (3H, 4 peaks)</p> 	5-6 ppm
<p>Case 6 (1H, 2 peaks)</p>  <p>C of DCPD</p> <p>Si of POSS</p>	7-8 ppm
<p>Case 7 (1H, 2 peaks)</p> 	<p>CH CH CH CH₂CH</p> <p>7-8 ppm CH₂</p> <p>C CH CH CH</p> <p>C of Phenyl ring</p>

APPENDIX F

Diagrams of Fourier transform infrared spectrometry

(FTIR) Characterization

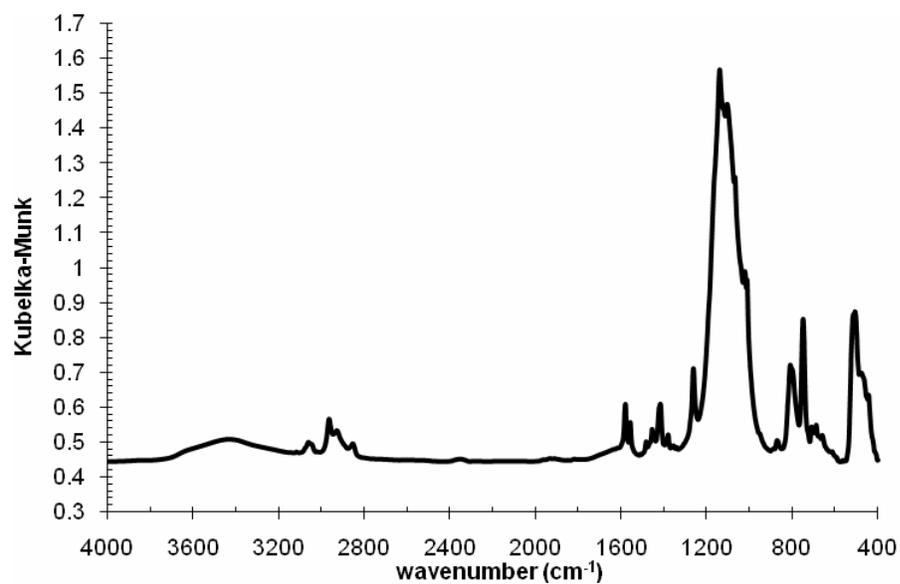


Figure F.1 FT-IR Diagram of Entry 2

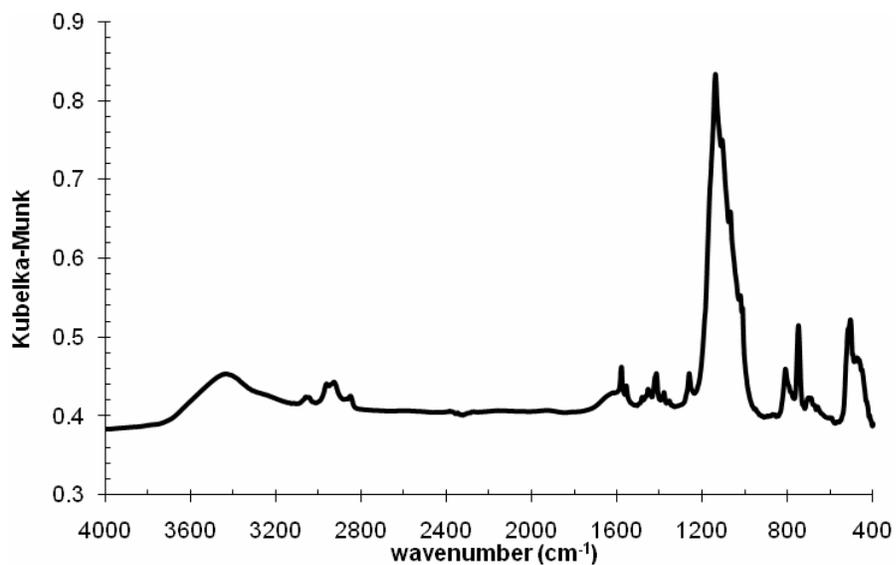


Figure F.2 FT-IR Diagram of Entry 3

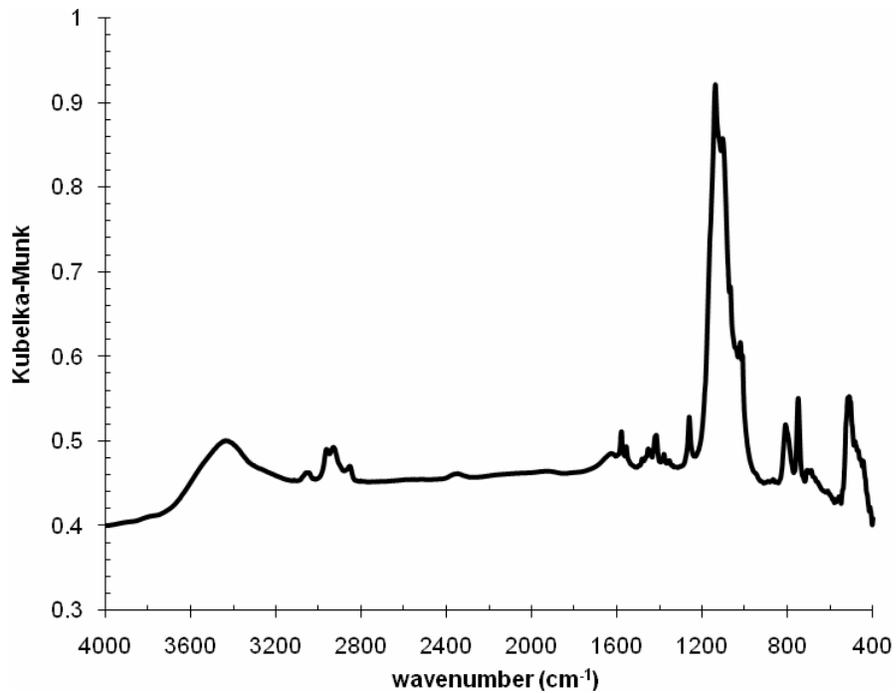


Figure F.3 FT-IR Diagram of Entry 4

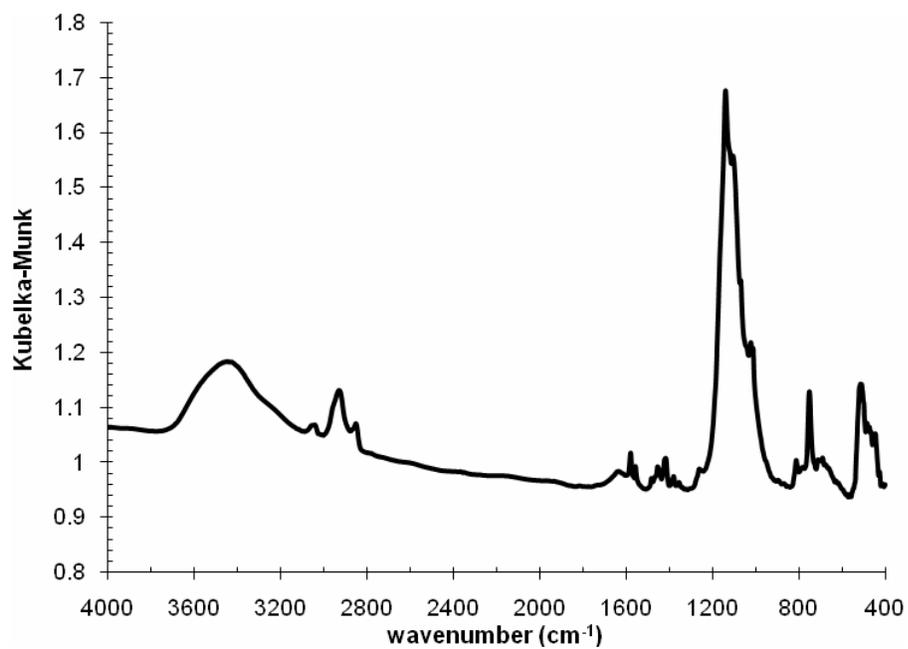


Figure F.4 FT-IR Diagram of Entry 5

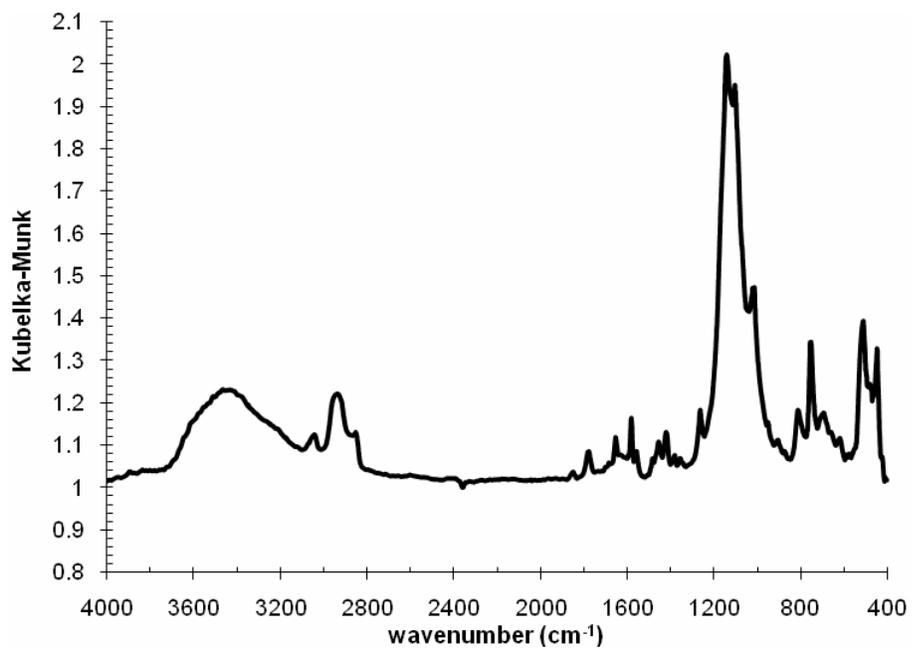


Figure F.5 FT-IR Diagram of Entry 6

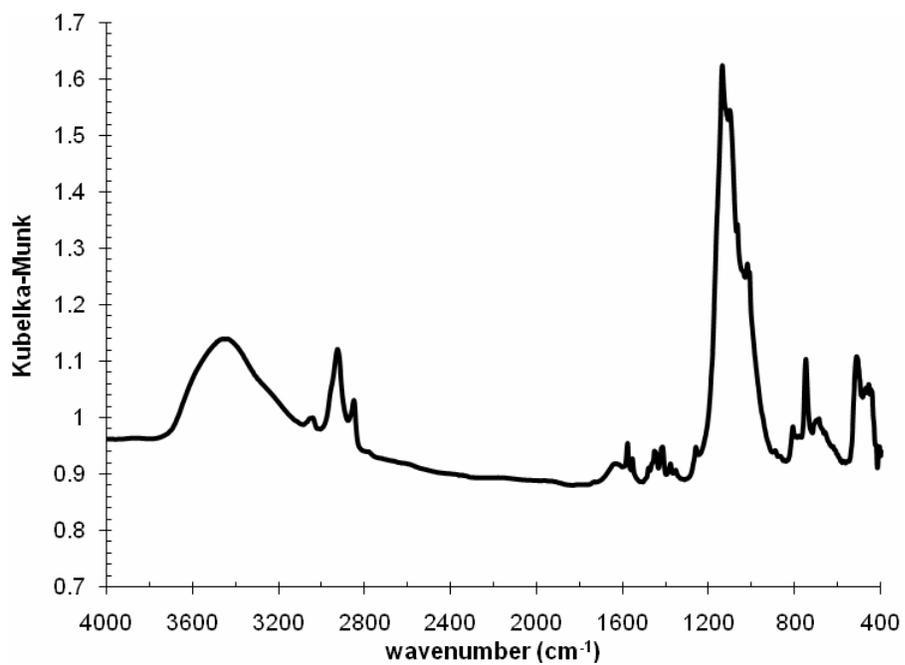


Figure F.6 FT-IR Diagram of Entry 7

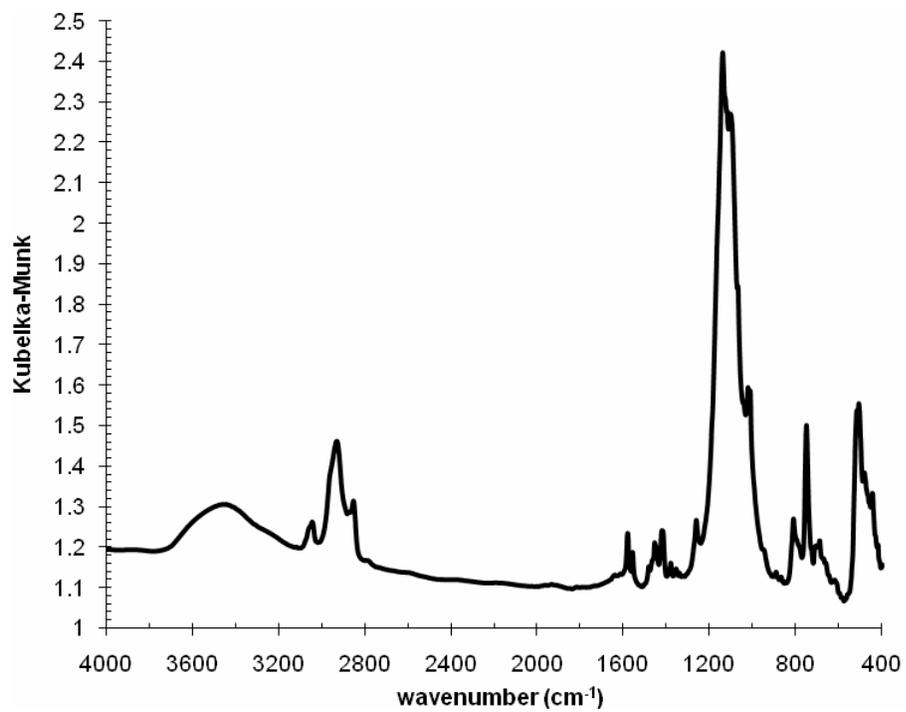


Figure F.7 FT-IR Diagram of Entry 8

APPENDIX G

Diagrams of Nuclear Magnetic Resonance Spectra

Characterization

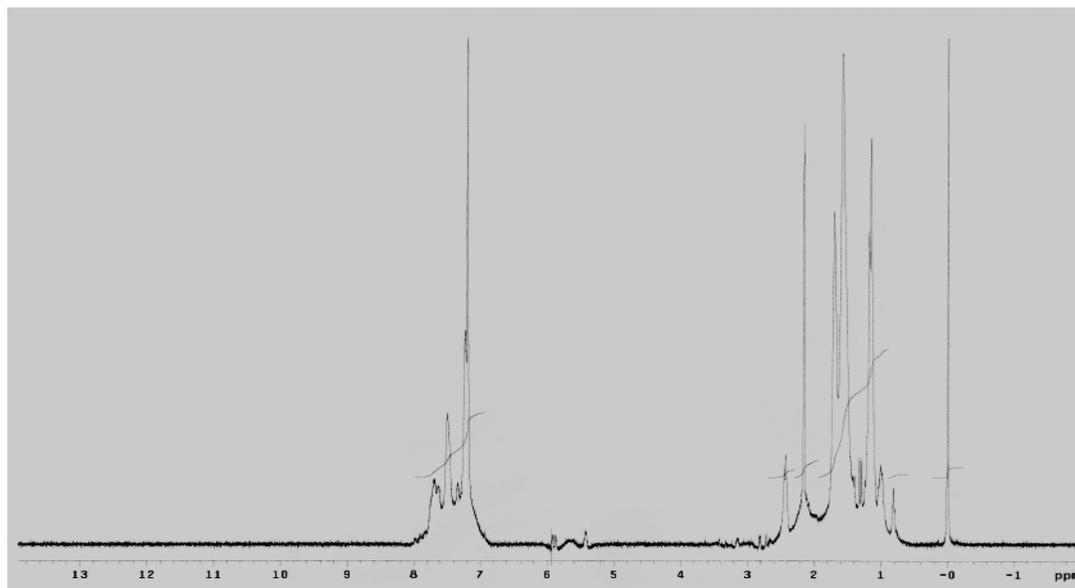


Figure G.1 NMR Diagram of Entry 3

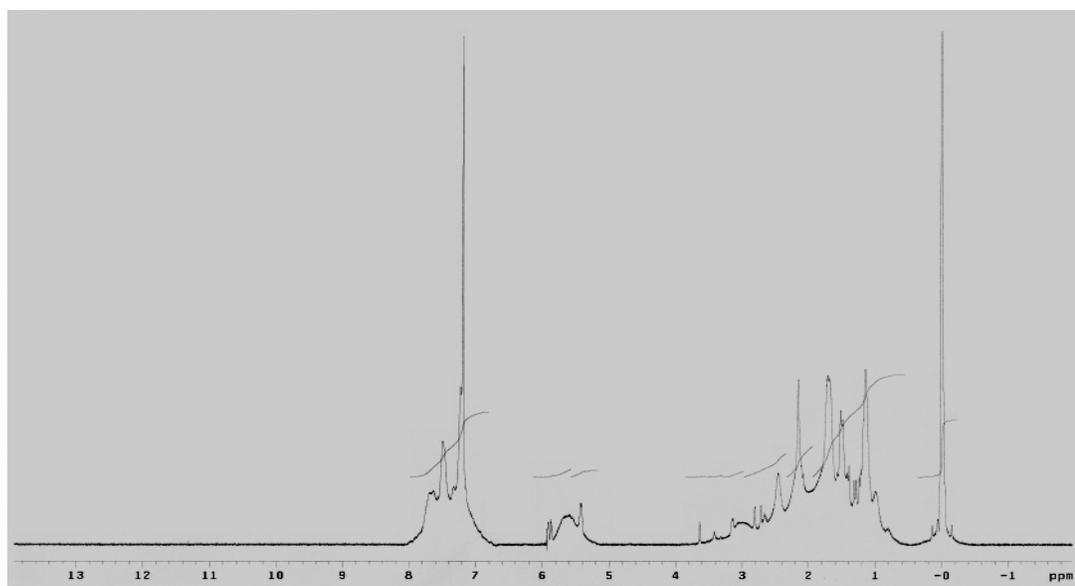


Figure G.2 NMR Diagram of Entry 4

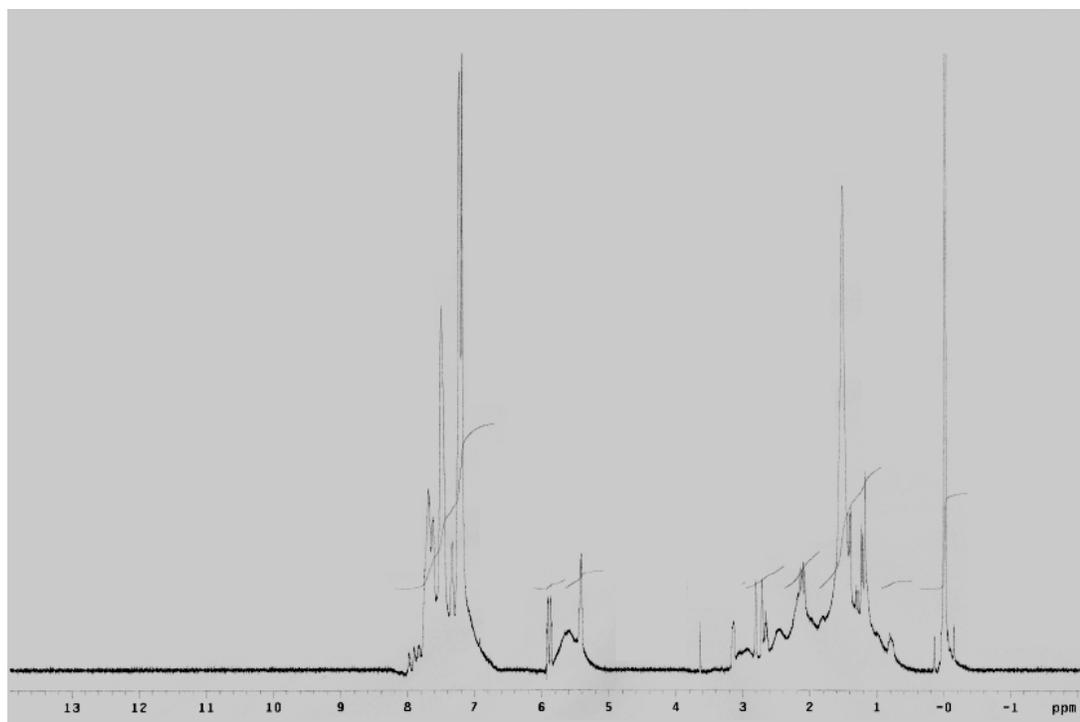


Figure G.3 NMR Diagram of Entry 5

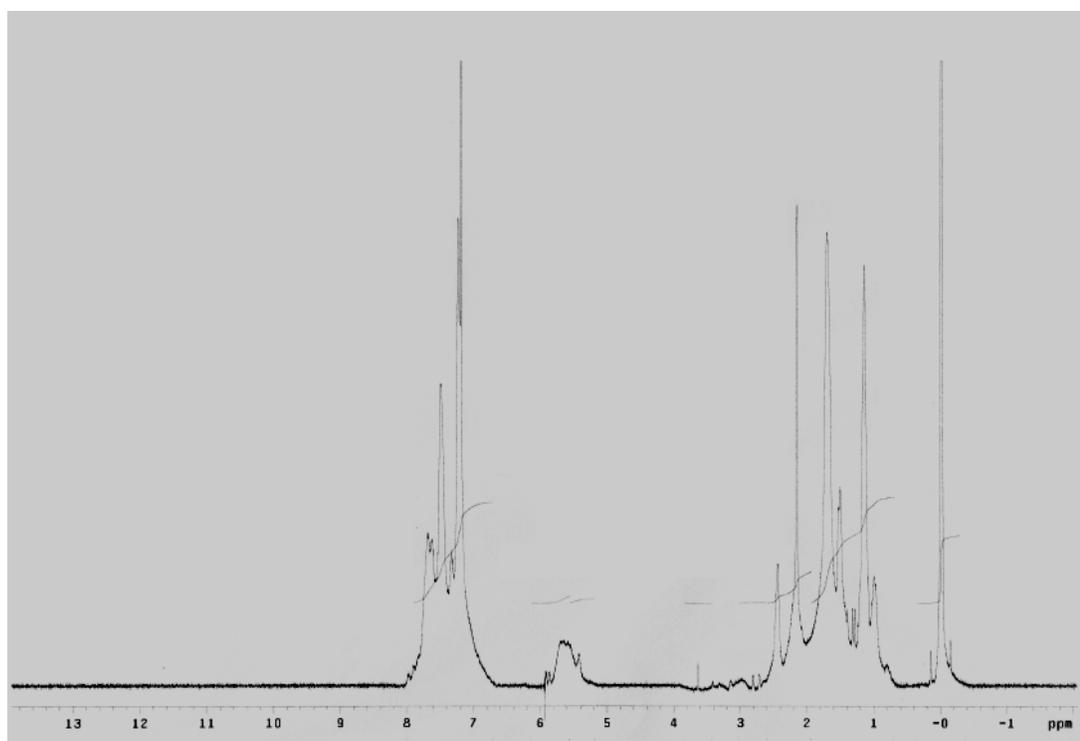


Figure G.4 NMR Diagram of Entry 6

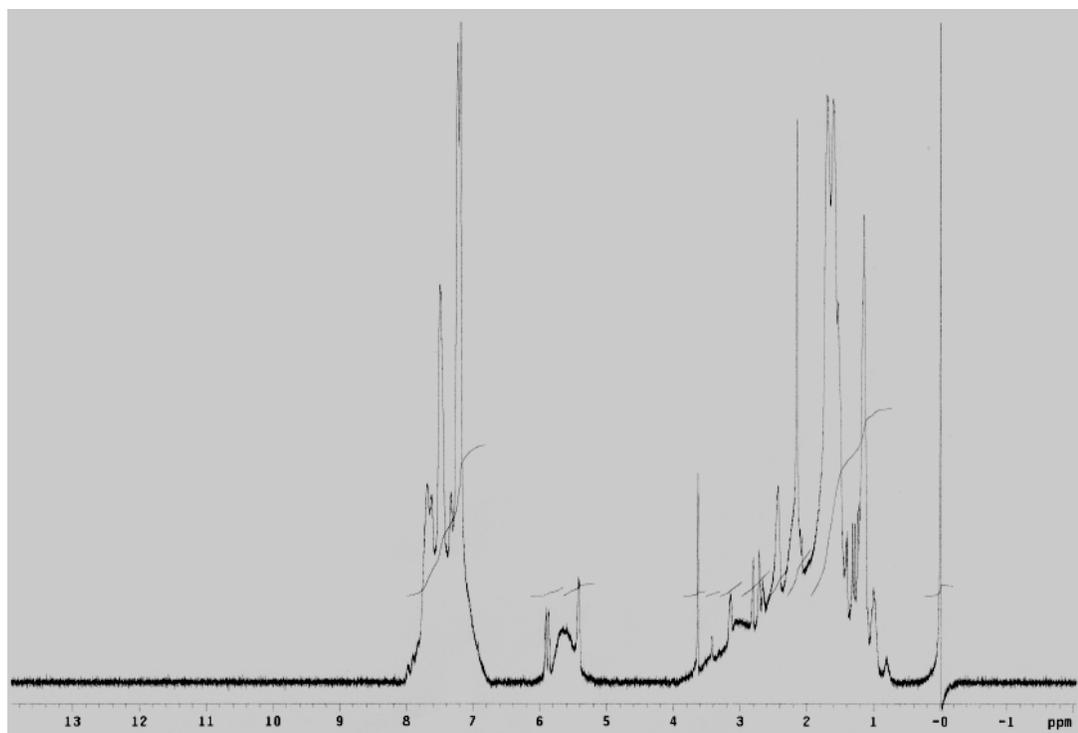


Figure G.5 NMR Diagram of Entry 7

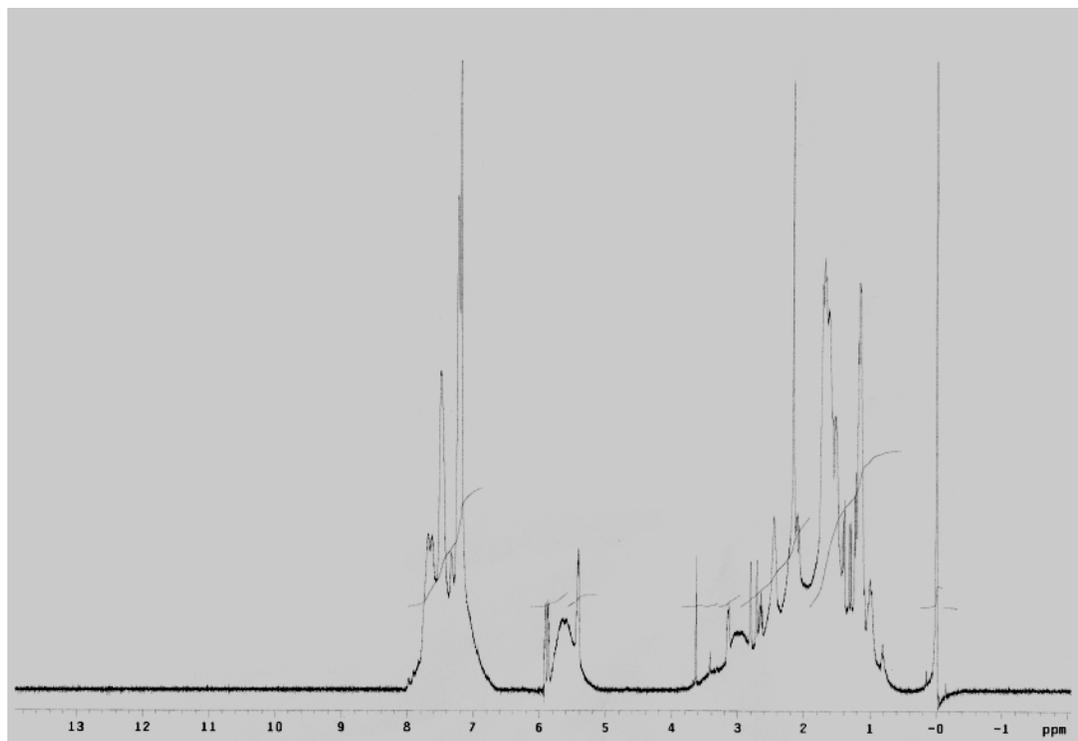


Figure G.6 NMR Diagram of Entry 8

APPENDIX H

Diagrams of Matrix-assisted laser desorption/ionization

Characterization

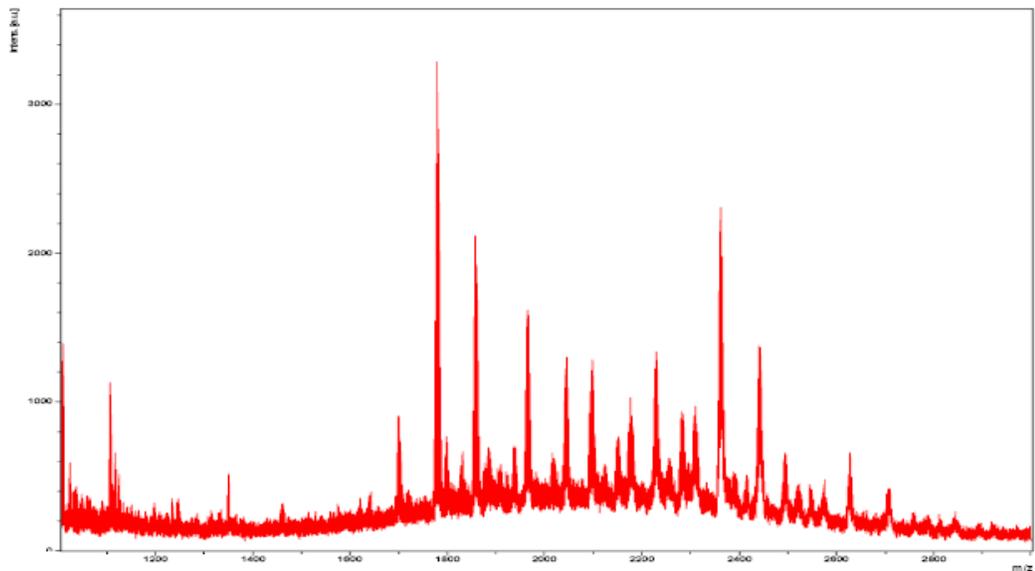


Figure H.1 MALDI-TOF Diagram of Entry 2

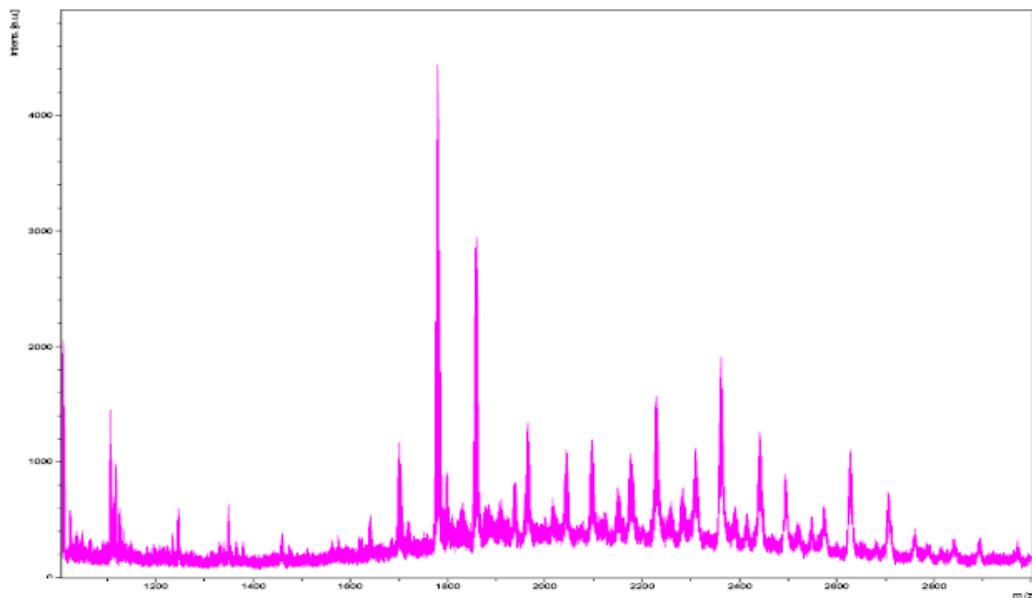


Figure H.2 MALDI-TOF Diagram of Entry 3

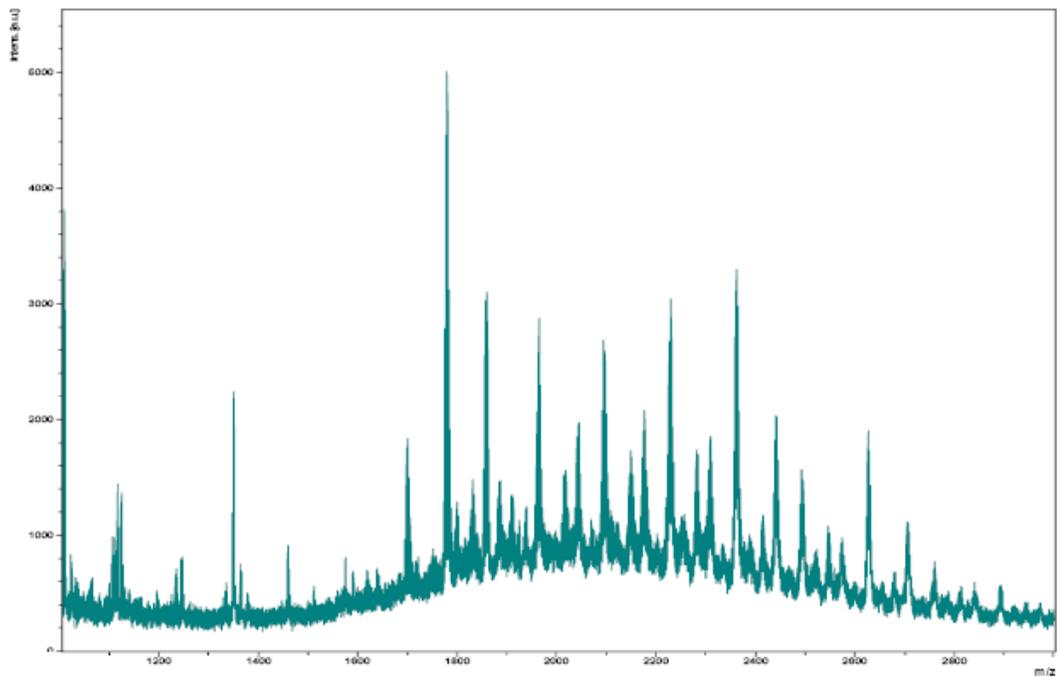


Figure H.3 MALDI-TOF Diagram of Entry 4

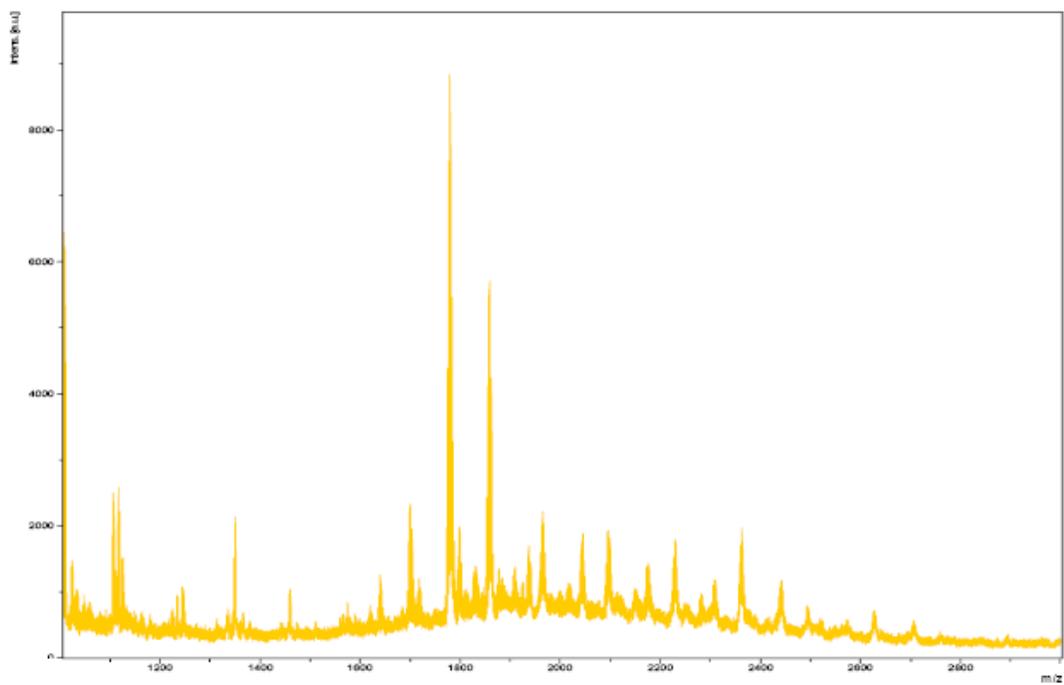


Figure H.4 MALDI-TOF Diagram of Entry 5

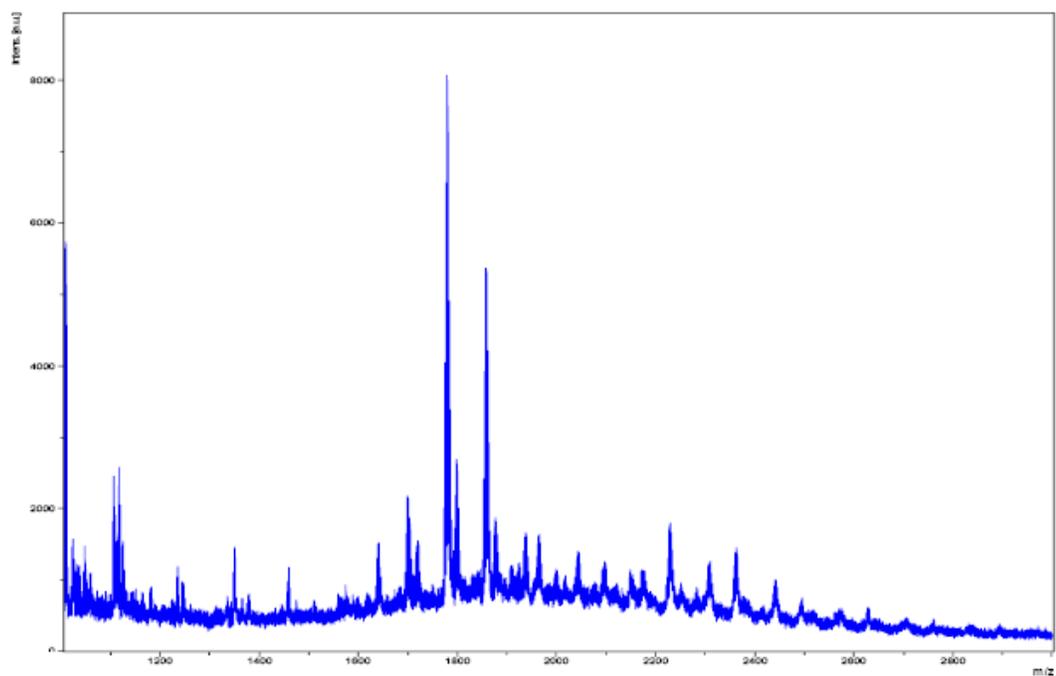


Figure H.5 MALDI-TOF Diagram of Entry 6

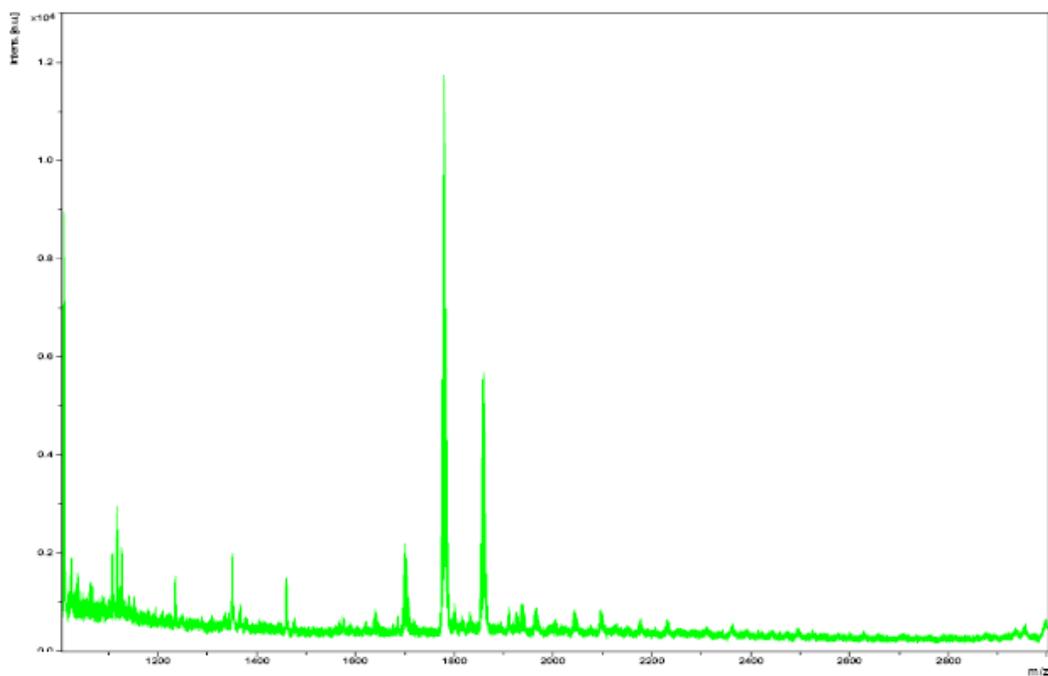


Figure H.6 MALDI-TOF Diagram of Entry 7

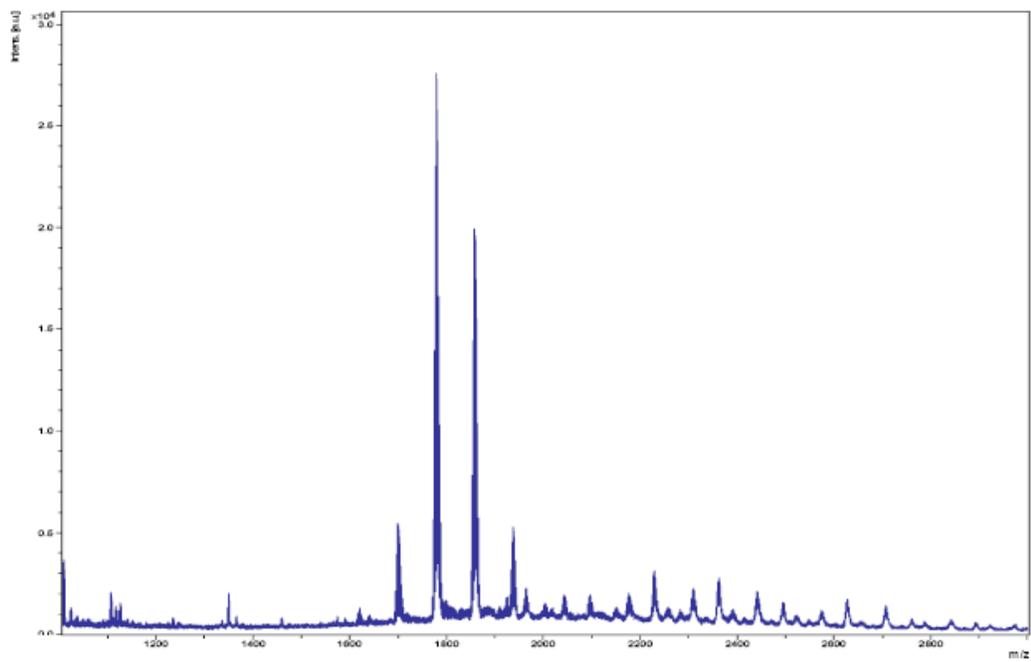


Figure H.7 MALDI-TOF Diagram of Entry 8

VITA

Miss Pratyaporn Tepmatee was born on February 12, 1984 in Khon Kaen, Thailand. She received the Bachelor's Degree in Chemical Engineering from Department of Chemical Engineering, Faculty of Engineering, Burapha University in March 2007. She entered the Master of Engineering in Chemical Engineering at Chulalongkorn University in June, 2007.