CATALYTIC HYDROGENATION OF ESTERS AND POLYMERS

Master of Science Thesis

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CATALYTIC HYDROGENATION OF ESTERS AND POLYMERS

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MASTER OF SCIENCE THESIS
Department of Chemistry

Programme in Organic Chemistry

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Eskişehir Technical University
Institute of Graduate Programs
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FINAL APPROVAL FOR THESIS

This thesis titled “Catalytic Hydrogenation of Esters and Polymers” has been prepared and submitted by Volkan CIRIK in partial fullfillment of the requirements in “Eskişehir Technical University Directive on Graduate Education and Examination” for the Degree of Master of Science in Chemistry Department has been examined and approved on 20/05/2019.

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ABSTRACT

CATALYTIC HYDROGENATION OF ESTERS AND POLYMERS

Volkan CIRIK

Department of Chemistry

Programme in Organic Chemistry

Eskişehir Technical University Institute of Graduate Programs, May 2019

Supervisor: Assist. Prof. Dr. Dilek ELMALI

In this thesis work, palladium catalyst was synthesized to be used in hydrogenation of carboxylic acid ester. Synthesized palladium catalyst was used in environmentally benign, atom-efficient and industrially important process homogeneous catalytic hydrogenation of benzyl benzoate, methyl benzoate and dimethyl terephthalate. Reduction of carboxylic acid esters to corresponding alcohols by using molecular hydrogen was not successful. It was aimed to hydrogenate the unsaturated heteroaromatic polymers in a heterogeneous catalytic manner to obtain saturated quaternary amine polymers for use in polymer electrolyte membrane fuel cells (PEMFC) which convert chemical energy into electrical energy and have the potential to reduce dependence on fossil fuels. Poly(*N*-methyl-4-vinylpyridiniumiodide) was successfully hydrogenated to saturated hetero aromatic ring containing polymers with ruthenium (IV) oxide.

Keywords: Hydrogenation, Catalysis, Esters, Polymers, Green Chemistry

ÖZET

ESTERLERİN VE POLİMERLERİN KATALİK HİDROJENLENDİRİLMESİ

Volkan CIRIK

Kimya Anabilim Dalı

Organik Kimya

Eskişehir Teknik Üniversitesi, Lisansüstü Eğitim Enstitüsü, Mayıs 2019

Danışman: Dr. Öğr. Üyesi Dilek ELMALI

Bu tez çalışmasında, karboksilik asit esterlerin homojen katalitik olarak hidrojenlendirilmesinde kullanılmak üzere paladyum katalizörü sentezlendi. Sentezlenen paladyum katalizörü benzil benzoat, metil benzoat, dimetil tereftalatın çevre dostu, atom ekonomik ve endüstriyel açıdan önemli olan homojen katalitik hidrojenlendirilmesinde kullanıldı. Karboksilik asit esterlerin moleküler hidrojen kullanılarak ilgili alkollere indirgenmesi başarıyla gerçekleştirilemedi. Fosil yakıtlara olan bağımlılığı azaltma potansiyeline sahip, kimyasal enerjiyi elektrik enerjisine çeviren polimer elektrolit membran yakıt hücrelerinde (PEMFC) kullanılmak üzere doymuş kuaterner amin polimerleri elde etmek için doymamış heteroaromatik polimerlerin heterojen katalitik olarak hidrojenlendirilmesi amaçlandı. Heteroaromatik halka içeren polimerlerin farklı metal katalizörler ile hidrojenlendirilmesinde Poli (*N*-metil-4-vinilpiridinyum iyodür) rutenyum(IV) oksit kullanılarak başarıyla hidrojenlendirildi.

Anahtar Kelimeler: Hidrojenlendirme, Kataliz, Esterler, Polimerler, Yeşil Kimya

STATEMENT OF COMPLIANCE WITH ETHICAL PRINCIPLES AND RULES

I hereby truthfully declare that this thesis is an original work prepared by me; that I have behaved in accordance with the scientific ethical principles and rules throughout the stages of preparation, data collection, analysis and presentation of my work; that I have cited the sources of all the data and information that could be obtained within the scope of this study, and included these sources in the references section; and that this study has been scanned for plagiarism with “scientific plagiarism detection program” used by Anadolu University, and that “it does not have any plagiarism” whatsoever. I also declare that, if a case contrary to my declaration is detected in my work at any time, I hereby express my consent to all the ethical and legal consequences that are involved.

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Volkan CIRIK

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SYMBOLS AND ABBREVIATIONS INDEX

^{13}C NMR:	Carbon-13 nuclear magnetic resonance spectroscopy
^{1}H NMR:	Proton Nuclear magnetic resonance spectroscopy
AEMFC:	Anion exchange membrane fuel cells (AEMFC)
°C:	Celsius
Cat1:	Catalyst 1
CP:	Capillary column
DCM:	Dichloromethane
dd:	Doublet of doublets
ddd:	Double-double-doublet
DMF:	Dimethylformamide
DMT:	Dimethyl terephthalate
dq:	Doublet of quartets
FID:	Flame ionization detector
GC:	Gas chromatography
GC-MS:	Gas chromatography-mass spectroscopy
Hz:	Hertz
J:	Coupling constant
m:	Multiplet (denotes complex pattern)
MeOH:	Methanol
MHz:	Megahertz
$NaHBEt_3$:	Sodium triethylborohydride
NMR:	Nuclear magnetic resonance spectroscopy
P:	Pressure
PEM:	Proton exchange membrane
PEMFC:	Polymer electrolyte membrane fuel cells
Pol1:	Poly(N-methyl-4-vinylpyridiniumiodide)
Pol2:	Poly(N-methyl-4-vinylpyridiniumiodide-co-styrene)
Pol3:	Polymer 3
q:	Quartet
QA:	Quaternary ammonium
s:	Singlet
T:	Temperature

t: Time

t: Triplet

t-BuOK: Potassium *tert*-butoxide

TFA: Trifluoroacetic acid

THF: Tetrahydrofuran

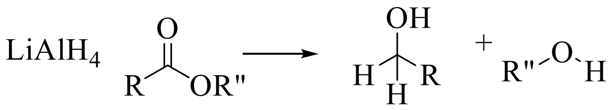
TLC: Thin-layer chromatography

USD: United States Dollar

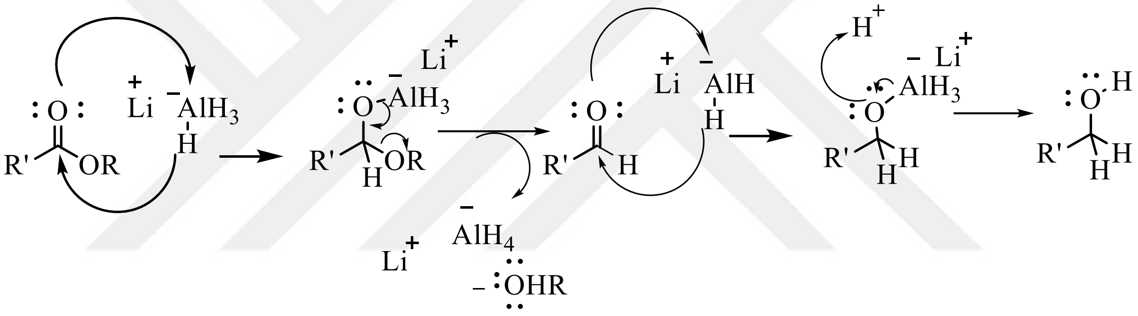
δ: Chemical shift

1. INTRODUCTION

The reduction of esters to corresponding alcohols is an important procedure in organic chemistry. Requirement of stoichiometric amounts of metal hydrides, generating waste, using precious metals makes classical reduction procedures (Scheme 1, Scheme 2) less advantages [1]

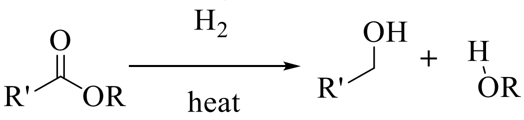


Scheme 1. *The reduction of esters to corresponding alcohols*



Scheme 2. *Mechanism of the reduction of esters*

Catalytic reduction of esters (Scheme 3) is environmentally benign, generates no waste or less waste compared to classical procedure, provides an atom-economical synthetic method at mild temperatures and under mild hydrogen pressure[2].



Scheme 3. *Catalytic hydrogenation of esters to corresponding alcohols*

Global fatty alcohol consumption was 2.2 million metric tons in 2012. It is estimated that fatty alcohol market was 4.72 billion USD in 2017 and predicted to increase 6.01 billion USD by 2020 [3]. Almost half of the fatty alcohols are formed from natural fatty alcohols by hydrogenating them [4].

Polymer electrolyte membrane fuel cells (PEMFC) (Figure 1) are devices that convert the chemical energy into the electricity[5]. PEMFCS have big capacity to lower our usage of the energy such as fossil fuels, and pollutant emissions from burning the fossil fuels [6].

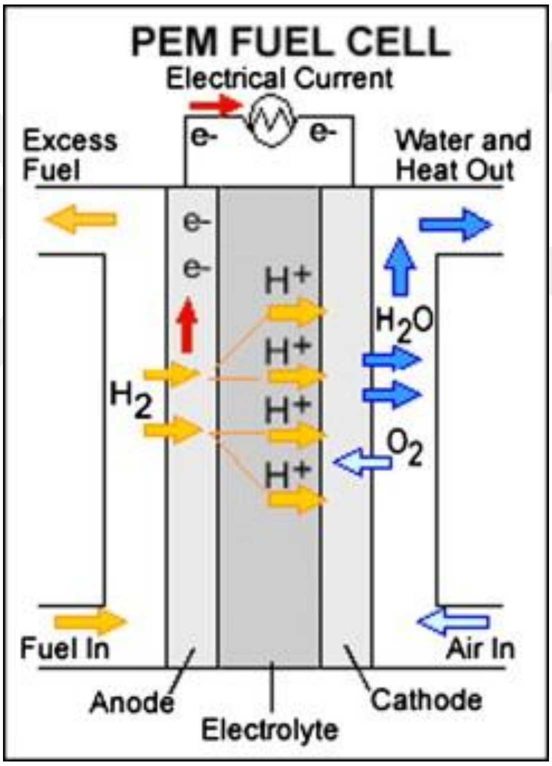


Figure 1. *Illustration of PEMFC* [6]

As shown in Figure 2, atmospheric levels of CO_2 is increasing every year [7]. CO_2 is one of the greenhouse gases. CO_2 is released during the combustion of fossil fuels. Increase in CO_2 leads to heat increase at the Earth’s surface. Greenhouse gases traps outgoing infrared radiation which results with increasing of the temperature[8].

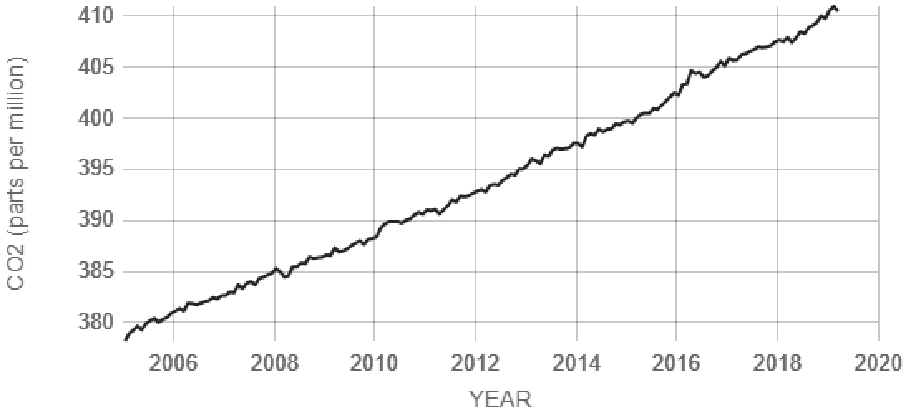


Figure 2. *Atmospheric CO_2 levels*

While PEMFCs are reducing the dependence on fossil fuels, they are also reducing the air pollution. They release water vapor instead of CO_2, which is completely clean.

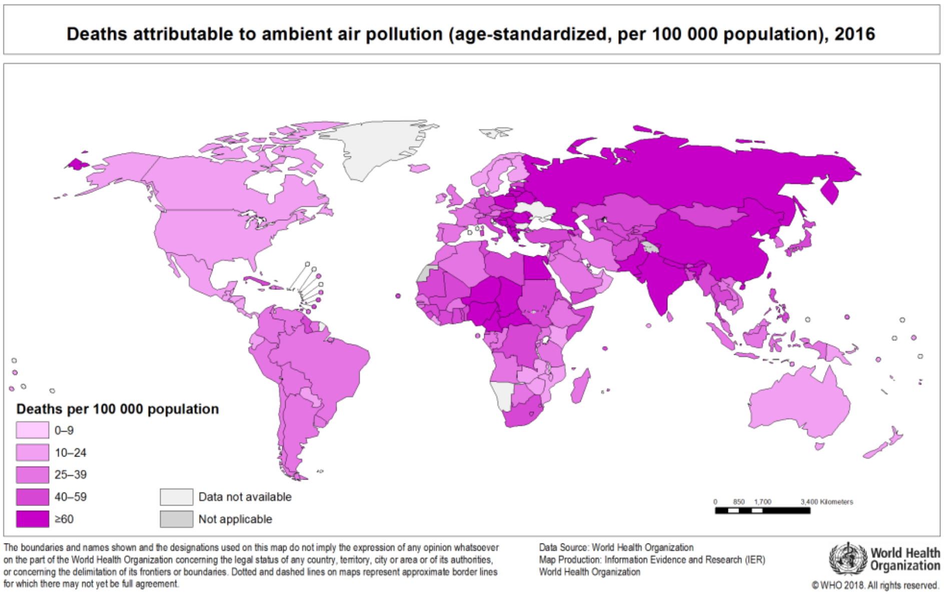


Figure 3. *Deaths attributable to ambient air pollution*

One of the major CO_2 release is coming from burning fossil fuels. Release of CO_2 is resulting with air pollution and it causes fatal diseases. The number of deaths because of air pollution is continuously increasing (Figure 3) [9].

One PEMFC made up off an anode, a cathode, and a polymer electrolyte membrane (PEM) [10]. Saturated polymers of quaternary amines are difficult to achieve easily from the corresponding monomers. Therefore, hydrogenation of heteroaromatic polymers with nitrogen in the ring is useful procedure to obtain quaternary amine polymers [11].

Hereby in this study it is reported that the attempt of catalytic hydrogenation of esters to corresponding alcohols and hydrogenation of heteroaromatic polymers to obtain quaternary amine polymers.

2. CATALYSIS

Catalysis is the process of modifying which is the increase in the rate of a chemical reaction with the use of a reagent called catalyst that is not itself consumed.

The term of catalysis was introduced for the first time by J. J. Berzelius in 1820. Berzelius was defined the catalysis a compound which effects the reaction remaining unaffected till the end of the reaction [12].

The next period in the catalysis started with the discovery of new catalytic processes. The most important process of the period was the ammonia process. It was developed to produce fertilizers but it ended up in the production of nitrogen based explosives. W. Oswalt can be accredited by developing a process for synthesis of nitric acid by oxidation of ammonia (Scheme 4) in 1902 [13].

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O \qquad (2.1.)$$

Scheme 4. *Synthesis of nitric acid by oxidation of ammonia*

Oswalt defined the catalyst as “A substance which affects the rate of a chemical reaction without being part of its end products”. According to this definition, the catalysis is considered as a kinetic phenomenon [14].

The catalyst lowers the activation energy of the reaction and as a result, the rate of the reaction increases and the reaction goes faster [15]. Figure 4 shows the required activation energy difference between reaction with catalyst, and reaction without catalyst.

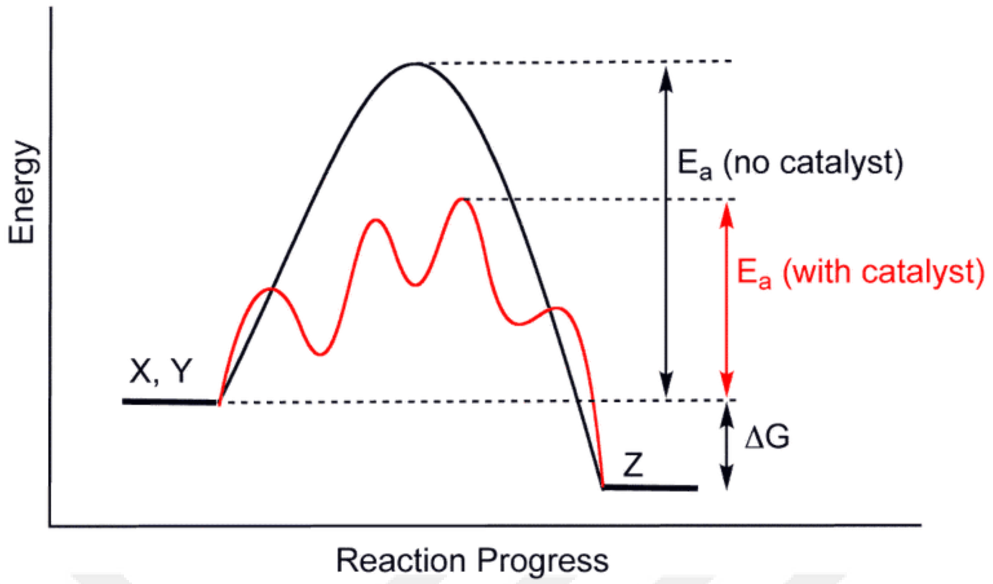


Figure 4. *Catalytic reaction progress*

The catalyst directs reaction to an alternative path which is more complex however energetically more favorable. The activation energy is the rate determining step, activation energy of catalyzed reaction is smaller than uncatalyzed reaction therefore catalytic reaction's rate is faster. The catalyst affects the kinetics not the thermodynamics therefore if reaction is thermodynamically unfavorable, a catalyst can't affect the situation. The catalyst catalyzes both the forward and the reverse reaction. If the bonding of catalyst to substrate is weak, there may not be a formation of products [16].

3. HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

Catalysis can be divided into two categories according to phase of the reaction that occurs. Homogeneous catalysis is a process that the catalyst and reactants are in the same phase. Usually homogeneous catalysis occurs in gas phase or in liquid phase. Both reactant and catalyst dissolve in the solvent and reaction occur [17].

Heterogeneous catalysis is a process which catalyst and reactants are in the different phase. Usually heterogeneous catalyst is solid while the reactant is in gas phase. The catalytical reaction happens on the catalyst surface.

Both types of catalysis could be considered as an environment friendly and green processes. Heterogeneous catalysis has a wide range in the industry on the contrary homogeneous catalysis has a narrow range in the industry. High selectivity, faster reaction rate, and milder conditions of the homogeneous catalysis makes it advantages over heterogeneous catalysis. Differently, easier catalyst separation and recycling of the catalyst are the advantages of the heterogeneous catalysis [18]

4. HISTORY OF HYDROGENATION OF ESTERS

To use molecular hydrogen is a good synthetic application to reduce organic compounds. To make hydrogenation reactions applicable, crucial factor is a good catalyst. There are still traditional paths that uses stoichiometric amounts of inorganic hydrides and produces enormous amounts of waste. For this reason, using molecular hydrogen in catalytic reduction of esters is considered as a environment friendly alternative for traditional procedure [19].

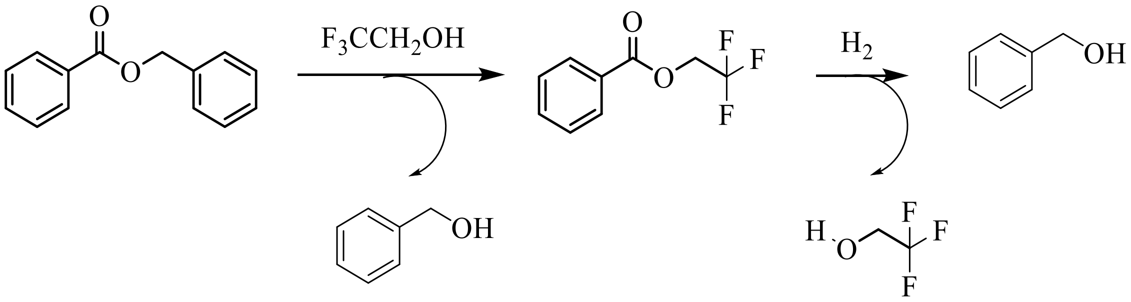
Paul Sabatier has received The Nobel Prize in 1912 for his work on hydrogenation of organic compounds by using metals as catalysts [20].

Catalytic hydrogenation of esters to corresponding alcohols is an important industrial process since the consumption of personal care ingredients and use of fatty alcohols in various industries is increasing [3].

First homogeneous catalytic hydrogenation of a simple ester was achieved by Grey and coworkers in 1981. Hydrogenation of non-activated ethyl ester to ethanol in only 8% yield and aromatic esters were not able to be hydrogenated with this catalyst [21].

Herman T. Elsevier and Cornelis J. Teunissen reported in 1998 that hydrogenation of esters to corresponding alcohols by Rutheniun-catalyst in an alcoholic solvent under H_2 pressure of 85 bar at 100–120 °C" [22].

Existence of electron withdrawing substituents in esters increase catalytic activity of substrate. Therefore Elsevier et al. conducted hydrogenation with influence of fluorinated alcohols. Fluorinated alcohol leads transesterification (Scheme 5) that results with electron withdrawing substitute esters.



Scheme 5. *Transesterification of benzyl benzoate*

Kotohiro Nomura reported hydrogenation of benzyl acetate with ruthenium catalyst to corresponding alcohols under relatively mild conditions [23].

Major breakthrough was achieved by David Milstein group. Milstein *et. al.* reported that hydrogenation of non-activated esters by using ruthenium-catalyst under relatively mild, neutral conditions, without additives in 2006 [24].

Scientists were aimed to replace the expensive noble-metal catalysts with earth-abundant metal catalysts. First in 2014 iron-catalyzed[25], in 2015 cobalt-catalyzed [26], and in 2017 manganese-catalyzed [27] hydrogenations of esters to corresponding alcohols were achieved by Milstein group.

5. POLYMER ELECTROLYTE MEMBRANE FUEL CELL

PEMFC (Figure 5) is the device which it converts chemical energy stored in fuels to the electricity[28]. In these electrochemical reactions, only product is water. Therefore, there is a big potential to reduce air pollution that caused from burning of fossil fuels. Electrochemical reactions are very similar reactions to battery. Battery could store the energy nevertheless fuel cells do not store the energy [6].

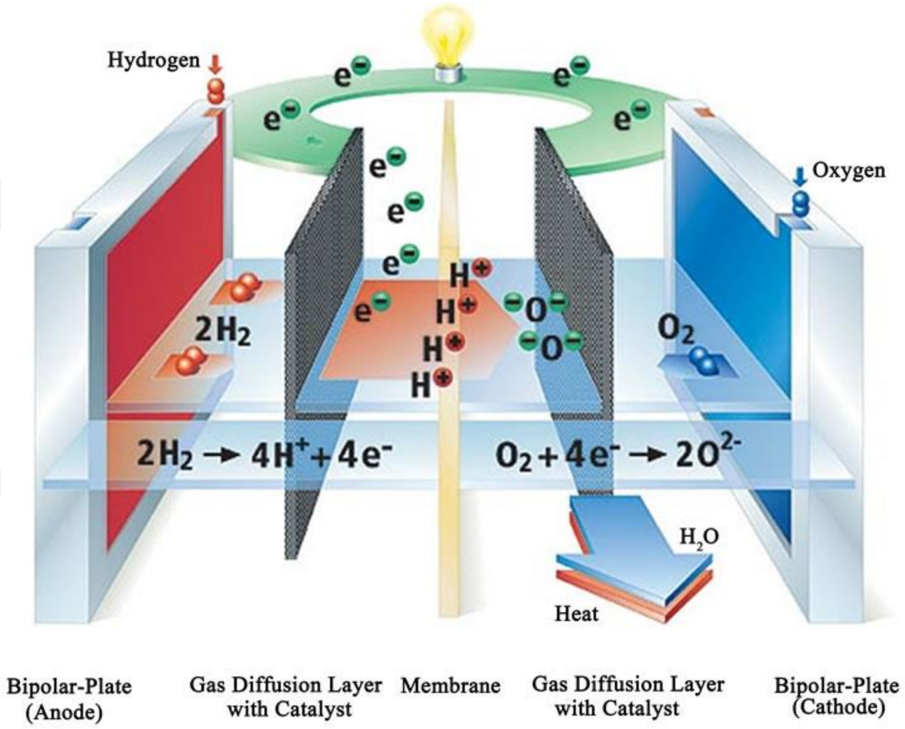


Figure 5. *Proton exchange membrane membrane fuel cell*

There are an anode, a cathode, and polymer electrolyte membrane [(proton exchange membrane (PEM)] in one PEMFC. At the anode, hydrogen flows over the gas diffusion layer to catalyst layer. Hydrogen splits into hydrogen ions and electrons in the anode. While hydrogen ions go over the membrane to the cathode catalyst layer, electrons go over an external circuit to the cathode and generate electricity. Simultaneously, oxygen flows through the gas diffusion later to the catalyst layer at the cathode part of PEMFC. In the cathode catalyst layer oxygen reacts with electrons coming from anode and form oxygen ions. These ions reacts with hydrogen ions and produce water and heat (Scheme 6) [29].

$$H_2 \longrightarrow 2H^+ + 2e^- \tag{5.1.}$$

$$1/2\ O_2 + 2H^+ + 2e^- \longrightarrow H_2O \tag{5.2.}$$

$$1/2\ O_2 + H_2 \longrightarrow H_2O + \text{Electrical energy} + \text{Heat} \tag{5.3.}$$

Scheme 6. *The reactions occur in the fuel cell* [30]

At the moment there are multiple PEMFC application areas, mainly in transportation [31]. Dependence on platinum type catalysts of PEMFCs makes them expensive. And in case of replacement of petrol driven cars to hydrogen cars, platinum would not be enough.

There is a big interest in anion exchange membrane fuel cells (AEMFC) over the PEMFCs. They both are very similar to each other. The main difference (Figure 6) is that AEM is a solid alkaline membrane instead of an acidic PEM. The OH^- anion flows from the cathode through the anode, opposite to the H^+ ion in PEMFC. Pt-free catalyst makes advantageous over PEMFC [32].

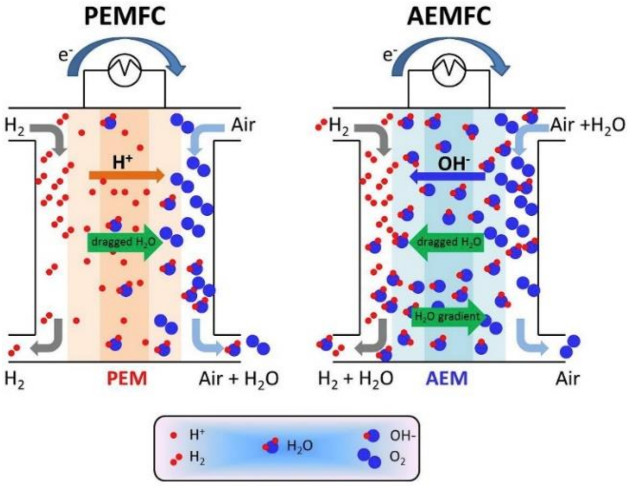
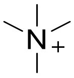
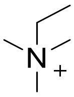
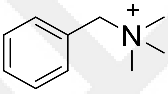
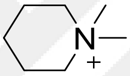
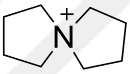
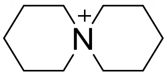


Figure 6. *Comparison of PEMFC and AEMFC* [30]

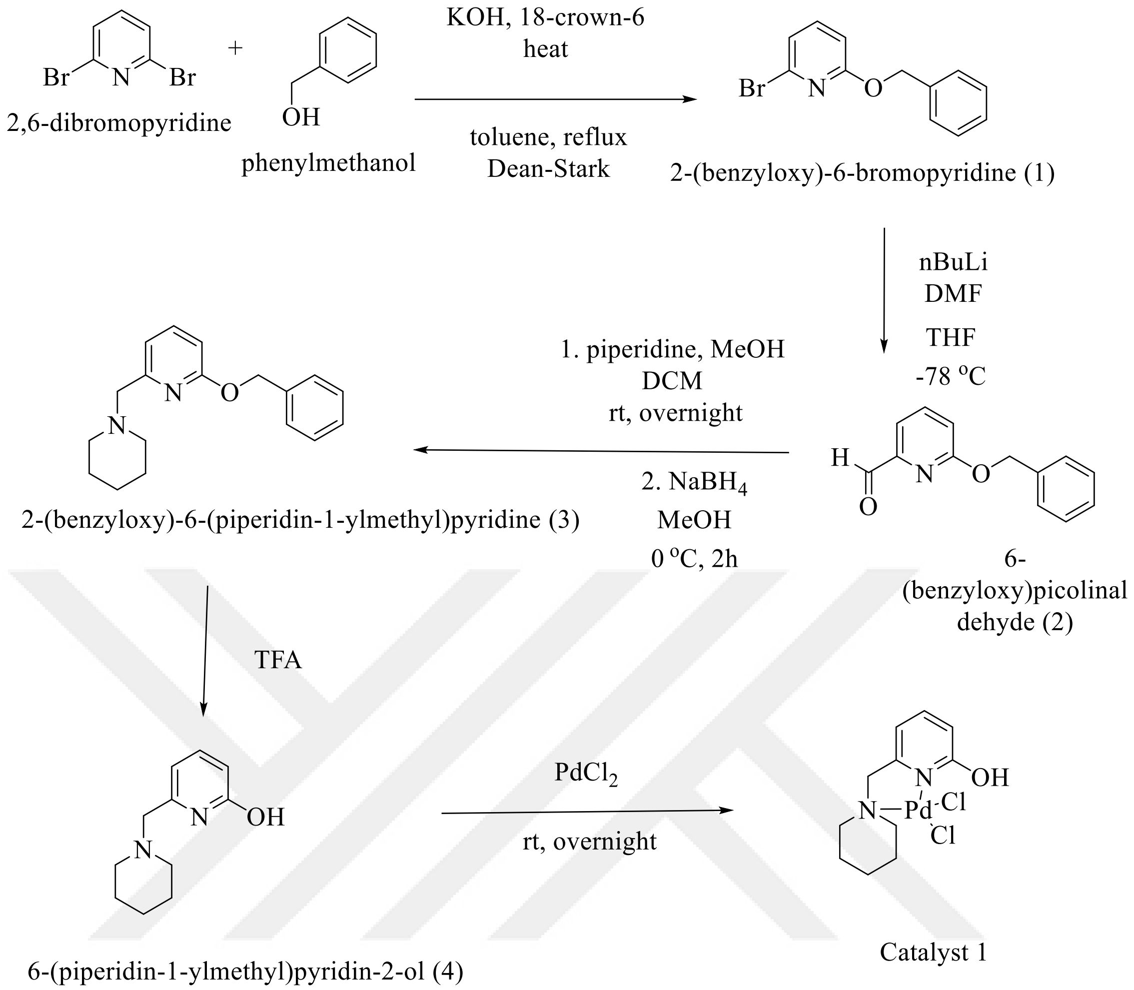
AEM consists of a rigid polymer backbone with cations attached. The cations are normally of the quaternary ammonium type and can be located anywhere in the polymer. The data (Table 1) from Marino et al. shows the excellent stability of these piperidinium-based cations [33].

Table 1. *Half-life of some common quarternary ammonium cations*

Quaternary ammonium cations	Half-life [h]
	61.9
	2.8
	4.18
	87.3
	28.4
	110

Saturated polymers of quaternary amines are difficult to achieve easily from the corresponding monomers. Therefore, hydrogenation of heteroaromatic polymers with nitrogen in the ring is useful procedure to obtain quaternary amine polymers [34].

In this study Catalyst 1 (Cat1) was synthesized (Scheme 7) according to reactions listed below. The synthesized catalyst and other catalysts were used hydrogenation of benzyl benzoate, methyl benzoate and dimethyl terephthalate (DMT). Base, catalyst and solvent effect were screened in these hydrogenation experiments.



Scheme 7. *Synthesis of Cat1*

Hydrogenation experiments were continued with polymers. Hetero aromatic polymers that contains pyridine rings were aimed to be hydrogenated.

6. EXPERIMENTAL SECTION

6.1. General Information

All experiments were carried out under an atmosphere of nitrogen using standard Schlenk unless otherwise noted. Unless stated otherwise, commercially available reagents were purchased from Sigma-Aldrich or Acros Organics and used as received. NMR-spectra were recorded on Bruker Avance 400 MHz spectrometers. Gas chromatographic analyses (GC) were made using a HewlettPackard 5890 II instrument with a flame ionization detector (FID) and a capillary column (CP-Sil 19CB 14% cyanopropyl-phenyl/86% dimethylpolysiloxane, 0.2 µm, 0.2 mm, 25 m) with decane as an internal standard. All catalytic hydrogenation experiments were carried out by using molecular hydrogen in a HEL autoclave CAT 24.

6.2. Synthesis of Catalyst 1 (Cat1)

6.2.1. Synthesis of 2-(benzyloxy)-6-bromopyridine (1)

2,6-dibromopyridine (5.03 g, 21.2 mmol), benzyl alcohol (2.64 g, 24.4 mmol), potassium hydroxide (2.60 g, 46.4 mmol) and 18-crown-6 (0.24 g, 0.91 mmol) were dissolved in toluene (70 mL) and was heated under reflux for 3 hours by using a Dean–Stark apparatus. After three hours, TLC [silica, petroleum ether-ethyl acetate (20:1)] showed complete consumption of the starting material. The reaction mixture was cooled and quenched with ice/water (50 mL). The layers were separated, and the aqueous layer extracted with toluene (in total 100 mL). Organic layers were combined and dried over Na_2SO_4, filtered and evaporated to dry-ness to give 2-(benzyloxy)-6-bromopyridine as an orange liquid (5.59 g, 93%) [35]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.34 (m, 6H), 7.10 (dd, *J* = 7.5, 0.7 Hz, 1H), 6.77 (dd, *J* = 8.2, 0.7 Hz, 1H), 5.39 (s, 2H).

6.2.2. Synthesis of 6-(benzyloxy)picolinaldehyde (2)

2-(benzyloxy)-6-bromopyridine (2,01 mL, 7,57 mmol) was dissolved in THF (9 mL). Temperature was set to -78ºC with acetone and dry ice. n-Buthyllithium (3,63 mL, 9,09 mmol) was added to a solution, and stirred for 1 hour. Dry DMF (0,70 mL, 9,09 mmol) was added to a solution and stirred for 1 hour. Solution was taken from the bath and let it to cool down to room temperature. Solution of $NaHCO_3$ was added to mixture and stirred for 20 minutes. Product was extracted with diethyl ether. TLC [silica, petroleum ether-ethyl acetate (20:1)] indicated complete consumption of starting material. Column purification [petroleum ether-ethyl acetate (20:1)] was done. The combined organic layers were dried over Na_2SO_4, filtered and evaporated to dry-ness to give 6-(benzyloxy)picolinaldehyde as a colorless liquid (5.59 g, 93%) [36]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.00 (d, J = 0.8 Hz, 1H), 7.77 (ddd, J = 8.1, 7.2, 0.8 Hz, 1H), 7.61 (dd, J = 7.2, 0.9 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.44 – 7.34 (m, 3H), 7.06 (dd, J = 8.3, 0.9 Hz, 1H), 5.52 (s, 2H).

6.2.3. Synthesis of 2-(benzyloxy)-6-(piperidin-1-ylmethyl)pyridine (3)

6-(benzyloxy)picolinaldehyde (0,30 mg, 1,41 mmol) was dissolved in dry DCM (10,00 mL) with molecular sieves. Piperidine (166,76 micro L, 1,69 mmol) was added to mixture and stirred for overnight. Molecular sieves were removed and solvent was evaporated. Compound was dissolved in methanol (5,00 mL). Soldiumborohydride (0,064 mg, 1,69 mmol) was added to solution and stirred for 1 hour. Solution was quenched with acetic acid. Product was extracted with ethyl acetate. Column purification [petroleum ether-ethyl acetate (1:1)] was done. The combined organic layers were dried over Na_2SO_4, filtered and evaporated to dry-ness to give 2-(benzyloxy)-6-(piperidin-1-ylmethyl)pyridine as a dark orange liquid [37]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (dd, J = 8.2, 7.2 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.41 – 7.31 (m, 3H), 7.04 (d, J = 7.2 Hz, 1H), 6.69 (d, J = 8.2 Hz, 1H), 5.40 (s, 2H), 3.63 (s, 2H), 2.52 (s, 4H), 1.64 (d, J = 5.7 Hz, 4H), 1.44 (d, J = 16.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.93, 128.39, 128.02, 127.69, 67.40, 54.51, 26.12

6.2.4. Synthesis of 6-(piperidin-1-ylmethyl)pyridin-2-ol (4)

TFA (1,5 mL) was added to 2-(benzyloxy)-6-(piperidin-1-ylmethyl)pyridine and reaction mixture was stirred for overnight. Neutralized with saturated $NaHCO_3$ and compound was extracted with chloroform. Column purification [chloroform-methanol (20:1)] was done. The combined organic layers were dried over Na_2SO_4, filtered and evaporated to dry-ness to give 6-(piperidin-1-ylmethyl)pyridin-2-ol (200mg, 60%) [38]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.01 (s, 1H), 7.30 (dd, J = 9.2, 6.7 Hz, 1H), 6.41 (dd, J = 9.2, 1.0 Hz, 1H), 6.01 (dq, J = 6.7, 1.1 Hz, 1H), 3.33 (s, 2H), 2.40 (t, J = 5.4 Hz, 4H), 1.57 (q, J = 5.5 Hz, 4H), 1.44 (q, J = 6.4, 6.0 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.62, 145.11, 141.02, 119.07, 104.12, 59.21, 54.45, 25.79, 23.80.

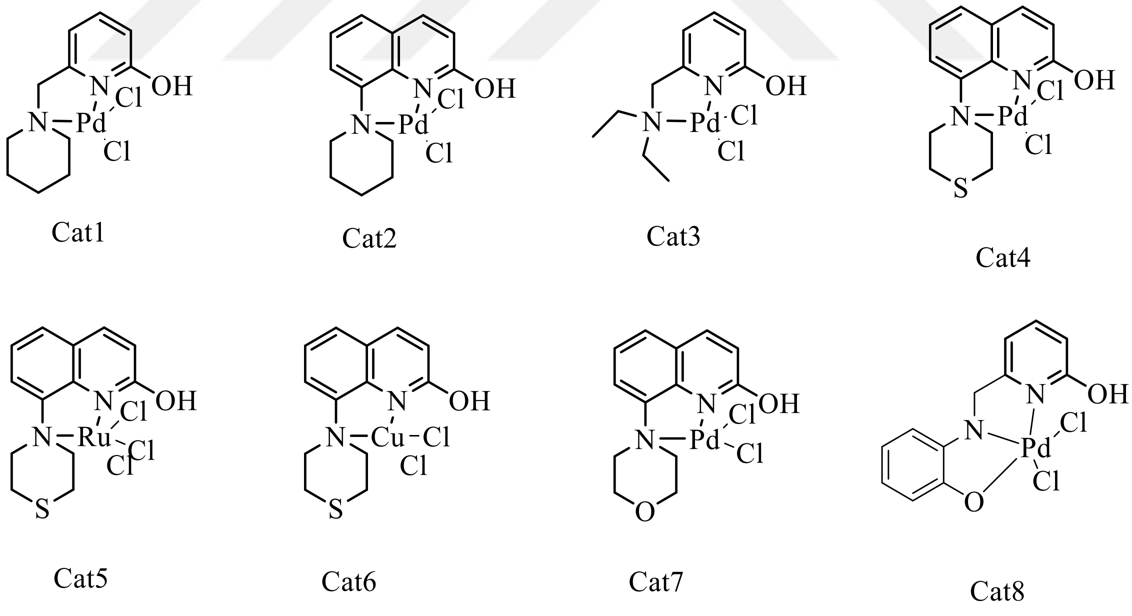
6.2.5. Synthesis of Cat1

6-(piperidin-1-ylmethyl)pyridin-2-ol (30 mg, 0,156 mmol) was dissolved in methanol (2 mL). $PdCl_2$ (25,7 mg, 27.67 mmol) was dissolved in acetonitrile (1 mL) and heated. Two solutions were combined and left stirring for overnight in room temperature. The compound was filtered and evaporated to dry-ness to give Cat1.

6.3. Hydrogenation Experiments

6.3.1. General procedure for hydrogenation of esters

A catalyst (Scheme 8), ester, and base were dissolved in a solvent. The solution was stirred slowly for 3-5 minutes. The vial was taken into the alloy plate, and then alloy plate was placed into the autoclave. After sealing and purging autoclave at least three times with hydrogen gas, it is pressurized to the desired bar. It is heated at the desired temperature for desired time. Once the reaction is over, autoclave was cooled down to room temperature and the pressure was released. Reaction mixture was analyzed by GC and GC-MS. Every GC data were given in Appendix [24].



Scheme 8. *Catalysts for experiments of hydrogenation of esters*

6.3.2. General procedure for hydrogenation of polymers

The polymer was dissolved in water or DMF. A catalyst was added into reaction vial. The solution was stirred slowly for 3-5 minutes. The vial was placed in an alloy plate, which was then placed into an autoclave. Once sealed, the autoclave was purged three times with hydrogen, then pressurized to desired bar, and heated at desired temperature for 72 hours. Catalyst was removed by filtration and solvent was evaporated. The filtrated product was dissolved in 0.2 mL of water, afterwards added drop-by-drop into 2 mL of isopropanol. The formed precipitates were decantated. The saturated polymer was dried up by vacuum [11].

7. RESULTS AND DISCUSSION

7.1. Results and Discussion of Synthesis of Catalyst 1

Compound (1) were synthesized by following the procedure that was described in section 6.2.1. The singlet peak of two hydrogens of methyl that appeared at 5.39 ppm in NMR spectra (Figure 7) shows that reaction was occurred successfully. Disappearance of alcohol peak of benzyl alcohol, remaining of aromatic peaks of pyridine and benzene support the result.

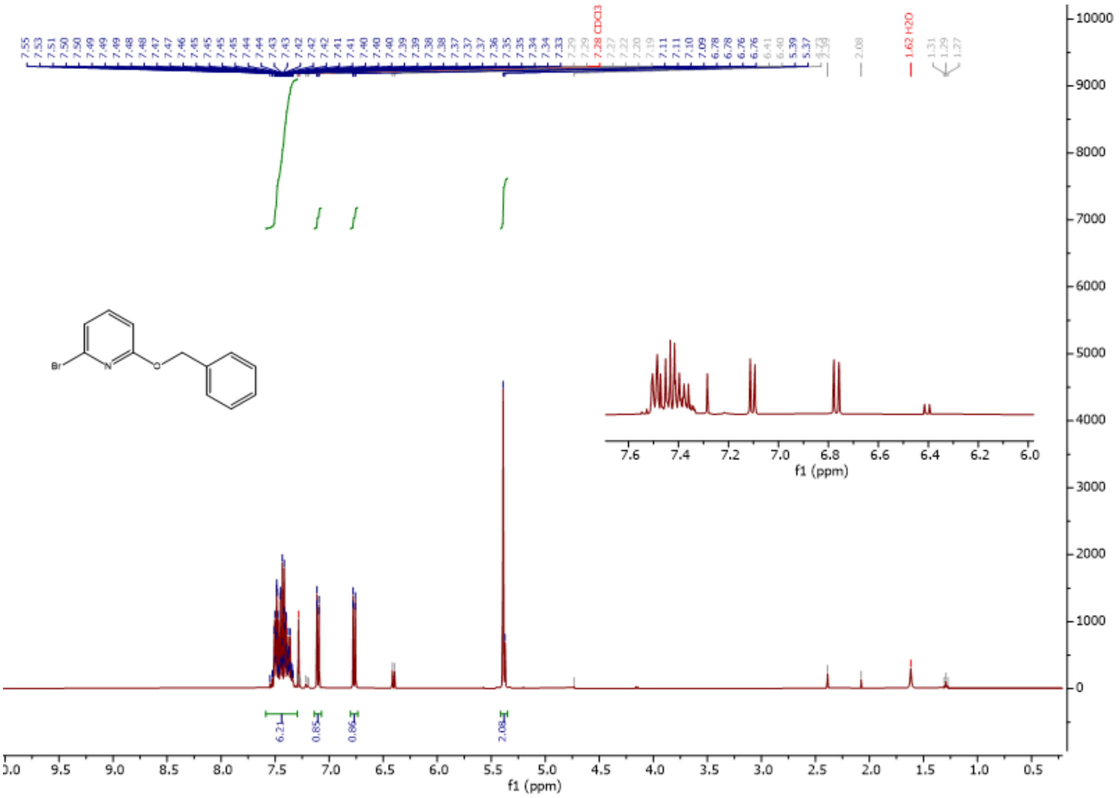


Figure 7. *^{1}H NMR spectra of (1)*

Compound (2) were synthesized by following the procedure that was described in section 6.2.2. The singlet peak of aldehyde hydrogen peak at 10 ppm in NMR spectra (Figure 8) shows that reaction was occurred successfully. Remaining of aromatic peaks of pyridine and benzene and aliphatic peak of two hydrogens of methyl support the result.

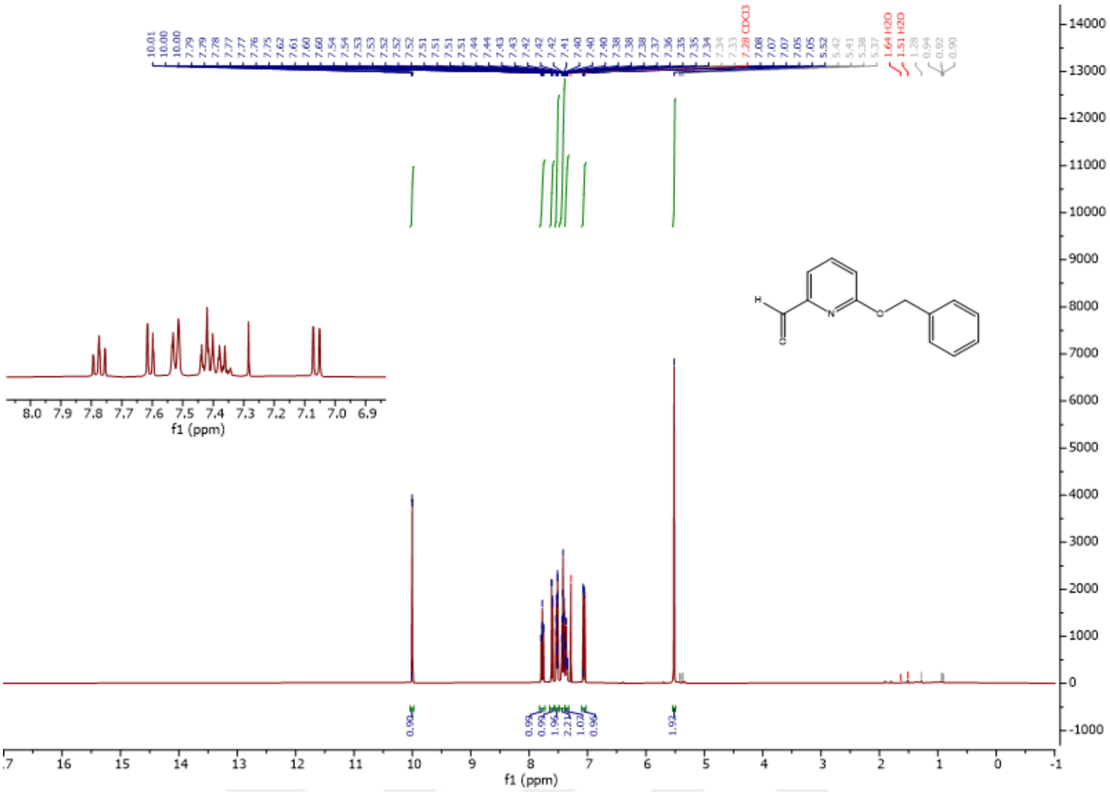


Figure 8. *^{1}H NMR spectra of (2)*

Compound (3) were synthesized by following the procedure that was described in section 6.2.3. Disappearance of singlet peak of aldehyde hydrogen peak at 10 ppm, appearance of aliphatic peaks of piperidine at 1.44-2.52 ppm, and singlet peak of two hydrogens at 3.63 ppm in ^{1}H NMR spectra (Figure 9) shows that reaction was occurred successfully. ^{13}C NMR spectra of (3) (Figure 10) shows carbons of pyridine and benzene rings at between 127-138 ppm, 5 carbons of piperidine ring at between 26-54 ppm, carbon adjacent to oxygen and carbon between pyridine and piperidine rings at 67.40 ppm.

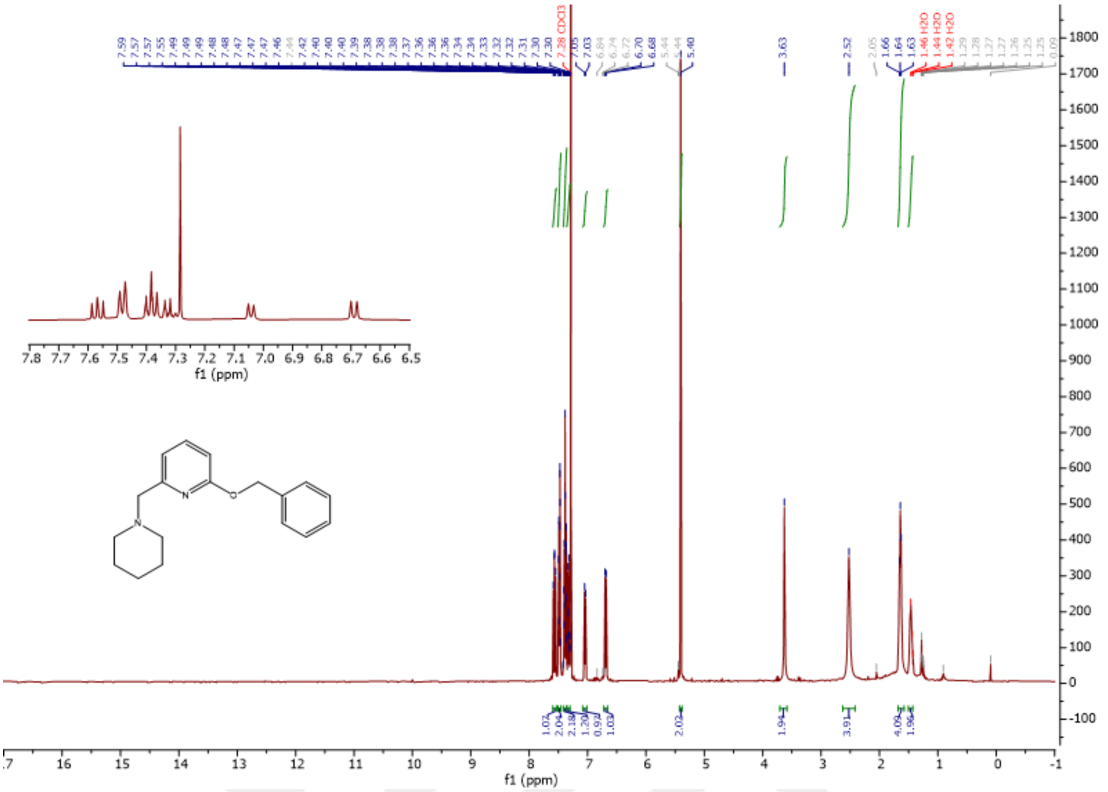


Figure 9. *^{1}H NMR spectra of (3)*

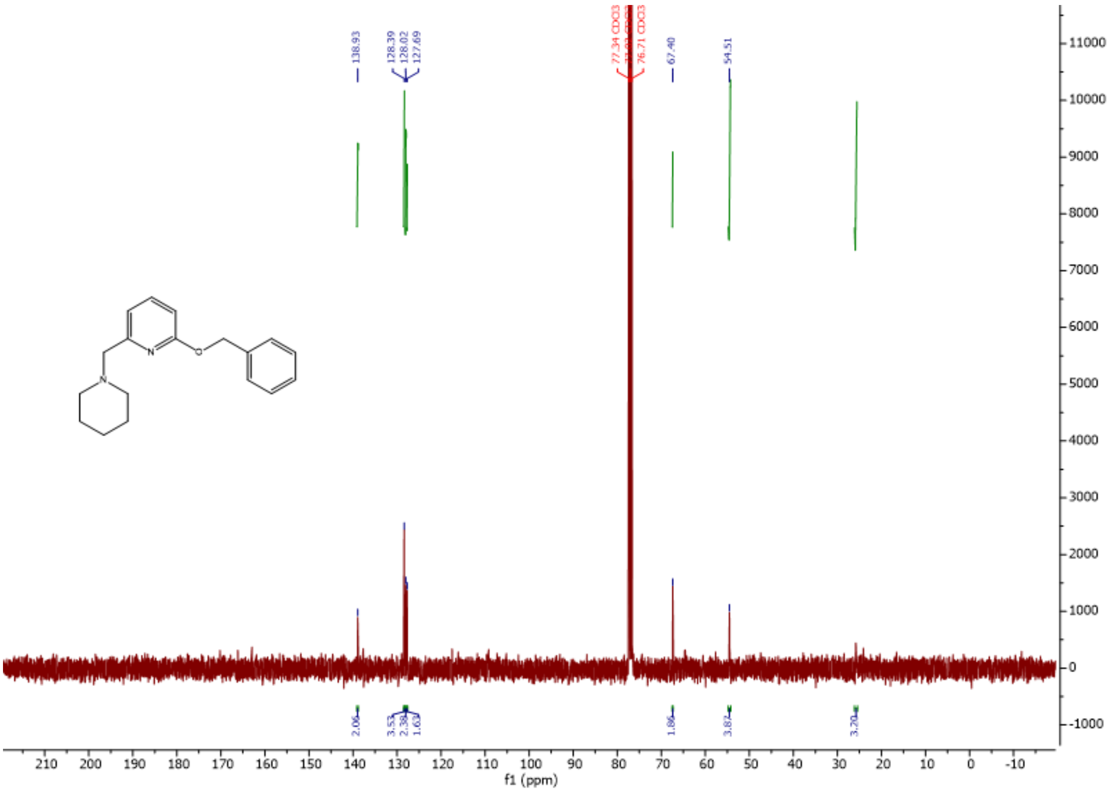


Figure 10. *^{13}C NMR spectra of (3)*

Compound (4) were synthesized by following the procedure that was described in section 6.2.4. In ^{1}H NMR spectra (Figure 11) appearance of singlet alcohol peak at 10.08 ppm, disappearance of aromatic peaks of benzene and hydrogen peaks of methyl adjacent to oxygen and remaining of aromatic peaks of pyridine and peaks of two hydrogen in methyl shows that reaction was occurred successfully. ^{13}C NMR spectra of (4) (Figure 12) shows 5 carbons of pyridine ring at between 104-163 ppm, 5 carbons of piperidine ring at between 23-54 ppm, carbon between pyridine and piperidine rings at 59.21 ppm.

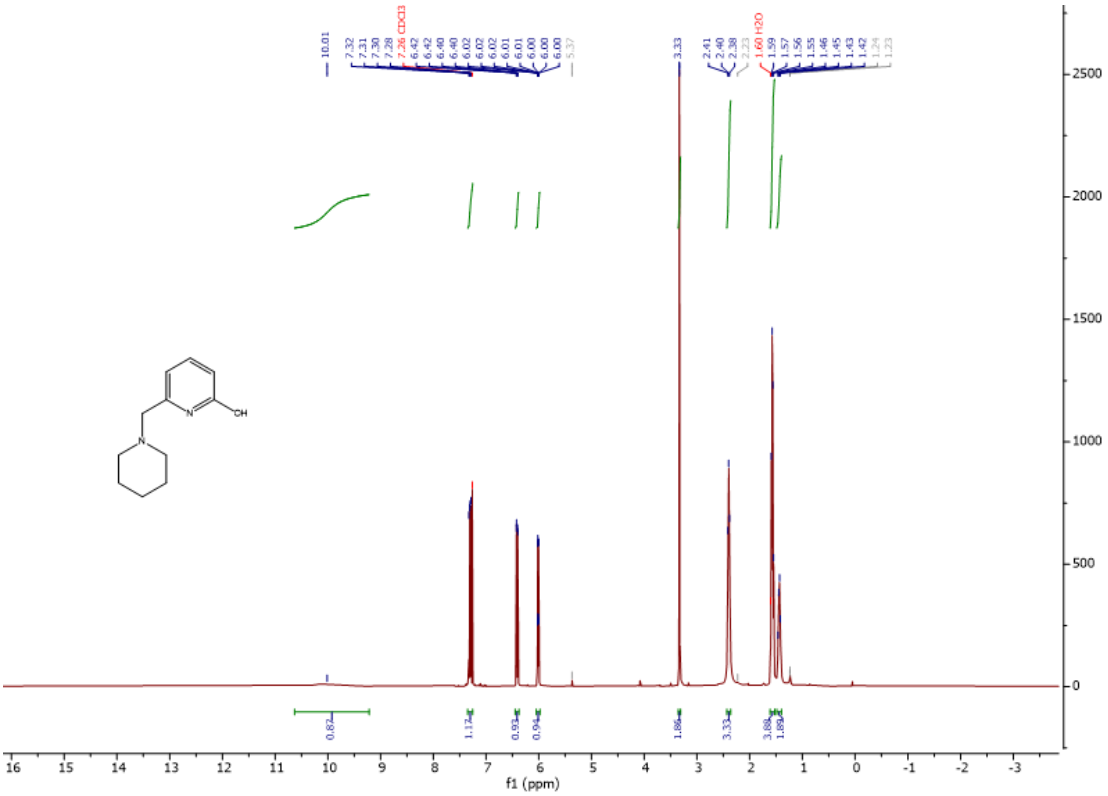


Figure 11. *^{1}H NMR spectra of (4)*

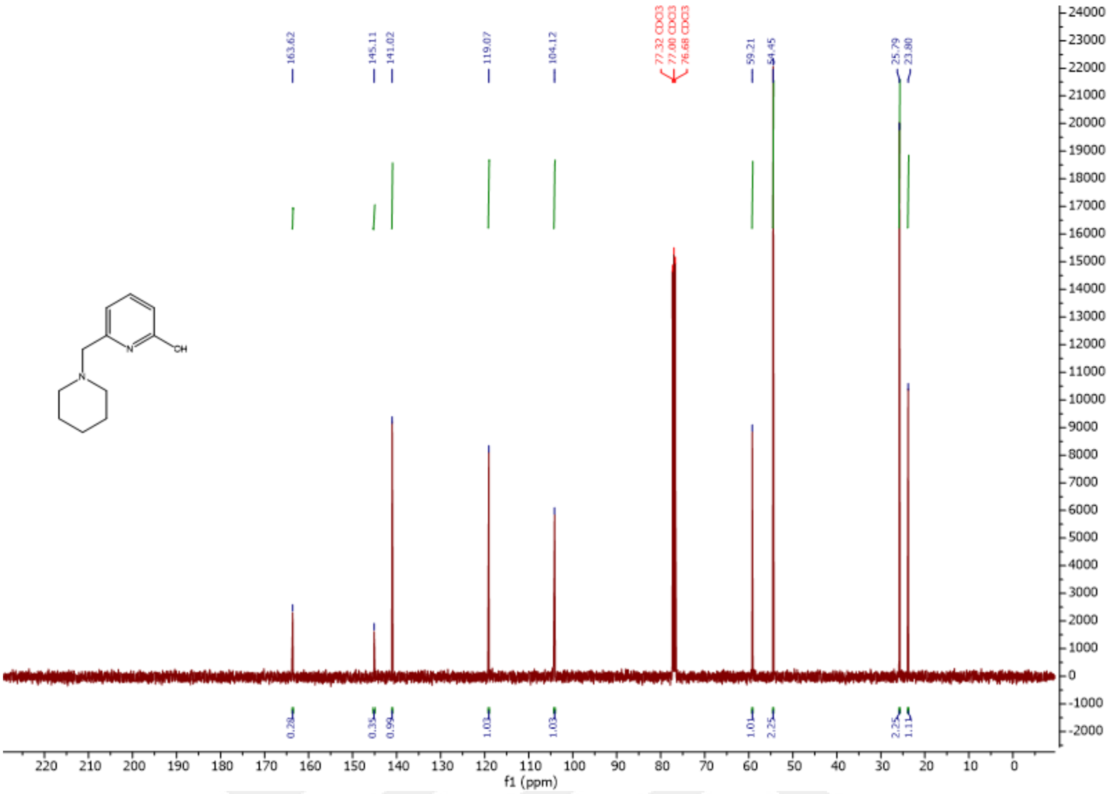
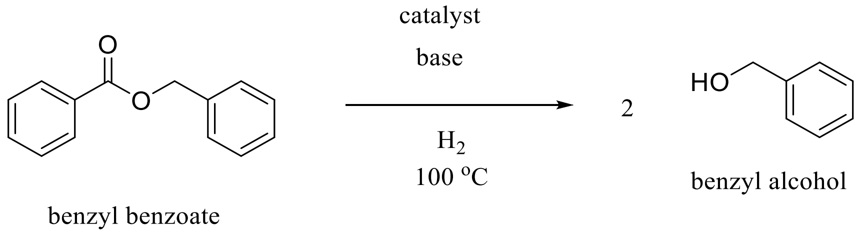


Figure 12. *^{13}C NMR spectra of (4)*

7.2. Results and Discussion of Hydrogenation of Esters

Table 2. *Catalyst screening of hydrogenation of benzyl benzoate* [a]

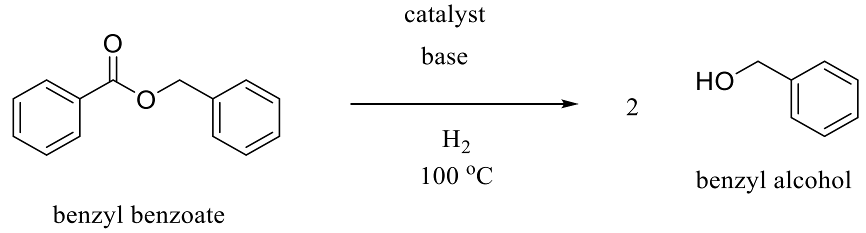


Entry	**Catalyst [mol%]**	**Base (*t*-BuOK) [mol%]**	**P (H_2) [bar]**	**t [h]**	**T [°C]**	**Yield[b] [%]**
1	Cat1 (0.05 mol%)	1.41	25	24	100	41.28
2	Cat2 (0.05 mol%)	1.41	25	24	100	36.70
3	Cat3 (0.05 mol%)	1.41	25	24	100	30.88

Reaction conditions: [a] substrate (0.16 mmol), base (0.22 mmol), 1 mL of Toluene, 25 bar H_2, 24 hours, 100 °C. [b] Products were confirmed by GC-MS. Yields were calculated by GC.

Exploration of catalytic hydrogenation of benzyl benzoate (Table 2) was started with 0.05 mol% catalyst, 1.41 mol% *t*-BuOK, under 25 bar of H_2 at 100 °C for 24 hours. Products were confirmed by GC-MS and yield calculations were determined by GC with a decane as an internal standard. Hydrogenation of benzyl benzoate was successfully achieved by catalysts Cat1, Cat2, Cat3 with 41.28%, 36.70%, 30.88% yields, respectively.

Table 3. *Amount of the base optimization of the hydrogenation of benzyl benzoate* [a]

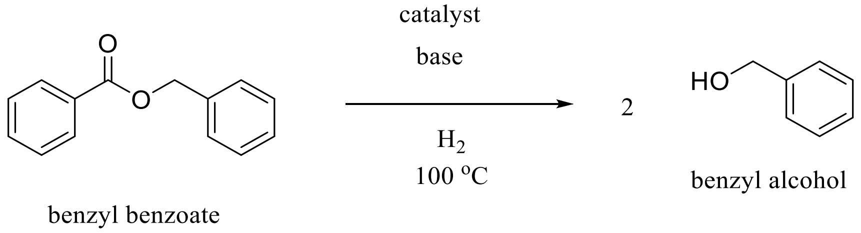


Entry	Catalyst [mol%]	Base (t-BuOK) [mol%]	P (H_2) [bar]	t [h]	T [°C]	Yield[b] [%]
1	Cat1 (0.05 mol%)	1.41	30	24	100	55.87
2	Cat1 (0.05 mol%)	0.85	30	24	100	- [c]
3	Cat2 (0.05 mol%)	1.41	30	24	100	26.15
4	Cat2 (0.05 mol%)	0.85	30	24	100	11.46
5	Cat3 (0.05 mol%)	1.41	30	24	100	32.52
6	Cat3 (0.05 mol%)	0.85	30	24	100	29.68

Reaction conditions: [a] substrate (0.16 mmol), base, 1 mL of Toluene, 30 bar H_2, 24 hours, 100 °C. [b] Products were confirmed by GC-MS. Yields were calculated by GC. [c] Yield couldn't calculated.

The amount of the base optimization (Table 3) with 0.85 % and 1.41% t-BuOK under 30 bar of H_2 at 100 °C for 24 hours showed that decrease in the amount of base resulted decrease in the yields.

Table 4. *Control experiments for the catalysts of the hydrogenation of benzyl benzoate* [a]

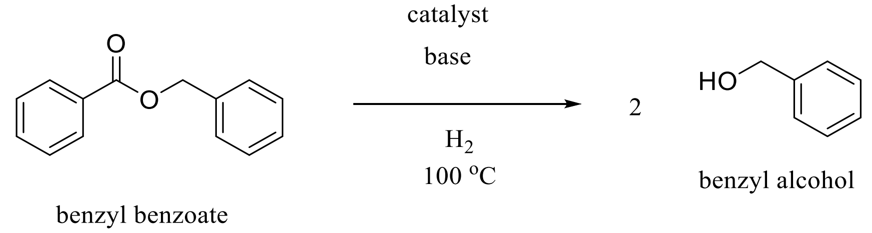


Entry	**Catalyst [mol%]**	**Base (*t*-BuOK) [mol%]**	**P (H_2) [bar]**	**t [h]**	**T [°C]**	**Yield[b] [%]**
1	$PdCl_2$ (0.05 mol%)	1.41	25	24	100	38.43
2	No use	1.41	25	24	100	36.65
3	$PdCl_2$ (0.05 mol%)	1.41	30	24	100	27.18
4	No use	1.41	30	24	100	41.29

Reaction conditions: [a] substrate (0.16 mmol), base (0.22 mmol), 1 mL of Toluene, H_2, 24 hours, 100 °C. [b] Products were confirmed by GC-MS. Yields were calculated by GC.

To control the previous experiments which resulted with hydrogenation of benzyl benzoate to benzyl alcohol, without ligand only $PdCl_2$ and without catalyst conditions were screened under 25 bar and 30 bar of H_2 at 100 °C for 24 hours (Table 4). Surprisingly, using $PdCl_2$ as catalyst was resulted with 38.43%, 27.18% yields in Entry 1 and 3, respectively. Likewise, without catalyst benzyl benzoate were converted to benzyl alcohol with 36.55% and 41.29% yields in Entry 2 and 4, respectively.

Table 5. *Base optimization of the hydrogenation of benzyl benzoate without catalyst in toluene* [a]

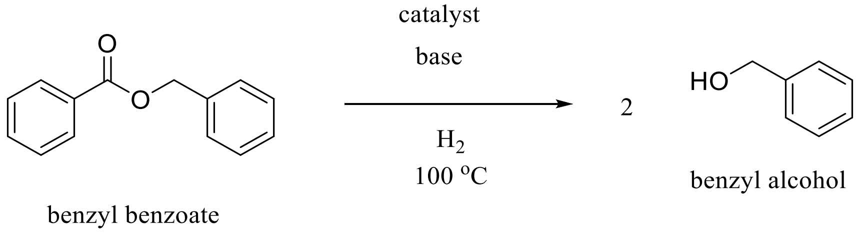


Entry	Catalyst [mol%]	Base (*t*-BuOK) [mol%]	P (H_2) [bar]	t [h]	T [°C]	Yield[b] [%]
1	No use	Sigma Aldrich *t*-BuOK (1.41)	30	24	100	28.89
2	No use	Acros *t*-BuOK (1.41)	30	24	100	33.61
3	No use	KOH (1.41)	30	24	100	46.61
4	No use	*t*-BuONa (1.41)	30	24	100	48.02
5	No use	No use	30	24	100	- [c]

Reaction conditions: [a] substrate (0.16 mmol), base (0.22 mmol), 1 mL of Toluene, 30 bar H_2, 24 hours, 100 °C. [b] Products were confirmed by GC-MS. Yields were calculated by GC. [c] 97.86% benzyl benzoate remains without any expected product.

To examine base optimization of the hydrogenation of benzyl benzoate (Table 5), using 1.41 mol% of *t*-BuOK (Sigma Aldrich), *t*-BuOK (Acros), KOH, *t*-BuONa were resulted with yield range between 28.89-48.02%. In contrast, no base usage in reaction was resulted with remaining of 97.86% of benzyl benzoate.

Table 6. *Base optimization of the hydrogenation of benzyl benzoate without catalyst in THF*[a]

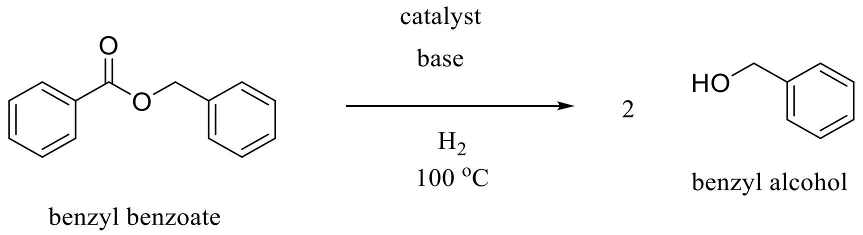


Entry	**Catalyst [mol%]**	**Base (*t*-BuOK) [mol%]**	**P (H_2) [bar]**	**t [h]**	**T [°C]**	**Yield[b] [%]**
1	No use	Sigma Aldrich *t*-BuOK (1.41)	30	24	100	22.37
2	No use	Acros *t*-BuOK (1.41)	30	24	100	24.49
3	No use	KOH (1.41)	30	24	100	0
4	No use	*t*-BuONa (1.41)	30	24	100	48.79
5	No use	No use	30	24	100	0

Reaction conditions: [a] substrate (0.16 mmol), base (0.22 mmol), 1 mL of THF, 30 bar H_2, 24 hours, 100 °C. [b] Products were confirmed by GC-MS. Yields were calculated by GC.

To screen solvent effect on hydrogenation of benzyl benzoate (Table 6), solvent was changed to THF from toluene. In Entry 4 which *t*-BuONa used as a base showed almost same result with where the toluene used as a solvent. The yield decreasing was noticed in the Entry 2 *t*-BuOK used as a base, and no conversion with KOH. The same result was showed in no base usage in THF also.

Table 7. *Screening of pressure effect on hydrogenation of benzyl benzoate in absence of catalyst* [a]

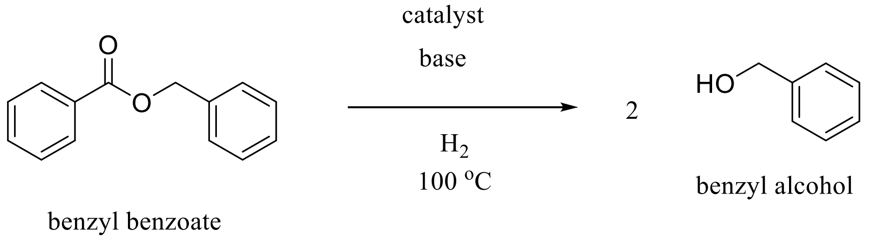


Entry	Solvent	Base (*t*-BuOK) [mol%]	P (H_2) [bar]	t [h]	T [°C]	Yield[b] [%]
1	THF	Sigma Aldrich *t*-BuOK (1.41)	20	24	100	34.83
2	THF	Acros *t*-BuOK (1.41)	20	24	100	33.67
3	THF	KOH (1.41)	20	24	100	0
4	THF	*t*-BuONa (1.41)	20	24	100	25.16
5	THF	No use	20	24	100	0
6	Toluene	Acros *t*-BuOK (1.41)	20	24	100	+[c]
7	Toluene	KOH (1.41)	20	24	100	+[c]
8	Toluene	*t*-BuONa (1.41)	20	24	100	+[c]
9	Toluene	No use	20	24	100	0

Reaction conditions: [a] substrate (0.16 mmol), base (0.22 mmol), 1 mL of THF, 20 bar H_2, 24 hours, 100 °C. [b] Products were confirmed by GC-MS. Yields were calculated by GC. [c] Yield couldn't be calculated.

So far pressure was kept at 30 bar. To examine the pressure effect on hydrogenation of benzyl benzoate (Table 7), pressure was drop to 20 bar. In entries which THF was used as a solvent were showed similar result with entries in Table 9 at 30 bar. In entries Table 8 which toluene was used as a solvent were showed different result than THF.

Table 8. *Screening of base effect on hydrogenation of benzyl benzoate* [a]

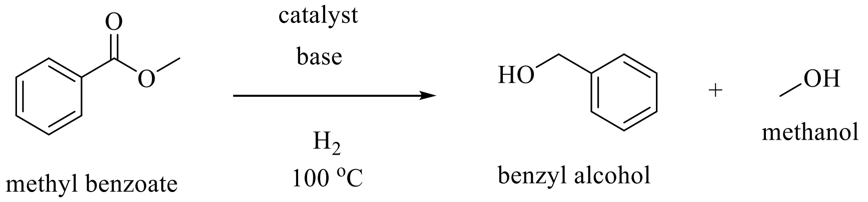


Entry	**Catalyst [mol%]**	**Base (t-BuOK) [mol%]**	**P (H_2) [bar]**	**t [h]**	**T [°C]**	**Yield[b] [%]**
1	Cat1	No use	30	24	100	0
2	Cat2	No use	30	24	100	0
3	Cat3	No use	30	24	100	0
4	$PdCl_2$	No use	30	24	100	0
5	Cat2	1.41	30	24	100	0
6	Cat2	No use	30	24	100	0
7	No use	1.41	30	24	100	+[c]
8	$PdCl_2$	1.41	30	24	100	0

Reaction conditions: [a] substrate (0.16 mmol), base (0.22 mmol), 1 mL of toluene, 30 bar H_2, 24 hours, 100 °C. [b] Products were confirmed by GC-MS. Yields were calculated by GC. [c] Yield couldn't be calculated.

Exploration of the effect of base on benzyl benzoate (Table 8) was conducted with 0.05 mol% catalyst, 0.10 mol% t-BuOK (not in all entries), under 30 bar of H_2 at 100 °C for 24 hours. Products were confirmed by GC-MS and yield calculations were determined by GC with a decane as an internal standard. Only in Entry 7 desired product were achieved, unfortunately yield couldn't calculated.

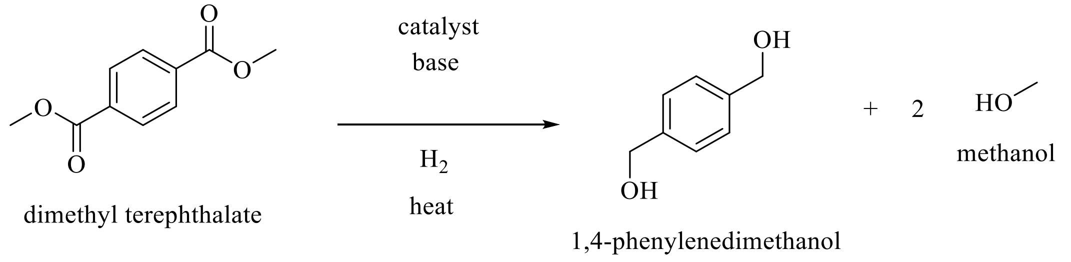
Table 9. *Hydrogenation of Methyl Benzoate* [a]



Entry	Catalyst [mol%]	Base (t-BuOK) [mol%]	P (H_2) [bar]	t [h]	T [°C]	Yield[b] [%]
1	Cat1	1.41	30	24	100	0
2	Cat4	1.41	30	24	100	0
3	Cat5	1.41	30	24	100	0
4	Cat6	1.41	30	24	100	0
5	Cat7	1.41	30	24	100	0
6	Cat1	1.41	30	24	100	0

Reaction conditions: [a] substrate (0.16 mmol), base (0.22 mmol), 1 mL of toluene, 30 bar H_2, 24 hours, 100 °C. [b] Products were confirmed by GC-MS. Yields were calculated by GC.

Table 10. *Hydrogenation of DMT*[a]



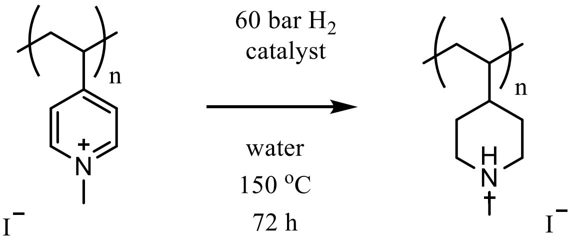
Entry	Catalyst [mol%]	Base (*t*-BuOK) [mol%]	Solvent	P (H_2) [bar]	t [h]	T [°C]	Yield[b] [%]
1	Cat1	1.41	Toluene	30	24	100	0
2	Cat1	1.41	Toluene	30	24	100	0
3	Cat1	1.41	THF	30	24	75	0
4	Cat7	1.41	THF	20	24	120	0
5	Cat8	1.41	THF	20	24	120	0
6	Cat7	1.41	THF	50	24	80	0
7	Cat8	1.41	THF	50	24	80	0
8	Cat1	1.41	THF	50	24	120	0
9	Cat1	1.41	THF	50	24	120	0

Reaction conditions: [a] substrate (0.16 mmol), base (0.22 mmol), 1 mL of solvent, H_2, 24 hours, 100 °C.
[b] Products were confirmed by GC-MS. Yields were calculated by GC.

After unsuccessful attempt of catalytical hydrogenation of benzyl benzoate, methyl benzoate (Table 9) and DMT (Table 10) were chosen to perform in hydrogenation reaction. Products were confirmed by GC-MS. Unfortunately, hydrogenation of methyl benzoate and DMT were not successful.

7.3. Results and Discussions of Hydrogenation of Polymers

Table 11. *Catalyst screening of hydrogenation of poly(N-methyl-4-vinylpyridiniumiodide) (Pol1)* [a]



Entry	Catalyst	P (H_2) [bar]	t [h]	T [°C]
1	Pd/C	60	72	150
2	RuO_2	60	72	150

Reaction conditions: [a] substrate (0,079708 micromol), catalyst (0,079708 mmol), 1 mL of water, 60 bar of H_2, 72 hours, 150 °C. [b] Products were confirmed by ^1H NMR spectroscopy.

Exploration of catalytic hydrogenation of Pol1 (Table 11) was started with excess amount of catalyst under 60 bar of H_2 at 150 °C for 72 hours. Products were confirmed by ^1H NMR spectroscopy. Stacked NMR spectra of the entries were given in Figure 13. In Entry 2, disappearing of aromatic peak of ^1H NMR spectroscopy, showed complete conversion to saturated polymer.

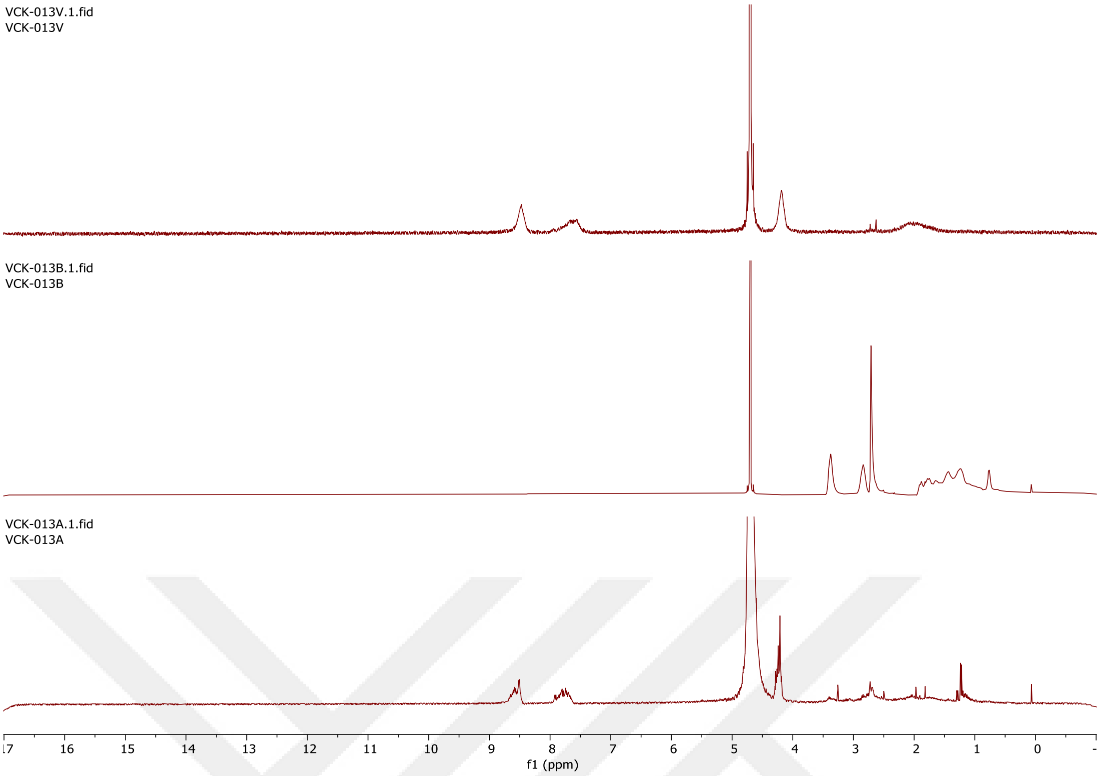
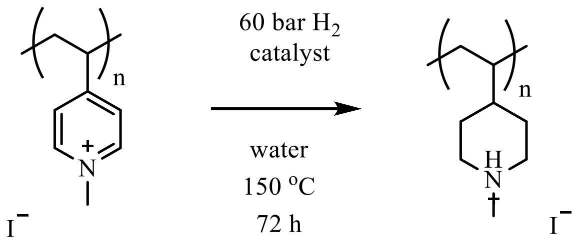


Figure 13. *^{1}H NMR spectra of entries in Table 21. VCK-013V is for polymer, VCK-013A is for Entry 1, VCK-013B is for Entry 2.*

Table 12. *Hydrogenation of Pol1* [a]



Entry	**Catalyst**	**P (H_2)** **[bar]**	**t** **[h]**	**T** **[°C]**
1	Pd/C	60	72	150
2	RuO_2	60	72	150
3	Rh/C	60	72	150
4	PtO_2	60	72	150

Reaction conditions: [a] substrate (0,079708 micromol), catalyst (0,079708 mmol), 1 mL of water, 60 bar of H_2, 72 hours, 150 °C. Products were confirmed by ^{1}H NMR spectroscopy.

In these experiments (Table 12), control experiments of Pd/C and RuO_2 and trial of new catalysis were checked. RuO_2 was succeeded to full conversion while Rh/C showed similar achievement with RuO_2. Desired results weren't achieved with Pd/C and PtO_2. Stacked NMR spectra of the entries were given in Figure 14.

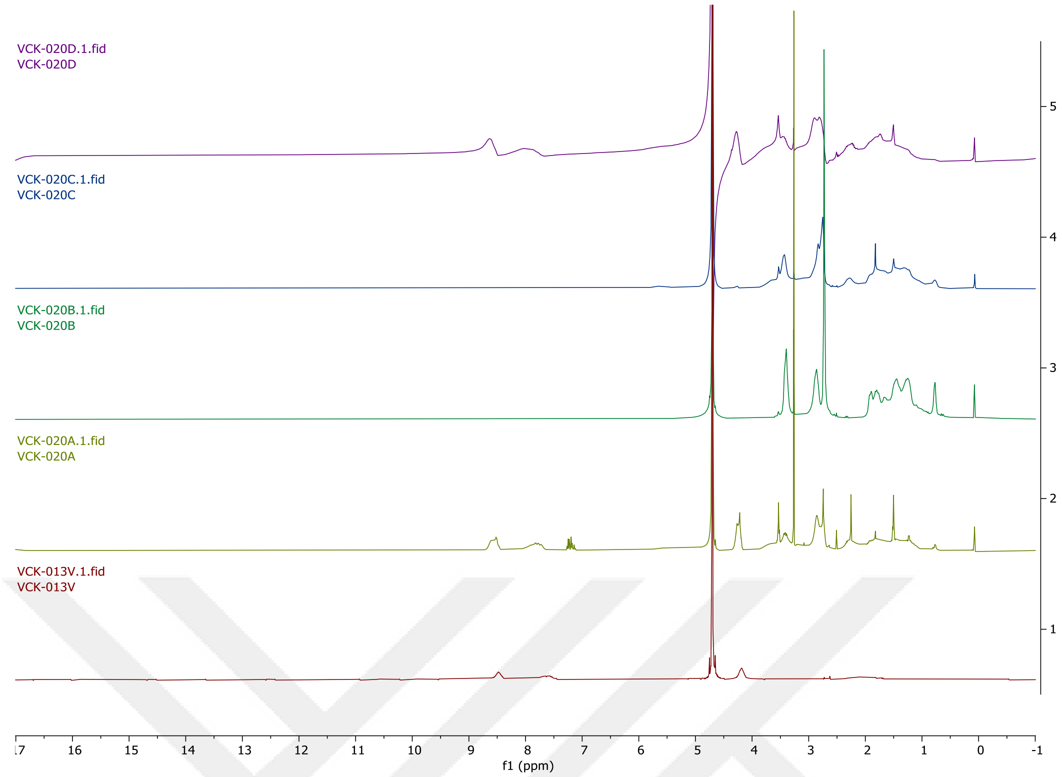
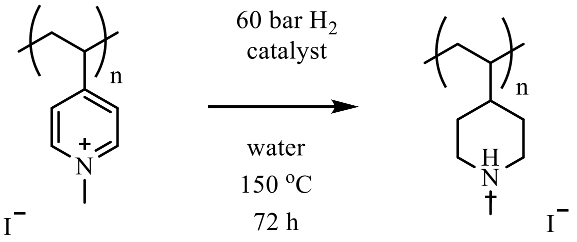


Figure 14. *^{1}H NMR spectra of entries in Table 22. VCK-013V is for polymer, VCK-020A is for Entry 1, VCK-020B is for Entry 2, VCK-20C is for Entry 3, VCK-020D is for Entry 4.*

Table 13. *Hydrogenation of Pol1 with RuO$_2$* [a]

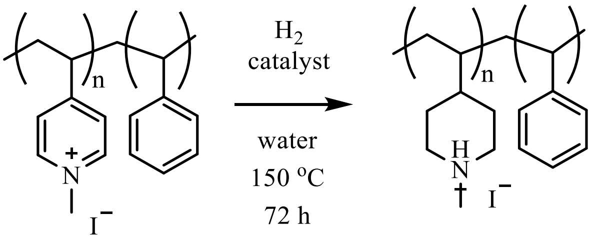


Entry	Catalyst	P (H$_2$) [bar]	t [h]	T [°C]	[g] [b]
1	RuO$_2$	60	72	150	0.6138
2	RuO$_2$	60	72	150	0.6053
3	RuO$_2$	60	72	150	0.4546

Reaction conditions: [a] substrate (0,079708 micromol), catalyst (0,079708 mmol), 1 mL of water, 60 bar of H$_2$, 72 hours, 150 °C. [b] Products were confirmed by ^{1}H NMR spectroscopy.

After achieving desired results of hydrogenation of Pol1 with RuO$_2$, sets of experiments (Table 13) were conducted. In these three experiments, 24 hydrogenation reactions were prepared at the same time. 1.6737 g of saturated polymer, product of hydrogenation of Pol1 were obtained.

Table 14. *Hydrogenation of poly(N-methyl-4-vinylpyridiniumiodide-co-styrene) (Pol2)* [a]



Entry	Catalyst	$P (H_2)$ [bar]	t [h]	T [°C]
1	Pd/C	75	72	150
2	RuO_2	75	72	150
3	Rh/C	75	72	150
4	PtO_2	75	72	150
5	Pd/C	80	72	150
6	RuO_2	80	72	150
7	Rh/C	80	72	150
8	PtO_2	80	72	150
9	Pd/C	75	72	150
10	RuO_2	75	72	150
11	PtO_2	75	72	150

Reaction conditions: [a] substrate (0.03 g), catalyst (0,079708 mmol), 1 mL of water, 75/80 bar of H_2, 72 hours, 150 °C. Products were confirmed by ^{1}H NMR spectroscopy.

After having successful results on hydrogenation of Pol1, next step was selective hydrogenation of Pol2. Exploration of catalytic hydrogenation of Pol2 (Table 14) was started with excess amount of catalyst under 75 bar of H_2 at 150 °C for 72 hours. Products were confirmed by ^{1}H NMR spectroscopy. Only in Entry 4 which PtO_2 were used as a catalyst showed selective hydrogenation of Pol2. When the pressure increased to 80 bar desired hydrogenated polymer products weren't obtained. Stacked NMR spectra of the entries were given in Figure 15.

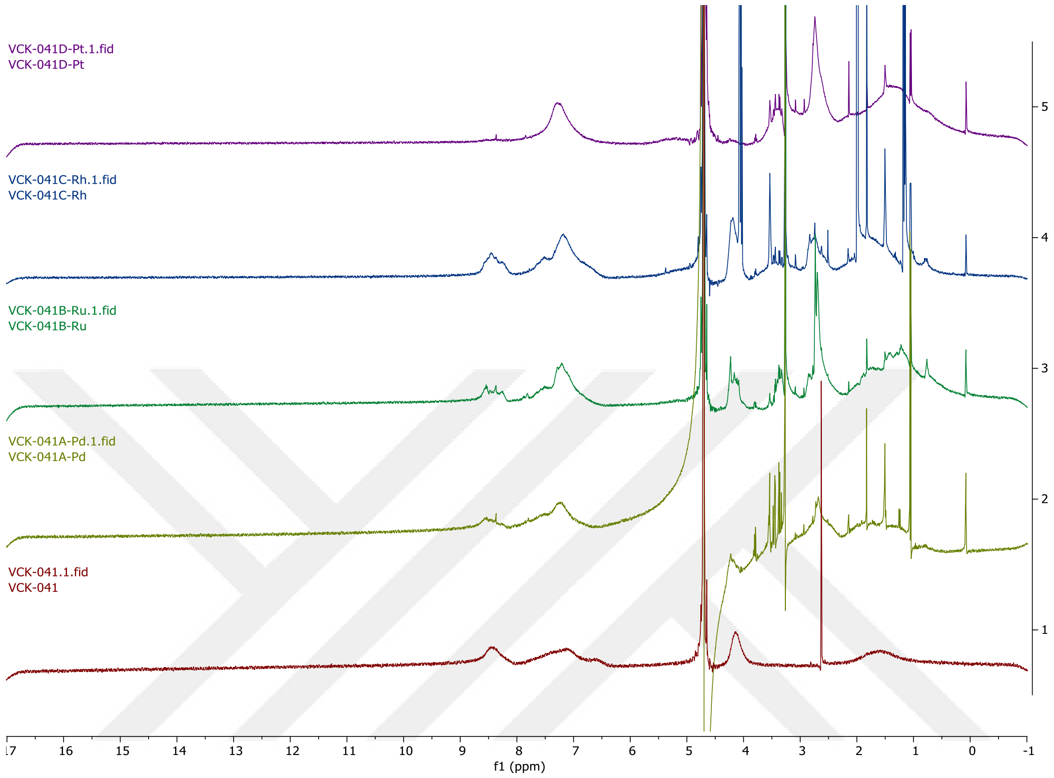
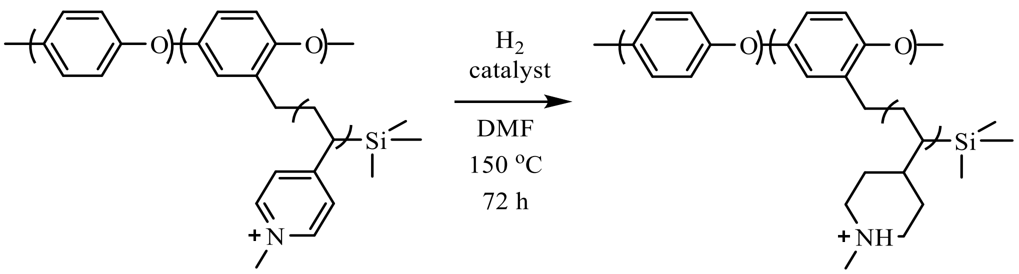


Figure 15. *^{1}H NMR spectra of entries in Table 16. VCK-041 is for polymer, VCK-041A is for Entry 1, VCK-041B is for Entry 2, VCK-43C is for Entry 3, VCK-044D is for Entry 4.*

Table 15. *Hydrogenation of polymer 3 (Pol3)* [a]



Entry	Catalyst	P (H_2) [bar]	t [h]	T [°C]
1	Pd/C	75	72	150
2	RuO_2	75	72	150
3	Rh/C	75	72	150
4	PtO_2	75	72	150

Reaction conditions: [a] substrate (0.03 g), catalyst (0.079708 mmol), 1 mL of DMF, 75 bar of H_2, 72 hours, 150 °C. Products were confirmed by ^{1}H NMR spectroscopy.

Selective hydrogenation of Pol3 were attempted by using four different heterogeneous catalysts (Table 15). ^{1}H NMR spectroscopy of products shows that ruthenium-catalyst and platinum-catalyst were able to selectively hydrogenate Pol3. Unfortunately, due to time constraint and technical errors of autoclave further control experiments weren't able to run. Stacked NMR spectra of the entries were given in Figure 16.

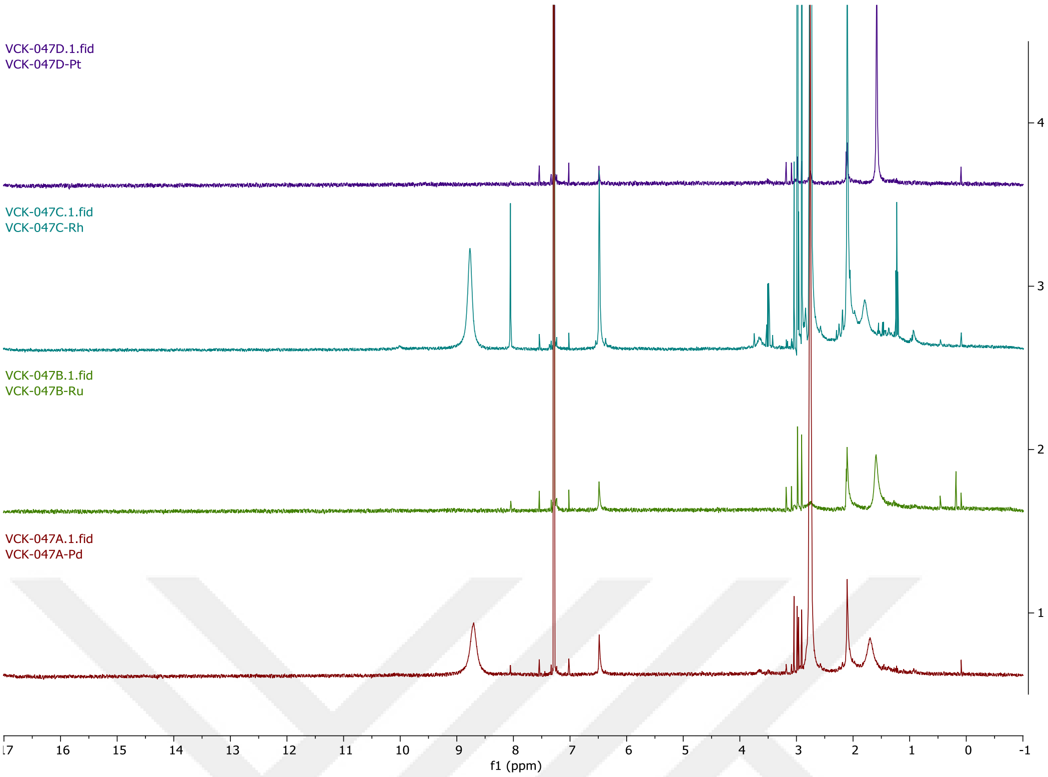


Figure 16. *^{1}H NMR spectra of entries in Table 17. VCK-047A-Pd is for Entry 1, VCK-047B-Ru is for Entry 2, VCK-47C-Rh is for Entry 3, VCK-047D-Pt is for Entry 4.*

In this thesis work Pd-catalyst was synthesized. Catalytic hydrogenation of some of the esters and polymers were attempted. Three different esters, benzyl benzoate, methyl benzoate, and dimethyl terephthalate were tried to be hydrogenated to corresponding alcohols by using various homogeneous catalysts. Unfortunately, hydrogenation of esters was not successful. Three different polymers that contains pyridine rings were tried to be hydrogenated by using various heterogeneous catalysts. Only poly(N-methyl-4-vinylpyridiniumiodide) were successfully hydrogenated. 1.6737 g of saturated polymer, product of hydrogenation of Pol1 were obtained.

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APPENDIX-1 GC Chromatograms of Hydrogenation of Benzyl Benzoate Experiments

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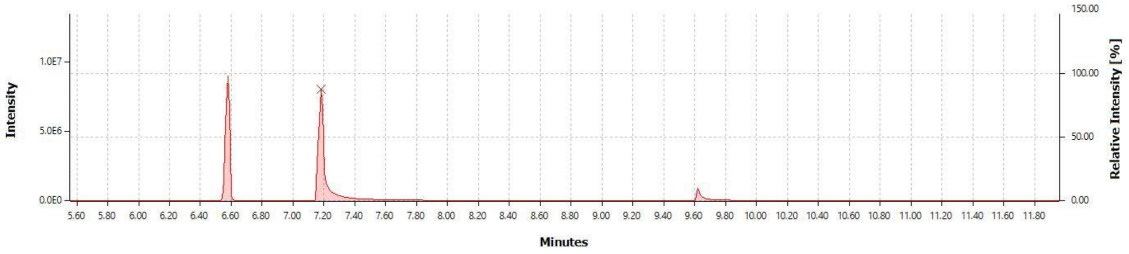

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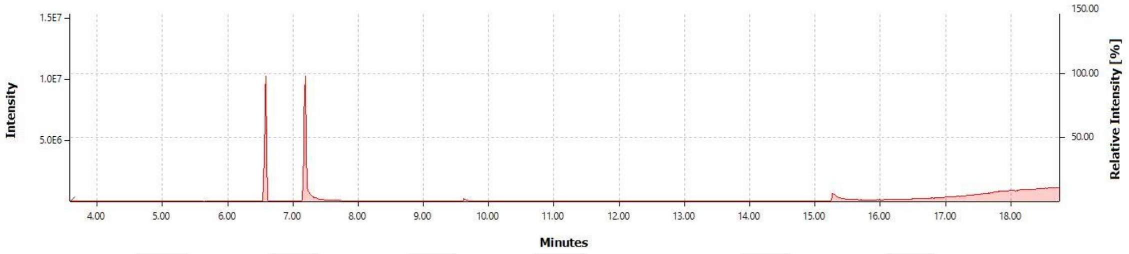

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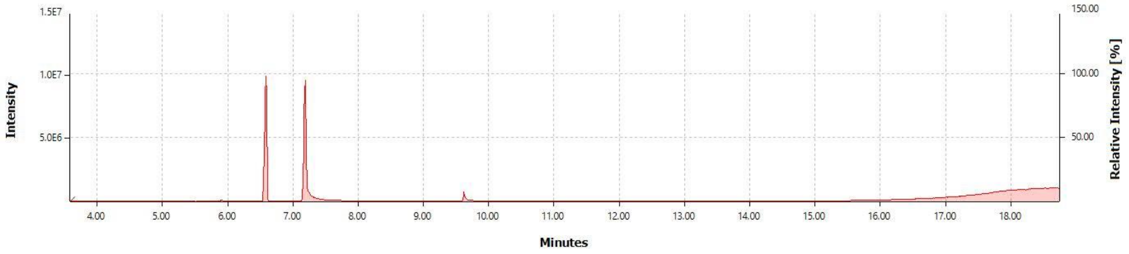

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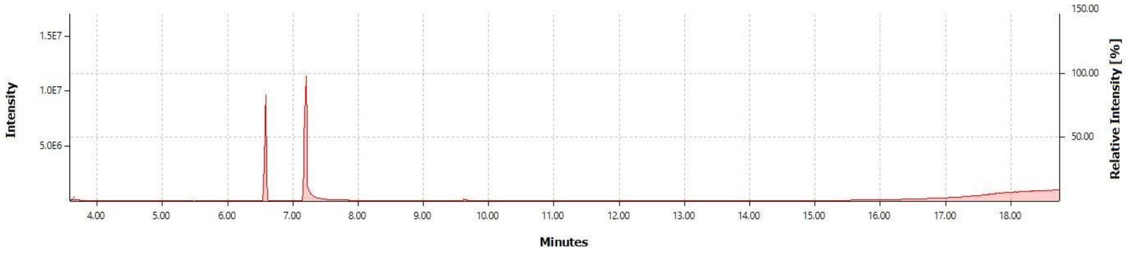

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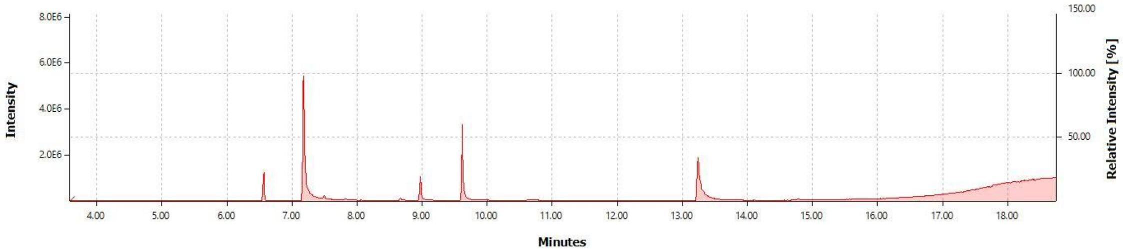

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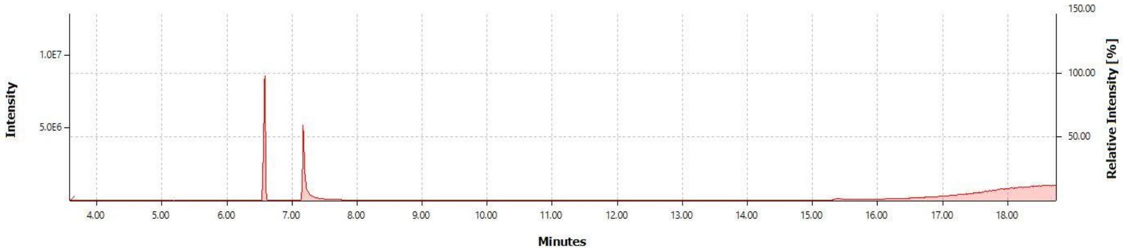

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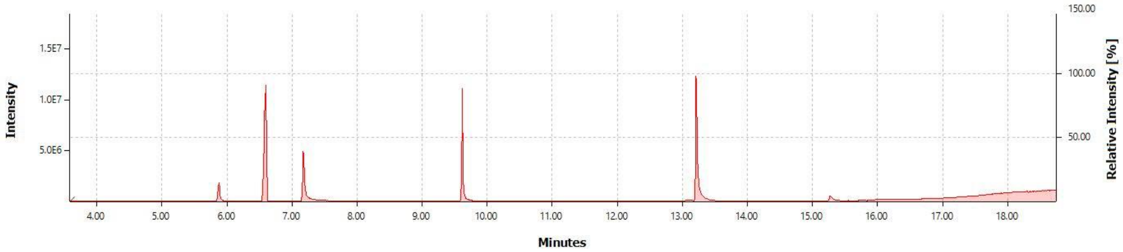

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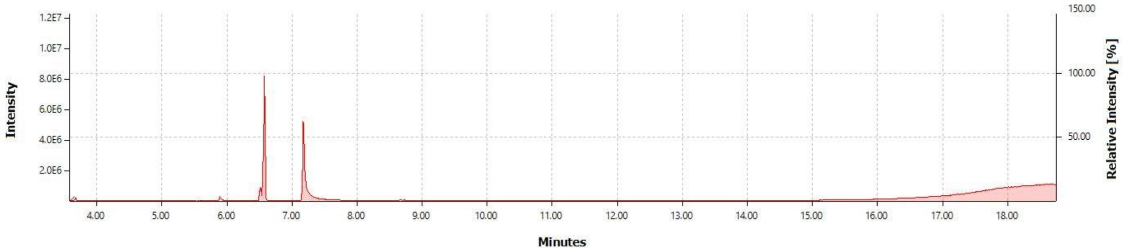

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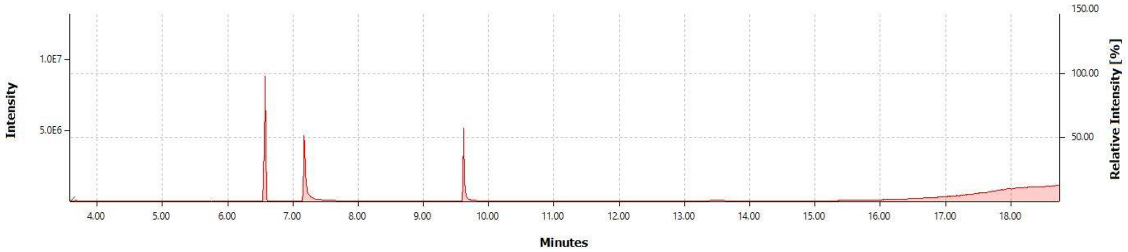

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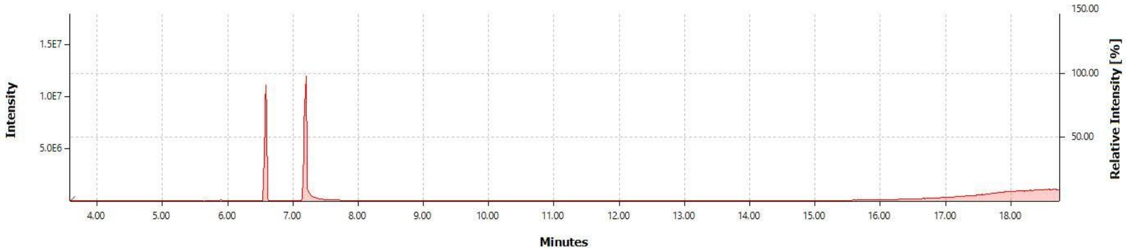

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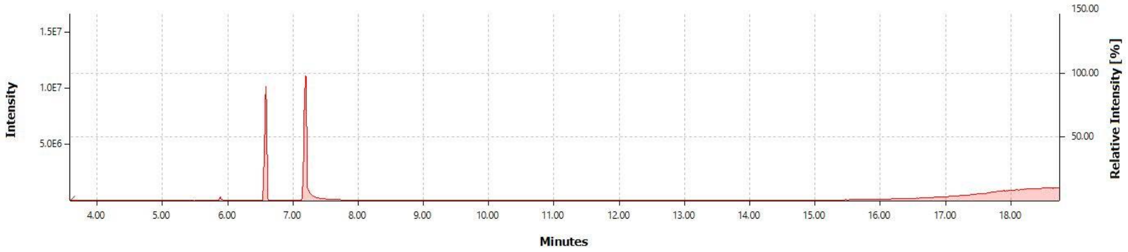

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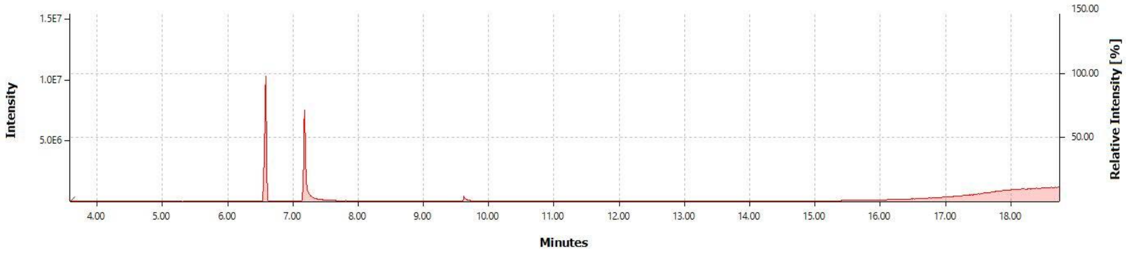

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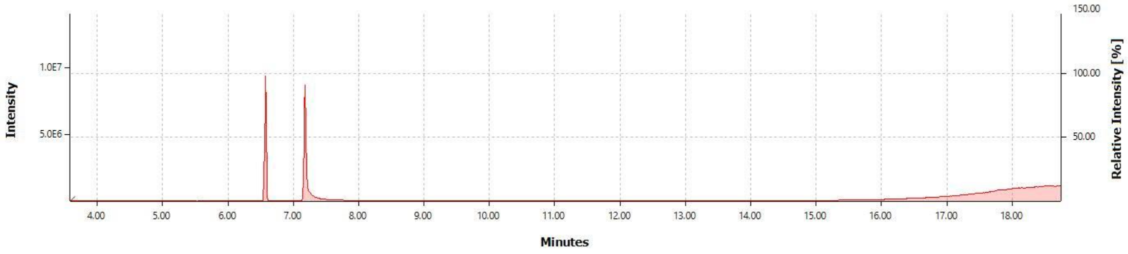

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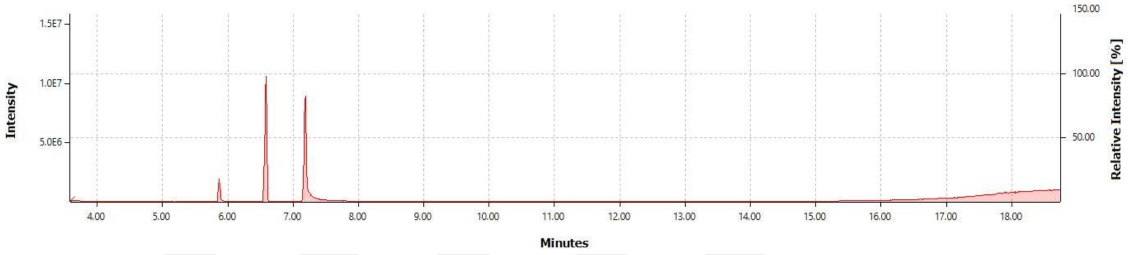

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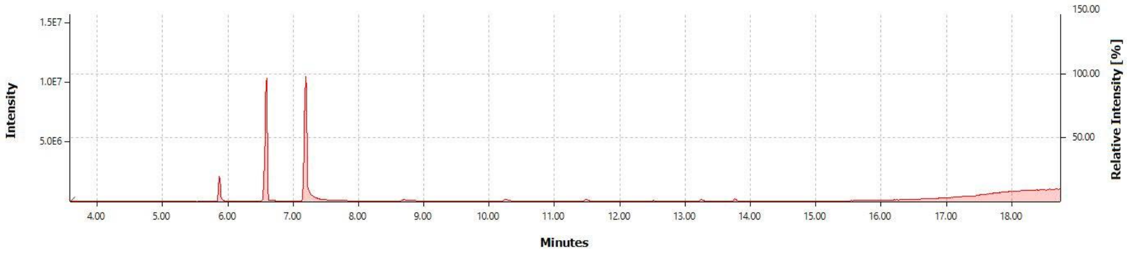

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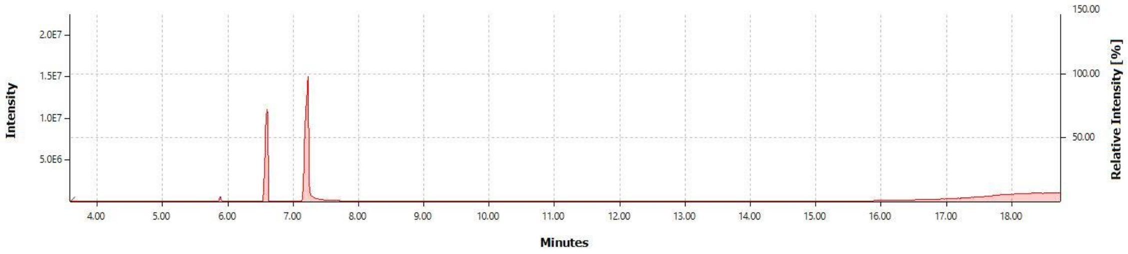

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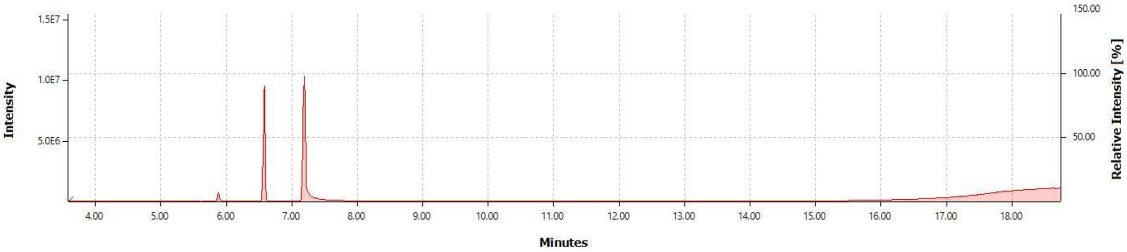

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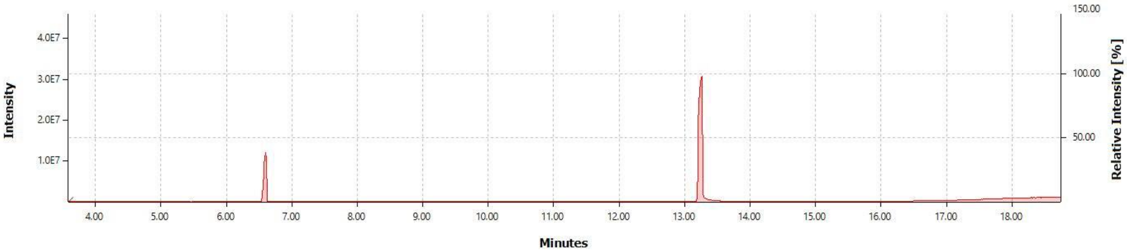

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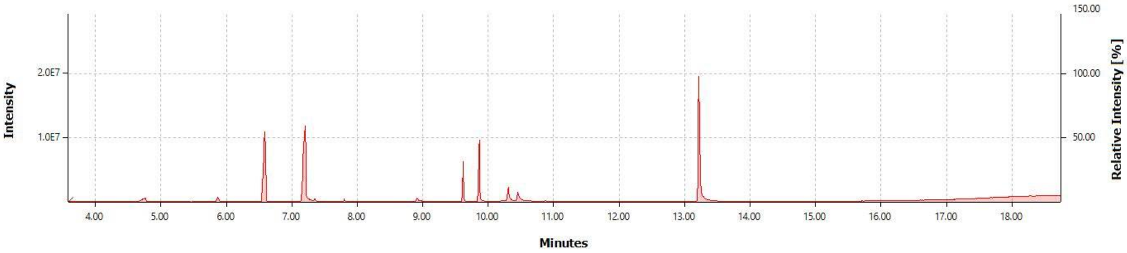

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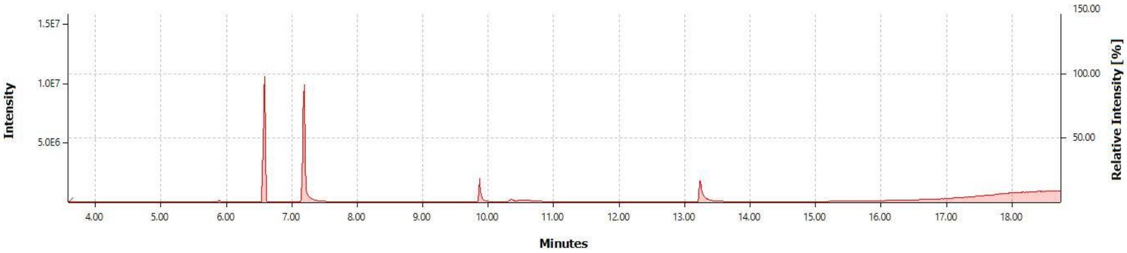

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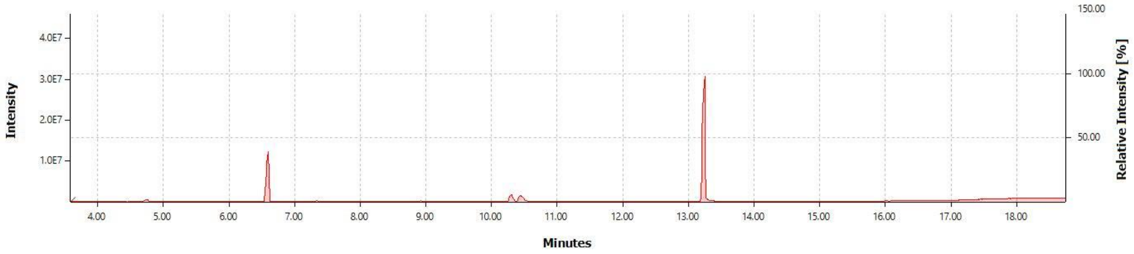

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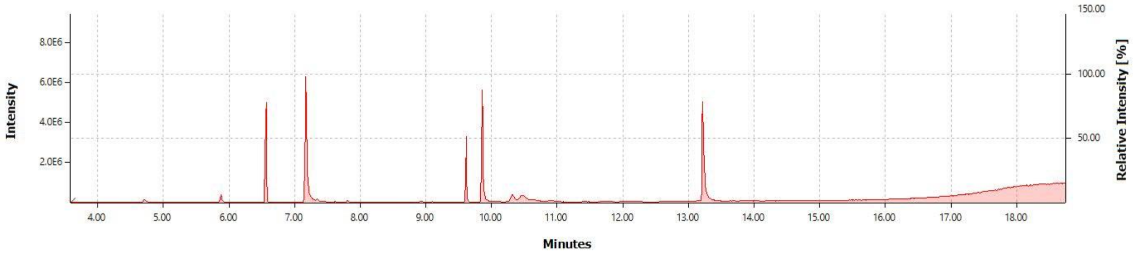

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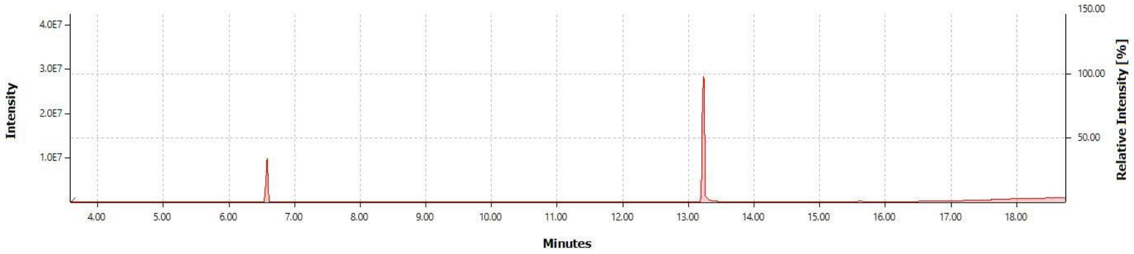

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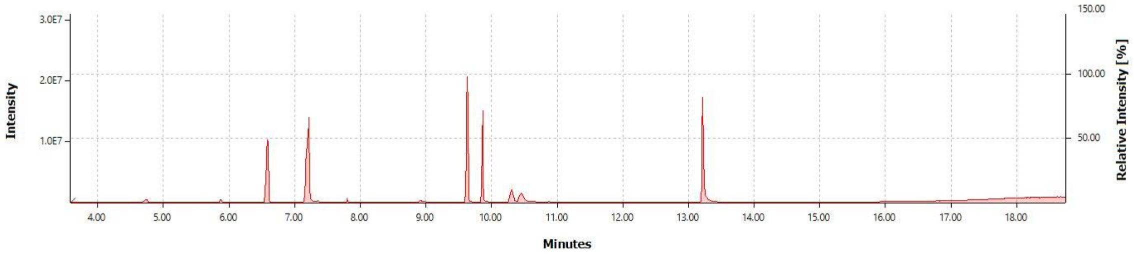

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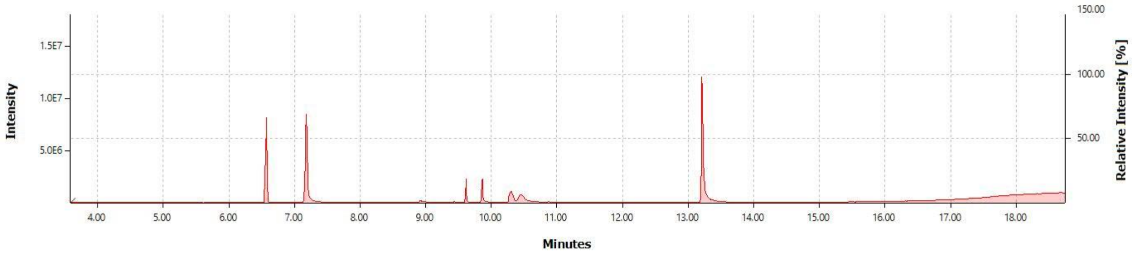

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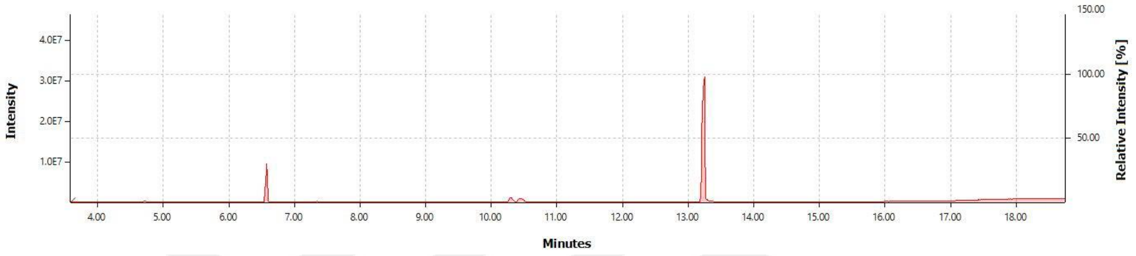

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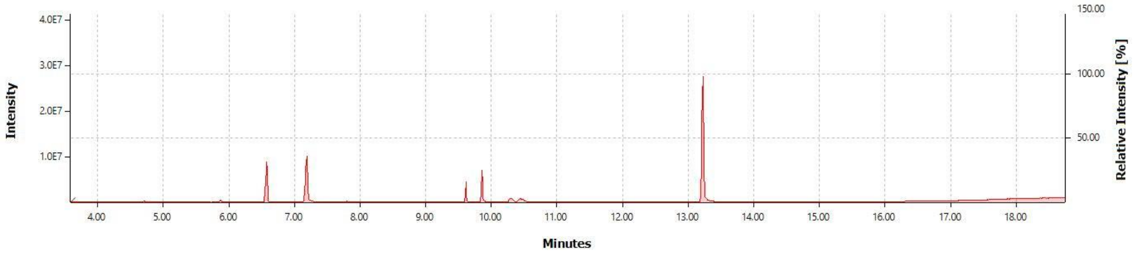

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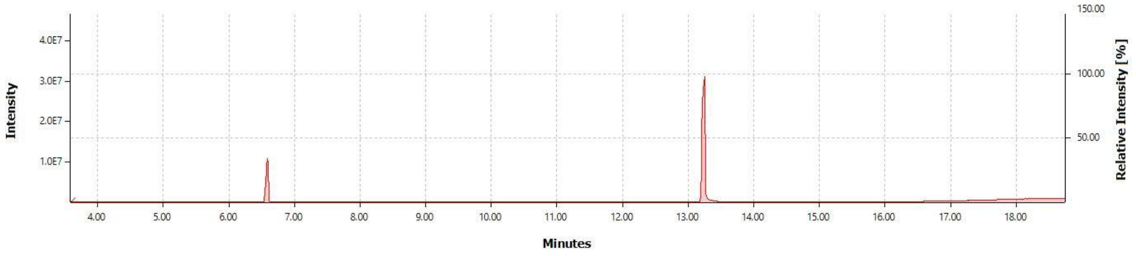

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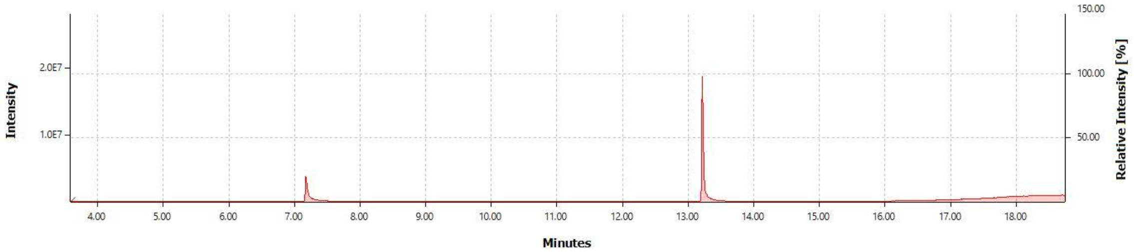

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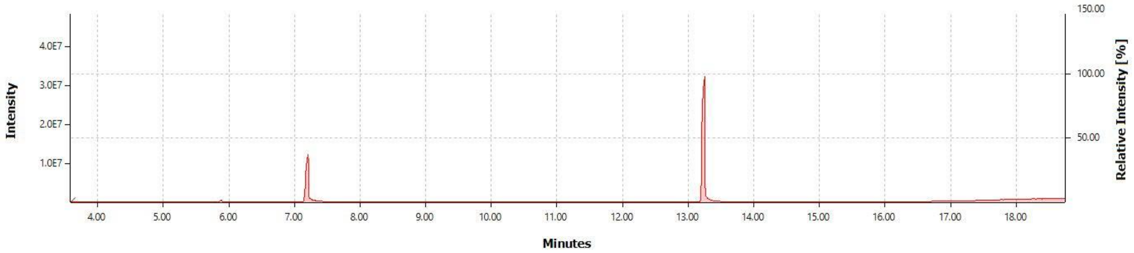

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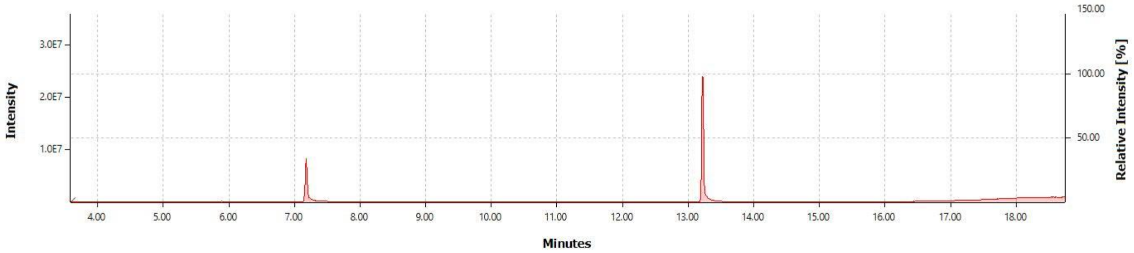

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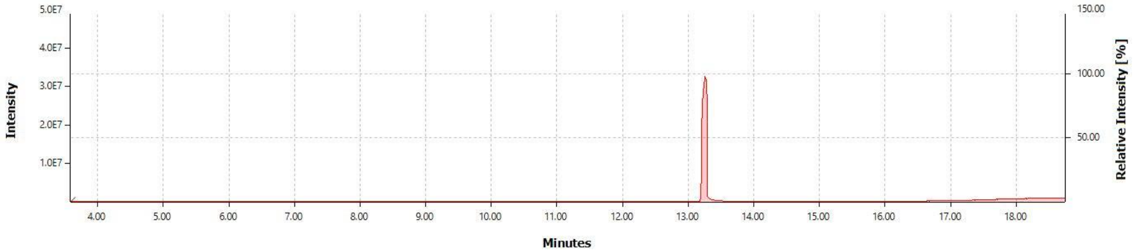

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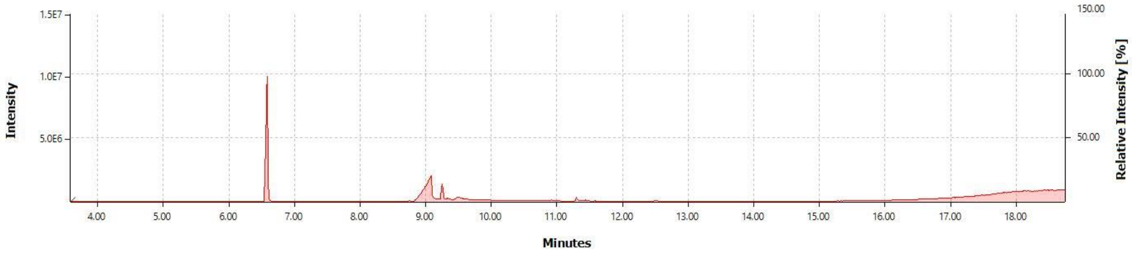

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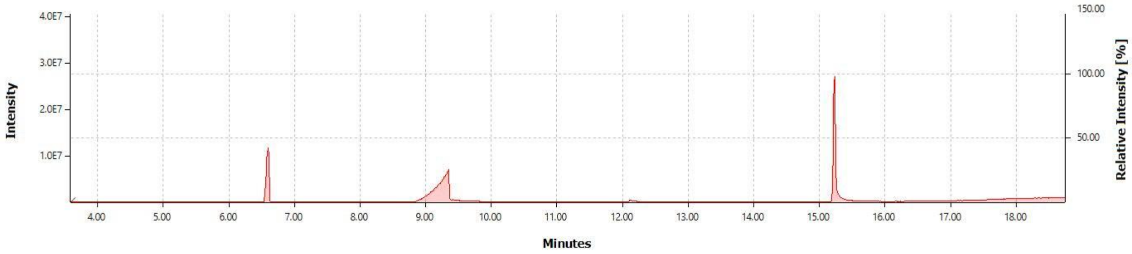

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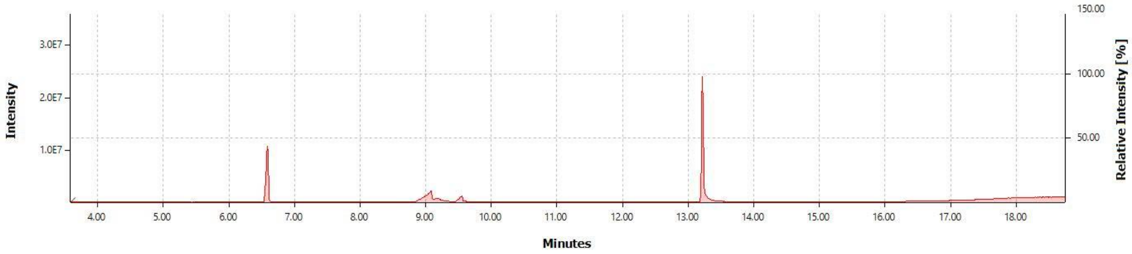

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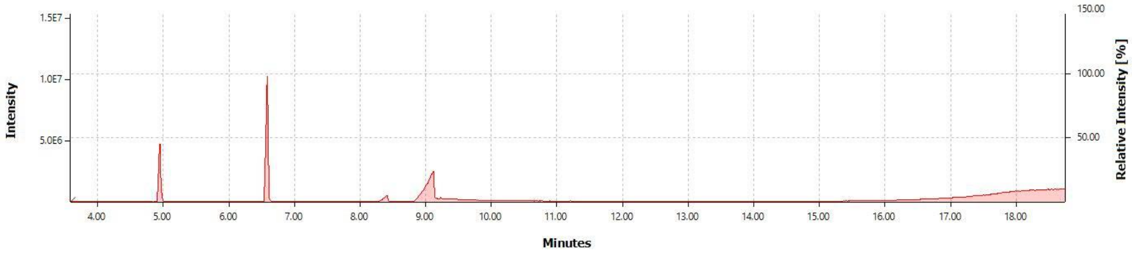

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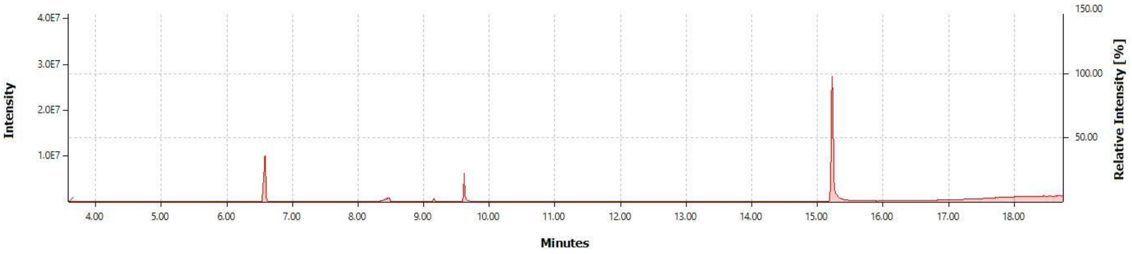

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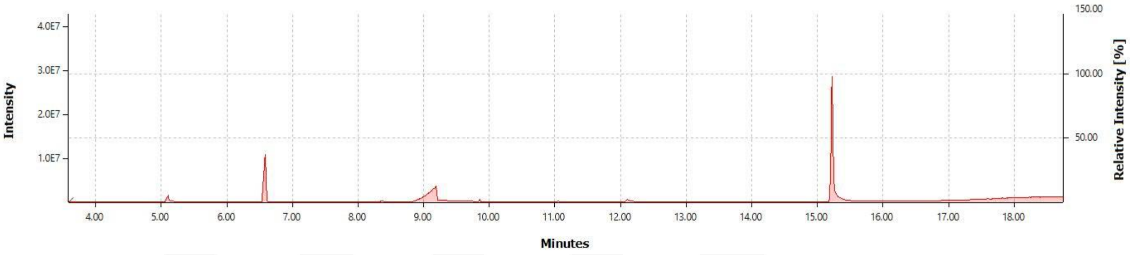

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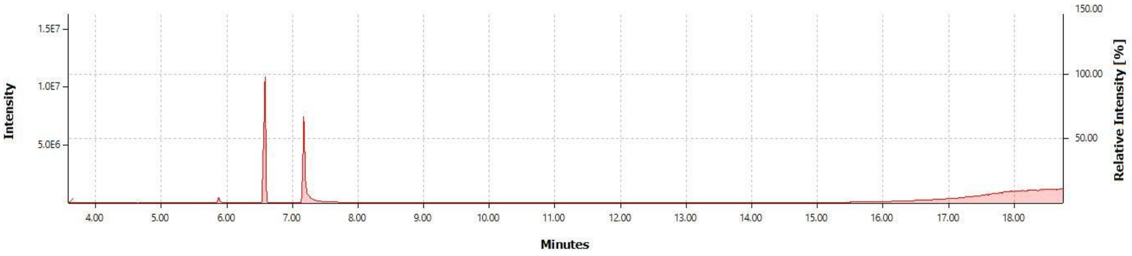

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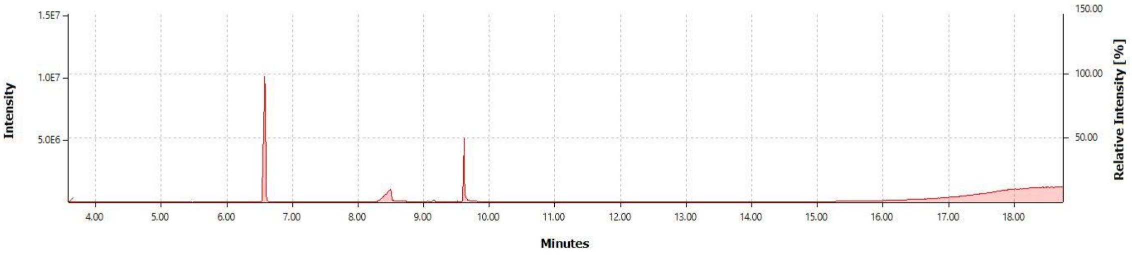

APPENDIX-2 GC Chromatograms of Hydrogenation of Methyl Benzoate

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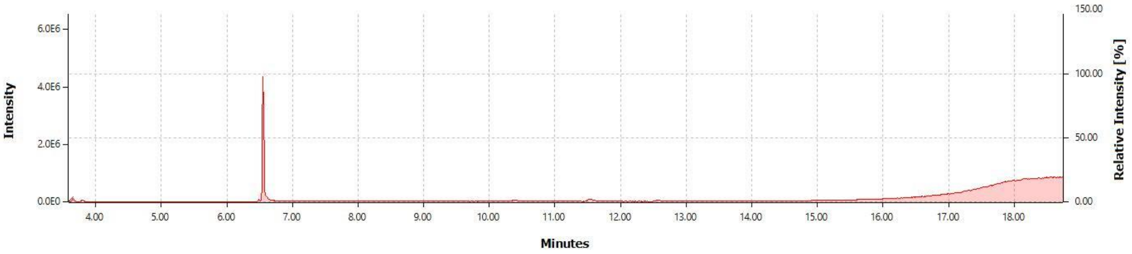

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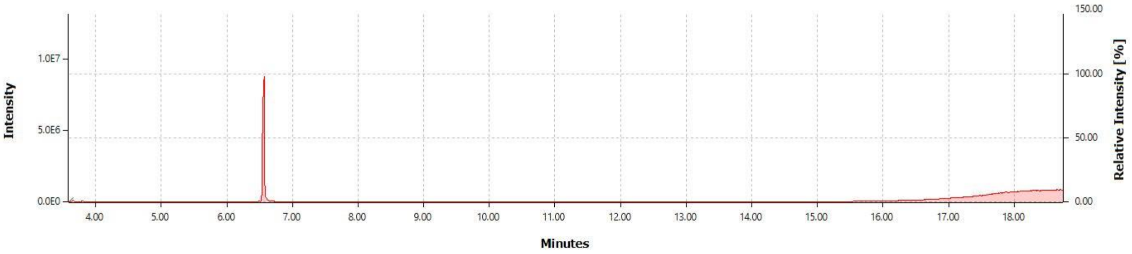

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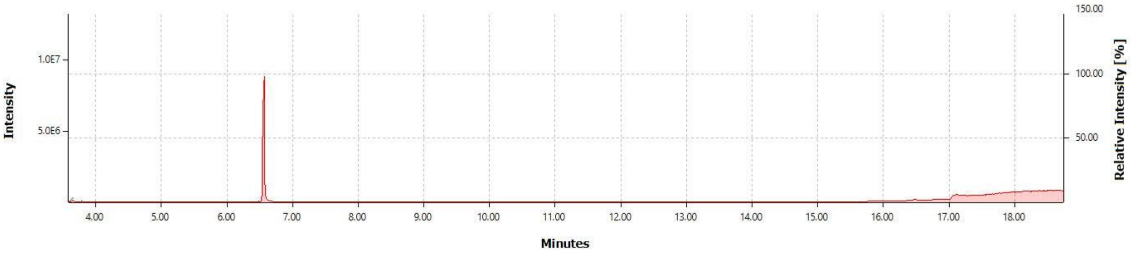
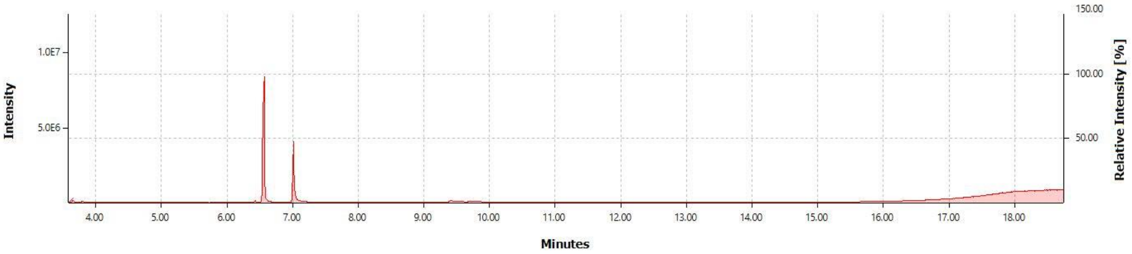


Table 9, Entry 4



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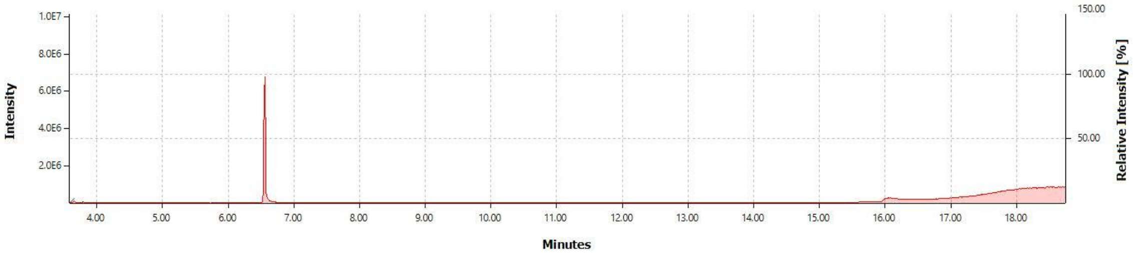

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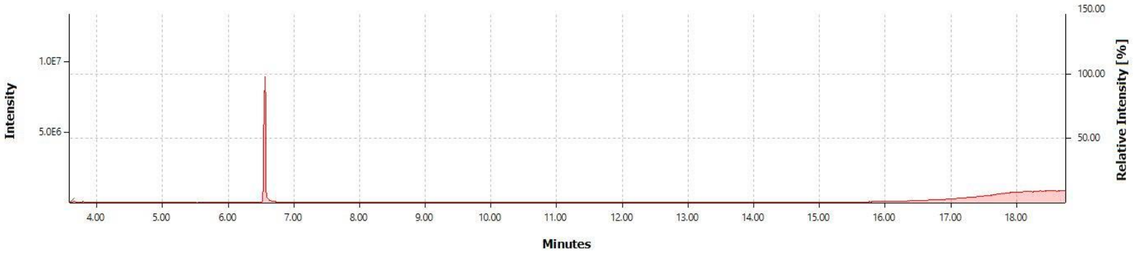


APPENDIX-3 GC Chromatograms of Hydrogenation of DMT

Table 10, Entry 1

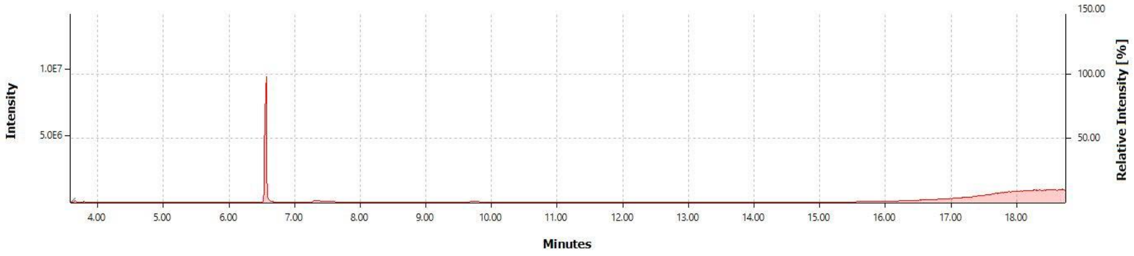


Table 10, Entry 2

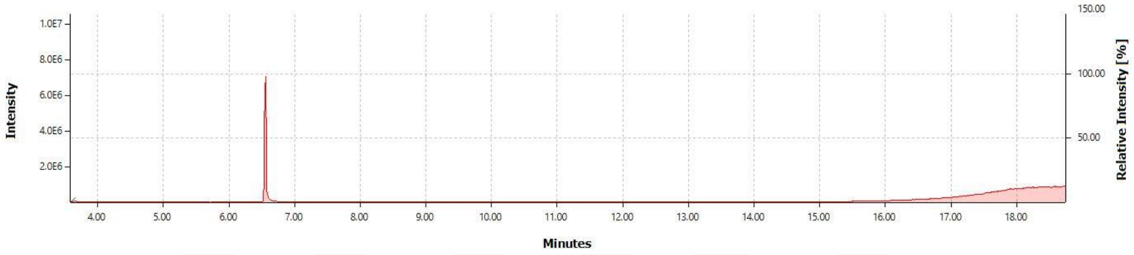
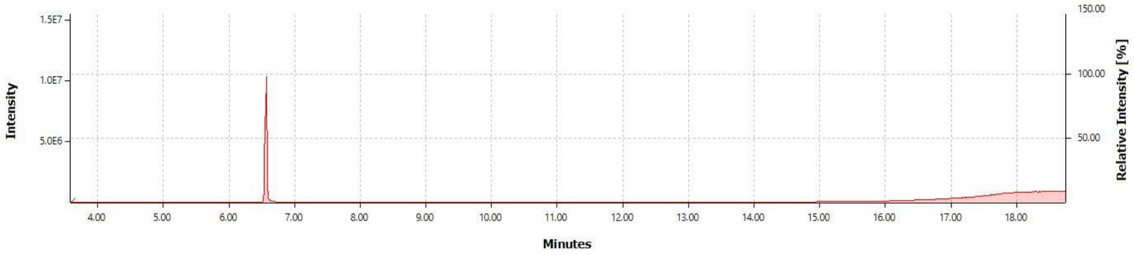


Table 10, Entry 3



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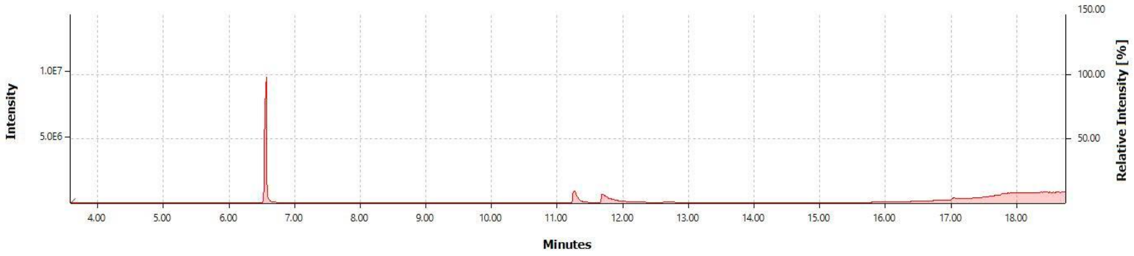

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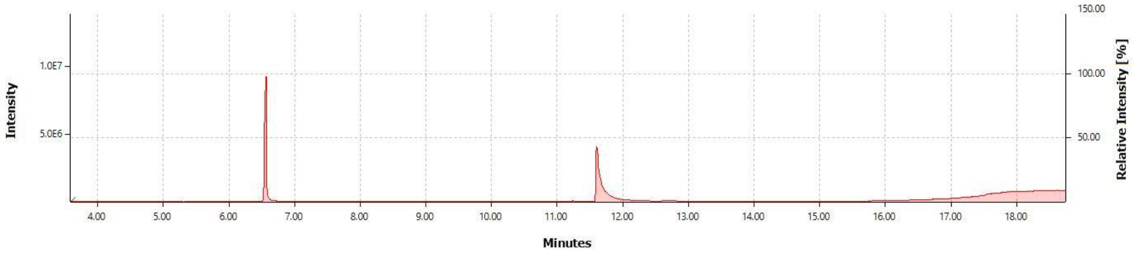

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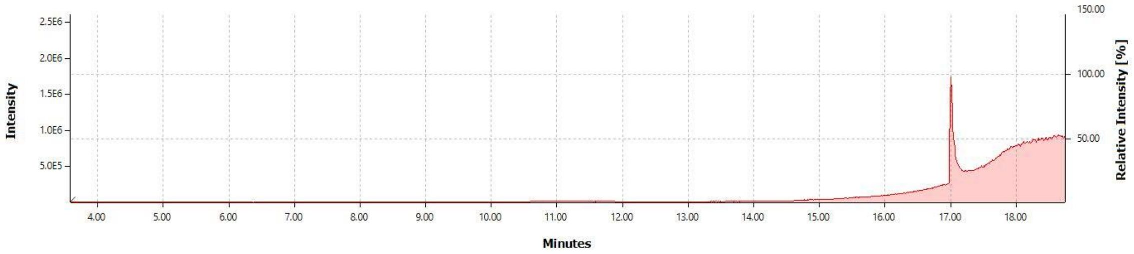


Table 10, Entry 7

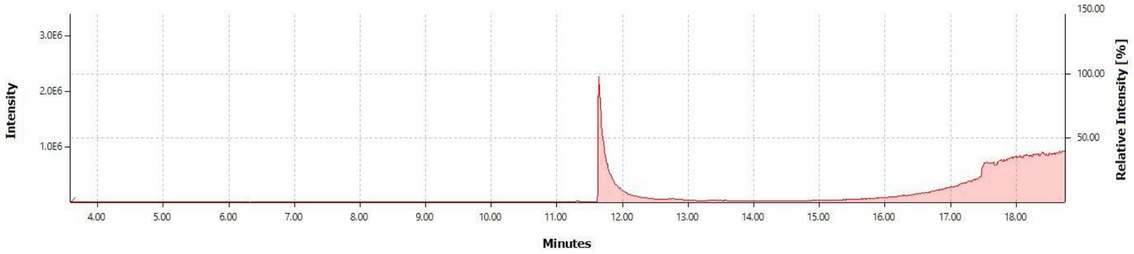
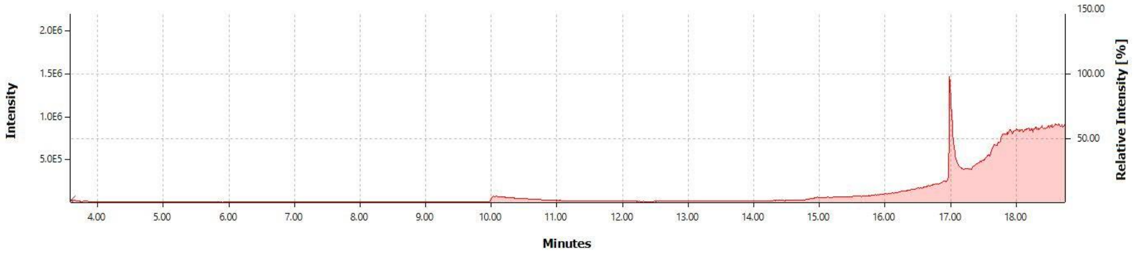


Table 10, Entry 8



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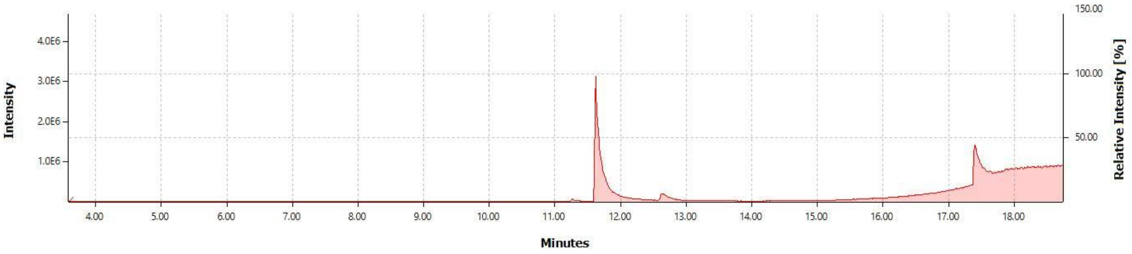


APPENDIX-4 NMR Spectra of Hydrogenation of Pol1

Table 11, Entry 1

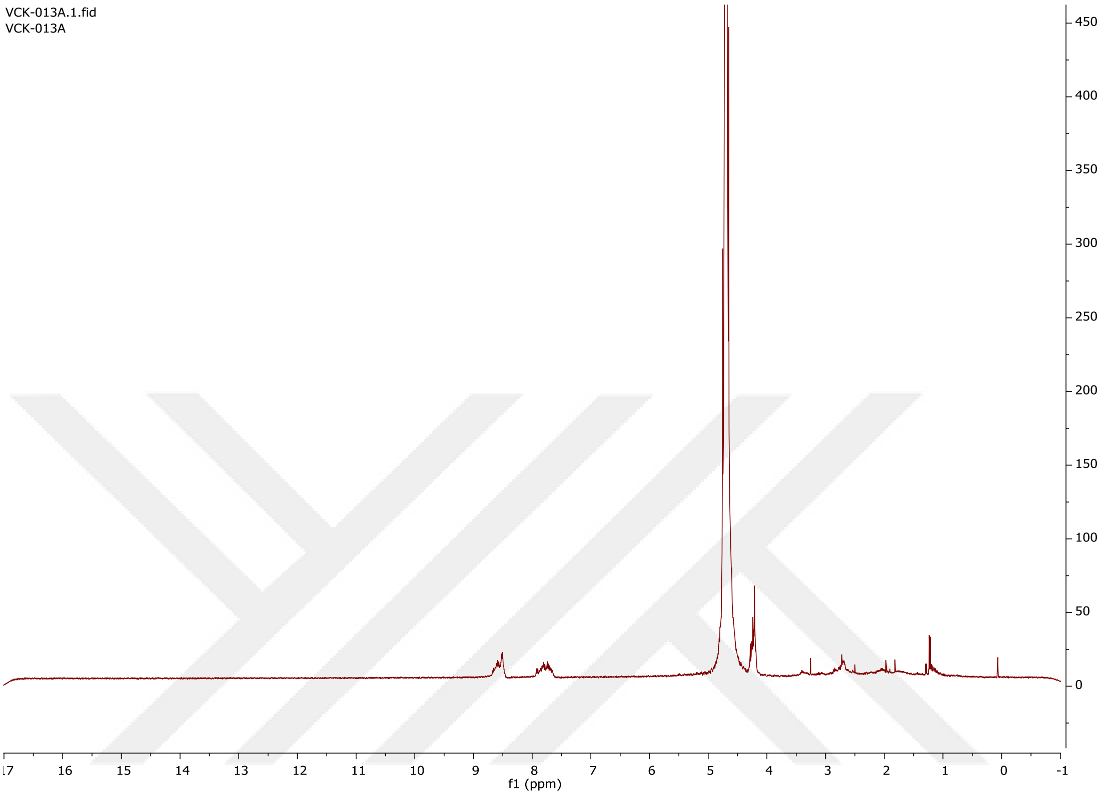


Table 11, Entry 2

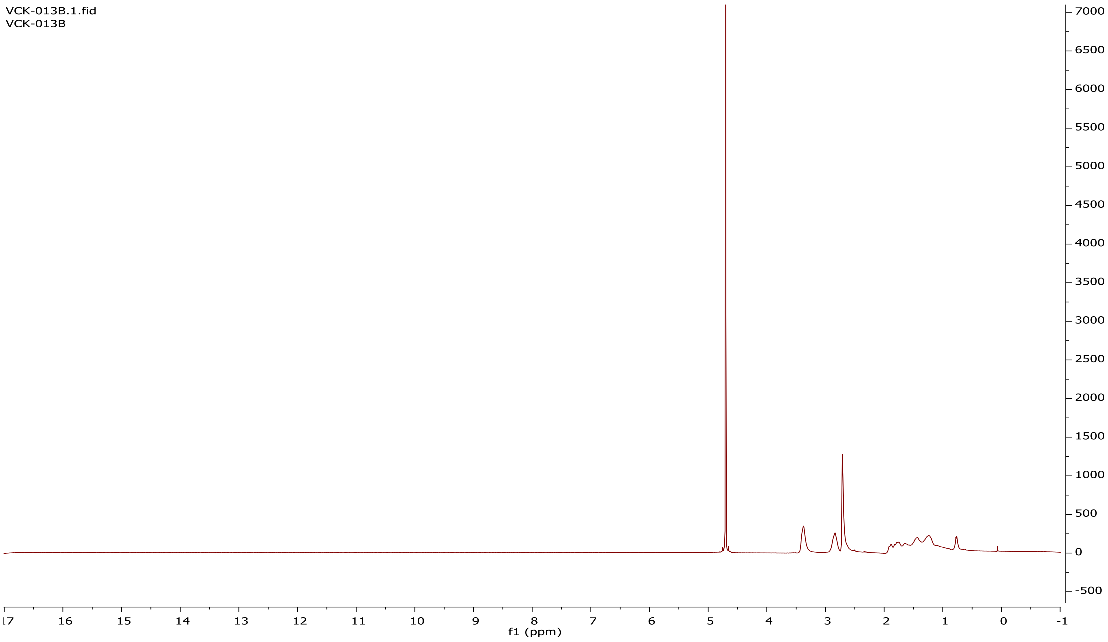


Table 12, Entry 1

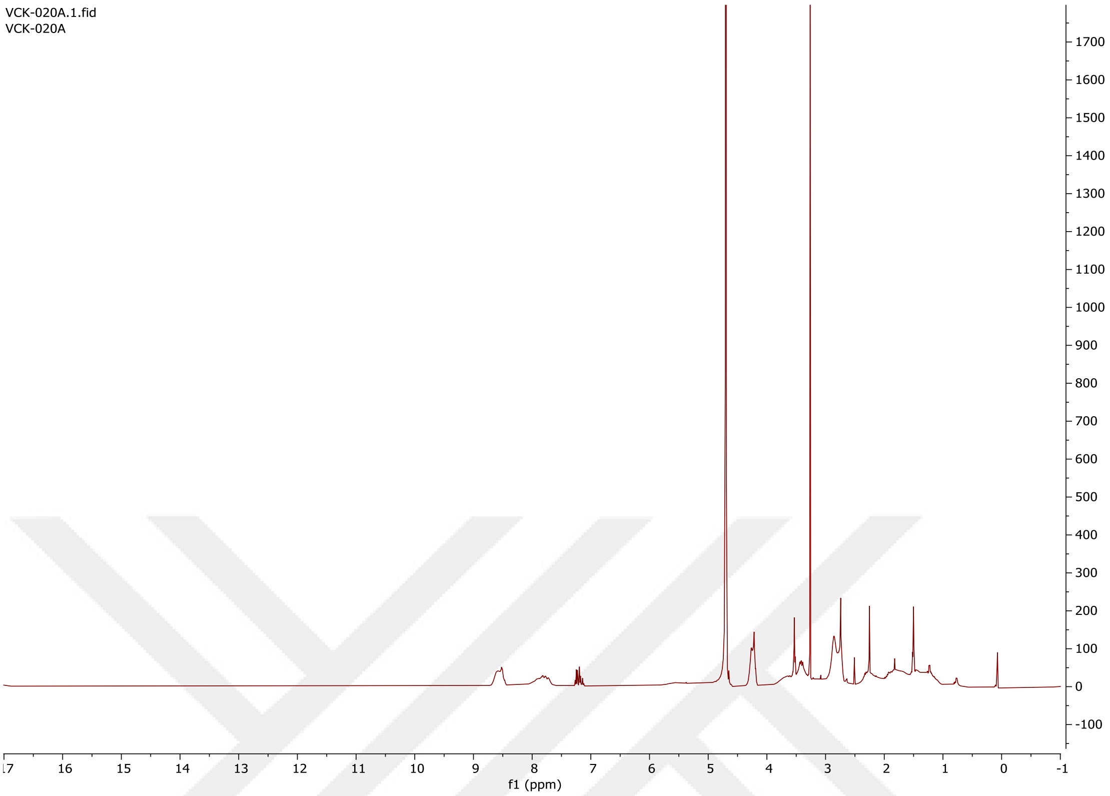


Table 12, Entry 2

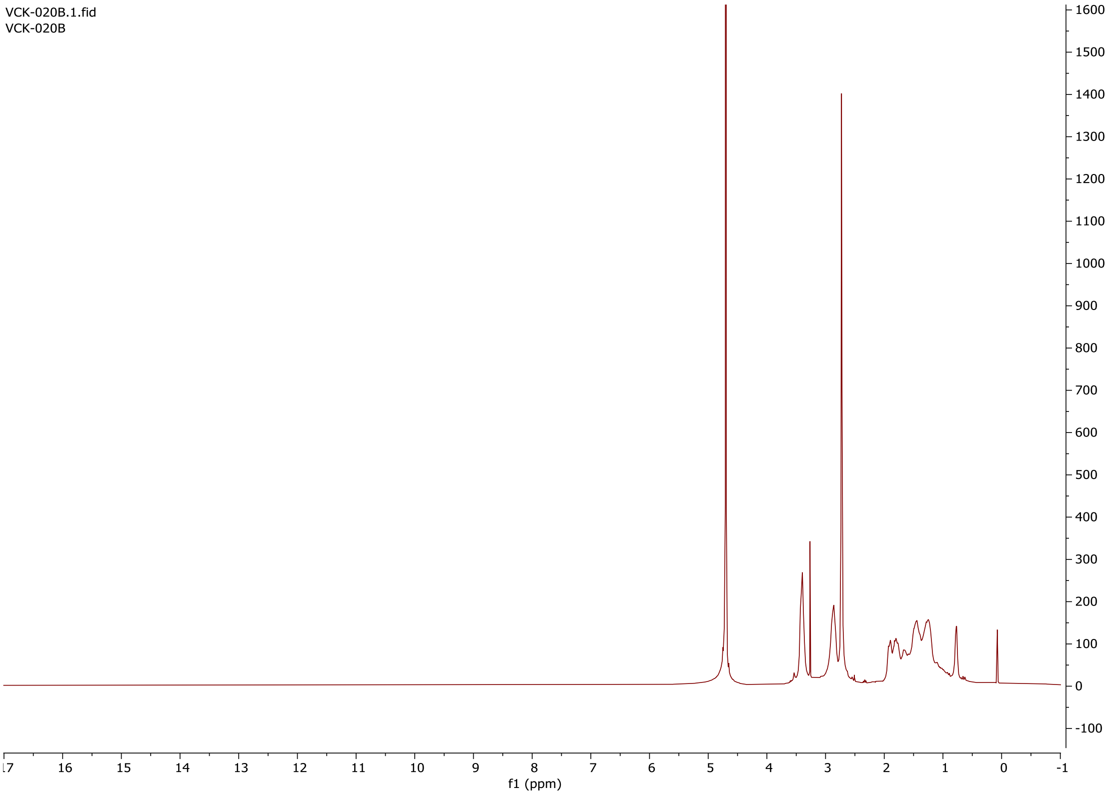


Table 12, Entry 3

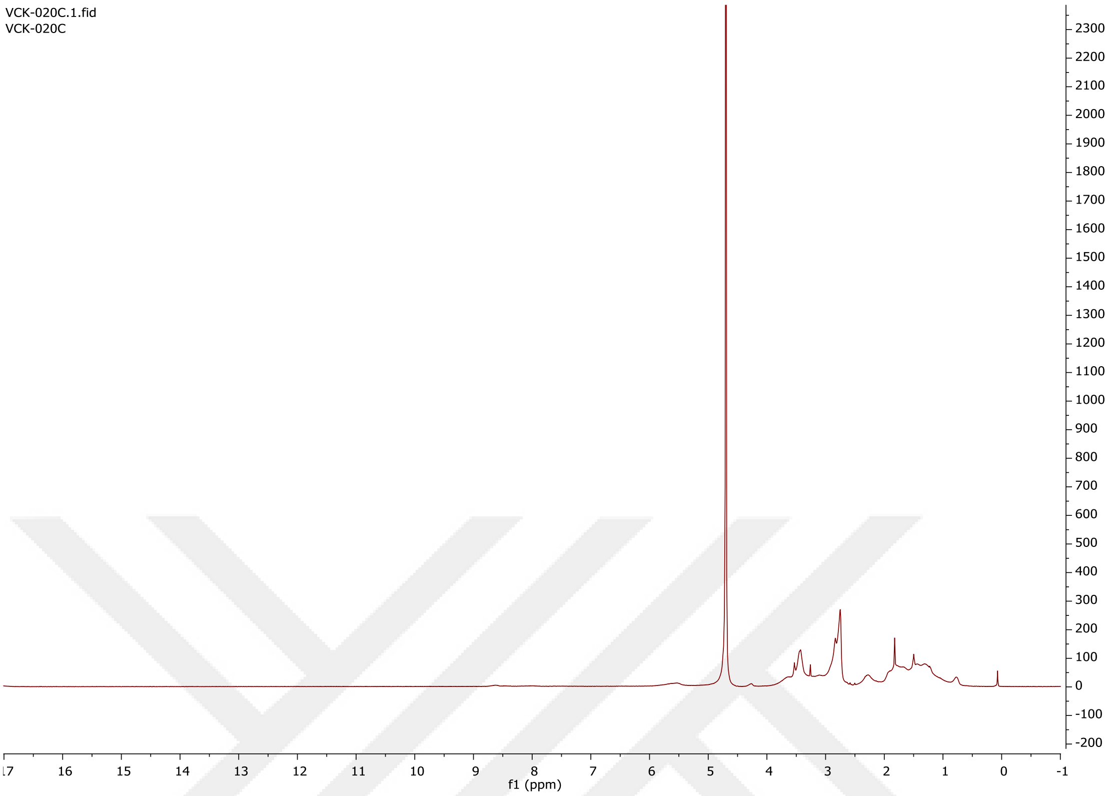


Table 12, Entry 4

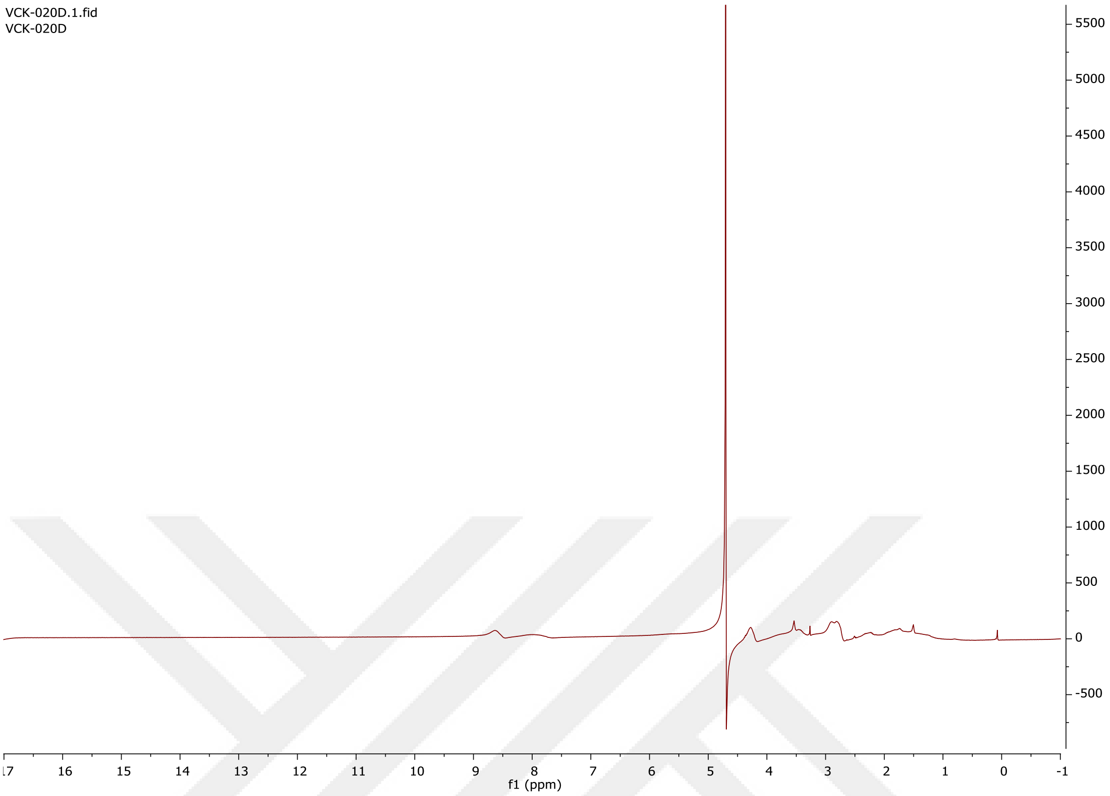


Table 13, Entry 1

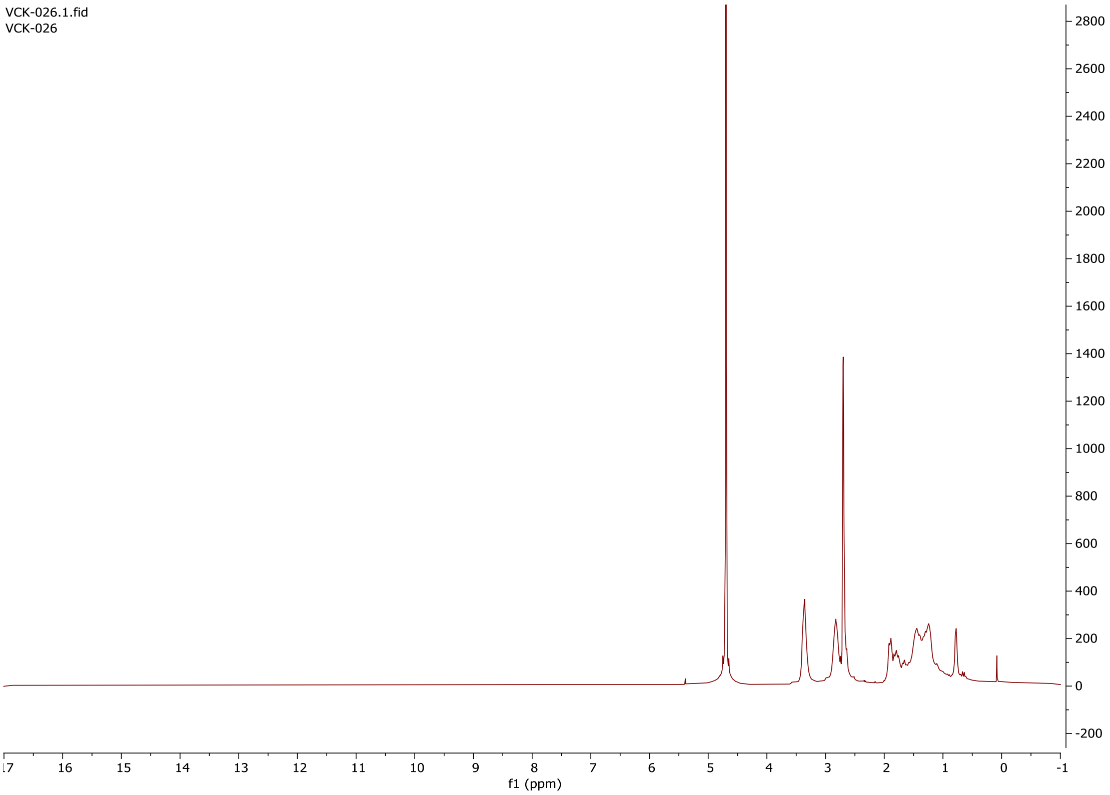


Table 13, Entry 2

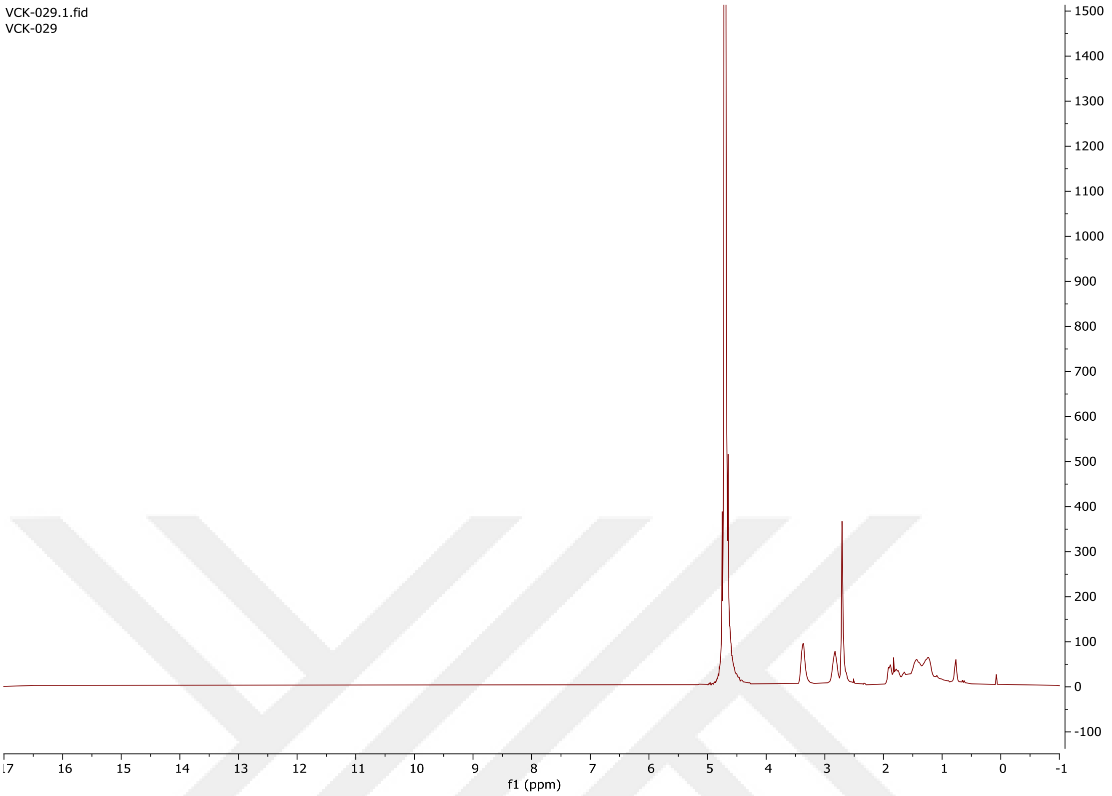
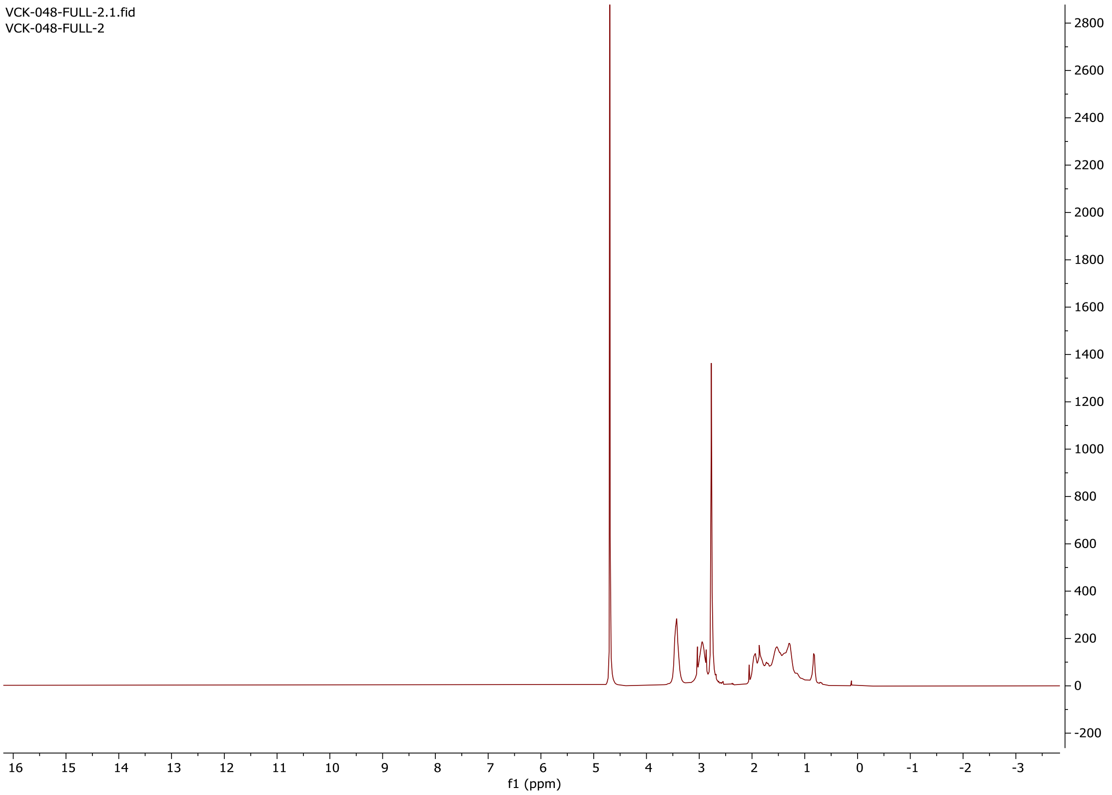


Table 13, Entry 3



APPENDIX-5 NMR Spectra of Hydrogenation of Pol2

Table 14, Entry 1

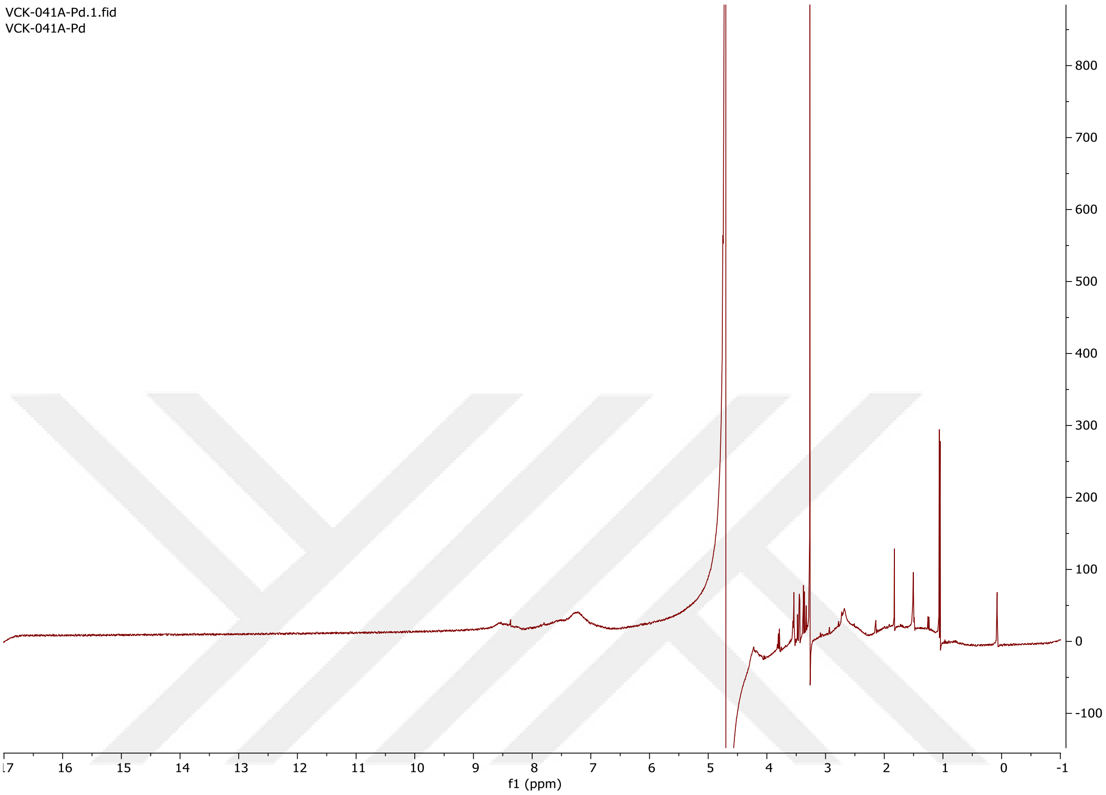
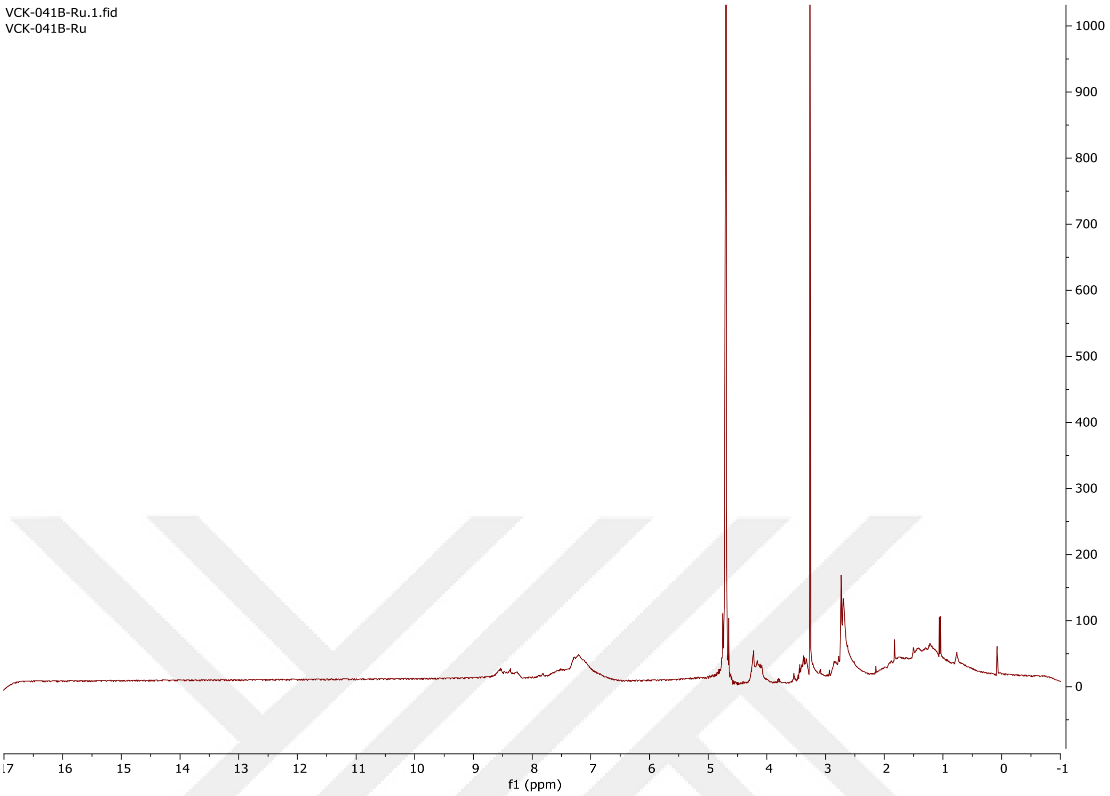


Table 14, Entry 2



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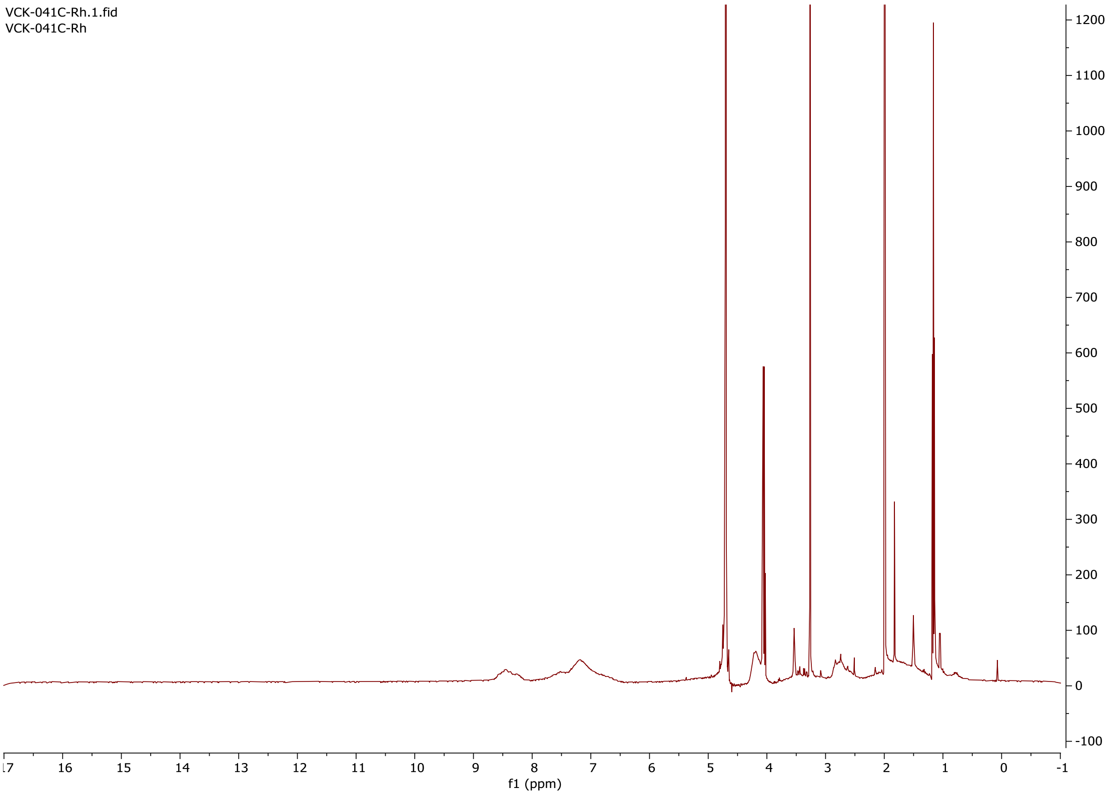


Table 14, Entry 4

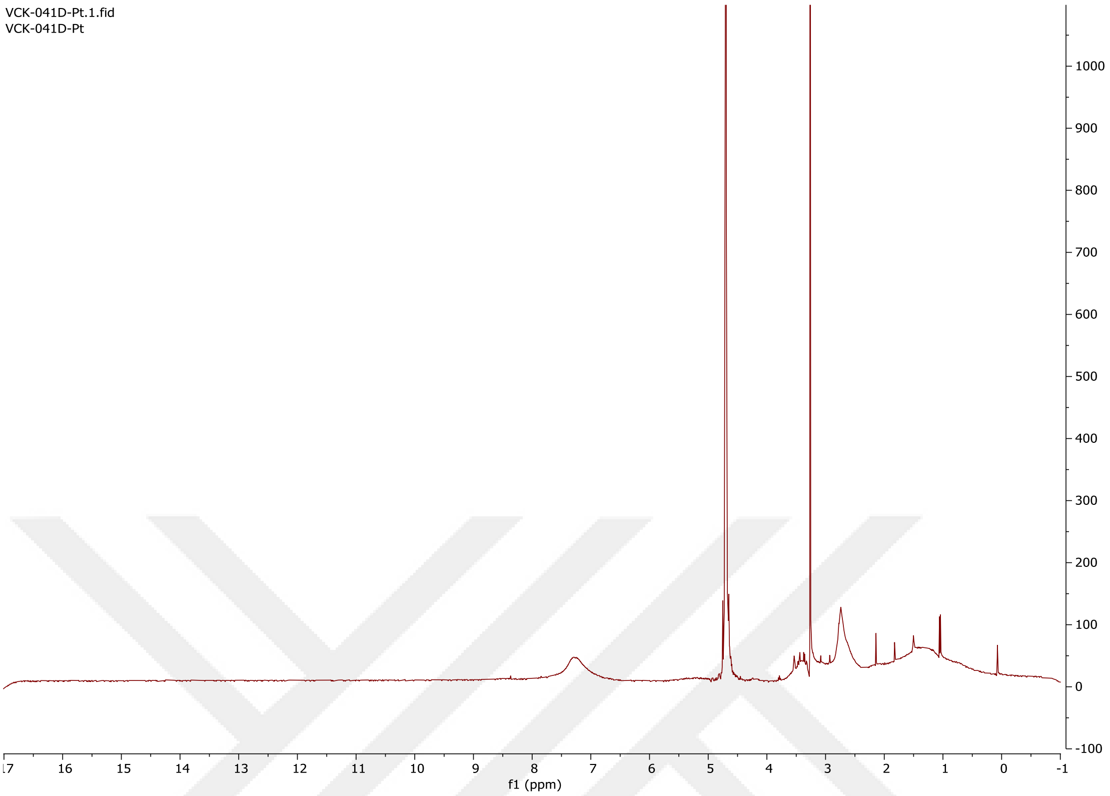
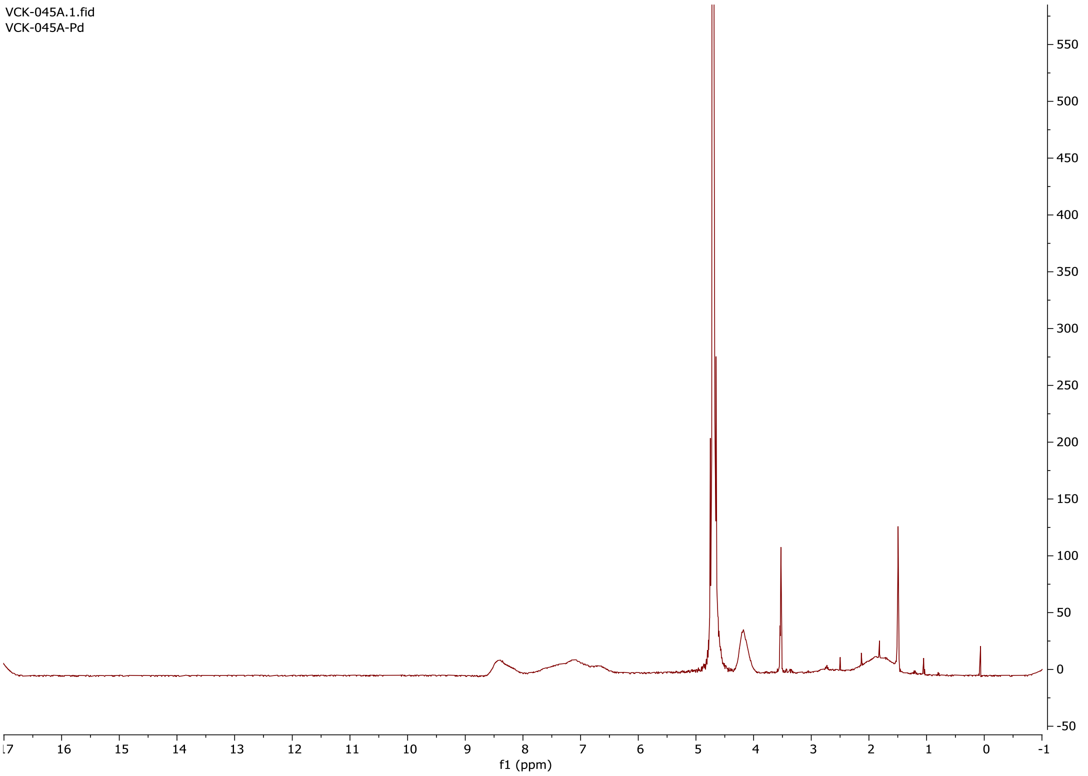


Table 14, Entry 5



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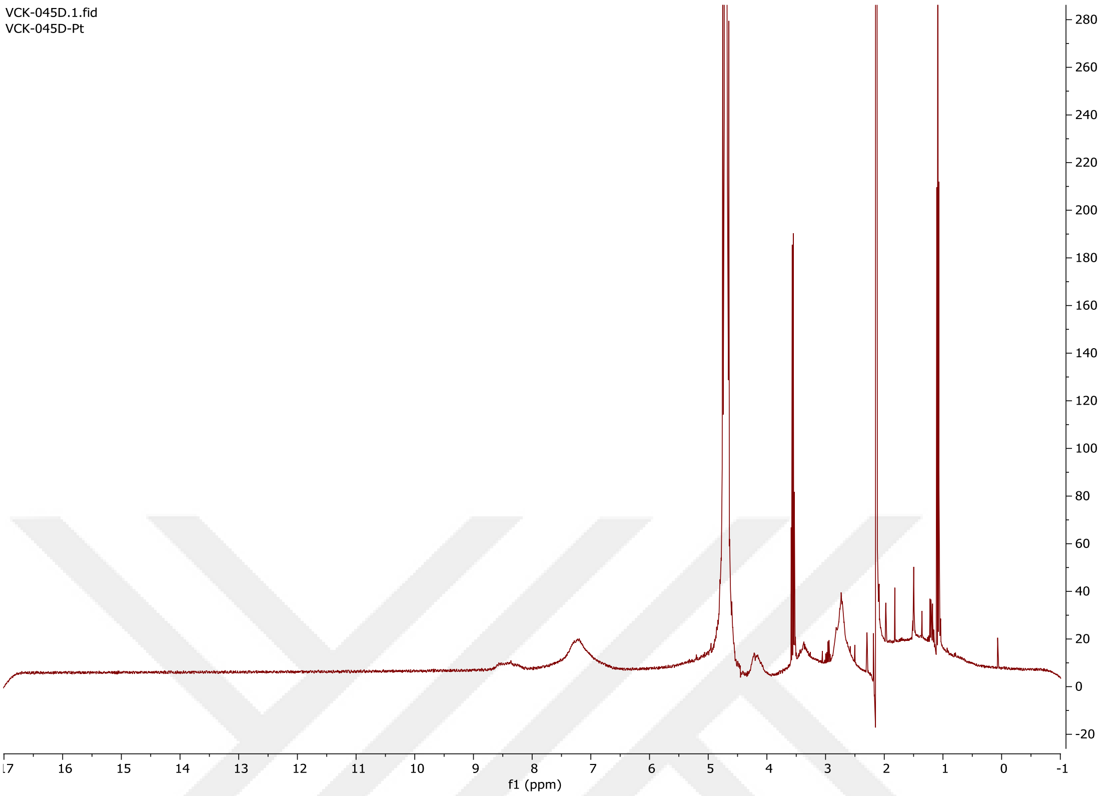

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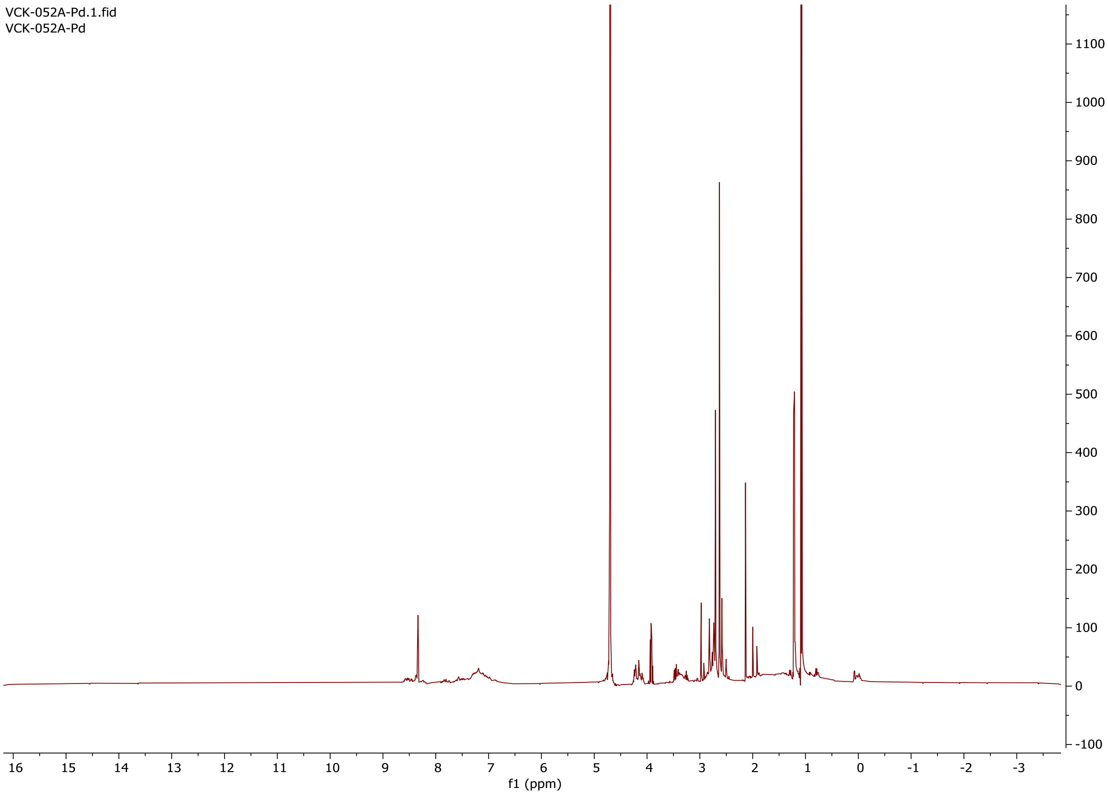

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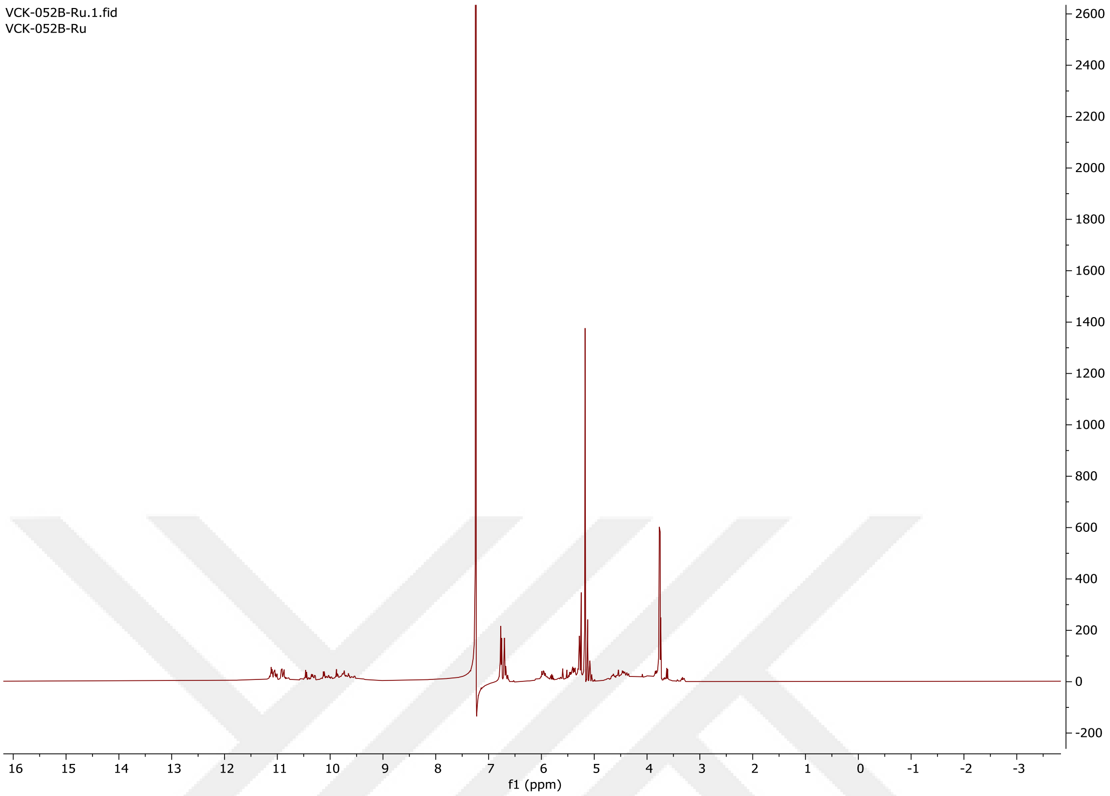

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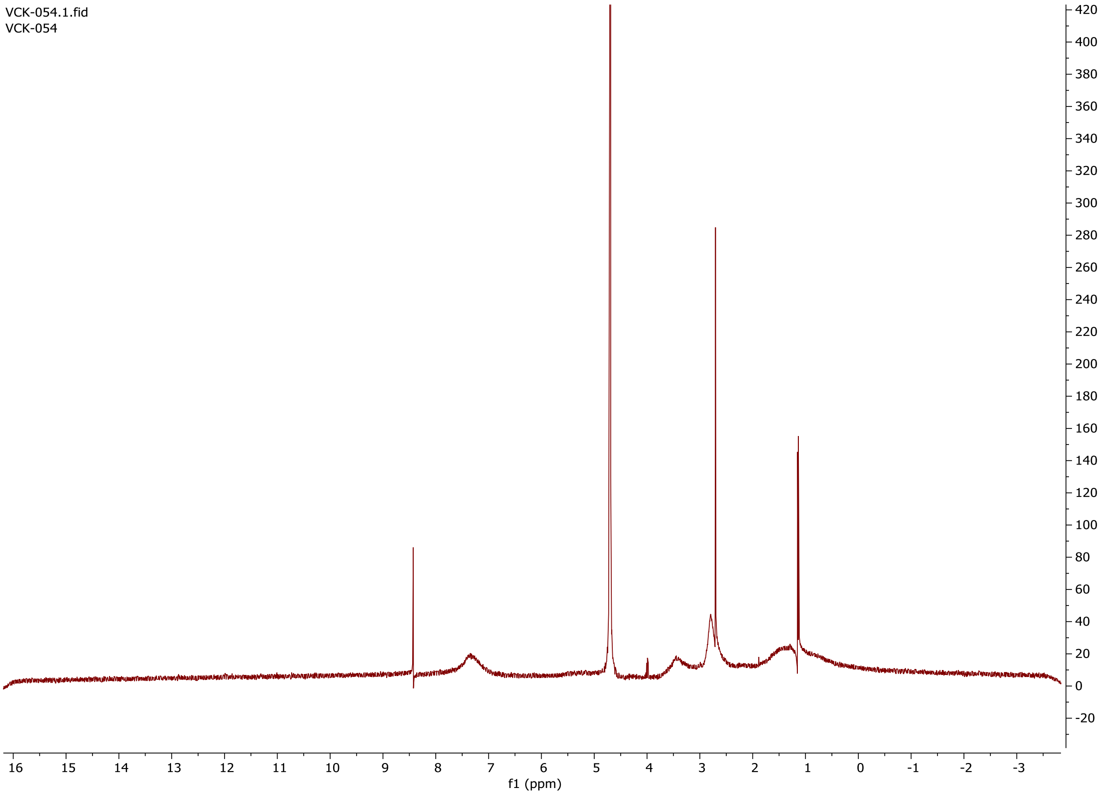


APPENDIX-6 NMR Spectra of Hydrogenation of Pol3

Table 15, Entry 1

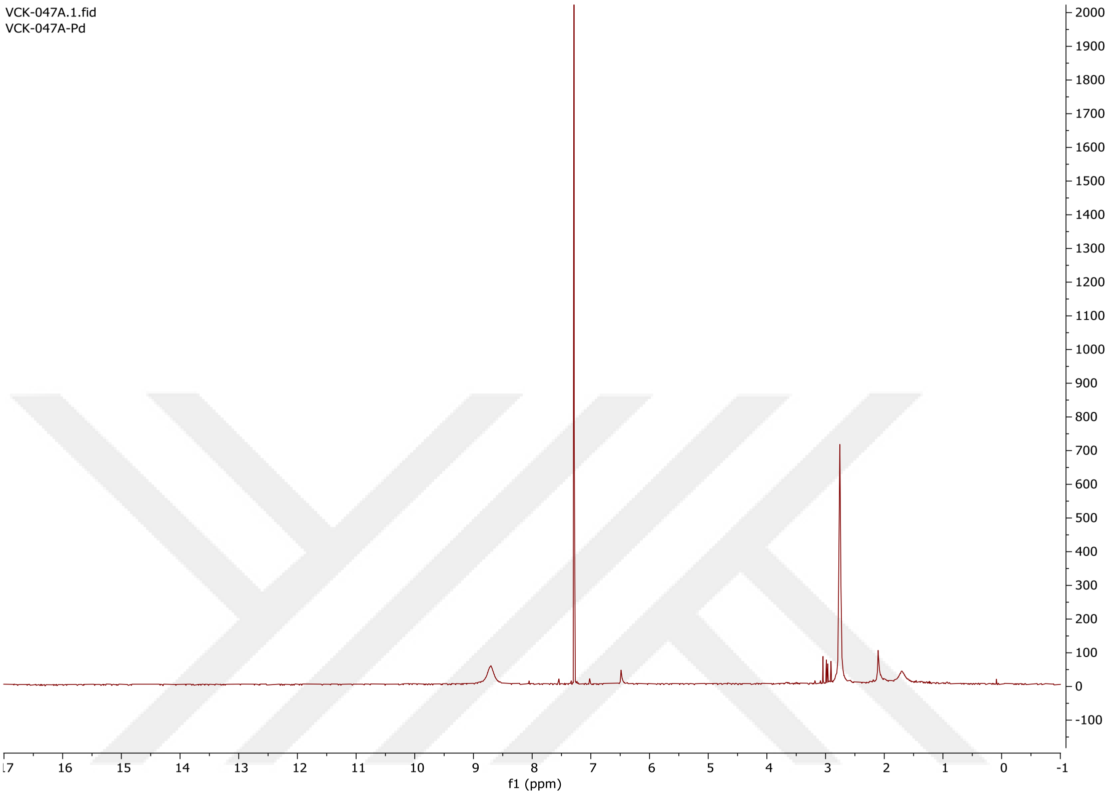
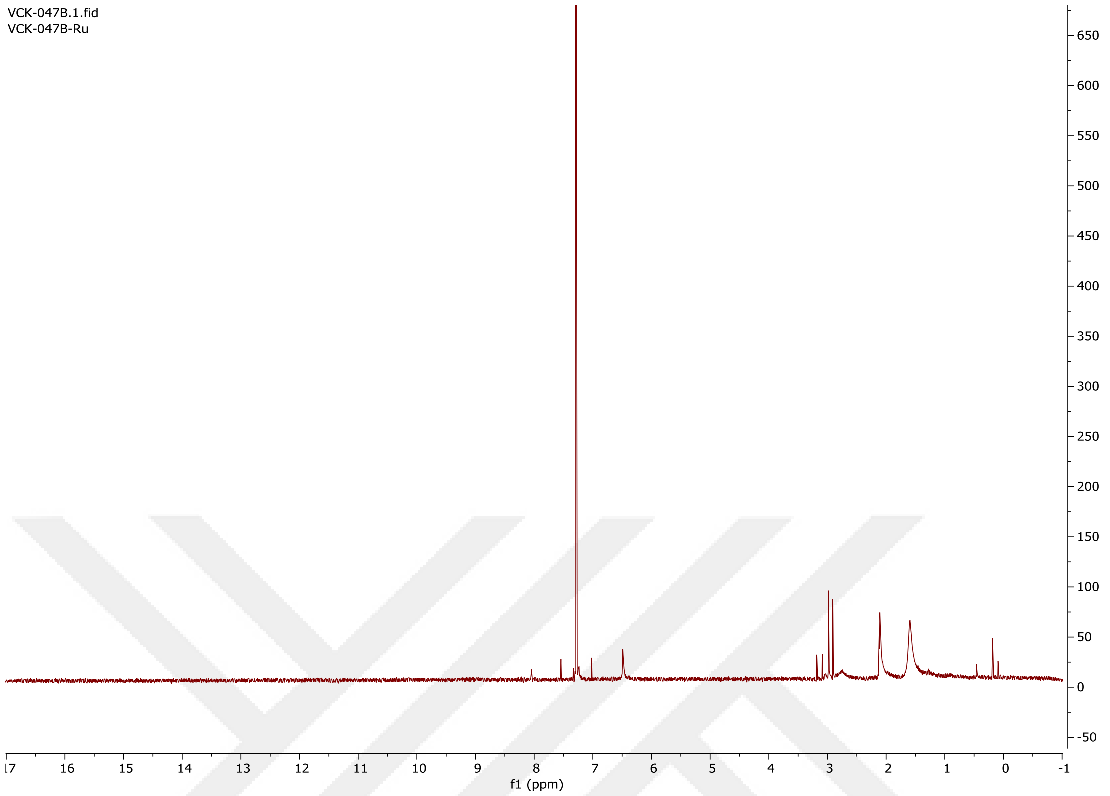


Table 15, Entry 2



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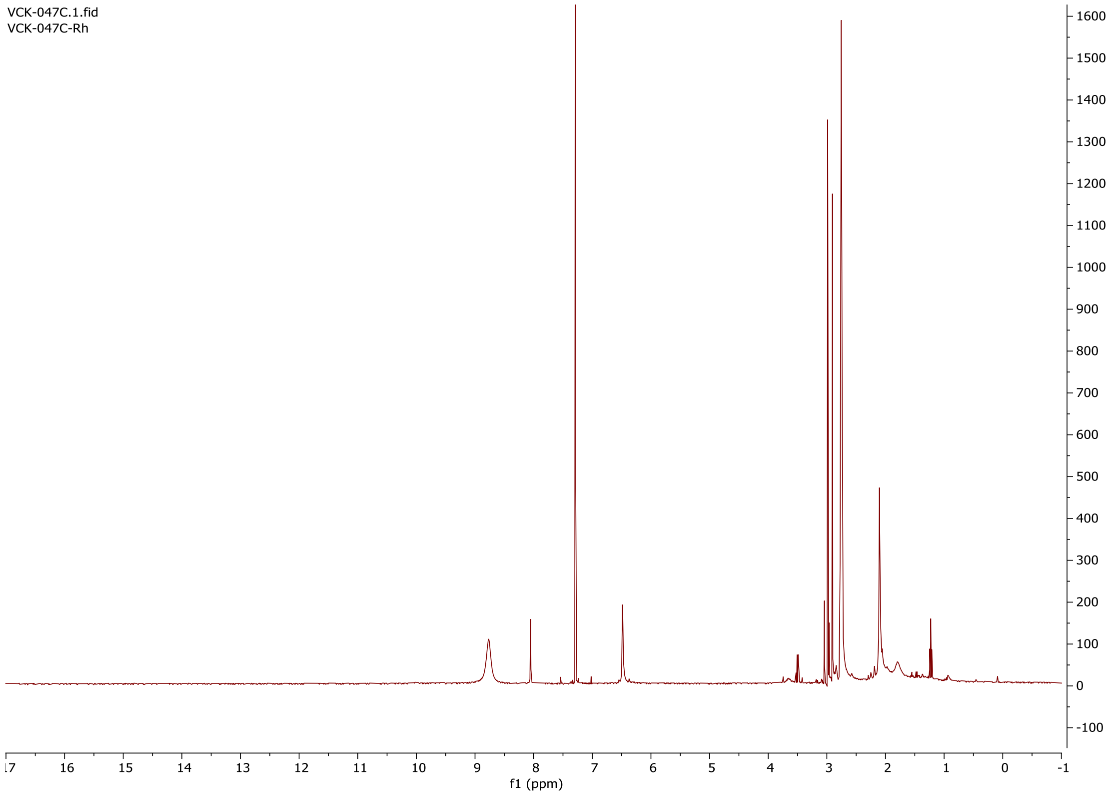

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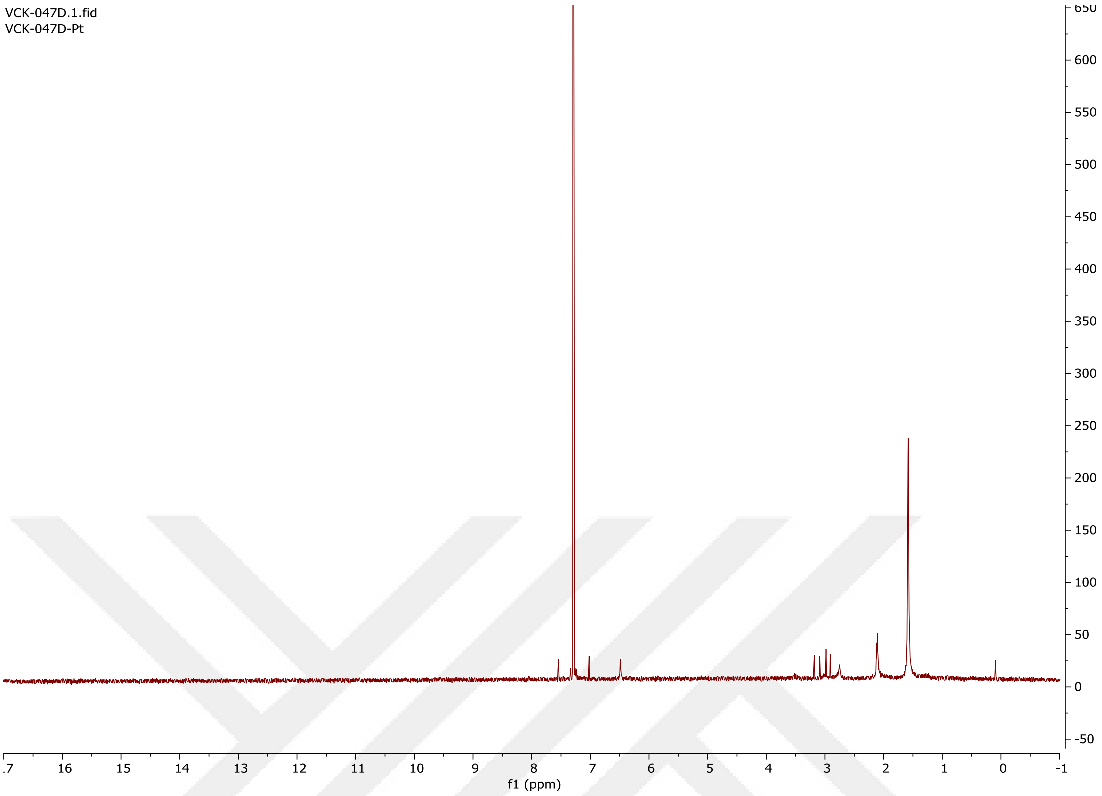

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2005 – 2009	Fatih Anadolu High School

Work Experience

June 2017 - May 2018	Intern, Lund University, Lund/Sweden
June 2015 - September 2015	Intern, University of Copenhagen, Copenhagen/Denmark
June 2013 - July 2013	Intern, Charles University, Prague/Czech Republic

Additional Skills

Language Skills:	Turkish - Native language
	English - Highly proficient in both spoken and written
	Swedish - Good knowledge in written and oral
Computer Skills:	Highly proficient in Microsoft Office Suite
	Acquainted with Cambridge Structural Database and Inorganic Crystal Structure Databese
	Skilled with Adobe Illustrator and PhotoShop Fireworks