

**ÇUKUROVA UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES**

PhD THESIS

Asım EĞİTMEN

**PREPARATION OF SBA-15 SUPPORTED METALLIC NANOPARTICLES
IN SCCO₂ USING SCHIFF BASE DERIVATIVE PRECURSORS AND
USABILITY AS CATALYST IN SUZUKI-MIYAUURA REACTIONS**

DEPARTMENT OF CHEMISTRY

ADANA, 2016

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ABSTRACT

PhD THESIS

PREPARATION OF SBA-15 SUPPORTED METALLIC NANOPARTICLES IN SCCO₂ USING SCHIFF BASE DERIVATIVE PRECURSORS AND USABILITY AS CATALYST IN SUZUKI-MIYaura REACTIONS

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DEPARTMENT OF CHEMISTRY

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In this thesis, a novel Schiff base derivatives ligands and their palladium complexes have been synthesized and characterized via spectral (FT-IR, ¹H NMR, ¹³C NMR) techniques. Single crystal X-ray diffraction spectroscopy has been used to determine the structure of suitable crystals. The synthesized complexes used as precursor to preparation of metallic nanoparticles on support material. Mesoporous silica derivative Santa Barbara Amorphous-15 (SBA-15) have been used as support material due to high surface area, high chemical and thermal stability. ICP-OES, XRD, TEM and FE-SEM have been used to characterize the morphology of SBA-15 supported metallic nanoparticles. The results have been showed that highly dispersed palladium nanoparticles obtained on SBA-15 with %2-%8 metal loading. The catalytic efficiency of obtained SBA-15 supported palladium nanoparticles have been tested over Suzuki- Miyaura reactions and the conversions monitored by gas chromatography (GC). The effect of electron-donating and electron-withdrawing group on aryl halides has been also investigated.

Key Words: Schiff-base, Supercritical Carbon Dioxide, Deposition, Catalyst, Suzuki-Miyaura

ÖZ

DOKTORA TEZİ

SCHIFF BAZ TÜREVİ ÖNCÜLLER KULLANILARAK SCCO_2 ORTAMINDA SBA-15 DESTEKLİ METALİK NANOPARTİKÜL HAZIRLANMASI VE KATALİZÖR OLARAK SUZUKI-MIYAUURA REAKSİYONUNDA KULLANIMI

Asım EĞİTMEN

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Tez kapsamında, daha önce sentezine rastlanmamış yeni Schiff baz türevi ligandlar ve bunların paladyum kompleksleri sentezlenerek yapıları, spektral (FT-IR, ^1H NMR, ^{13}C NMR) tekniklerle karakterize edilmiştir. Kristal formu elde edilen bileşiklerin yapıları tek kristal X-Ray spektroskopisi ile aydınlatılmıştır. Elde edilen kompleksler, Süperkritik karbon dioksit (scCO_2) ortamında kati destek üzerinde metalik nanopartikül oluşturmada öncül olarak kullanılmışlardır. Destek katisi olarak ise, yüksek yüzey alanına, yüksek kimyasal ve termal kararlılığa sahip olmasından dolayı mezogözenekli silika türevi olan Santa Barbara Amorf-15 (SBA-15) kullanılmıştır. Elde edilen SBA-15 destekli metalik nanopartiküllerin yüzey morfolojileri ICP-OES, XRD, TEM ve FE-SEM kullanılarak karakterize edilmiştir. Analiz sonuçları incelendiğinde, SBA-15 üzerine %2 - %8 aralığında değişen ve de yüksek yoğunlukta homojen olarak dağılmış paladyum nanopartiküllerinin elde edildiği görülmektedir. SBA-15 destekli metal nanopartiküllerin katalitik etkinlikleri Suzuki-Miyaura reaksiyonu üzerinden incelenmiş olup, dönüşümleri gaz kromatografi (GC) cihazı ile kaydedilmiştir. Bu reaksiyon sırasında, aril halojenür türevleri üzerindeki hem elektron çekici hem de elektron sağlayıcı substitüenlerin dönüşüm üzerine etkisi incelenmiştir.

Anahtar Kelimeler: Schiff-baz, Süperkritik Karbon Dioksit, Depozisyon, Katalizör, Suzuki-Miyaura,

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I would like to thank all of the people who have helped and supported me throughout the process of this whole doctorate program and research. This research would not have been possible without the support, help and guidance from many people. First of all, I would like to thank my supervisor, Prof. Dr. Bilgehan GÜZEL, who is largest shareholder for carrying out of this thesis by giving me chance to work with his group, for helping me choose this research topic, directing me in the researches, sharing their knowledge and experience.

I would like to thank the members of my committee, Prof. Dr. Selahattin SERİN, Prof. Dr. Ramazan ESEN, Prof. Dr. Mehmet TÜMER, Prof. Dr. Hüseyin KÖKSAL. I would like to special thanks to Prof. Dr. Ramazan ESEN for XRD measurments. I would like to thank to the head of the chemistry department, Prof. Dr. İlyas DEHRİ and the all of the members of chemistry department. I am deeply thankful, Prof. Dr. Tunç TÜKEN for his helping and suggestions.

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I would like to thank Burak AY and Serkan KARACA for sharing his experience and helping me for spectral analyses. I would like to thank, Kemal CELLAT, Fatih TEZCAN and Berk KAZANCI for DSC/TGA analyses, I would like to thank Dr. Onur Şahin for single crystal X-Ray analyses. Also I am really thankfulness to Dr. Mustafa Kemal YILMAZ for sharing his research experiences.

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LIST OF ABBREVIATIONS

°C	Santigrat Degree
DSC	Differential Scanning Calorimetry
FE-SEM	Field Emission-Scanning Electron Microscopy
EDX	Energy Dispersive X-Ray Spectroscopy
Si	Silicon
TEM	Transmission Electron Microscopy
TGA	Thermal Gravimetric Analysis
XRD	X-Ray Powder Diffraction Spectroscopy
SCF	Supercritical Fluids
SCFD	Supercritical Fluids Deposition
ScCO ₂	Supercritical Carbon Dioxide
SBA-15	Santa Barbara Amorphous-15
Pd	Palladium
PdCl ₂	Palladium(II) Chloride
FT-IR	Fourier Transform Infrared Spectroscopy
NMR	Nuclear Magnetic Resonance Spectroscopy
XRD	X-Ray Powder Diffraction
NMP	1-Methyl-2- Pyrrolidone
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
GC	Gas Chromatography
FID	Flame Ionization Detector
<i>s</i>	Singlet
<i>d</i>	Dublet
<i>m</i>	Multiplet
DMSO-d ₆	Deutero-Dimethylsulfoxide
CDCl ₃ -d ₆	Deutero-Chloroform
Cat	Catalyst
DMF	Dimethylformamide
CH ₂ Cl ₂	Dichloromethane

Hr	Hour
SCFD	Supercritical Fluid Deposition
Psi	Pound Per Square Inch
cm	Centimeters
nm	Nanometers
SiO ₂	Silicon dioxide
g	Gram



1. INTRODUCTION

Over past decades, supported metallic nanoparticles grabbed much attention due to their unique properties and numerous applications of their composite materials in such areas; magnetic-materials, microelectronics, optoelectronics and catalyst (Cabanas *et al.*, 2002; Erkey, 2009; Morero *et al.*, 2005, Zhang *et. al*, 2005).). In catalyst area, palladium is the most studied metal due to its versatility. There has been exponential rise in the number of work using supported-palladium nanoparticles as catalyst in the reaction of hydrogenation, cracking, oxidation and C-C cross coupling reactions for both industrial and scientific purpose (Blaser *et al.*, 2001; Bozbag *et al.*, 2012 and Morero *et al.*, 2011)

Last Decades, different kind of materials have been used as support material such as, carbon nanotubes, polymers, carbon black, activated carbon, carbon aerogel, alumina and silica. Among them ordered mesoporous silica have been extensively investigated due to the their larger surface area, high chemical and thermal stability. There are several ways to prepare supported metallic nanoparticles, such as; impregnation, deposition-precipitation, chemical vapor deposition and sol-gel method (Angelucci *et al*, 2007; Arvela *et al*, 2013; Bozbag *et al*, 2011; Cangul *et al.*, 2009; Zhang and Erkey, 2006). However, conventional preparation methods often fail to offer adequate control of particle size and morphology because deposition of metal particles on the external surface is unavoidable (Han *et. al*, 2000; Yu *et al.*, 2003; Yin *et al.*, 2010). Due to these limitations, Supercritical fluid deposition (SCFD) technique has been developed as alternative to prepare supported metallic nanoparticles (Bozbag *et al*, 2011; Hunt *et al.*, 2014;. Zhang and Erkey, 2006). As compared with conventional liquid solvents, supercritical fluids exhibit unique features of gas-like and liquid-like states Similarly liquid, they can dissolve compounds and like gases, it can be provide low viscosity, high diffusivity, and zero surface tension (Yin *et al*, 2005; 2008; 2010). In this technique, scCO₂ used extensively as reaction media due to the inexpensive, non-flammable, non-toxic properties (Cansell *et al.*, 2003 and Erkey,. 2009).

This SCFD process occurs in three steps; (i) the dissolution of an

organometallic precursor in a supercritical fluid (ii) impregnation of metal complex (precursor) onto the solid support material. (iii) Reduction of the organometallic precursor to its metallic form by reducing agent such as hydrogen into the supercritical solution or thermal reductions after depressurization.

On the other hand, There are limited number of precursors have been known that use in SCFD technique (acetylacetonate, β -diketonate, hexamethyl triethylene, cyclooctadiene) (Bayrakceken *et al.*, 2007). Among them, β -diketonate derivatives are mostly used ligand type due to their stability, high-energy transfer efficienct and related solubility values in scCO_2 (Cabanass *et al.*, 2002). However, limited number of precursor is insufficient to explain SCFD tecchnique.

The effect of different parameters (solubility, ligand type, metal type, etc.) on deposition process would be investigate. Due to the these limitations,, novel schiff base derivative ligands and their palladium complexes have been synthesized. The synthesized palladium complexes have been used alternative to the current precursors for preparing metallic nanoparticles.

1.1 Schiff Bases

Schiff bases are considered “privileged ligands” because they are easily prepared by the condensation of primary amine with an aldehyde or a ketone under specific conditions. Structurally, Schiff base (also known as imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (CO) has been replaced by an imine or azomethine group (Schiff, *et al.*, 1986, Abdel Latif *et al.*, 2007 and Xavier, *et al.*, 2015).

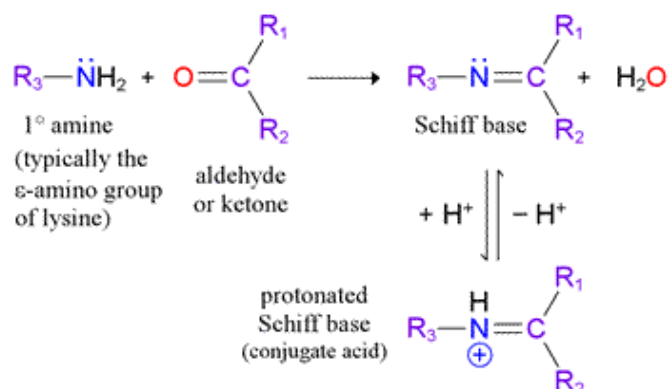


Figure 1.1. General scheme for synthesis of Schiff base

Schiff bases that contain aryl substituents are substantially more stable and more readily synthesized, while those that contain alkyl substituents are relatively unstable. The formation of a Schiff base from an aldehydes or ketones is a reversible reaction and generally takes place under acid catalyzed. The formation is generally completion by separation of the product or removal of water, or both. Many Schiff bases can be hydrolyzed back to their aldehydes or ketones and amines by aqueous acid or base.

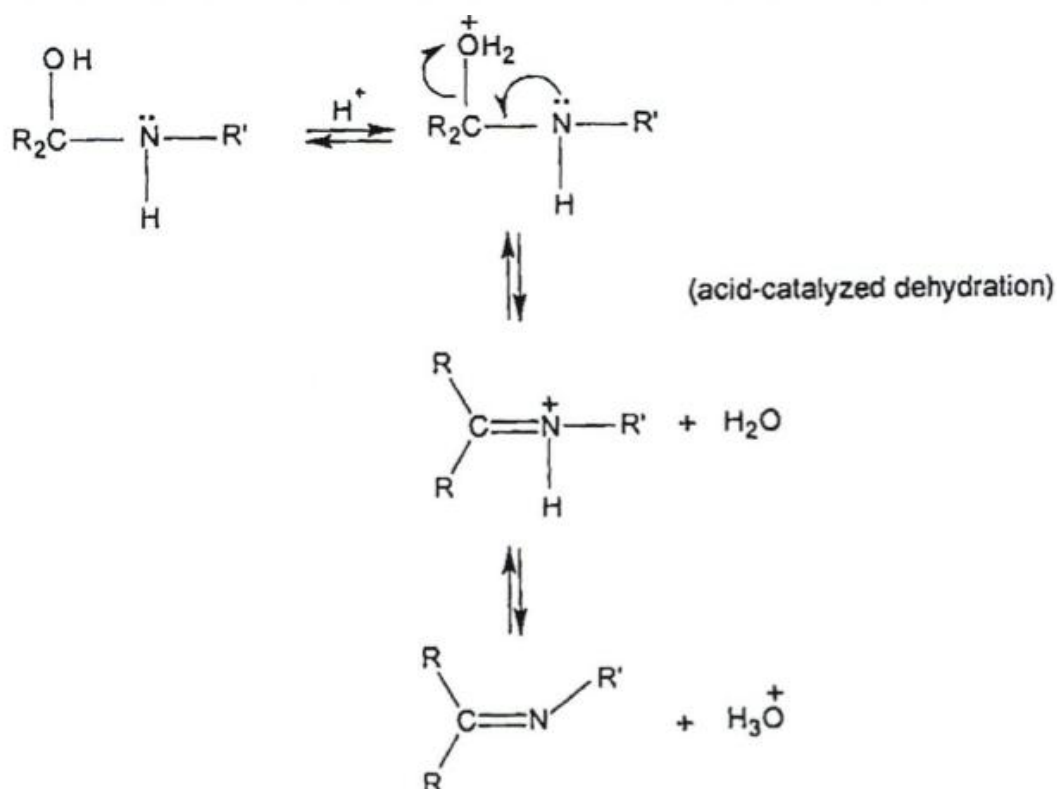


Figure 1.2. General mechanism for Schiff base synthesis

The mechanism of Schiff base formation is another variation on the theme of nucleophilic addition to the carbonyl group. In this case, the nucleophile is the amine. In the first part of the mechanism, the amine reacts with the aldehyde or ketone to give an unstable addition compound called carbinolamine. The carbinolamine loses water by either acid or base catalyzed pathways. Since the carbinolamine is an alcohol, it undergoes acid catalyzed dehydration. (Gilani and Mahmood, 2003).

Typically the dehydration of the carbinolamine is the rate-determining step of Schiff base formation and that is why the reaction is catalyzed by acids. Yet the acid concentration cannot be too high because amines are basic compounds. If the amine is protonated and becomes non-nucleophilic, equilibrium is pulled to the left and carbinolamine formation cannot occur. Therefore, many Schiff bases synthesis are best carried out at mildly acidic pH (Gilani and Mahmood, 2003).

Schiff base ligands are able to coordinate many different metals (Cindric *et al.*, 2003; Sallam *et al.*, 2006 and Abdel Latif *et al.*, 2007) and to stabilize them in various oxidation states.

During the past two decades, Schiff bases and their complexes have widely used in the area of biological including antioxidant, antifungal, antibacterial, anticancer, and also potential application as catalyst in various reactions; hydrosilylation, hydroformylation, oxidation, epoxidation and C-C cross coupling reactions. (Nishinaga *et al.*, 1988; Xi *et al.*, 1986; Abdel Latif *et al.*, 2007; Kumar *et al.*, 2009).

The high thermal and moisture stabilities of many Schiff base complexes were useful attributes for their application as catalysts in reactions involving at high temperatures. The activity is usually increased by complexation therefore to understand the properties of both ligands and metal can lead to the synthesis of highly active compounds.

1.2. Catalysis

Catalysis is a term that was first employed by J. J. Berzelius in 1835 to describe the property of substances that facilitate chemical reactions without being consumed in them and this term is the increase in the rate of a chemical reaction due to the participation of an additional substance called a catalyst. With a catalyst, reactions occur faster and require less activation energy. Because catalysts are not consumed in the catalyzed reaction, they can continue to catalyze the reaction of further quantities of reactant. Often only tiny amounts are required. Catalysts work by providing an (alternative) mechanism involving a different transition state and lower activation energy. Consequently, more molecular collisions have the energy needed to reach the transition state. Hence, catalysts can enable reactions that would otherwise be blocked or slowed by a kinetic barrier. The catalyst may increase reaction rate or selectivity, or enable the reaction at lower temperatures. This effect can be illustrated with an energy profile diagram.

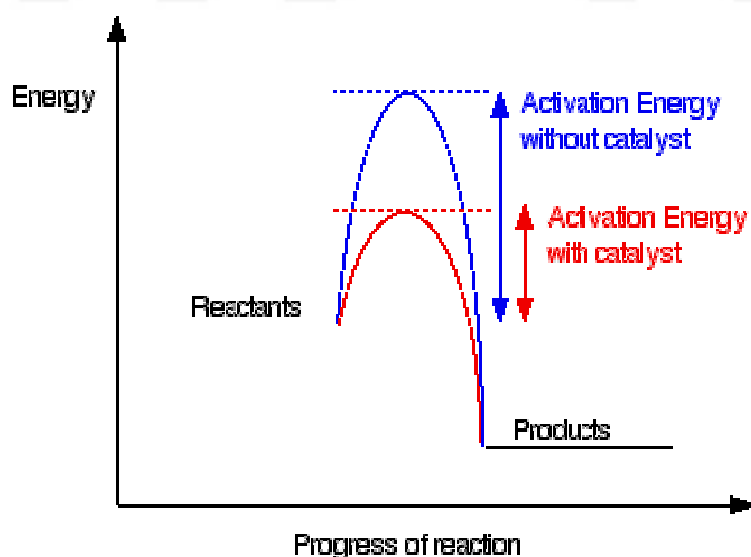


Figure 1.3. Potential energy diagram of reaction with catalyst and without catalyst

Catalysts can be divided into two types depending on the reaction phase that they occupy; homogeneous and heterogeneous.

1.2.1 Homogenous Catalyst

Homogeneous catalysts occupy in the same phase as the reaction media and are generally dissolved in the same solution with reactants. This catalyst type is used extensively in organometallic chemistry. It is more selective and also very effective with low concentration. But homogeneous catalyst systems have major drawbacks; it's very difficult to remove catalyst from reaction media and this situation is limited the catalyst recycling.

1.2.2 Heterogeneous Catalyst

Heterogeneous catalyst exists in a different phase than the substrates. Commonly, they are solids and the reaction media is liquid or gaseous. These type catalysts have been designed as alternative to the homogeneous catalyst due to the easily catalyst separation and simple recycling.

Table 1.1. Comprasion of advantages/ disadvantages of Homogenous and Heterogeneous Catalyst

	Homogeneous	Heterogeneous
Form	Soluble metal complexes,	Metals, usually supported or metal oxides
Phase	Liquid phase	gas/solid phase
Selectivity	High selectivity	Low selectivity
Catalyst separation	Difficult	Easy catalyst separation
Catalyst recycling	Expensive recycling	Simple recycling
Active site	Well-defined active site	Poorly defined active site
Catalyst modification	Easy	Difficult catalyst modification
Reaction mechanism	Well understood	poorly understood

Catalyst Separation: *Homogeneous:* The separation of the products from the catalyst is generally expensive, the only exception being in biphasic catalysis.

Heterogeneous: The separation of the products from the catalyst is usually straightforward.

- **Recycling:** *Homogeneous:* Recycling is expensive due to difficult treatment of the spent catalyst. *Heterogeneous:* Recycling is usually straightforward, although the catalyst might need reactivating treatment.

- **Active site** *Homogeneous:* Usually well defined. Catalysts are generally single atom transition metal stabilized by ligands. □ *Heterogeneous:* Mainly not well-defined. When dealing with metal particles on a support, the active site might be only a few percent of the metal (usually small particles), and different zones of the same particle might have different catalytic properties.

- **Catalyst modification** *Homogeneous:* Relatively easy. Tuning of the electronic and steric properties on the metal can be done by varying donor atoms in the ligands or by tuning the donating abilities of the ligands. For example, if triphenylphosphine is the ligand and one needs to have a less donating phosphine, the phenyl groups on the phosphine could be tuned (adding CF₃, F, and other electron withdrawing groups). Synthetic methods available are numerous and all based on basic concepts developed in organic and organometallic chemistry. *Heterogeneous:* Relatively difficult. Control of the particle size and of the active site in general at the molecular level is extremely difficult. Few synthetic methods are available.

- **Reaction Mechanism** *Homogeneous:* Easier to find out due to more techniques available. Direct methods are available (they look at catalyst and not at the products of the reaction). In addition to those of heterogeneous catalysis (see below) the most common techniques are; Liquid state NMR: Useful in kinetics for relatively slow reactions and to identify intermediate states *of the catalyst*. Limited to diamagnetic metal complexes. Single crystal X-ray diffraction: Useful to identify the intermediate states *of the catalyst*. Computational methods are more accurate due to discrete molecular orbitals as theoretical model. *Heterogeneous:* Difficult to find out. Mainly by indirect methods (they look at products and not at the catalyst itself). Available techniques are: Infrared spectroscopy: Useful to determine the species absorbed on

active site. Strongly limited by the presence of groups that can be distinguished in the IR spectrum. Computational model might help to determine the structure of the reactive intermediates. Useful in kinetics as well. Liquid State NMR, GC-MS: Useful to determine the intermediates *of the organic reaction*. Electron microscopy: Ex-situ determination of particle-size. X-ray absorption: Ex-situ and in-situ determination of the surrounding of the metal. MUST be supported by computational models.

- **Selectivity** *Homogeneous*: High. It is a consequence of the easier fine-tuning of the steric and electronic properties of the catalyst and of the easier way of finding out the reaction mechanism. *Heterogeneous*: Low. It is a consequence of more difficult fine-tuning of the steric and electronic properties of the catalyst and of the more difficult way of finding out the reaction mechanism.

1.2.2.1 Nano-catalyst

A heterogeneous catalyst is generally adsorbed onto/into second solid material that called a support. This type of catalyst referred by the name of Nano-catalyst or solid support -catalyst.

A nano-catalyst is defined as a material that has a structure such that at least one of its phases has one or more dimension (length, width or thickness) in the nanometer size range, usually ranging from 1 to 100 nm.(Zhang *et al.*, 2006) This catalyst include polycrystalline materials with nanometer sized crystallites, materials with surface protrusions spatially separated by distances on the order of nanometers, granular or porous materials with grain sizes in the nanometer range or nanometer sized metallic clusters dispersed within a porous matrix.

Solid supported metal nanoparticles has become the focus of increasing interest and research in the scientific community due to their unique (physical and chemical) properties and numerous applications of its composite materials in such areas; microelectronics, magnetics, electrochemistry, optics and catalysis (Zhang *et al.*, 2006). The special properties provided by these materials in such applications depend on the size, distribution and concentration of the metal clusters within the porous matrix as well as the properties of the support.

On the other hand, activity and selectivity of catalyst depend on several factors such as; particle size, structure of support material surface area and its acidity and basicity. There are several methods for preparation of supported metal catalyst, for example, micro-emulsion (Xiong *et al.*, 2005 and Cangul *et al.*, 2009) sol-gel (Arvela *et al.*, 2013 and Erkey, 2009), impregnation (Dawidzuik *et al.*, 2009), sonochemical (Angelucci *et al.*, 2007), deposition-precipitation (Durant *et al.*, 2013) and chemical vapor deposition (CVD) (Moshkalyov *et al.*, 2004) methods have been reported. These techniques were used widely in literature, but metal particle size and uniform distribution with these methods still in challenge. Most crucial problem with these techniques is larger particle size and this situation is limited the catalytic performance of the catalyst. Due to these limitations, supercritical fluid deposition (SCFD) (Bozdag *et al.*, 2012; Cabanas *et al.*, 2002, Zhang and Erkey, 2006) technique has been developed as alternative to these techniques. SCFD is a demonstrated technology that provides excellent coverage area for the deposition of metals and metal oxides within narrow size.

1.3. Supercritical Fluids (SCF)

SCF is known as a single homogenous phase that occurs above critical temperature and pressure. Supercritical fluids are sometimes referred to as gas-liquid phase hybrid and employ properties of both phases. The supercritical region can be found above the critical point, which is at the end of the two-phase line between the gas and liquid regions, Figure 1.4.

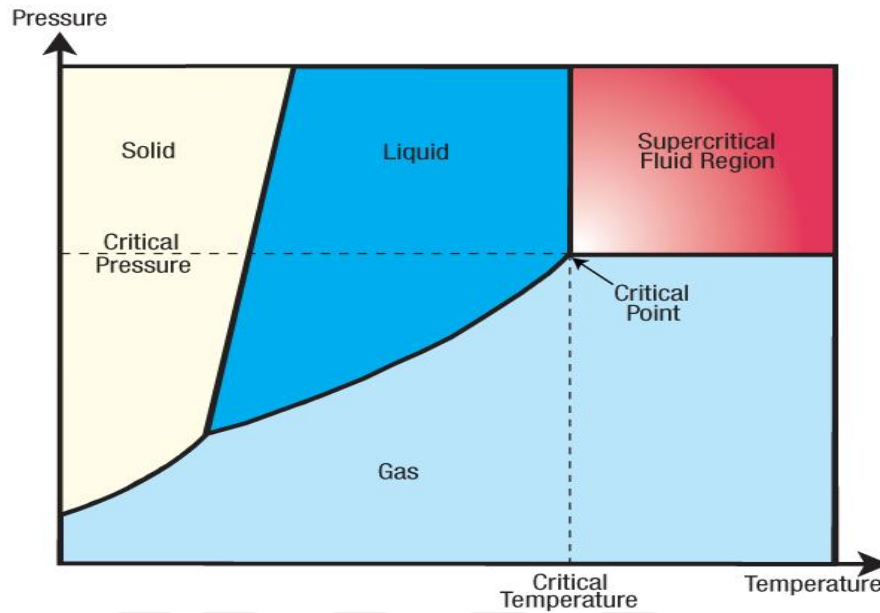


Figure 1.4. Phase diagram of supercritical fluids

The most distinguishing properties for SCF are their enhanced mass transfer properties compared to liquids and its variable density. The density of a SCF is changeable with related temperature and pressure values. The density of SCF is increasing with increasing pressure at constant temperature while decreasing with increasing temperature at constant pressure. The mass transport properties of SCFs shows similarity with conventional gases and add to the desirability of SCF processes, as their gas like diffusivity and viscosity allow for faster penetration into/onto solid support materials. These properties enable to the deposition of compounds into/onto support materials (Teoh *et al.*, 2013).

Supercritical carbon dioxide (scCO₂) is the most used supercritical fluids due to the related properties; low cost, non-flammability, non- toxicity and in particular the mild critical pressure and temperature ($T_C = 31.1\text{ }^{\circ}\text{C}$, $P_C = 7.38\text{ MPa}$) (Mchugh *et al.*, 1986; Saquing *et al.*, 2005; Tenorio *et al.*, 2012; Zhang and Erkey, 2006).

Table 1.2. Critical properties of various solvents (Reid et al., 1987)

Solvent	Critical Temperature (K)	Critical Pressure (Mpa)	Critical Density (g/cm ³)
Carbon dioxide	304.1	7.38	0.469
Water	647.096	22.064	0.322
Methane	190.4	4.60	0.162
Ethane	305.3	4.87	0.203
Ethylene	282.4	5.04	0.215
Methanol	512.6	8.09	0.272
Ethanol	513.9	6.14	0.276
Acetone	508.1	4.70	0.278

Supercritical fluid technologies have grabbed much attention of researchers and industries due to their unique properties (Mchugh *et al.*, 1986). These green technology especially supercritical carbon dioxide have been successfully employed for industrial and scientific approach.

Last two decades Supercritical fluids have been widely used as reaction media for preparation of supported metal nanoparticles.

1.3.1. Supercritical Fluid Deposition Technique (SCFD)

Supercritical fluid deposition (SCFD) is a hybrid process that combines both vapor and liquid phase deposition characteristics in order to reduce organometallic compounds with hydrogen or other reducing agents in the presence of a supercritical fluid (SCF) as the solvent. SCFD uses a supercritical fluid as the solvent and enables a higher solubility. To date, many metals have been deposited from the SCFD process, some of which include: Au, Cu, Co, Ni, Ir, Rh, Ru, Pd, Pt. Supercritical carbon dioxide has been widely used in supercritical fluid deposition process due to the related properties. The choice of supercritical carbon dioxide as a solvent for the SCFD system is the result of many considerations. It has an easily attainable critical point as well as zero surface tension at its critical point and above. It also has a highly tunable density, (Figure 1.5), which allows for much higher precursor

concentrations. This is an enabling feature of SCFD that changes the deposition from a mass transfer limited regime to a reaction rate limited regime. This means that the reaction can proceed at the same speed across the entire surface of the substrate, resulting in nanoparticles growth at relatively fast growth rates.

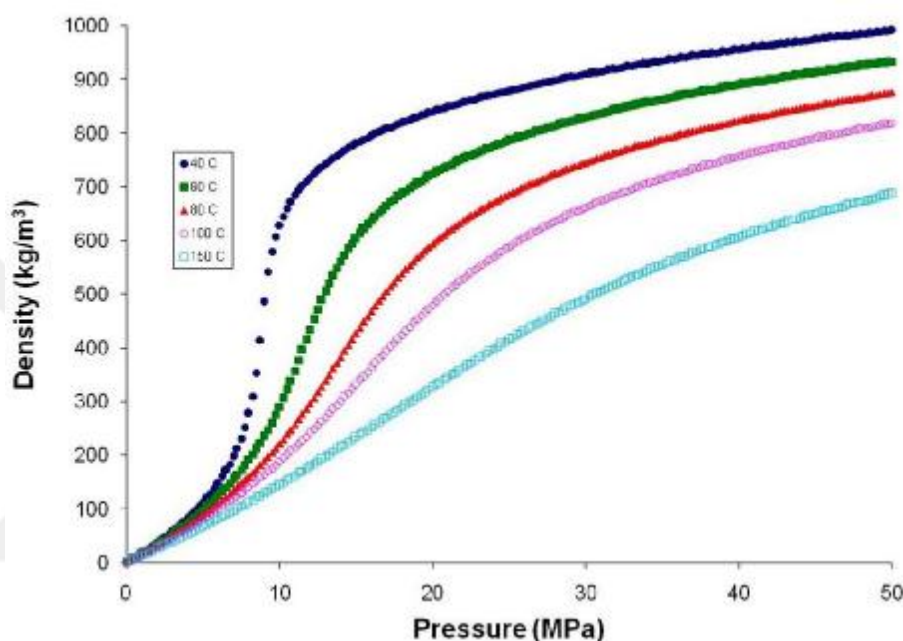


Figure 1.5. Density values of CO₂ with increasing pressure at desired temperatures

SCFD technique occurs in three steps; i) dissolution of precursor (metal complex) in Supercritical fluids (SCF), ii) deposition (adsorption) of precursor onto the support material surface, iii) reduction of metallic precursor to its metallic form by a chemical reduction with reducing agent (hydrogen gas or alcohols) or thermal reduction under inert atmosphere. The most commonly used supercritical fluid (SCF) is carbon dioxide (CO₂) because CO₂ is non-toxic, non-reactive, non-flammable and inexpensive (Morero *et al.*, 2011; Zhang and Erkey, 2006) like most SCFs, supercritical CO₂ (scCO₂) combines both the good solvent properties of a gas and a liquid. The gas-like diffusivity and viscosity of scCO₂ are favorable for rapid diffusion and permeation into porous substrates whereas the liquid-like density allows for the dissolution of a wide range of organometallic precursors. The low surface tension of scCO₂ not only permits better penetration and wetting of pores

than is usually possible with liquid solvents, but also avoids the pore collapse which can occur on certain structures such as organic and silica aerogels with organic liquid solvents. Furthermore, residual CO₂ is negligible in the processed product because of the gaseous character of CO₂ near ambient conditions.

1.4. Support Materials

Investigation of supported metal nanoparticles has grabbed much attention. Silica, alumina, MW-CNT, activated carbon, zeolites, molecular sieves, organic polymers and porous materials have been used as support in SCFD technique. Among them, porous composite materials have received widespread interest because of their potential applications as supports for catalysis, separation, selective adsorption and novel functional materials, due to their extremely high surface areas combined with large and uniform pore sizes (Alothman, 2012).

Porous materials created by nature or by synthetic design have found great utility in all aspects of human activities. Their pore structure is usually formed in the stages of crystallization or by subsequent treatment and consists of isolated or interconnected pores that may have similar or different shapes and sizes. Depending on the predominant pore sizes, the porous materials are classified by IUPAC (Alothman *et al.*, 2012; Zhao *et al.*, 1996) ;

- Microporous materials, pore diameters up to 2.0 nm
- Mesoporous materials, pore size between 2.0 and 50 nm
- Macroporous materials, pore diameters larger than 50 nm

Mesoporous materials based on SBA-15 show excellent thermal, hydrothermal and chemical stabilities and also high surface area (Han *et al.*, 2007; Zhang *et al.*, 2008; Yang *et al.*, 2011, Hunt *et al.*, 2014).

In this thesis, SBA-15 has been choosing as support material due to the outstanding properties that given in above.

1.5. C-C cross coupling reactions

Palladium-catalyzed carbon-carbon bond-forming reactions developed by Heck, Negishi and Suzuki, among others (Figure 1.6) have made a critical impact on synthetic organic chemistry. In this regard, coupling reactions present wide applications in the production of polymers, agrochemicals, pharmaceutical intermediates, and high-tech materials.

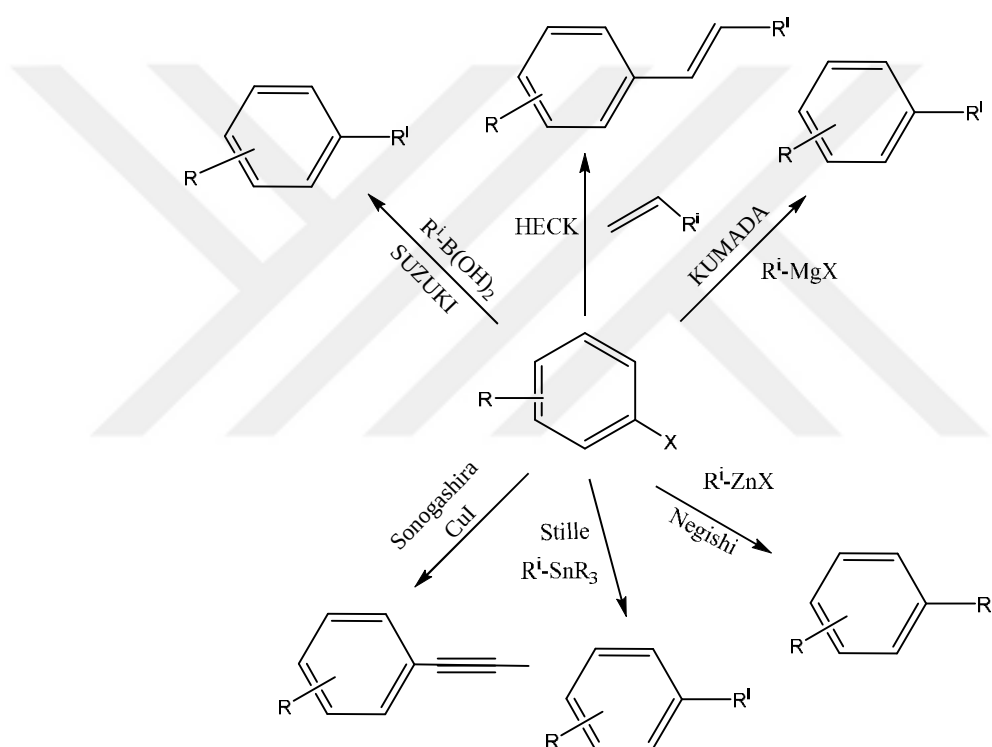


Figure 1.6. Classification of C-C cross coupling reactions

This widespread use is mainly due to the mild conditions associated with these reactions together with their tolerance to a wide variety of functional groups. However, the significance of carbon-carbon coupling reactions for both academic and industrial research is far from settled down. The recent methods for the development of new catalysts have broadened enormously the potential uses of these processes. Thus, if palladium has been considered as one of the most efficient metals in catalysis of carbon-carbon bond formation in the last decades, Pd nanoparticles (PdNPs) have also attracted great interest recently. Their high surface-to-volume

ratio and their highly active surface atoms compared to those of the bulk catalysts establish PdNPs as a promising alternative in the search for milder reaction conditions as well as more environmentally friendly methods. Hence, if coupling reactions have been traditionally catalyzed by PdII/Pd0 complexes in the presence of phosphines or other ligands, the use of PdNPs allows “ligandfree” synthesis, which reduces costs, simplifies workup procedures, and facilitates the separation of the final product. In addition, the use of colloidal-suspended or solid-supported PdNPs also allows the easy recovery of the nanocatalysts, considering their multiple recycling and continuous processing (Lorenzo *et al.* 2012).

Mechanism for the PdNP-Catalyzed Suzuki Cross-Coupling: Homogeneous versus Heterogeneous Catalysis. Understanding the nature of the active sites that drive certain chemical transformations has been an important but often elusive goal in catalytic studies. In recent years, a great body of reviews and original papers has been published related to the homogeneous or heterogeneous nature of the mechanism of PdNP-catalyzed carbon–carbon bond-forming reactions. As a matter of fact, this topic constitutes the key issue in order to comprehend and control the operational properties of Pd nanocatalysts. Among the many synthetic strategies to produce carbon–carbon bonds, Suzuki cross-coupling reactions have been especially investigated given the small loading of metal required by these processes to achieve very high TONs, the so-called “homeopathic” catalysis. However, the nature of the true catalytic species in this reaction has somehow remained controversial. On one hand, a substantial number of reports have been published pointing toward a soluble Pd species-operated catalysis (Figure 1.7) analogous to the one proposed by de Vries for all high-temperature Heck reactions. On the other hand, many authors have claimed a heterogeneous nature for the Suzuki reaction mechanism. In this case, both aryl halide and boronic acid would come into contact by colliding on the nanoparticle surface and not within the solution (figure 1.7) (Lorenzo *et al.* 2012).

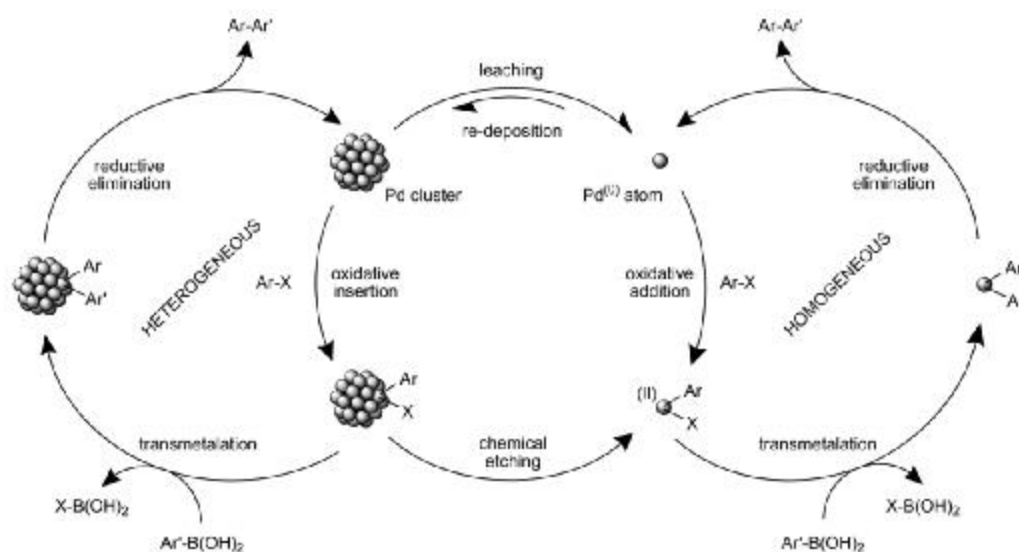


Figure 1.7. Proposed mechanism for the PdNP-catalyzed Suzuki Cross-Coupling involving both homogeneous and heterogeneous pathways

Among C-C cross coupling reactions, Heck and Suzuki couplings are fascinating reactions from a catalysis science perspective. Only few metals (Cu, Pd, Ni, Ag and Fe) can be used in C-C cross coupling reactions. But palladium is the most used metal for this type of reactions due to its versatility. An enormous number of new Pd complexes, organometallic compounds, and supported Pd catalysts for these reactions have been reported in the last decades. There are some reasons why the Pd is the most efficient metal for these reactions;

- Electronegativity
- Atomic radius
- Oxidation state
- Electronic configuration

1.5.1 Suzuki-Miyaura Cross coupling reactions

In 1981, Suzuki and Miyaura developed the Suzuki-Miyaura cross-coupling reaction of organoboron compounds and organic halides or pseudohalides (figure 1.7.) can be considered as one of the most efficient methods for the construction of

aromatic carbon-carbon bonds. It has seen enormous use in the synthesis of pharmaceuticals and specialty chemicals. As a result of its great importance, Suzuki shared the 2010 Nobel Prize with other workers Heck and Negishi.

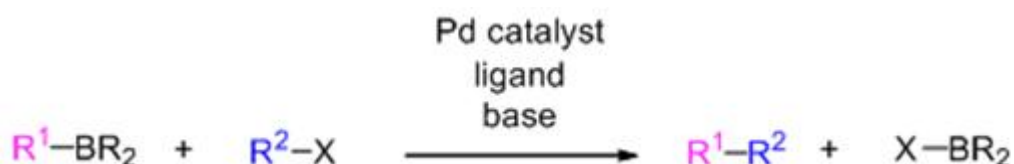


Figure 1.8. Schematic representation of Suzuki-Miyaura cross coupling reaction

In general, the commercial availability of the starting materials, the relatively mild reaction conditions required, the tolerance of a broad range of functionalities and the insignificant effect of steric hindrance, makes the reaction feasible. In addition, the ease of handling and removal of the nontoxic boron-containing by-products, as well as the possibility of using water as a solvent or co-solvent, have widened the scope of this reaction. Because of all these features, it has gained prominence in recent years at an industrial level, mainly in the synthesis of pharmaceuticals and fine chemicals. In academic laboratories, it has been largely applied as the key step in the total synthesis of natural products and polymer synthesis. Various modifications, however, have been recently introduced involving catalysts, substrates, reaction media, reaction conditions, synthetic techniques, etc. in order to develop environmentally friendly and more efficient Suzuki cross-coupling reactions. One current limitation in the scope of the Suzuki reaction is the lower activity of aryl chlorides.

1.5.1.1 Suzuki –Miyaura Mechanism

The commonly accepted mechanism of the Suzuki-Miyaura coupling reaction involves an initial oxidative addition of the aryl halide to active palladium (0) species followed by transfer of the aryl group from the boronic acid to the Pd(II) centre (transmetallation). Base is required to generate quarternized boron species in order to enhance the nucleophilicity of aryl group on boron; a pre-requirement for

transmetallation step and the last step is reductive elimination (Alonso, 2008).

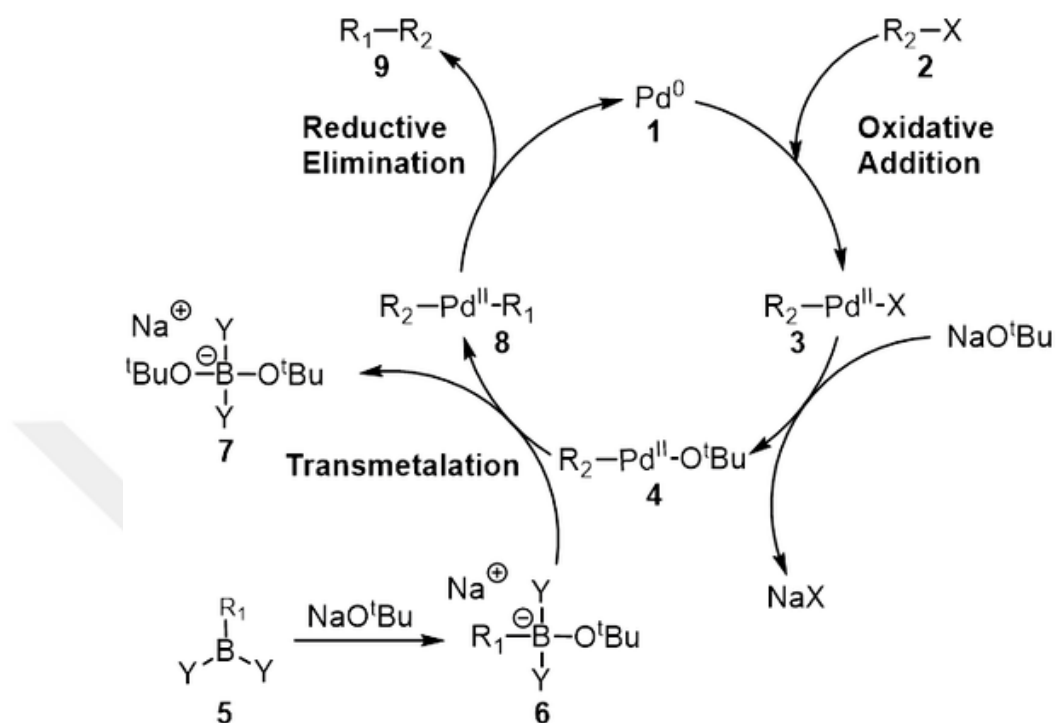


Figure 1.9. Reaction mechanism of Suzuki- Miyaura reaction.

2. PRELIMINARY WORK

2.1. Schiff Base

Schiff base derivative ligand and its metal complexes have much attention in scientific researches as catalyst. Schiff base derivatives have used extensively in many area of catalyst. But, there is no more application in supercritical fluid deposition technique.

- ▼ Hong *et al.* (2005), reported a highly active *in situ* catalytic system for the Suzuki-Miyaura reaction based on an N,O-bidentate Schiff base ligand, 2-[1-(2,4,6-trimethyl-phenylimino)-ethyl]-phenol (L22) and [Pd(OAc)₂]. A wide array of electronically different aryl bromides can be coupled efficiently with arylboronic acids at room temperature with a Pd loading of 1 mol%. A deprotonated chelated Pd acetate complex, [Pd(L22)(OAc)(solv)], was proposed as precursor of the catalytically active species.
- ▼ Sarkar and Srimani (2008), reported a series of N,O-bidentate Schiff base ligands derived from substituted benzaldehydes and explored their catalytic potential for use in Suzuki-Miyaura reactions. The reaction between *p*-bromoanisole and phenylboronic acid was selected as a model reaction for screening the performances of ligands. The highest yield of the coupling product (92%) was obtained with the ligand L25, which was derived from *o*-anisaldehyde and α -methylbenzylamine. Increasing the steric bulkiness using an *o*-OPr group (L26) instead of an *o*-OMe group could not improve the yield. The yields were also low or moderate when Schiff bases were derived from cyclohexylamine (L28) or *tert*-butylamine (L29). Using L25 as the ligand, various aryl bromides, benzyl bromides, and even heteroaryl bromides can be conveniently coupled with arylboronic acids; however, this catalytic system is inactive with aryl chlorides.
- ▼ Cui *et al.* (2010), reported the synthesis of some new amino-salicyldiimine Pd(II) complexes bearing 5-methyl-3-(*R*-1-ylmethyl)-salicylaldimine ligands (*R*

= morpholine, piperidine, pyrrolidine, 4- methylpiperazin, or diisopropylamine), which are highly effective as catalysts for Suzuki-Miyaura reactions with aryl chlorides in DMF under air. During the initial screening of the catalysts and optimization studies, the coupling reaction between *p*-chlorobenzaldehyde and phenylboronic acid was taken as the model reaction. C9 and C12 were found to be very efficient complexes. Thus, using complex C12 as the catalyst and under optimized conditions (K₂CO₃, DMF, 110 °C), many electronically and structurally different aryl chlorides can be activated with good to excellent yields. However, sterically hindered *ortho*-substituted substrates such as *o*-dichlorobenzene or *o*-chlorotoluene give very poor yields.

- ▼ Tajuddin *et al.* (2012), reported the synthesis of schiff base derivatives ligands from condensation of *o*-vanilin and 4-methyl or 4-fluoro benzylamine and their palladium (II) complexes. They were investigated the catalytic performance of their catalyst over heck reaction between iodobenzene and methyl acrylate and observed 100% conversion after 6 hours.
- ▼ Shahnaz *et al.* (2013), have been reported highly efficient palladium complex derived from bidentate Schiff base ligand for Suzuki-Miyaura Reaction. They noted that, similarly with phosphine derivatives excellent yield were obtained with less reactive aryl chlorides at a relatively low catalyst loading (0.2%).
- ▼ Keles et al., were investigated the catalytic application of Pd(II) Schiff base complexes as catalyst in Suzuki-Miyaura and Heck ceoss-coupling reactions. For determination of optimum conditions both Suzuki-Miyaura and Heck reactions, they were tested the effect of different bases and solvents on product yield. Under optimized conditions, they obtained good yields with *para*-substituted aryl bromides with electron-withdrawing groups. On the other hand, they were investigated the effect of ligands with methy, methoxy and trifluoromethyl groups on catalytic activity and they were observed that different groups no influence on catalytic performance of catalyst.

2.2. Supercritical Fluids

2.2.1 Solubility in ScCO₂

For preparing supported metal nanoparticles via SCFD technique, ScCO₂-soluble metal complexes have been used which are called precursor. Within this scope, acetylacetonate, β -diketonate, cyclooctadiene, etc. Derivatives ligands have been used. The main factor that limited the usability of ligand for this purpose is the solubility behaviour in scCO₂. There is no work about the solubility of schiff base derivatives ligand metal complexes in scCO₂.

- ▼ Aschenbrenner *et al.*, (2007), were investigated the wide variety of metal complexes including acetylacetonate, β -diketonate, cyclooctadiene, etc. They were investigated, the effect of ligand type, ligand charge, metal and its oxidation step on the solubility behaviour in scCO₂.
- ▼ Cabanas *et al.*, (2012a), were investigated the solubility behaviour of hexafluoroacetylacetonate palladium (II) and Ni(II) complexes in scCO₂. They found that the solubility for palladium complex is 3.15×10^{-3} (mol fraction) at 313.2 K ve 8.9 Mpa, while nickel complex solubility is between 2.95×10^{-5} - 2.02×10^{-4} mol fraction at between 313-333 K.

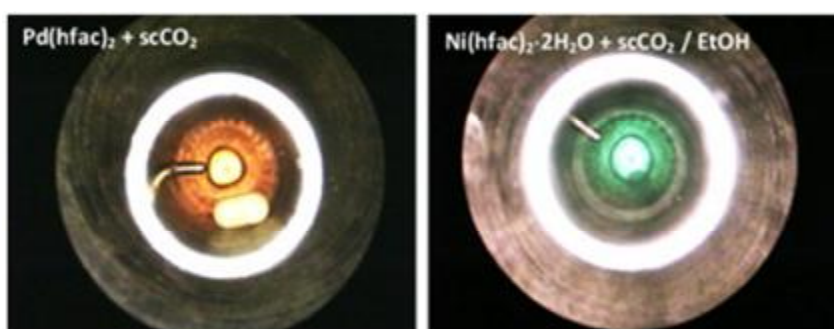


Figure 2.1. Solubility Behaviour of Pd(Hfac)₂ and Ni(hfac)₂ in scCO₂

- ▼ Cabanas *et al.*, (2012b), was investigated the solubility of ruthenium(III)acetylacetonate [Ru(acac)₃] and bis-(2,2,6,6-tetramethyl-3,5-

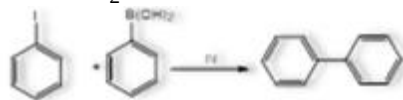
heptanedionato)(1,5-cyclooctadiene) ruthenium(II) $[\text{Ru}(\text{tmhd})_2(\text{COD})]$ complexes a range of 313 K - 353 K and up to 20 MPa. They found that, solubility of $\text{Ru}(\text{tmhd})_2(\text{COD})$ is 5 times higher than those $\text{Ru}(\text{acac})_3$

2.2.2 Supercritical Fluid Deposition Technique (SCFD)

In literature, there are many of publications about silica as support material. Nowadays, SCFD is developing technique for preparing metallic nanoparticles on silica surface. Due to lack of optimization experiments about this technique, more publications is needed with different kind of precursors.

- V** Saffarzadeh *et al.*, (2006), were prepared polydimethylsiloxane derivatives palladium complexes and used as precursor for preparing silica supported palladium nanoparticles. Then, they investigated catalytic efficiency of obtained palladium nanoparticles over C-C cross coupling reactions such as; Suzuki and Heck reactions. Within this scope, different organic solvents and scCO_2 used as reaction media. They compared the catalytic recycling of organic solvents with scCO_2 . There is no decrease in catalytic activity efficiency in scCO_2 while significant decrease (96-65 %) was occurred in toluene. This results is promising result for using scCO_2 as reaction media.

Table 2.1. Suzuki reaction conditions and % conversion of SBA-15 supported Pd nanoparticles in scCO_2 and toluene.



Reaction conditions	Conversion %
Toluen 75 °C, 3hrs	1-96
	2-65
scCO ₂ 75 °C, 100 bar, 18 hrs	1-96
	2-93
	3-93
	4-91

- ▼ Zhang and Erkey, (2006) were investigated the solubility behaviour of fluorinated organometallic precursors in scCO₂ and the effect of thermal stability on the deposition process. In this way, carbon black, silica and alumina were used as support material. According to their results, impregnation of precursor on support surface increasing with increasing solubility behaviour, but lower thermal stability of precursor may cause agglomeration.
- ▼ Erkey, (2009), was reported a review about a deposition process on different kind of support materials for preparing metallic nanoparticles. Within this context, silica, carbon aerogel, carbon nanotube, alumina and etc. Support materials and the effect of wide variety of metals including Pd, Pt, Cu, Ag, Rh and Ni on deposition process have been also reported. According to his review, he said that, the researches about SCFD is insufficient to explanation of SCFD technique. On the other hand, controlling particle size, distribution and morphology is more difficult, to overcome this problem more experiments are required.
- ▼ Morero *et al.*, (2011) were investigated the deposition process Pd(hfac)₂. For this purpose, they were impregnated Pd(hfac)₂ precursor on SBA-15 surface at a temperature of 40 °C and a pressure of 85 bar in scCO₂. Then, reduced the metallic palladium by using different technique; (i) reduction by H₂(g) in H₂/CO₂ mixture, (ii) depressurization and reduction at 40 °C 60 bar. They used TEM, SEM, XRD and ICP-OES to determine the surface morphology of support. According to results they indicated that better results obtained when the reduction realized under pure H₂(g).

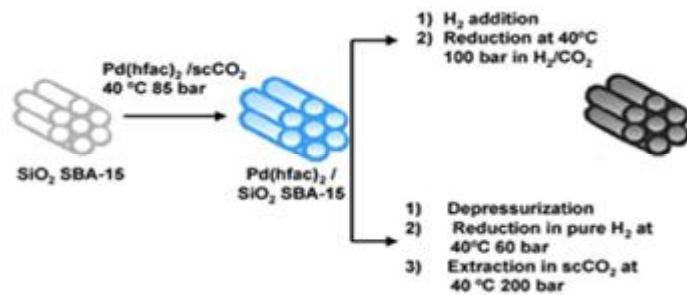


Figure 2.2. Schematic representation for preparation of SBA-15 supported Pd nanoparticles in scCO₂

- ▼ Hunt *et al.*, (2014) were used scCO_2 as reaction media to prepared palladium nanoparticles in SBA-15. XPS and TEM were used characterized obtained palladium nanoparticles. On the other hand, they compared scCO_2 media with organic solvents. As shown in figure 2.3. average particles size in TEM image that obtained from scCO_2 solution are smaller than those obtained from organic solvent.

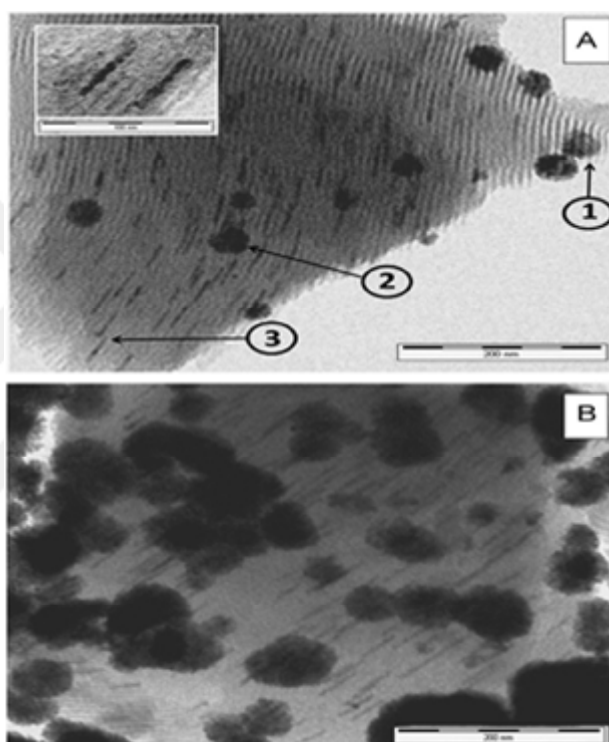


Figure 2.3. (a) Sc-Pd at 100 nm and 200 nm resolution, (b) Ac-Pd at 200 nm resolution.

2.3. Suzuki-Miyaura Reaction with supported heterogeneous catalyst

- ▼ Jana *et al.*, (2009), developed an efficient palladium(0) immobilized MCM-41 catalytic system for C–C cross-coupling reaction. They obtained excellent yields with aryl halides including less reactive chlorobenzene. On the other hand, there is no deficiency on catalytic activity after 4 run.

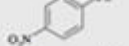
Entry	Aryl halide	Product	Time (h)	Conversion ^a (wt %)	Yield ^b (wt %)
1			20	100	93
2			12	100	90
3			24	24	24
4			12	97	97
5			20	97	97
6			24	65	64

Figure 2.4. Pd/MCM-41 catalyzed Suzuki reaction of aryl halides

Vaghei *et al.*, (2014), described the synthesis of a novel SBA-15/AO/Pd(II) nanocatalyst by grafting of amidoxime on SBA-15 and subsequent deposition of palladium chlorides. The materials were characterized via XRD, SEM, TEM, EDX and ICP. The obtained material was used as heterogeneous catalyst for Suzuki coupling reaction of aryl halides (I, Br, Cl) with phenylboronic acid to provide the corresponding products. They were obtained excellent yields with low palladium loading (0.2 mol %). They were tested the recyclability of their catalyst and they observed that about 20% of catalytic activity was lost after six cycles of reaction.

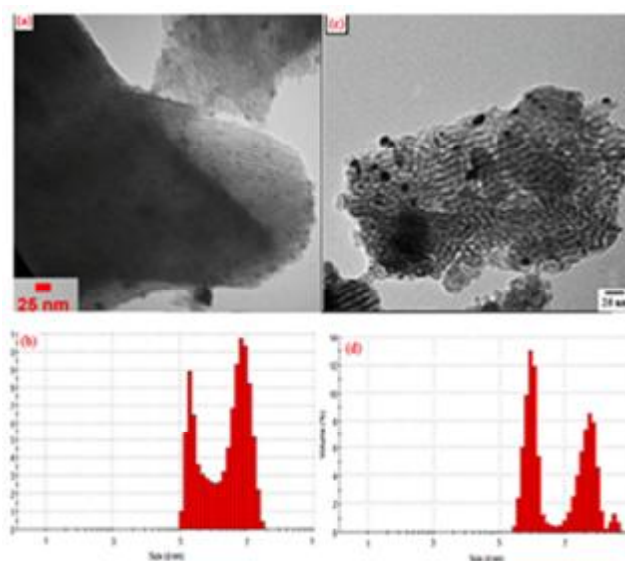


Fig. 2.5. TEM images and histogram showing the size distribution for (a and b) fresh SBA-15/AO/Pd(0), and for (c and d) reused 6 cycles SBA-15/AO/Pd(0)

- ▼ Ncube *et al.*, (2015) were prepared palladium nanoparticles using the dendrimer-template method and then immobilized on SBA-15. The obtained SBA-15 supported palladium nanoparticles characterized by SEM-EDX and TEM analyses. According to SEM images, the morphology of support consist rod-shaped particles. and the presence of metallic palladium confirmed by EDX analysis. as shown in figure 2.5

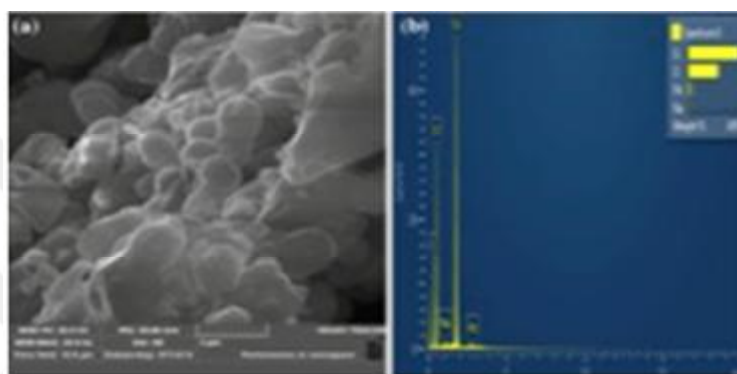


Figure 2.6. (a) SEM micrograph of Pd⁰/SBA-15 catalyst and (b) EDX spectrum showing elemental composition of the catalyst

On the other hand, they investigated the catalytic activity of their heterogenous catalyst over Suzuki- Miyaura reactions. During catalytic activity experiments, they investigated the influence of base, solvent, temperature and % metal loading on catalytic activity. They were also tested the recyclability of their catalyst and they observed that catalytic activity did not change after 4 cycles.

- ▼ Begum *et al.* (2015), recently reported highly effective and robust silica-supported Pd-Schiff base catalyst that exhibits excellent activity in Suzuki-Miyaura reactions with aryl bromides and arylboronic acids. It is interesting that the catalytic reactions proceed well in protic and aprotic solvents, but there are significant variations in the yields obtained. The reaction also depends on the nature of the base. Using PrOH:H₂O (1:1) as the solvent and Na₂CO₃ as the base, a wide range of substrates can be conveniently converted into their corresponding biphenyls under mild conditions. The catalyst is highly recyclable and the mercury-poisoning test confirmed the heterogeneous nature.

3. MATERIAL AND METHOD

3. 1. Material

All chemicals were purchased from Sigma-Aldrich were used without any purification. All solvents were analytical grade and were used as received from Merck. All reactions were carried out in air, without any special precautions. Column chromatography was performed over silica gel (mesh 60-120) and hexane/ethyl acetate combination was used as the eluent. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature in $\text{CDCl}_3/\text{DMSO-D}_6$. The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively on Bruker Avance 400 MHz instrument. Elemental analysis of the products was performed by using Thermo Scientific Flash 2000 elemental analyzer. FT-IR analysis was performed via Perkin Elmer Spectrum RX I FT-IR System. DSC/TGA analysis was performed with Perkin Elmer Simultaneous Thermal Analyzer STA 6000, Single Crystal X-Ray analysis was performed via Bruker/D8 Quest.

3.1.1. Chemicals

- 2-hydroxy-4-methylbenzaldehyde (4-methylsalicylaldehyde)
- 2-hydroxy-5-methylbenzaldehyde (5-methylsalicylaldehyde)
- 2-fluoro-3-(trifluoromethyl)aniline
- 2-fluoro-4-(trifluoromethyl)aniline
- 2-fluoro-5-(trifluoromethyl)aniline
- Palladium acetate
- SBA-15(Santa Barbara Amorphous-15)
- Hydrochloric Acid
- Ethanol
- Methanol
- Acetonitrile
- Tetrahydrofuran

- Toluen
- 1,4 dioxane
- H₂O
- Dichloromethane
- Hexane
- Chloroform
- Phenylboronic acid
- Bromobenzene
- 4-bromotoluene
- 2-bromo-6-methoxynapthalene
- 1-bromonaphtahalene
- 1-bromo-4-nitrobenzene
- 4-bromoaniline
- 4-bromobenzaldeheyde
- 4-bromoacetophenone
- 2-bromoanisol
- 2-bromoprydine
- 4-bromoanisoile
- 1-bromo-2-nitrobenzene
- 2-bromoacetophenone

3.1.2 Instruments

The following instruments and lab equipment were used for this thesis.

- Magnetic Stirrer with Contact Thermometer : IKA
- Amar Brand High Pressure Reactor Equipped with Mechanic Stirrer (100 ml, Max. Pressure 5000 Psi)
- Parr Brand High Pressure View Cell (50 Ml, Max. Pressure 3500 Psi)
- Syringe Type High Pressure Pump: ISCO, 266.4 ml
- Elemental Analysis: Thermo Scientific Flash 2000 (CHNS Analyses)
- FT-IR: Perkin Elmer Spectrum RX I FT-IR System

- Melting Point Measurement Device: Gallenkamp
- ^1H NMR(400 Mhz) And ^{13}C NMR(100.6 Mhz) : Bruker Avance 400 Mhz
- DSC/TGA: Perkin Elmer Simultaneous Thermal Analyzer STA 6000
- Single Crystal X-Ray Spectroscopy: Bruker/D8 Quest
- UV-Visible: Thermo Scientific Genesis 10S UV-Vis
- XRD: Rigaku Miniflex $\text{CuK}\alpha$, $\lambda=0.154\text{nm}$
- ICP-OES: Perkin Elmer 2100 DV
- FE-SEM with EDX: ZEISS Supra 55 VP
- TEM: Jeol JEM 1400 Plus 120kV
- GC: Agilent 6850 Series With FID Detector

3.2. Method

3.2.1. Synthesis of Schiff Base Ligands

3.2.1.1. Synthesis of (E)-2-(((2-fluoro-3-(trifluoromethyl)phenyl)imino) methyl)-5-methylphenol (FSB-1):

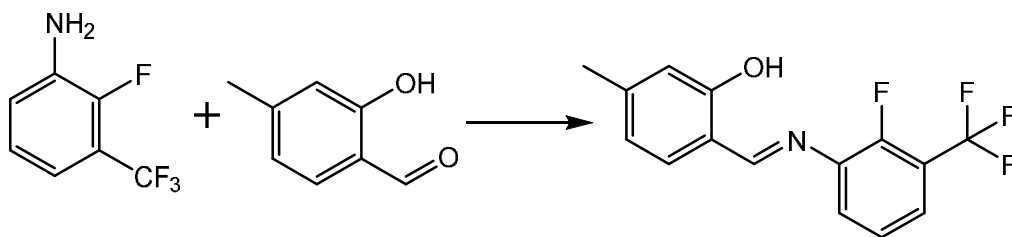


Figure 3.1. Schematic representation for synthesis of FSB-1 ligand

5 mmol 4-methylsalicylaldehyde (0.68 g) was dissolved in methanol (15 ml), then a methanolic solution of 5 mmol 2-fluoro-3-(trifluoromethyl)aniline (0.895 g, 0.64 ml) was added to the mixture and stirred continuously by refluxed for 2 hours. The reaction mixture was checked by TLC and allowed to cool room temperature. Upon cooling, yellow solid product was occurred. The product was filtered, washed with ice-cold methanol and n-hexane, and finally dried under vacuum. Further purification was conducted via re-crystallization from DCM/

hexane (1:5) mixture, to obtain yellow crystalline. Finally, the product yield was 1.25 g (83%) and the m.p. value was 128.2 °C, Elemental Anal. Calc. for $C_{15}H_{11}F_4NO$: C, 60.61; H, 3.73; N, 4.71. Found: C, 61.62; H, 3.67; N, 3.85 %. FT-IR (KBr, cm^{-1}): $\nu(O-H)$ 3444 cm^{-1} ; $\nu(C-H_{aromatic})$ 3100 cm^{-1} ; $\nu(C-H_{aliphatic})$ 2870 cm^{-1} ; $\nu(C=N)$ 1626 cm^{-1} ; $\nu(C=C_{aromatic})$ 1480 cm^{-1} , $\nu(C-O_{phenolic})$ 1333 cm^{-1} ; $\nu(C-F)$ 1240, 1170 cm^{-1} . ^1H NMR(300 MHz, $CDCl_3-d_6$): δ = 2.38 (s, 3H, CH_3), 6.77-7.50 (m, 6H, Ar-H), 8.65 (s, 1H, $HC=N$), 12.69 (s, 1H, OH) ppm. ^{13}C NMR (76 MHz, $CDCl_3-d_6$): δ = 22.00 (CH_3), 116.62-138 (Ar-C), 125.23 ($C-F_{CF_3}$), 145.99 (C-F), 161.39 (HO-C(Ar)), 166.03 ($HC=N$), ppm.

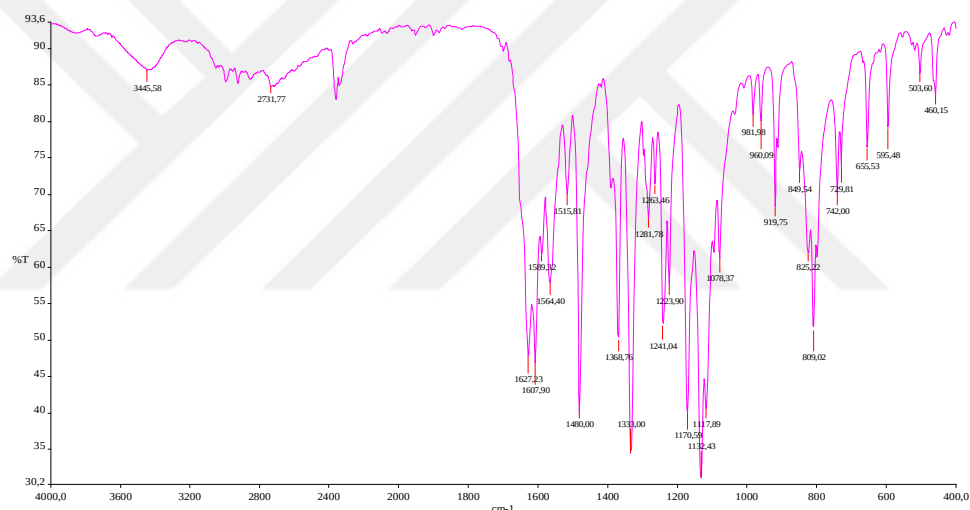


Figure 3.2. FT-IR spectrum of FSB-1

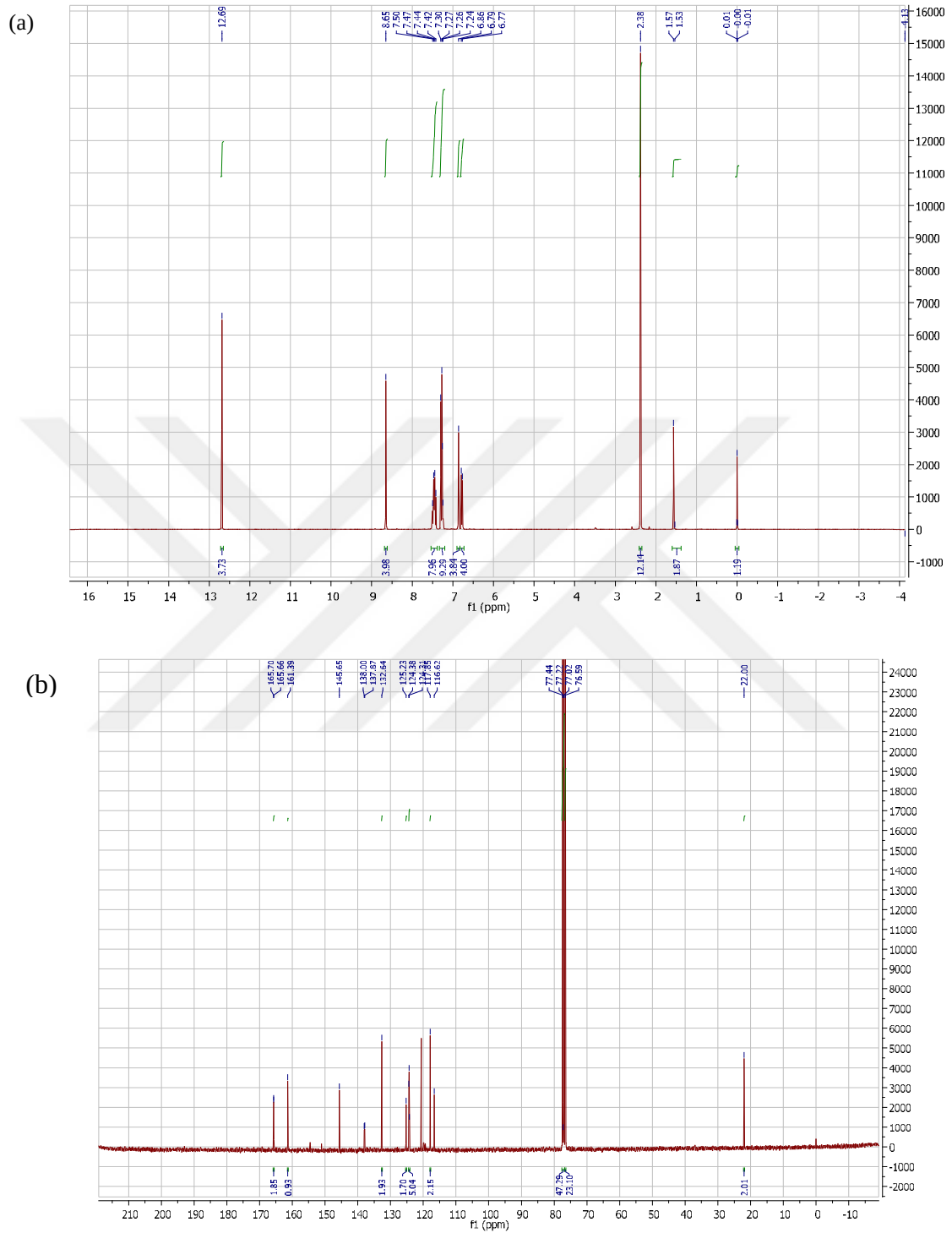


Figure 3.3. (a) ^1H NMR and (b) ^{13}C NMR spectra of FSB-1



Figure 3.4. Ortep diagram of FSB-1

Table 3.1. Single X-Ray crystal data for FSB-1

Crystal data	
Chemical formula	$C_{15}H_{11}F_4NO$
M_r	297.25
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	296
a, b, c (Å)	4.7831 (5), 12.5673 (14), 22.266 (3)
V (Å ³)	1338.4 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.13
Crystal size (mm)	0.21 × 0.15 × 0.13
Data collection	
Diffractometer	Bruker APEX-II CCD
Absorption correction	Multi-scan Bruker
T_{min}, T_{max}	0.691, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	24381, 3287, 2173
R_{int}	0.064
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.666
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.046, 0.106, 1.03
No. of reflections	3287
No. of parameters	193
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.14, -0.18
Absolute structure	Refined as an inversion twin.
Absolute structure parameter	0.3 (1)

Table 3.2. Selected bond angles and lengths for FSB-1

Bond Length	Bond Angle
N1—C9 : 1.405	C6—O1—H1 : 109.5
C9—C10 : 1.385	C10—C9—N1 : 117.0
O1—H1 : 0.8200	F1—C10—C9 : 118.1
C13—C14 : 1.370	

3.2.1.2. Synthesis of (E)-2-(((2-fluoro-3-(trifluoromethyl)phenyl)imino) methyl)-4-methyl phenol (FSB-2):

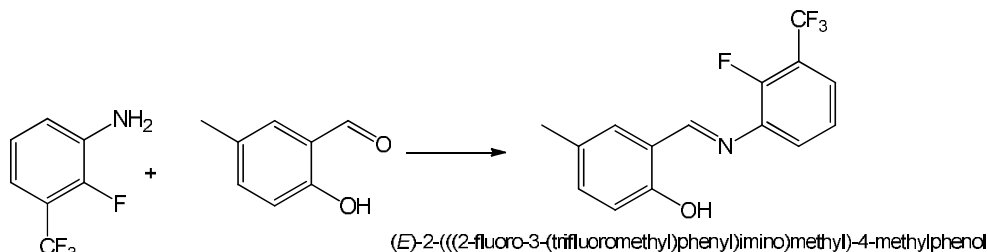


Figure 3.5. Schematic representation for synthesis of FSB-2 ligand

5 mmol 5-methylsalicylaldehyde (0.68 g) was dissolved in methanol (15 ml), a methanolic solution of 5 mmol 2-fluoro-3-(trifluoromethyl)aniline (0.895 g, 0.64 ml) was added and the mixture was stirred continuously and refluxed for 2 hours. Then, the reaction mixture was checked by TLC and allowed to cool room temperature. Upon cooling yellow solid product was occurred. The product was filtered, washed with ice-cold methanol and N-hexane, and finally dried under vacuum. Further purification was conducted via re-crystallization from DCM/Hexane (1:5) mixture. Finally, orange product was obtained with a yield of 1.17 g (78%) and the m.p. value was 109.9 °C, Elemental Anal. Calc. for $C_{15}H_{11}F_4NO$: C, 60.61; H, 3.73; N, 4.71. Found: C, 64.28; H, 3.79; N, 3.93 %. FT-IR (KBr, cm^{-1}): $\nu(O-H)$ 3422 cm^{-1} ; $\nu(C-H_{aromatic})$ 3080 cm^{-1} ; $\nu(C-H_{aliphatic})$ 2921 cm^{-1} ; $\nu(C=N)$ 1630.20 cm^{-1} ; $\nu(C=C_{aromatic})$ 1496.35 cm^{-1} , $\nu(C-O_{phenolic})$ 1320 cm^{-1} ; $\nu(C-F)$ 1231, 1171.08 cm^{-1} . ^1H NMR(400 MHz, $DMSO-d_6$) : δ = 2.29 (s, 3H, CH_3), 6.90-7.88 (m, 6H, Ar-H), 9.01 (s, 1H, $HC=N$), 12.23 (s, 1H, OH) ppm. ^{13}C NMR (100.6 MHz, $DMSO-d_6$) : δ = 19.84 (CH_3), 116.67-137.94 (Ar-C), 125.70 ($C-F_{CF_3}$), 150.86 (C-F), 158.21 ($HO-C(Ar)$), 166.03 ($HC=N$), ppm.

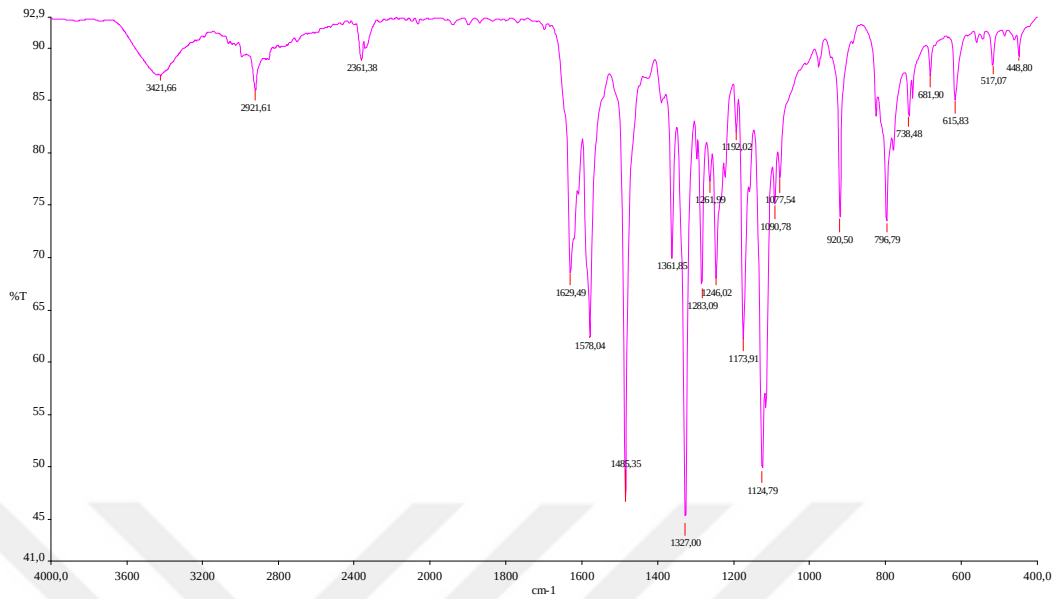
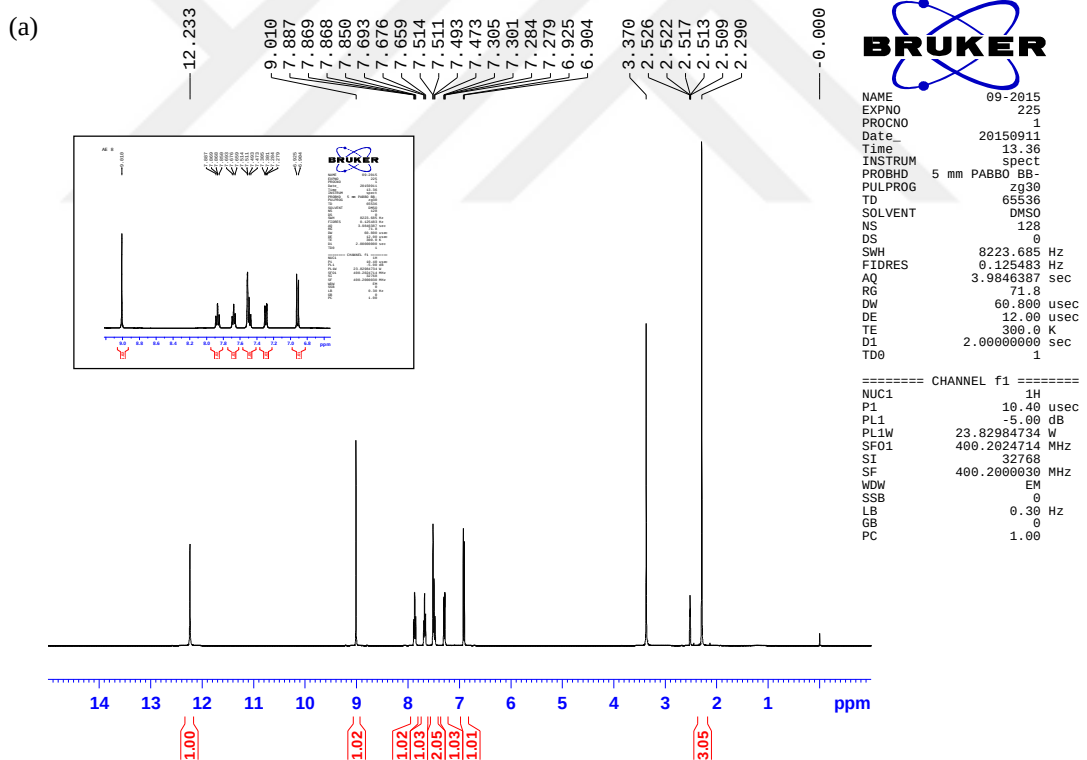
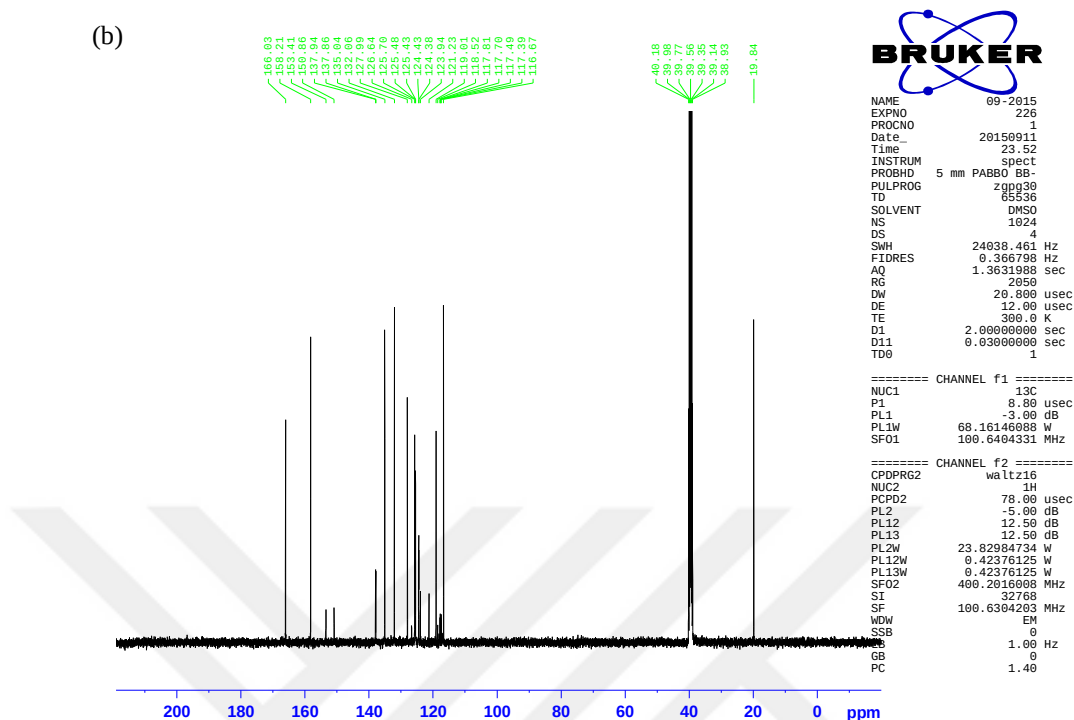


Figure 3.6. FT-IR spectrum of FSB-2



Figure 3.7. (a) ^1H NMR and (b) ^{13}C NMR spectra of FSB-2

3.2.1.3. Synthesis of (E)-2-(((2-fluoro-4-(trifluoromethyl)phenyl)imino) methyl)-5-methylphenol (FSB-3) Sentezi:

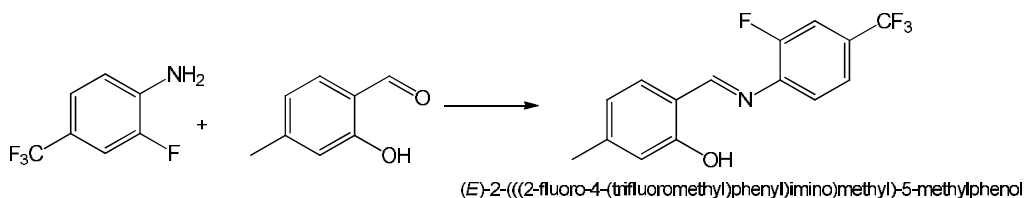


Figure 3.8. Schematic representation for synthesis of FSB-3 ligand

5 mmol 4-methylsalicylaldehyde (0.68 g) was dissolved in methanol (15 ml), a methanolic solution of 5 mmol 2-fluoro-4-(trifluoromethyl)aniline (0.895 g, 0.64 ml) was added and the mixture was stirred continuously and refluxed for 2 hours. Then, the reaction mixture was checked by TLC and allowed to cool room temperature. Upon cooling yellow solid product was occurred. The product was filtered, washed with ice-cold methanol and N-hexane, and finally dried under vacuum. Further purification was conducted via re-crystallization from DCM/Hexane (1:5) mixture. Finally, yellowish product was obtained with a yield of 1.065 g (71%) and the m.p. value was 147.1 °C, Elemental Anal. Calc. for $\text{C}_{15}\text{H}_{11}\text{F}_4\text{NO}$: C,

60.61; H, 3.73; N, 4.71. Found: C, 63.88; H, 3.92; N, 3.87 %. FT-IR (KBr, cm^{-1}): $\nu(\text{O-H})$ 3416.69 cm^{-1} ; $\nu(\text{C-H}_{\text{aromatic}})$ 3090 cm^{-1} ; $\nu(\text{C-H}_{\text{aliphatic}})$ 2924 cm^{-1} ; $\nu(\text{C=N})$ 1614.32 cm^{-1} ; $\nu(\text{C=C}_{\text{aromatic}})$ 1496.35 cm^{-1} , $\nu(\text{C-O}_{\text{phenolic}})$ 1332.82 cm^{-1} ; $\nu(\text{C-F})$ 1275, 1171.55 cm^{-1} . $^1\text{H NMR}$ (400 MHz, DMSO-d_6) : δ = 2.34 (s, 3H, CH_3), 6.83-7.82 (m, 6H, Ar-H), 9.02 (s, 1H, HC=N), 12.54 (s, 1H, OH) ppm. $^{13}\text{C NMR}$ (100.6 MHz, DMSO-d_6) : δ = 21.46 (CH_3), 113-140 (Ar-C), 132.06 (CF_3), 153.58 (C-F), 160.50 (HO-C(Ar)), 166.27 (HC=N), ppm.

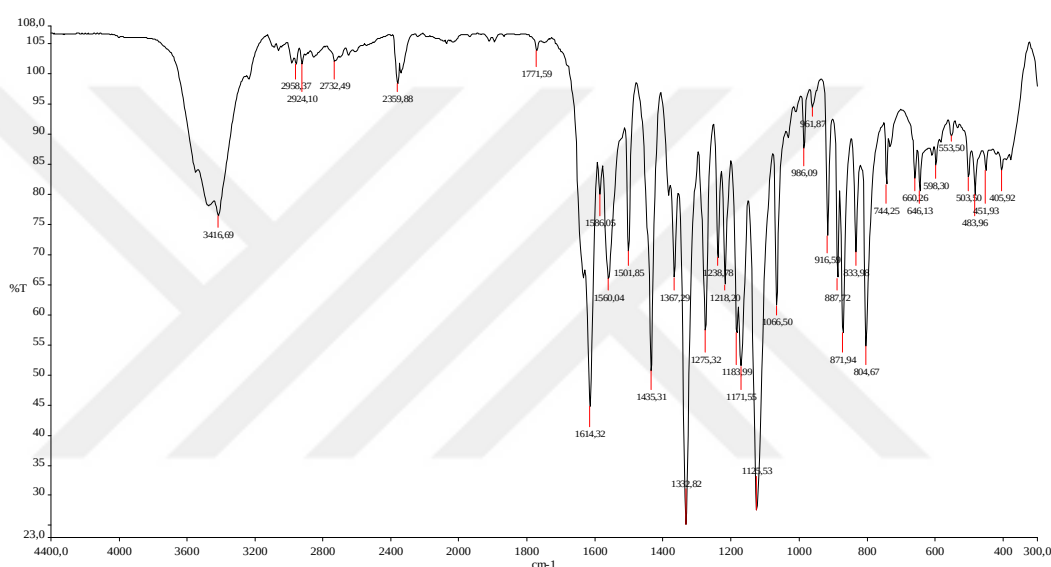
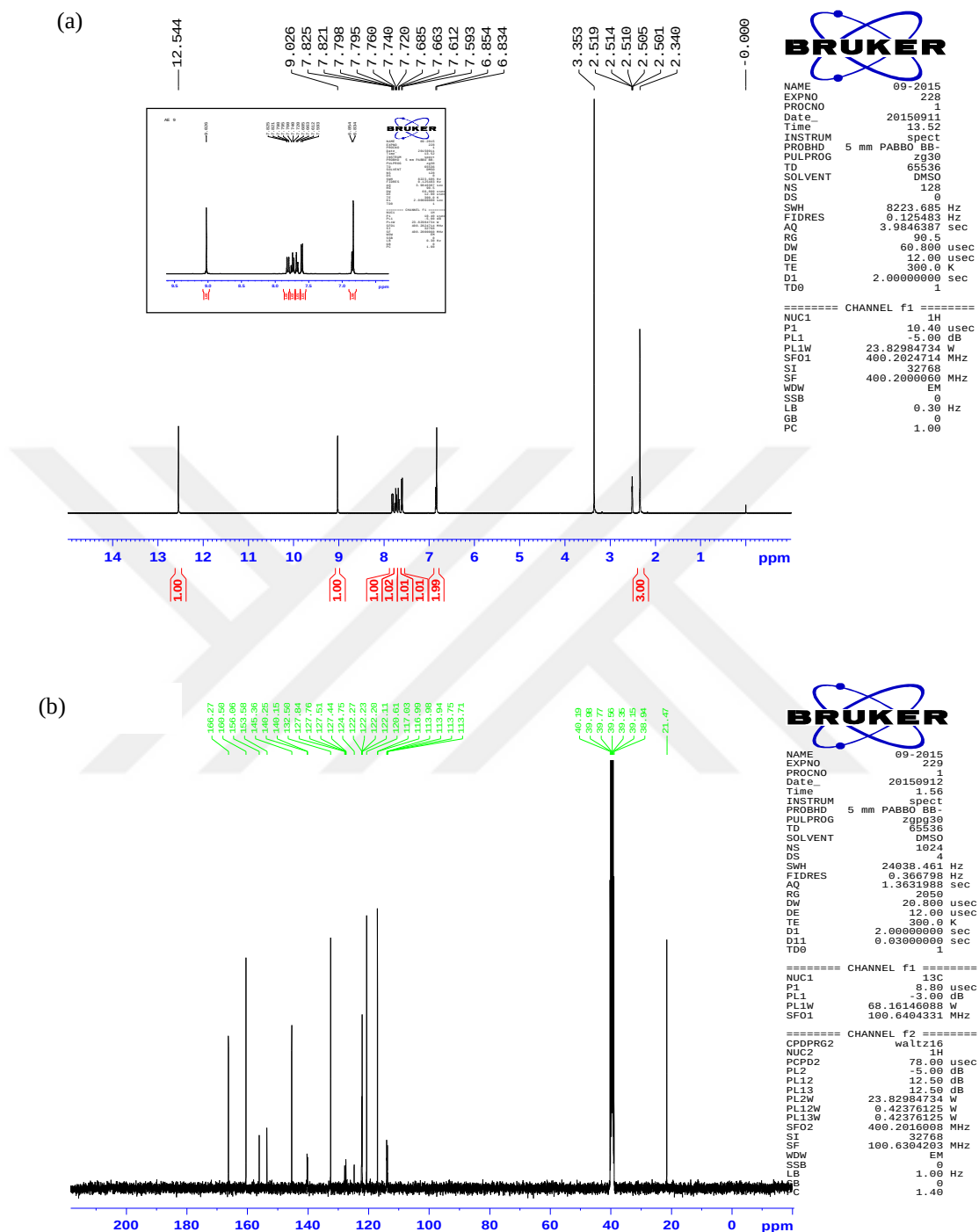


Figure 3.9. FT-IR spectrum of FSB-3

Figure 3.10. (a) ^1H NMR and (b) ^{13}C NMR spectra of FSB-3

3.2.1.4. Synthesis of (E)-2-(((2-fluoro-4-(trifluoromethyl)phenyl)imino) methyl)-4-methylphenol (FSB-4):

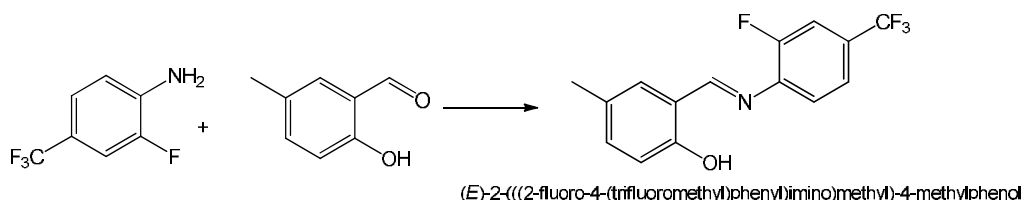


Figure 3.11. Schematic representation for synthesis of FSB-4 ligand

5 mmol 5-methylsalicylaldehyde (0.68 g) was dissolved in methanol (15 ml), a methanolic solution of 5 mmol 2-fluoro-4-(trifluoromethyl)aniline (0.895 g, 0.64 ml) was added and the mixture was stirred continuously and refluxed for 2 hours. Then, the reaction mixture was checked by TLC and allowed to cool room temperature. Upon cooling yellow solid product was occurred. The product was filtered, washed with ice-cold methanol and N-hexane, and finally dried under vacuum. Further purification was conducted via re-crystallization from DCM/Hexane (1:5) mixture. Finally, light orange product was obtained with a yield of 1.035 g (69%) and the m.p. value was 116.12 °C, Elemental Anal. Calc. for $C_{15}H_{11}F_4NO$: C, 60.61; H, 3.73; N, 4.71. Found: C, 61.81; H, 3.65; N, 3.65 %. FT-IR (KBr, cm^{-1}): $\nu(O-H)$ 3419.20 cm^{-1} ; $\nu(C-H_{aromatic})$ 3060 cm^{-1} ; $\nu(C-H_{aliphatic})$ 2927 cm^{-1} ; $\nu(C=N)$ 1617.08 cm^{-1} ; $\nu(C=C_{aromatic})$ 1487.52 cm^{-1} , $\nu(C-O_{phenolic})$ 1332.30 cm^{-1} ; $\nu(C-F)$ 1280.87, 1192.41 cm^{-1} . ^1H NMR(400 MHz, DMSO- d_6) : δ = 2.28 (s, 3H, CH_3), 6.90-7.81 (m, 6H, Ar-H), 8.99 (s, 1H, $HC=N$), 12.18 (s, 1H, OH) ppm. ^{13}C NMR (100.6 MHz, DMSO- d_6) : δ = 19.83 (CH_3), 113.68-140 (Ar-C), 131.98 (CF_3), 153.52 (C-F), 158.25 (HO-C(Ar)), 166.26($HC=N$), ppm.

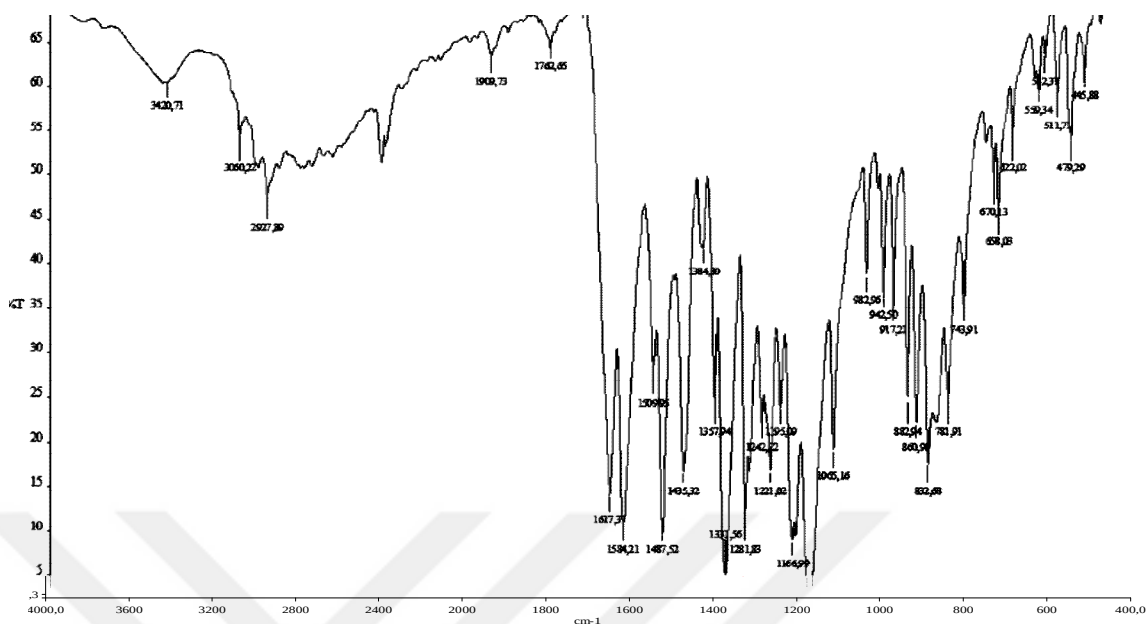
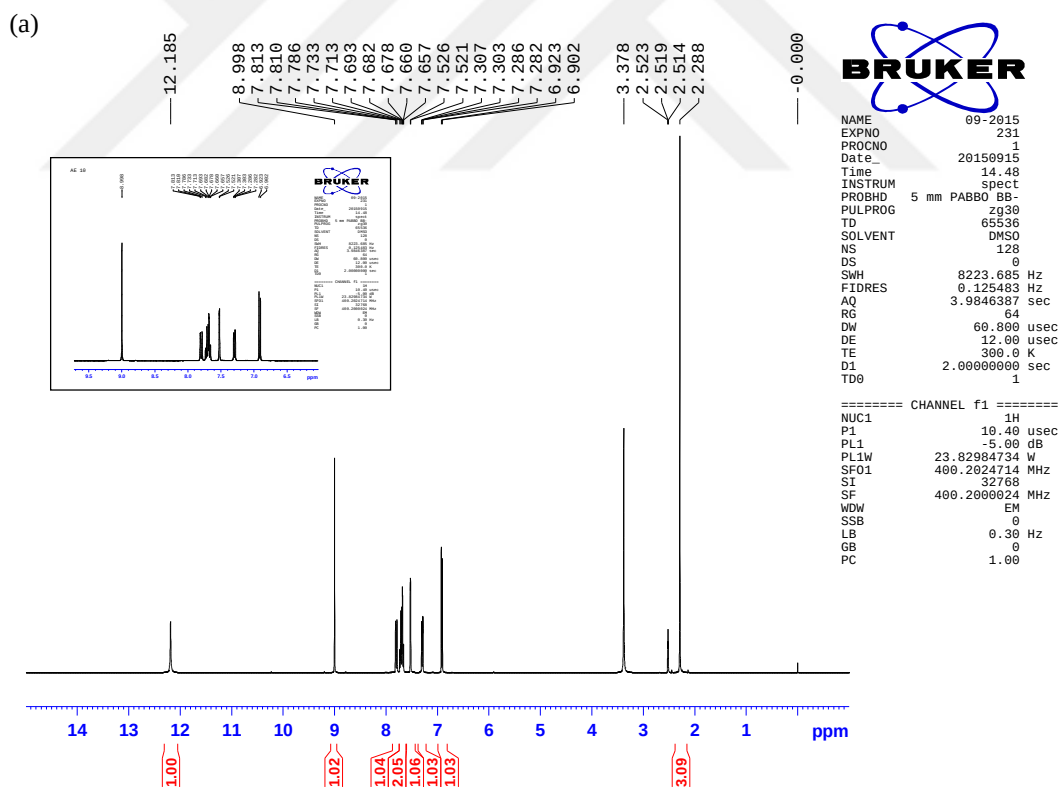
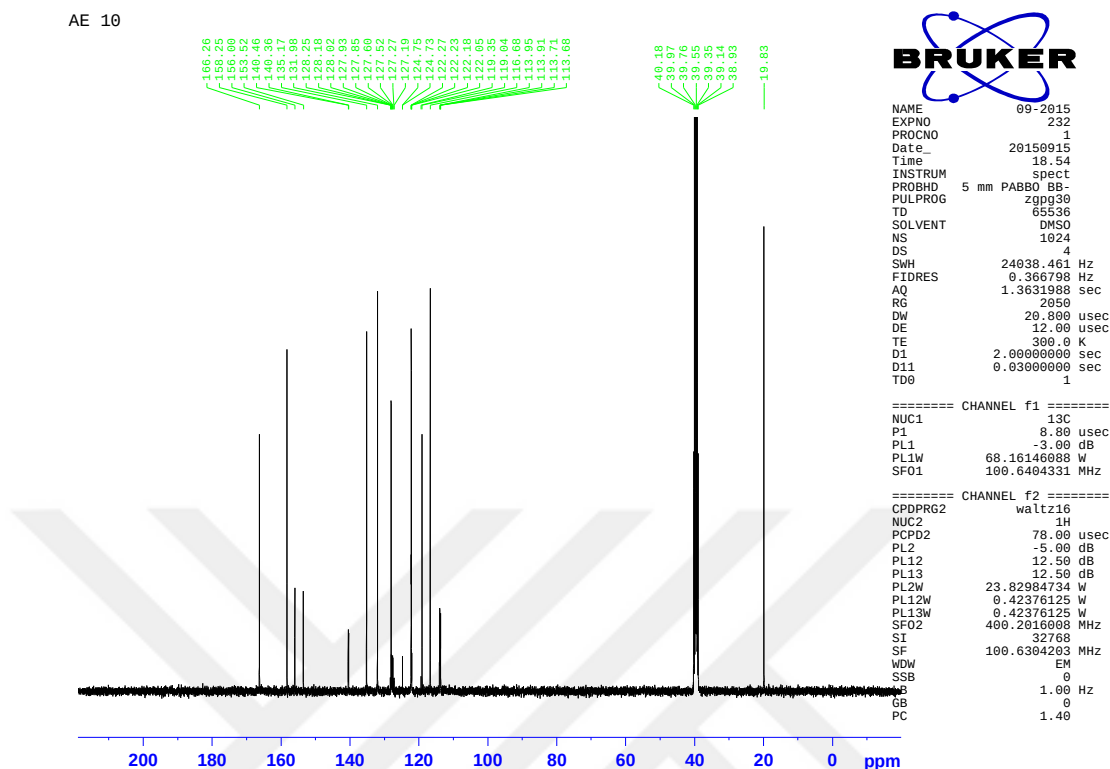


Figure 3.12. FT-IR spectrum of FSB-4



(b)

Figure 3.13. (a) ^1H NMR and (b) ^{13}C NMR spectra of FSB-4

3.2.1.5. Synthesis of (E)-2-(((2-fluoro-5-(trifluoromethyl)phenyl)imino) methyl)-5-methylphenol (FSB-5):

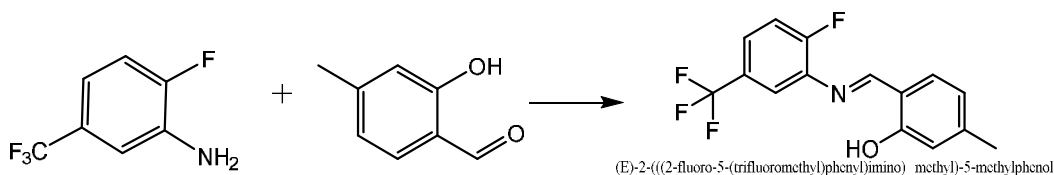


Figure 3.14. Schematic representation for synthesis of FSB-5 ligand

5 mmol 4-methylsalicylaldehyde (0.68 g) was dissolved in methanol (15 ml), a methanolic solution of 5 mmol 2-fluoro-5-(trifluoromethyl)aniline (0.895 g, 0.64 ml) was added and the mixture was stirred continuously and refluxed for 2 hours. Then, the reaction mixture was checked by TLC and allowed to cool room temperature. Upon cooling yellow solid product was occurred. The product was filtered, washed with ice-cold methanol and N-hexane, and finally dried under vacuum. Further purification was conducted via re-crystallization from DCM/

Hexane (1:5) mixture. Finally, light orange product was obtained with a yield of 0.675 g (45%) and the m.p. value was 100.77 °C, Elemental Anal. Calc. for $C_{15}H_{11}F_4NO$: C, 60.61; H, 3.73; N, 4.71. Found: C, 65.03; H, 3.65; N, 3.86 %. FT-IR (KBr, cm^{-1}): $\nu(O-H)$ 3420.39; $\nu(C-H_{aromatic})$ 3020 cm^{-1} ; $\nu(C-H_{aliphatic})$ 2927 cm^{-1} ; $\nu(C=N)$ 1621.07 cm^{-1} ; $\nu(C=C_{aromatic})$ 1487.52 cm^{-1} , $\nu(C-O_{phenolic})$ 1332.30 cm^{-1} ; $\nu(C-F)$ 1228, 1170 cm^{-1} . ^1H NMR(400 MHz, DMSO- d_6) : δ = 2.24 (s, 3H, CH_3), 6.69-7.45 (m, 6H, Ar-H), 8.58 (s, 1H, $HC=N$), 12.62 (s, 1H, OH) ppm. ^{13}C NMR (100.6 MHz, DMSO- d_6) : δ = 21.91 (CH_3), 116-137 (Ar-C), 132.31 (CF_3), 145.71(C-F), 161.44 (HO-C(Ar)), 166.49 (HC=N), ppm.

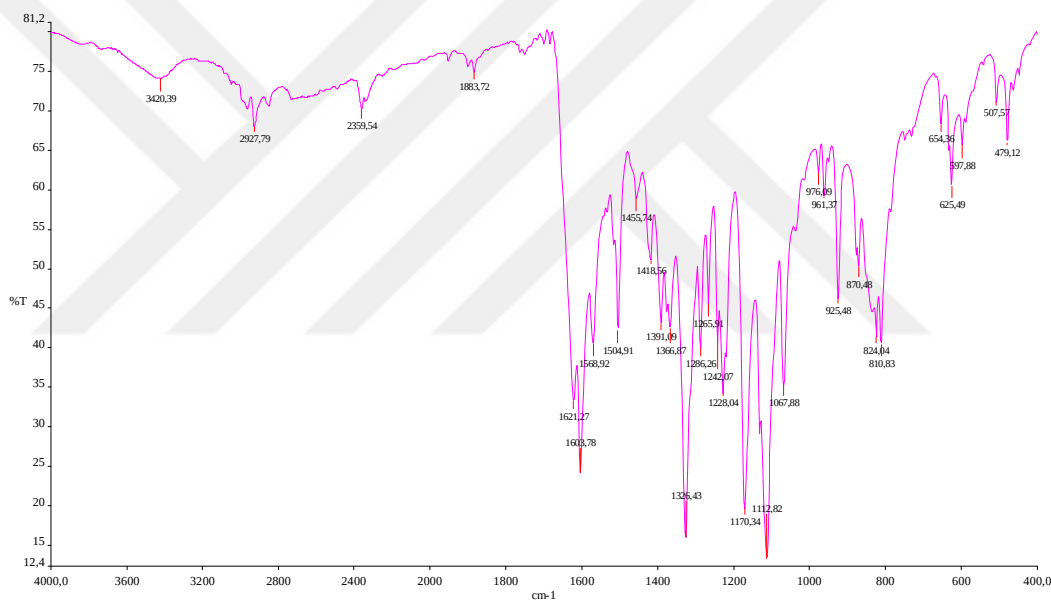
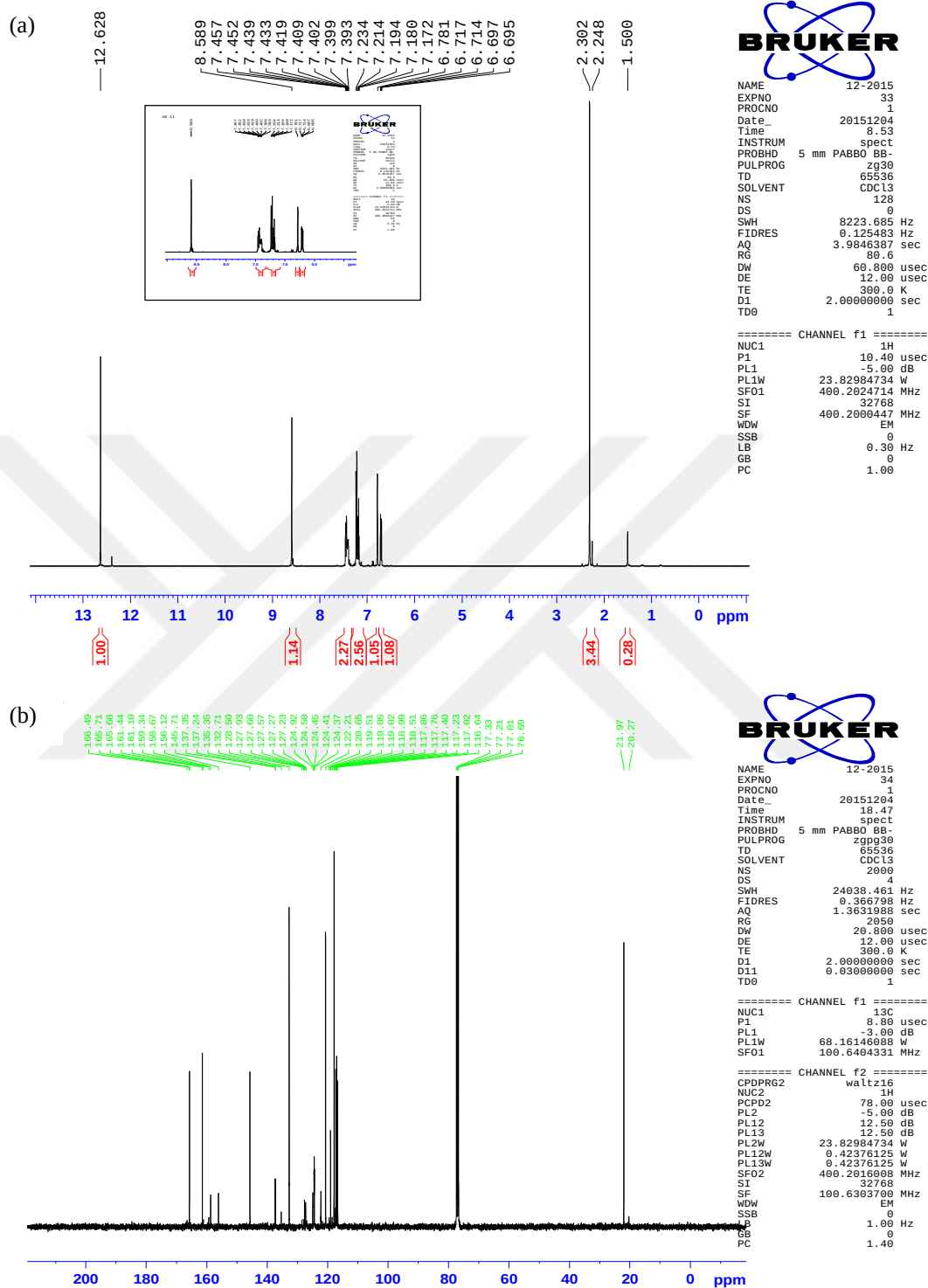


Figure 3.15. FT-IR spectrum of FSB-5

Figure 3.16. (a) ^1H NMR and (b) ^{13}C NMR spectrum of FSB-5

3.2.1.6. Synthesis of (E)-2-(((2-fluoro-5-(trifluoromethyl)phenyl)imino) methyl)-4-methylphenol (FSB-6):

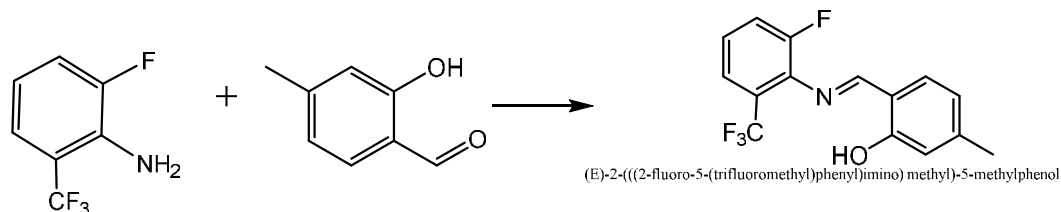


Figure 3.17. Schematic representation for synthesis of FSB-6 ligand

5 mmol 5-methylsalicylaldehyde (0.68 g) was dissolved in methanol (15 ml), a methanolic solution of 5 mmol 2-fluoro-5-(trifluoromethyl)aniline (0.895 g, 0.64 ml) was added and the mixture was stirred continuously and refluxed for 2 hours. Then, the reaction mixture was checked by TLC and allowed to cool room temperature. Upon cooling yellow solid product was occurred. The product was filtered, washed with ice-cold methanol and N-hexane, and finally dried under vacuum. Further purification was conducted via re-crystallization from DCM/Hexane (1:5) mixture. Finally, dark yellow product was obtained with a yield of 0.675 g (45%) and the m.p. value was 92.3 °C, Elemental Anal. Calc. for $C_{15}H_{11}F_4NO$: C, 60.61; H, 3.73; N, 4.71. Found: C, 64.81; H, 3.75; N, 3.79 .

FT-IR (KBr, cm^{-1}): $\nu(O-H)$ 3447.0 cm^{-1} ; $\nu(C-H_{aliphatic})$ 2920.33 cm^{-1} ; $\nu(C=N)$ 1624.90 cm^{-1} ; $\nu(C=C_{aromatic})$ 1582.09 cm^{-1} , $\nu(C-O_{phenolic})$ 1332.82 cm^{-1} ; $\nu(C-F)$ 1272, 1159 cm^{-1} . ^1H NMR(400 MHz, DMSO- d_6) : δ = 2.31 (s, 3H, CH_3), 6.72-7.46 (m, 6H, Ar-H), 8.60 (s, 1H, $HC=N$), 12.63 (s, 1H, OH) ppm. ^{13}C NMR (100.6 MHz, DMSO- d_6) : δ = 21.98 (CH_3), 116.64-137.36 (Ar-C), 132.70 (CF_3), 145.71(C-F), 161.44 ($HO-C(Ar)$), 165.72 ($HC=N$), ppm.

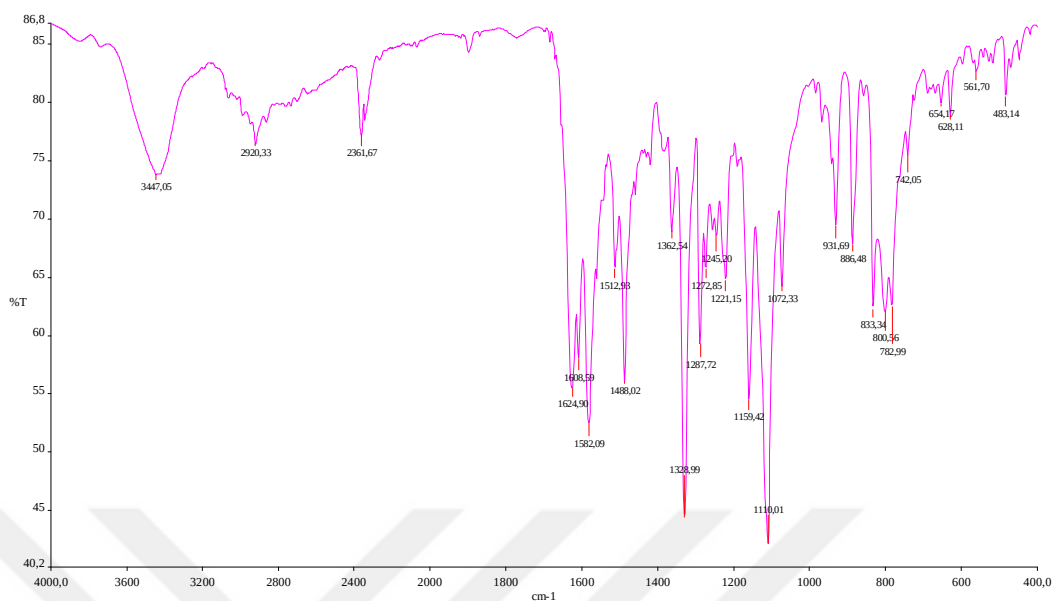
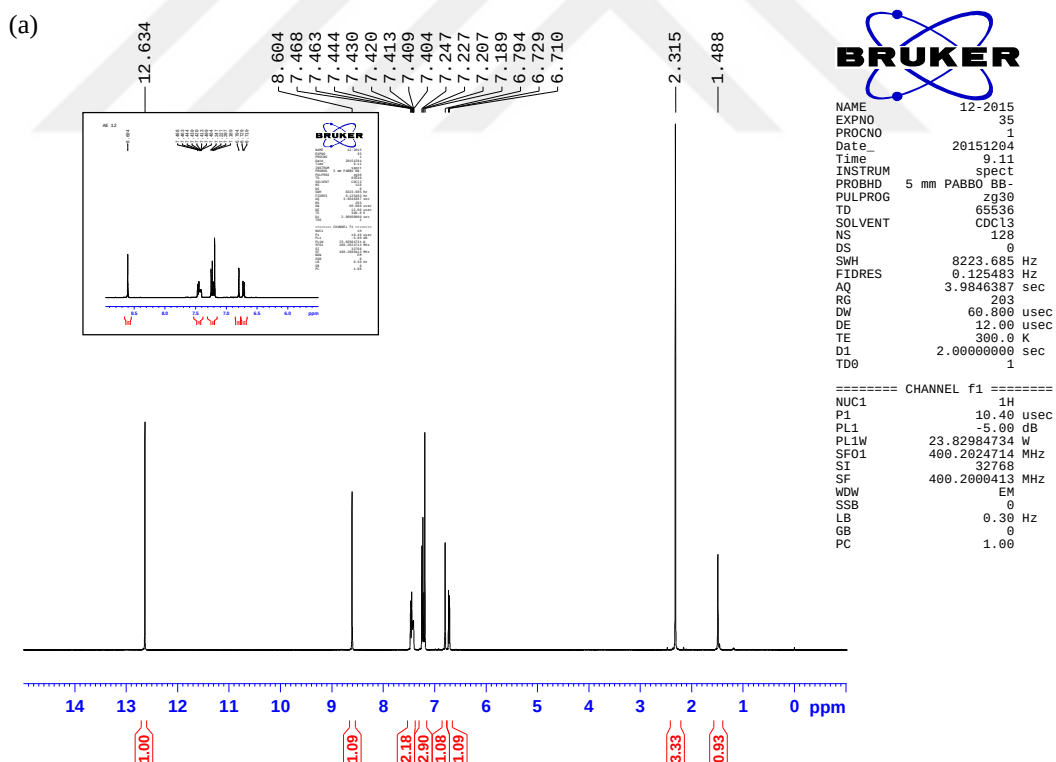
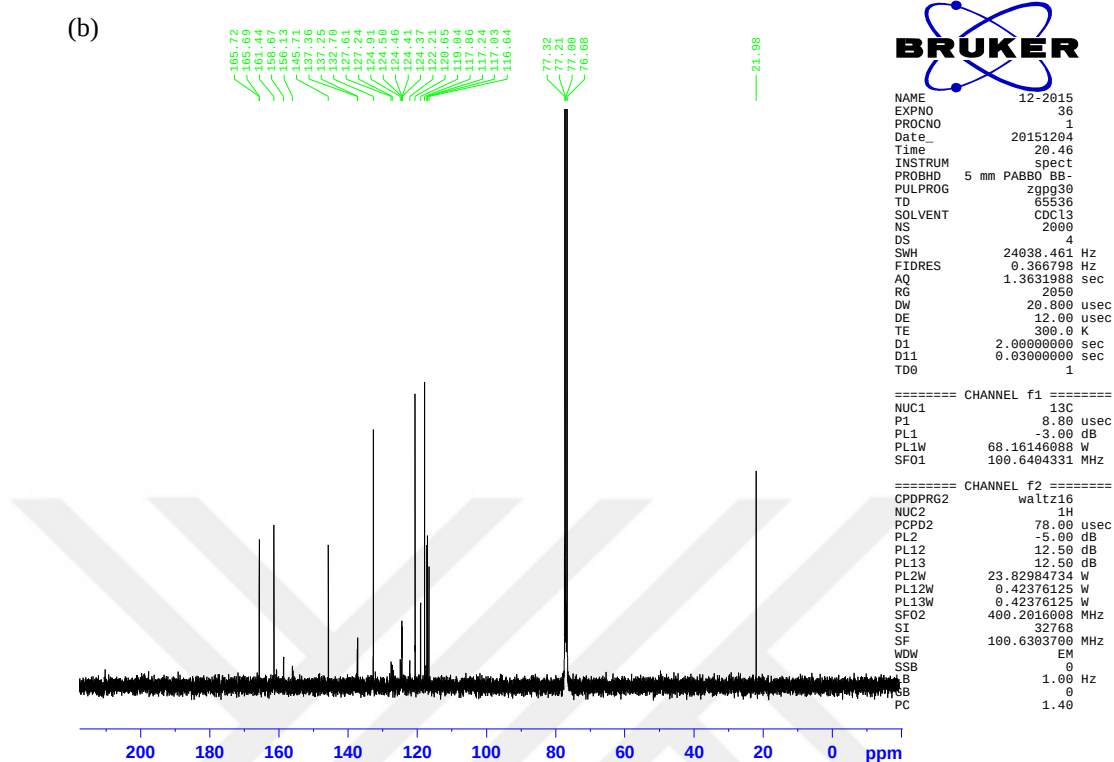


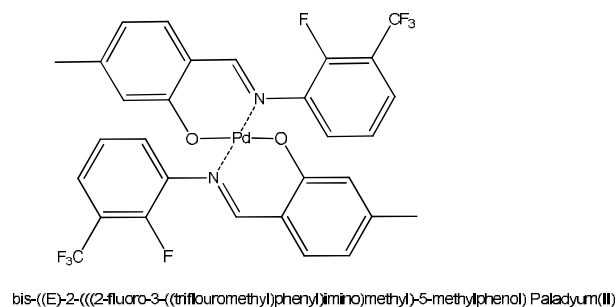
Figure 3.18. FT-IR spectrum of FSB-6



Figure 3.19. (a) ^1H NMR and (b) ^{13}C NMR spectrum of FSB-6

3.2.2. Synthesis of Schiff Base Palladium complexes

3.2.2.1. Synthesis of *bis*-((*E*)-2-(((2-fluoro-3-(trifluoromethyl)phenyl)imino)methyl)-5-methylphenol) Palladium (II) [Pd(FSB-1)₂], K1:

Figure 3.20. Schematic representation for Pd(FSB-1)₂

1 mmol Palladium (II) acetate (0.2246 g) was dissolved in 10 ml acetonitrile solution. Then, added to the 10 ml acetonitrile solution of 2 mmol Schiff base (FSB-1, 0.594 g). The mixture was stirred and refluxed for 2 hours until orange colour solid product was obtained. The product filtered and washed with ice-cold acetonitrile and dried under vacuum. Further purification was realized with re-crystallization over chloroform to obtain high purity crystalline product. Yield: 0.60 g (87%), m.p. 297.39 °C, Elemental Anal. Calc. for $C_{30}H_{20}F_8N_2O_2Pd$: C, 51.56; H, 2.88; N, 4.01. Found: C, 51.84; H, 2.73 ; N, 3.85 %. FT-IR (KBr, cm^{-1}): $\nu(C=N)$ 1597,42 cm^{-1} ; $\nu(C=C_{aromatik})$ 1475 cm^{-1} ; $\nu(C-O)$ 1377 cm^{-1} ; $\nu(C-F)$ 1247.25 cm^{-1} , $\nu(Pd-O)$ 560 cm^{-1} , $\nu(Pd-N)$ 469 cm^{-1} . ^1H NMR (400 MHz, $CDCl_3-d_6$): δ = 2.06 (s, 6H, CH_3), 5.83-7.57 (m, 12H, Ar-H), 7.59 (s, 2H, $HC=N$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3-d_6$): δ = 19.94 (CH_3), 117.57-138.56 (Ar-C), 147.65 (C-F), 163.94 (C=N), ppm.

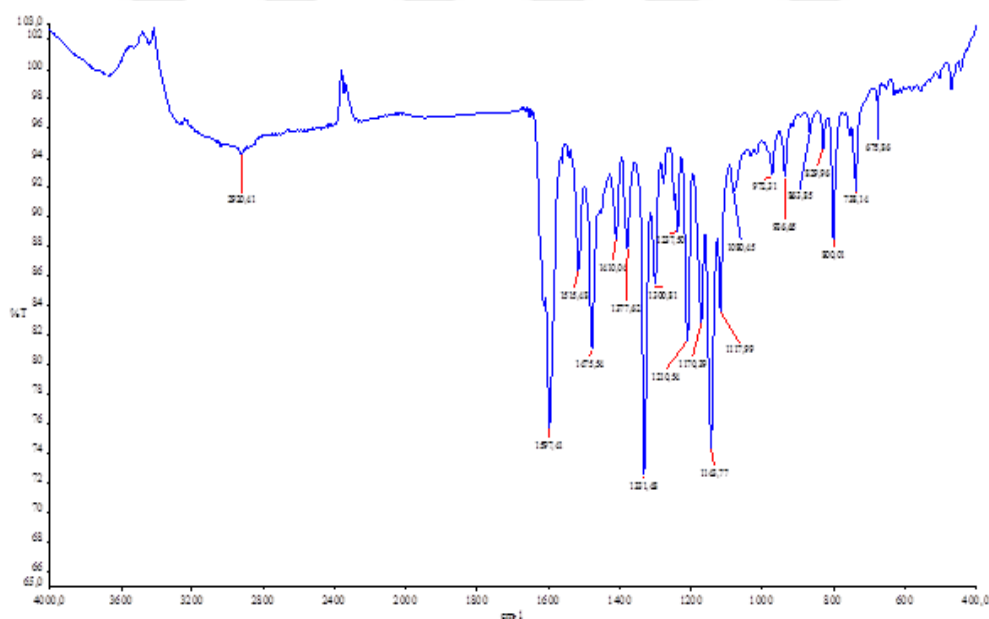


Figure 3.21. FT-IR spectrum of $Pd(FSB-1)_2$

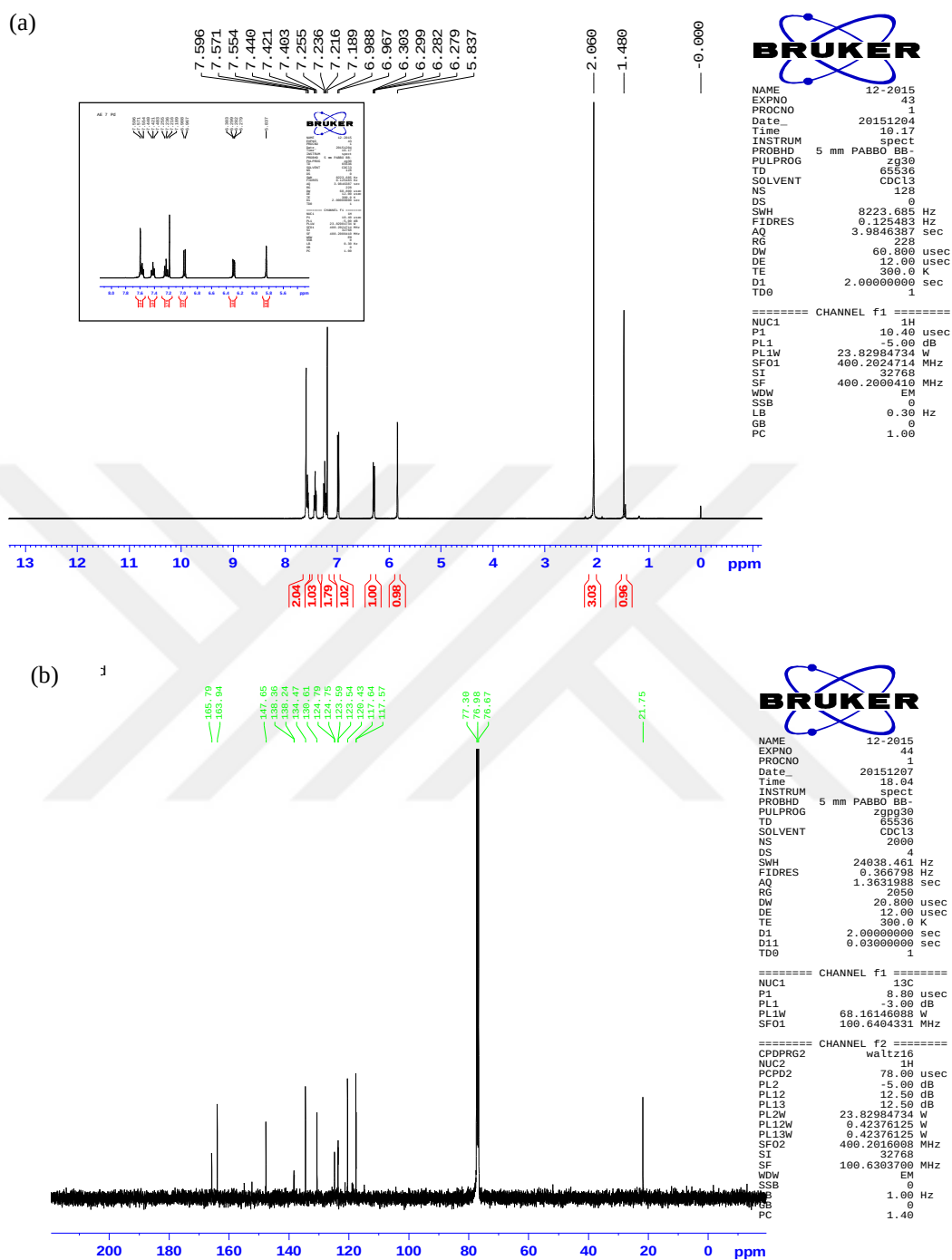
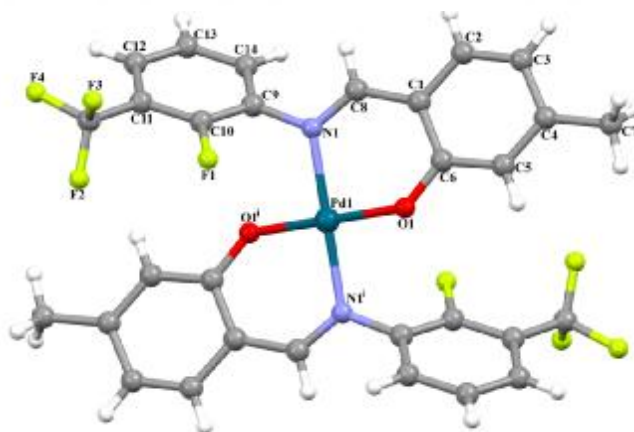
Figure 3.22. (a) ^1H NMR and (b) ^{13}C NMR spectra of $\text{Pd}(\text{FSB-1})_2$

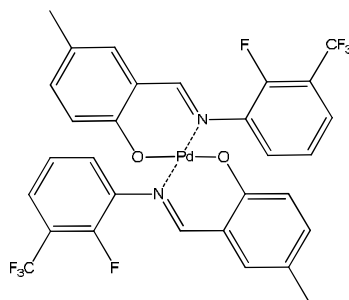
Table 3.3. Single X-Ray crystal data for Pd(FSB-1)₂

Crystal data	
Empirical formula	C ₃₀ H ₂₀ F ₈ N ₂ O ₂ Pd
Formula weight	698.88
Crystal system	Monoclinic
Space group	P2 ₁ /c
<i>a</i> (Å)	12.863 (4)
<i>b</i> (Å)	11.003 (3)
<i>c</i> (Å)	10.024 (3)
β (°)	96.18 (1)
<i>V</i> (Å ³)	1410.4 (7)
<i>Z</i>	2
<i>D_c</i> (g cm ⁻³)	1.646
μ (mm ⁻¹)	0.74
θ range (°)	3.1–28.3
Measured refls.	34753
Independent refls.	3527
<i>R</i> _{int}	0.086
<i>S</i>	1.23
<i>R</i> ₁ / <i>wR</i> ₂	0.121/0.259
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (eÅ ⁻³)	1.03/-1.02

Figure 3.23. Ortep diagram for Pd(FSB-1)₂Table 3.4. Selected bond angles and lengths for Pd(FSB-1)₂

Bond Length	Bond Angle
C8-N1: 1.278	O1-Pd1-N1: 91.0
Pd1-N1: 12.037	C1-C8-N1-C9: -179.0
Pd1-O1: 1.989	

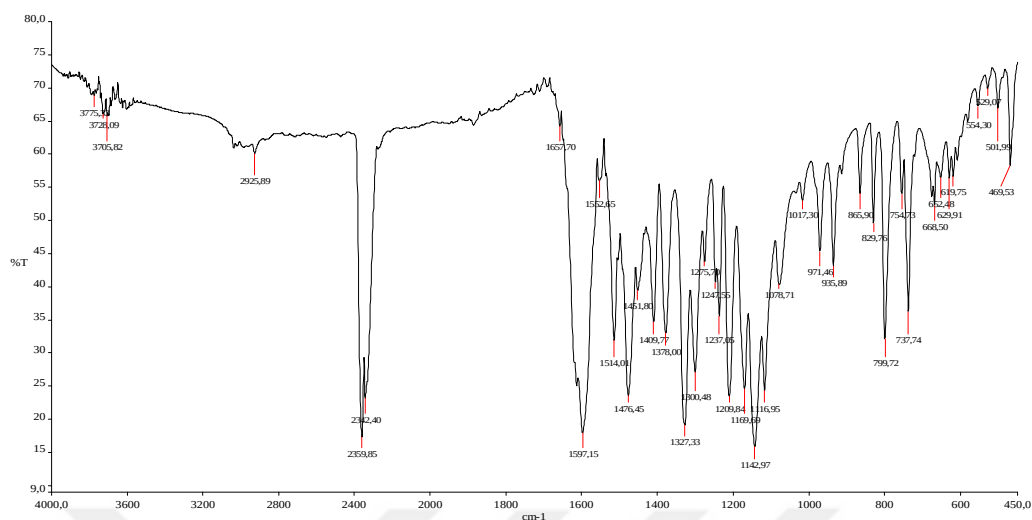
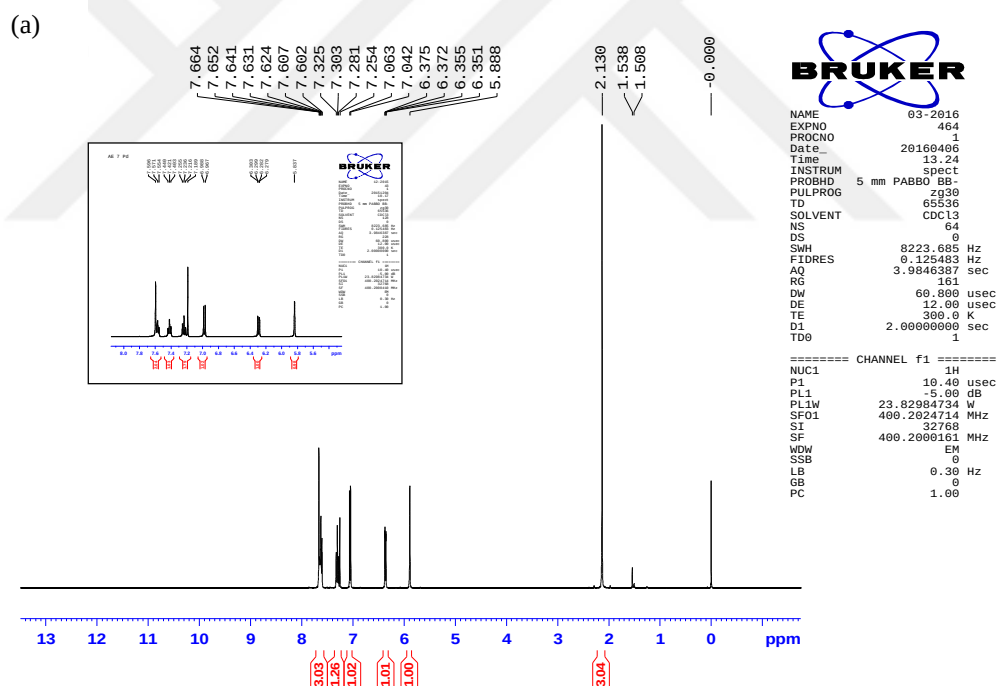
3.2.2.2 Synthesis of *bis-((E)-2-(((2-fluoro-3-(trifluoromethyl)phenyl)imino)methyl)-4-methylphenol)Paladium (II) Pd(FSB-2)₂*, K2:

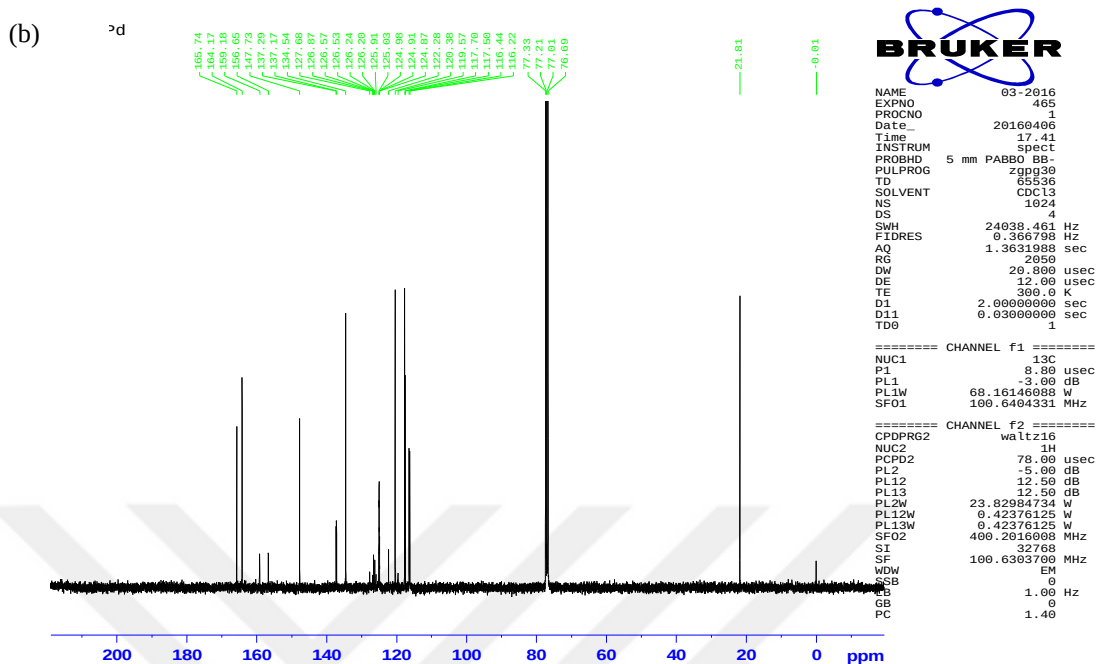


bis-((E)-2-(((2-fluoro-3-(trifluoromethyl)phenyl)imino)methyl)-4-methylphenol) Paladyum(II)

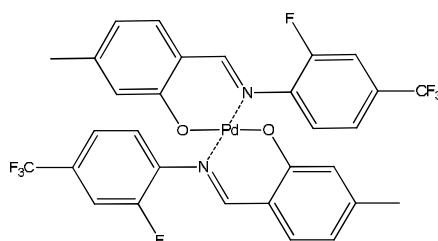
Figure 3.24. Schematic representation for Pd(FSB-2)₂

1 mmol Palladium (II) acetate (0.2246 g) was dissolved in 10 ml acetonitrile solution. Then, added to the 10 ml acetonitrile solution of 2 mmol Schiff base (FSB-2, 0.594 g). The mixture was stirred and refluxed for 2 hours until orange colour solid product was obtained. The product filtered and washed with ice-cold acetonitrile and dried under vacuum. Further purification was realized with re-crystallization over chloroform to obtain high purity crystalline product. Yield: 0.638 g (91 %), m.p. 346.70 °C, Elemental Anal. Calc. for C₃₀H₂₀F₈N₂O₂Pd: C, 51.56; H, 2.88; N, 4.01. Found: C, 51.72 ; H, 2.81 ; N, 3.81 %. FT-IR (KBr, cm⁻¹): ν(C=N) 1597,54 cm⁻¹; ν(C=C_{aromatic}) 1476.45 cm⁻¹; ν(C-O) 1377 cm⁻¹; ν(C-F) 1237.05 cm⁻¹, ν(Pd-O) 554 cm⁻¹, ν(Pd-N) 469 cm⁻¹. ¹HNMR(400 MHz, CDCl₃-d₆) : δ= 2.13 (s, 6H, CH₃), 5.88-7.62 (m, 12H, Ar-H), 7.66 (s, 2H, HC=N) ppm. ¹³CNMR (100.6 MHz, CDCl₃-d₆) : δ= 21.01 (CH₃), 116.22-137.29 (Ar-C), 147.73 (C-F) 164.17(C=N), ppm.

Figure 3.25. FT-IR spectrum of Pd(FSB-2)₂

Figure 3.26. (a) ¹H NMR and (b) ¹³C NMR spectra of Pd(FSB-2)₂

3.2.2.3. Synthesis of bis-((E)-2-(((2-fluoro-4-(trifluoromethyl)phenyl)imino)methyl)-5-methylphenol)Palladium (II) [Pd(FSB-3)₂], K3:

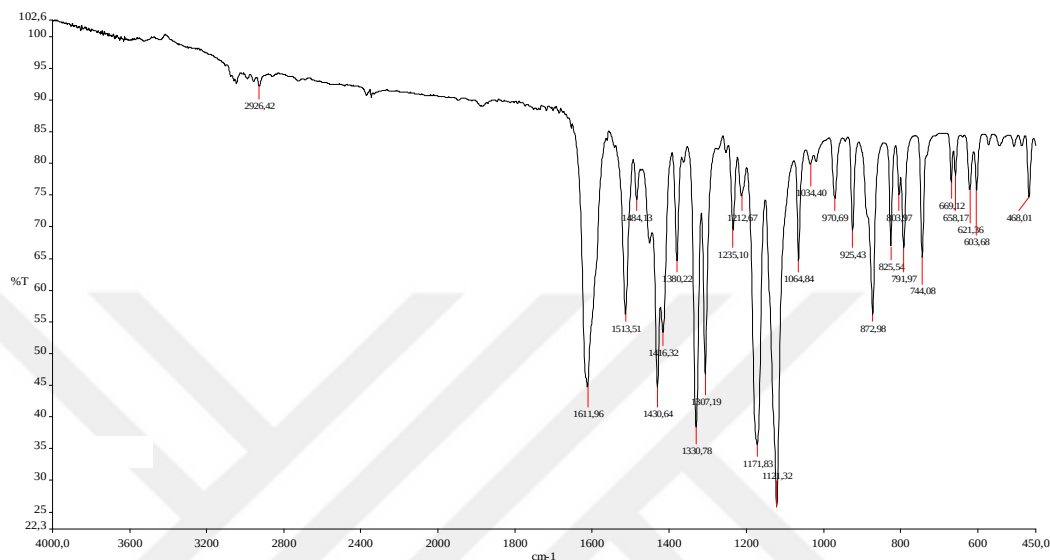
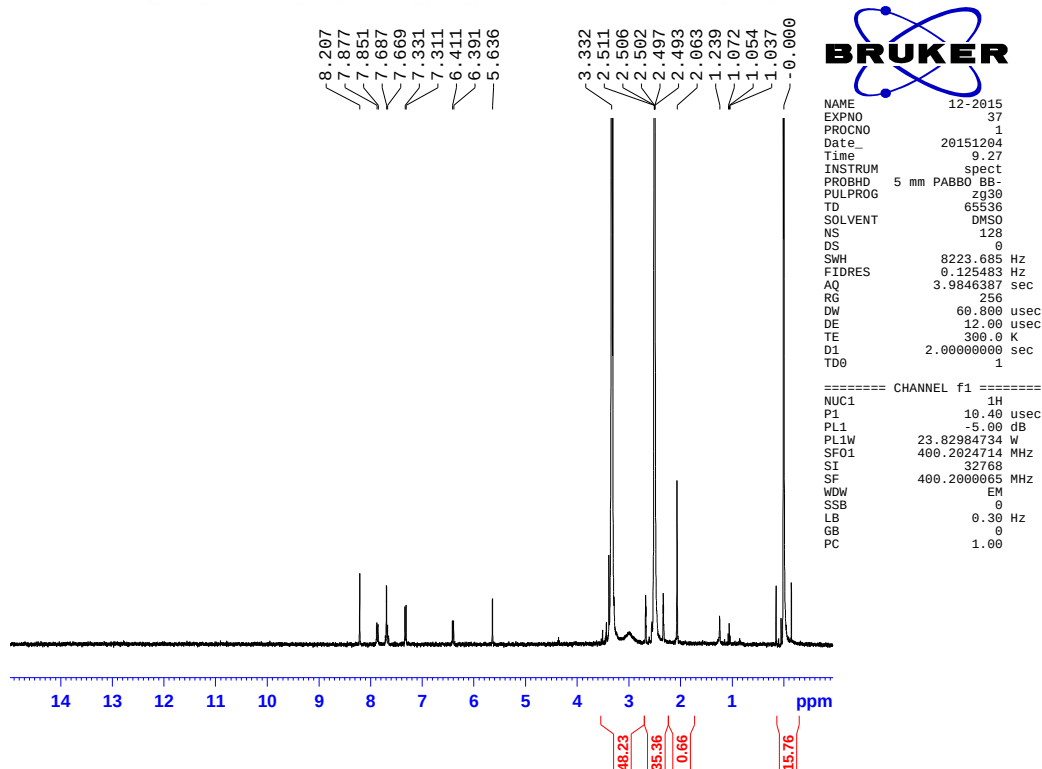


bis-((E)-2-(((2-fluoro-4-(trifluoromethyl)phenyl)imino)methyl)-5-methylphenol) Palladium(II)

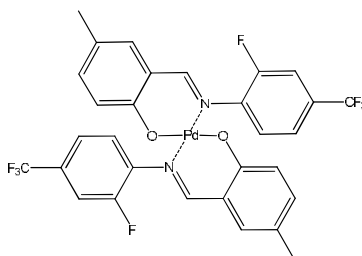
Figure 3.27. Schematic representation for Pd(FSB-3)₂

1 mmol Palladium (II) acetate (0.2246 g) was dissolved in 10 ml acetonitrile solution. Then, added to the 10 ml acetonitrile solution of 2 mmol Schiff base (FSB-3, 0.594 g). The mixture was stirred and refluxed for 2 hours until dark yellow colour solid product was obtained. The product filtered and washed with ice-cold acetonitrile and dried under vacuum. Further purification was realized with re-crystallization over chloroform to obtain high purity crystalline product. Yield: 0.624 g (89 %), m.p. 264.01°C, Elemental Anal. Calc. for C₃₀H₂₀F₈N₂O₂Pd: C, 51.56; H, 2.88; N, 4.01. Found: ,52.15 ; H, 2.93 ; N, 3.51 %. FT-IR (KBr, cm⁻¹): ν(C=N) 1611

cm^{-1} ; $\nu(\text{C}=\text{C}_{\text{aromatic}})$ 1430.64 cm^{-1} ; $\nu(\text{C}-\text{O})$ 1330.78 cm^{-1} ; $\nu(\text{C}-\text{F})$ 1171.33 cm^{-1} , $\nu(\text{Pd}-\text{O})$ 604 cm^{-1} , $\nu(\text{Pd}-\text{N})$ 468 cm^{-1} . $^1\text{H NMR}$ (400 MHz, DMSO- d_6) : $\delta = 2.06$ (s, 6H, CH_3), 5.63-7.85 (m, 12H, Ar-H), 7.87 (s, 2H, $\text{HC}=\text{N}$) ppm.

Figure 3.28. FT-IR spectrum of Pd(FSB-3)₂Figure 3.29. ^1H NMR spectrum of Pd(FSB-3)₂

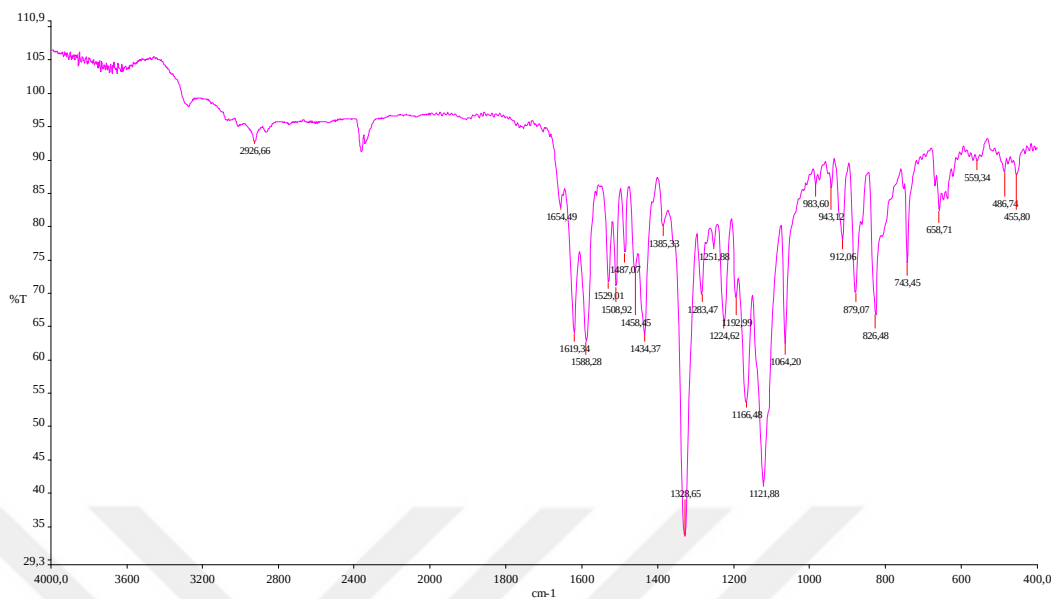
3.2.2.4. Synthesis of *bis*-(*E*)-2-(((2-fluoro-4-(trifluoromethyl)phenyl)imino)methyl)-4-methylphenol) Palladium(II) [Pd(FSB-4)₂], K4:



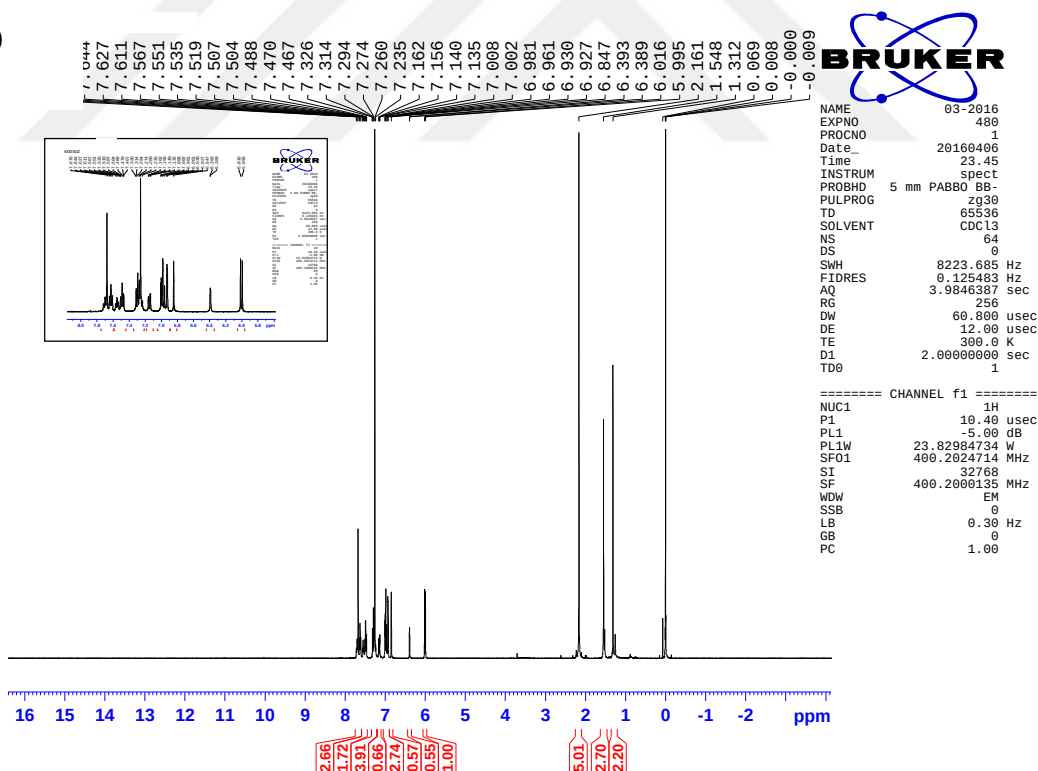
bis-((*E*)-2-(((2-fluoro-4-(trifluoromethyl)phenyl)imino)methyl)-4-methylphenol) Palladium(II)

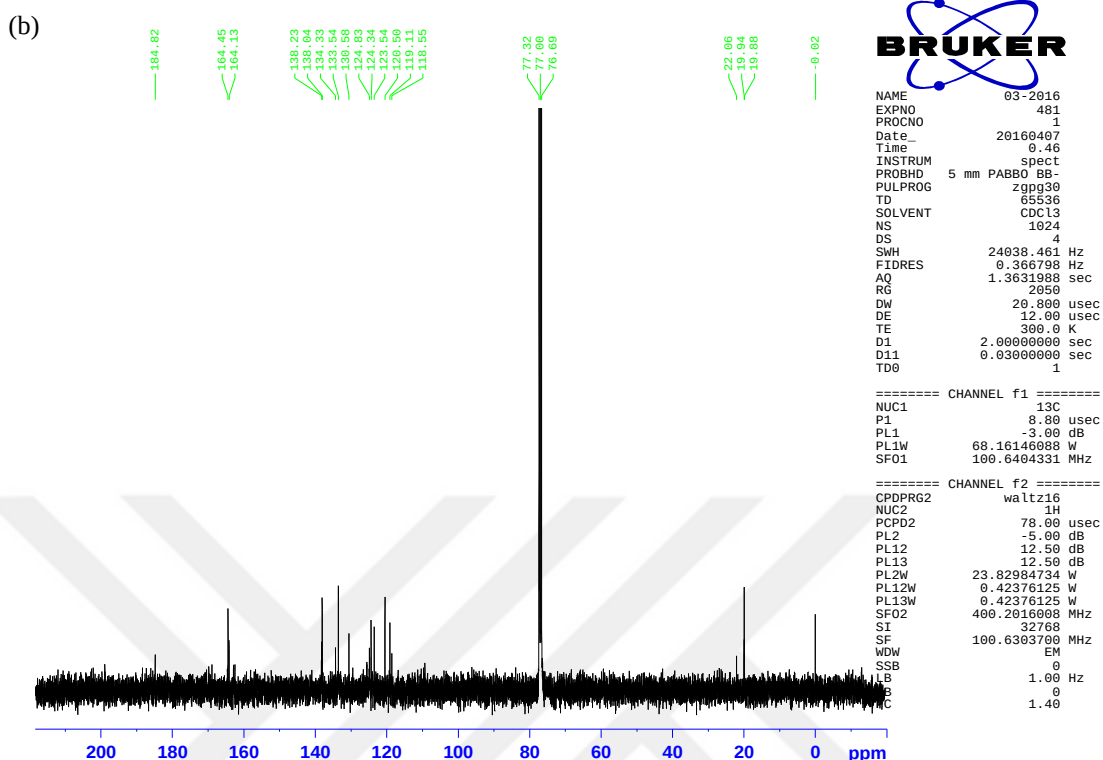
Figure 3.30. Schematic representation for Pd(FSB-4)₂

1 mmol Palladium (II) acetate (0.2246 g) was dissolved in 10 ml acetonitrile solution. Then, added to the 10 ml acetonitrile solution of 2 mmol Schiff base (FSB-4, 0.594 g). The mixture was stirred and refluxed for 2 hours until dark yellow colour solid product was obtained. The product filtered and washed with ice-cold acetonitrile and dried under vacuum. Further purification was realized with re-crystallization over chloroform to obtain high purity crystalline product. Yield: 0.624 g (89 %), m.p. 260.83°C, Elemental Anal. Calc. for C₃₀H₂₀F₈N₂O₂Pd: C, 51.56; H, 2.88; N, 4.01. Found: C, 51.95 ; H, 2.79 ; N, 3.65 %. FT-IR (KBr, cm⁻¹): ν(C=N) 1588,28 cm⁻¹; ν(C=C_{aromatic}) 1434.37 cm⁻¹; ν(C-O) 1323.65 cm⁻¹; ν(C-F) 1224.62 cm⁻¹, ν(Pd-O) 618 cm⁻¹, ν(Pd-N) 484 cm⁻¹. ¹HNMR(400 MHz, CDCl₃-d₆) : δ= 2.16 (s, 6H,CH₃), 5.99-7.69 (m, 12H, Ar-H), 7.71 (s,2H,HC=N) ppm.¹³CNMR (100.6 MHz, CDCl₃-d₆): δ= 19.94 (CH₃), 118.55-138.04 (Ar-C), 138.25(C-F) , 164.45(C=N), ppm.

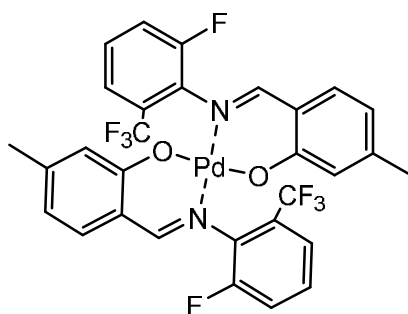
Figure 3.31. FT-IR spectrum of Pd(FSB-4)₂

(a)



Figure 3.32. (a) ^1H NMR and (b) ^{13}C NMR spectra of $\text{Pd}(\text{FSB-4})_2$

3.2.2.5. Synthesis of *bis*-((E)-2-(((2-fluoro-5-(trifluoromethyl)phenyl)imino) methyl)-5-methylphenol) Palladium(II) [$\text{Pd}(\text{FSB-5})_2$], K5:



bis-((E)-2-(((2-fluoro-5-(trifluoromethyl)phenyl)imino) methyl)-5-methylphenol) Palladium(II)

Figure 3.33. Schematic representation for $\text{Pd}(\text{FSB-5})_2$

1 mmol Palladium (II) acetate (0.2246 g) was dissolved in 10 ml acetonitrile solution. Then, added to the 10 ml acetonitrile solution of 2 mmol Schiff base (FSB-5, 0.594 g). The mixture was stirred and refluxed for 2 hours until light orange colour solid product was obtained. The product filtered and washed with ice-cold

acetonitrile and dried under vacuum. Further purification was realized with re-crystallization over chloroform to obtain high purity crystalline product. Yield: 0.45 g (65 %), m.p. 237.50°C, Elemental Anal. Calc. for $C_{30}H_{20}F_8N_2O_2Pd$: C, 51.56; H, 2.88; N, 4.01. Found: C, 51.85 ; H, 2.54 ; N, 3.44 %. FT-IR (KBr, cm^{-1}): $\nu(C=N)$ 1578,23 cm^{-1} ; $\nu(C=C_{aromatic})$ 1499.10 cm^{-1} ; $\nu(C-O)$ 1312.86 cm^{-1} ; $\nu(C-F)$ 1186.39 cm^{-1} , $\nu(Pd-O)$ 592 cm^{-1} , $\nu(Pd-N)$ 466 cm^{-1} . ^1H NMR(400 MHz, $CDCl_3-d_6$) : δ = 2.09 (s, 6H, CH_3), 5.87-7.42 (m, 12H, Ar-H), 7.58 (s, 2H, $HC=N$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3-d_6$) : δ = 19.81 (CH_3), 119.20-133 (Ar-C), 138.23(C-F), 164.16 (C=N), ppm.

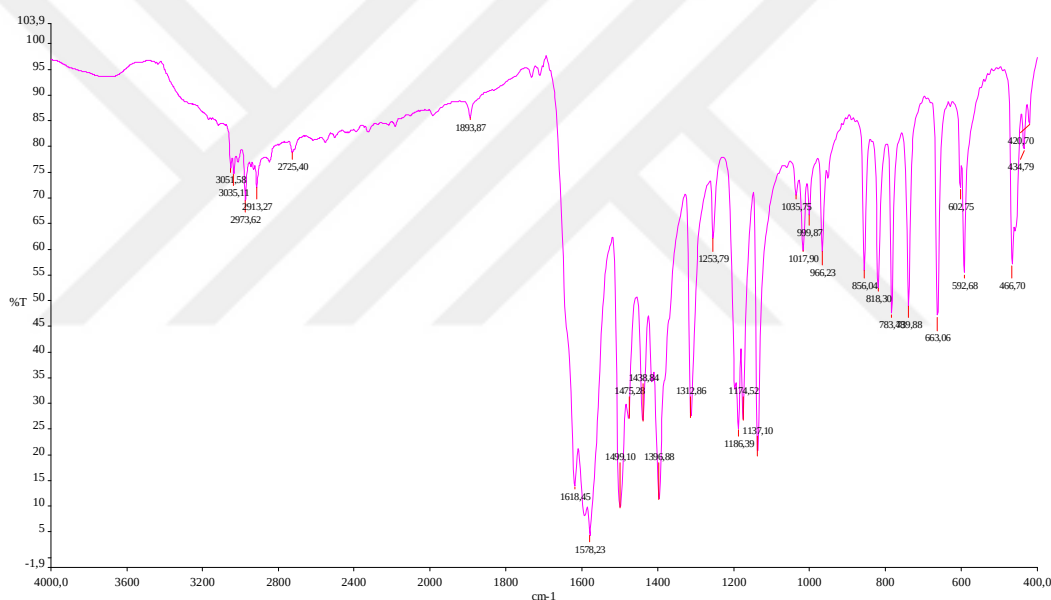
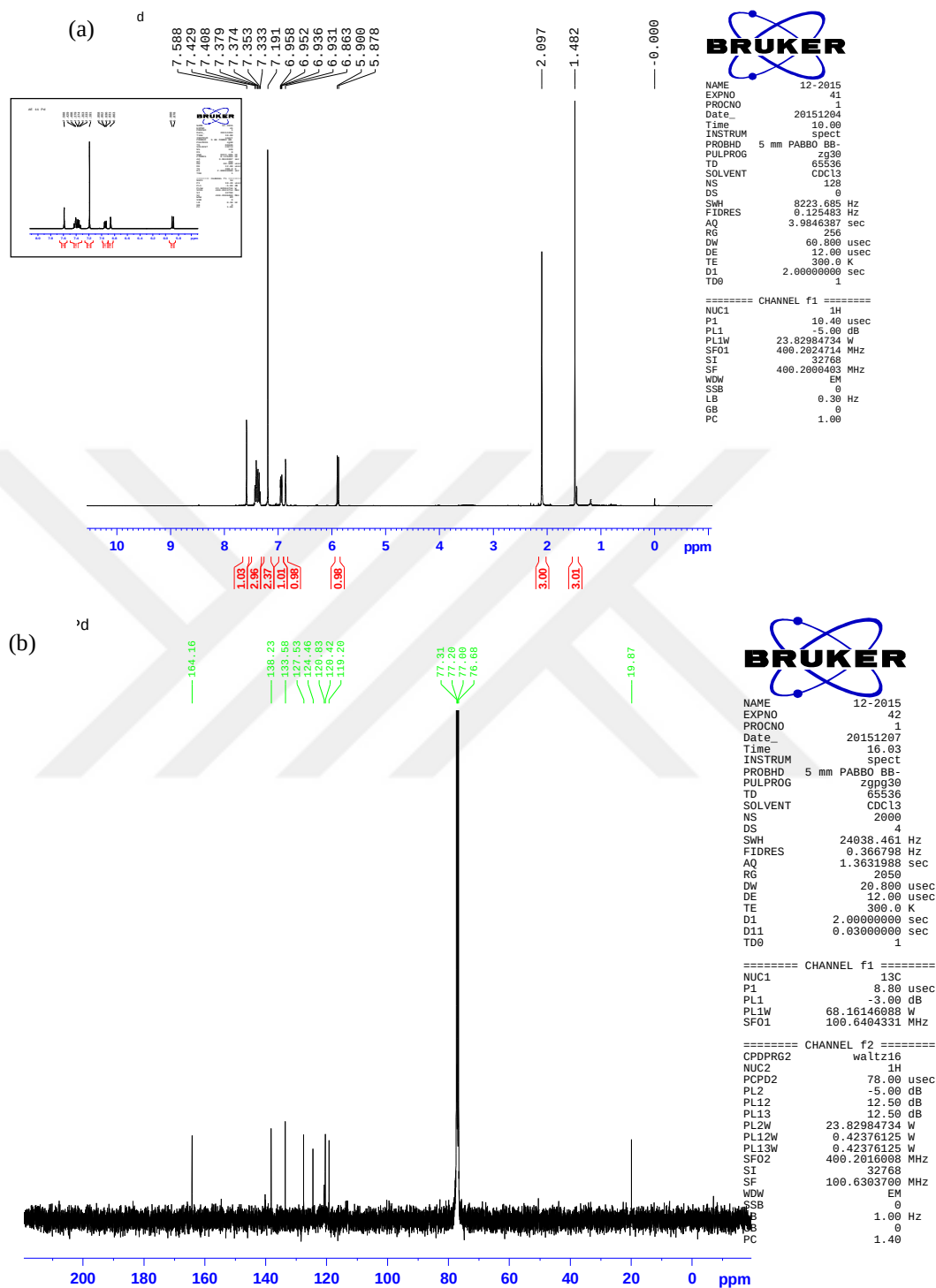
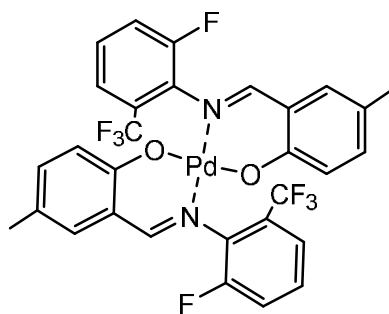


Figure 3.34. FT-IR spectrum of $Pd(FSB-5)_2$



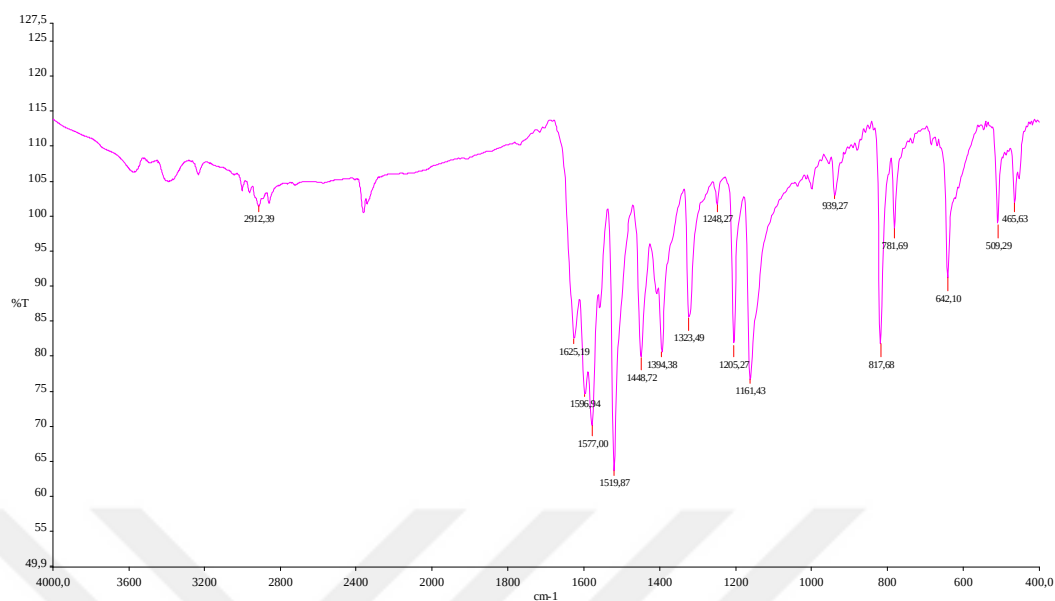
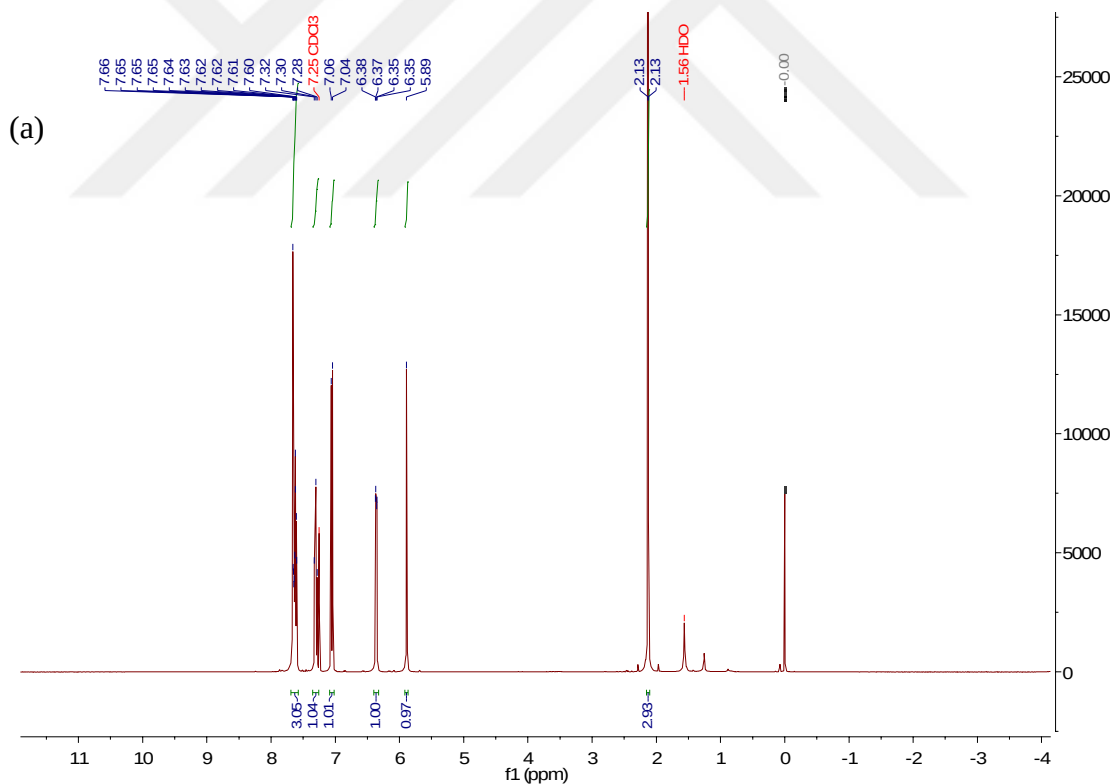
3.2.2.6. Synthesis of bis-((E)-2-(((2-fluoro-6-(trifluoromethyl)phenyl)imino) methyl)-4-methylphenol) Palladium(II) [Pd(FSB-6)₂], K6:



bis-((E)-2-(((2-fluoro-5-(trifluoromethyl)phenyl)imino) methyl)-4-methylphenol) Palladium(II)

Figure 3.36. Schematic representation for Pd(FSB-6)₂

1 mmol Palladium (II) acetate (0.2246 g) was dissolved in 10 ml acetonitrile solution. Then, added to the 10 ml acetonitrile solution of 2 mmol Schiff base (FSB5, 0.594 g). The mixture was stirred and refluxed for 2 hours until orange colour solid product was obtained. The product filtered and washed with ice-cold acetonitrile and dried under vacuum. Further purification was realized with re-crystallization over chloroform to obtain high purity crystalline product. Yield: 0.483 g (69 %), m.p. 272.35°C, Elemental Anal. Calc. for C₃₀H₂₀F₈N₂O₂Pd: C, 51.56; H, 2.88; N, 4.01. Found: C, 53.34 ; H, 2.27 ; N, 3.23 %. FT-IR (KBr, cm⁻¹): ν(C=N) 1577.0 cm⁻¹; ν(C=C_{aromatic}) 1519.87 cm⁻¹; ν(C-O) 1323.49 cm⁻¹; ν(C-F) 1205.27 cm⁻¹. , ν(Pd-O) 642 cm⁻¹, ν(Pd-N) 466 cm⁻¹. ¹HNMR(400 MHz, CDCl₃-d₆) : δ= 2.13 (s, 6H,CH₃), 5.89-7.22 (m, 12H, Ar-H), 7.65 (s,2H,HC=N) ppm.¹³CNMR (100.6 MHz, CDCl₃-d₆) : δ= 21.81 (CH₃), 116.22-134.54 (Ar-C), 137.29(C-F), 164.17 (C=N), ppm.

Figure 3.37. FT-IR spectrum of Pd(FSB-6)₂

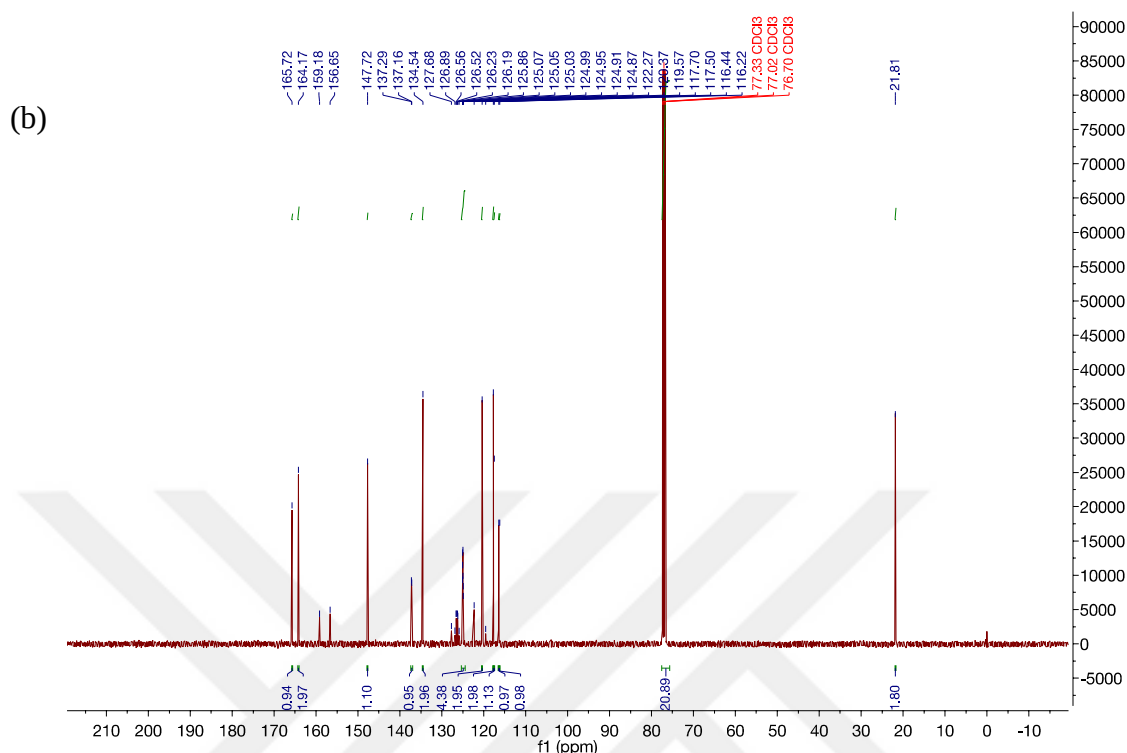


Figure 3.38. (a) ^1H NMR and (b) ^{13}C NMR spectra of $\text{Pd}(\text{FSB-6})_2$

3.3. Solubility of Palladium Complexes (Precursor) in scCO_2

Solubility measurements were carried out using high-pressure reactor (figure 3.40). Reactor is made up of high-pressure stainless steel vessel (54 mL) and equipped with two sapphire windows for visual observation. The solubility is determined by following method below.

Metal complex (precursor) (20 mg) was loaded into the reactor; cell closed and CO_2 was sent into cell by using syringe pump (ISCO, 260D) until the reactor reached 20.6 Mpa and was heated up to 363 K by means of heating tape connected to a Proportional Integral Derivative (PID) temperature controller and the temperature controlled by J calibrated thermocouple. At these conditions, cell was mixed for 3 hours by using magnetic stirrer. The dissolution of the precursor was observed via sapphire window. At the end of this time, samples were taken from the vent valve into the small tube whose inner volume 5ml, after that the tube was washed with dichloromethane to obtain complex whose dissolve in scCO_2 . Finally Solubility of

complexes was calculated quantitatively via UV–visible spectroscopy. The solubility values given in table 3.5.

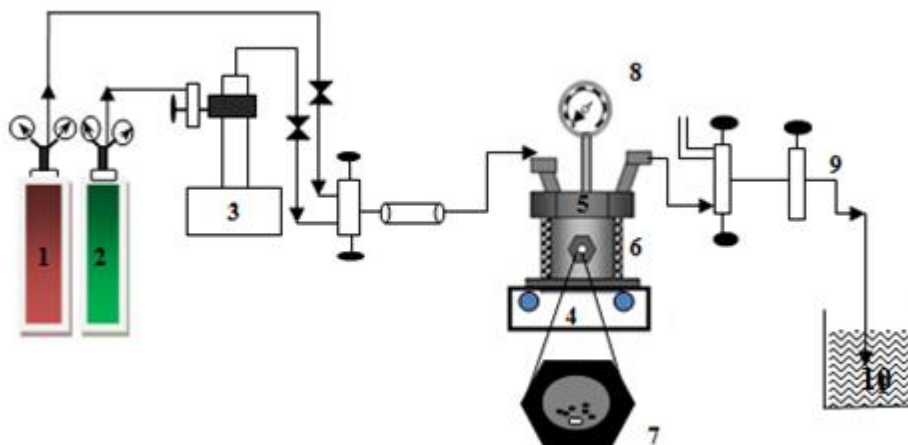


Figure 3.39. The apparatus that use for determination of solubility in scCO₂ (1: H₂ tube, 2: CO₂ tube, 3: High pressure syringe pump (ISCO 260 D), 4: magnetic stirrer, 5: Parr brand 50 mL lik high pressure view cell with sapphire window, 6: heating system, 7: Sapphire window (25 mm x 14 mm), 8: pressure gauge, 9:sampling valve, 10: sample tube).

Table 3.5. Solubility data for complexes in scCO₂ (mol/mol CO₂)

	2000 psi	2500 psi	3000 psi
K1	3.16 x10 ⁻⁵	3,41 x10 ⁻⁵	5,06 x10 ⁻⁵
K2	2,64 x10 ⁻⁵	2,98 x10 ⁻⁵	3.94 x10 ⁻⁵
K3	2.85 x10 ⁻⁵	3,93 x10 ⁻⁵	3,89 x10 ⁻⁵
K4	2,46 x10 ⁻⁵	2,87 x10 ⁻⁵	3,05 x10 ⁻⁵
K5	4.58 x 10 ⁻⁵	4.65 x 10 ⁻⁵	5.71 x 10 ⁻⁵
K6	4,33 x 10 ⁻⁵	4,45 x 10 ⁻⁵	5,66 x 10 ⁻⁵

3.4. Deposition of Palladium Complexes onto SBA-15 Using ScCO₂ as Reaction Media

Deposition of metal complexes (precursor) onto SBA-15 was performed in AMAR brand 100ml stainless steel reactor (fig. 3.40) in scCO₂ as reaction media. In terms of SCFD technique, precursor was dissolved in scCO₂ at a pressure of 20.6

Mpa and a temperature of 363 K. After dissolution of the precursor, adsorbed onto SBA-15 support material. Then, reduced its elemental form by using H_2 (g).

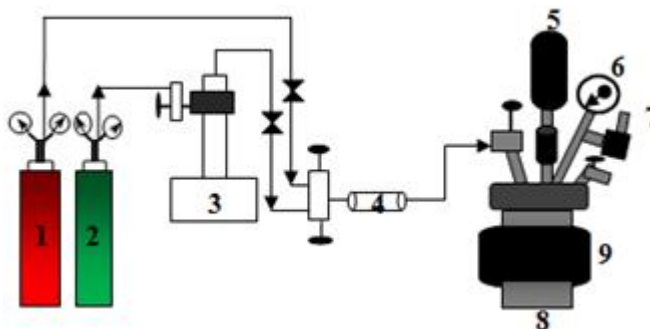


Figure 3.40. The apparatus that use for deposition process in $scCO_2$ (1: H_2 tube, 2: CO_2 tube, 3: High pressure syringe pump (ISCO 260 D), 4: (H_2+CO_2 mixing tube), 5: magnetic stirrer, 6: pressure gauge heating system, 7: Rupture Disc, 8: Amar brand high pressure reactor(100ml) , 9: heating jacket).

In a typical deposition experiments, Precursor SBA-15 were placed in a reactor as include theoretically %10 or %5 Pd. Then the cell was sealed and heated up to 363 K and pressurized with CO_2 by using a syringe pump (ISCO, 260D) until reached 20.6 Mpa and stirrer 3 hours to reach the equilibrium. Following this step, H_2 (0.5 Mpa) and CO_2 (20.6 Mpa) which were mixed in mixing tube, were sent to the cell and stirred 3 hours at desired pressure and temperature. At the end of this time, the reactor was cooling until room temperature. Then, the system was depressurized slowly by using vent valve. After that, thermal treatment under inert atmosphere applied to obtained material to reduce the precursor which is not reduced to its metallic form by $H_2(g)$.

3.5. Catalytic Efficiency of Synthesized SBA-15 Supported Palladium Nanoparticles over Suzuki- Miyaura Reaction

3.5.1. Determination of Optimum Conditions for Suzuki reactions

For the catalytic efficiency of catalysts, Suzuki-Miyaura C-C cross coupling reaction was chosen as target reaction. It is known that solvent and base preferences

play key role for the performance of catalyst in Suzuki-Miyaura reactions. Within this context, different solvents (DMF, toluene, 1,4-dioxane, NMP, acetonitrile and ethanol) and bases (Et_3N , K_2CO_3 , Na_2CO_3 and NaOAc) were studied to optimize reaction conditions. Initial reactions were realized with model substrates; bromobenzene and phenylboronic acid with catalyst 1 (Cat. 1) which was obtained from the deposition of $\text{Pd}(\text{FSB-1})_2$ onto SBA-15. Due to the optimization experiments, K_2CO_3 and ethanol were determined as most efficient base-solvent combination at 80 °C with 0.5 % mole catalyst. The optimization results are given below.

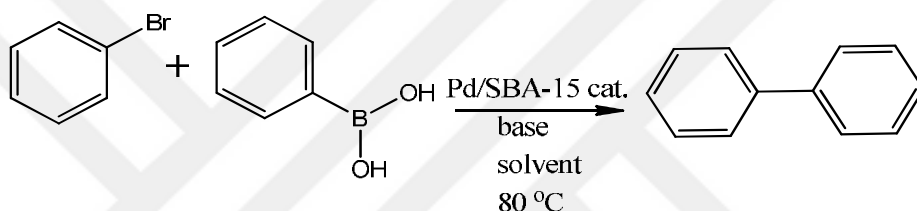


Figure 3.41. Suzuki-Miyaura reaction of aryl bromides with phenylboronic acid by Pd/SBA-15 catalyst

Table 3.6. Optimization conditions of Suzuki reactions

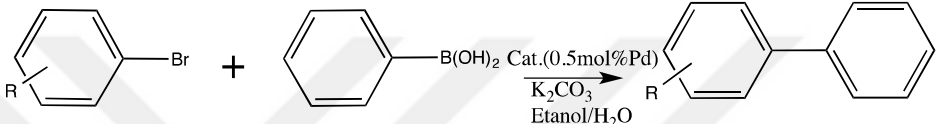
Entry	Catalyst	Base	Solvent	Time(h)	Yield ^a (%)
1	Cat. 1.	Na_2CO_3	Acetonitrile	8	72
2	Cat. 1.	Na_2CO_3	DMF	8	43
3	Cat. 1.	Na_2CO_3	1,4- dioxane	8	67
4	Cat. 1.	Na_2CO_3	Toluene	8	-
5	Cat. 1.	Na_2CO_3	NMP	8	79
6	Cat. 1.	Na_2CO_3	Etanol	8	91
7	Cat. 1.	K_2CO_3	Acetonitrile	8	78
8	Cat. 1.	K_2CO_3	DMF	8	53
9	Cat. 1.	K_2CO_3	1,4- dioxane	8	68
10	Cat. 1.	K_2CO_3	Toluene	8	5
11	Cat. 1.	K_2CO_3	NMP	8	81
12	Cat. 1.	K_2CO_3	Etanol	8	96
13	Cat. 1.	NaOAc	Acetonitrile	8	30
14	Cat. 1.	NaOAc	DMF	8	17
15	Cat. 1.	NaOAc	1,4- dioxane	8	27
16	Cat. 1.	NaOAc	Toluene	8	-
17	Cat. 1.	NaOAc	NMP	8	41
18	Cat. 1.	NaOAc	Etanol	8	53
19	Cat. 1.	Et_3N	Acetonitrile	8	14
20	Cat. 1.	Et_3N	DMF	8	7
21	Cat. 1.	Et_3N	1,4- dioxane	8	-
22	Cat. 1.	Et_3N	Toluene	8	-
23	Cat. 1.	Et_3N	NMP	8	21
24	Cat. 1.	Et_3N	Etanol	8	32

^a: conversion yields are based bromobenzene

3.5.2. Suzuki-Miyaura reactions of Arylbromide and arylchloride derivatives with phenylboronic acid

Following the optimization reactions, the catalytic performance of catalysts were tested over Suzuki-Miyaura reactions of wide variety of arylbromides and arylchlorides with phenylboronic acid and results given in table 3.7 and 3.8.

Table 3.7. Suzuki reactions of catalysts with arylbromide derivatives and phenylboronic acid



Entry	R	Cat.1	Cat.2	Cat.3	Cat.4	Cat.5	Cat.6
1	4-CH ₃	84 %	77%	74%	79%	61%	55%
2	1-naphth.	94%	91%	87%	87%	78%	75%
3	4-NO ₂	99%	99%	94%	93%	83%	77%
4	4-NH ₂	93%	92%	86%	88%	77%	71%
5	4-CHO	99%	97%	90%	91%	86%	75%
6	4-COCH ₃	99%	94%	91%	92%	87%	84%
7	2-OCH ₃	79%	77%	67%	69%	62%	58%
8	2-pry	58%	44%	39%	41%	27%	21%
9	4-OCH ₃	89%	85%	82%	83%	79%	74%

^a : Conditions: 0.1 mmol ArBr, 0.12 mmol PhB(OH)₂, 0.12 mmol base, catalyst / substrate ratio:1/200 (0,5 mol %Pd), 2.0 ml solvent / water (1:1), 80°C, in air. 8 h

^b: conversion yields are based arylbromide derivatives

4. RESULTS AND DISCUSSION

First step of this thesis, new Schiff base ligands and their palladium complexes were synthesized and characterized via elemental analysis, spectral analyses (FT-IR, ^1H NMR, ^{13}C NMR) and single crystal X-Ray crystallography for suitable compounds. In the FT-IR spectra of ligands, O-H, C-H_(aromatic), C-H_(aliphatic), C=C_(aromatic), C=N and C-F peaks were observed. The difference between the wavenumber of imine groups in infrared spectra of ligands and metal complexes give us useful information about the coordination between metal centre and ligand atoms. (Xavier *et al.*, 2015) Furthermore, the disappearance of O-H peak in metal complexes spectra showed that the metal atom completely coordinated over oxygen atom (Tajuddin *et al.*, 2012) In the NMR spectra of compounds, chemical shifts and peak areas gave us significant information about the structure. Furthermore, in ^1H NMR spectra of complexes imine group proton's shifted to the lower value due to complexation with metal centre.

In the second step, the solubility of synthesized palladium complexes (precursor) were measured in scCO_2 and determined quantitatively using UV-Vis spectroscopy. Then, palladium complexes used as precursor at supercritical carbon dioxide(scCO_2) deposition process. Mesoporous silica derivative SBA-15 was chosen as support material due to its higher surface area, chemical and thermal stability. The obtained SBA-15 supported palladium nanoparticles were analyzed using ICP-OES, XRD, FE-SEM with EDX application and TEM. ICP-OES was used to determine % palladium content on SBA-15, From XRD measurements the average particle size was calculated by using Scherer equation. FE-SEM and TEM were used to determine the distribution on SBA-15.

For determination catalytic activity of SBA-15 supported palladium nanoparticles, Suzuki-Miyaura C-C cross coupling reaction was elected as target reaction. The conversion yield of the biphenyl products were determined by gas chromatography (GC).

All of the spectra, data and images that illustrated with ligands, metal complexes and supported metal nanoparticles are given in the appendix.

4.1 Characterization of Ligands

The Schiff base ligands were synthesized without difficulty and generally in good yields. The spectral data that collected matched with expected data based on publication for similar molecules. The synthesis of all Schiff base ligands were reported for the first time. Elemental analysis, FT-IR, ^1H NMR and ^{13}C NMR were used to characterize synthesized ligands.

All of the Schiff base ligands are stable at room temperature and soluble in common solvents; ethanol, methanol, chloroform, 1,4-dioxane, DMSO and acetonitrile.

4.1.1. Characterization of FSB-1

Differential scanning calorimetry (DSC) was used to investigate thermal behaviour of compounds. According to results that obtained, FSB-1 melting point determined as; 128.26°C . Elemental analysis result matched with theoretical data.

In the FT-IR spectrum of FSB-1, a sharp band was appeared at 3444 cm^{-1} and demonstrated the phenolic group $\nu(\text{OH})$ vibration. The characteristic peak for the imine formation is the $\nu(\text{C}=\text{N})$ vibration and observed at 1626 cm^{-1} . The other peaks that observed in spectrum, $\nu(\text{C}-\text{H}_{\text{aromatic}})$ 3100 cm^{-1} , $\nu(\text{C}-\text{H}_{\text{aliphatic}})$ 2870 cm^{-1} , $\nu(\text{C}=\text{C}_{\text{aromatic}})$ 1480 cm^{-1} , $\nu(\text{C}-\text{F})$ $1240, 1170\text{ cm}^{-1}$.

In the ^1H NMR Spectrum of FSB1, singlet signal that observed at 2.38 ppm illustrated with methyl group's protons. Multiplet signal was observed between 6.77-7.50 ppm which is illustrated with aromatic protons. Singlet signal was observed at 8.65 ppm and showed characteristic peak for schiff base formation. Singlet signal was observed at 12.69 ppm and illustrated with phenolic O-H group proton.

Total number of carbon atoms in ^{13}C NMR spectrum matched with total carbon atoms in the structure. Peaks in the spectrum; 22.00 (CH_3), 116.62-138 (Ar-C), 125.23 ($\text{C}-\text{F}_{\text{CF}_3}$), 145.99 (C-F), 161.39 ($\text{HO}-\text{C}(\text{Ar})$), 166.03 ($\text{HC}=\text{N}$), ppm.

4.1.2. Characterization of FSB-2

Differential scanning calorimetry (DSC) was used to investigate thermal behaviour of compounds. According to results that obtained, FSB-2 melting point determined as; 109.9 °C. Elemental analysis result compatible with theoretical data.

In the FT-IR spectrum of FSB-2, wide band at 3422 cm⁻¹ showed the phenolic group $\nu(\text{OH})$ vibration. The characteristic peak for the imine formation is the $\nu(\text{C}=\text{N})$ vibration and observed at 1630.20 cm⁻¹. The other peaks in spectrum are $\nu(\text{C}-\text{H}_{\text{aromatic}})$ 3080 cm⁻¹, $\nu(\text{C}-\text{H}_{\text{aliphatic}})$ 2921 cm⁻¹, $\nu(\text{C}=\text{C}_{\text{aromatic}})$ 1496 cm⁻¹, $\nu(\text{C}-\text{F})$ 1231, 1171 cm⁻¹.

In the ¹H NMR Spectrum of FSB-2, the main evidence for schiff base (imine) formation is the singlet signal that observed at 9.01 ppm. singlet signal at 2.29 ppm demonstrated the methyl group's protons. Multiplet signal was observed between 6.90-7.88 ppm which is illustrated with aromatic protons. Phenolic O-H group proton was observed as a singlet at 12.23 ppm.

Total number of carbon atoms in ¹³C NMR spectrum matched with total carbon atom. Peaks in the spectrum; 21.46 (CH₃), 113-140 (Ar-C), 132.06 (CF₃), 153.58 (C-F), 160.50 (HO-C(Ar)), 166.27 (HC=N), ppm.

4.1.3. Characterization of FSB-3

Differential scanning calorimetry (DSC) was used to investigate thermal behaviour of compounds. According to results that obtained, FSB-3 melting point determined as; 147.12 °C. Elemental analysis result matched with theoretical data.

In the FT-IR spectrum of FSB-3, a sharp band was appeared at 3416 cm⁻¹ and demonstrated the phenolic group $\nu(\text{OH})$ vibration. The characteristic peak for the imine formation is the $\nu(\text{C}=\text{N})$ vibration that observed at 1614 cm⁻¹. The other peaks that observed in spectrum, $\nu(\text{C}-\text{H}_{\text{aromatic}})$ 3090 cm⁻¹, $\nu(\text{C}-\text{H}_{\text{aliphatic}})$ 2924 cm⁻¹, $\nu(\text{C}=\text{C}_{\text{aromatic}})$ 1496 cm⁻¹, $\nu(\text{C}-\text{F})$ 1275, 1171 cm⁻¹.

In the ¹H NMR Spectrum of FSB-3, singlet signal that observed at 2.34 ppm illustrated with methyl group's protons. Multiplet signal was observed between 6.83-

7.82 ppm which is illustrated with aromatic protons. Singlet signal was observed at 9.02 ppm and showed characteristic peak for schiff base formation. Singlet signal that observed at 12.54 ppm and illustrated with phenolic O-H group proton.

Total number of carbon atoms in ^{13}C NMR spectrum matched with structure and the peaks in the spectrum demonstrated; 22.00 (CH_3), 116.62-138 (Ar-C), 125.23 (C-F_{CF_3}), 145.99 (C-F), 161.39 (HO-C(Ar)), 166.03 (HC=N), ppm.

4.1.4. Characterization of FSB-4

Differential scanning calorimetry (DSC) was used to investigate thermal behaviour of compounds. According to results that obtained, FSB-4, melting point determined as; 116.12 °C. Elemental analysis result compatible with theoretical data.

In the FT-IR spectrum of FSB-4, wide band at 3419 cm^{-1} showed the phenolic group $\nu(\text{OH})$ vibration. The characteristic peak for the imine formation is the $\nu(\text{C=N})$ vibration and observed at 1617 cm^{-1} . The other peaks in spectrum are $\nu(\text{C-H}_{\text{aromatic}})$ 3060 cm^{-1} , $\nu(\text{C-H}_{\text{aliphatic}})$ 2927 cm^{-1} , $\nu(\text{C=C}_{\text{aromatic}})$ 1487 cm^{-1} , $\nu(\text{C-F})$ 1228, 1170 cm^{-1} .

In the ^1H NMR Spectrum of FSB-4, the main evidence for schiff base (imine) formation is the singlet signal that observed at 8.99 ppm. singlet signal at 2.28 ppm demonstrated the methyl group's protons. Multiplet signal was observed between 6.90-7.81 ppm which is illustrated with aromatic protons. Phenolic O-H group proton was observed as a singlet at 12.18 ppm.

Total number of carbon atoms in ^{13}C NMR spectrum matched with total carbon atom. Peaks in the spectrum; 19.83 (CH_3), 113.68-140 (Ar-C), 131.98 (CF_3), 153.52 (C-F), 158.25 (HO-C(Ar)), 166.26(HC=N), ppm.

4.1.5. Characterization of FSB-5

Differential scanning calorimetry (DSC) was used to investigate thermal behaviour of compounds. According to results that obtained, FSB-5 melting point determined as; 100.7 °C.

Elemental analysis result compatible with theoretical data. In the FT-IR spectrum of FSB-5, wide band at 3420 cm^{-1} showed the phenolic group $\nu(\text{OH})$ vibration. The characteristic peak for the imine formation is the $\nu(\text{C}=\text{N})$ vibration and observed at 1621 cm^{-1} . The other peaks in spectrum are $\nu(\text{C-H}_{\text{aromatic}})$ 3020 cm^{-1} , $\nu(\text{C-H}_{\text{aliphatic}})$ 2927 cm^{-1} , $\nu(\text{C}=\text{C}_{\text{aromatic}})$ 1487 cm^{-1} , $\nu(\text{C-F})$ $1228, 1170\text{ cm}^{-1}$.

In the ^1H NMR Spectrum of FSB-5, the main evidence for schiff base (imine) formation is the singlet signal that observed at 8.58 ppm. singlet signal at 2.24 ppm demonstrated the methyl group's protons. Multiplet signal was observed between 6.69-7.45 ppm which is illustrated with aromatic protons. Phenolic O-H group proton was observed as a singlet at 12.62 ppm.

Total number of carbon atoms in ^{13}C NMR spectrum matched with total carbon atom. Peaks in the spectrum; 21.91 (CH_3), 116-137 (Ar-C), 132.31 (CF_3), 145.71 (C-F), 161.44 ($\text{HO-C}(\text{Ar})$), 166.49 ($\text{HC}=\text{N}$), ppm.

4.1.6. Characterization of FSB-6

Differential scanning calorimetry (DSC) was used to investigate thermal behaviour of compounds. According to results that obtained, FSB-6 melting point determined as; 92.3°C .

Elemental analysis result was matched with theoretical data. In the FT-IR spectrum of FSB-6, a sharp band was appeared at 3416 cm^{-1} and demonstrated the phenolic group $\nu(\text{OH})$ vibration. The characteristic peak for the imine formation is the $\nu(\text{C}=\text{N})$ vibration was observed at 1614 cm^{-1} . The other peaks that observed in spectrum, $\nu(\text{C-H}_{\text{aromatic}})$ 3018 cm^{-1} , $\nu(\text{C-H}_{\text{aliphatic}})$ 2920 cm^{-1} , $\nu(\text{C}=\text{C}_{\text{aromatic}})$ 1504 cm^{-1} , $\nu(\text{C-F})$ $1273, 1171\text{ cm}^{-1}$.

In the ^1H NMR Spectrum of FSB1, singlet signal that observed at 2.31 ppm illustrated with methyl group's protons. Multiplet signal was observed between 6.72-7.46 ppm which is illustrated with aromatic protons. Singlet signal was observed at 8.60 ppm and showed characteristic peak for schiff base formation. Singlet signal was observed at 12.63 ppm and illustrated with phenolic O-H group proton.

Total number of carbon atoms in ^{13}C NMR spectrum matched with structure and the peaks in the spectrum demonstrated; 21.98 (CH_3), 116.64-137.36 (Ar-C), 132.70 (CF_3), 145.71(C-F), 161.44 (HO-C(Ar)), 165.72 ($\text{HC}=\text{N}$), ppm.

4.2. Characterization of Complexes

Schiff base palladium complexes were synthesized via similar method in literature (Tajuddin *et. al*,2012). The spectral data that collected matched with expected data based on publication for similar molecules. All of the complexes were reported for the first time. Elemental analysis, FT-IR, ^1H NMR and ^{13}C NMR were used to characterize the obtained palladium complexes.

4.2.1. Characterization of $\text{Pd}(\text{FSB-1})_2 \cdot \text{K1}$

Differential scanning calorimetry (DSC) was used to investigate thermal behaviour of compounds. According to results that obtained, $\text{Pd}(\text{FSB-1})_2$ melting point determined as; 297.39 $^\circ\text{C}$. Elemental analysis that found matched with calculated data.

In the FT-IR spectrum of FSB-1, vibrations of the imine ($\text{C}=\text{N}$) group was observed at 1626 cm^{-1} . This value shifted to lower wavenumber in the complex spectrum and appeared at 1597.42 cm^{-1} . This shift could be attributed to decreasing strength of the M–N bonds on adduct formation, due to donation of electrons from the nitrogen atom to the empty d-orbitals of the metal atom. On the other hand, in the FT-IR spectrum of ligands exhibited a wide band, that appeared at 3404 cm^{-1} is the characteristic peaks of O-H vibration of phenolic group. (Abu-Dief and Mohammed, 2015). It should be noted that phenolic O-H peak disappeared due to the new bond forming between phenolic oxygen and metal centre. The phenolic protons were replaced by Pd^{2+} cations and new band appeared at 560 cm^{-1} , this situation is the proof of Pd-O bonding, thus formation of Palladium-Schiff base complexes. The other proof of for the complex formation is the new band around $\sim 469 \text{ cm}^{-1}$ which was demonstrated Pd-N.

^1H NMR spectrum of K1 may differ from those of ligand and the most remarkable change is the shifted to lower fields. The signal for the imine proton in the spectrum of FSB-1 appear at 8.65 ppm, upon the complexion with palladium metal centre imine (H-C=N), this value shifted to 7.59 ppm. On the other hand, phenolic O-H proton that appear at 12.69 ppm in ligand (FSB-1) spectrum, was disappeared in K1 complex indicated that the hydroxyl group are fully deprotonated and the oxygen atoms are most likely coordinated to the metal ion.

4.2.2. Characterization of $\text{Pd}(\text{FSB-2})_2$, K2

Differential scanning calorimetry (DSC) was used to investigate thermal behaviour of compounds. According to results that obtained, $\text{Pd}(\text{FSB-2})_2$ melting point determined as; 346.70 °C. Elemental analysis that found matched with calculated data.

In the FT-IR spectrum of FSB-2, vibrations of the imine (C=N) group was observed at 1630.20 cm^{-1} . This value shifted to lower wavenumber in the complex spectrum and appeared at 1597.54 cm^{-1} . This shift could be attributed to decreasing strength of the Pd–N bonds on adduct formation, due to donation of electrons from the nitrogen atom to the empty d-orbitals of the metal atom. On the other hand, in the FT-IR spectrum of ligands exhibited a wide band, that appeared at 3422 cm^{-1} is the characteristic peaks of O-H vibration of phenolic group. It should be noted that phenolic O-H peak disappeared due to the new bond forming between phenolic oxygen and metal centre. The phenolic protons were replaced by Pd^{2+} cations and new band appeared at 554 cm^{-1} , this situation is the proof of Pd-O bonding, thus formation of Palladium-Schiff base complexes. The other proof of for the complex formation is the new band around $\sim 469 \text{ cm}^{-1}$ which was demonstrated Pd-N.

^1H NMR spectrum of K2 may differ from those of ligand and the most remarkable change is the shifted to lower fields. The signal for the imine proton in the spectrum of FSB-2 appear at 9.01 ppm, upon the complexion with palladium metal centre imine (H-C=N), this value shifted to 7.66 ppm. On the other hand, phenolic O-H proton that appear at 12.23 ppm in ligand (FSB-2) spectrum, was

disappeared in K2 complex indicated that the hydroxyl group are fully deprotonated and the oxygen atoms are most likely coordinated to the metal ion.

4.2.3. Characterization of Pd(FSB-3)₂, K3

Differential scanning calorimetry (DSC) was used to investigate thermal behaviour of compounds. According to results that obtained, Pd(FSB-3)₂ melting point determined as; 264.01 °C. Elemental analysis that found matched with calculated data.

In the FT-IR spectrum of FSB-3, vibrations of the imine (C=N) group was observed at 1614 cm⁻¹. This value shifted to lower wavenumber in the complex spectrum and appeared at 1611 cm⁻¹. This shift could be attributed to decreasing strength of the Pd–N bonds on adduct formation, due to donation of electrons from the nitrogen atom to the empty d-orbitals of the metal atom. On the other hand, in the FT-IR spectrum of ligands exhibited a wide band, that appeared at 3416 cm⁻¹ is the characteristic peaks of O-H vibration of phenolic group. It should be noted that phenolic O-H peak disappeared due to the new bond forming between phenolic oxygen and metal centre. The phenolic protons were replaced by Pd²⁺ cations and new band appeared at 604 cm⁻¹, this situation is the proof of Pd-O bonding, thus formation of Palladium-Schiff base complexes . The other proof of for the complex formation is the new band around ~469 cm⁻¹ which was demonstrated Pd-N.

¹H NMR spectrum of K3 may differ from those of ligand and the most remarkable change is the shifted to lower fields. The signal for the imine proton in the spectrum of FSB-3 appear at 9.02 ppm, upon the complexion with palladium metal centre imine (H-C=N), this value shifted to 7.88 ppm. On the other hand, phenolic O-H proton that appear at 12.54 ppm in ligand (FSB-3) spectrum, was disappeared in K1 complex indicated that the hydroxyl group are fully deprotonated and the oxygen atoms are most likely coordinated to the metal ion.

4.2.4. Characterization of Pd(FSB-4)₂, K4

Differential scanning calorimetry (DSC) was used to investigate thermal behaviour of compounds. According to results that obtained, Pd(FSB-4)₂ melting point determined as; 260.83 °C. Elemental analysis that found matched with calculated data.

In the FT-IR spectrum of FSB-4, vibrations of the imine (C=N) group was observed at 1617 cm⁻¹. This value shifted to lower wavenumber in the complex spectrum and appeared at 1588.28 cm⁻¹. This shift could be attributed to decreasing strength of the Pd–N bonds on adduct formation, due to donation of electrons from the nitrogen atom to the empty d-orbitals of the metal atom. On the other hand, in the FT-IR spectrum of ligands exhibited a wide band, that appeared at 3419 cm⁻¹ is the characteristic peaks of O-H vibration of phenolic group. It should be noted that phenolic O-H peak disappeared due to the new bond forming between phenolic oxygen and metal centre. The phenolic protons were replaced by Pd²⁺ cations and new band appeared at 618 cm⁻¹, this situation is the proof of Pd-O bonding, thus formation of Palladium-Schiff base complexes. The other proof of for the complex formation is the new band around ~484 cm⁻¹ which was demonstrated Pd-N.

¹H NMR spectrum of K4 complex may differ from those of ligand and the most remarkable change is the shifted to lower fields. The signal for the imine proton in the spectrum of FSB-4 appear at 8.99 ppm, upon the complexion with palladium metal centre imine (H-C=N), this value shifted to 7.71 ppm. On the other hand, phenolic O-H proton that appear at 12.18 ppm in ligand (FSB-4) spectrum, was disappeared in K4 complex indicated that the hydroxyl group are fully deprotonated and the oxygen atoms are most likely coordinated to the metal ion.

4.2.5. Characterization of Pd(FSB-5)₂, K5

Differential scanning calorimetry (DSC) was used to investigate thermal behaviour of compounds. According to results that obtained, Pd(FSB-5)₂ melting

point determined as; 237.50 °C. Elemental analysis that found matched with calculated data.

In the FT-IR spectrum of FSB-5, vibrations of the imine (C=N) group was observed at 1621.07 cm⁻¹. This value shifted to lower wavenumber in the complex spectrum and appeared at 1578.23 cm⁻¹. This shift could be attributed to decreasing strength of the Pd-N bonds on adduct formation, due to donation of electrons from the nitrogen atom to the empty d-orbitals of the metal atom. On the other hand, in the FT-IR spectrum of ligands exhibited a wide band, that appeared at 3420 cm⁻¹ is the characteristic peaks of O-H vibration of phenolic group. It should be noted that phenolic O-H peak disappeared due to the new bond forming between phenolic oxygen and metal centre. The phenolic protons were replaced by Pd²⁺ cations and new band appeared at 592 cm⁻¹, this situation is the proof of Pd-O bonding, thus formation of Palladium-Schiff base complexes. The other proof of for the complex formation is the new band around ~466 cm⁻¹ which was demonstrated Pd-N.

¹H NMR spectrum of K5 may differ from those of ligand and the most remarkable change is the shifted to lower fields. The signal for the imine proton in the spectrum of FSB-5 appear at 8.58 ppm, upon the complexion with palladium metal centre imine (H-C=N), this value shifted to 7.58 ppm. On the other hand, phenolic O-H proton that appear at 12.62 ppm in ligand (FSB-5) spectrum, was disappeared in K5 complex indicated that the hydroxyl group are fully deprotonated and the oxygen atoms are most likely coordinated to the metal ion.

4.2.6. Characterization of Pd(FSB-6)₂, K6

Differential scanning calorimetry (DSC) was used to investigate thermal behaviour of compounds. According to results that obtained, Pd(FSB-6)₂ melting point determined as; 272.35 °C. Elemental analysis that found matched with calculated data.

In the FT-IR spectrum of FSB-6, vibrations of the imine (C=N) group was observed at 1624.90 cm⁻¹. This value shifted to lower wavenumber in the complex spectrum and appeared at 1577 cm⁻¹. This shift could be attributed to decreasing

strength of the M–N bonds on adduct formation, due to donation of electrons from the nitrogen atom to the empty d-orbitals of the metal atom. On the other hand, in the FT-IR spectrum of ligands exhibited a wide band, that appeared at 3447 cm^{-1} is the characteristic peaks of O-H vibration of phenolic group. It should be noted that phenolic O-H peak disappeared due to the new bond forming between phenolic oxygen and metal centre. The phenolic protons were replaced by Pd^{2+} cations and new band appeared at 642 cm^{-1} , this situation is the proof of Pd-O bonding, thus formation of Palladium-Schiff base complexes. The other proof of for the complex formation is the new band around $\sim 466\text{ cm}^{-1}$ which was demonstrated Pd-N.

^1H NMR spectrum of K6 may differ from those of ligand and the most remarkable change is the shifted to lower fields. The signal for the imine proton in the spectrum of FSB-6 appear at 8.60 ppm, upon the complexion with palladium metal centre imine (H-C=N), this value shifted to 7.65 ppm. On the other hand, phenolic O-H proton that appear at 12.63 ppm in ligand (FSB-6) spectrum, was disappeared in K6 complex indicated that the hydroxyl group are fully deprotonated and the oxygen atoms are most likely coordinated to the metal ion.

4.3. Single Crystal X-Ray diffraction analyses of compounds

Suitable crystals of FSB-1 and its Pd complex were selected for data collection, which was performed on a D8-QUEST diffractometer equipped with a graphite-monochromatic Mo-K_α radiation at 296 K. Structures were evaluated by direct methods using SHELXS-97 (Sheldrick *et al.*, 2008) and refined by full-matrix least-squares methods on F^2 using SHELXL-2013 (Sheldrick *et al.*, 2015) from within the WINGX (Farugia *et al.*, 1999) suite of software. All non-hydrogen atoms were refined with anisotropic parameters. The H atoms were located from different maps and then treated as riding atoms with C-H distance of 0.93-0.96 Å and O-H distance of 0.82 Å. Molecular diagrams were created using MERCURY. Supramolecular analyses were conducted and the diagrams were prepared with the aid of PLATON. Details of data collection and crystal structure determinations are given in Table 4.1.

Compounds FSB1 and K1: The molecular structures of FSB1 and K1, with the atom numbering schemes, are shown in Figs. 4.2 and 4.3. The X-ray single crystal study shows that compound FSB1 adopts the phenol-imine tautomeric form. In the case of structure K1, the Pd(II) ion is located on a centre of symmetry and is coordination by two oxygen (O1 and O1ⁱ) and two nitrogen (N1 and N1ⁱ) atoms, thus showing a distorted square planar coordination geometry [(i) 1-x, 1-y, 1-z]. The N=C bond distance is 1.280 (3) Å in **1** and 1.278 (12) Å in Pd(FSB-1)₂, respectively. The dihedral angle between phenyl rings is 12.45 (15)° in FSB-1 and 43.39 (37)° in K1. The molecules of FSB-1 are connected by C-H... π interactions (Table 4.6), while the molecules of K1, are connected by C-H...Pd interactions. For the structure FSB-1, atom C7 in the molecule at (x, y, z) acts as hydrogen-bond donors to the C1-C6 phenyl ring in the molecule at (x-1, y, z), so forming a C(4) chain which is running parallel to the [100] direction (Fig. 4.1). The most striking feature of K1 is the presence of the intermolecular C-H...Pd interaction: Pd1...H2=2.939(2) Å, Pd1...C2=3.589(3) Å and C2-H2...Pd1=128°.

Table 4.1. Crystal data and structure refinement parameters for FSB1- K1.

Crystal data	FSB1	K1
Empirical formula	C ₁₅ H ₁₁ F ₄ NO	C ₃₀ H ₂₀ F ₈ N ₂ O ₂ Pd
Formula weight	297.25	698.88
Crystal system	Orthorhombic	Monoclinic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c
<i>a</i> (Å)	4.8731 (5)	12.863 (4)
<i>b</i> (Å)	12.5673 (14)	11.003 (3)
<i>c</i> (Å)	22.266 (3)	10.024 (3)
β (°)	90.00	96.18 (1)
<i>V</i> (Å ³)	1338.4 (3)	1410.4 (7)
<i>Z</i>	4	2
<i>D_c</i> (g cm ⁻³)	1.475	1.646
μ (mm ⁻¹)	0.13	0.74
θ range (°)	3.2-24.3	3.1-28.3
Measured refls.	24381	34753
Independent refls.	3287	3527
<i>R</i> _{int}	0.064	0.086
<i>S</i>	1.03	1.23
<i>R</i> ₁ / <i>wR</i> ₂	0.046/0.106	0.121/0.259

Table 4.2. Selected bond distances and angles for FSB1- K1 (Å, °)

FSB1			
N1-C8	1.280 (3)		
C9-N1-C8-C1	-179.2 (2)		
Pd(FSB-1) ₂			
C8-N1	1.278 (12)	Pd1-O1	1.989 (7)
Pd1-N1	2.037 (7)		
O1-Pd1-N1	91.0 (3)	C1-C8-N1-C9	-179.0 (9)

Table 4.3. Hydrogen bonds and C-H... π interaction parameters for FSB1 (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A
O1—H1...N1	0.82	1.89	2.618 (3)	147
C7-H7C...Cg(1) ⁱ	0.96	2.81	3.583 (4)	138

Symmetry code: (i) x-1, y, z; Cg(1)=C1-C6.

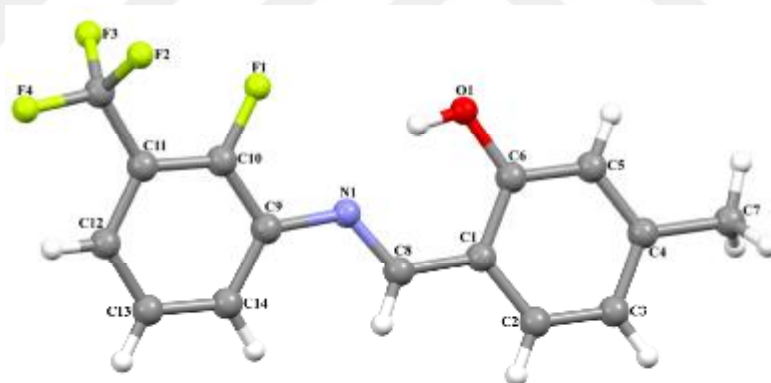


Fig. 4.1. The molecular structure of FSB-1 showing the atom numbering scheme.

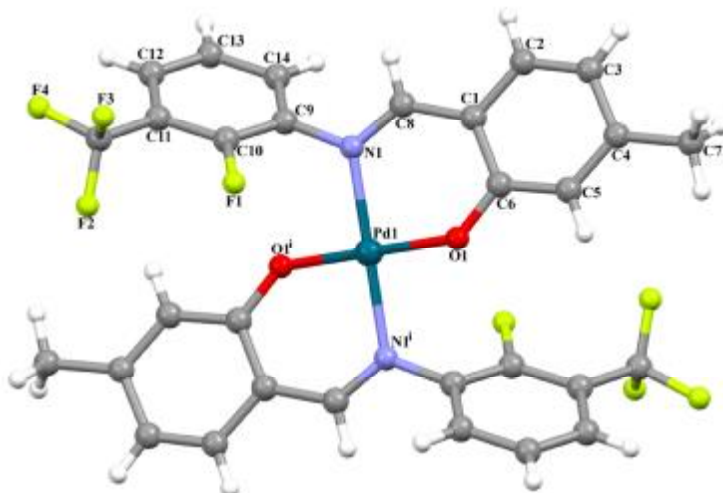


Fig. 4.2. The molecular structure of K1 showing the atom numbering scheme.

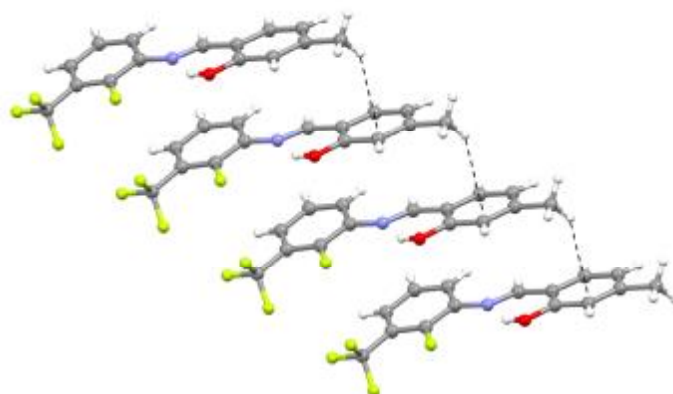


Fig. 4.3. Crystal structure of FSB-1, showing the formation of a chain along [100] generated by C-H... π interactions

4.4. Determination of Complexes (Precursor) Solubility in scCO_2

It has been known that, precursor solubility has essential role at deposition process. According to literature data, due to the higher solubility values of fluorinated complexes in scCO_2 (Erkey, 2012), palladium complexes of Schiff base derivatives has been chosen as precursor for deposition process.

The solubility behaviours of all the complexes in scCO_2 were determined under a pressure range of 2000, 2500 and 3000 psi and 90 °C by UV-Vis spectroscopy.

Table 4.4. Solubility of metal complexes in scCO₂ (mol/ mol CO₂)

	2000 psi	2500 psi	3000 psi
K1	3.16 x10 ⁻⁵	3,41 x10 ⁻⁵	5,06 x10 ⁻⁵
K2	2,64 x10 ⁻⁵	2,78 x10 ⁻⁵	3.94 x10 ⁻⁵
K3	2.85 x10 ⁻⁵	3,23 x10 ⁻⁵	3.89 x10 ⁻⁵
K4	2,46 x10 ⁻⁵	2,87 x10 ⁻⁵	3,05 x10 ⁻⁵
K5	4.58 x 10 ⁻⁵	4.65 x 10 ⁻⁵	5.71 x 10 ⁻⁵
K6	4,33 x 10 ⁻⁵	4,45 x 10 ⁻⁵	5,66 x 10 ⁻⁵

As shown in table 4.9., solubility values for K3 and K4 complexes slightly lower than the other complexes. This situation is related with the *para*- position of -CF₃ group on the structure. Due to the *para*-position, the solubility of these complexes affected by stability and higher stability may cause lower solubility behaviours.

4.5. Deposition of Metal Complexes (Precursor) on Mesoporous Silica Derivative SBA-15 in scCO₂

K1-K6 complexes were used as precursor as include theoretically %10 or %5 Pd to prepare SBA-15 supported palladium nanoparticles via supercritical fluid deposition method in scCO₂. The obtained SBA-15 supported palladium nanoparticles named as Cat. 1, Cat. 2 , Cat. 3, Cat. 4, Cat. 5 and Cat. 6 for derived from the deposition process of Pd(FSB-1)₂ - Pd(FSB-6)₂ on SBA-15, respectively. Their characterization were realized by ICP-OES, XRD, SEM-EDX and TEM to determine the distribution of particles, particle size and the amount of metal percentage.

4.6. Characterization of SBA-15 Supported Metal Nanoparticles

ICP-OES, XRD, SEM-EDX and TEM were used to characterized SBA-15 supported palladium nanoparticles. ICP-OES analysis were carried out by Perkin

Elmer 2100 DV and were used to determine the percentage of impregnated palladium nanoparticles on SBA-15 surface.

XRD analysis were carried out by Rigaku Miniflex CuK α , $\lambda=0.154\text{nm}$. XRD measurements carried out with 2θ angle and scanning with a range of 10-80. XRD patterns were interpreted by using JCPDS (Joint Committee on Powder Diffraction Standarts) database (*pd card no: 01-089-4897*) (Morero *et al.*, 2011). TEM images were collected via Jeol JEM 1400 Plus 120kV and FE-SEM images were obtained via Zeiss Supra 55 VP.

4.6.1 Characterization Cat. 1

The Pd content of the SBA-15 supported palladium nanoparticles was measured by ICP-OES as % 2.79 for % 10 Pd and % 0.95 for % 5 Pd.

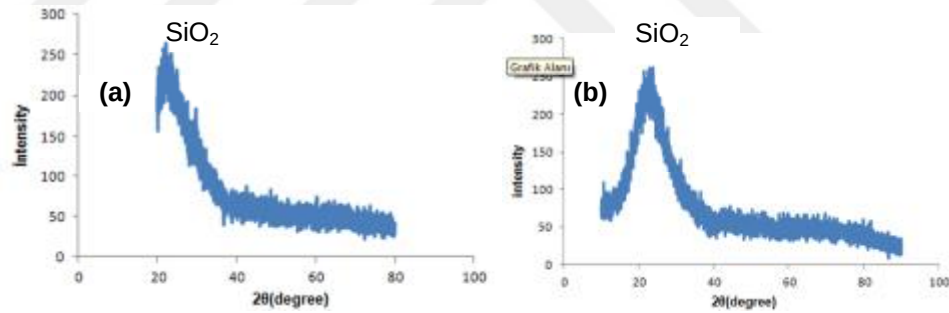


Figure 4.4. XRD pattern of SBA-15 (without Pd nanoparticles) (a) measurement between 20-80 degree (b) measurement between 10-90 degree.

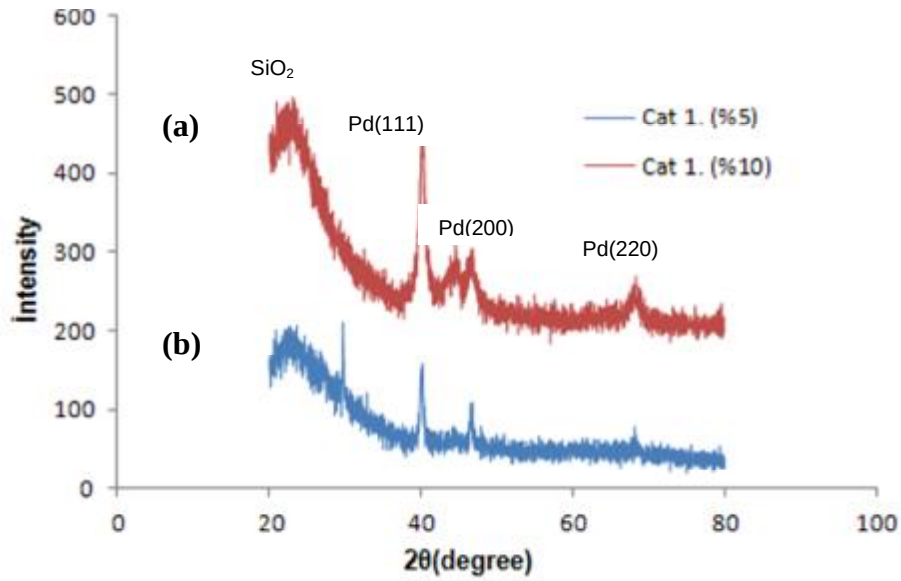


Figure 4.5. XRD pattern of Cat.1 (a) % 10 Pd (b) % 5 Pd

Figure 4.5. show the XRD pattern of Cat. 1 . The Characteristic peaks for SBA-15 supported palladium nanoparticles were observed at 22.19° , 40.19° , 44.20° , 68.24° that corresponding to the SiO_2 , Pd(111), Pd(200) and Pd(220), respectively. These values are in agreement with literature data. The average particle size for the palladium nanoparticles was calculated by applying the Scherrer equation to the Pd(111) peak at 40.19° to estimate the crystallite size. Average crystallite sizes were calculated as 9.7 nm(%10 Pd) and 6.5 nm (%5 Pd).

A typical FE-SEM image of the SBA-15(without Pd nanoparticles) Cat. 1 with % 10 Pd and % 5 Pd were given in figure 4.6, 4.7 and 4.8 , respectively. In comparison SEM image of SBA-15 and the material with palladium nanoparticles prepared in scCO_2 , there is not significant change in the macrostructure of the support after the deposition process. The presence of metallic palladium nanoparticles in the catalyst was confirmed via EDX-point analysis and the image for the distribution of palladium nanoparticles on support surface was performed by EDX-mapping analysis

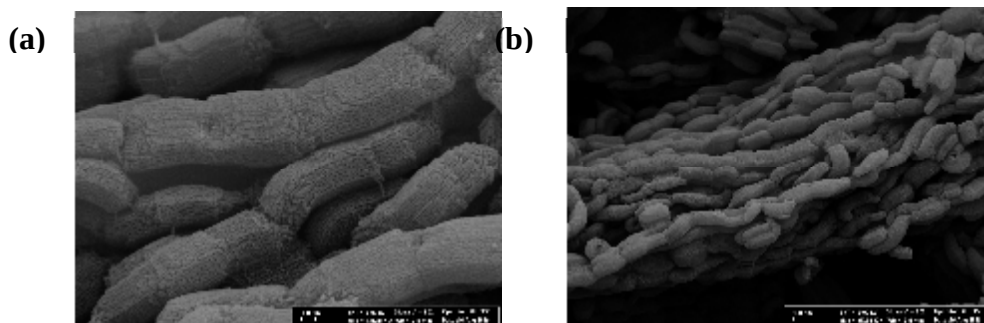


Figure 4.6. FE-SEM micrograph of SBA-15 (a) 100kx (b) 50 kx

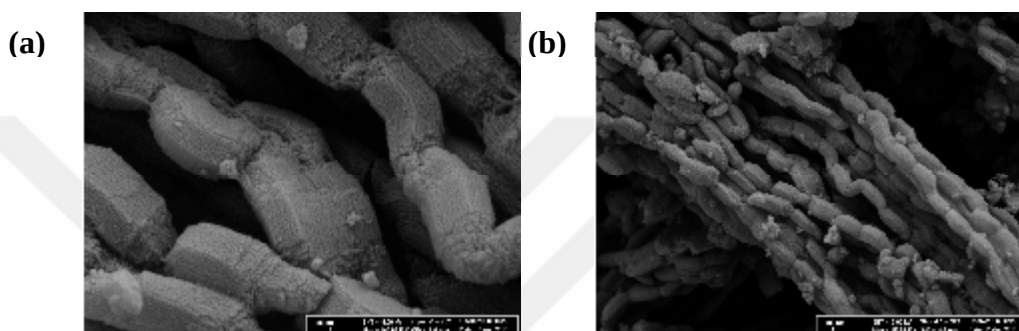


Figure 4.7. FE-SEM micrograph of Cat. 1 with % 10 Pd (a) 100 kx (b) 50 kx

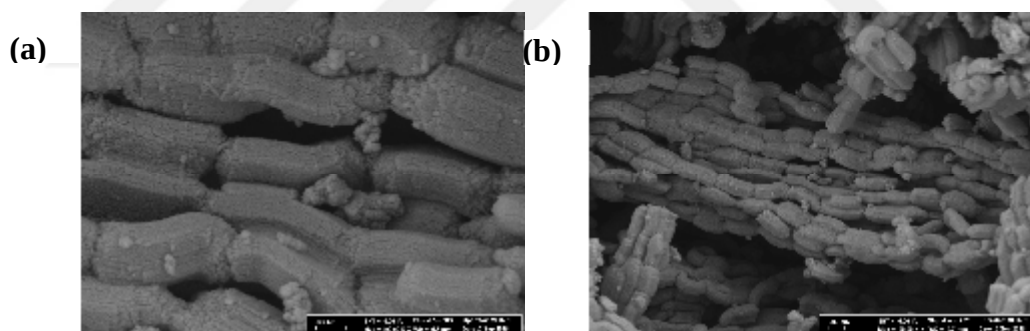


Figure 4.8. FE-SEM micrograph of Cat. 1 with % 5 Pd (a) 100 kx (b) 50 kx

Mapping spectrum of the cat. 1, showed the distribution of palladium nanoparticles on the support surface with a size range of 10-20 nm. As shown in fig. 4.9. a and 4.10 a. Palladium nanoparticles were deposited uniformly on SBA-15 without agglomeration. The percentages of Pd nanoparticles were calculated from point spectrum as 2.74 and 0.80 % . The percentage of Pd nanoparticles that calculated via ICP-OES may differ from that calculated by EDX- Point application. Because, EDX-Point data are local measurements and give the metal content of only special area that selected while, ICP-OES data show that the average amount of Pd deposited onto support material. The agreement of Pd content that obtained both

EDX and ICP-OES have been showed that the palladium nanoparticles deposited homogenously on SBA-15. (Morero *et al.*, 2011 and Erkey *et al.*, 2009).

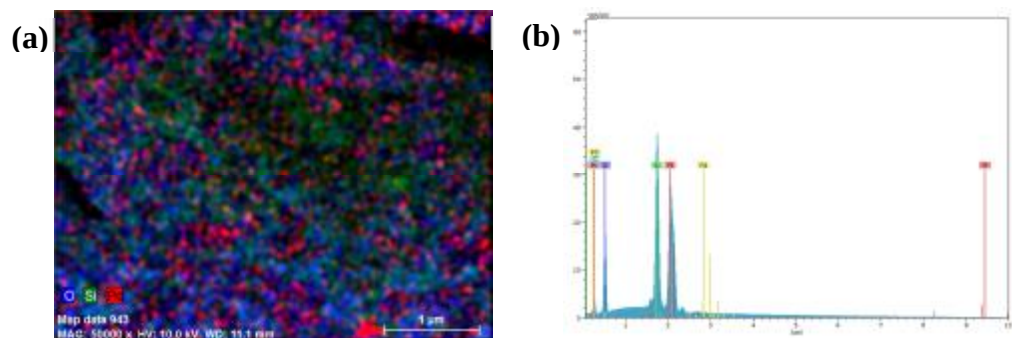


Figure 4.9. EDX Spectrum of Cat. 1 with %10 Pd content (a) mapping spectrum (b) point spectrum

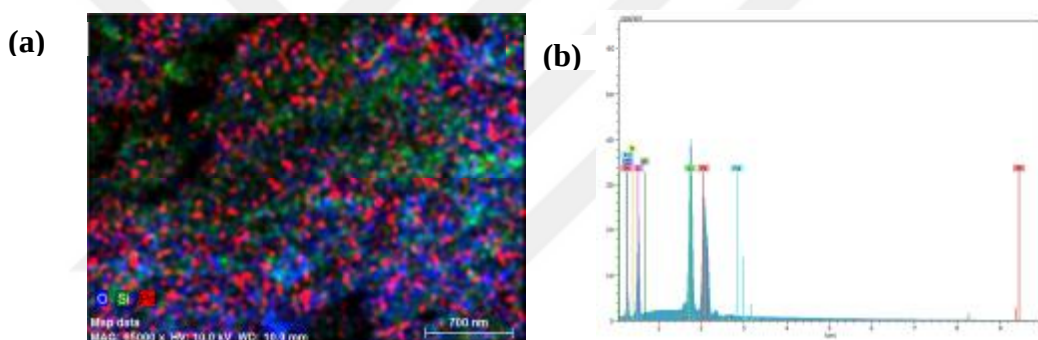


Figure 4.10. EDX Spectrum of Cat. 1 with %5 Pd (a) mapping spectrum (b) point spectrum

TEM micrographs of the Pd/SBA-15 (Cat.1) are shown in fig. 4.11. TEM images Show the presence of nanoparticles on SBA-15: (i) as spherical spots on the outer surface of SBA-15, (ii) as dark lines following the porous structure. As shown in fig. 4.11, palladium nanoparticles evenly distributed on SBA-15 surface. Due to movement of image while TEM analysis was performed, the some of palladium nanoparticles on surface were shown as extended spot.

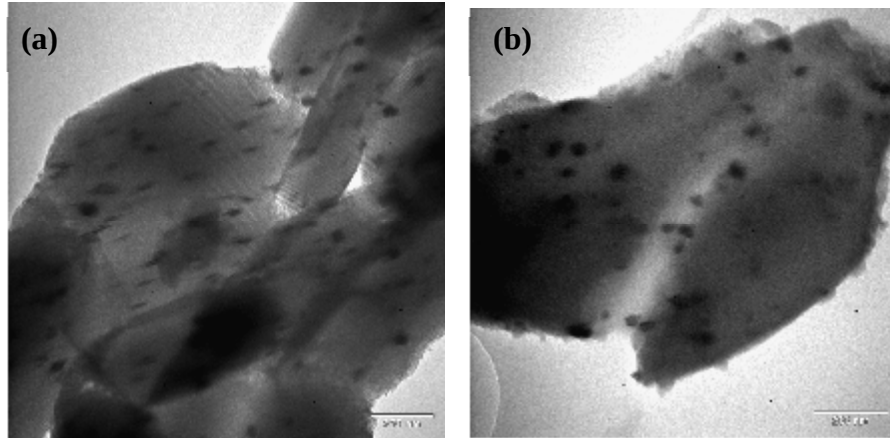


Figure 4.11. TEM micrographs of Cat. 1 with % 10 Pd (a) 250 nm (b) 200 nm

4.6.2 Characterization of Cat. 2

The Pd content of the SBA-15 supported palladium nanoparticles was measured by ICP-OES as % 6.56 for % 10 Pd and % 1.89 for % 5 Pd.

Figure 4.9. shows the XRD pattern of Pd/SBA-15 (cat. 2). The characteristic peaks for SBA-15 supported palladium nanoparticles were observed at 40.27° , 46.64° , 68.09° that corresponding to the Pd(111), Pd(200) and Pd(220), respectively. These values are in agreement with literature data. (Bozbag and Erkey, 2012). The average particle sizes for the palladium nanoparticles were calculated by applying the Scherrer equation to the Pd(111) peak at 46.64° to estimate the crystallite size. Average crystallite sizes were determined as 17.3 and 6.98 nm.

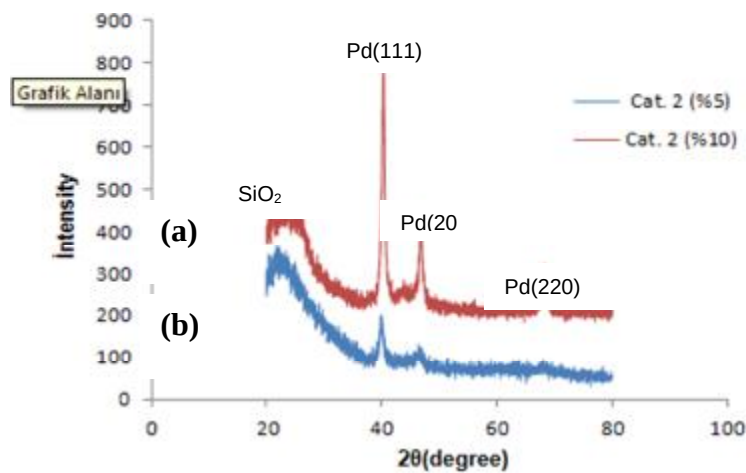


Figure 4.12. XRD pattern of Cat.2 (a) %10 Pd (b) %5 Pd

FE-SEM micrograph of the Pd⁰/SBA-15 catalyst shown in figure 4.13 and 4.14 as 100kx and 50kx magnification, respectively. From SEM images, The presence of metallic palladium nanoparticles on SBA-15 was observed clearly.

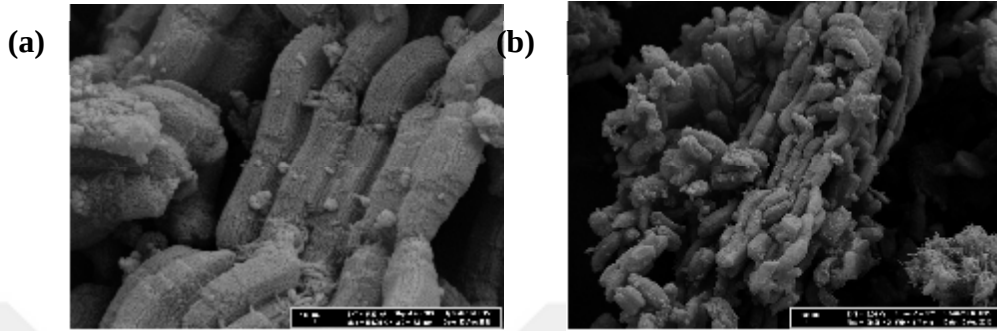


Figure 4.13. FE-SEM micrograph of Cat. 2 with % 10 Pd (a) 100 kx (b) 50 kx

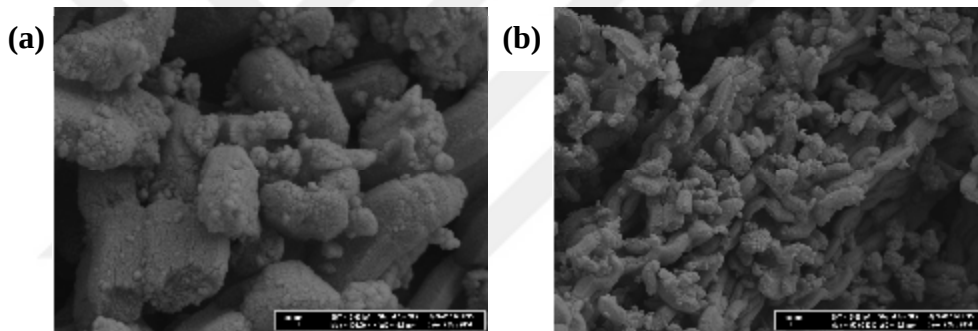


Figure 4.14. FE-SEM micrograph of Cat. 2 with % 5 Pd (a) 100 kx (b) 50 kx

Mapping spectrum of the cat. 2, showed the distribution of palladium nanoparticles on the support surface with uniformly size. As shown in fig. 4.15. a and 4.16 a, palladium nanoparticles were distributed homogeneously on SBA-15 without agglomeration. In the point spectrum of the cat.2, % percentage of elements on SBA-15 were shown. The percentages of Pd nanoparticles were calculated via EDX- point spectrum as 4.02 and 1.44 % . The percentage of Pd nanoparticles that calculated via ICP-OES may differ from that calculated by EDX-Point application. Because, EDX-Point data are local measurements and give the metal content of volume-based area whereas ICP-OES data show the average amount of Pd that deposited onto the SBA-15. The metal loading has an influence on particle size. The mean particle size increasing with increasing metal content. (Bozbag and Erkey, 2012). According to literature, particle size of palladium

nanoparticles increased due to higher amount of palladium content on SBA-15 surface.

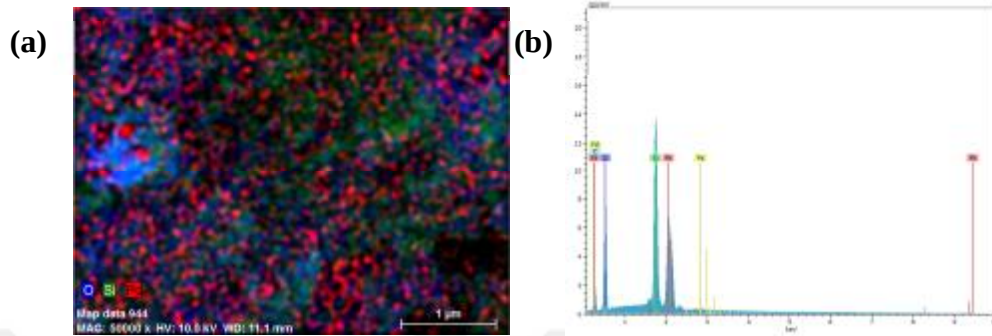


Figure 4.15. EDX Spectrum of Cat. 2 with %10 Pd (a) mapping spectrum (b) point spectrum

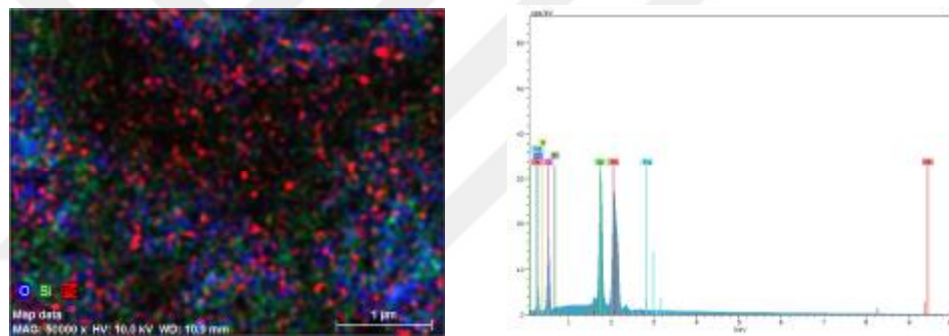


Figure 4.16. EDX Spectrum of Cat. 2 with %5 Pd (a) mapping spectrum (b) point spectrum

TEM micrographs of the Pd/SBA-15 (Cat.2) are shown in fig. 4.12. TEM images Show the distrubution of nanoparticles on SBA-15: (i) as spherical spots on the outer surface of SBA-15, (ii) as dark lines following the porous structure. As shown in fig. 4.17. palladium nanoparticles distrubuted on SBA-15 surface with 20-25 nm. Difference between the average particle sizes obtained from TEM and XRD micrographs was occurred. XRD measurements gives number-weighted value whereas TEM micrographs gives a volume-weighted value (Bozbag and Erkey, 2012).

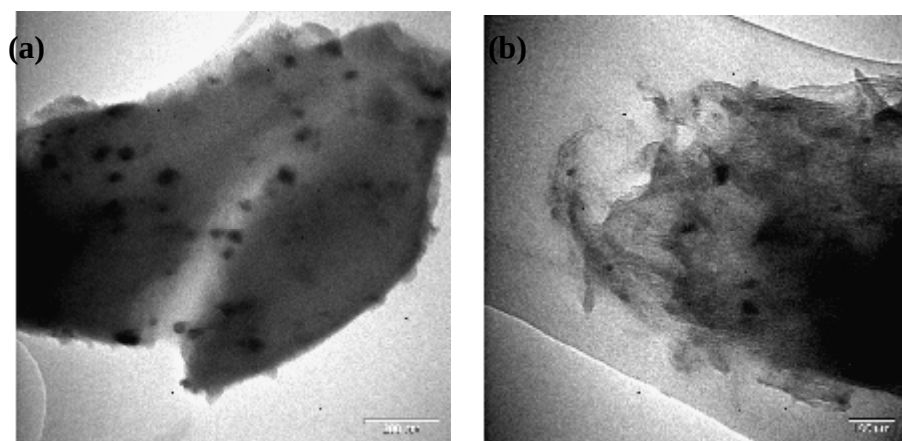


Figure 4.17. TEM micrographs of Cat. 2 with % 10 Pd (a) 200 nm (b) 100 nm

4.6.3 Characterization of Cat. 3

The Pd content of the SBA-15 supported palladium nanoparticles was measured by ICP-OES as % 9.48 and 1.27.

Figure 4.18. show the XRD pattern of Pd/SBA-15 (cat. 3). The Characteristic peaks for SBA-15 supported palladium nanoparticles were observed at, 40.32° , 46.78° , 68.32° that corresponding to the Pd(111), Pd(200) and Pd(220), respectively. These values are in agreement with literature data. The average particle size for the palladium nanoparticles was calculated by applying the Scherrer equation to the Pd(111) peak at 46.78° to estimate the crystallite size. Average crystallite sizes were determined as 20.2 and 12.5 nm.

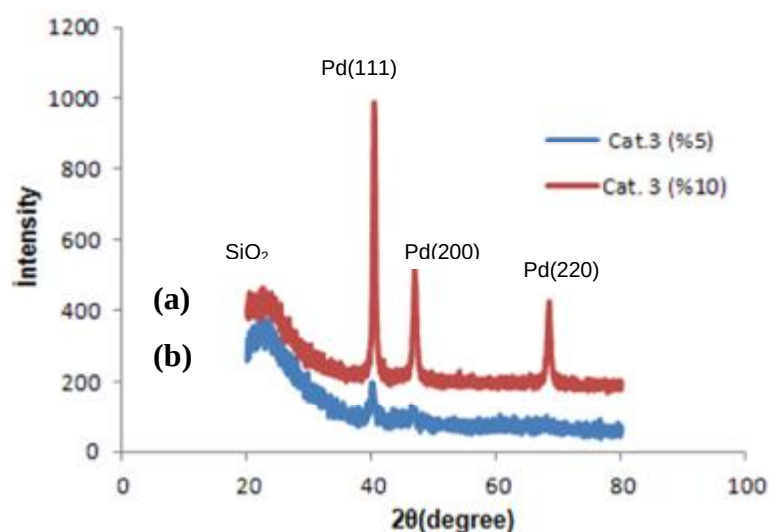


Figure 4.18. XRD pattern of Cat. 3 (a) % 10 Pd (b) % 5 Pd

FE-SEM micrograph of the Pd⁰/SBA-15 catalyst shown in figure 4.19 and 4.20 as 100kx and 50kx magnification, respectively. From SEM images, The presence of metallic palladium nanoparticles on SBA-15 was observed clearly.

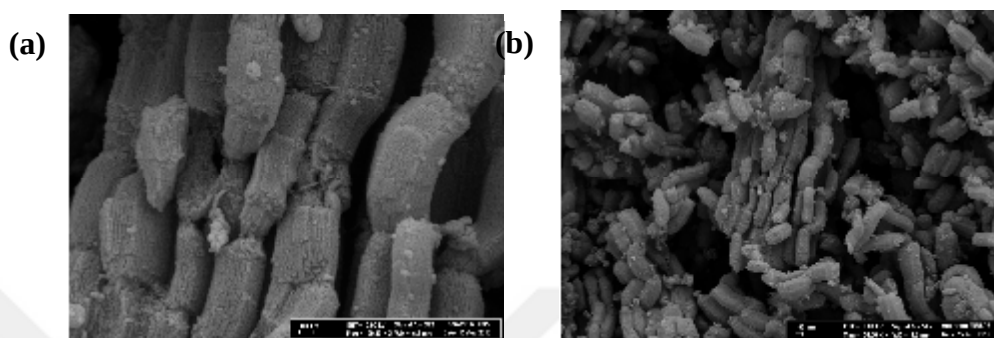


Figure 4.19. FE-SEM micrograph of Cat. 3 with % 10 Pd (a) 100 kx (b) 50 kx

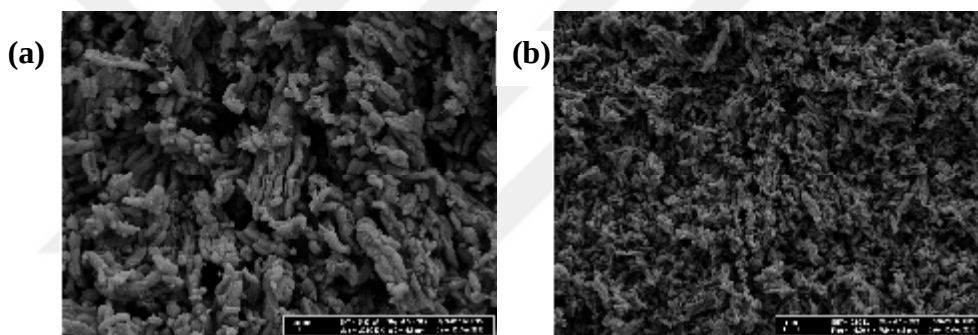


Figure 4.20. FE-SEM micrograph of Cat. 3 with % 5 Pd (a) 100 kx (b) 50 kx

Mapping spectrum of the cat. 3, showed the distribution of palladium nanoparticles on the support surface and also the Si and O elements that illustrated with SiO₂. As shown in fig. 4.21.a and 4.22.a, palladium nanoparticles were distributed uniformly on SBA-15 support material. In the point spectrum of the cat. 3, percentage of elements on SBA-15 have been shown. The percentage of Pd nanoparticles was calculated via EDX- point spectrum as 8.2 and 0.51% . The percentage of Pd nanoparticles that calculated via ICP-OES may differ from that calculated by EDX- Point application. Because, EDX-Point data are local measurements and give the metal content of volume-based area whereas ICP-OES data show the average amount of Pd that deposited onto the SBA-15. According to literature, particle size of palladium nanoparticles increased due to higher amount of palladium content on SBA-15 surface.

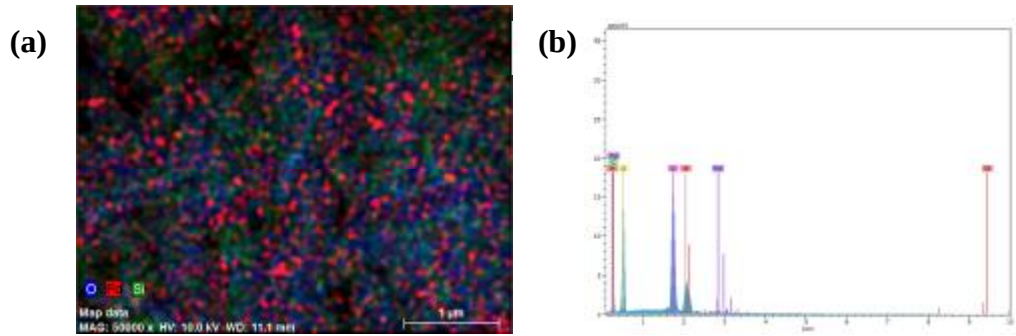


Figure 4.21. EDX spectrum of Cat. 3 with % 10 Pd (a) mapping spectrum (b) point spectrum

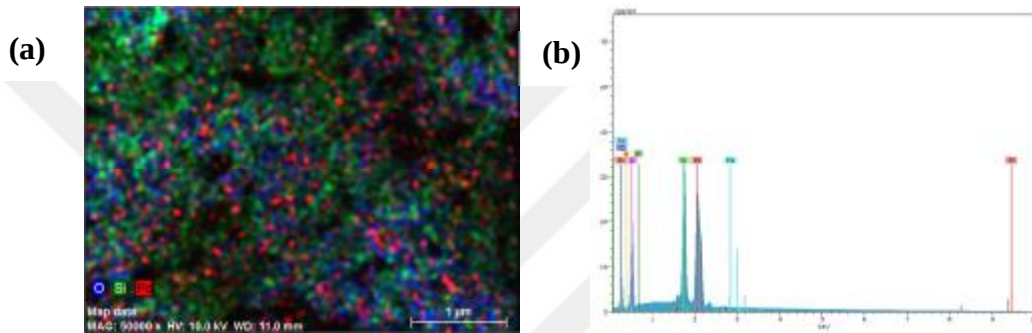


Figure 4.22. EDX spectrum of Cat. 3 with % 10 Pd (a) mapping spectrum (b) point spectrum

TEM micrographs of the Pd/SBA-15 (Cat.3) are shown in fig. 4.23. TEM images show the distribution of nanoparticles on SBA-15: (i) as spherical spots on the outer surface of SBA-15, (ii) as dark lines following the porous structure. As shown in fig. 4.23, palladium nanoparticles distributed on SBA-15 surface with 20-25 nm. Difference between the average particle sizes obtained from TEM and XRD micrographs was occurred. XRD measurements gives number-weighted value whereas TEM micrographs gives a volume-weighted value.

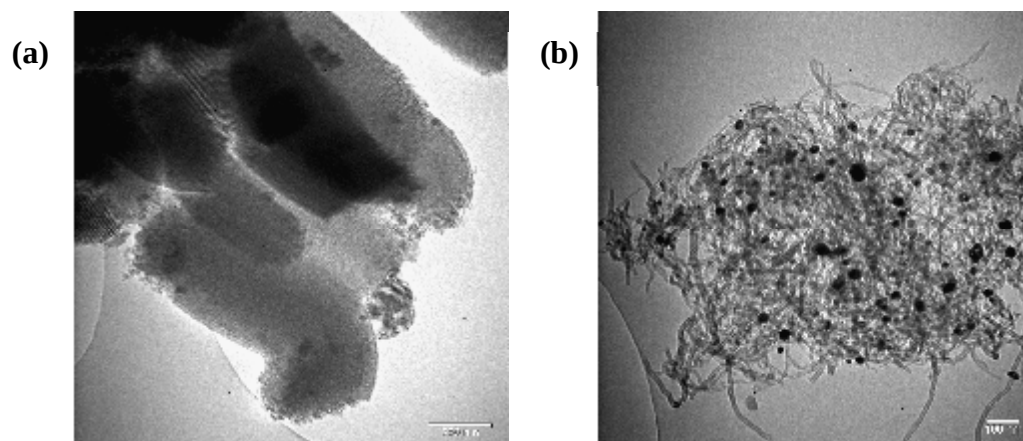


Figure 4.23. TEM micrographs of Cat. 3 with % 10 Pd (a) 250 nm (b) 100 nm

4.6.4. Characterization of Cat. 4

The Pd content of the SBA-15 supported palladium nanoparticles was measured by ICP-OES as % 5.60.

Figure 4.24. show the XRD pattern of Pd/SBA-15 (cat. 4). The Characteristic peaks for SBA-15 supported palladium nanoparticles were observed at, 40.07° , 46.27° , 68.20° that corresponding to the Pd(111), Pd(200) and Pd(220), respectively. These values are in agreement with literature data. The average particle size for the palladium nanoparticles was calculated by applying the Scherrer equation to the Pd(111) peak at 46.27° to estimate the crystallite size. Average crystallite size were determined as 13.5 and 9.5 nm.

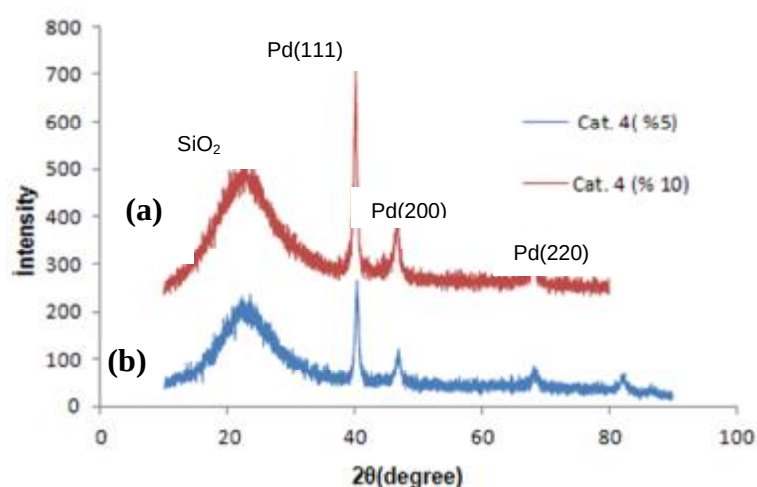


Figure 4.24. XRD pattern of Cat. 4 (a) % 10 Pd (b) % 5 Pd

FE-SEM micrograph of the Pd⁰/SBA-15 catalyst shown in figure 4.25. as 100kx, 50kx, 25kx and 10kx magnification, respectively. SEM images indicated that palladium complex deposited on SBA-15 with a size range of 10-20 nm.

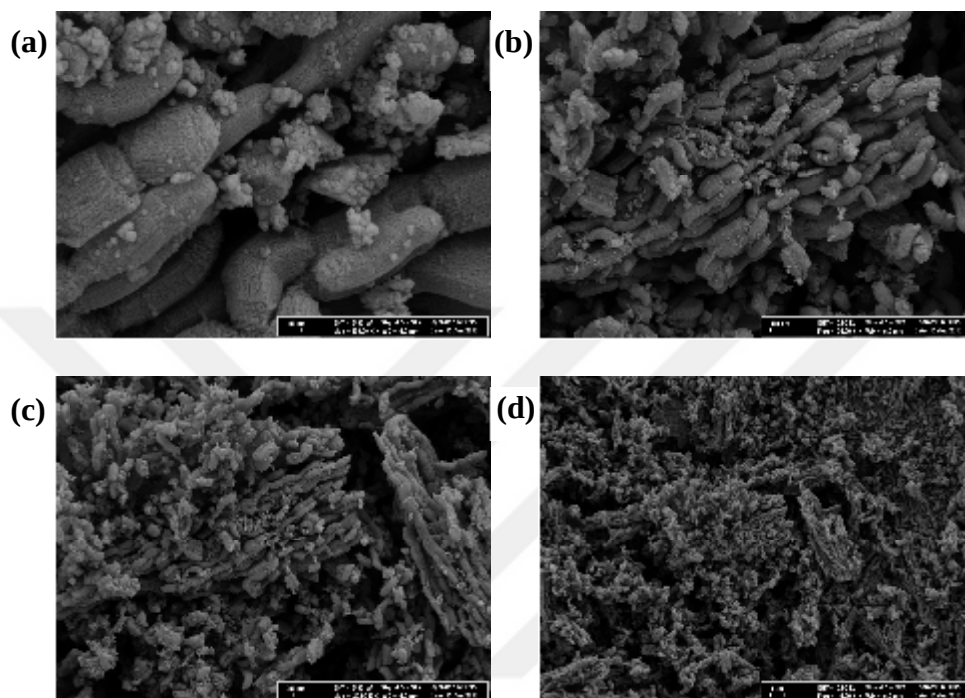


Figure 4.25. FE-SEM micrograph of Cat. 4 with % 10 Pd (a) 100 kx (b) 50 kx (c) 25 kx (d) 10 kx

Mapping spectrum of the cat. 4, showed the distribution of palladium nanoparticles on the support surface and also the Si and O elements that illustrated with SiO₂. As shown in fig. 4.26. (a), palladium nanoparticles were distributed on SBA-15 support material homogenously. However, There are some aggregate on the support. The max. Agglomeration was 250 nm. In the point spectrum of the cat. 4, elemental composition of elements on SBA-15 were shown. There are unexpected elements in point spectrum, Carbon atom was illustrated with carbon band during preparation of SEM sample and the platinum atom was observed due to the platinum coating of sample. The percentage of Pd nanoparticles was calculated via EDX-point spectrum as 2.95 %. The percentage of Pd nanoparticles that calculated via ICP-OES may differ from that calculated by EDX- Point application. Because, EDX-Point data are local measurements and give the metal content of volume-based area

whereas ICP-OES data show the average amount of Pd that deposited onto the SBA-15.

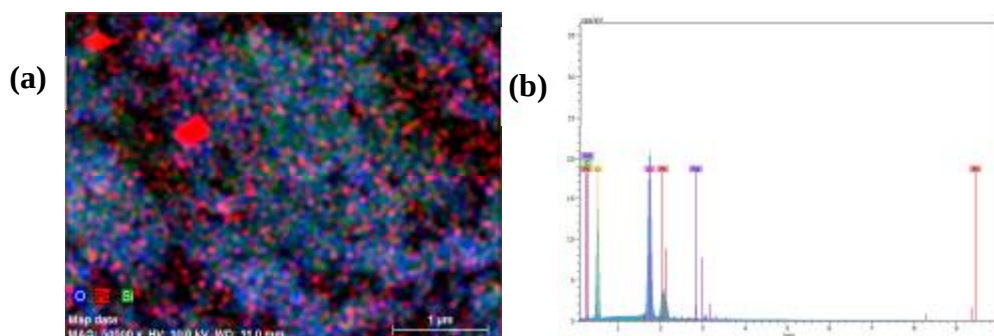


Figure 4.26. EDX spectrum of Cat. 4 with % 10 Pd (a) mapping spectrum (b)EDX point spectrum

TEM micrographs of the Pd/SBA-15 (Cat.4) are shown in fig. 4.27. TEM images show the distribution of nanoparticles on SBA-15: (i) as spherical spots on the outer surface of SBA-15, (ii) as dark lines following the porous structure. As shown in fig. 4.27, palladium nanoparticles distributed on SBA-15 surface. Difference between the average particle sizes obtained from TEM and XRD micrographs was occurred. XRD measurements give number-weighted value whereas TEM micrographs give a volume-weighted value.

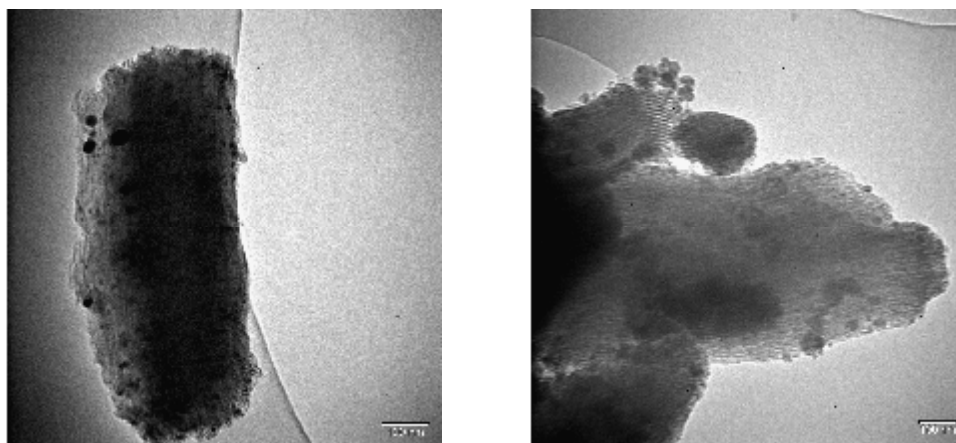


Figure 4.27. TEM micrographs of Cat. 4 with % 10 Pd at 100 nm

4.6.5 Characterization of Cat.5

The Pd content of the SBA-15 supported palladium nanoparticles was measured by ICP-OES as % 7.91.

Figure 4.21. show the XRD pattern of Pd/SBA-15 (cat. 5). The Characteristic peaks for SBA-15 supported palladium nanoparticles were observed at, 40.13° , 46.57° , 68.17° that corresponding to the Pd(111), Pd(200) and Pd(220), respectively. These values are in agreement wit literature data. The average particle size for the palladium nanoparticles was calculated by applying the Scherrer equation to the Pd(111) peak at 46.57° to estimate the crystallite size. Average crystallite size were determined as 13.04 and 10.8 nm.

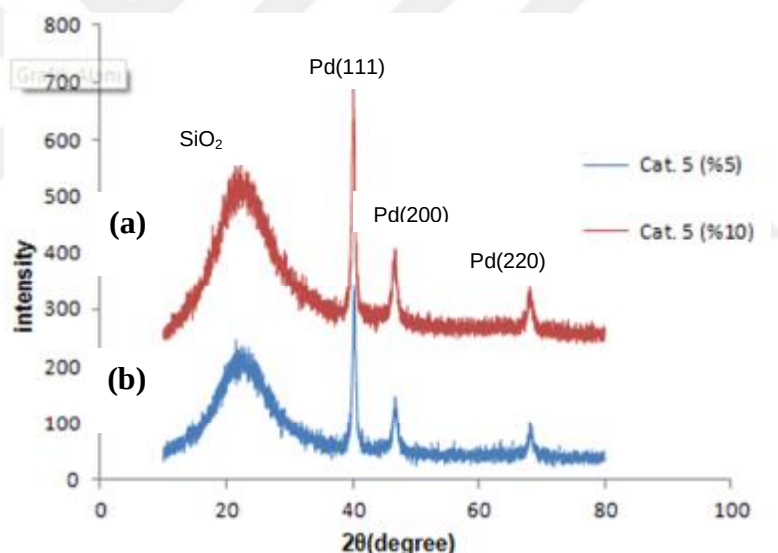


Figure 4.28. XRD pattern of Cat. 5 (a) % 10 Pd (b) % 5 Pd

FE-SEM micrograph of the Pd⁰/SBA-15 catalyst shown in figure 4.22. as 100kx, 50kx, 25kx and 10kx magnification, respectively. SEM images indicated that palladium nanoparticles distributed on the outer surface of SBA-15.

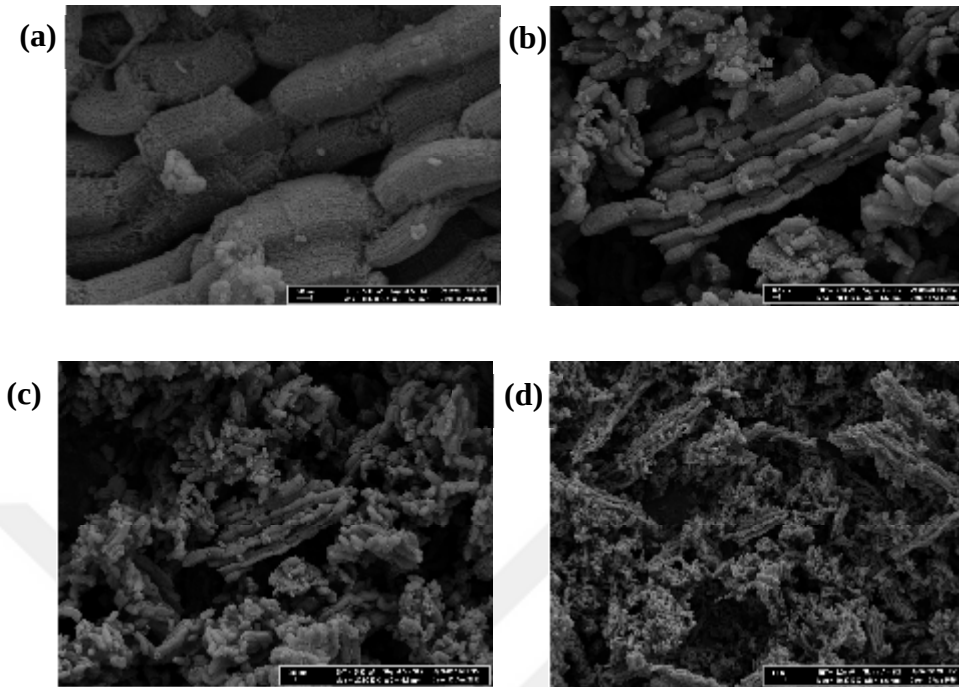


Figure 4.29. FE-SEM micrograph of Cat. 5 with % 10 Pd (a) 100 kx (b) 50 kx (c) 25 kx (d) 10 kx

Mapping application of the cat. 5, showed the elemental distribution of presence of palladium nanoparticles and silica. In mapping spectrum, Pd, Si and O were observed. % Pd amount on the SBA-15 have been also determined via EDX-point application. The percentage of Pd nanoparticles was calculated 4.78 %. The percentage of Pd nanoparticles that calculated via ICP-OES may differ from that calculated by EDX- Point application. Because, EDX-Point data are local measurements and give the metal content of volume-based area whereas ICP-OES data show the average amount of Pd that deposited onto the SBA-15.

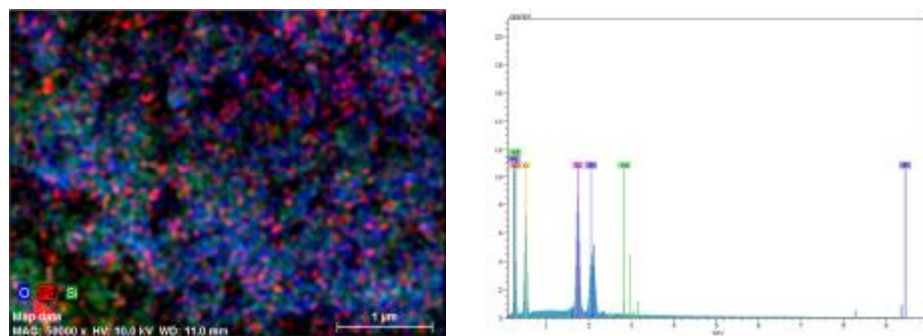


Figure 4.30. (a) EDX mapping spectrum (b) EDX point spectrum of Cat. 5 (%10 Pd)

TEM micrographs of the Pd/SBA-15 (Cat.5) are shown in fig. 4.31. TEM images show the distribution of nanoparticles on SBA-15: (i) as spherical spots on the outer surface of SBA-15, (ii) as dark lines following the porous structure. As shown in fig. 4.31. palladium nanoparticles distributed on SBA-15 surface with 10-20 nm. Difference between the average particle sizes obtained from TEM and XRD micrographs was occurred. XRD measurements gives number-weighted value whereas TEM micrographs gives a volume-weighted value.

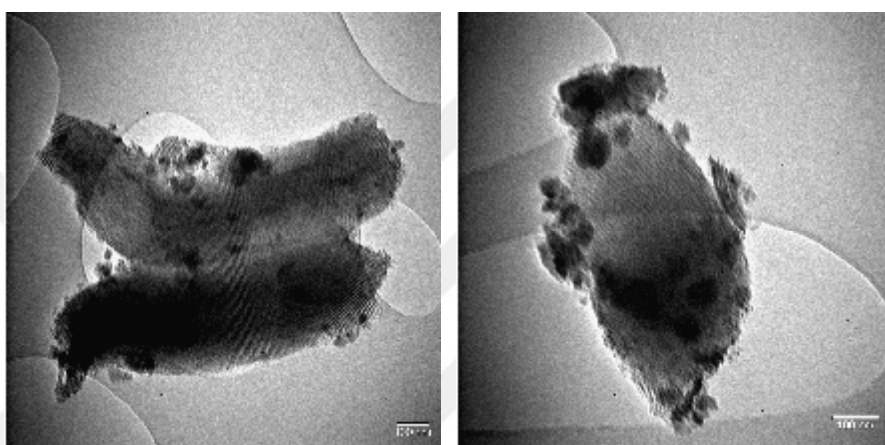


Figure 4.31. TEM micrographs of Cat. 5 at 100 nm

4.6.6 Characterization of Cat.6

The Pd content of the SBA-15 supported palladium nanoparticles was measured by ICP-OES as % 4.91.

Figure 4.32. show the XRD pattern of Pd/SBA-15 (cat. 6). The Characteristic peaks for SBA-15 supported palladium nanoparticles were observed at, 39.99° , 46.56° , 67.97° that corresponding to the Pd(111), Pd(200) and Pd(220), respectively. These values are in agreement with literature data. The average particle size for the palladium nanoparticles was calculated by applying the Scherrer equation to the Pd(111) peak at 46.56° to estimate the crystallite size. Average crystallite sizes were determined as 18.71 and 14.74 nm.

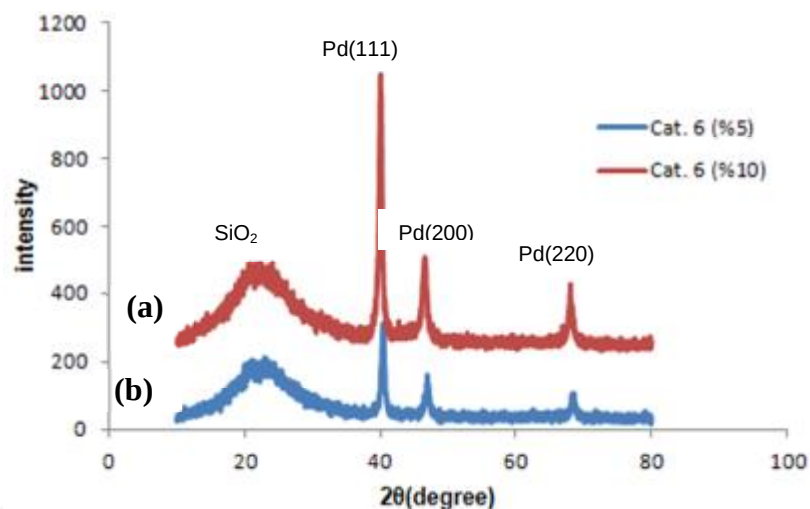


Figure 4.32. XRD pattern of Cat. 6 (a) % 10 Pd (b) % 5 Pd

FE-SEM micrograph of the $\text{Pd}^0/\text{SBA-15}$ catalyst shown in figure 4.33. as 100kx, 50kx, 25kx and 10kx magnification, respectively. From SEM images, The presence of metallic palladium nanoparticles on SBA-15 was observed with 15-20 nm.

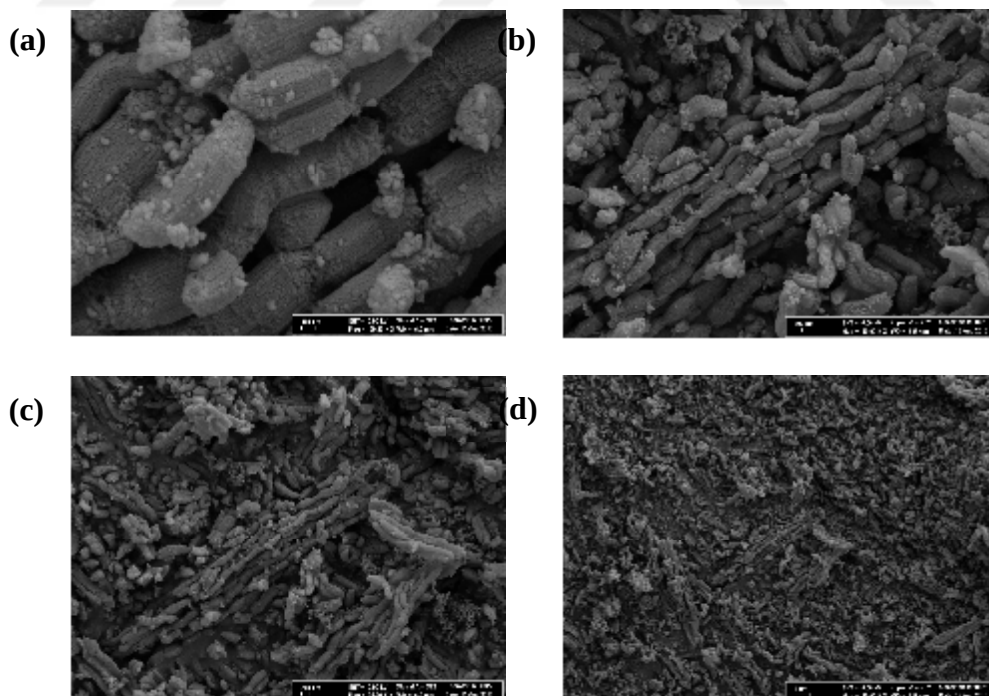


Figure 4.33. FE-SEM micrograph of Cat. 6 (a) 100 kx (b) 50 kx (c) 25 kx (d) 10 kx

Mapping spectrum of the cat. 6, showed the presence of palladium nanoparticles on the support surface and also the Si and O elements that illustrated with SiO_2 . As shown in fig. 4.34. (a) palladium nanoparticles were distributed only limited area of SBA-15 support material. Agglomeration was observed with max. size 50 nm. In the point spectrum of the cat. 6, elemental composition of cat. 3, percentage of elements on SBA-15 have been shown. The percentage of Pd nanoparticles was calculated via EDX- point spectrum as 2.02 % . The percentage of Pd nanoparticles that calculated via ICP-OES may differ from that calculated by EDX- Point application. Because, EDX-Point data are local measurements and give the metal content of volume-based area whereas ICP-OES data show the average amount of Pd that deposited onto the SBA-15. According to literature, particle size of palladium nanoparticles increased due to higher amount of palladium content on SBA-15 surface.

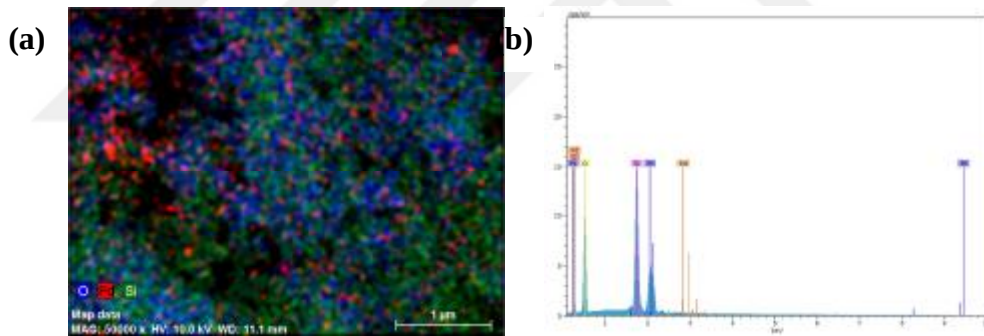


Figure 4.34. (a) EDX mapping spectrum (b) EDX point spectrum of Cat. 6

TEM micrographs of the Pd/SBA-15 (Cat.6) are shown in fig. 4.35. TEM images Show the distribution of nanoparticles on SBA-15: (i) as spherical spots on the outer surface of SBA-15, (ii) as dark lines following the porous structure. As shown in fig. 4.35, palladium nanoparticles distributed on SBA-15 surface with 20-25 nm. Difference between the average particle sizes obtained from TEM and XRD micrographs was occurred. XRD measurements gives number-weighted value whereas TEM micrographs gives a volume-weighted value.

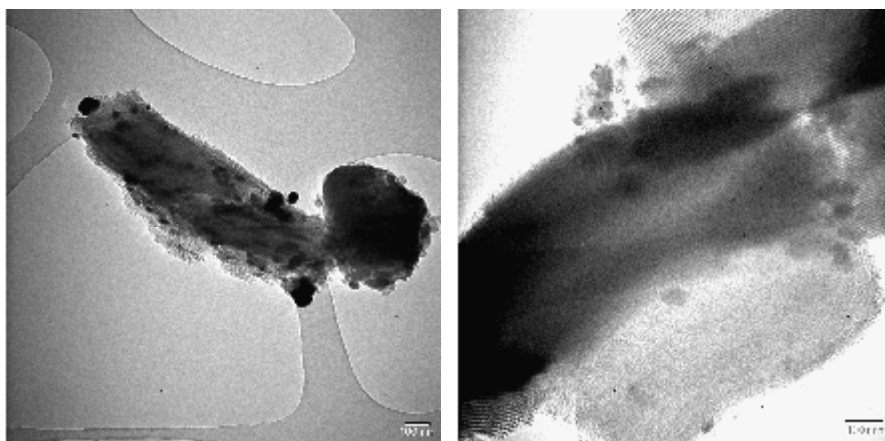


Figure 4.35. TEM micrographs of Cat. 6 at 100 nm

4.7. Catalytic Activity of SBA-15 Supported Palladium Catalysts

4.7.1. Determination of optimum conditions for Suzuki Reactions

To evaluate the catalytic activities of SBA-15 supported palladium nanocatalyst for the Suzuki-Miyaura reactions, we have chosen bromobenzene and phenylboronic acid as model substrate. Initial reaction was conducted using cat.1.(%10 Pd) for determination the optimum conditions.

It is known that in the Suzuki-Miyaura cross coupling reactions choice of solvent often plays a crucial role in the overall performance of a catalyst (Shahnaz *et al.*, 2013)., and to investigate this effect we have screened different solvents including, ethanol, acetonitrile, 1,4-dioxane, Toluene, DMF and NMP. Our study showed that, Etanol is the best solvent for our reaction. On the other hand, we have also investigated the effect of different bases including organic (Et_3N) and inorganic bases (K_2CO_3 , Na_2CO_3 and NaOAc . K_2CO_3 is found to be the most effective base. The effects of base and solvent on Suzuki-Miyaura reactions are summarized in table 4.5.

Table 4.5. Effect of base and solvent on the yield of coupling product

Entry	Catalyst	Base	Solvent	Time(h)	Yield ^b (%)
1	Cat. 1.	Na ₂ CO ₃	Acetonitrile	8	72
2	Cat. 1.	Na ₂ CO ₃	DMF	8	43
3	Cat. 1.	Na ₂ CO ₃	1,4- dioxane	8	67
4	Cat. 1.	Na ₂ CO ₃	Toluene	8	-
5	Cat. 1.	Na ₂ CO ₃	NMP	8	79
6	Cat. 1.	Na ₂ CO ₃	Etanol	8	91
7	Cat. 1.	K ₂ CO ₃	Acetonitrile	8	78
8	Cat. 1.	K ₂ CO ₃	DMF	8	53
9	Cat. 1.	K ₂ CO ₃	1,4- dioxane	8	68
10	Cat. 1.	K ₂ CO ₃	Toluene	8	5
11	Cat. 1.	K ₂ CO ₃	NMP	8	81
12	Cat. 1.	K ₂ CO ₃	Etanol	8	96
13	Cat. 1.	NaOAc	Acetonitrile	8	30
14	Cat. 1.	NaOAc	DMF	8	17
15	Cat. 1.	NaOAc	1,4- dioxane	8	27
16	Cat. 1.	NaOAc	Toluene	8	-
17	Cat. 1.	NaOAc	NMP	8	41
18	Cat. 1.	NaOAc	Etanol	8	53
19	Cat. 1.	Et ₃ N	Acetonitrile	8	14
20	Cat. 1.	Et ₃ N	DMF	8	7
21	Cat. 1.	Et ₃ N	1,4- dioxane	8	-
22	Cat. 1.	Et ₃ N	Toluene	8	-
23	Cat. 1.	Et ₃ N	NMP	8	21
24	Cat. 1.	Et ₃ N	Etanol	8	32

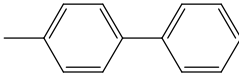
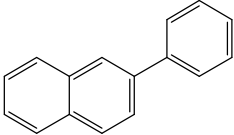
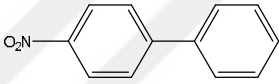
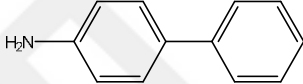
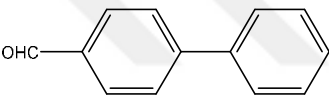
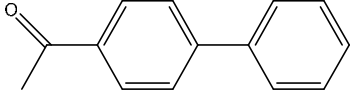
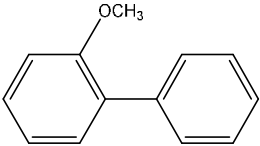
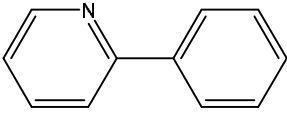
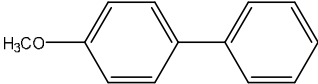
^a : Conditions: 0.1 mmol ArBr, 0.12 mmol PhB(OH)₂, 0.12 mmol base, catalyst / substrate ratio:1/200 (0,5 mol %Pd), 2.0 ml solvent / water (1:1), 80⁰C, in air. 8 h.

^b: conversion yields are based bromobenzene

4.7.2. Catalytic performance of catalyst over Suzuki reactions with arylbromide derivatives

For catalytic applications, catalysts with % 10 Pd content were chosen due to higher palladium content and uniform distribution. The effect of electron-withdrawing group or electron-donating group on substrates to the product yields were investigated.

Table 4.6. Using arylbromides derivatives and their cross coupled products

Entry	Arylbromide Derivatives	Cross-coupled product
1	4-bromotoluene	 4-methyl-1,1'-biphenyl
2	1-bromonaphthalene	 2-phenylnaphthalene
3	1-bromo-4-nitrobenzene	 4-nitro-1,1'-biphenyl
4	4-bromoaniline	 [1,1'-biphenyl]-4-amine
5	4-bromobenzaldehyde	 [1,1'-biphenyl]-4-carbaldehyde
6	4-bromoacetophenone	 1-([1,1'-biphenyl]-4-yl)ethan-1-one
7	2-bromoanisole	 2-methoxy-1,1'-biphenyl
8	2-bromopyridine	 2-phenylpyridine
9	4-bromoanisole	 4-methoxy-1,1'-biphenyl

It is known that, the steric hindrance and electronic effects of substituents have significant role on the catalytic performance(Shahnaz *et al.*, 2013). For this purpose, *ortho* and *para*-substituted arylbromides with electron-withdrawing groups such as nitro, aldehyde and acetyl and electron-donating groups such as methyl and methoxy have been used as substrate and their effect on yield of coupling product have been investigated. The results are summarized in table 4.6.

Table 4.7. Suzuki-Miyaura reactions of various aryl bromides with cat.1-6.

Entry	R	Cat.1	Cat.2	Cat.3	Cat.4	Cat.5	Cat.6
1	4-CH ₃	84 %	77%	74%	79%	61%	55%
2	1-naphth.	94%	91%	87%	87%	78%	75%
3	4-NO ₂	99%	99%	94%	93%	83%	77%
4	4-NH ₂	93%	92%	86%	88%	77%	71%
5	4-CHO	99%	97%	90%	91%	86%	75%
6	4-COCH ₃	99%	94%	91%	92%	87%	84%
7	2-OCH ₃	79%	77%	67%	69%	62%	58%
8	2-pyridyl	58%	44%	39%	41%	27%	21%
9	4-OCH ₃	89%	85%	82%	83%	79%	74%

^a : Conditions: 0.1 mmol ArBr, 0.12 mmol PhB(OH)₂, 0.12 mmol base, catalyst / substrate ratio:1/200 (0,5 mol %Pd), 2.0 ml solvent / water (1:1), 80°C, in air. 8 h.

^b: conversion yields are based on arylbromides.

^c: Yields were determined by GC-FID

For Suzuki-Miyaura reaction of Cat. 1, *para*-substituted aryl bromides bearing electron-withdrawing groups nitro (entry 3), aldehyde (entry 5) and acetyl (entry 6) showed excellent yields, while arylbromides bearing electron-donating group at their *para*-position methyl (1), amine(entry4), methoxy(entry 9) show slightly lower yields than those with electron-withdrawing group. It is noted that our catalyst can also tolerate sterically bulky *ortho*-substituted bromides. sterically hindrance *ortho*-substituted bromides 2-bromo anisol gave the desired product in reasonably good yields. On the other hand, *ortho*-substituted 2-bromopyridine gave poorer yields due to the its heterocyclic structure.

To compare the catalytic activities of complexes (cat. 1- cat. 6), we performed Suzuki cross-coupling reactions of arylbromides using the same set of experimental

conditions. Interestingly, a marked difference in catalytic activity has been noticed. For instance, as compared to 99% nitrophenyl formation (entry 3), cat.2 gave similarly yields with cat.1 While Cat. 3 and Cat. 4 gave slightly lower yields. But, Cat. 5 and Cat. 6 gave poorer yield due to thermal instability. Similarly, substantially poorer yields were also obtained with other aryl bromides. On the other hand, It is known that, the metal particle size is increasing with increasing percentage of palladium nanoparticles on support surface. The yields of products is decreased with increasing metal size due to the decreasing in surface area of support material.

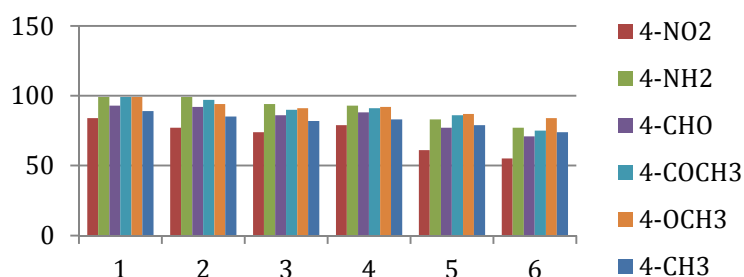


Figure 4.37. % Conversion of *p*-substituted aryl bromides

4.7.3. Recyclability of Catalysts

From an economic perspective, the reusability of catalysts is one of the most important benefits of heterogeneous catalytic systems. The recyclability of our catalyst was investigated for the reaction between 4-nitrobenzene and phenylboronic acid by carrying out four cycles at same reaction conditions. After each run, the catalyst was recovered by filtration, washed with ethanol and water, then dried at 130 °C. There is no significant change in the catalytic activity of the catalyst after four cycles except cat. 5 and cat. 6 (table 4.7).

Table 4.7. Recyclability of the catalysts after 4 run

Run	1 st	2 nd	3 rd	4 th
Cat. 1	99%	99%	99%	98%
Cat. 2	94%	94%	92%	92%
Cat. 3	91%	91%	88%	86%
Cat. 4	92%	92%	90%	90%
Cat. 5	87%	85%	78%	73%
Cat. 6	84%	81%	76%	69%

5. CONCLUSIONS

Suzuki-Miyaura carbon-carbon bond coupling reactions have grabbed much attention for the preparation of compounds such as pharmaceuticals and other fine chemicals. Generally, these transformations realized with homogenous palladium catalysts. In the recent years, for economic perspective, supported Pd catalysts have been shown great interest in scientific research area, due to the properties of better separation of the noble metal from the products and recycling of catalyst.

In this thesis, we have reported the syntheses and characterization of novel bidendate Schiff base ligands and their palladium complexes. Thermal analysis (DSC) and spectral analyses (FT-IR, ^1H NMR, ^{13}C NMR) were used to characterize synthesized compounds. Structure of suitable crystals FSB-1 and K1 were identified by single crystal X-ray crystallography. The obtained Pd-schiff base complex was employed as precursor in SCFD technique to obtain palladium nanoparticles. For this purpose, SBA-15 was elected as support material due to its thermal and chemical stability and also high surface area.

It has been known that, % metal loading has influence on particle size., increasing in % metal loading may cause increase on average the particle size of palladium nanoparticles. This situation has been affected the catalytic activity due to the limitation of surface area.

On the other hand, the obtained nanoparticles were act as catalyst on the Suzuki-Miyaura cross-coupling reactions of phenylboronic acid with wide range of aryl bromides. The particle size of complexes has been limited the catalytic activity of catalyst. The catalytic efficiency has been decreased with increasing particle size. However, excellent conversions were obtained with aryl bromides with both electron-withdrawing group and electron-donating groups. On the other hand, *ortho*-substituted aryl bromides show slightly lower catalytic activity due to the steric hindrance of its position. 2-bromopyridine which have hetero atom in its ring gave poorer yield. The results showed that, SBA-15 supported Pd nanoparticles are effective for Suzuki Miyaura C-C cross coupling reactions under 80 °C reasonable lower catalyst loading (0.5 mol %).

In Conclusion, the Schiff base derivatives ligands have a potential for using in supercritical fluid deposition method. Within this purpose, the effect of metal on deposition process can be investigated with such metals; Ni, W, Fe, Cu and Rh. The deposition of Schiff base derivatives metal complexes on different support materials including; carbon nanotubes, alumina, activated carbon and the effect of different support on catalytic activity can be investigated. The catalytic activity of catalyst can be investigated different C-C coupling reactions. Instead of organic solvents, scCO₂ can be used as reaction media due to environmental properties.



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CURRICULUM VITAE

He was born in Nicosia, T.R.N.C in 1987. He was graduated from Cukurova University chemistry department, Adana, Turkey, in 2009. In the same year, he was began his Master degree at the department of chemistry in Cukurova University. He received the M.Sc. degree in inorganic chemistry department from the Çukurova University, Adana, Turkey, in 2012. His master thesis includes the preparation of phosphine derivatives ligand and their metal complexes and investigation of their catalytic activity over styrene hydrogenation by using micro emulsion technique. During his master degree, he continued his education at Nottingham University, United Kingdom as Erasmus Exchange Student and worked in Martyn Poliakoff's "Hydrothermal depolymerization of Lignin Derivatives in ScH_2O " project as researcher (2011). In 2012, he was admitted into the PhD program at Cukurova University, chemistry department. During his MSc and PhD degrees, he was worked in TUBITAK projects;

- 2011-2013 (The Preparation and Determination of The Catalytic Effectiveness of Multi-Walled Carbon Nanotube Supported Metallic Nano-Particles Using New Precursors In A Supercritical Carbon Dioxide Solution)
- 2015- (The Synthesis of Schiff Base and vic-Dioxime Derivatives Of Palladium Complexes and Their Usability as Precursor for Preparing Silica Supported Nanoparticles)

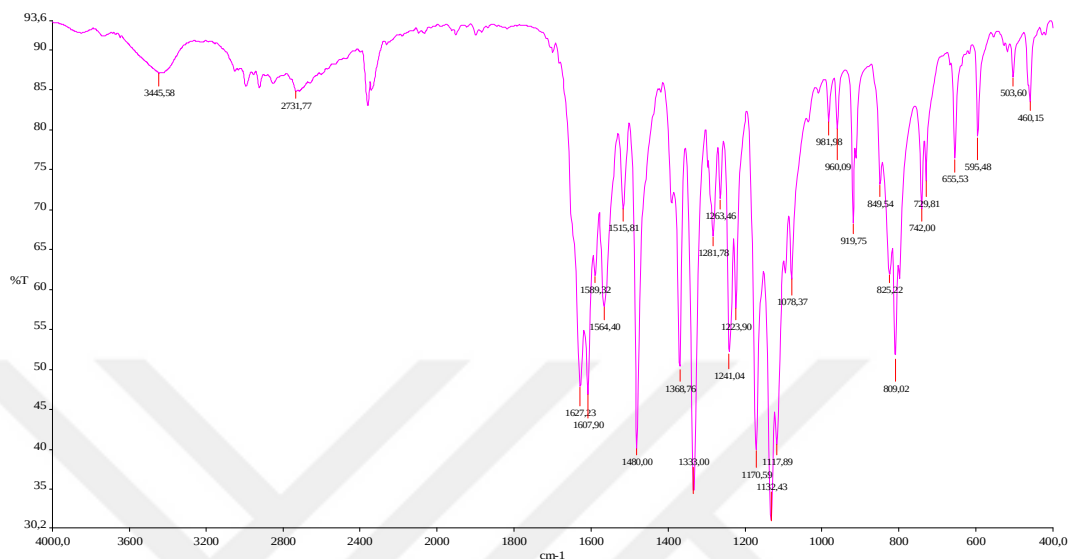


APPENDIX

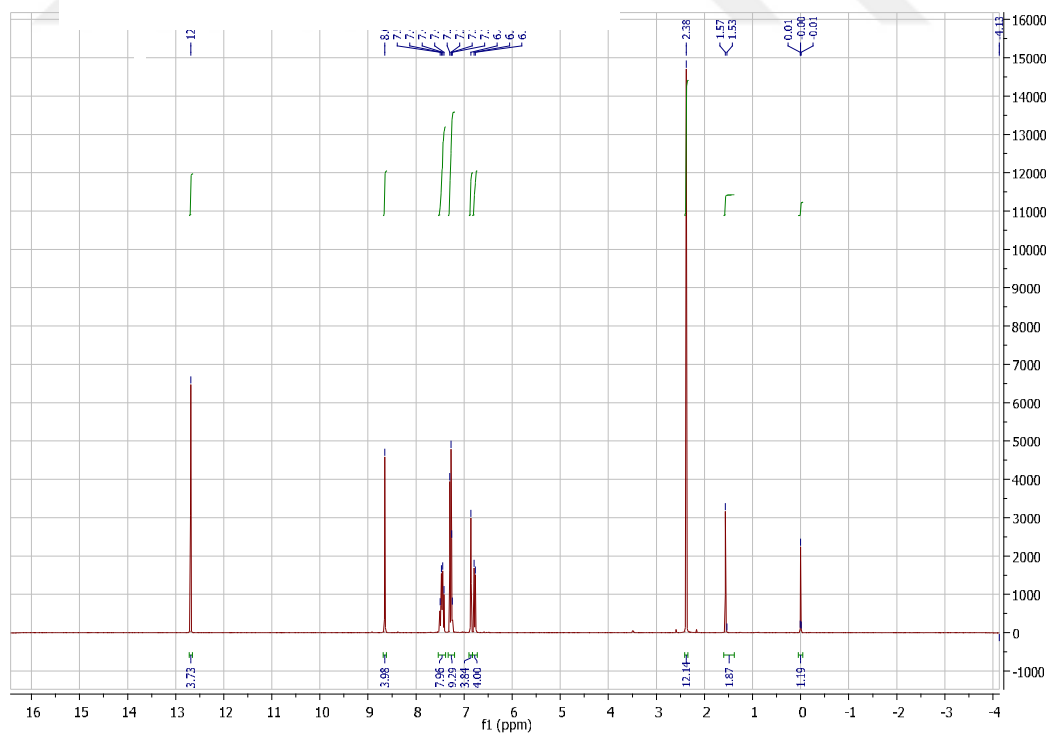


APPENDIX 1: FT-IR and NMR Spectra of Ligands

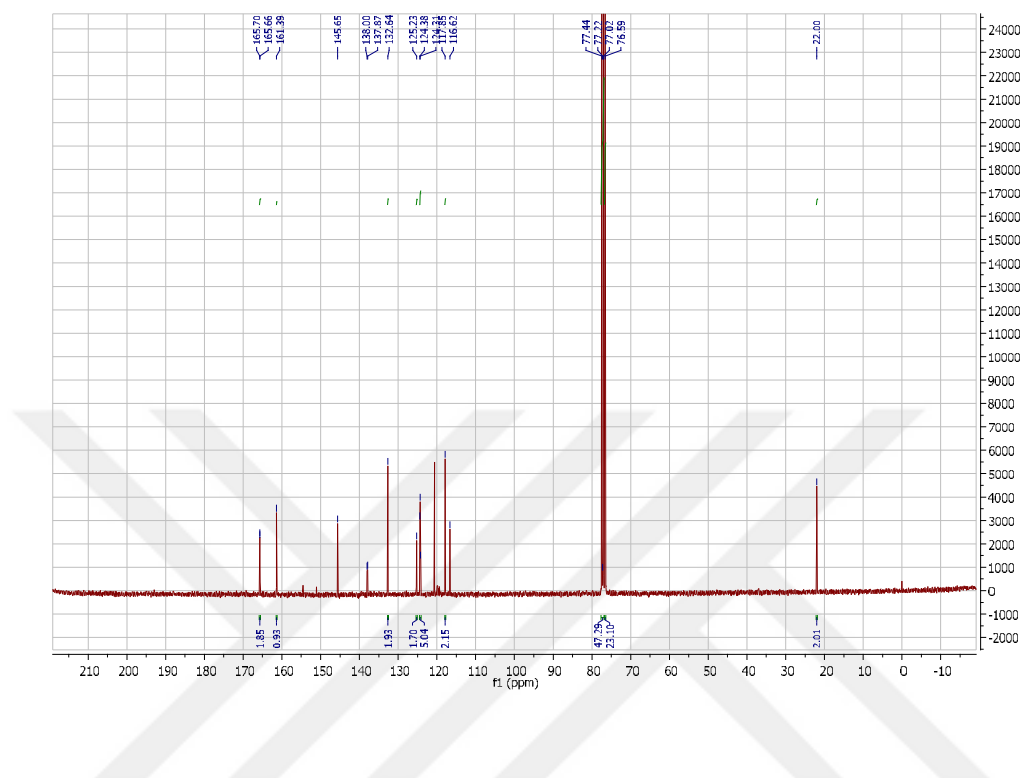
APPENDIX 1.1. FT-IR spectrum of FSB-1



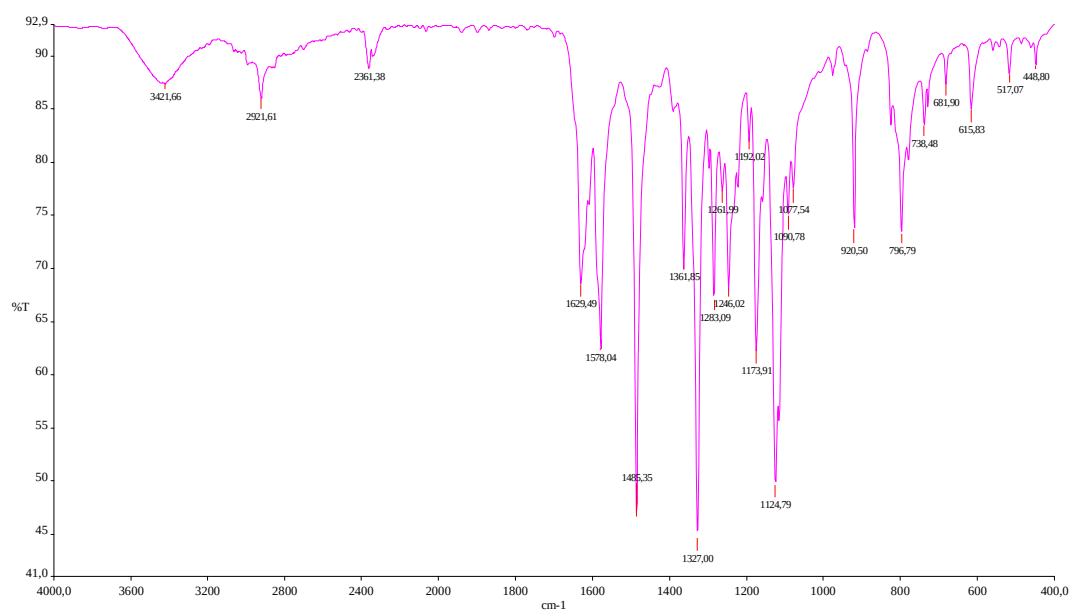
APPENDIX 1.2. ¹H NMR spectrum of FSB-1



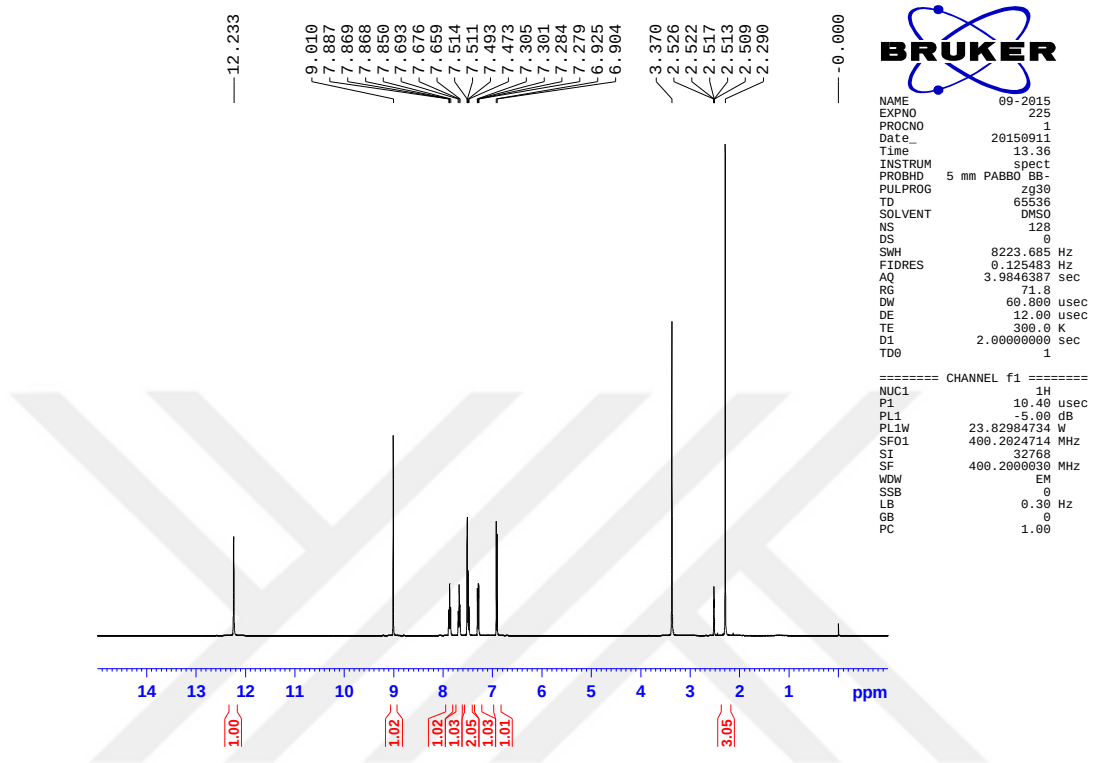
APPENDIX 1.3. ^{13}C NMR spectrum of FSB-1



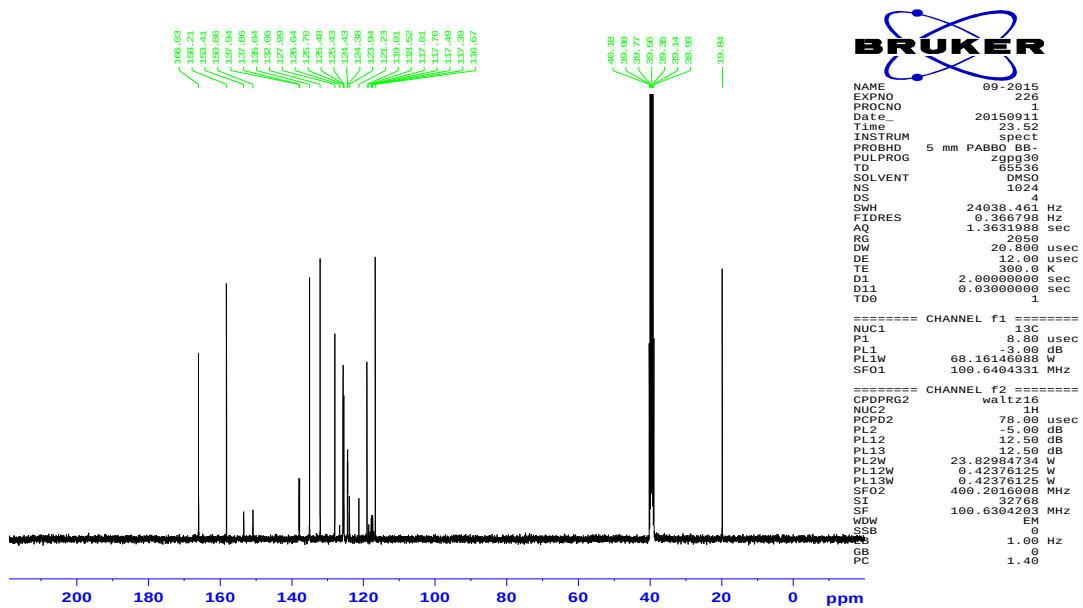
APPENDIX 1.4. FT-IR spectrum of FSB-2



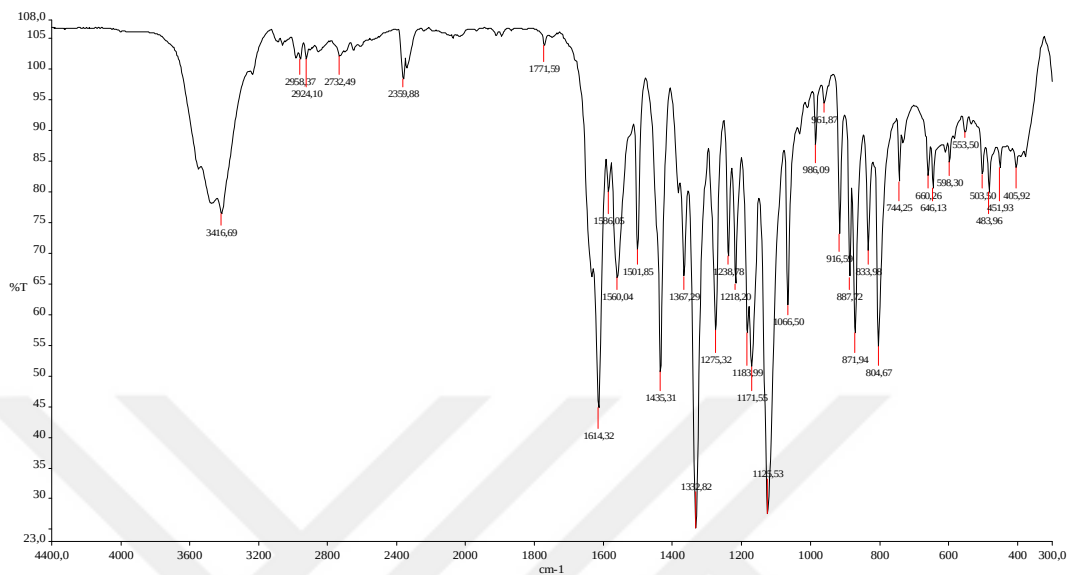
APPENDIX 1.5. ¹H NMR spectrum of FSB-2



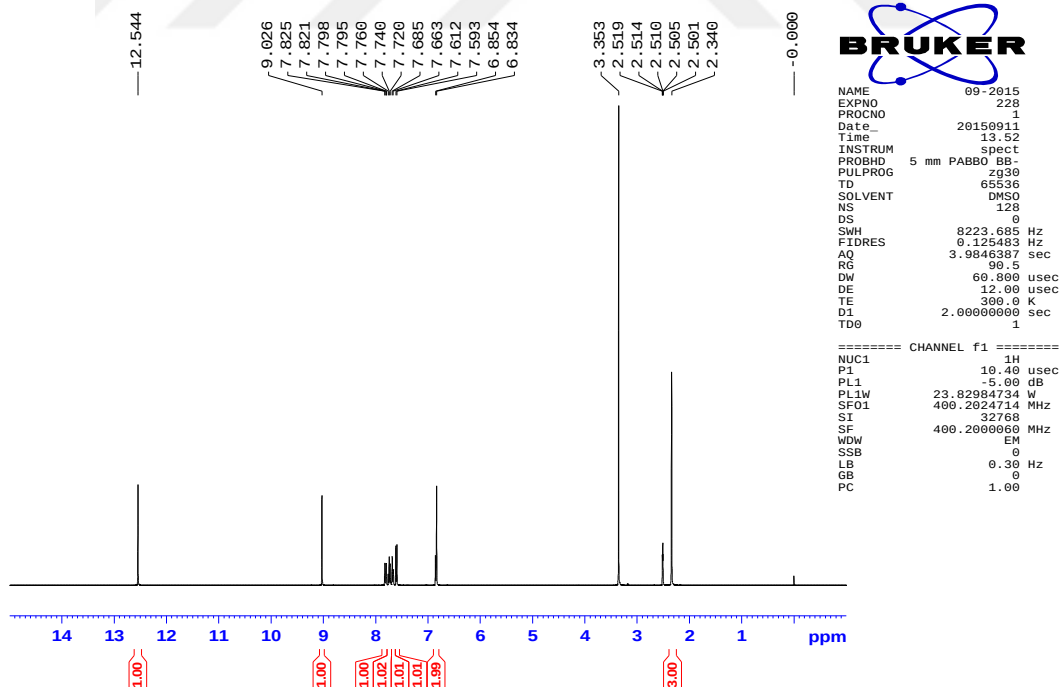
APPENDIX 1.6. ^{13}C NMR spectrum of FSB-2



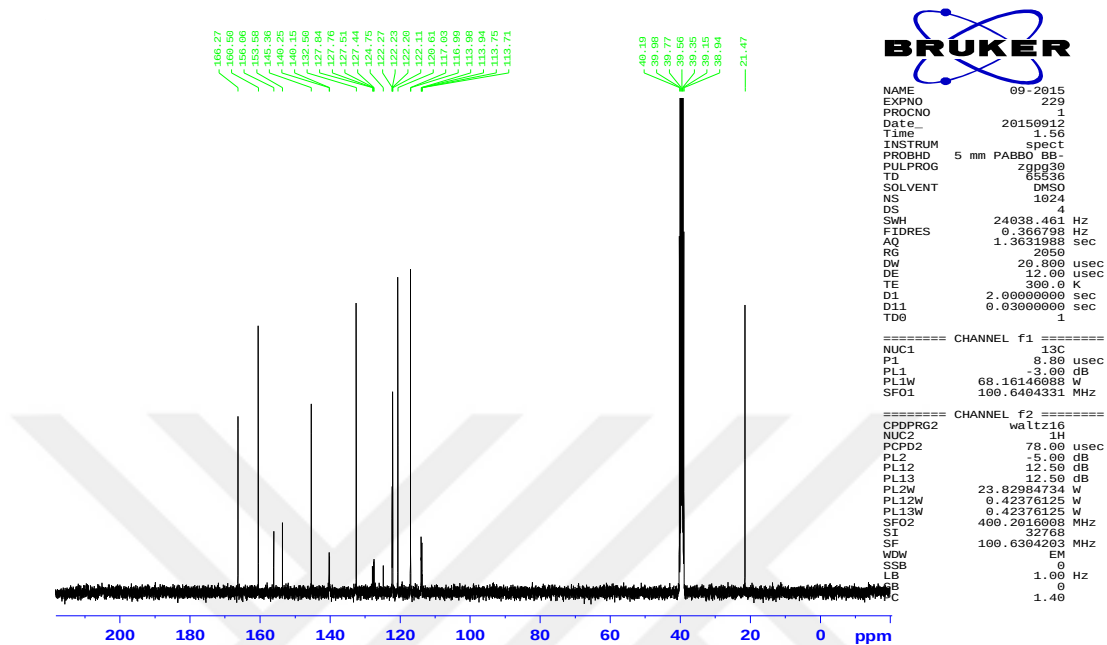
APPENDIX 1.7. FT-IR spectrum of FSB-3



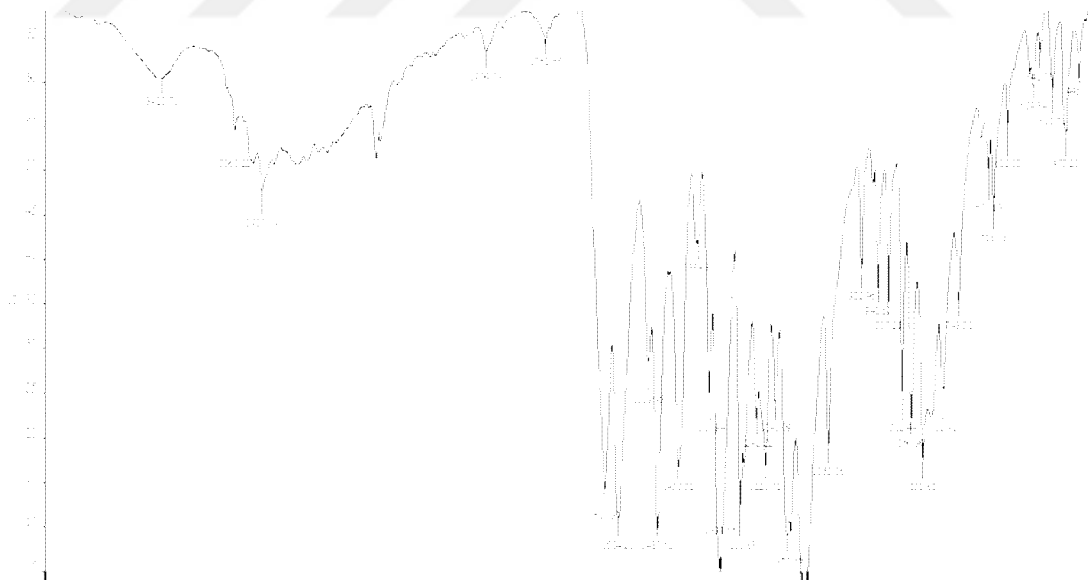
APPENDIX 1.8. ¹H NMR spectrum of FSB-3



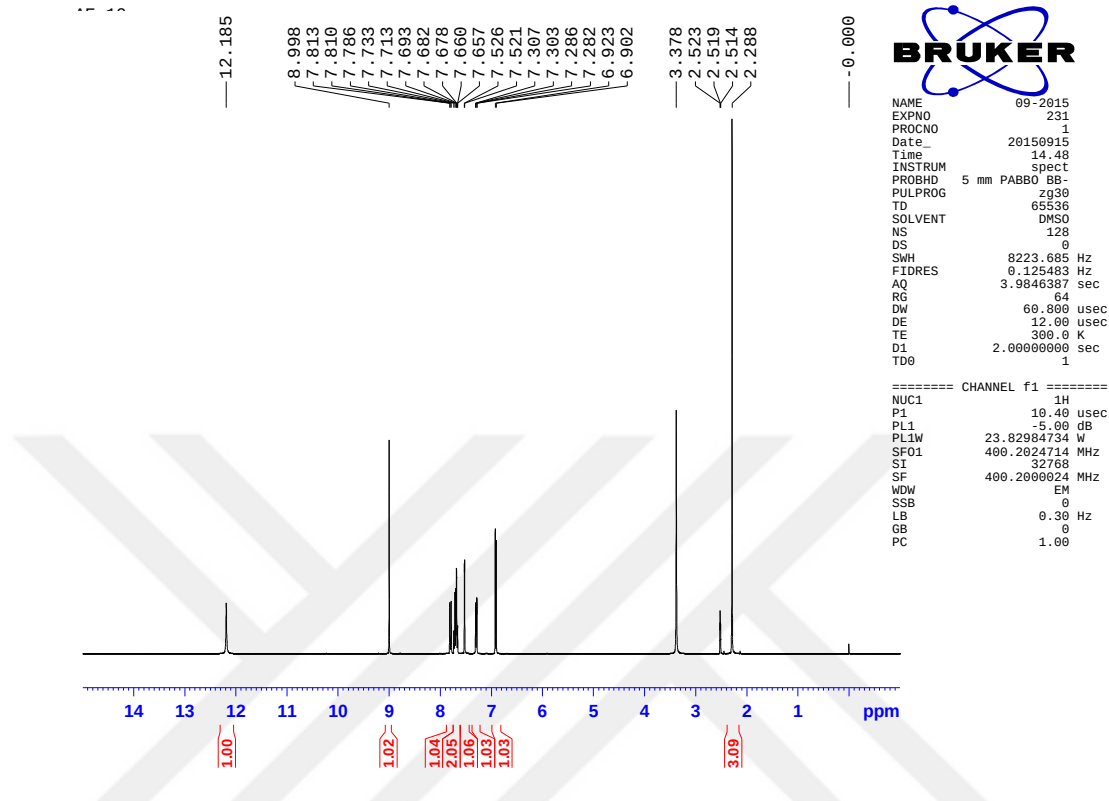
APPENDIX 1.9. ^{13}C NMR spectrum of FSB-3



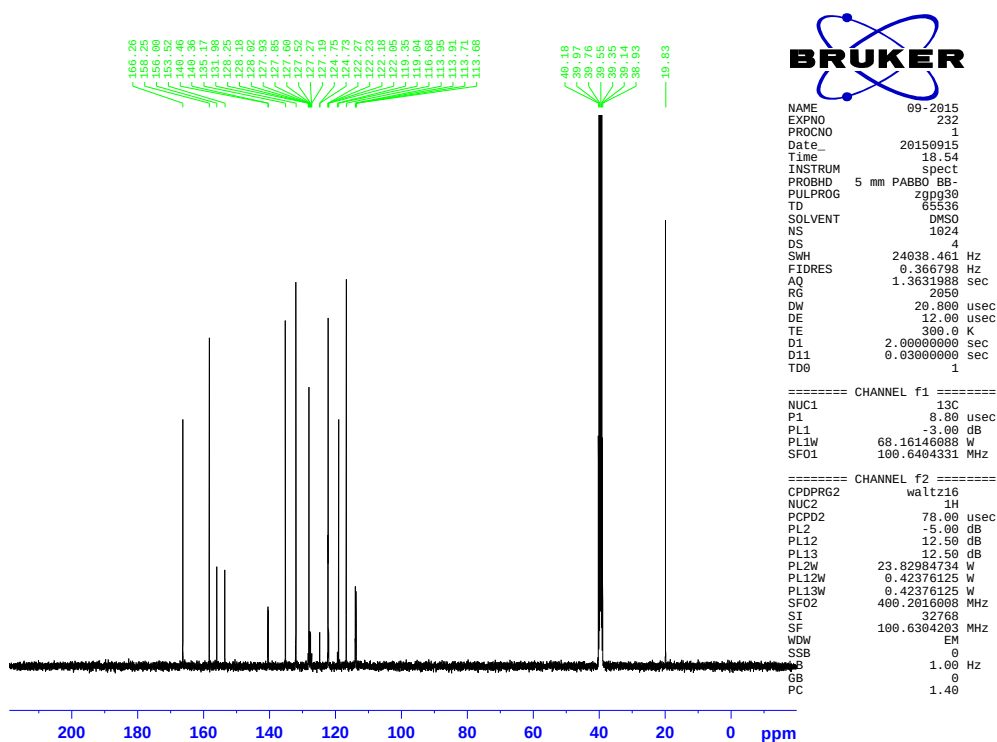
APPENDIX 1.10. FT-IR spectrum of FSB-4



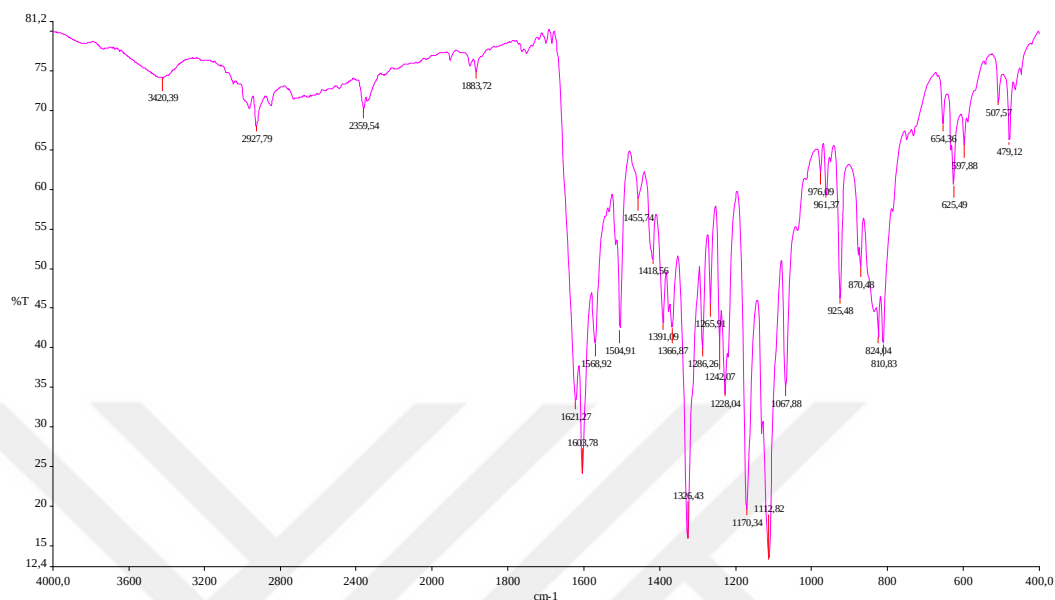
APPENDIX 1.11. ^1H NMR spectrum of FSB-4



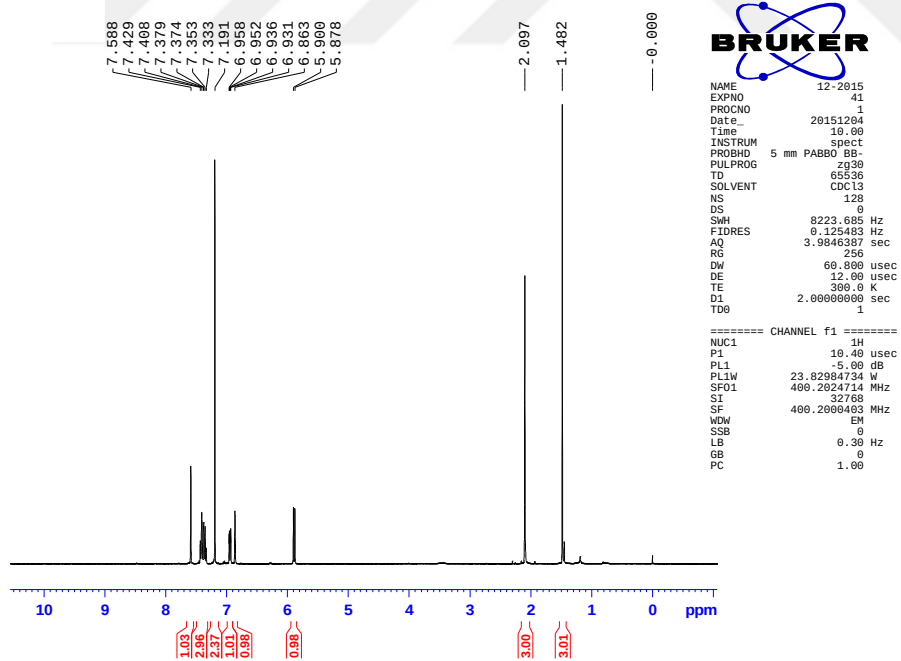
APPENDIX 1.12. ^{13}C NMR spectrum of FSB-4



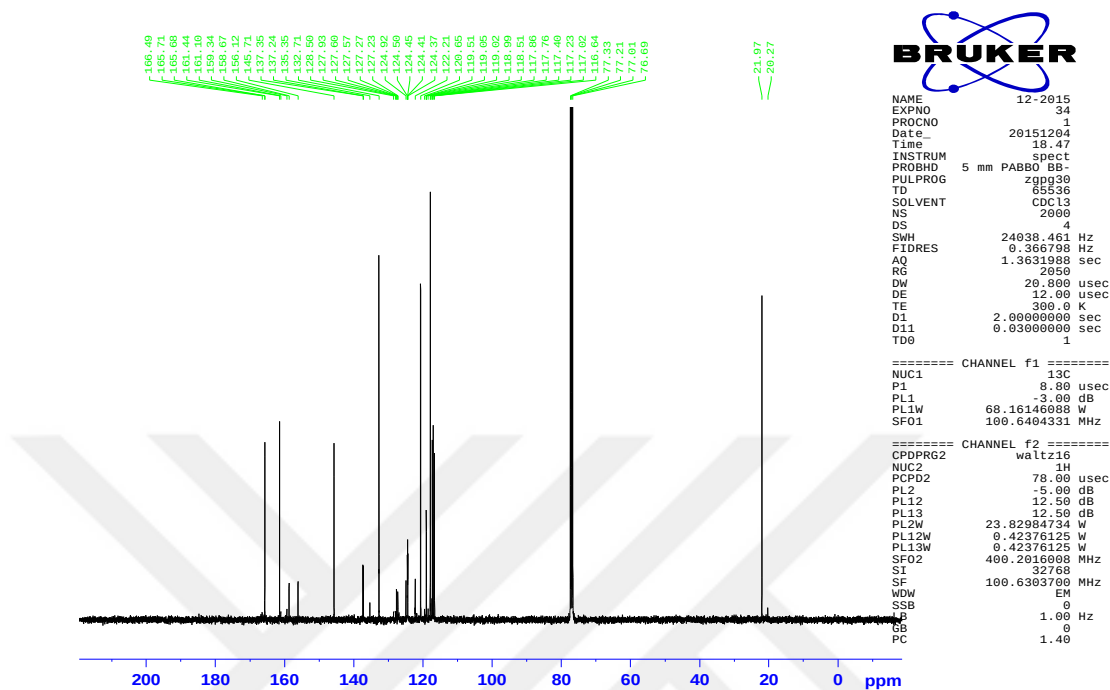
APPENDIX 1.13. FT-IR spectrum of FSB-5



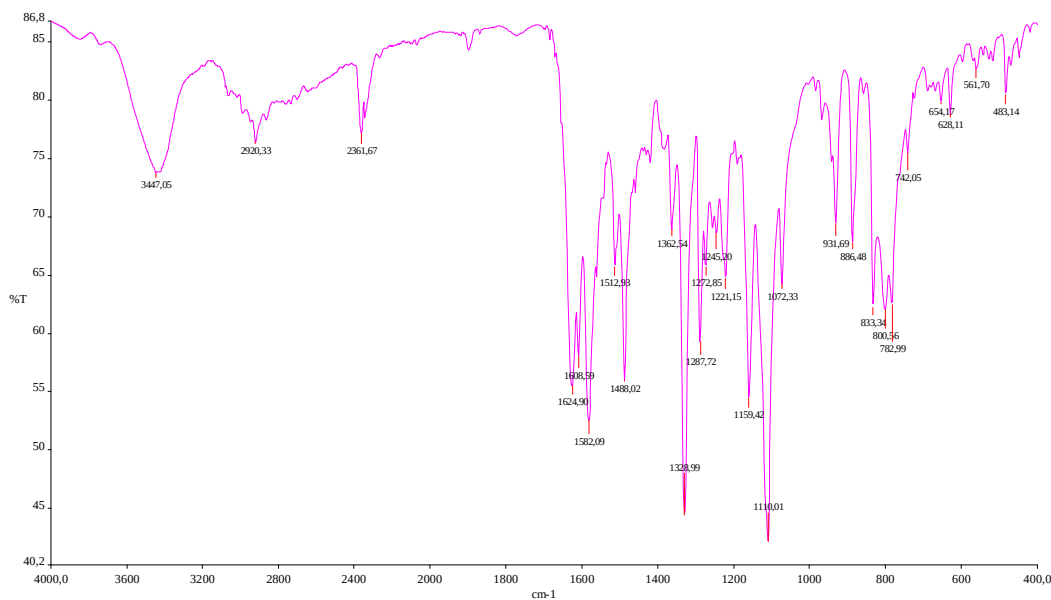
APPENDIX 1.14. ¹H NMR spectrum of FSB-5



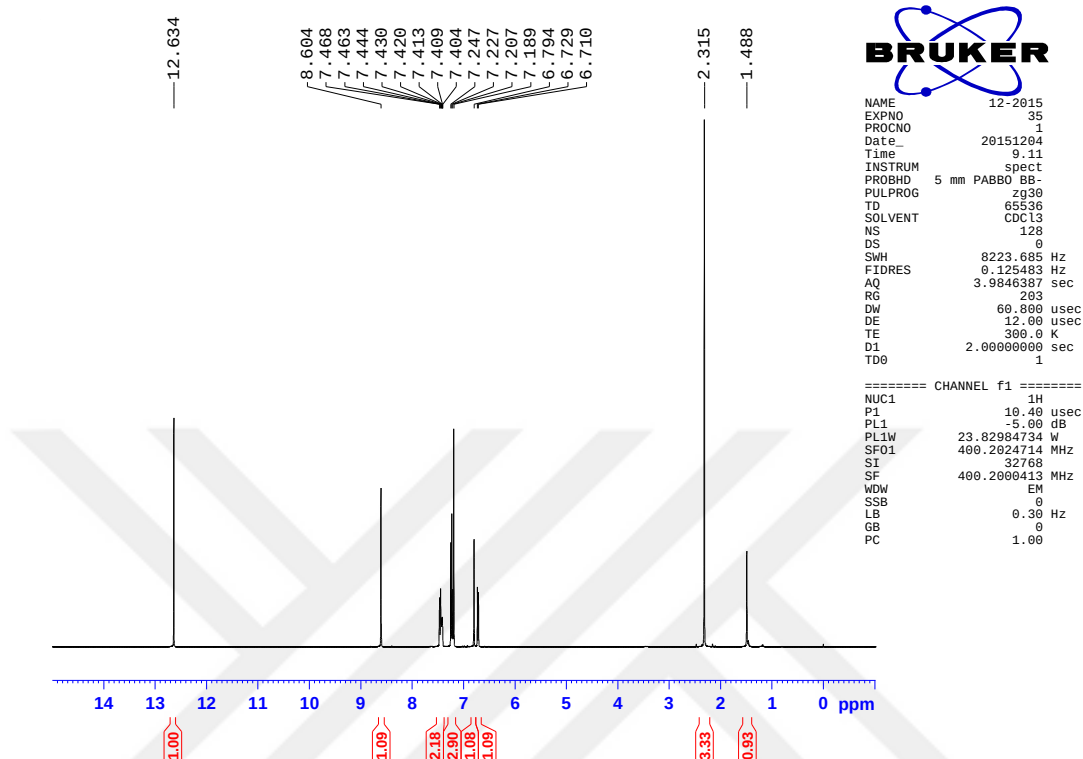
APPENDIX 1.15. ^{13}C NMR spectrum of FSB-5



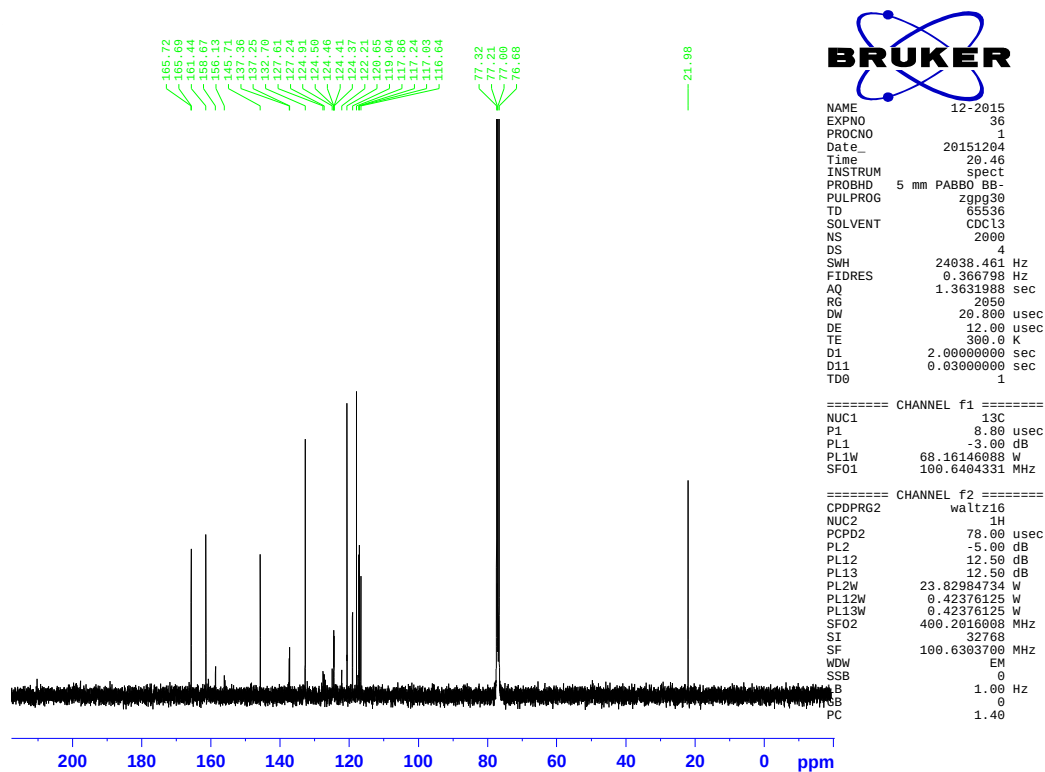
APPENDIX 1.16. FT-IR spectrum of FSB-6



APPENDIX 1.17. ^1H NMR spectrum of FSB-6

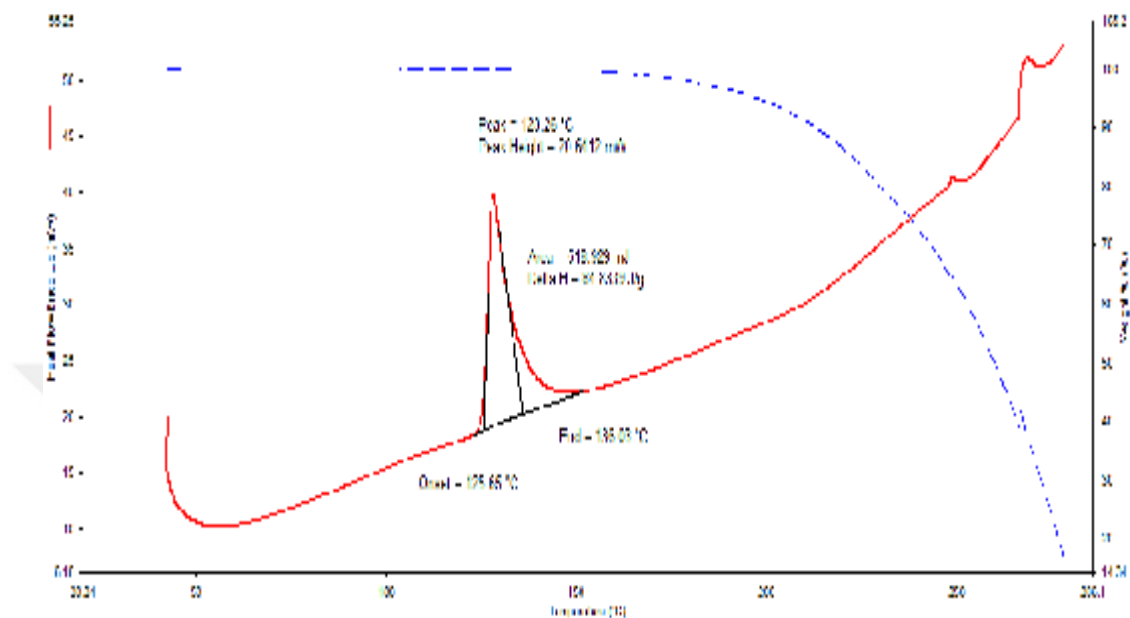


APPENDIX 1.18. ^{13}C NMR spectrum of FSB-6

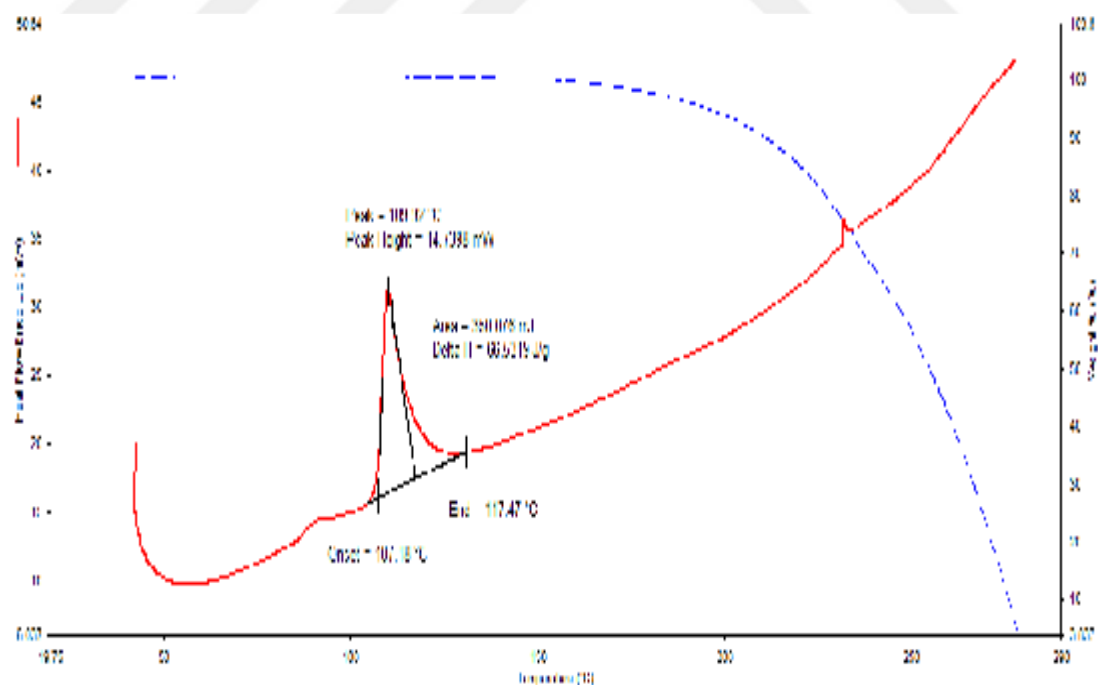


APPENDIX 2. DSC graphs of Ligands

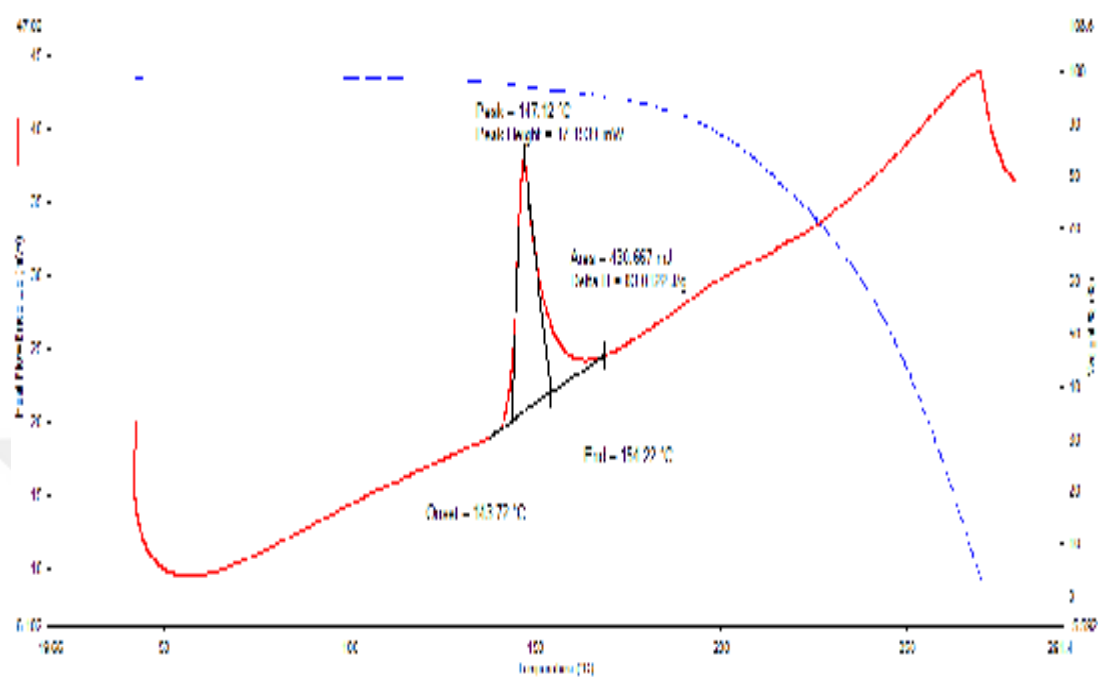
APPENDIX 2.1. DSC graph of FSB-1



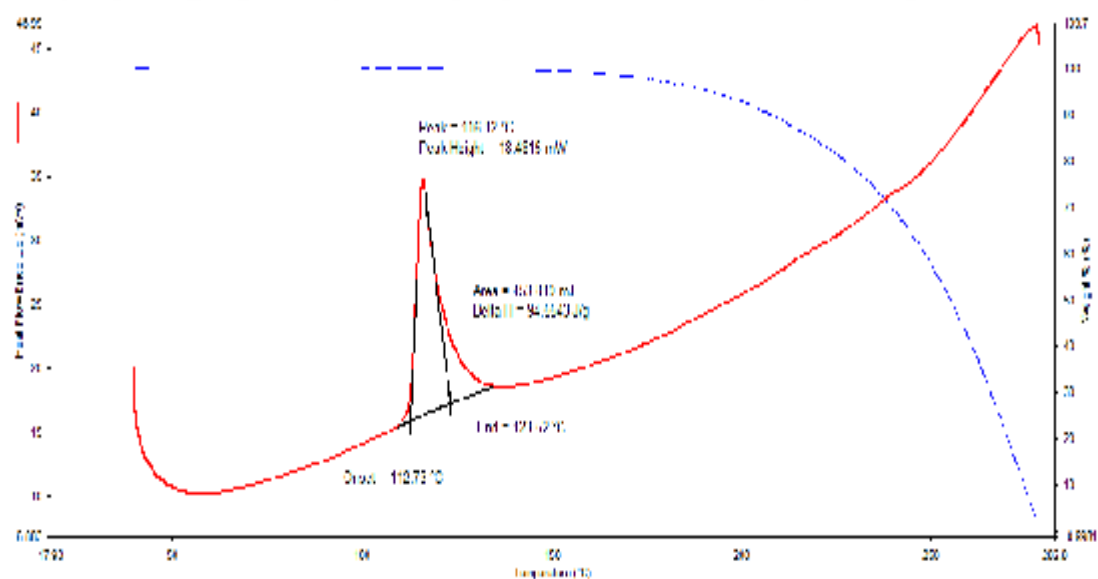
APPENDIX 2.2. DSC graph of FSB-2



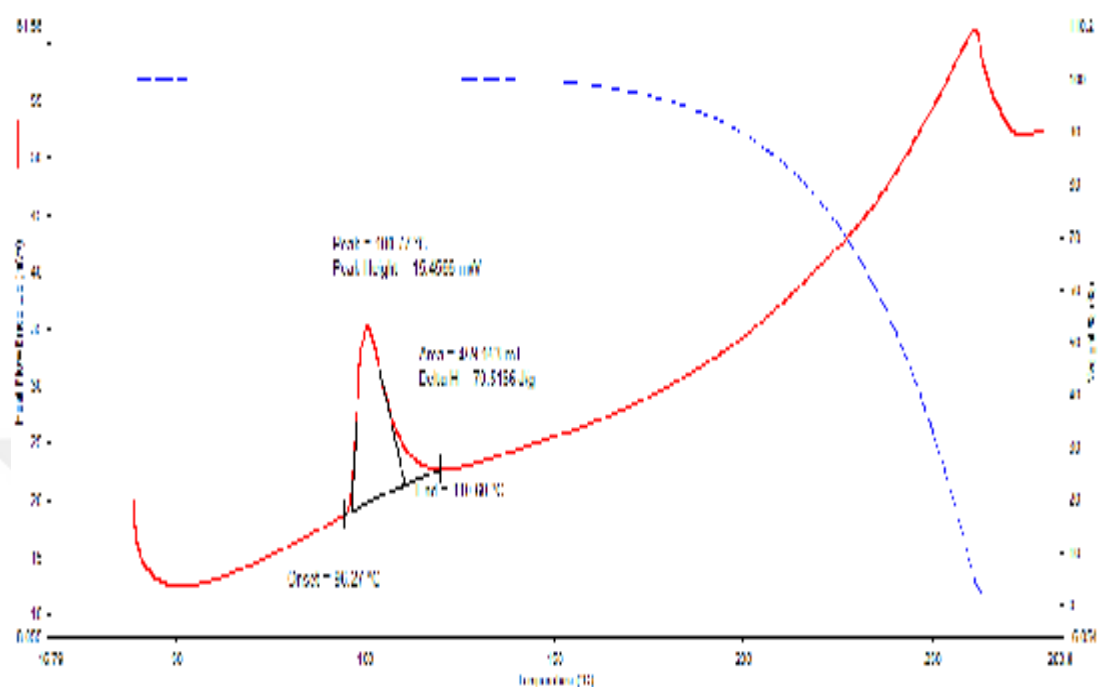
APPENDIX 2.3. DSC graph of FSB-3



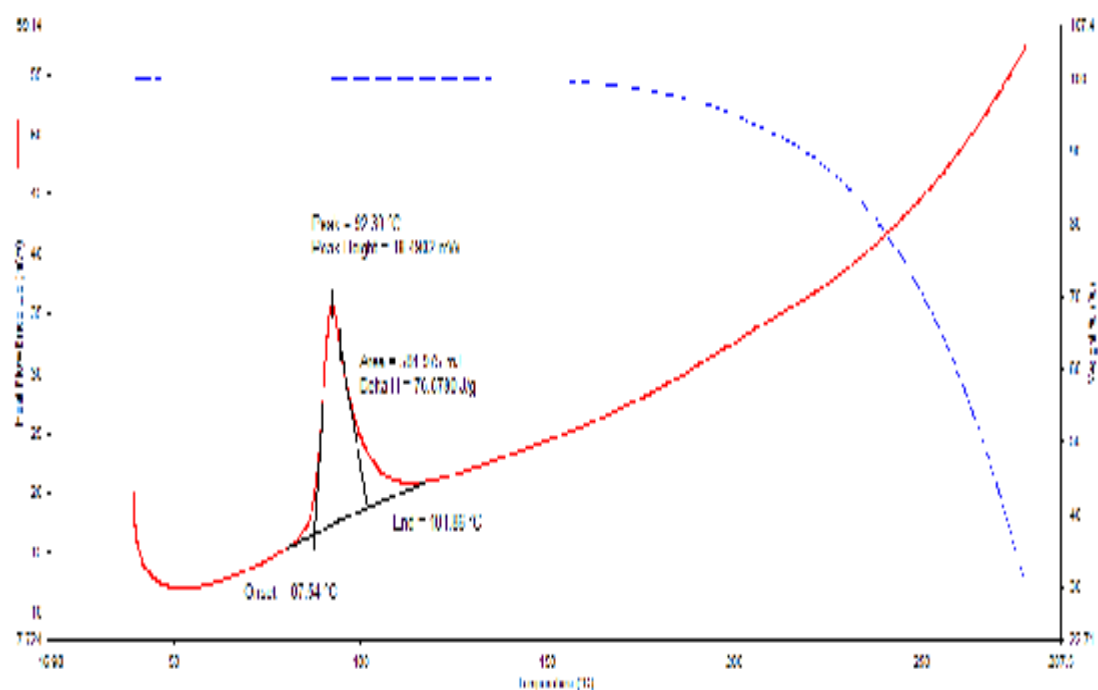
APPENDIX 2.4. DSC graph of FSB-4



APPENDIX 2.5. DSC graph of FSB-5

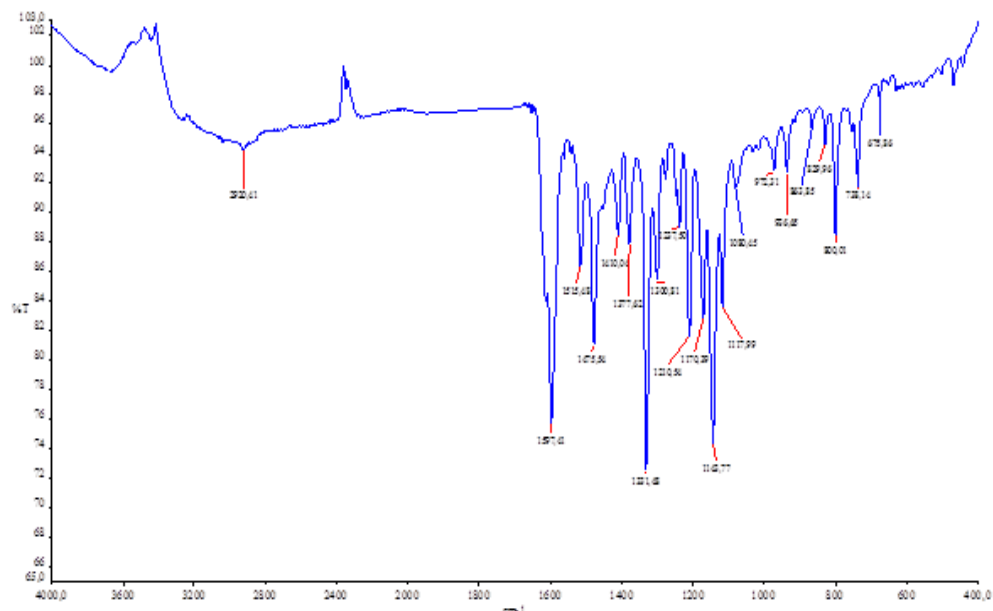


APPENDIX 2.6. DSC graph of FSB-6

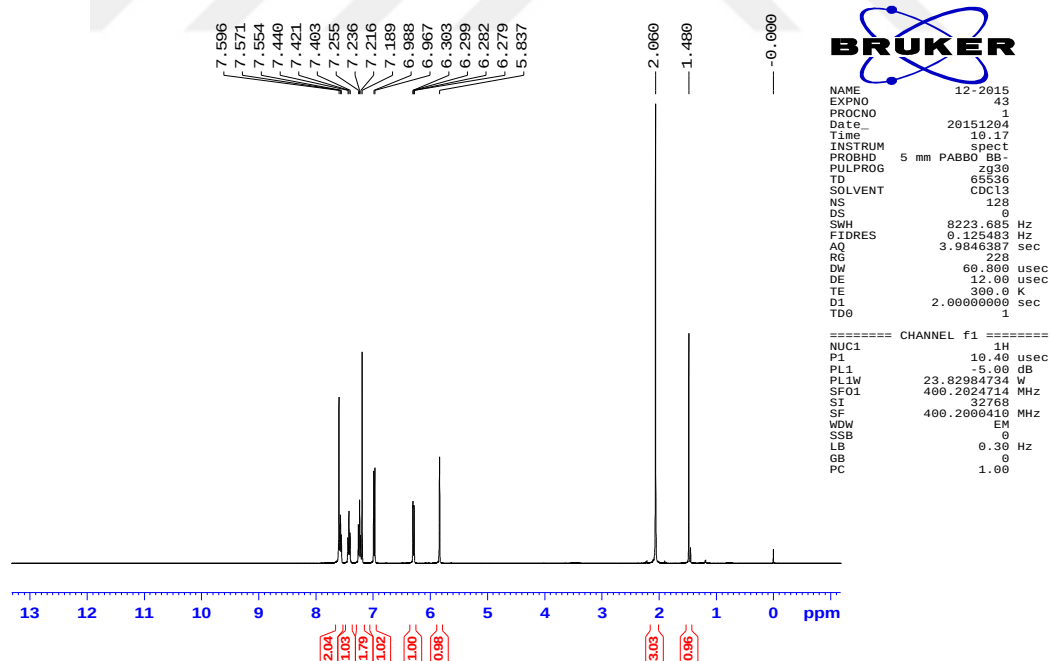


APPENDIX 3: FT-IR and NMR Spectra of Complexes

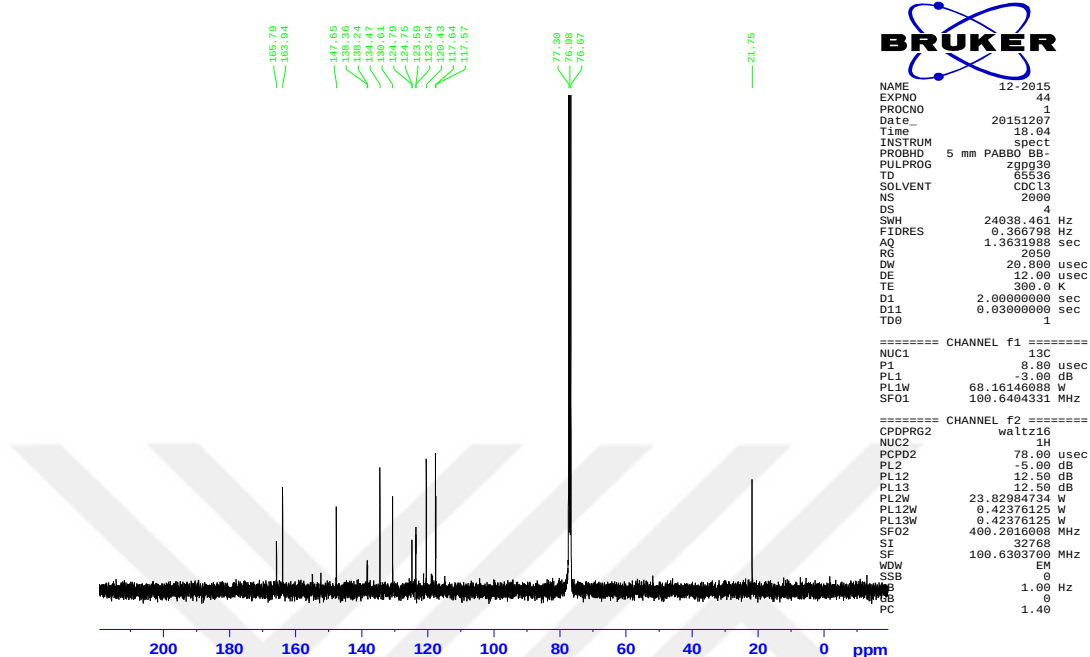
APPENDIX 3.1. FT-IR spectrum of K1



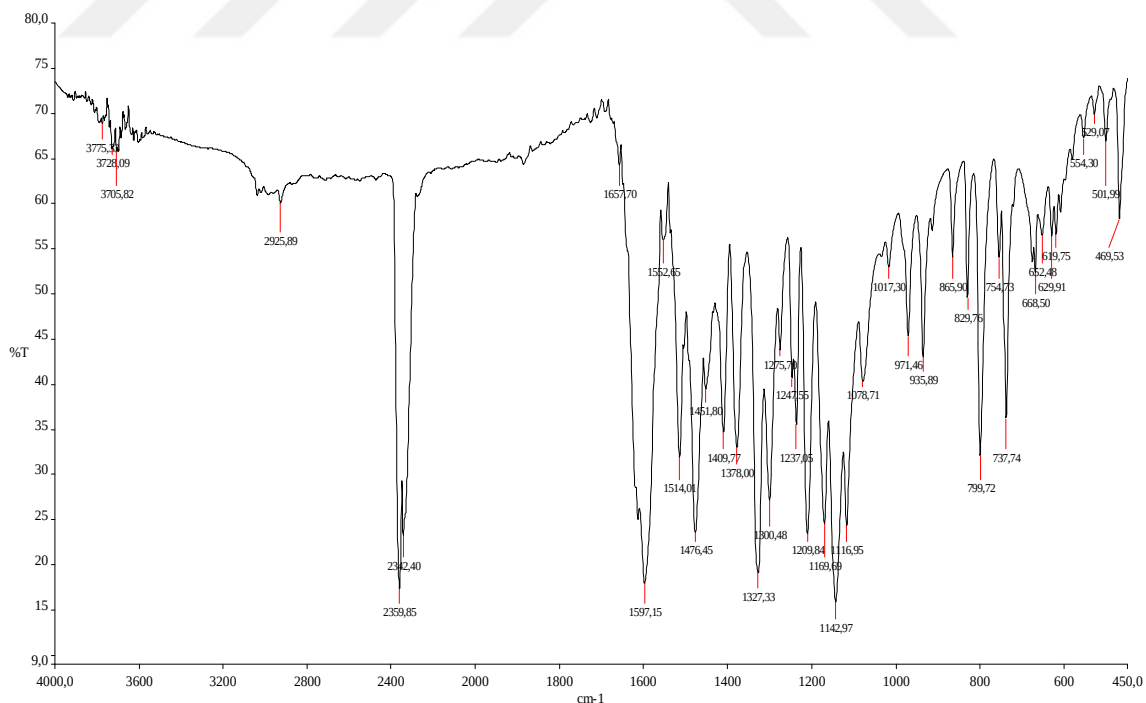
APPENDIX 3.2. ^1H NMR spectrum of K1



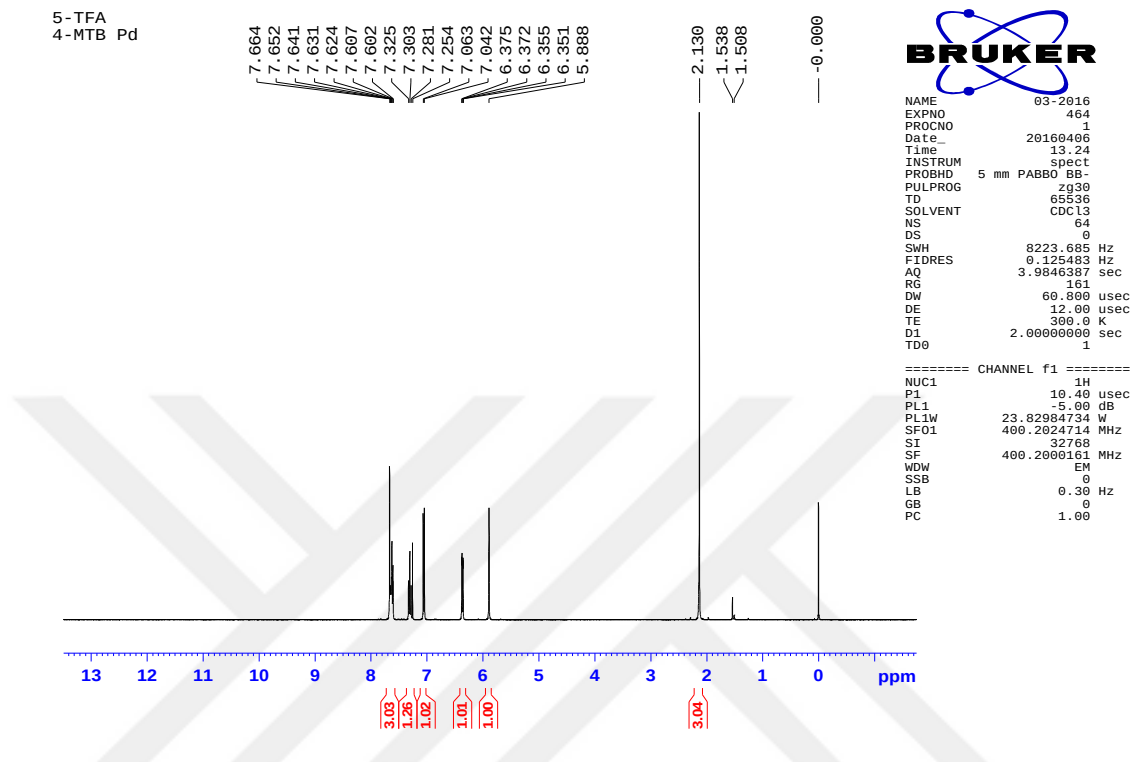
APPENDIX 3.3. ^{13}C NMR spectrum of K1



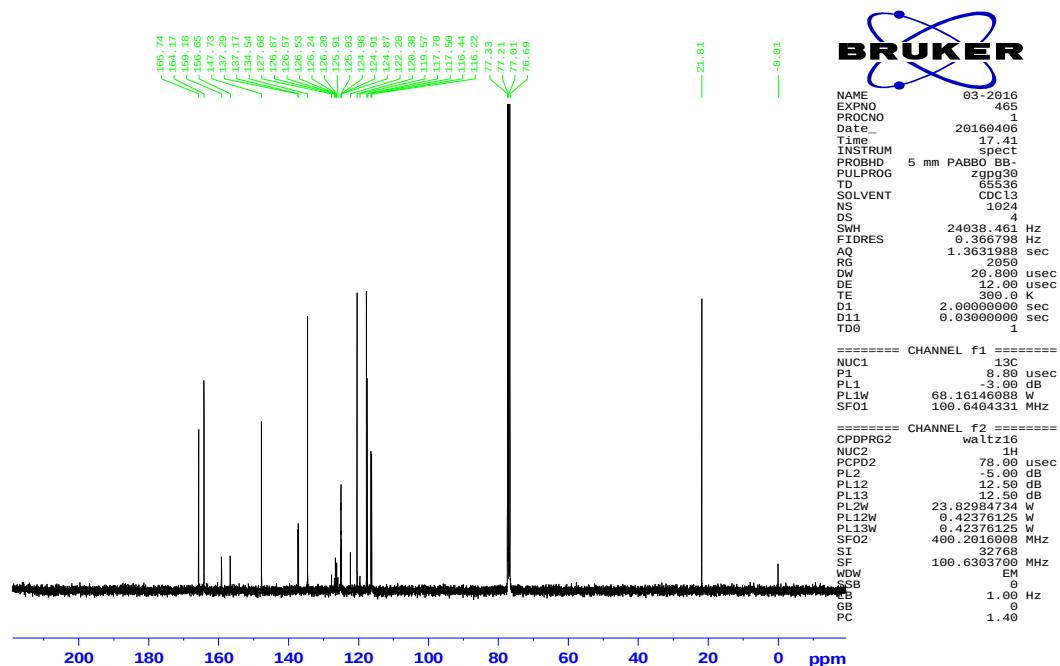
APPENDIX 3.4. FT-IR spectrum of K2



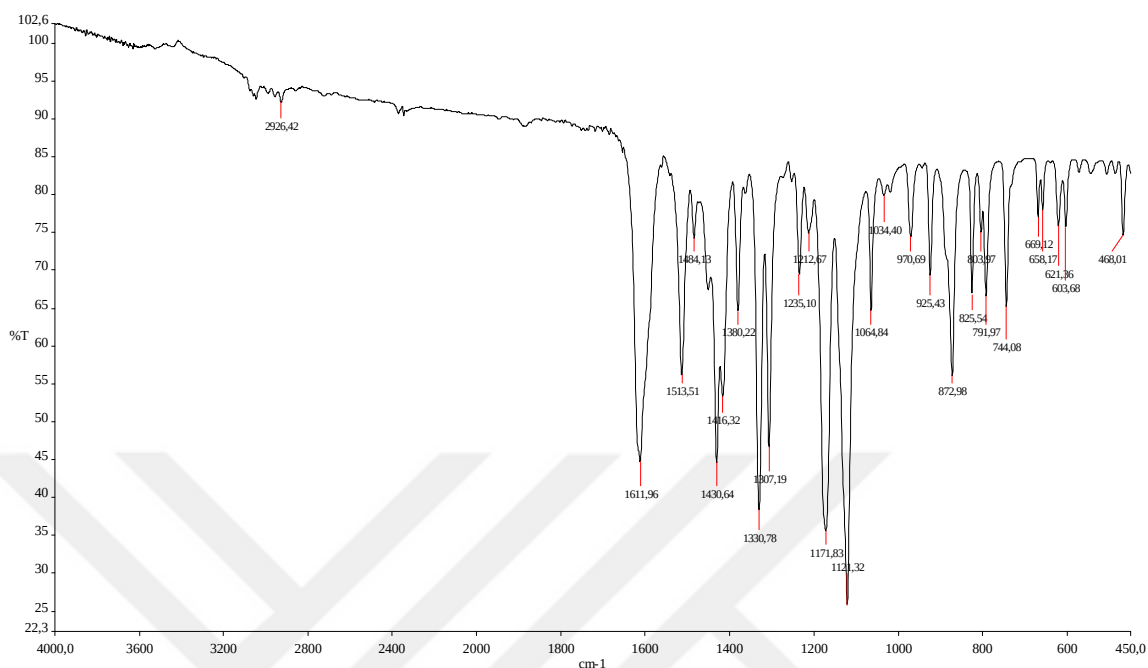
APPENDIX 3.5. ^1H NMR spectrum of K2



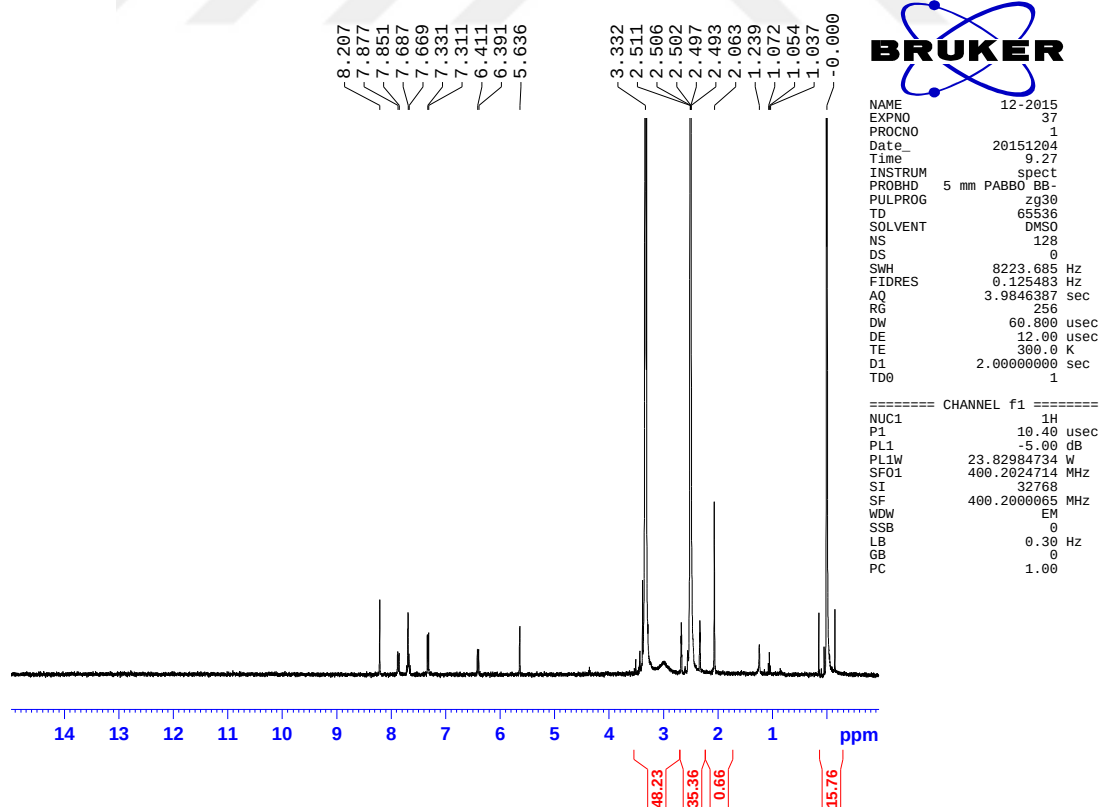
APPENDIX 3.5. ^{13}C NMR spectrum of K2



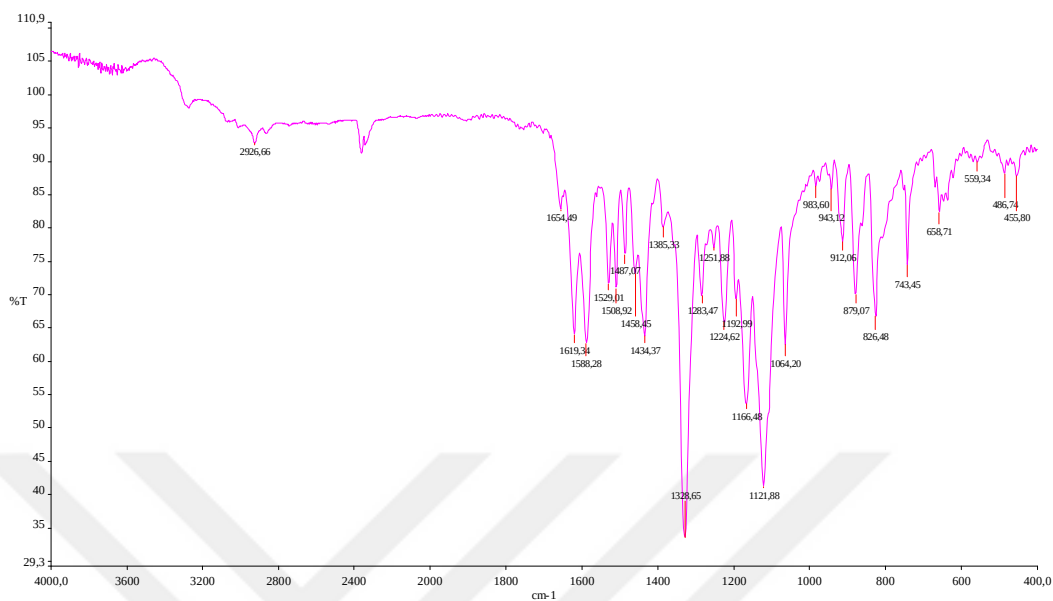
APPENDIX 3.6. FT-IR spectrum of K3



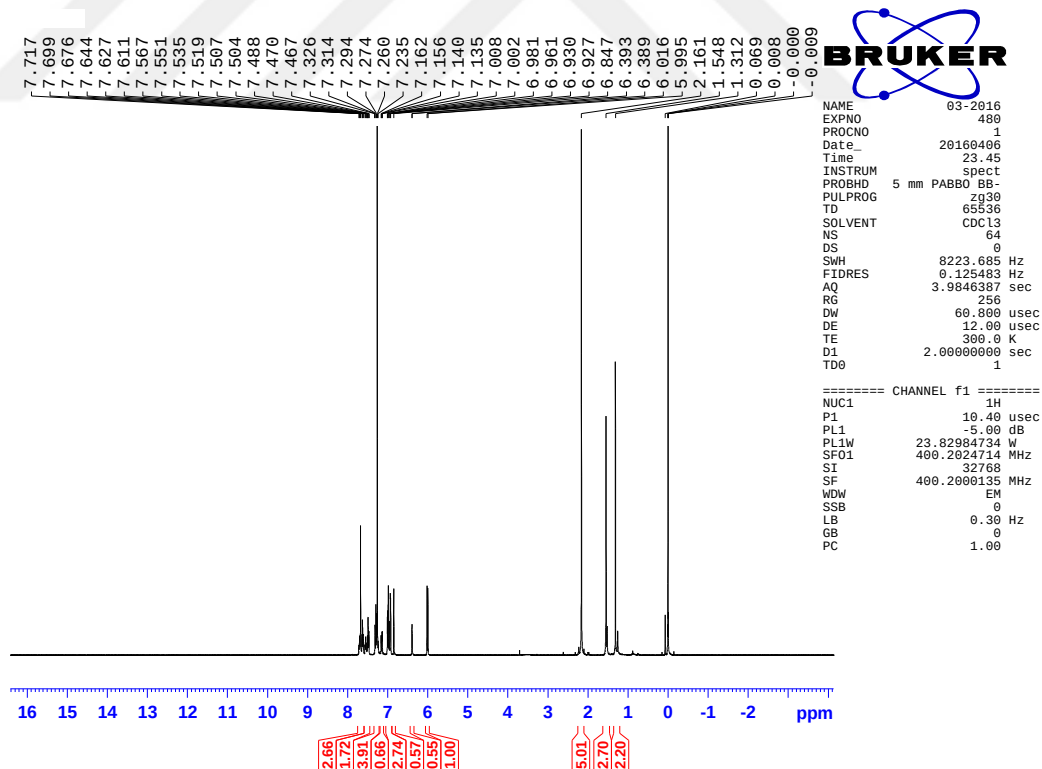
APPENDIX 3.7. ¹H NMR spectrum of K3



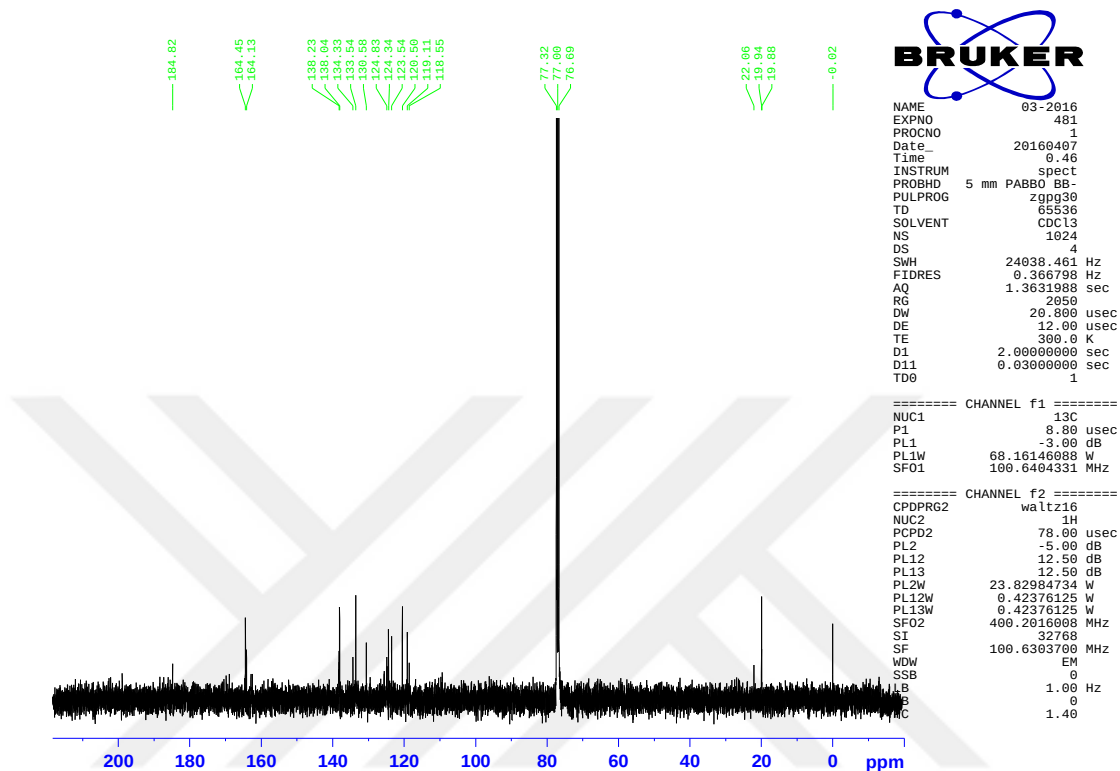
APPENDIX 3.8. FT-IR spectrum of K4



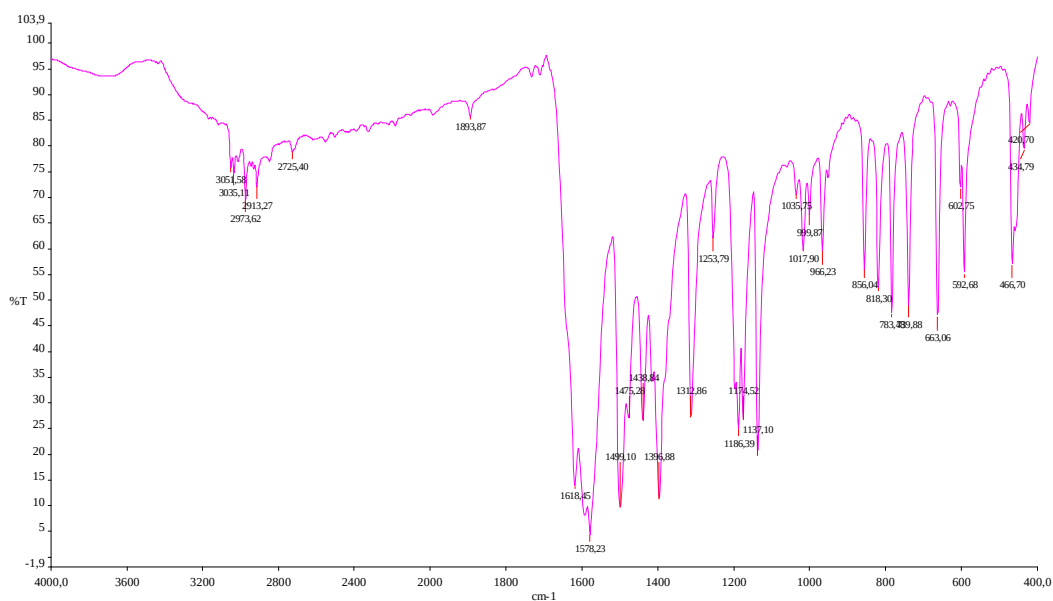
APPENDIX 3.9. ¹H NMR spectrum of K4



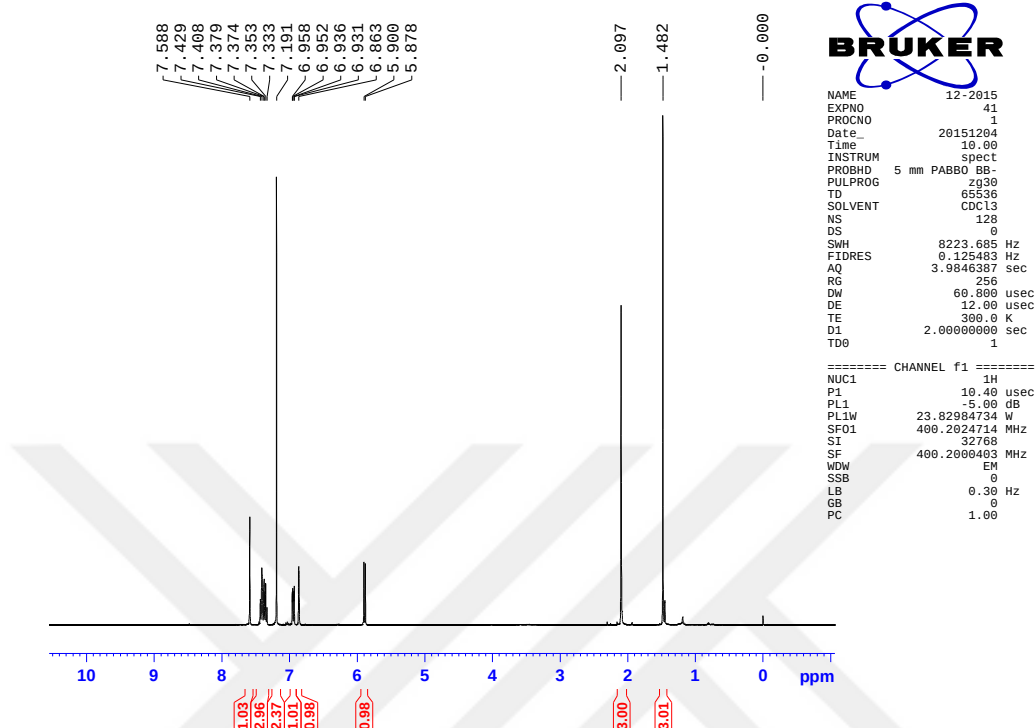
APPENDIX 3.10. ^{13}C NMR spectrum of K4



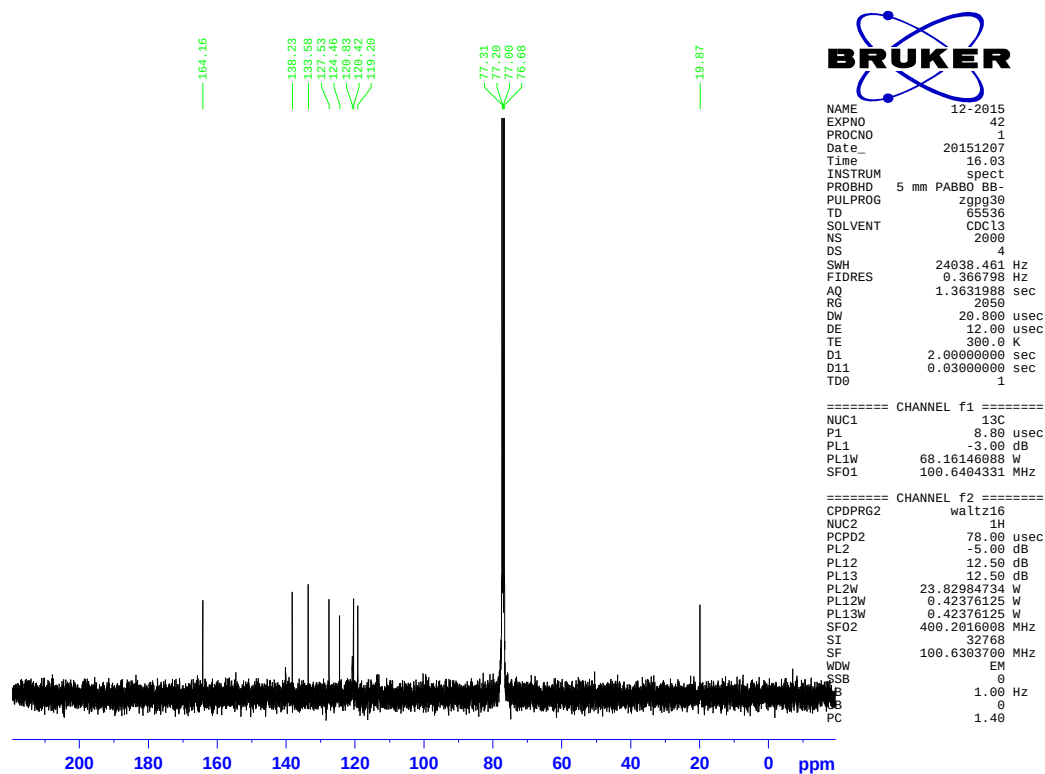
APPENDIX 3.11. FT-IR spectrum of K5



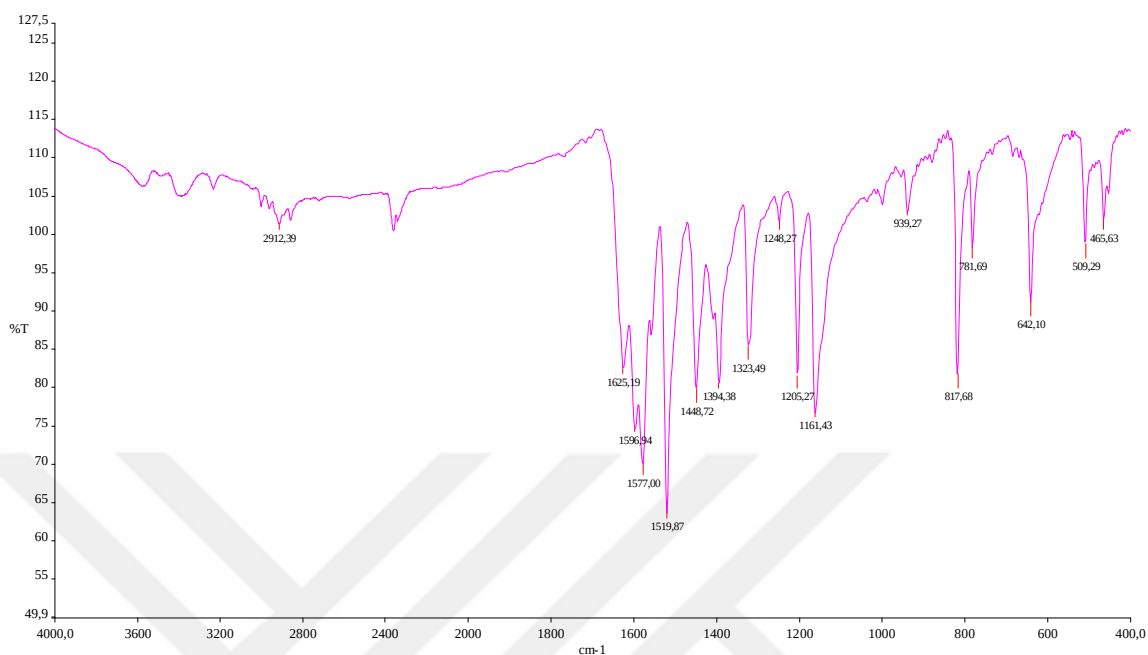
APPENDIX 3.12. ^1H NMR spectrum of K5



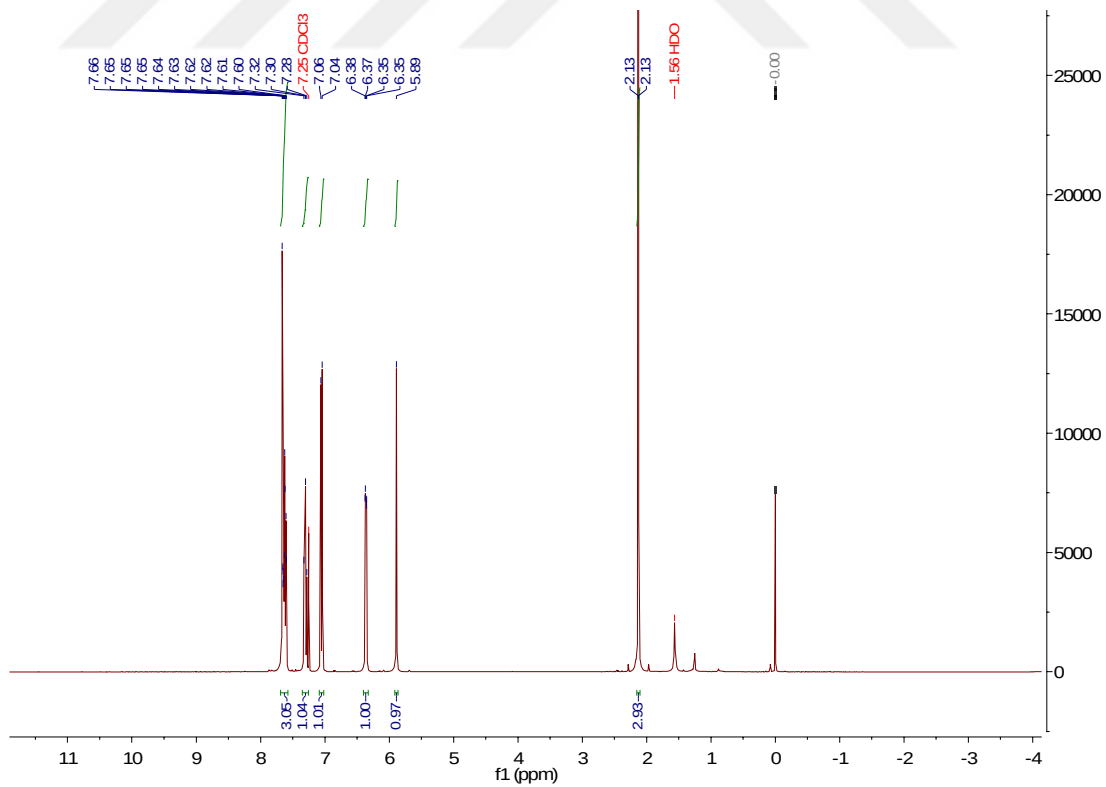
APPENDIX 3.13. ^{13}C NMR spectrum of K5



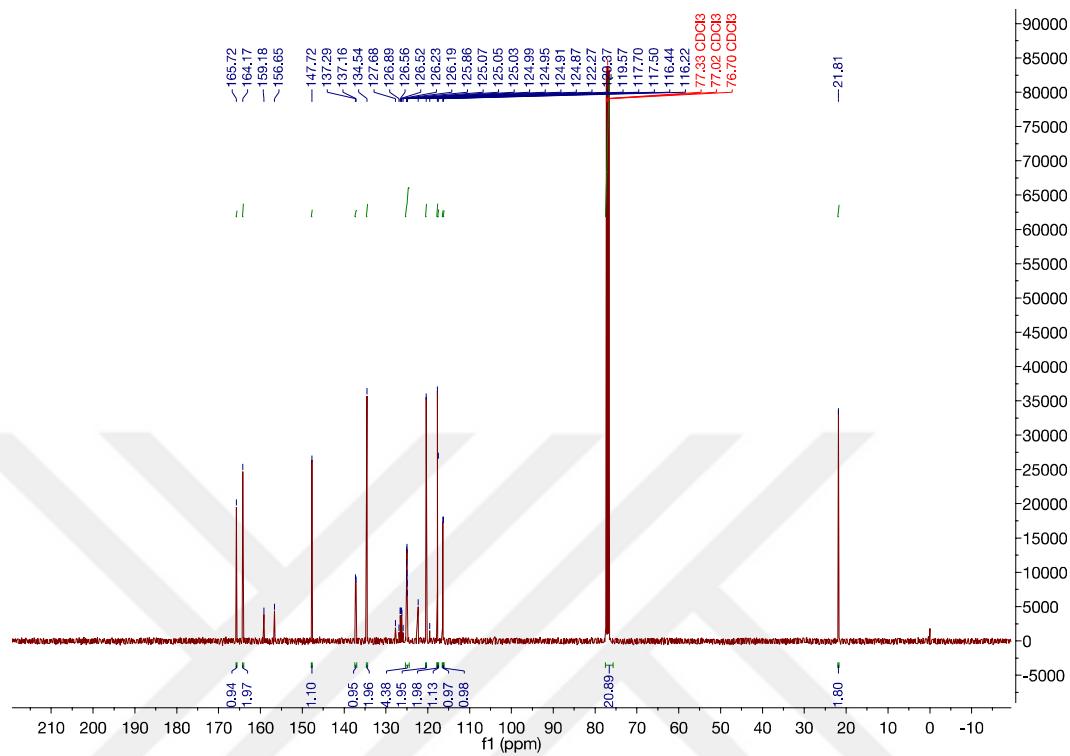
APPENDIX 3.14. FT-IR spectrum of K6



APPENDIX 3.15. ¹H NMR spectrum of K6

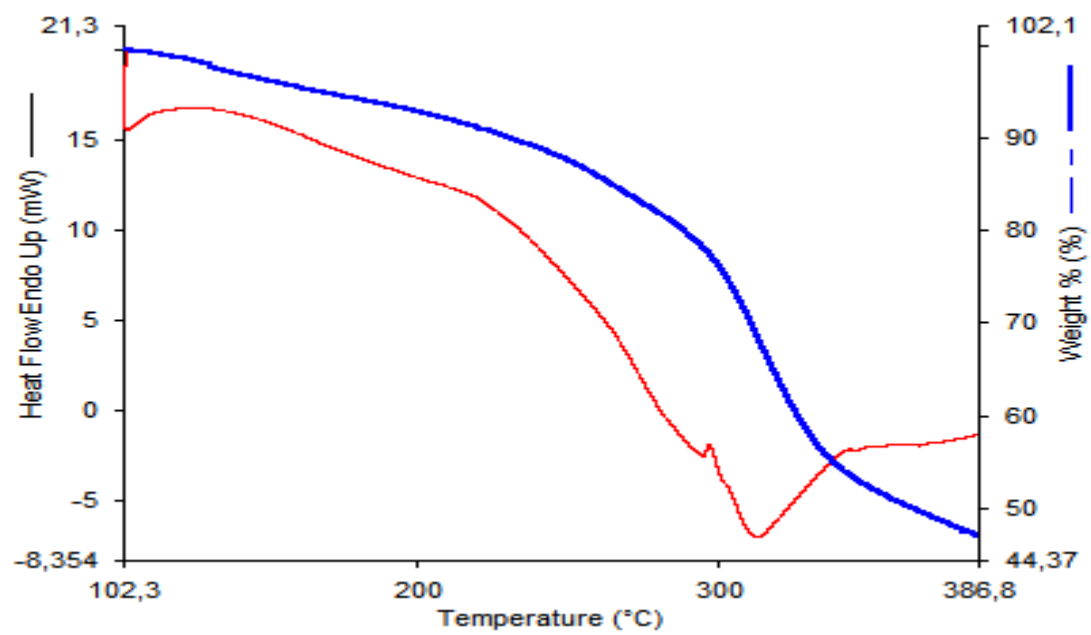


APPENDIX 3.16. ^{13}C NMR spectrum of K6

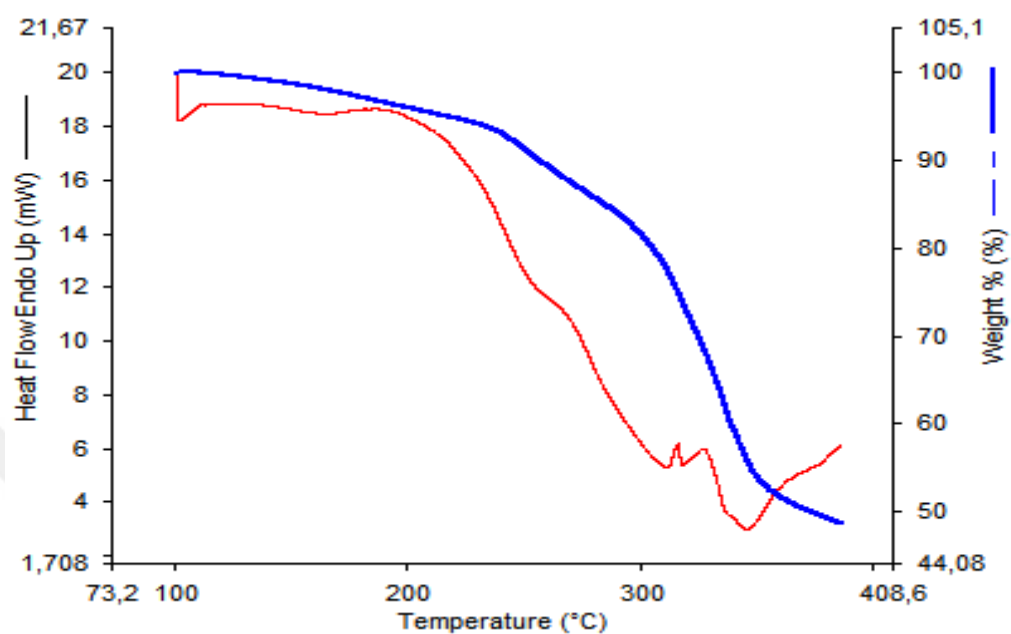


APPENDIX 4. DsSC graphs of Palladium-Schiff base complexes

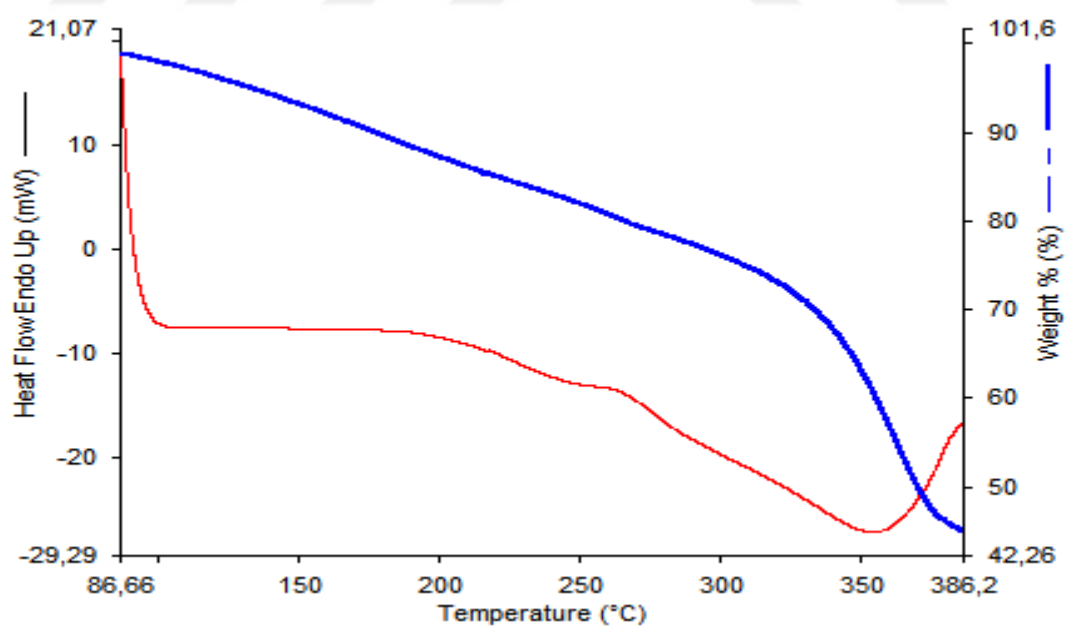
APPENDIX 4. 1 DSC graph of K 1



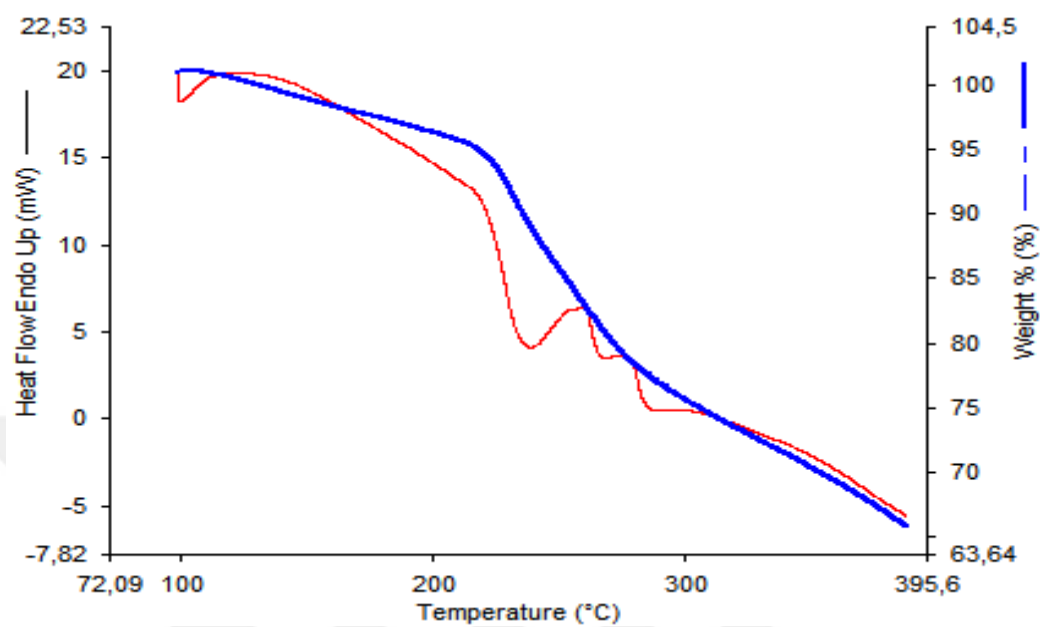
APPENDIX 4. 2. DSC graph of K2



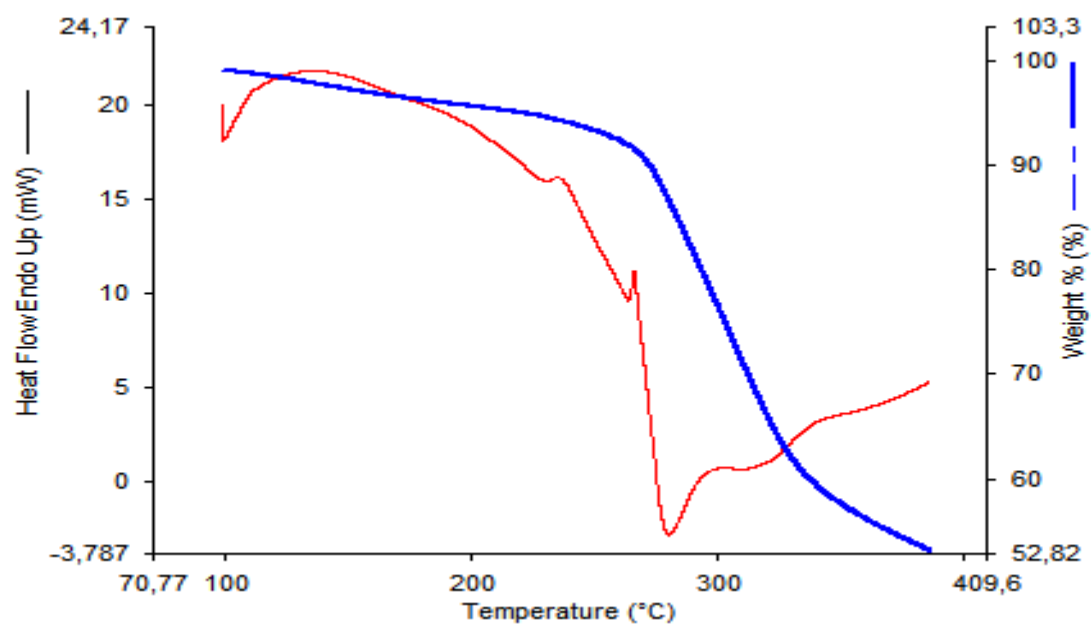
APPENDIX 4. 3 DSC graph of K 3



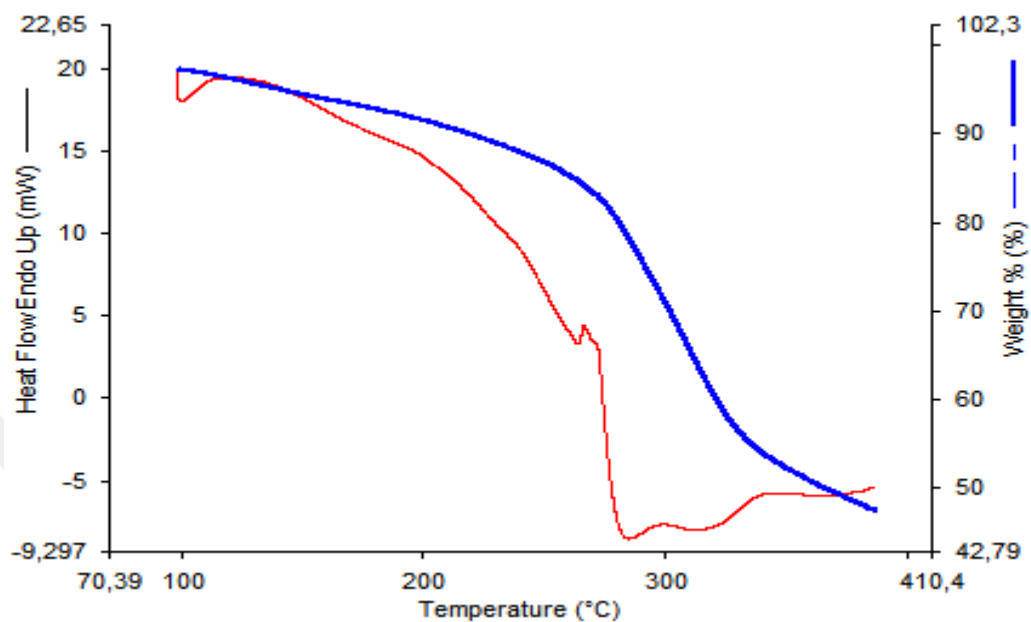
APPENDIX 4. 4. DSC graph of K 4



APPENDIX 4. 5. DSC graph of K 5

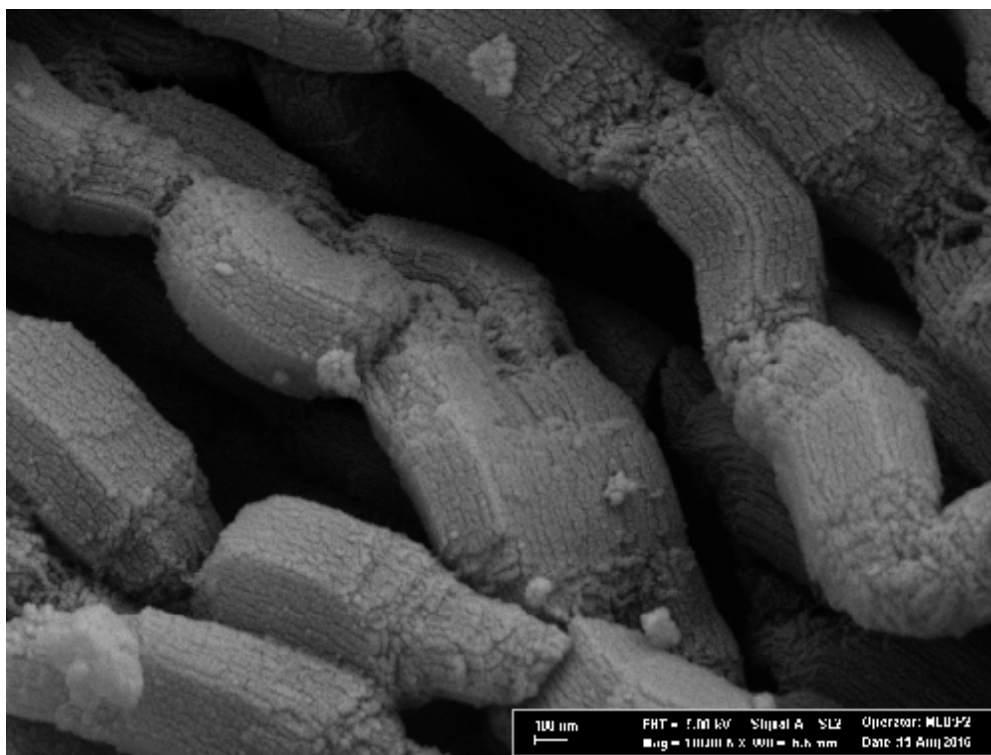


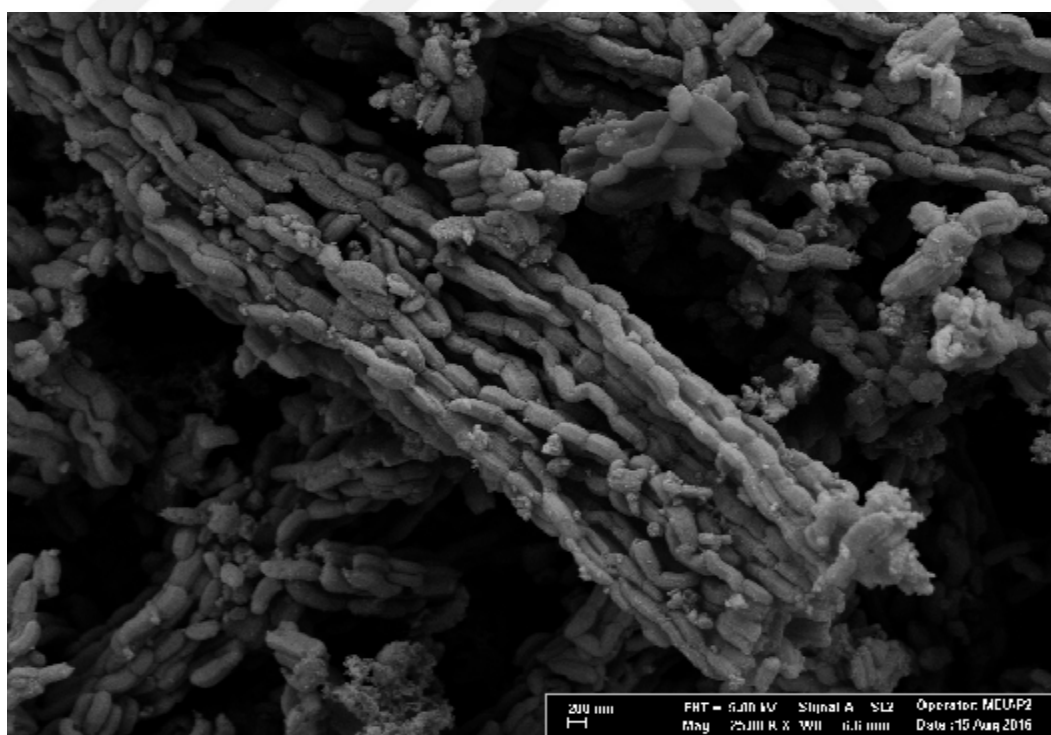
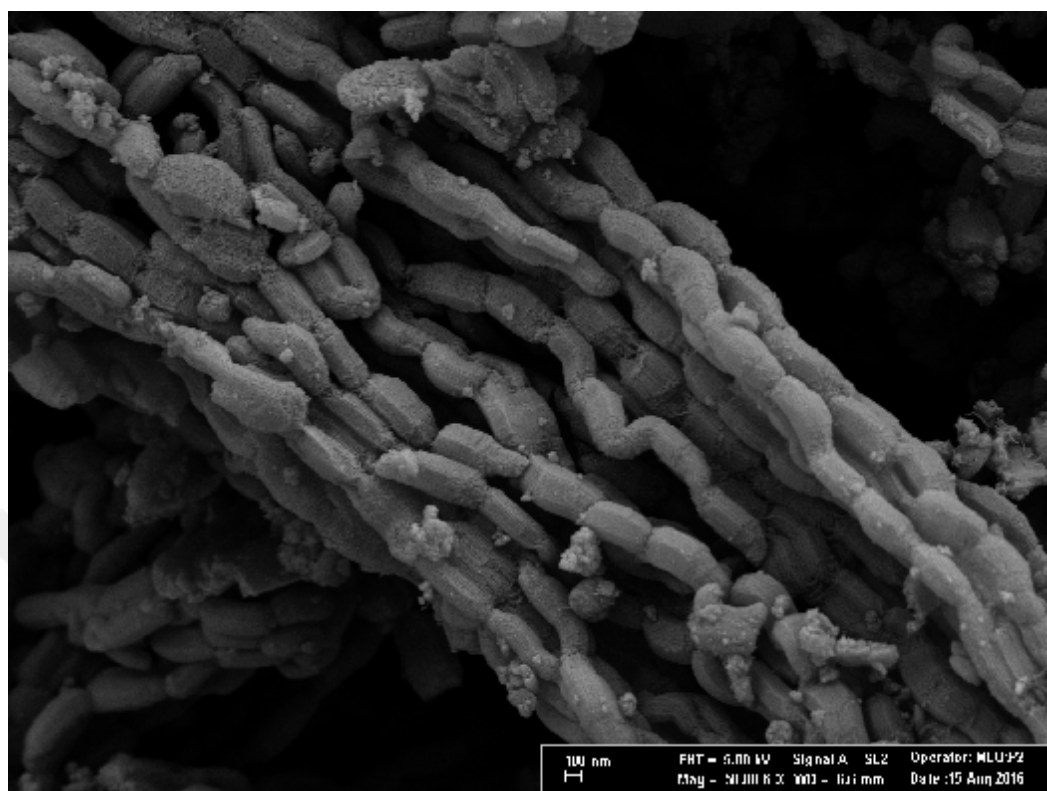
APPENDIX 4. 6. DSC graph of K 6

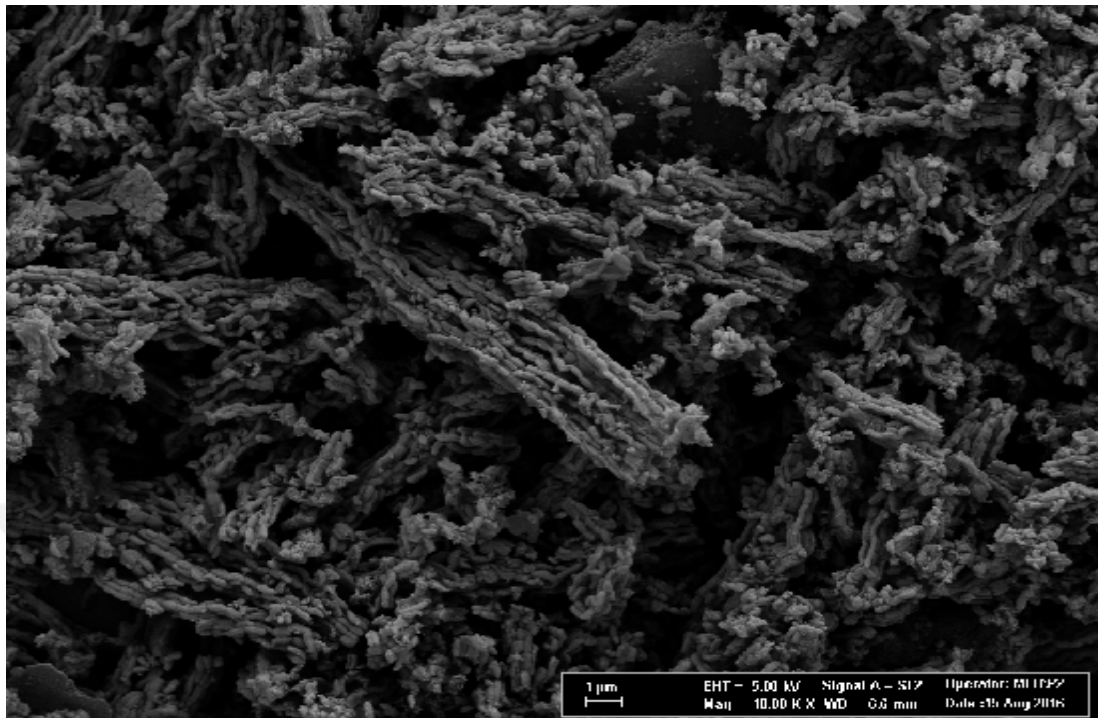


APPENDIX 5. SEM images of catalyst (100kx, 50kx, 25kx, 10 kx magnification)

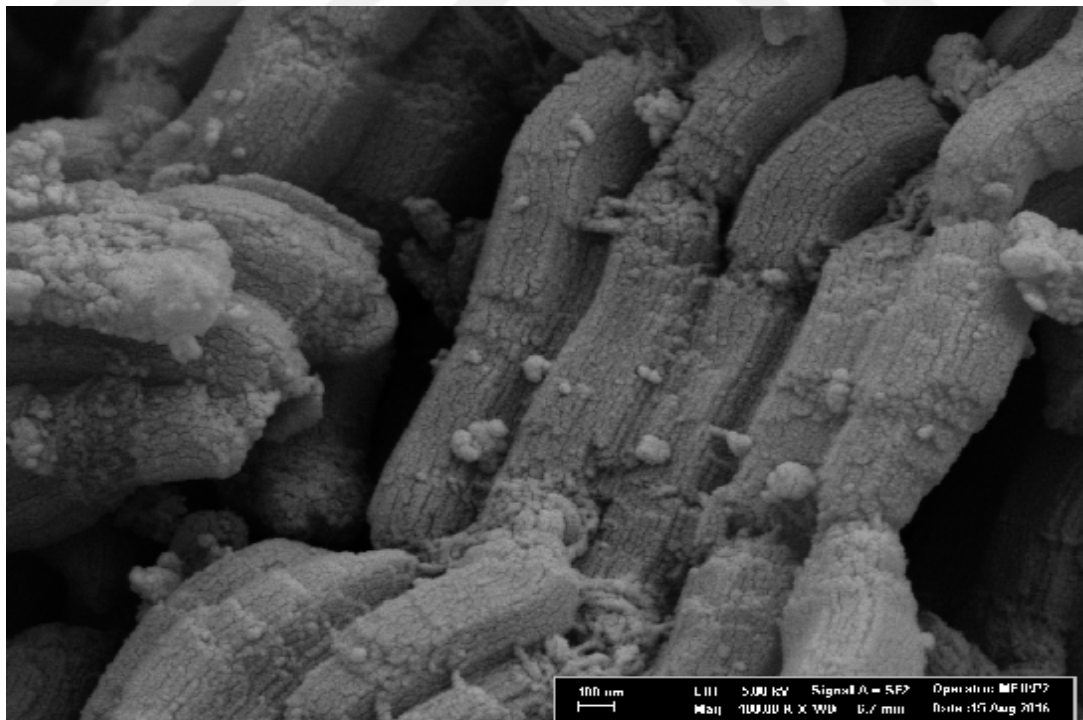
APPENDIX 5.1. SEM images of Cat. 1

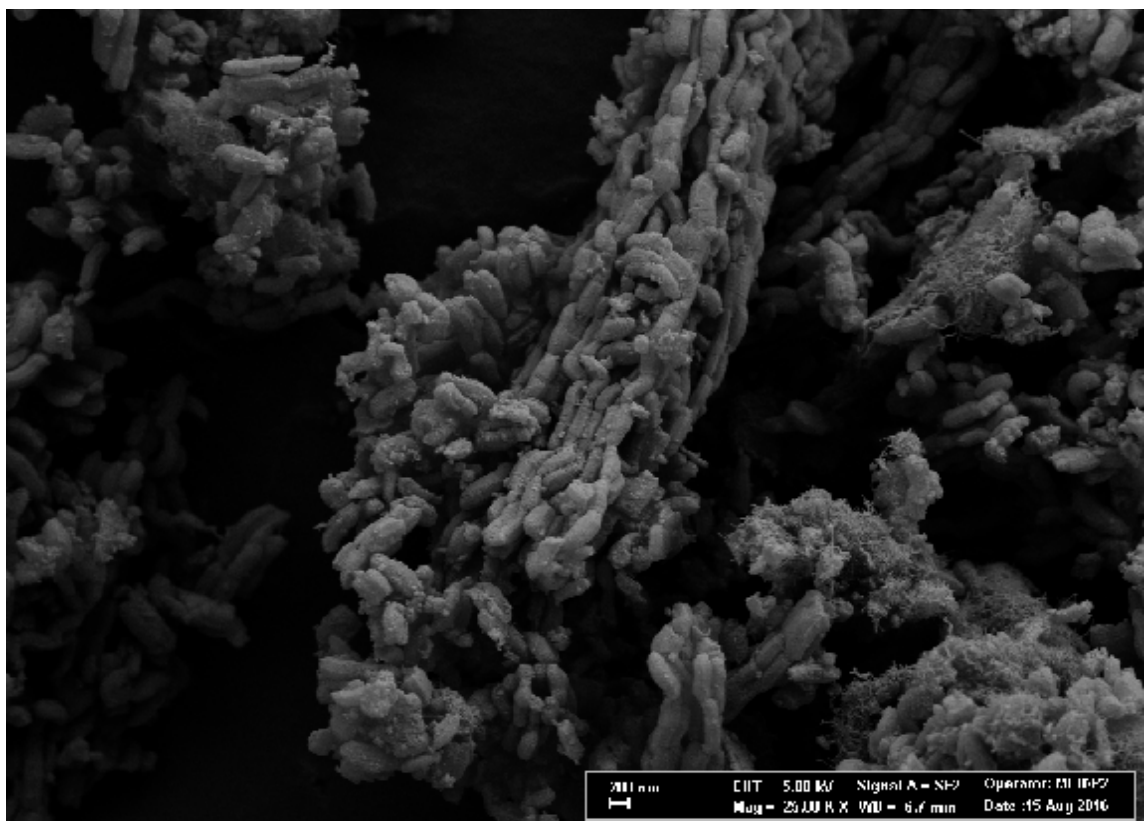
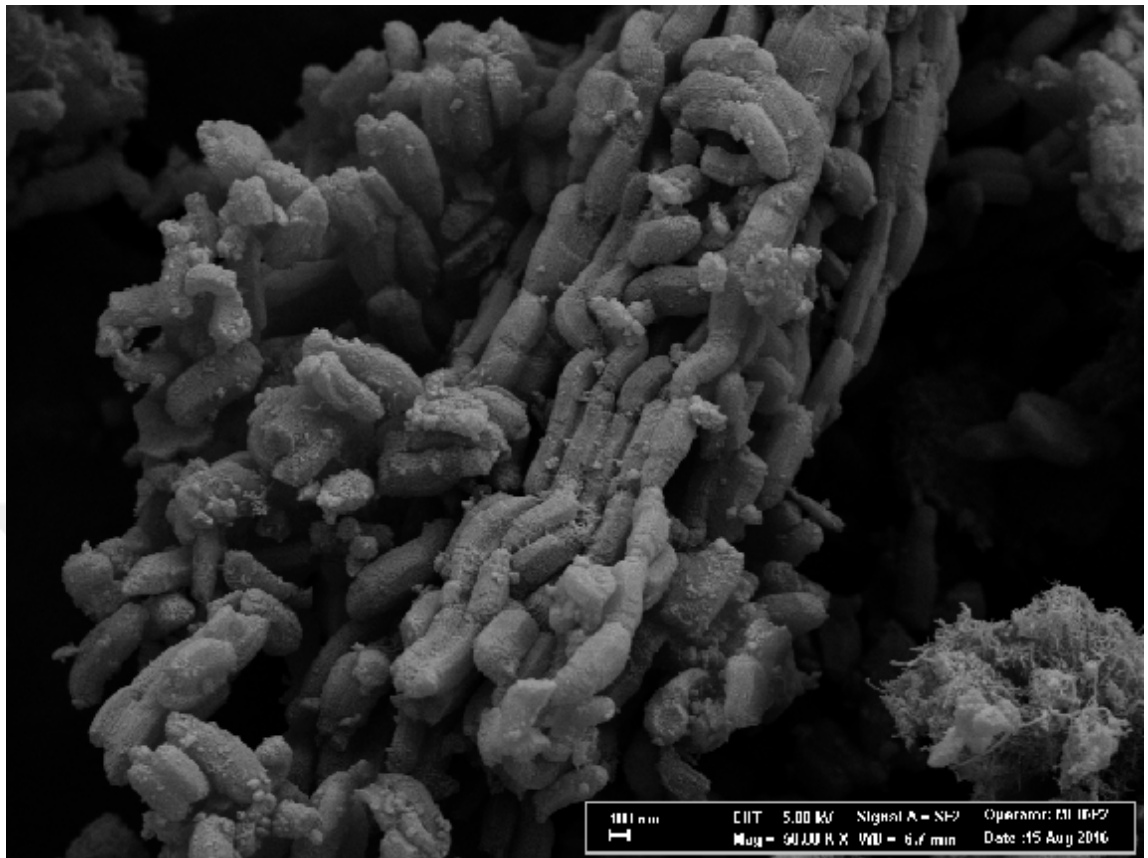


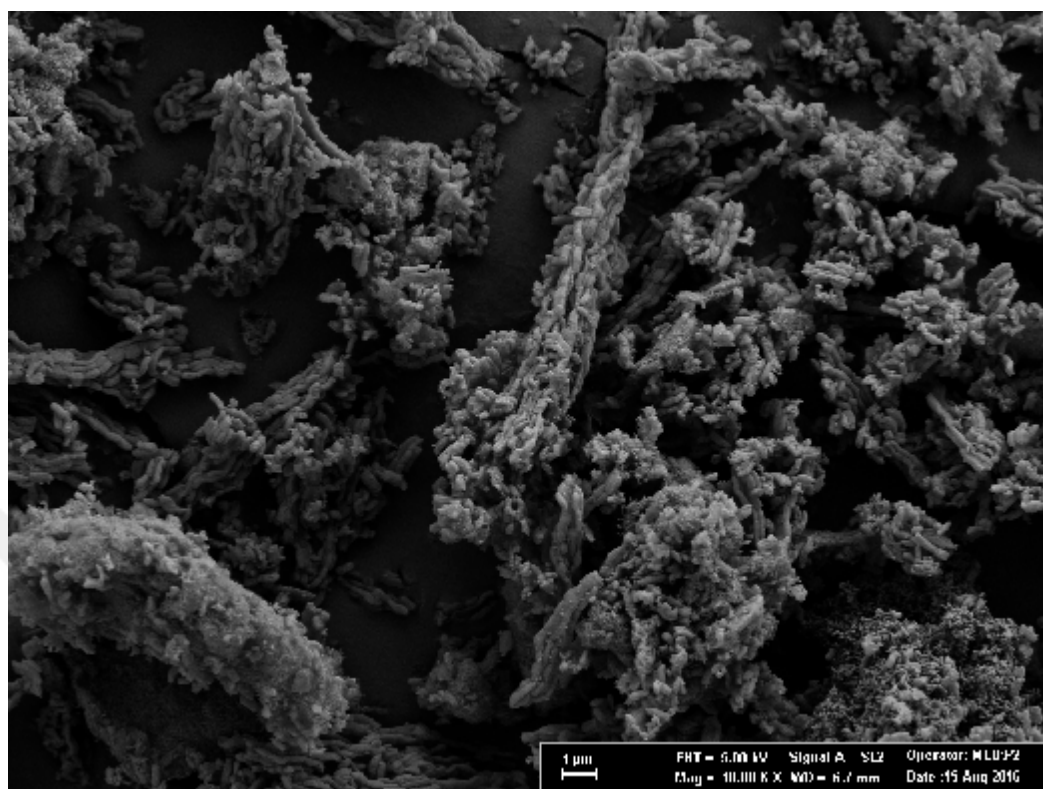




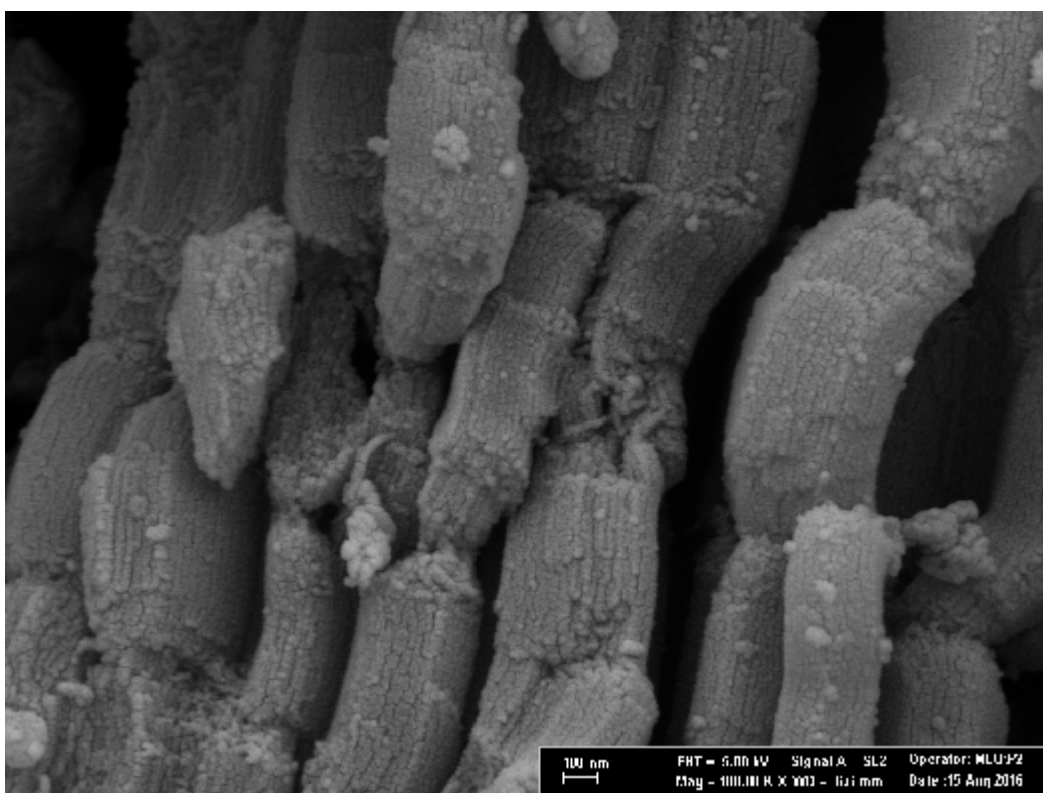
APPENDIX 5.2. SEM images of Cat. 2

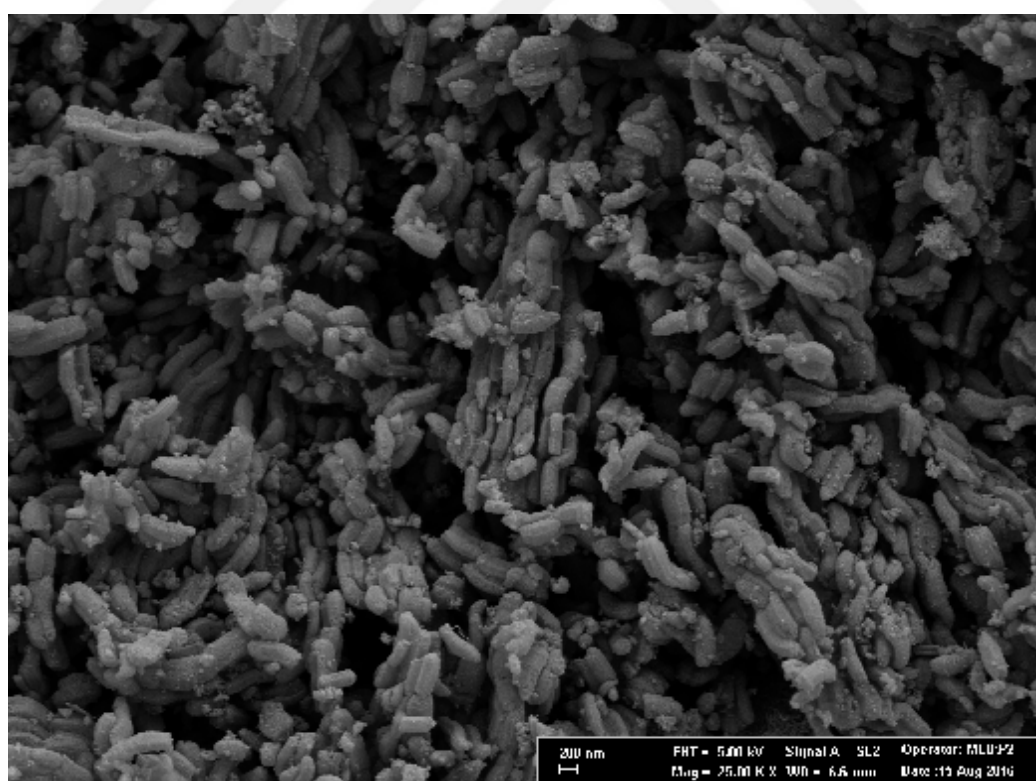
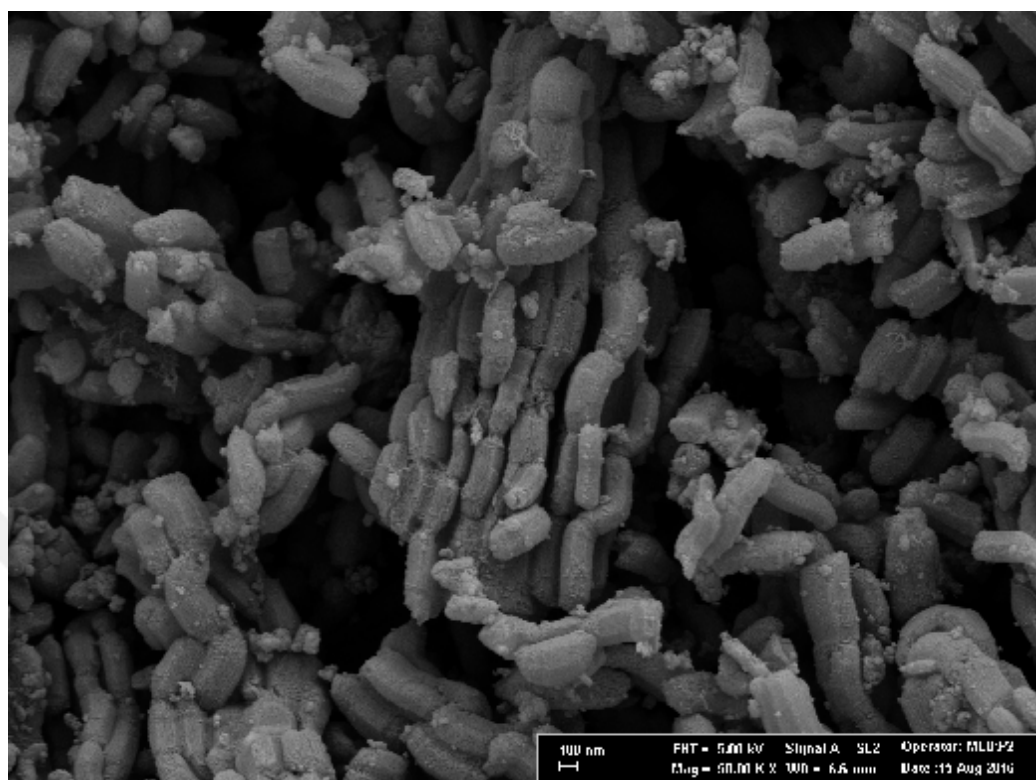


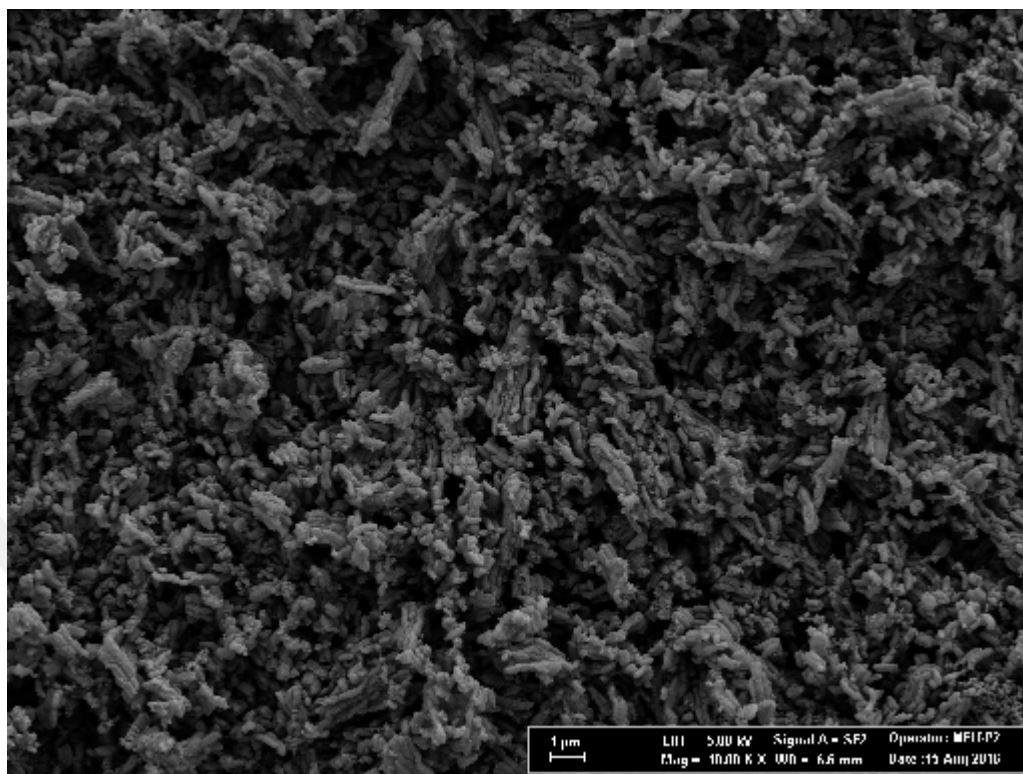




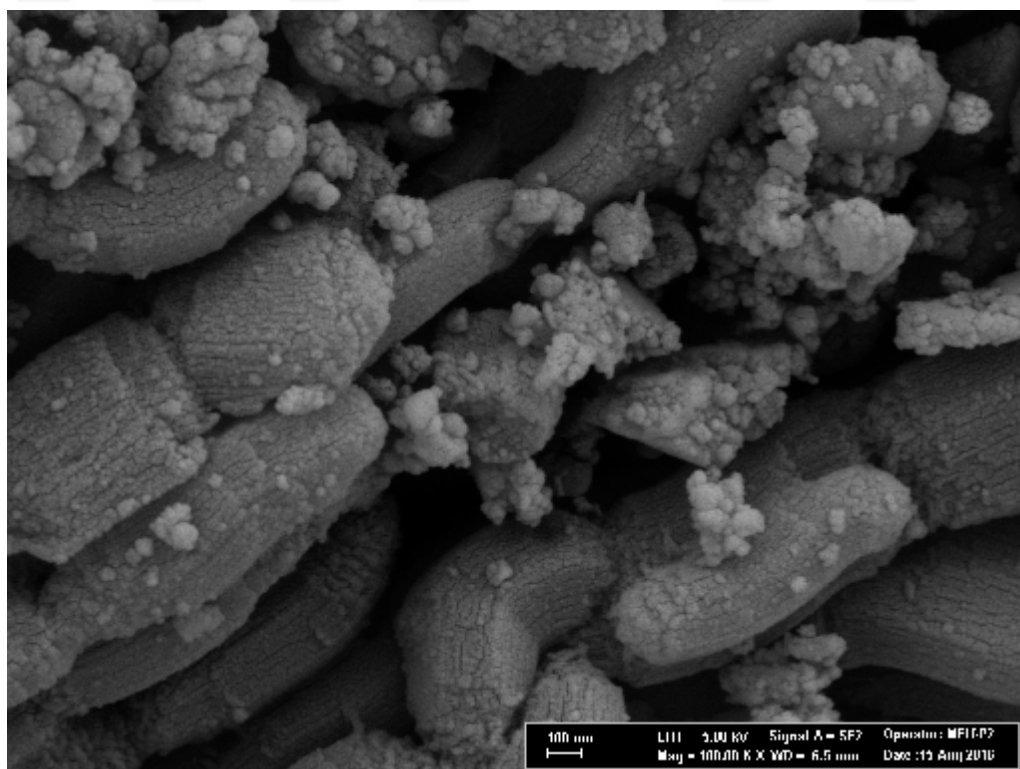
APPENDIX 5.3. SEM images of Cat. 3

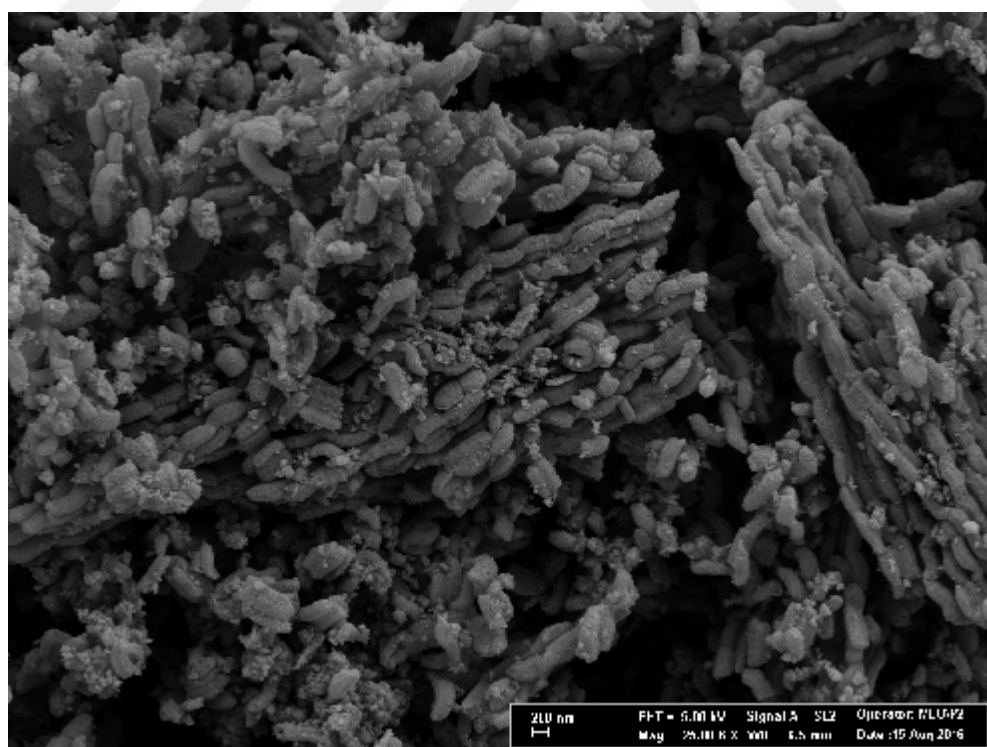
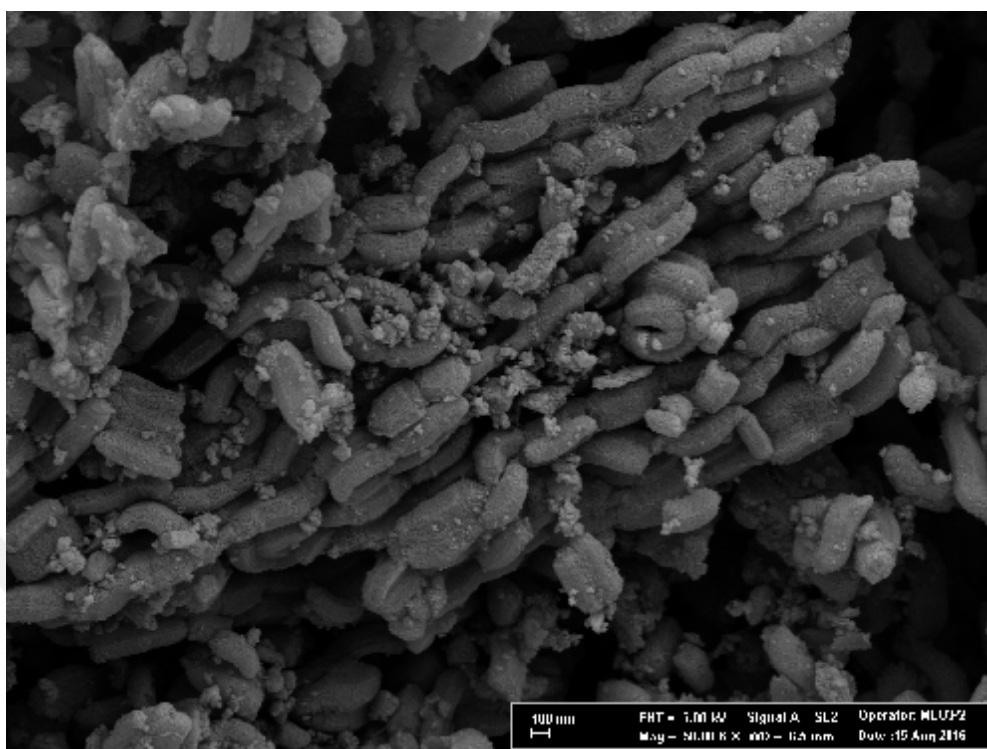


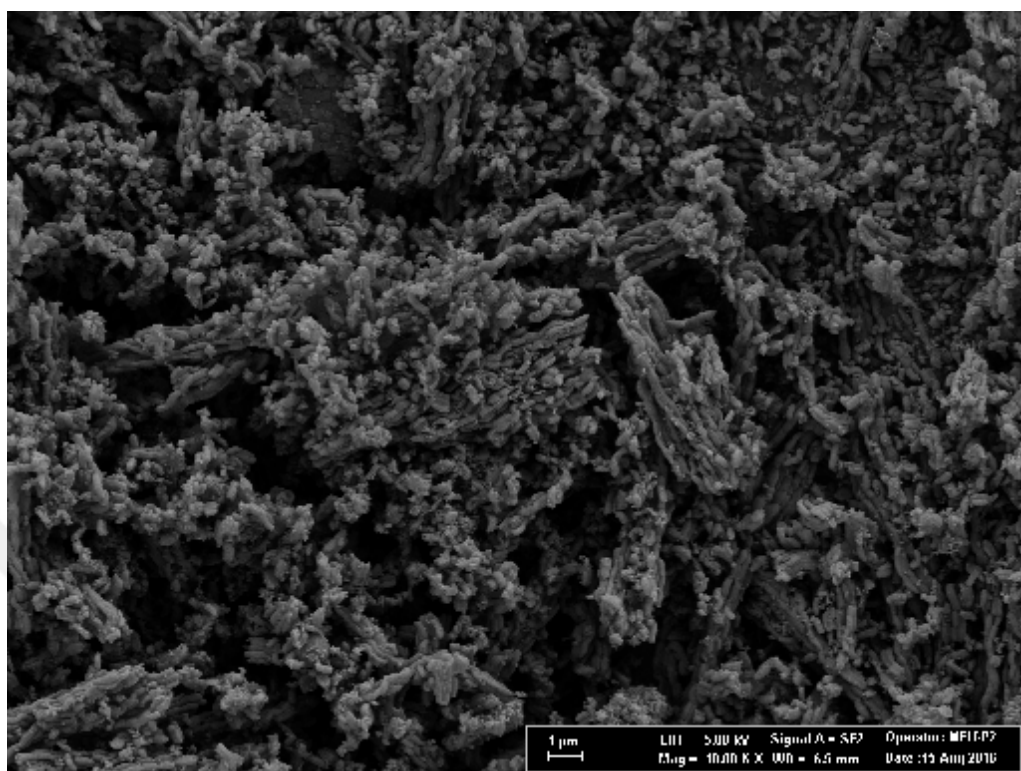




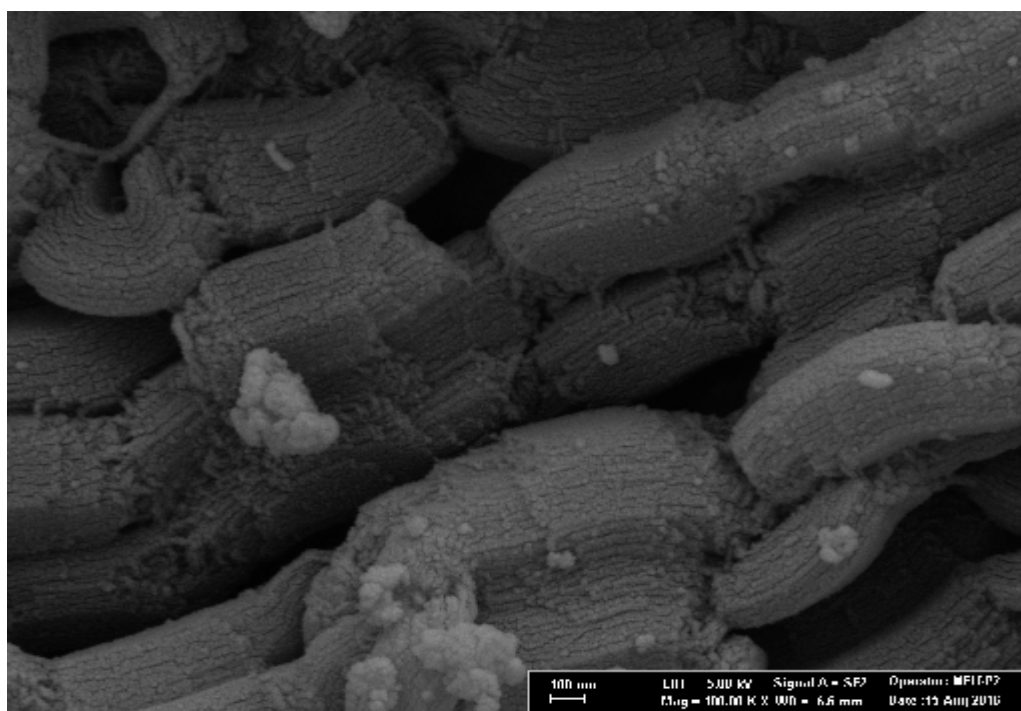
APPENDIX 5.4. SEM images of Cat. 4

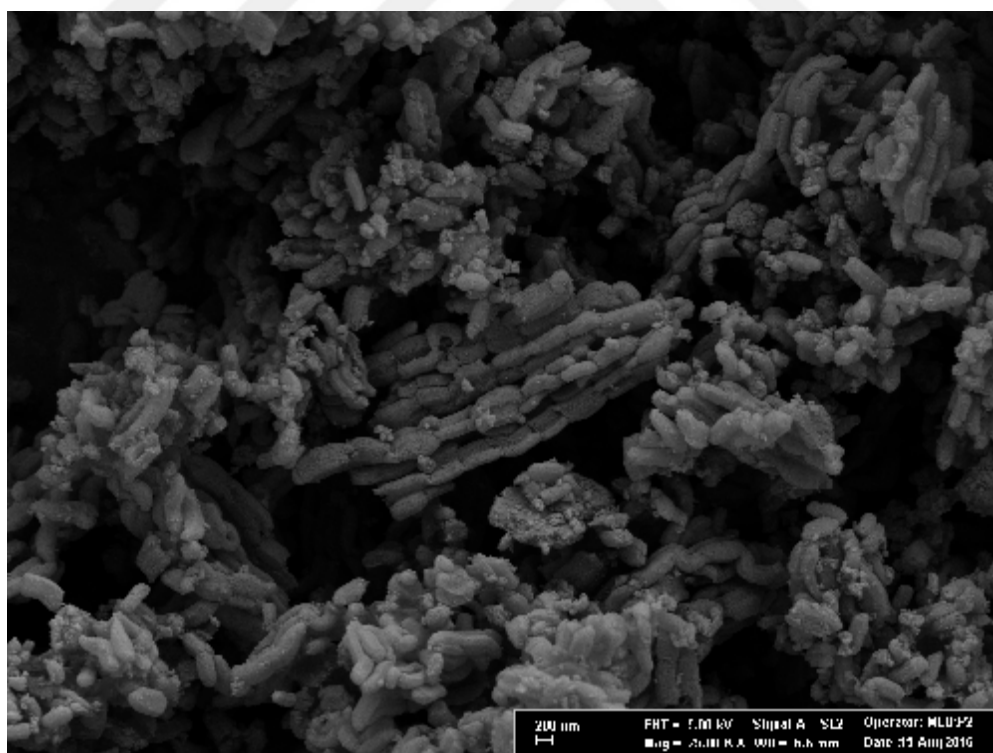
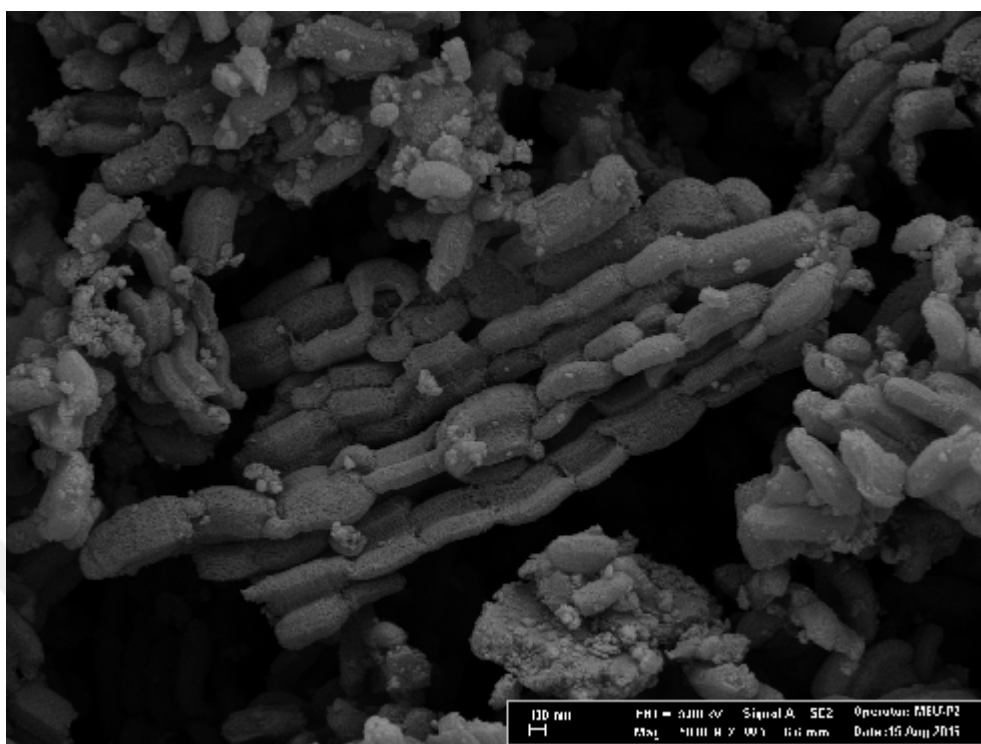


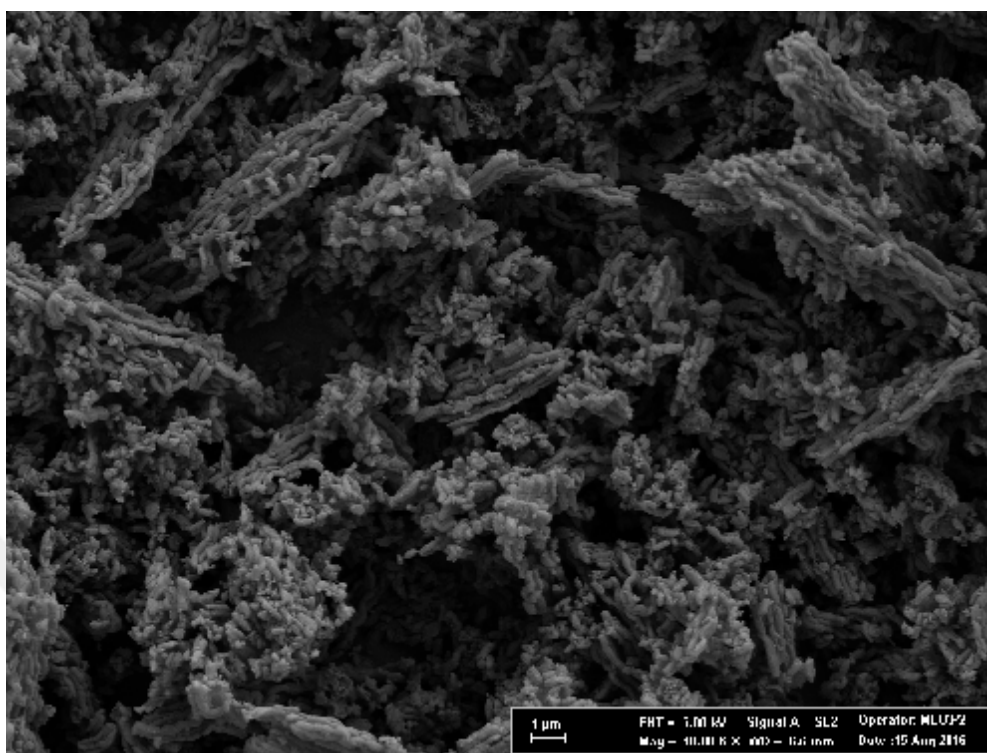




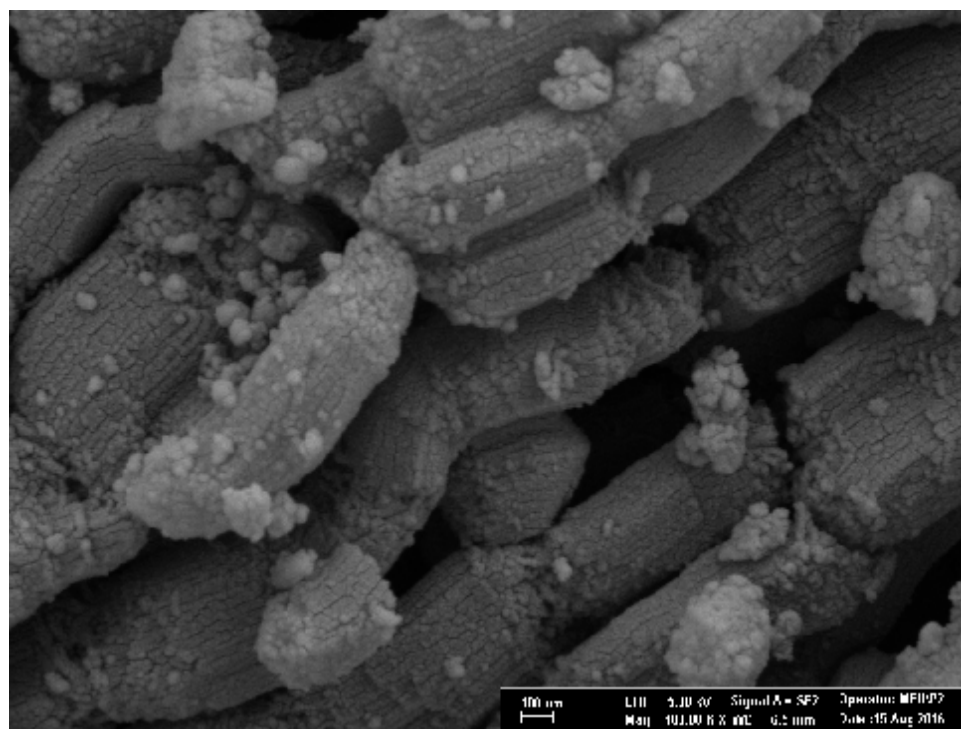
APPENDIX 5.5. SEM images of Cat. 5

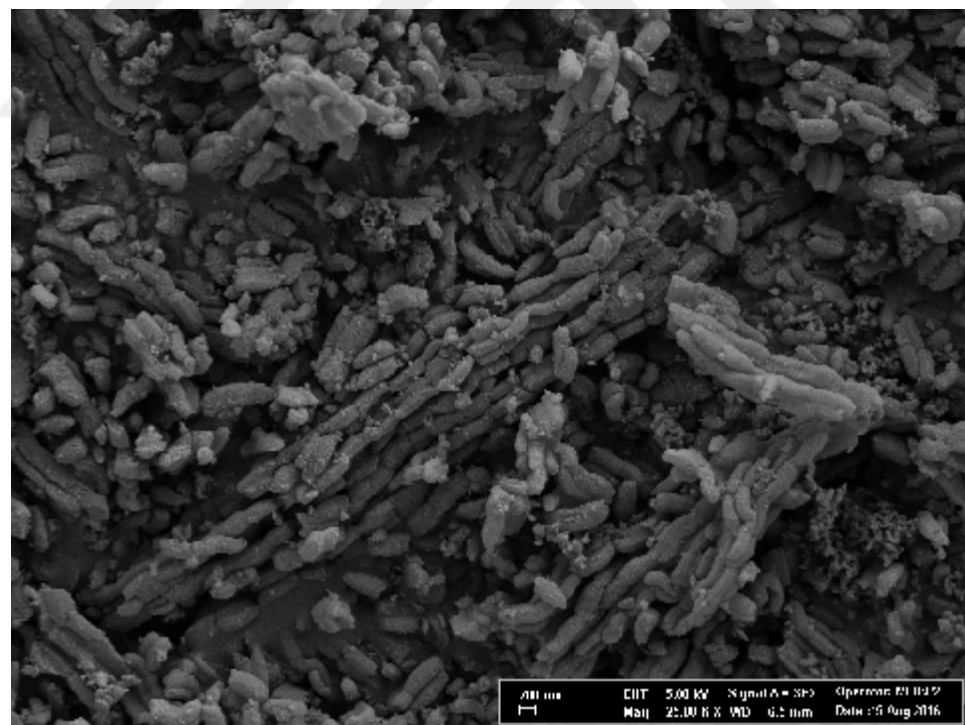
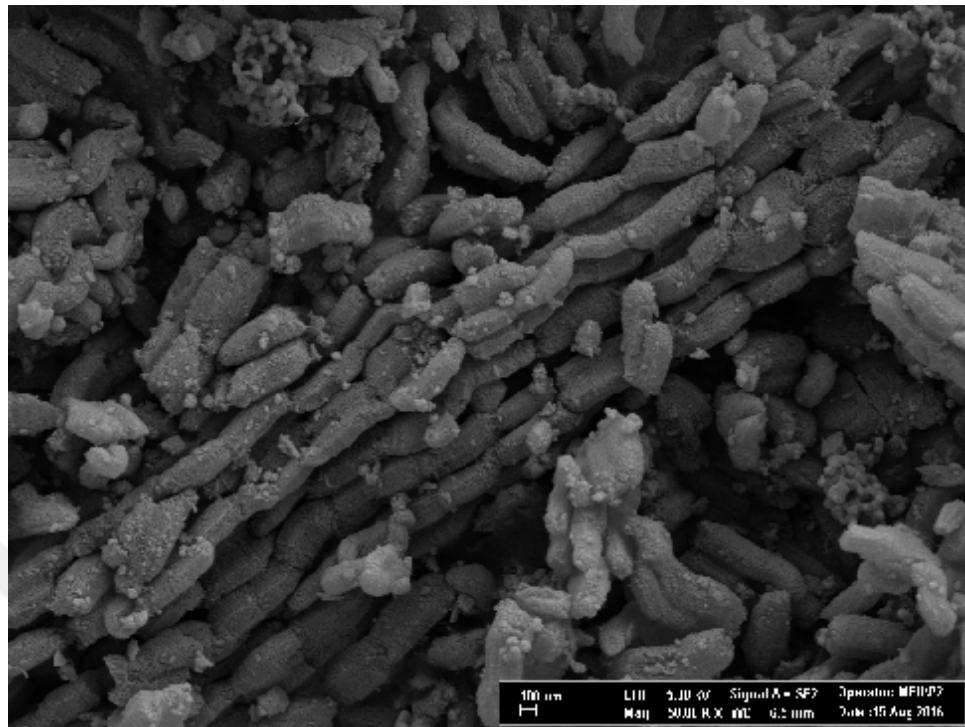


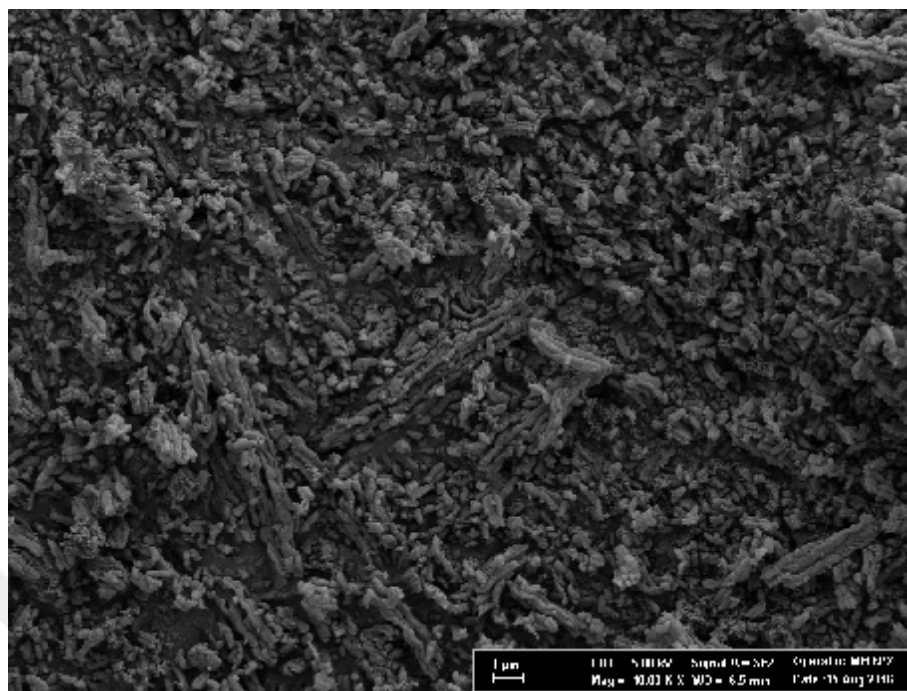




APPENDIX 5.6. SEM images of Cat. 6

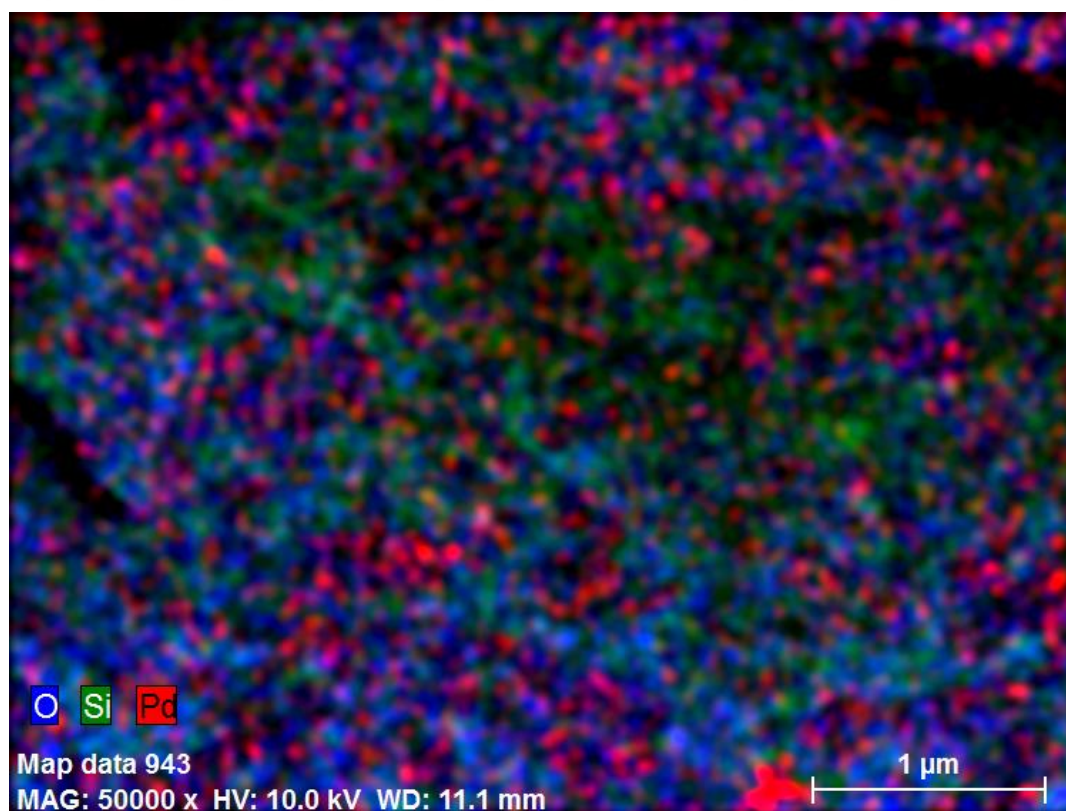




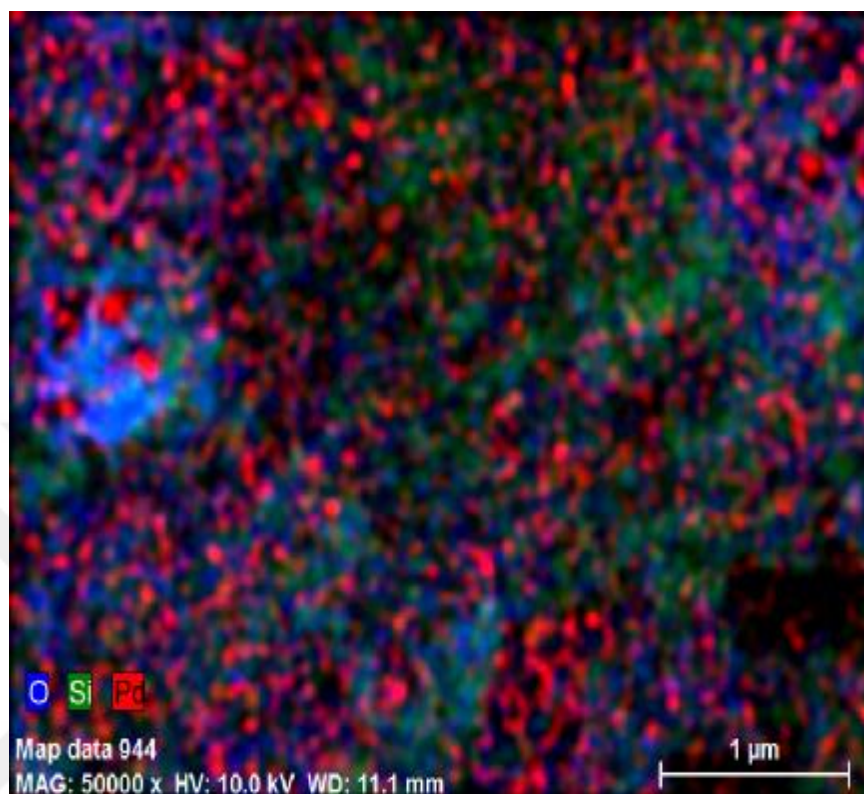


APPENDIX 6. EDX- mapping images of supported catalyst

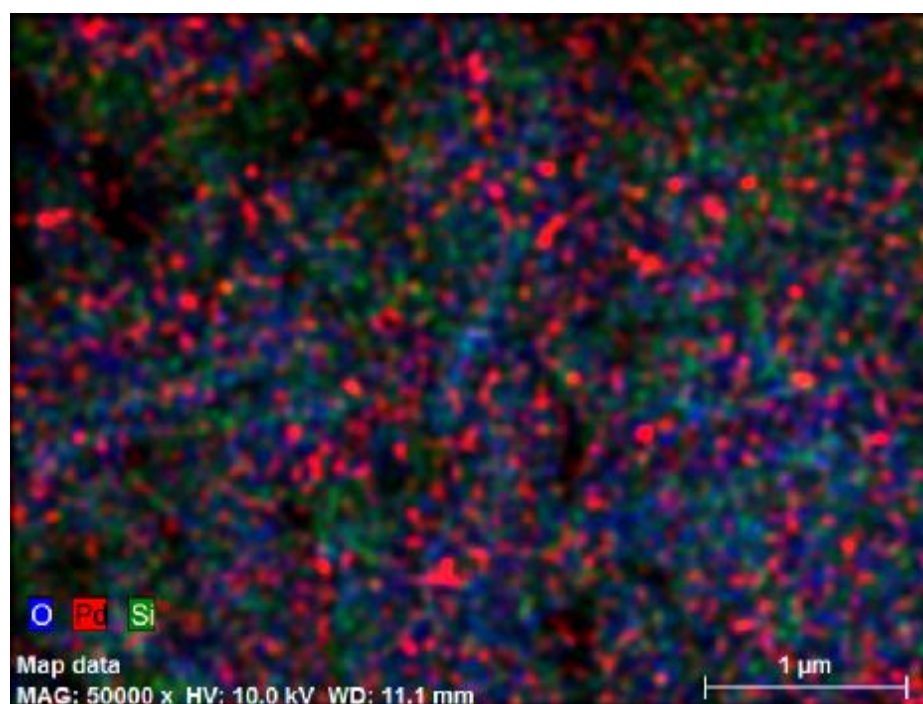
APPENDIX 6. 1 EDX- mapping images of Cat. 1



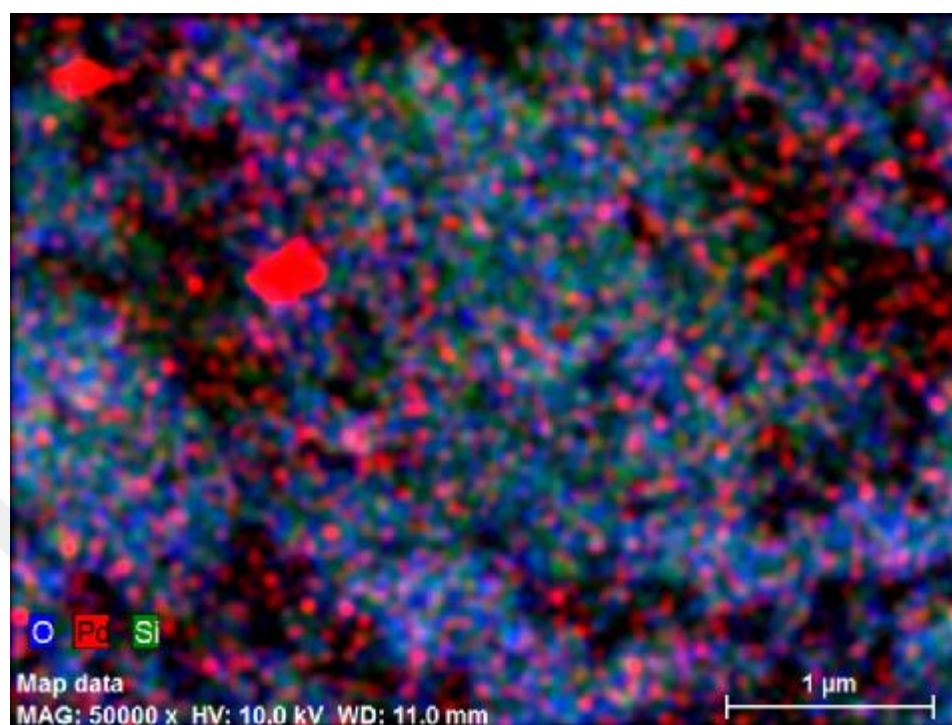
APPENDIX 6.2 EDX- mapping images of Cat. 2



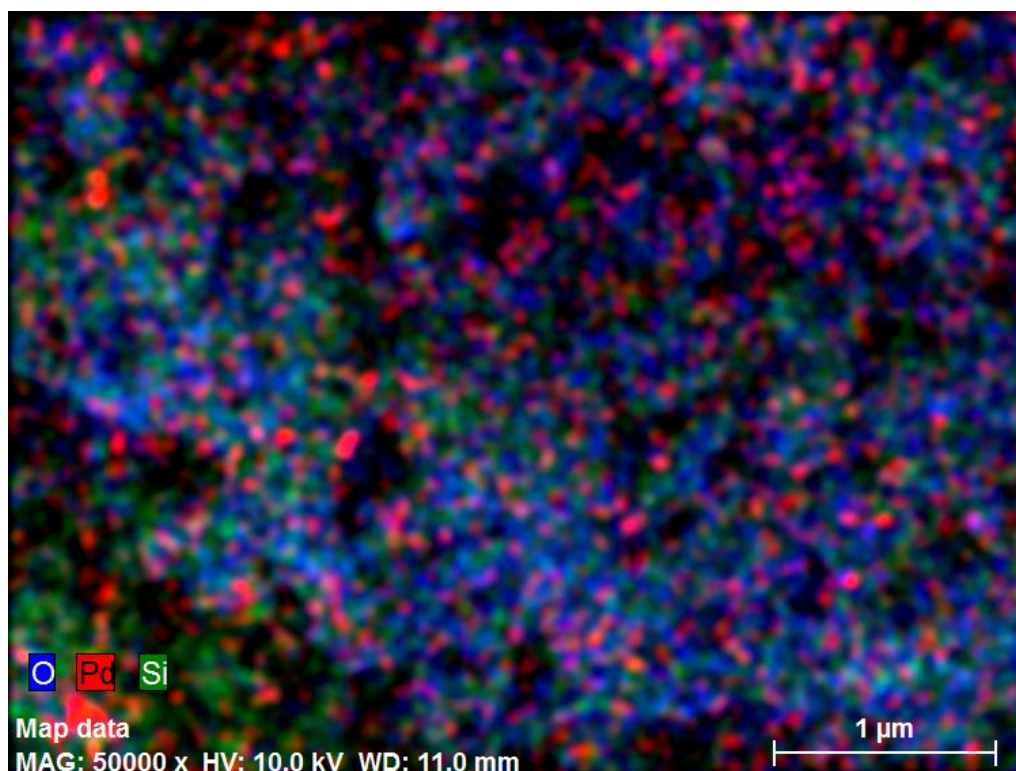
APPENDIX 6.3 EDX- mapping images of Cat. 3



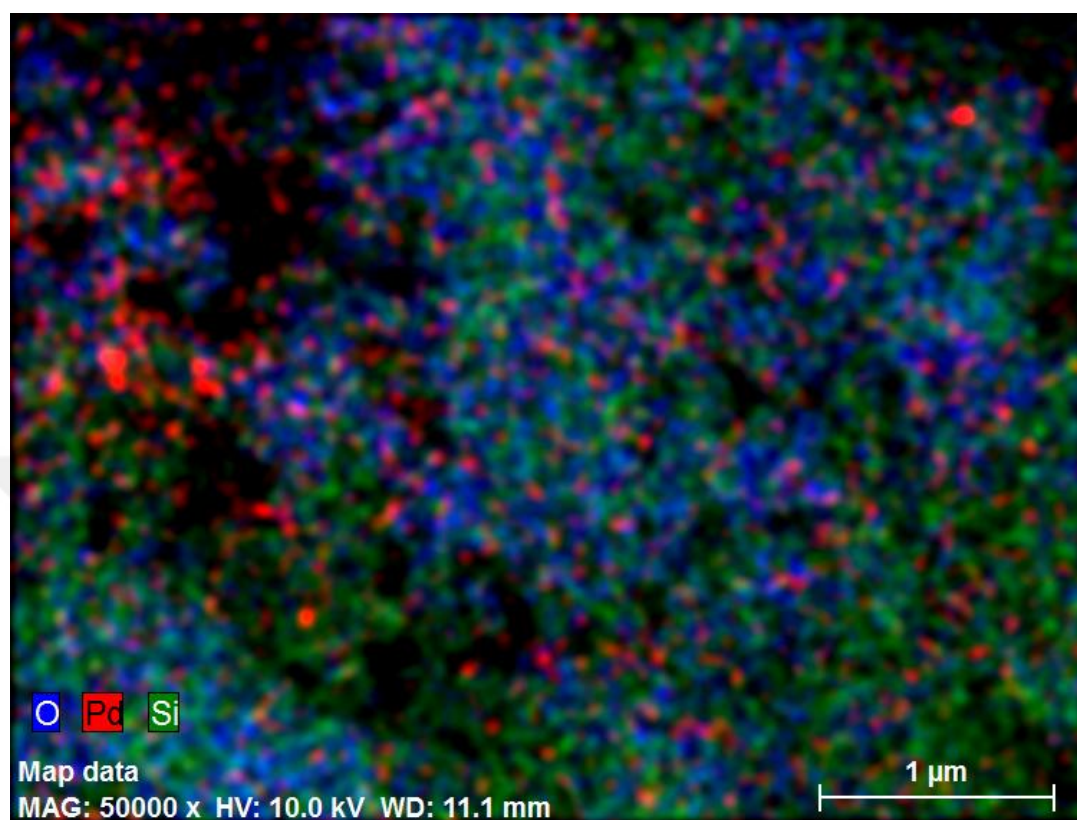
APPENDIX 6.4 EDX- mapping images of Cat. 4



APPENDIX 6.5 EDX- mapping images of Cat. 5

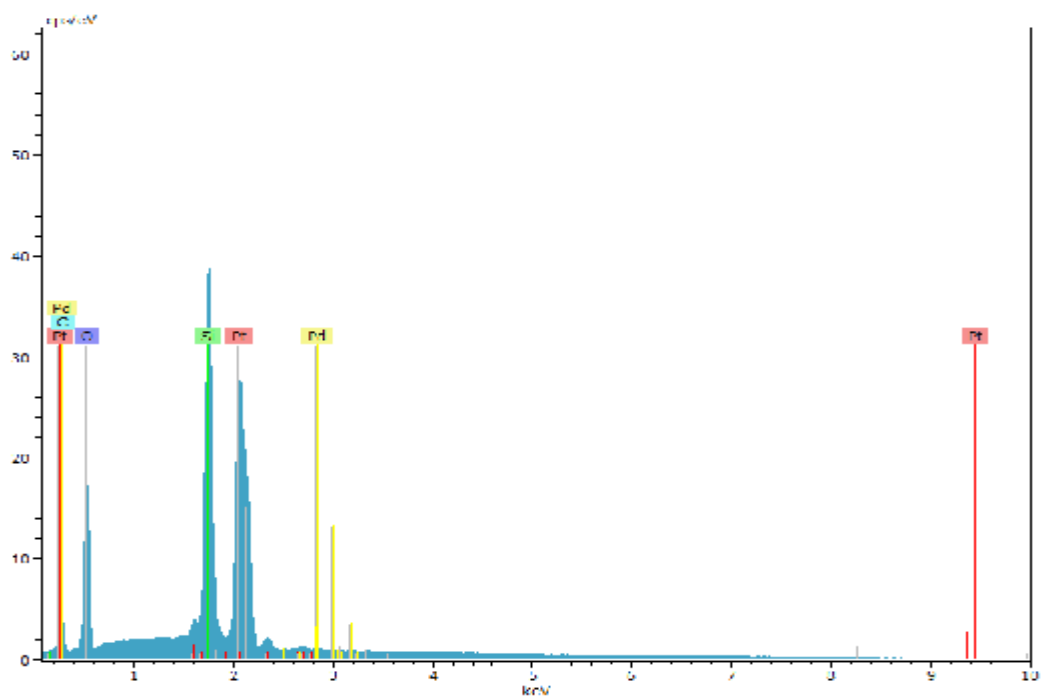


APPENDIX 6.6 EDX- mapping images of Cat. 6

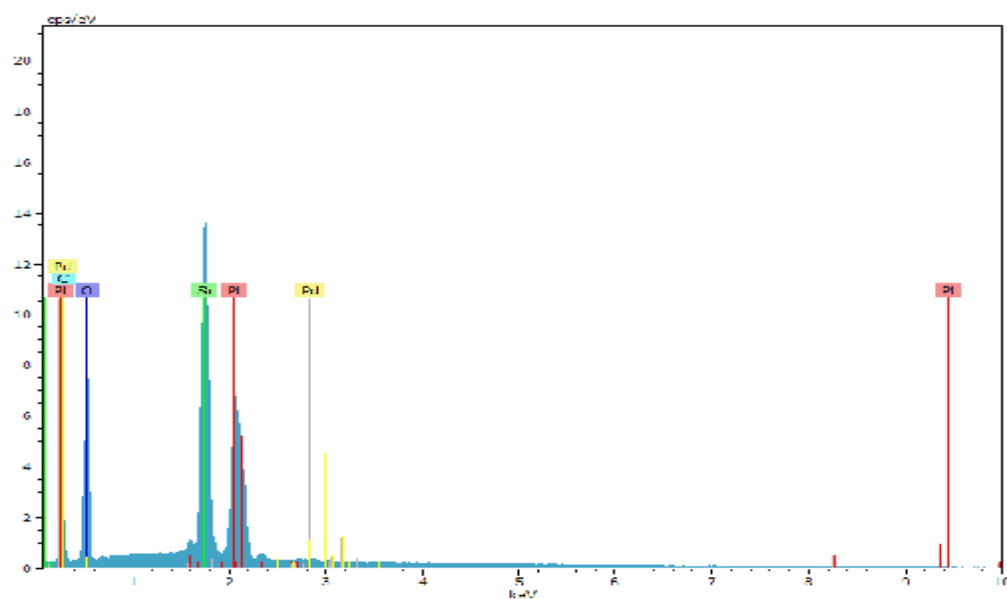


APPENDIX 7. Elemental composition of Catalyst with EDX-point application

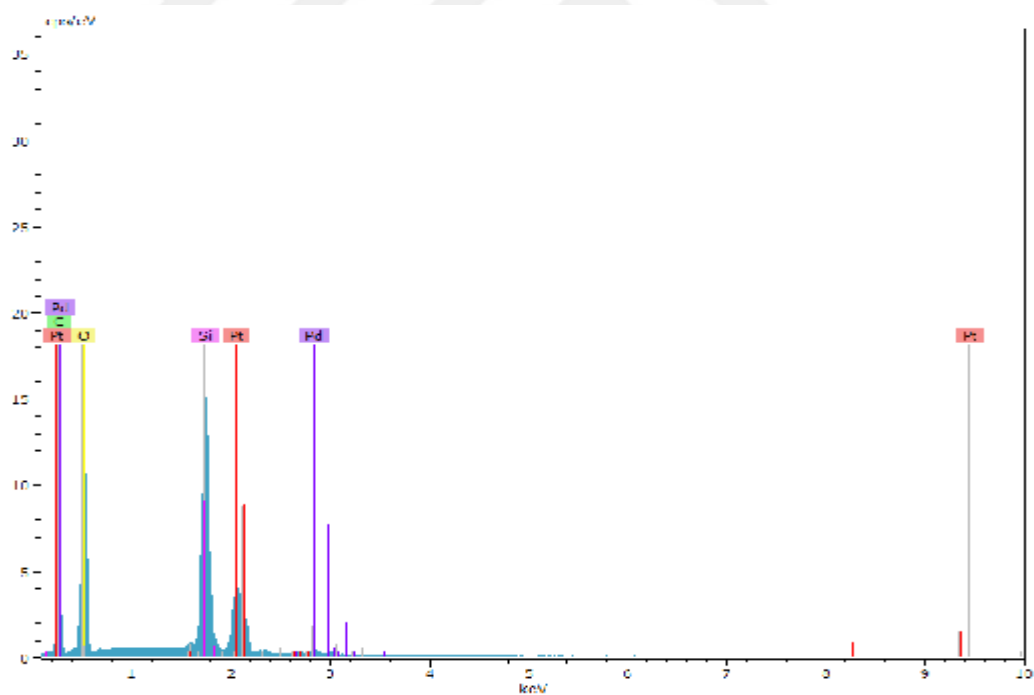
APPENDIX 7.1. EDX- point analysis of Cat.1



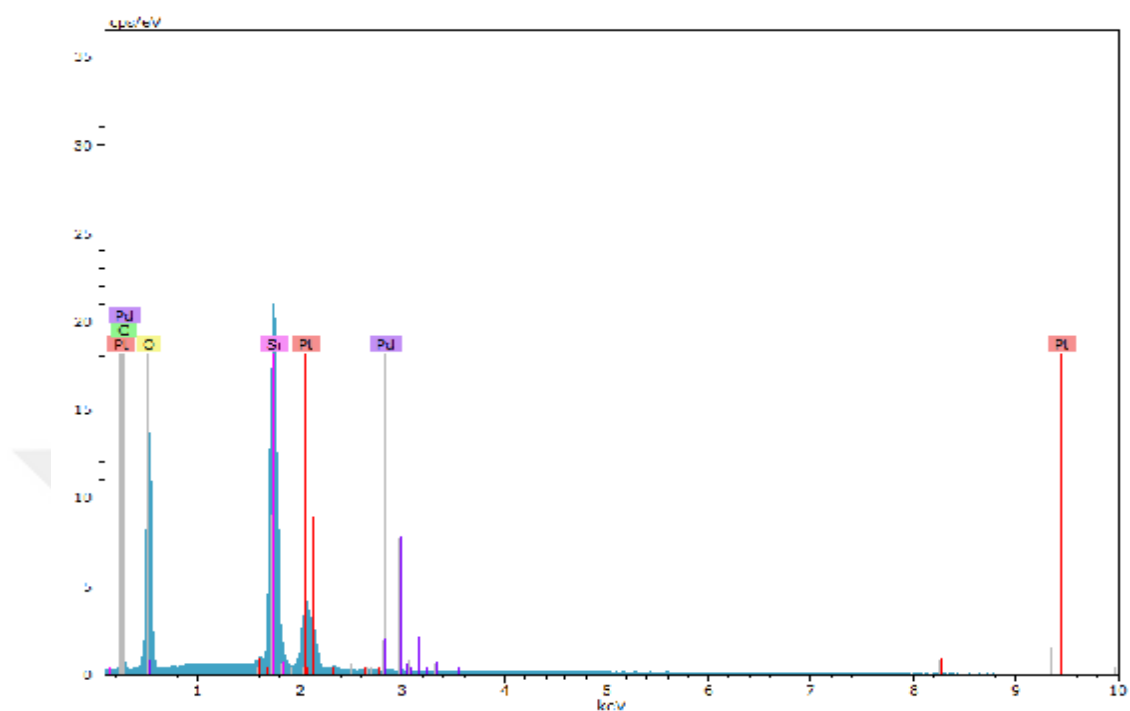
APPENDIX 7.2. EDX- point analysis of Cat.2



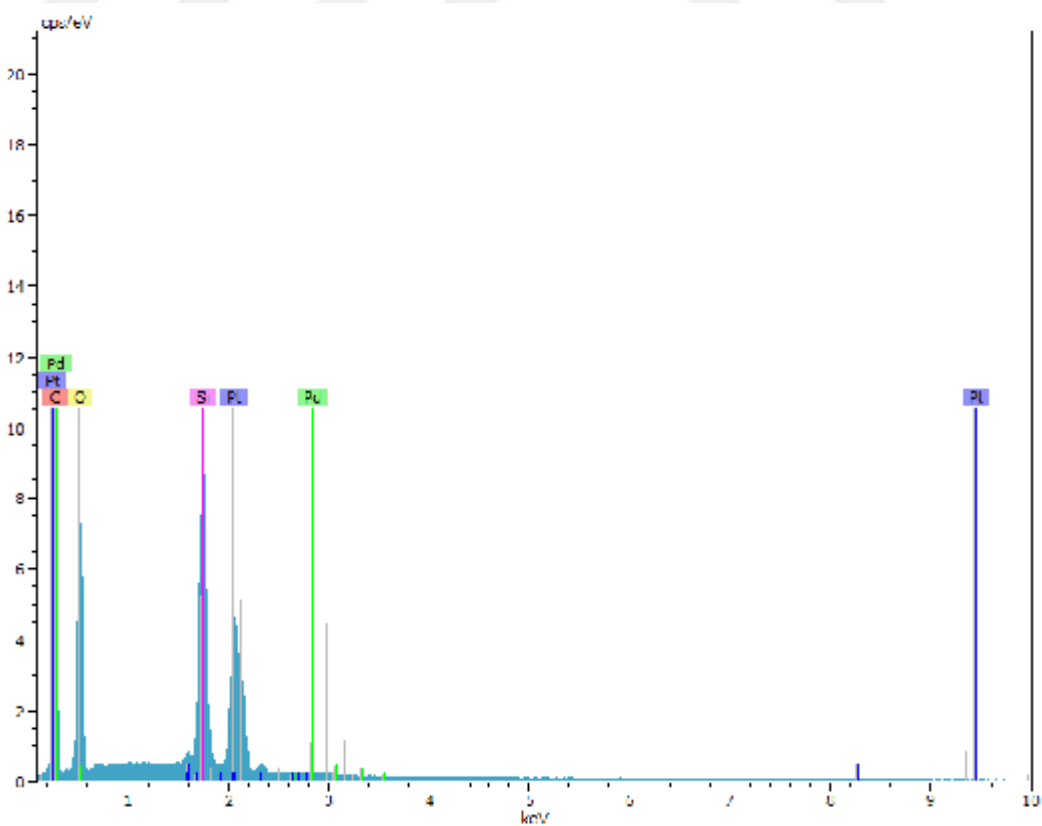
APPENDIX 7.3. EDX- point analysis of Cat.3



APPENDIX 7.4. EDX- point analysis of Cat.4



APPENDIX 7.5. EDX- point analysis of Cat.5



APPENDIX 7.6. EDX- point analysis of Cat.6

