공학석사학위논문

One-pot deoxydehydration/hydrogenation/esterification reactions for the synthesis of adipate from glucose

글루코스로부터 아디페이트 합성을 위한
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송민규

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이 논문을 공학석사학위논문으로 제출함

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Abstract

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The effort using biomass as one of the chemical feed stocks has been made by chemical industries producing petroleum-based products due to the depletion of fossil fuels. According to the trend, this paper suggests the method that synthesizes adipic acid and

HMDA, two monomers of nylon 6,6 from glucose. As a starting material, potassium D-glucarate is chosen, which is synthesized by simple oxidation of glucose that is most economical and most readily available biomass. The synthetic scheme of adipamide consists of two steps. One is the synthesis of diisopropyl adipate through one-pot reaction of deoxydehydration, hydrogenation and esterification in an autoclave reactor. The other is amination of adipate to adipamide.

The solvent, catalysts, additives, temperature and time were screened in order to optimize the condition of the one-pot reaction to reach the maximum yield of 76%. This paper is breakthrough in that it obtained diisopropyl adipate with high yield through one-pot reaction of potassium D-glucarate, which is significantly less responsive to deoxydehydration due to basicity and ultimately suggested an progressive method to the synthesis of monomer of bio-based nylon 6,6. Unfortunately, further study is needed for amination of diisopropyl adipate to synthesize adipamide.

Keyword : deoxydehydration, rhenium, nylon 6,6, biomass, one-pot reaction, glucaric acid

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LIST OF ABBREVIATIONS

DODH	Deoxydehydration
MeOH	Methanol
EtOH	Ethanol
IPA	Isopropyl alcohol
DCM	Dicholoromethane
HMDA	Hexamethylenediamine
HMDA formate	Hexamethylenediammonium formate
APR	Ammonium perrhenate
MTO	Methyltrioxorhenium
eq.	Equivalent
Pd/C	Palladium on carbon
m. p.	Melting point
$CDCl_3$	Chloroform-*d*
D_2O	Deuterium oxide
DMSO	Dimethylsulfoxide
dec.	Decomposed
NMR	Nuclear Magnetic Resonance
Quant.	Quantitative yield
TsOH	*p*-toluenesulfonic acid

Chapter 1. Introduction

1.1. Purpose of studies on bio-based plastics

Because of the problem of the depletion of fossil fuels and environmental pollution, biomass which can alternate fossil fuels is getting attention. Biomass is a living organism like animal or plant to be used for energy sources, including methane gas and ethanol. Since it doesn't emit pollutant and is recyclable, biomass is attracted as a next generation energy source. According to the trend, global market demand for biomass is sharply increasing. As shown in figure 1, biomass power market size will continue to increase by 2027.[1]

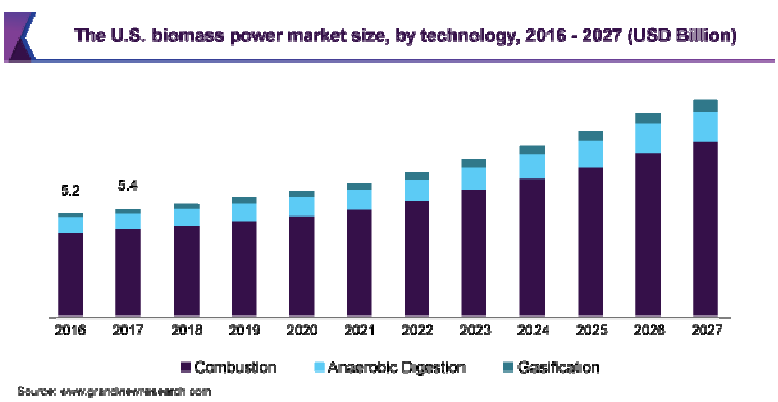


Figure 1. U.S. biomass market size, 2016-2027 [1]

Bio-based plastics are polymers which are made in whole or partially from renewable biological resources. Mostly, sources of bio-based plastics are polysaccharide such as starch, cellulose, and glycogen. It is significant in that they are eco-friendly although bio-based plastics are not more efficient and economical than conventional petroleum-based plastics. The demand for bio-based plastics gradually increases, and also research is being actively conducted. According to figure 2, it is estimated that global bioplastics and biopolymers market is 10.5 billion dollars in 2020 and it will rise to 27.9 in 2025 that is 2.65 times larger than 2020.[2]

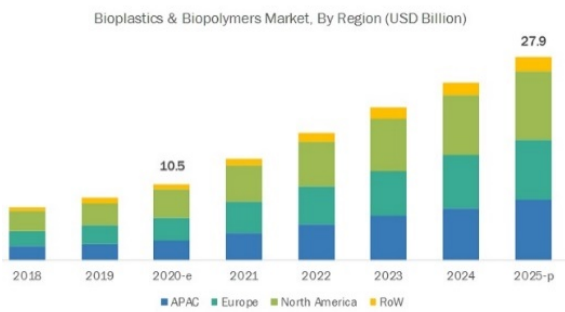


Figure 2. Global bioplastics & biopolymers market, 2018-2025 [2]

1.2. Previous studies on bio-based adipic acid

Adipic acid is a crucial material in polymer industries. Therefore the global market for adipic acid is gradually increased and the worldwide market volume of adipic acid was produced 3.9 million metric tons in 2018.[3] Among produced adipic acid, 60 % of the amount produced is consumed for the monomer of nylon 6,6 and the 40% remains are for the manufacture of other polymers including plasticizers, unsaturated polyester resins, polyurethanes. Traditionally, most of adipic acid is based on benzene that is extracted from petroleum. (Figure 3.) Benzene is converted into cyclohexane by hydrogenation and it reacts with oxygen to synthesize cyclohexanone and cyclohexanol. Then adipic acid is synthesized by oxidizing them.[4] However, this method that synthesizes adipic acid from petroleum sources causes severe damage to the environment by emitting a tremendous amount of pollutant such as NO and NO_2. Therefore, the synthetic process that can make adipic acid environmental-friendly is an important issue in polymer industries.

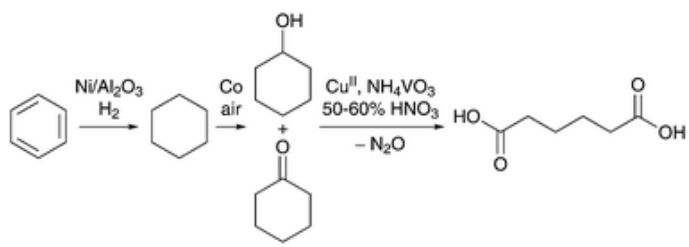


Figure 3. production of adipic acid from benzene [4]

Several kinds of research to substitute starting material of adipic acid from petroleum to biomass have been conducted in the industry and academic world. US Company Rennovia implemented a chemo-catalytic process to synthesize adipic acid from glucaric acid with hydrohalic acid and platinum catalyst. [5] Figure 4 describes the mechanism of the Rennovia process eliminating vicinal -OH groups of glucaric acid. But this process caused severe environmental problems like brominated byproducts.

Many alternative ways to synthesize adipic acid from biomass have been introduced over a decade and galactaric acid was chosen as a starting material in several articles. To convert oxygen-rich biomass such as galactaric acid into fossil resources which are composed of hydrocarbon, deoxydehydration is required as a method for eliminating oxygen efficiently.

Toste et al. introduced an efficient way to convert galactaric acid into adipate ester using deoxydehydration. (Figure 5A.)[6] They used perrhenic acid as a catalyst for deoxydehydration because it catalyzed both deoxydehydration and acid-catalyzed esterification. Yugen Zhang et al. also suggested synthetic process for the conversion of galactaric acid to adipic acid through deoxydehydration using MTO. (Figure 5B.)[7] Y. G. Kim et al. designed the large-scale adipic acid production from galactaric acid with microwave (Figure 5C.)[8]

Since galactaric acid is not economical material due to lack of abundance, another aldaric acid like glucaric acid can be an alternative option in order to improve economic efficiency. Potassium salt of glucaric acid is only commercially available due to the possibility of glucaric acid freely converted to three lactone structures.[9]

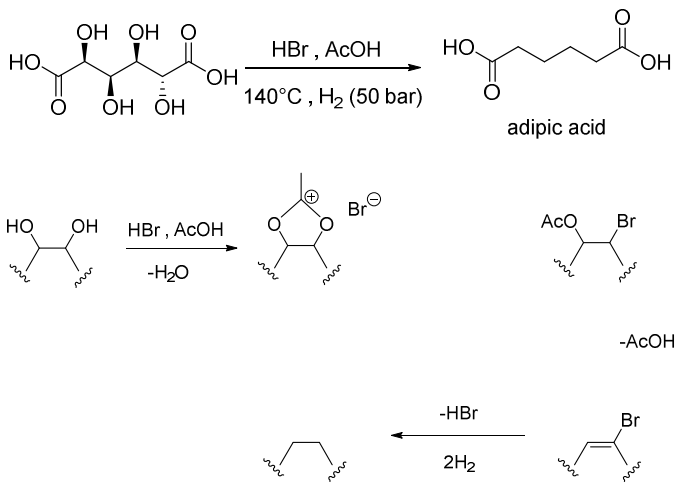


Figure 4. Rennovia process and possible mechanism [4]

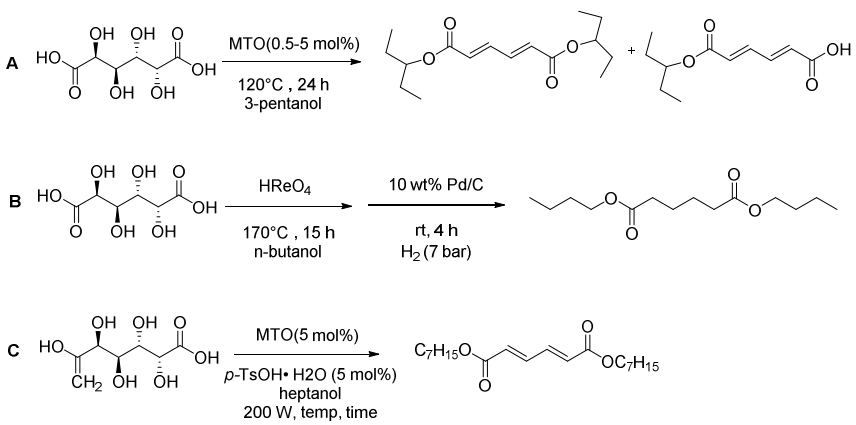


Figure 5. production of adipic acid from galactaric acid [6-8]

1.3. Previous studies on bio-based HMDA

Hexamethylenediamine(HMDA) is also a crucial material in polymer industries. Therefore, the worldwide market size of HMDA is getting larger and the market size of adiponitrile which is the precursor of HMDA is 3.53 billion dollars in 2015.[10] Most of the HMDA produced is consumed for the production of nylon 6,6 as a monomer and the other purpose of HMDA is the production of hexametylene diisocyanate (HDI) which is a monomer of polyurethane and serves as a cross-linking agent in epoxy resins. In industry, the Dupont process is normally conducted for producing HMDA (Figure 6.).[11] 1,3-butadiene is a starting material of the Dupont process and is converted to adiponitrile by continuous hydrocyanation and then HMDA is formed by hydrogenation of adiponitrile. Since this process generates toxic materials that cause contamination, the development of a greener method for the production of HMDA is needed.

Unfortunately, little research has been conducted on eco-friendly HMDA synthesis using biomass. *Pera-Titus* et al. suggested the synthetic process of HMDA from 5-(hydroxymethyl) furfural (HMF)(Figure 7.).[11] It is the environmental-friendly way in that HMF is synthesized from fructose that is a biomass material. But it is not an economical method because fructose is much more expensive than glucose.

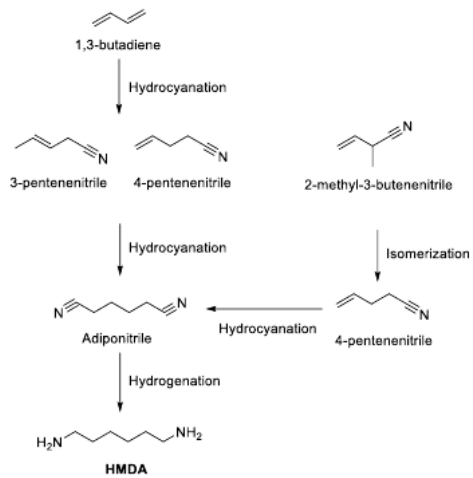


Figure 6. Production of HMDA from 1,3-butadiene [11]

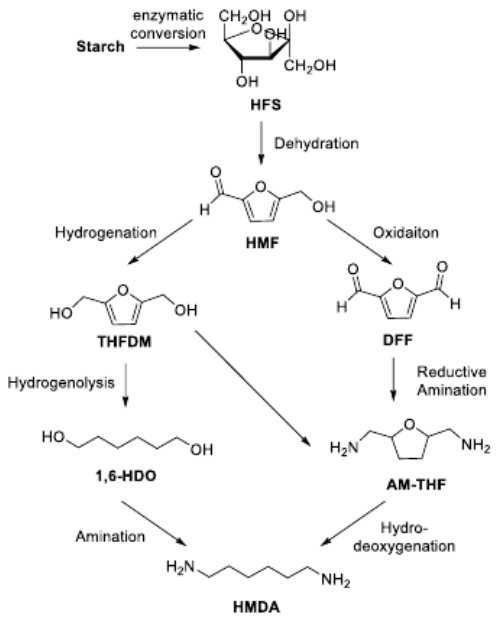


Figure 7. Production of HMDA from HMP [11]

1.4. Deoxydehydration

DODH has been a promising reaction to synthesize materials based on carbohydrates using biomass because it can eliminate a vicinal diol of sugar acids effectively. This reaction was firstly reported by Cook and his colleagues and remove two adjacent hydroxyl groups with rhenium catalyst.[12] The mechanism of DODH is composed of three steps; reduction, condensation, and extrusion and has been studied by density function theory (DFT). Toste, Abu-Omar, and Wang suggested different mechanisms, but the key three steps are the same.[13 (a)-(c)]

There are three major factors which affect DODH reaction; Catalyst, reductant, and solvent. Catalyst used in the reaction is usually rhenium. Although molybdenum and vanadium are chosen due to their less expensive price, they are not preferred because of their poor reactivity. There are various rhenium catalysts including Methyltrioxorhenium(MTO), Ammonium perrhenate (APR), sodium perrhenate, perrhenic acid, and recently alkyl-ammonium derived catalysts were applied. Also, solid-supported heterogeneous catalysts such as Re/CeO_2 were alternative options to recycle expensive rhenium catalysts. The purpose of reductant is that it can reduce oxidized rhenium catalyst to enhance the efficiency of the catalytic cycle. Metal, PPh_3, hydrogen gas, sulfite, alcohols are used in DODH as a reductant. Solvent such as toluene, benzene, and alcohols is the key element of DODH which can make a homogeneous solution to dissolve reagents and catalysts. Among

them, alcohols are used frequently in recent articles because they can play a role as both solvent and reductant.

Furthermore, one-pot DODH/hydrogenation reaction to enhance the efficiency has been conducted. Toste et al. conducted tandem DODH/hydrogenation reaction including bimetallic Pd/Re catalyst and using hydrogen gas as a terminal reductant.[14] They successfully synthesized adipate ester from the lactone form of D-glucaric acid. It was the key to stabilize a rhenium catalyst on the condition of high pressure and high temperature. Finding a stable rhenium catalyst and adding activated C and phosphoric acid as additives played an important role in improving the yield.

However, the starting material, ethyl glucarate-6,3-lactone is priceless and hard to synthesize. For that reason, our group suggested sequential deoxydehydration/hydrogenation reaction for the synthesis of adipamdie using less expensive potassium D-glucarate as a starting material. Unfortunately, the yield of sequential reaction didn't increased above 68%.

Developing the sequential reaction, this paper suggested one-pot DODH/hydrogenation/esterification reaction to synthesize adipate ester in order to improve efficiency.[15]

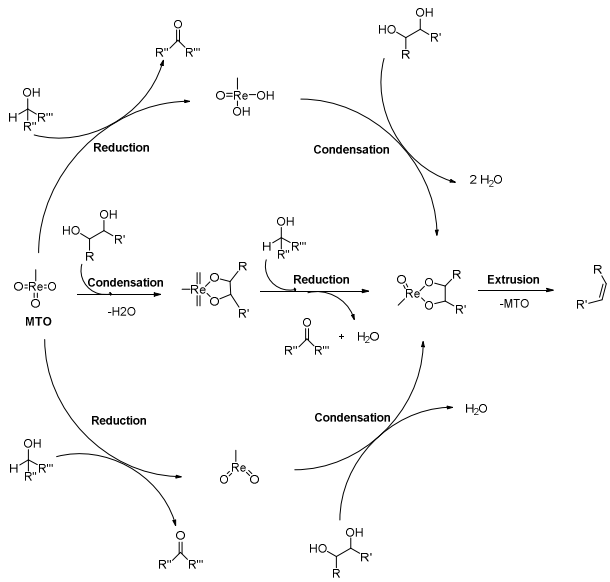


Figure 8. The three different mechanism of deoxydehydration suggested by Toste, Abu-Omar, and Wang [13 (a)-(c)]

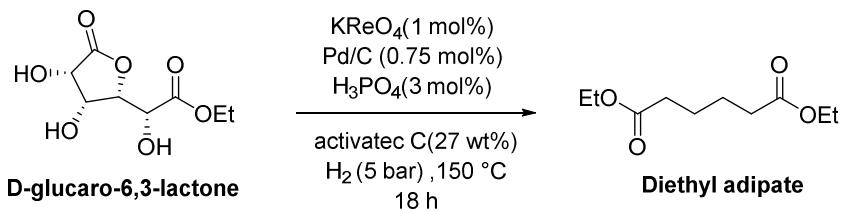


Figure 9. Tandem DODH/hydrogenation reaction with D-glucaro-6,3-lactone by Toste [14]

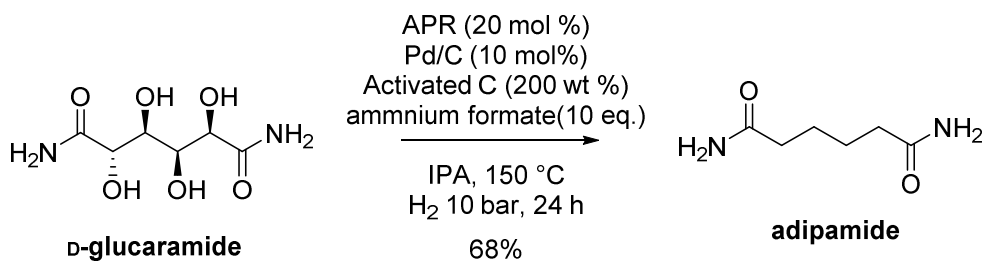


Figure 10. Sequential DODH/hydrogenation reactions by our group[15]

Chapter 2. Result and discussion

This paper suggested the synthesis of adipic acid and HMDA from glucose which are two monomers of nylon 6,6. The figure 10 shows the total process of the synthesis. Potassium D-glucarate was chosen as a starting material because it is the cheapest and linear form among the derivatives of glucose. The greatest advantage of this paper is that both monomers of nylon 6,6 can be synthesized from the same intermediate, adipamide. Furthermore, since DODH, hydrogenation, and esterification proceeded in only one step, the steps of the synthetic route shortened. As a result, D-glucaramide don't need to be synthesized.[15] In the case of the synthetic route of HMDA from adipamide, HMDA was easily obtained with salt form without Boc protection and deprotection. Finally, nylon 6,6 are synthesized as a salt form synthesized adipic acid and HMDA formate.

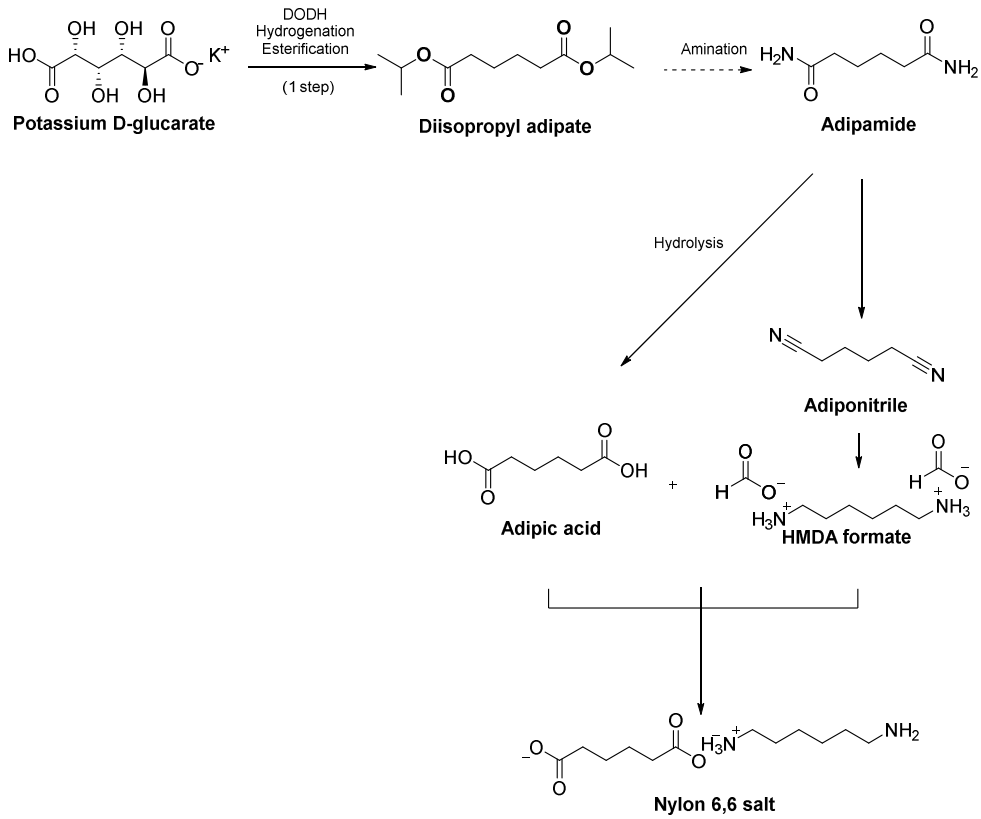


Figure 11. Synthetic process for adipic and and HMDA from potassium D-glucarate

2.1. One-pot DODH/hydrogenation/esterification reactions

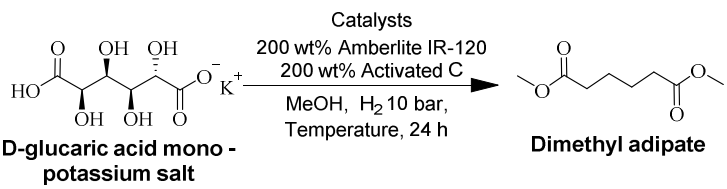
Tandem DODH/hydrogenation was already conducted by Toste group. However, as mentioned in chapter 1.4, D-glucarate-6,3-lactone is expensive and the ethyl ester form of it is difficult to be synthesized.[14] Therefore, we tried to one-pot DODH/hydrogenation/esterification reaction through the raw material, potassium D-glucarate which is easily affordable and reasonable.

As shown in Table 1, a similar condition that was applied in sequential DODH/hydrogenation reaction from D-glucaramide was tested on our substrate with some modifications. Since the product was not easy to isolate, the yield was confirmed by the proton NMR with an internal standard. Above all, Rhenium screening test was conducted to find a catalyst that fitted well and potassium perrhenate showed 30% yield. We suggested the reason that potassium perrhenate was stable under high pressure of H_2 due to ionic interaction.[14] Temperature was chosen as the next screening factor. Normally, deoxydehydration proceeds at the temperature between 130 degrees Celsius and 180 degrees Celsius, so mentioned range of temperature was tested. As a result, the experiment at 140 degrees Celsius showed better result giving a 52% yield. As reaction temperature goes higher, the reaction rate also faster but the decomposition of starting material started. Thus, we supposed that 140 degree Celsius was the optimum temperature

between decomposition and reaction rate.

Various alcohol solvents were studied and the results were shown in Table 2. Alcohol is an important factor in the reaction because it has the roles of reductant of DODH, reagent of esterification, and solvent. We tested primary and secondary alcohols. IPA, secondary alcohol increased the yield of diisopropyl adipate by 56%. It was assumed that the secondary alcohol was effective as reductant and IPA is the simplest of the secondary alcohols.

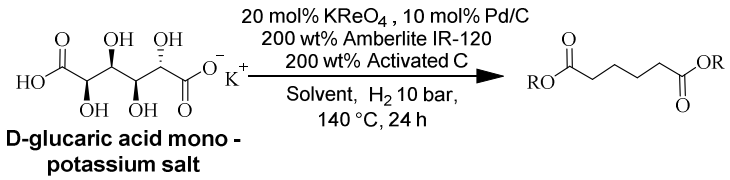
Table 1. Screening of rhenium catalysts and temperature



Entry	Catalysts	Temperature	Yield[a]
1	20 mol% Re_2O_7 ,10 mol% Pd/C	150 ° C	9%
2	20 mol% APR ,10 mol% Pd/C		21%
3	**20 mol% $KReO_4$,10 mol% Pd/C**		30%
4		130 ° C	10%
5		**140 ° C**	**38%**
6		160 ° C	25%

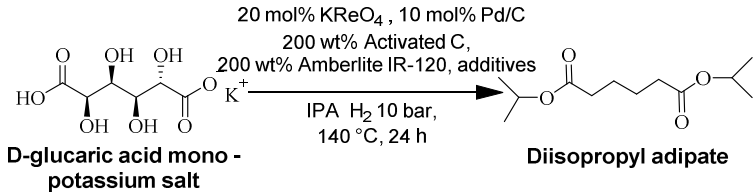
[a] The reaction yield was determined by ^{1}H NMR using an internal standard (maleic acid)

Table 2. Screening of various alcohol solvents



Entry	Solvent	Yield[a]
1	MeOH	38%[b]
2	EtOH	–
3	3-petanol	38%[c]
4	**IPA**	**56%[d]**

Table 3. Screening of acid catalysts



Entry	Additives	Yield[a]
1	0.05 eq. 10-CSA	56%
2	0.1 eq. H_2SO_4	60%
3	1 eq. HCl	–
4	0.5 eq. H_3PO_4	50%
5	**0.2 eq. TsOH**	**66%**

[a] The reaction yield was determined by ^{1}H NMR using an internal standard (maleic acid)

[b] dimethyl adipate

[c] di-3-pentyl adipate

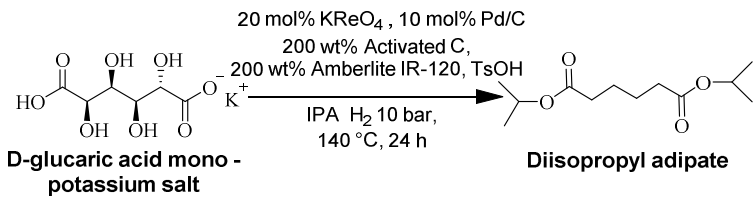
[d] diisopropyl adipate

According to the articles that synthesized adipate ester with DODH, Brønsted acids would be excellent cocatalysts to promote the esterification step and increase the solubility of reagents. Additionally, they also help olefin extrusion step by protonating the rhenium diolate intermediate.[16] To enhance the yield, various acid additives were applied in our one-pot system. Among them, TsOH gave the diisopropyl adipate yield of 66%. (Table 3.)

Spurred by the promising results, screening tests for the amount of TsOH between 0.1 eq. and 0.8 eq. were conducted to optimize reaction conditions. When the 0.5 eq. of TsOH are used, it gave 76% yield which is the highest. (Table 4)

Improving economic feasibility, we also tried to reduce the amount of other catalysts and additives. The equivalent of potassium perrhenate was reduced to 0.1 which is the half of the previous condition. Also, the amount of activated C and Amberlite IR-120 decreased to 150 wt% of starting material. (Table 5 and Table 6) Nevertheless, based on reduced amount of rhenium catalyst on Table 5, further studies are needed to improve economic feasibility such as recycling rhenium catalyst with Ionic liquids.

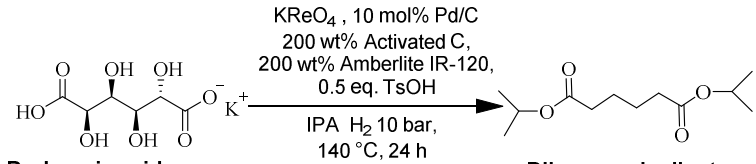
Table 4. Screening of the amount of TsOH



Entry	Amount of TsOH (eq.)	Yield[a]
1	0.1	65%
2	0.2	66%
3	0.3	63%
4	0.4	71%
5	**0.5**	**76%**
6	0.6	75%
7	0.7	39%
8	0.8	49%

[a] The reaction yield was determined by ^{1}H NMR using an internal standard (maleic acid)

Table 5. Screening of the amount of potassium perrhenate

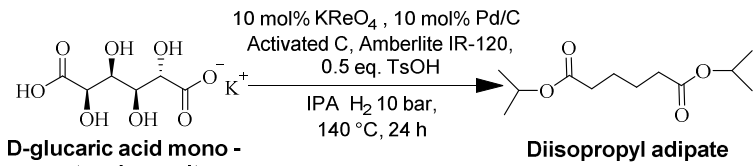


D-glucaric acid mono - potassium salt

Diisopropyl adipate

Entry	Amount of $KReO_4$(eq.)	Yield[a]
1	**0.2**	**76%**
2	0.1	76%
3	0.05	26%

Table 6. Screening of the amount of Amberlite and activated C



D-glucaric acid mono - potassium salt

Diisopropyl adipate

Entry	Amount of Amberlite (wt%)	Amount of activated C (wt%)	Yield[a]
1	200	200	76%
2	100		52%
3	**150**		76%
4		100	68%
5		**150**	**76%**

[a] The reaction yield was determined by ^1H NMR using an internal standard (maleic acid)

2.2. Synthesis of adipic acid and HMDA formate from adipamide

Adipic acid was synthesized by the hydrolysis of adipamide. Since amide group is poor leaving group, this reaction needs nucleophilic acyl substitution reaction with strong acid and base. Among strong acid reagents, the acidic ion-exchange resin, Amberlyst 15 was chosen as a proper catalyst because it can be easily removed by just filtration to enable work up simple.

Then, HMDA formate was synthesized from adipamide with indirct synthetic pathway. Adipamide can convert into adiponitrile which is an intermediate of the synthetic process of HMDA formate by nitrile formation. TsCl and pyridine were used to make adiponitrile without generating SO_2 gas, Finally, HMDA formate was obtained from adiponitrile by hydrogenation with high pressure.

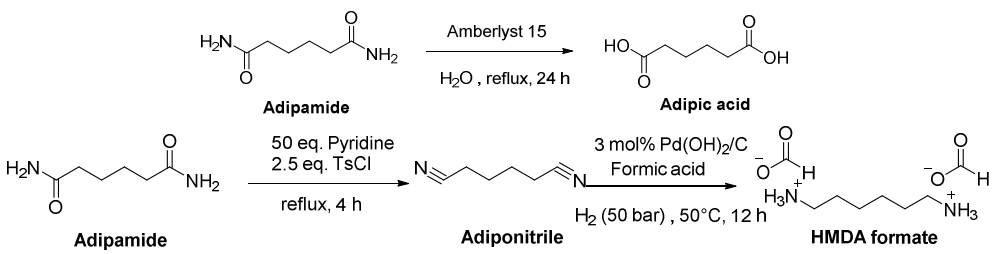


Figure 12. Synthetic route for adipic acid and HMDA

Chapter 3. Conclusion

This paper suggested a novel synthetic process for the monomers of nylon 6,6 from biomass. The commercially available potassium D-glucarate was chosen as a starting material. One-pot DODH/hydrogenation/esterification was performed with Re/Pd catalyst system and alcohol solvent. Potassium perrhenate was effective on our system among rhenium catalysts and IPA was chosen as a solvent due to the simplest secondary alcohol. To improve the yield, we used various additives such as activated C, Amberlite IR-120, and TsOH. Since Brønsted acid can be applied as a cocatalyst for both DODH and esterification, TsOH was the versatile additive for our one-pot reaction. Furthermore, the amount of catalysts and additives was reduced for optimization and we could obtain diisopropyl adipate with the highest yield of 76%.

Chapter 4. Experimental Details

4.1. General information

Unless otherwise noted, all commercially available materials were used without further purification. Thin layer chromatography analysis was carried out with Merck silica gel 60 F_{254} glass TLC plates pre-coated with a silica gel. UV light (254 nm), ninhydrin staining or phosphomolybdic acid staining were used to analyze TLC plates. Flash column chromatography was conducted on Merck Kieselgel 60 gel (70-230 mesh) using solvent mixtures of dichloromethane/methanol as eluents. An open capillary melting point apparatus (Electrothermal IA9100) was used to measure melting points. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance III 400 instrument with TMS as internal standard. (^{1}H at 400 MHz and ^{13}C at 100 MHz) Chemical shifts are reported in ppm from the internal standard (TMS, 0.0 ppm). The data are reported as (s : singlet, d : doublet, t : triplet, m : multiplet, br : broad single, coupling constant(s) in Hz, integration). High resolution mass spectra were obtained by the FAB ionization method and analyzed with a magnetic sector mass analyzer (Thermo Fisher Scientific, Flash2000).

4.2. General procedure

4.2.1 One-pot deoxydehydration/hydrogenation/esterification reactions of potassium D-glucarate

In autoclave were added potassium D-glucarate (0.5 mmol, 0.1241g), IPA (12 mL), potassium perrhenate (0.05 mmol, 0.0145g), 10 wt% Pd/C (0.05 mmol, 0.0532g), activated C (150 wt%, 0.1862g), Amberlite IR-120 (150 wt%, 0.1862g), TsOH (0.25 mmol, 0.0496g). The suspension was stirred at 140 ° C for 24 h under 10 bar hydrogen atmosphere. After completion of the reaction, the solution was filtered through cellite pad with methanol and the filtrate was concentrated under the reduced pressure. The product, diisopropyl adipate was obtained by 76% yield and yield was confirmed by NMR spectroscopy with maleic acid as an internal standard. ^{1}H NMR ($CDCl_3$) δ 4.99(quin, 2H), 2.28 (t, 4H), 1.64 (quin, 4H), 1.22 (d, 12H); ^{13}C NMR ($CDCl_3$) δ 172.93, 67.55, 34.30, 24,45, 21.84; HRMS (CI^+) : $C_{12}H_{22}O_4$ calc'd 231.1601 found 231.1598

4.2.2. Synthesis of adipic acid

To a solution of adipamide (0.72 g, 5 mmol) in water (60 mL) was added Amberlyst® 15 hydrogen form (strongly acidic, cation exchanger, 7.2 g, 1000 wt%) at room temperature. The reaction mixture was stirred vigorously at reflux condition for 24 h. After completion of reaction, the mixture was cooled to room temperature then filtered with filter paper to recover the resin The filtrate was concentrated under the reduced pressure giving the pale yellow solid. The crude product was recrystallized with acetonitrile and dried on vacuum oven at 50 ° C for overnight. Adipic acid was obtained as a white solid in quantitative yield. ^{1}H NMR (DMSO−d_6) δ 2.19 (t, 4H), 1.49 (quin, 4H); ^{13}C NMR (DMSO− d_6) δ 174.80, 33.78, 24.45

4.2.3. Synthesis of adiponitrile

To a solution of adipamide (0.72 g, 5 mmol) in pyridine (20mL, 100 mmol), p-Toluenesulfonyl chloride (2.38 g, 12.5 mmol), was added carefully at room temperature. The resulting mixture was stirred at reflux condition for 6 h. After completion of reaction, the mixture was cooled to room temperature then concentrated under reduced pressure. The yellow syrup mixture was purified by column chromatography on silica gel using solvent mixtures hexane/ethyl acetate eluents affording desired adiponitrile as yellow liquid. ^{1}H NMR (DMSO-d_6) δ 2.61 (t, 4H), 1.86(quin, 4H) ; ^{13}C NMR ($CDCl_3$) δ 11874, 24.43, 16.82; HRMS (CI^+) : $C_6H_{12}N_2O_6[M+H]^+$ calc' d 109.0765; found 109.0766

4.2.3. Synthesis of hexamethylenediammonium formate

To a solution of adiponitrile (0.216 g, 2 mmol) in formic acid (10 mL) was added 20 wt% palladium hydroxide on carbon (0.0042 g, 0.06 mmol) at room temperature. The reaction mixture was stirred at 50 ° C for 12 h under 50 bar hydrogen atmosphere. After the reaction, the reaction mixture was filtered through cellite pad with with excess methanol and the filtrate was concentrated under the reduced pressure. The crude was the syrup not the solid because of incomplete evaporation of formic acid fue to hydrogen bonding. The crude was dried on freeze drier for overnight to remove residual formic acid. After freeze drying, precipitation with acetonitrile was carried out. As a result, the solid was obtained and it was recrystallized with IPA/acetonitrile for further purification. Mp 126.4~127.3 ° C ; ^{1}H NMR (DMSO−d_6) δ 8.46 (s, 2H), 3.00 (t, 4H), 1.68 (t, 4H), 1.42 (quin, 4H) ; ^{13}C NMR (DMSO−d_6) δ 166.73, 38.64, 27.22, 25.44

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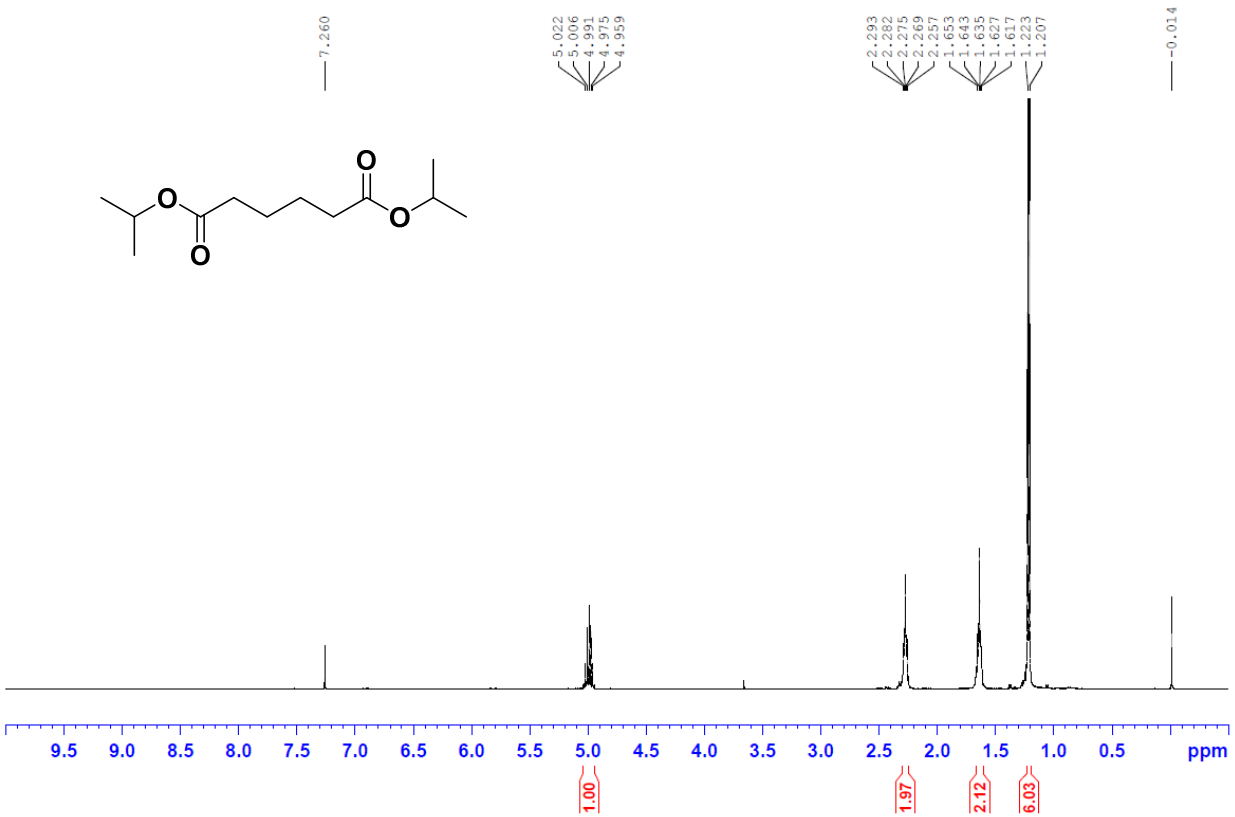
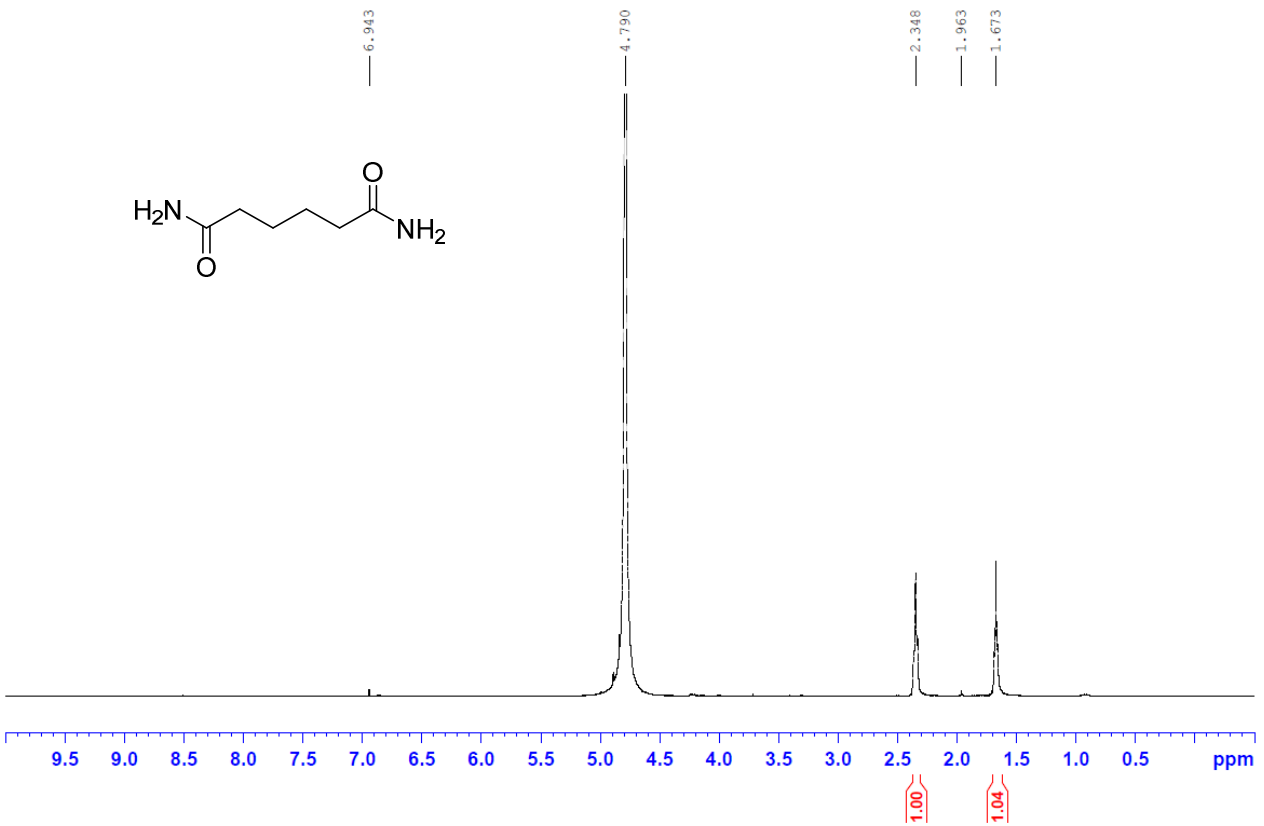
APPENDICES

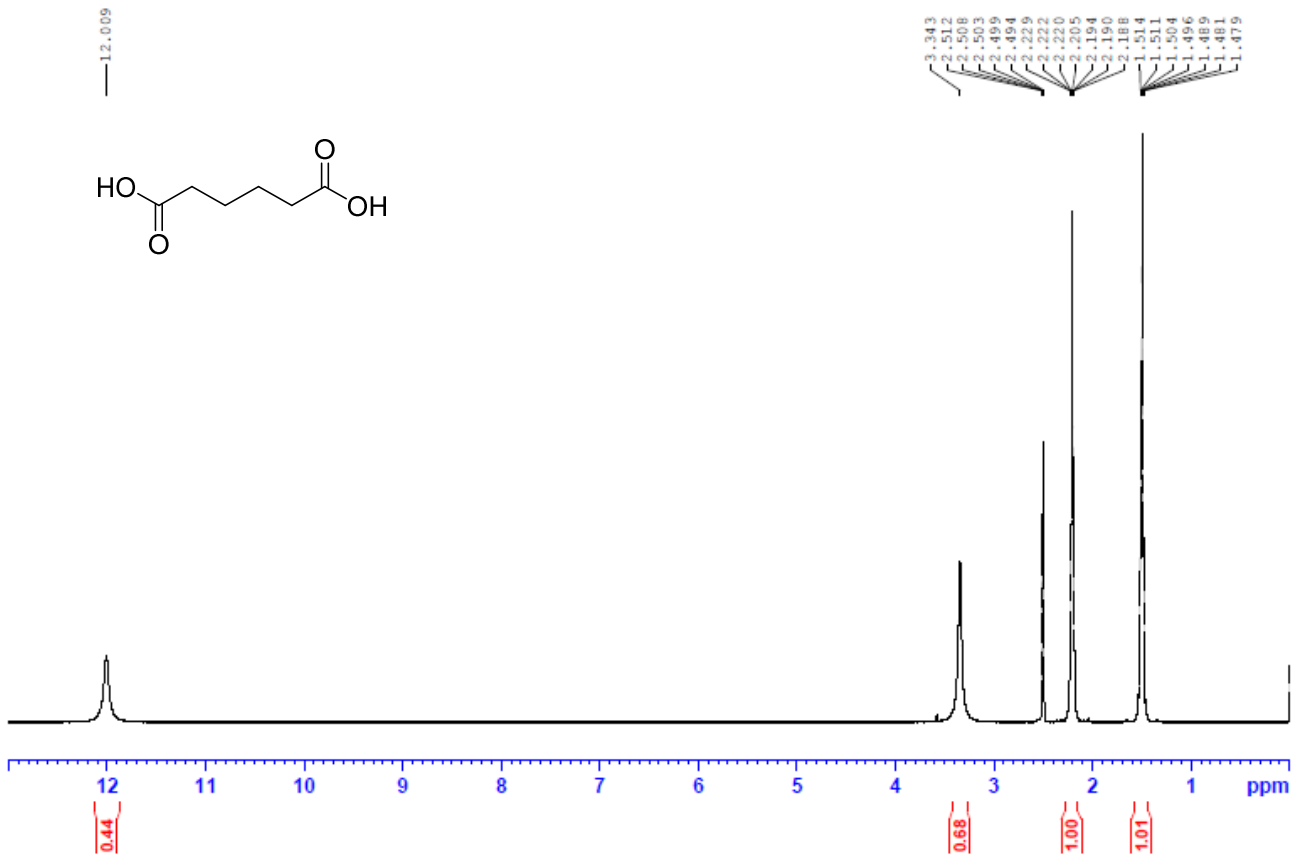
List of ^{1}H NMR Spectra



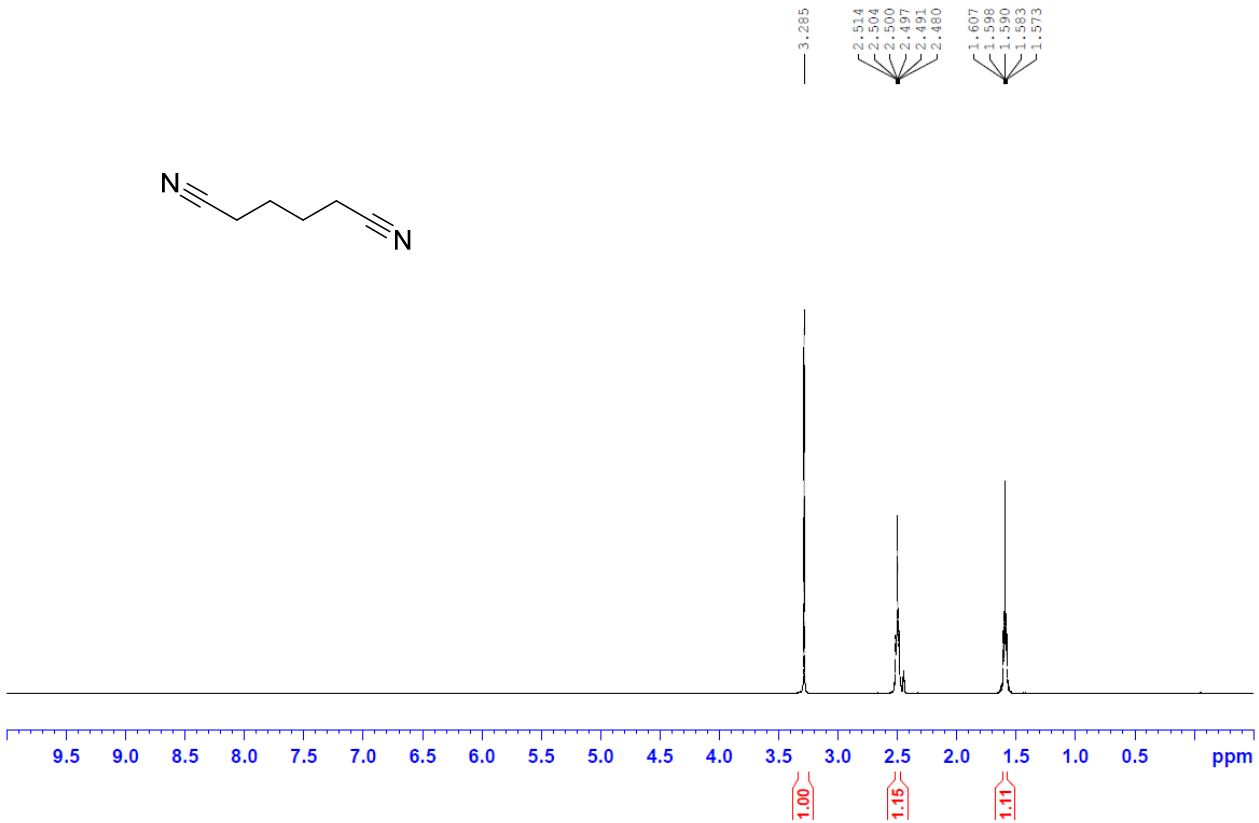
1. 400 MHz 1 H NMR Spectrum ($CDCl_3$) of diisopropyl adipate



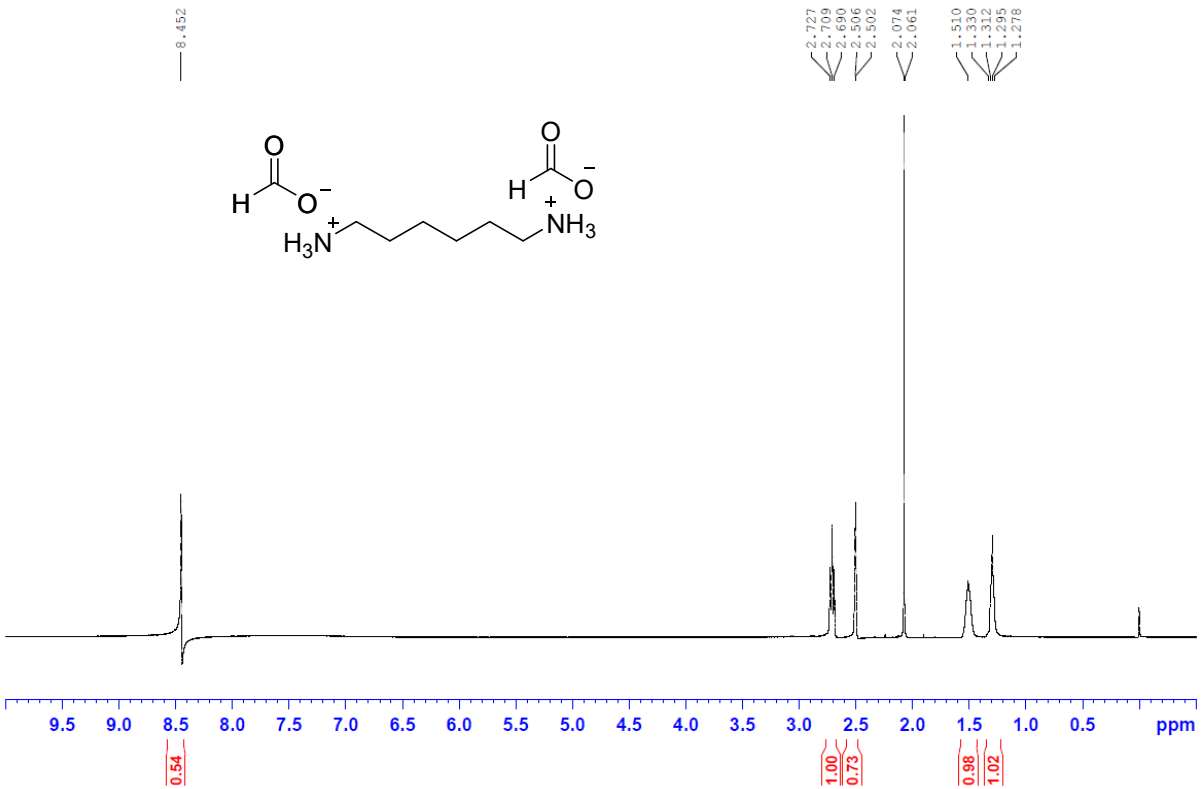
2. 400 MHz 1 H NMR Spectrum (D2O) of adipamide



3. 400 MHz 1 H NMR Spectrum (DMSO−d_6) of adipic acid

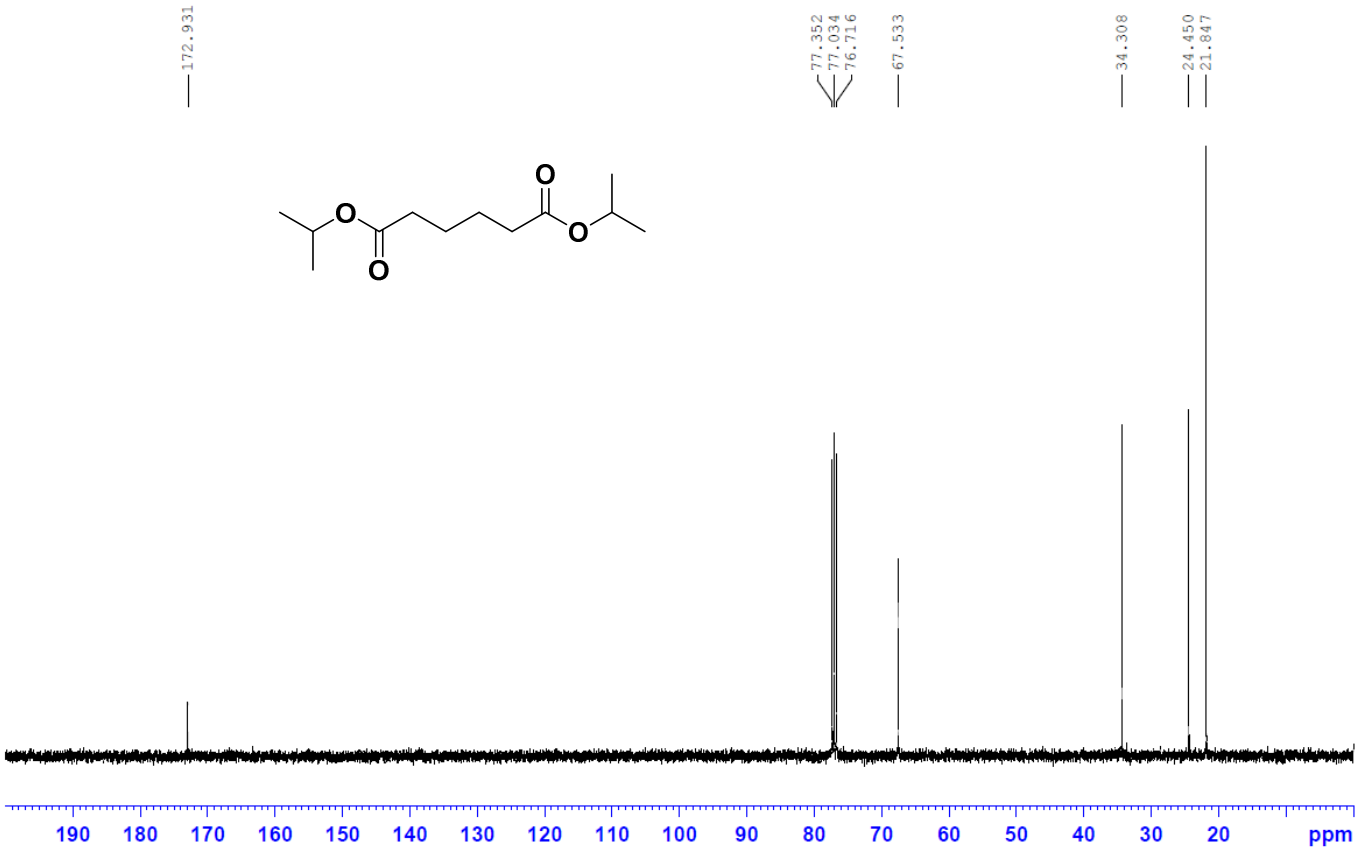


4. 400 MHz 1 H NMR Spectrum (DMSO−d_6) of adiponitrile



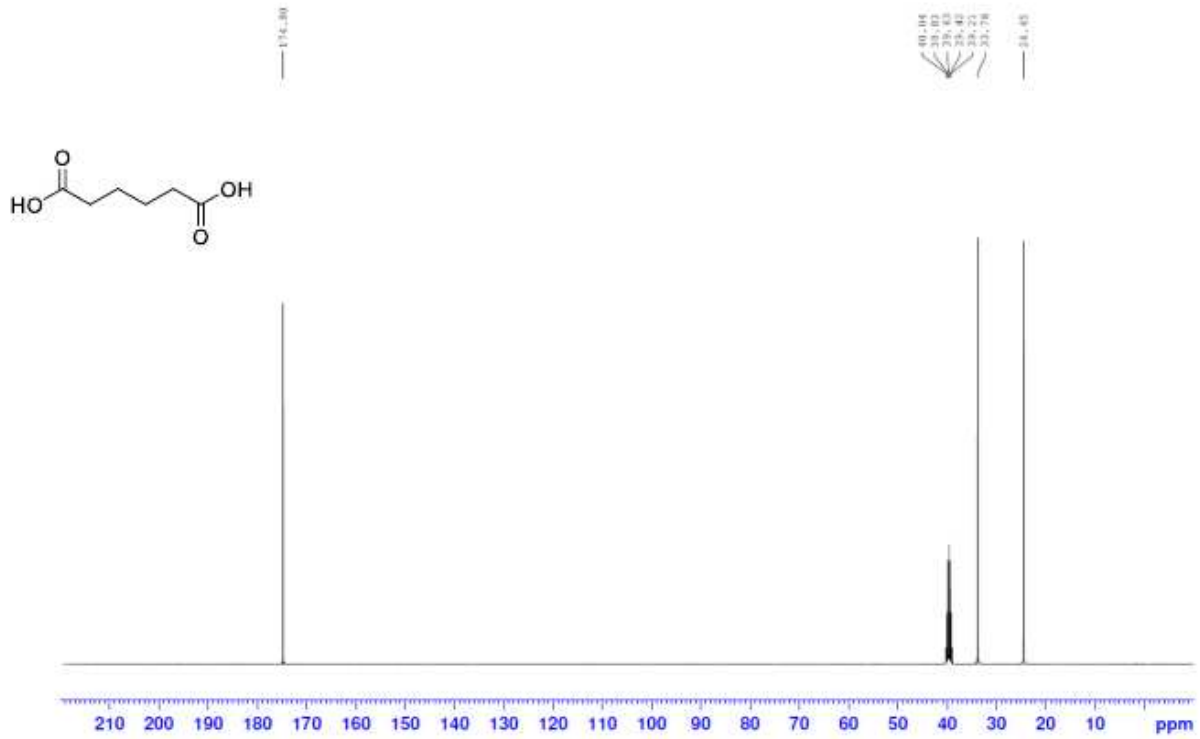
5. 400 MHz 1 H NMR Spectrum (DMSO−d_6) of HMDA formate

List of ^{13}C NMR Spectra

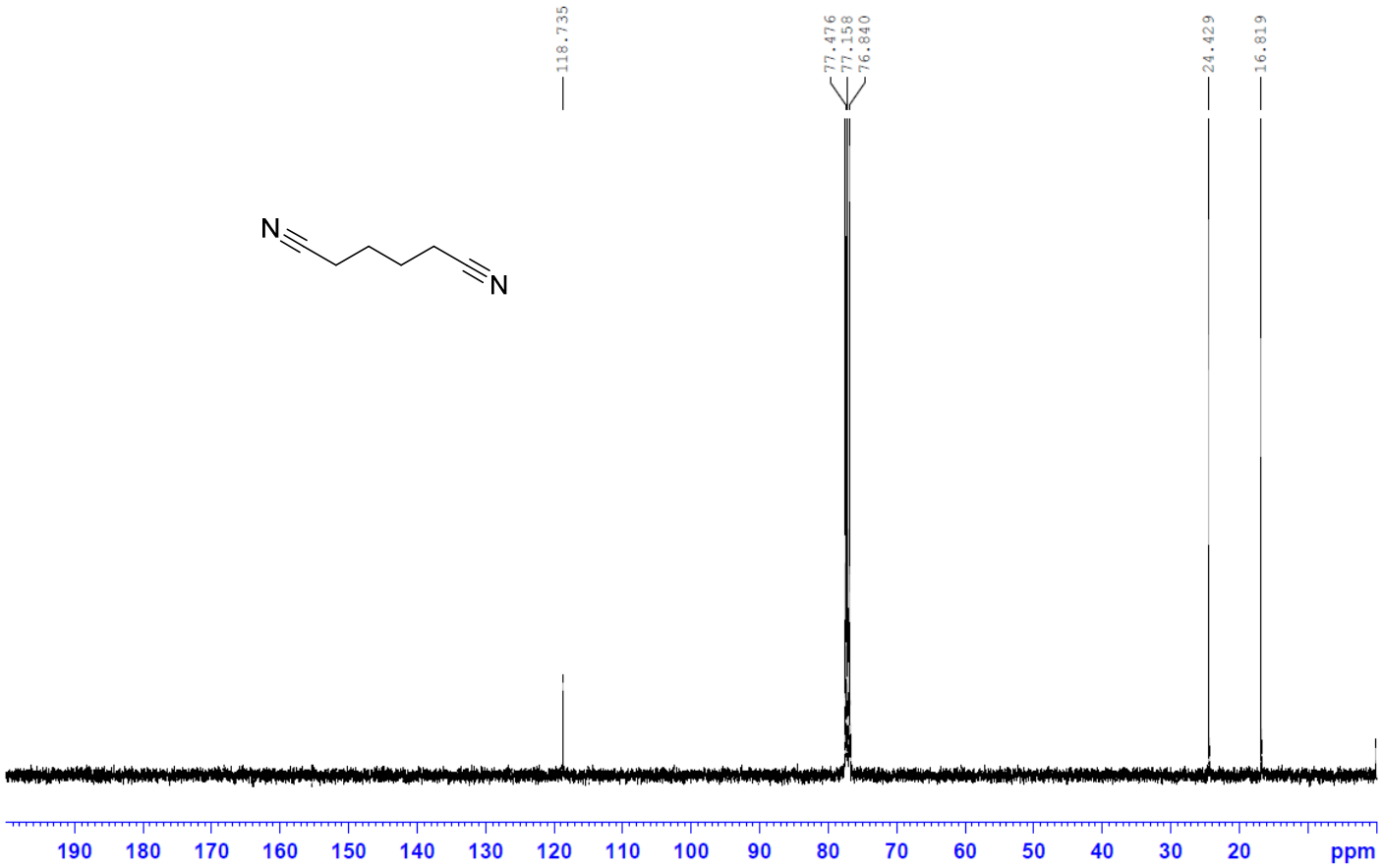


1. 400 MHz ^{13}C NMR Spectrum ($CDCl_3$) of diisopropyl adipate

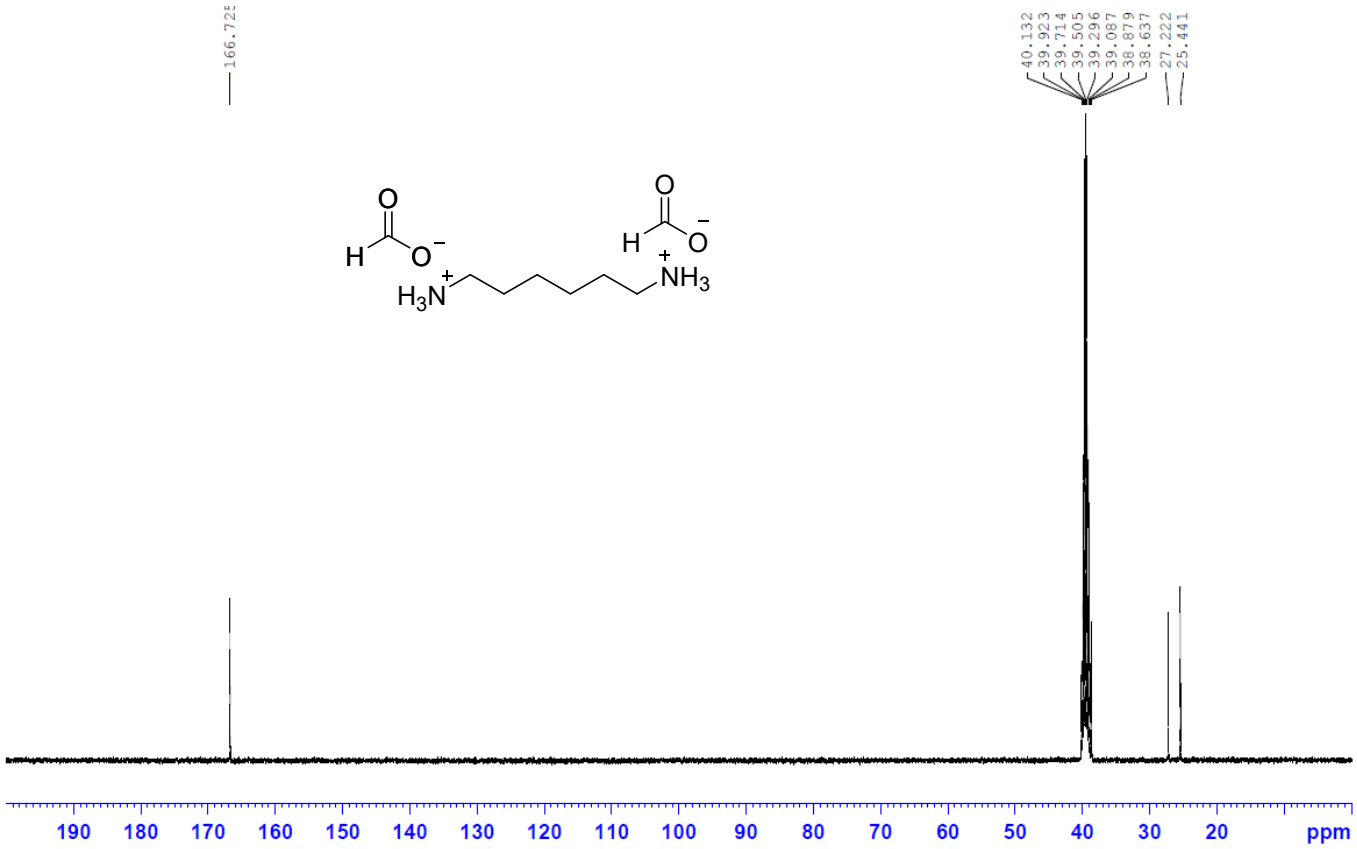
2. 400 MHz ^{13}C NMR Spectrum (DMSO−d_6) of adipamide



3. 400 MHz ^{13}C NMR Spectrum (DMSO−d_6) of adipic acid



4. 400 MHz ^{13}C NMR Spectrum ($CDCl_3$) of adiponitrile



5. 400 MHz ^{13}C NMR Spectrum (DMSO−d_6) of HMDA formate

국 문 초 록

화석 연료의 고갈로 인해 석유 기반 물질을 생산하는 많은 석유화학 기업들에서 바이오매스를 화학 공급 원료 중의 하나로 사용하려는 노력이 계속 되어 왔다. 따라서, 본 연구에서는 글루코스로부터 나일론 6,6 의 단량체인 아디프산와 헥사메틸렌다이아민을 합성하는 실험을 진행하였다. 시작 물질로는 포타슘 글루카릭산을 사용하였는데, 이는 가장 저렴하고 구하기 쉬운 글루코스를 산화시켜서 만들어진다. 아디파마이드를 합성하는 공정은 두 단계로 이루어져있다. 첫 번째는 가장 중요한 반응인 탈산소탈수, 수소화반응 그리고 에스터화 반응을 고압반응기에서 연속반응으로 다이이소프로필 아디페이트를 합성하는 단계이며, 두 번째 단계는 합성된 아디페이트를 아민화하여 아디파마이드를 합성하는 것이다. 연속반응의 조건 최적화를 위해 용매, 촉매, 첨가제, 온도, 압력, 시간을 스크리닝하여 최대 수율 76% 에 도달할 수 있었다. 본 논문은 염기성 때문에 탈산소탈수 반응에 대한 반응성이 현저히 떨어지는 포타슘 글루카릭산을 연속 반응을 통해 다이이소프로필 아디페이트를 높은 수율로 얻었고, 궁극적으로 바이오 기반으로 한 나일론 6,6 의 단량체 합성에 혁신적인 방법을 제시함에 의의가 있다. 또한, 다이이소프로필 아디페이트를 아디파마이드로 전환하는 아민화 반응에 대한 연구가 더 필요하다고 판단된다.

주요어: 탈산소탈수, 레늄, 나일론 6,6, 바이오매스, 원팟반응, 글루카릭산

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