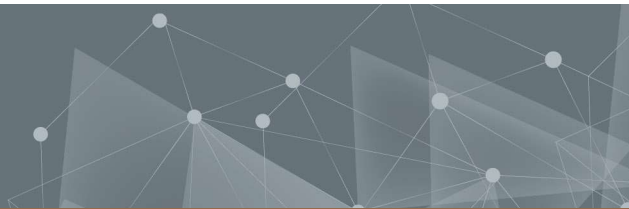




CHALMERS
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Synthesis of β -O-4 Linkage Containing Lignin Model Compound

Bachelor's Thesis in Chemistry and Chemical Engineering

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DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING

DIVISION OF ORGANIC CHEMISTRY

CHALMERS UNIVERSITY OF TECHNOLOGY

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ABSTRACT

In today, energy consumption on this planet has continuously increased. One of the destinations in green chemistry is the development of efficient conversion of lignin polymer into useable chemical compounds. The aim of this study is to synthesize lignin models and streamlining the synthesis route by adjusting different parameters.

After a series of researches and tests. Few of the synthesized steps were streamlined, but the synthesis of the lignin model compound did not accomplish, due to the time limit. The protecting step of starting material, vanillin, to benzyl vanillin by adding benzylated derivate as protecting group has been founded to give the best result by using acetone as the solvent and K_2CO_3 as the base, according to the NMR. Although the recrystallization was failed and, therefore, the actual yield could not be estimated. The conversion of benzyl vanillin to an α,β -unsaturated ester was succeeded through Wittig reaction by using water as the medium. The yield was good according to the NMR, but a better processing method needs to be founded. Epoxidizing of the α,β -unsaturated ester was failed. But in the test with trans-cinnamaldehyde, α,β -unsaturated aldehyde, some traces of epoxide have shown. The possible reasons may be the steric hindrance of the protecting group and the reactivity of the ester, which differed from the trans-cinnamaldehyde.

Keywords: Lignin model compound, β -O-4 linkage, biomass

TABLE OF CONTENT_Toc41145127

1	Introduction	1
1.1	Background	1
1.2	Purpose	1
2	Theory	2
2.1	Composition of Lignin	2
2.2	Lignin in Wood	2
2.3	Green Chemistry.....	3
2.4	Reaction Flows.....	4
2.4.1	Reaction I – II.....	4
2.4.2	Reaction III-VI	5
2.4.3	The Reaction Mechanism for Wittig Reaction.....	6
3	Experimental	8
3.1	Synthesis of Benzyl Vanillin (2)	8
3.2	(2-methoxy-2-oxoethyl)triphenylphosphonium bromide	8
3.3	Synthesis of 3-(4-(benzyloxy)-3- methoxyphenyl)acrylate (3).....	9
3.3.1	Non-one-pot	9
3.3.2	One-pot	9
3.3.3	Purification	9
3.4	Synthesis of Tetrabutylammonium Peroxydisulfate (4).....	10
3.5	Synthesis of Methyl 3-(4-(benzyloxy)-3-methoxyphenyl) oxirane-2-carboxylate (5).....	10
4	Result and Discussion	11
4.1	Benzyl Vanillin.....	11
4.1.1	Interpretation of Samples	12
4.2	3-(4-(benzyloxy)-3- methoxyphenyl)acrylate	14
4.3	Tetrabutylammonium Peroxydisulfate	16
4.4	Methyl 3-(4-(benzyloxy)-3-methoxyphenyl)oxirane-2-carboxylate	16
5	Conclusion and Future Outlook.....	19
6	Acknowledgment.....	20

1 INTRODUCTION

1.1 BACKGROUND

In today's society, the environmental impact caused by various energy consumption has led to a serious problem [1]. The greenhouse gas effect is getting worse and climate change destroys the ecosystems. Therefore, a more sustainable and energy-saving method needs to develop. A choice for this is biomass [2].

Lignin is the generic name for a series of polymeric aromatic compounds contained in plant cell walls. It is lignocellulosic biomass together with cellulose and hemicellulose [3] and is one of the biggest naturally occurring biomass in nature. Since lignin is available as renewable products in large quantities, it has a high potential to become renewable sources of aromatic chemicals and fuels [4].

The development of the lignin process is a new technique that has been more attentive in recent years. But the current situation is that lignin treats as a major waste product in the pulp and paper industry, which is only used for heat supply [3, 4]. Therefore, the development of an efficient and inexpensive conversion from lignin to useful material will be an important advance in chemistry and today's society.

1.2 PURPOSE

In this study, the β -O-4 linkage containing lignin model is synthesized based on the article "Synthesis of lignin model compound containing β -O-4 linkage" written by Mukthar et al. [4]. The aim is to synthesize and understand the theory for the lignin model compound.

The study will also aim at finding an alternative reaction route that is more time-efficiency and environmentally friendly than what the article concluded. This will provide an efficient and convenient synthesis route for the future study of the lignin model compound. But due to the timeframe, the study will be mainly focusing on streamlining the reaction route.

2 THEORY

2.1 COMPOSITION OF LIGNIN

Lignin is a complex three-dimensional amorphous which is composite by different kind of monolignol monomers [5]. But only three of them are the most common; p-coumaryl, coniferyl, and sinapyl alcohols. Monomers in lignin usually are linked by various C-O and C-C linkage (see figure 1). Two-third or more of all the linkage belongs to C-O linkage and the rest are C-C. In all of the linkages, the β -O-4 linkage is the most dominant one in lignin, which consists of 50-60% of all C-O linkages [4, 5]. Therefore, the main challenge in transform lignin to useable chemicals will be cleavage of these linkages, especially the β -O-4 linkage.

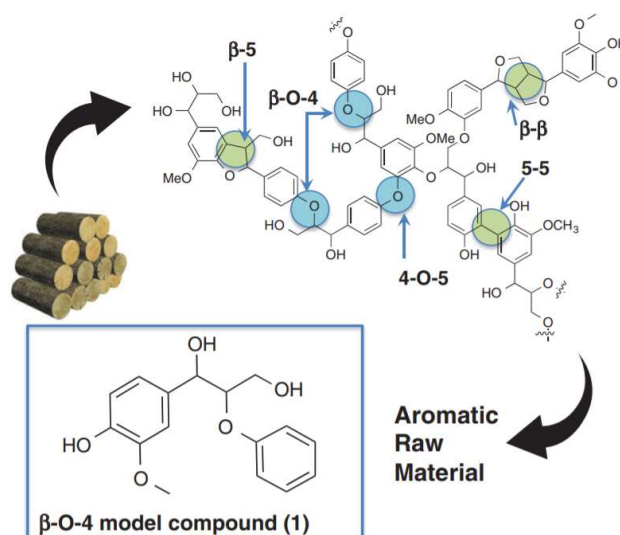


Figure 1. Different linkage on lignin. Blue circles stand for C-O linkages and green circles stand for C-C linkages. Source: Asma Mukhtar et al. [4].

2.2 LIGNIN IN WOOD

Wood is mainly composed of three components; lignin, cellulose, and hemicellulose [6]. These components interact with each other which results in structural and mechanical properties, through primary and secondary bonds, in the wood [6].

Lignin is the second most abundant of the biopolymers in the wood [6]. In various types of wood, the composition of lignin will be different [5]. In softwood, lignin accounts for 30% by the weight, but in hardwood, lignin only accounts for 20-25%.

As earlier mentioned, most of the monomers in lignin are p-coumaryl, coniferyl, and sinapyl alcohols. These compounds also known as syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H) units (see figure 2) [5]. G-unit usually classified as softwood lignin. This is because most of the units in softwood are G-unit. For the same reason are G-S is classified as hardwood lignin.

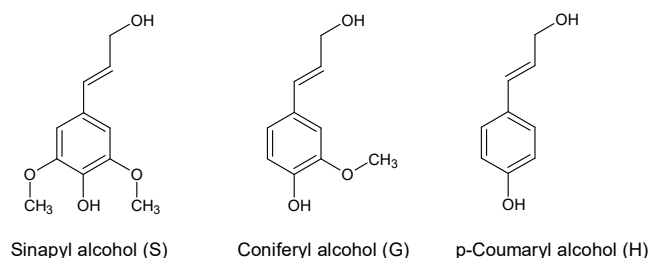


Figure 2. Chemical structure for sinapyl (S), coniferyl (G), and p-coumaryl alcohols (H). Source: Changzhi Li et al. [5]

	Syringyl unit % (sinapyl)	Guaiacyl unit % (coniferyl)	p-hydroxyphenyl unit % (p-coumaryl)
Hardwood ¹	50	50	2
Softwood	1	95	4

Table 1. Composition of the phenylpropane unit in hardwood and softwood. ¹Most hardwood consists of an equal amount of syringyl unit and guaiacyl unit. But some hardwood that consists of the p-hydroxyphenyl unit has been founded. Source: Brunow and Lundquist. [7].

2.3 GREEN CHEMISTRY

In today's society, Earth's resources are being consumed more and more. As an effect, global warming has been a serious problem that is threatening different species on this planet. Therefore, the trend in chemistry has been to make the reactions more energy-efficient, environmentally friendly, and recyclable. This concept is named as green chemistry.

The definition of green chemistry is "design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances.", which mentioned in Anastas and Eghbali's article [8]. This definition has already established in the early 1990s.

In 1998, a guiding framework of green chemistry was introduced by Paul Anastas and John Warner. The framework including twelve different principles, thereby, is called The Twelve Principles of

Table 2. Detail explanation of twelve principles. Source: Anastas and Eghbali [8].

- Prevention.** It is better to prevent waste than to treat or clean up waste after it is formed.
- Atom Economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- Less Hazardous Chemical Synthesis.** Whenever practicable, synthetic methodologies should be designed to use and generate substances that pose little or no toxicity to human health and the environment.
- Designing Safer Chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
- Safer Solvents and Auxiliaries.** The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
- Design for Energy Efficiency.** Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
- Use of Renewable Feedstocks.** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- Reduce Derivatives.** Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
- Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- Design for Degradation.** Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
- Real-Time Analysis for Pollution Prevention.** Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
- Inherently Safer Chemistry for Accident Prevention.** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Green Chemistry (see table 2). In recent years, this framework has been summarized into a more memorable acronym, PRODUCTIVELY (see figure 3) [8–10].

Condensed Principles of Green Chemistry

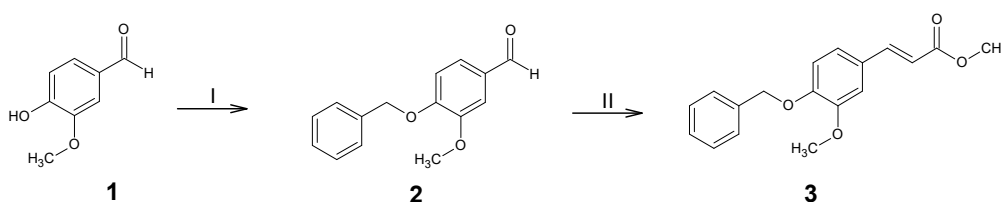
- P - Prevent wastes
- R - Renewable materials
- O - Omit derivatization steps
- D - Degradable chemical products
- U - Use safe synthetic methods
- C - Catalytic reagents
- T - Temperature, Pressure ambient
- I - In-Process Monitoring
- V - Very few auxiliary substances
- E - E-factor, maximise feed in product
- L - Low toxicity of chemical products
- Y - Yes, it is safe

Figure 3. Condensed principles of green chemistry, PRODUCTIVELY. Source: Tang et al. [9].

2.4 REACTION FLOWS

In this section, the overall reaction flow will be described. This section is divided into three parts. In the first part, the reaction I and II will be described, as well as the synthesis of an oxidant that will be used in reaction iii. In the second part, the step that was failed (reaction III) and unperformed (reaction IV-VI) will be described. But in this case, the explanation will only be based on what expected to happen. The third part will describe the detailed mechanism for reaction II.

2.4.1 Reaction I – II



Scheme 1. Synthesis routes that were succeeded. [(i) K_2CO_3 , BnBr, Acetone, r.t., 3 h; (ii) PPh_3 , $NaHCO_3$, water, 50 °C, 1 h]

In the first step (see scheme 1), the vanillin (1) is deprotonated by a base, in a solvent, which leads to a nucleophilic reaction to a benzylated derivate, in this case, benzyl bromide. The purpose of this step is

to give the OH group protection to prevent an unwilling reaction. Benzyl vanillin (**2**) has been synthesized.

The synthesis of methyl 3-(4-(benzyloxy)-3-methoxyphenyl)acrylate (**3**) referred to the article of El-Batta et al. [11]. This article describes the synthesis of α,β -unsaturated ester through Wittig reaction, and by using water as the medium. Wittig reaction is a reaction that produces alkene by a reaction between triphenylphosphonium ylide and ketone or aldehyde. In this case, the reaction is accomplished by reacting triphenylphosphine, methyl 2-bromoacetate in a saturated aqueous NaHCO_3 .

In step **II**, the reaction is performed in one pot, which means all reaction was performed continuously in one container without any processing between. This was different from the Mukhtars et al.' method [4], which has the synthesis for Wittig salt, (2-methoxy-2-oxoethyl)triphenylphosphonium bromide, and the synthesis of **3** separately. After the reaction solution was washed and separated. The solution was washed again by sodium bisulfite, by using the extraction method from Furigay et al. [12]. This method will extract the unwilling aldehyde from the product.

The synthesis of **5** referred to the article by Yang et al. [13]. This article discusses how to epoxide different electron-deficient olefins by using an oxidant, tetrabutylammonium peroxydisulfate (**4**). This oxidant can create from a reaction between tetrabutylammonium hydrogensulfate and potassium persulfate in water as a solvent (see figure 4).

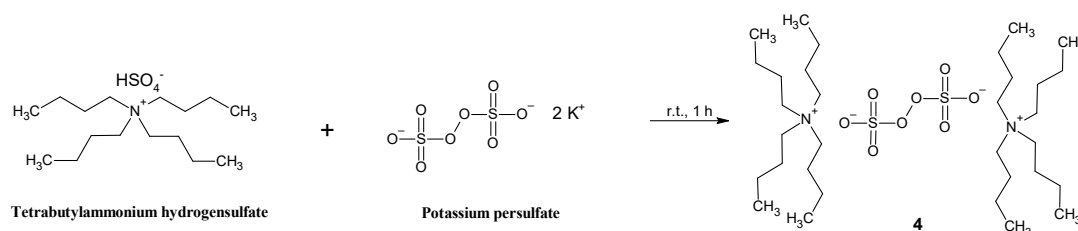
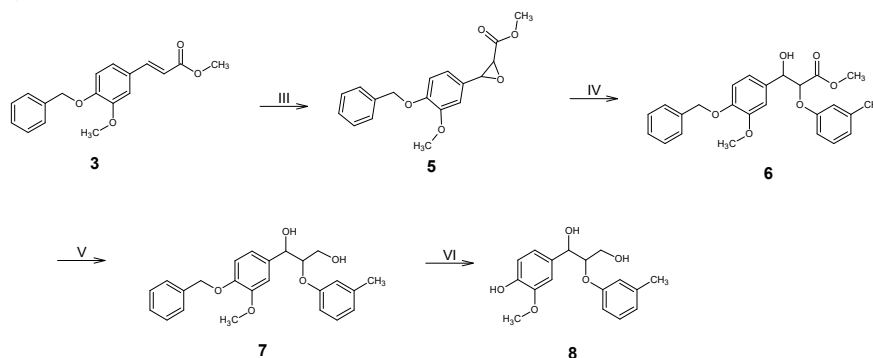


Figure 4. Synthesis of tetrabutylammonium peroxydisulfate (**4**).

2.4.2 Reaction III-VI



Scheme 2. Uncompleted reactions.

The **3** reacts with **4** together with H_2O_2 and NaOH to form the epoxide. First, H_2O_2 and NaOH will form HOO^- which will future react with **4** to form a peroxysulfate anion intermediate [13]. This intermediate has a strong nucleophile oxidizing ability toward substrates **3**. As a result, a 1,4-addition occurs to **3**, which is α,β -unsaturated ester, and the double bond will be replaced by epoxide. The methyl 3-(4-(benzyloxy)-3-methoxyphenyl)oxirane-2-carboxylate (**5**) will be synthesized. After synthesis of **5**, m-cresol is using as the reagent. m-cresol is deprotonated by KOH . This will make the deprotonated cresol have a nucleophile attack on the epoxide and form methyl 3-(4-(benzyloxy)-3-methoxyphenyl)-3-hydroxy-2-(m-tolyloxy)propanoate (**6**).

In the last two steps, V and VI, reductions occur. The method that would have used is the method in Asma Mukhtar et al.'s method [4]. These are well-established reduction methods. Therefore, any side reactions are less expected to happen. But possible optimization for the product may be necessary. First, the **6**, α,β -unsaturated ester, is reduced to primary alcohol by using LiAlH_4 in diethyl ester. 1-(4-(benzyloxy)-3-methoxyphenyl)-2-(m-tolyloxy)propane-1,3-diol (**7**) is formed. Then, the protecting group, benzyl group, is removed by using Pd/C and H_2 gas. 1-(4-hydroxy-3-methoxyphenyl)-2-(m-tolyloxy)propane-1,3-diol (**8**) is formed.

2.4.3 The Reaction Mechanism for Wittig Reaction

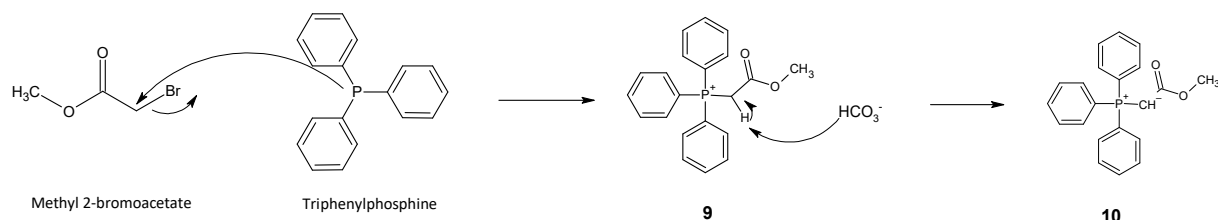


Figure 5. Synthesis of methyl 3-(4-(benzyloxy)-3-methoxyphenyl)acrylate (**3**), part 1.

Firstly, triphenylphosphine will make a nucleophile attack on the methyl 2-bromoacetate (see figure 5). This causes bromide to leaves the molecule and form (2-methoxy-2-oxoethyl)triphenylphosphonium cation (**9**). Then, HCO_3^- will deprotonate the α -hydrogen and cause a negatively charged α -carbon. **10** is formed.

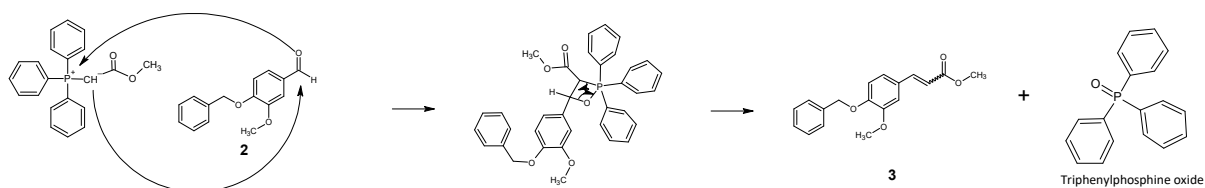


Figure 6. Synthesis of methyl 3-(4-(benzyloxy)-3-methoxyphenyl)acrylate (**3**), part 2.

The α -carbanion makes a nucleophile attack to the aldehyde carbon on **2** (see figure 6). A double bond on oxygen will also release to form O-P with phosphorus. Finally, the C-P bond and C-O bond will break to form C=C and O=P bond. **3** and Triphenylphosphine oxide are synthesized.

3 EXPERIMENTAL

3.1 SYNTHESIS OF BENZYL VANILLIN (2)

In a stirred solution of 1 g vanillin (5.00 mmol) and 20 mL of acetone, 8 g of K_2CO_3 and 0.63 mL benzyl bromide (5.30 mmol) was added respectively. The suspension is then stirred in 3 hours and monitored by TLC (ethyl acetate : hexane, 1 : 9) was taken. After the reaction was completed, the suspension was suction filtrated and evaporated to remove the base and the solvent. The remaining oil was mixed with 10 mL DCM and extracted together with 10 mL of water. The organic phase was collected and two more extractions with DCM were made. The combined organic phase was dried with Na_2SO_4 and evaporated in reduced pressure. A yellow solid was collected and NMR was conducted.

1H NMR ($CDCl_3$): δ = 9.84 (s, 1 H, aldehyde), 7.46 - 6.95 (m, 7 H, Ph), 6.98 (d, 1 H, Ph-H), 5.25 (s, 2 H, Ph- CH_2 -), 3.95 (s, 3 H, CH_3) (Appendix 1).

3.2 (2-METHOXY-2-OXOETHYL)TRIPHENYLPHOSPHONIUM BROMIDE

A mixture of 8.50 g triphenylphosphine (33.5 mmol) and 10 mL ethyl acetate was prepared and stirred at room temperature. To the stirred mixture, a solution of 4.97 g methyl 2-bromoacetate (32.5 mmol) in ethyl acetate was further added. The resulting mixture was stirred in 17 h at room temperature.

When the reaction was completed, the mixture was extracted with 30 mL diethyl ether three times and dried with Na_2SO_4 . The dried solution was then evaporated in reduced pressure. A white solid was furnished, (2-methoxy-2-oxoethyl)triphenylphosphonium bromide. NMR check for the solid was conducted.

1H NMR ($CDCl_3$): δ = 7.91 (m, 4 H, Ph-H), 7.78 (m, 2 H, Ph-H), 7.67 (m, 4 H, Ph-H) (Appendix 2).

3.3 SYNTHESIS OF 3-(4-(BENZYLOXY)-3-METHOXYPHENYL)ACRYLATE (3)

In this section, both experimental methods and purification steps of synthesis **3** were described.

3.3.1 Non-one-pot

A mixture of 0.886 g of sodium ethoxide in 10 mL of ethanol was prepared. To the mixture, 5.22 g phosphonium bromide (12.6 mmol) and 2.61 g **2** (12.4 mmol) were added respectively. The reaction was stirred in at 50 °C for 1 h and monitored by TLC (ethyl acetate : hexane, 1 : 9). After the completion of the reaction, the mixture was added with water and extracted with 30 mL diethyl ether four times. The organic phase was dried with Na₂SO₄ and evaporated under reduced pressure. A white solid was collected and an NMR check was conducted.

3.3.2 One-pot

A mixture of 0.482 g triphenylphosphine (1.90 mmol), 5 mL saturated aqueous NaHCO₃, 0.340 g methyl 2-bromoacetate (2.22 mol), and 0.245 g (1.01 mmol) **2** was prepared. The mixture was stirred at room temperature in 4 h and the process is monitored by TLC. After the completion of the reaction, the solution was dissolved in 25 mL distilled water and extracted with 25 ml diethyl ether three times. The combined organic phase was dried with Na₂SO₄ and evaporated in reduced pressure. A white solid was remaining after the evaporation and NMR check for the solid was conducted.

3.3.3 Purification

The solids in **3.3.1** and **3.3.2** were mixed. Purification on the solid by using column chromatography (ethyl acetate : hexane, 3 : 7) was performed. After the chromatography, the desired product was collected and evaporated. The white solid after evaporation was dissolved by a small amount of diethyl ether and blend with saturated NaHSO₃. The mixture was future added by 25 mL diethyl ether and extracted. The organic phases evaporated and an NMR check was conducted. Further purification of recrystallization was performed by using ethanol. The crystal, **3**, was collected and an NMR check was conducted. The total weight was 0.245 g and a yield of 7.00 %.

¹H NMR (CDCl₃): δ= 7.62 (d, 1 H, olefinic proton), 7.46–7.28 (m, 6 H, Ph-H), 7.27-7.25 (s, 1 H, Ph-H), 7.08-7.00 (d, J = 8.3 Hz, 1 H, Ph-H), 6.30 (d, 1 H, olefinic proton), 5.1 (s, 2 H, Ph-CH₂-), 3.92 (s, 3 H, CH₃), 3.79 (s, 3 H, CH₃) (Appendix 3).

3.4 SYNTHESIS OF TETRABUTYLAMMONIUM PEROXYDISULFATE (4)

A mixture of 21.2 g (64.0 mmol) tetrabutylammonium hydrogensulfate and 0.870 g potassium persulfate (32.0 mmol) in distilled water, was stirred for 60 min at room temperature. The resulting solution was then extracted with 30 mL of CH₂Cl₂ three times and the organic phases were collected. The combined organic phase was then dried with Na₂SO₄ and evaporated under reduced pressure to form a white solid. NMR check for the solid was conducted.

¹H NMR (CDCl₃): δ = 3.31 (t, 8 H, CH₂), 1.63 (t, 8 H, CH₂), 1.45 (m, 8 H, CH₂), 0.98 (t, 12 H, CH₃) (Appendix 4).

3.5 SYNTHESIS OF METHYL 3-(4-(BENZYLOXY)-3-METHOXYPHENYL) OXIRANE-2-CARBOXYLATE (5)

To a stirred solution of 0.746 g **3** (2.5 mmol) in 10 mL of methanol, 1.70 g **4** (2.54 mmol), 0.25 mL H₂O₂, 100 mg NaOH were added respectively. The mixture was stirred for 2 h and monitored by TLC (DCM). After the completion of the reaction, the resulting solution was mixed with 30 ml saturated NH₄Cl and extracted with 30 ml diethyl ether three times. The combined organic phases were dried Na₂SO₄ and evaporated under reduced pressure. NMR check for the product was conducted.

4 RESULT AND DISCUSSION

4.1 BENZYL VANILLIN

As earlier mentioned, the initial recipe that was used was from Mukhtar et al.'s article [4]. In the initial recipe, DMF was used as the solvent, and K_2CO_3 was used as the base. However, the process did not go as expected. In Mukhtar et al.'s article [4], the suspension after the reaction has not been any processed before extraction. This makes some difficulty in extraction.

Firstly, the excessive amount of K_2CO_3 that was used in reaction caused the third layer in extraction. This might be due to the excess amount base dissolves in water, the high density of the base solution caused another layer that comes below the organic layer. Secondly, DMF dissolves in water. So, without any processing for the DMF, the DMF will mix with water and cause a bad extraction. Lastly, DMF has a high boiling point which makes evaporation difficult.

Due to the causes above, the reaction has made some changes. Firstly, different solvents were tested; acetone and ethanol (see table 3). The choice of ethanol referred to Nakatsubo et al.'s article [14]. In this article, ethanol was used in the synthesis of benzyl vanillin. The reason for choosing acetone was because of the similarity in polarity to ethanol. In Nakatsubo et al.'s article [13] KOH was used for the base. Therefore, KOH was also tested for an alternative base. Secondly, the extra steps of filtration and evaporation were added. Filtration was used for removal of the excessive base and evaporation was used for removal of acetone, since acetone mix with water. The amount of benzyl bromide was also changed since the original rate is almost 1:1.7 for vanillin to benzyl bromide. The rate after changing is 1:1.05.

The yield of the step could not be estimated. This is because the recrystallization of the reaction failed. The reason is too much impurity in the solution.

Number	Solvent	Base	Result (TLC and NMR)
Sample 1	DMF	K_2CO_3	All vanillin consumed
Sample 2	Ethanol	K_2CO_3	Some vanillin was left
Sample 3	Ethanol	KOH	Some vanillin was left
Sample 4	Acetone	K_2CO_3	All vanillin consumed
Sample 5	Acetone	KOH	Unknown substance created ¹

Table 3. Result for testing of different solvents and bases. ¹Only TLC data is available.

4.1.1 Interpretation of Samples

The signal on 9.84 ppm will indicate both aldehyde proton on **1** and **2**. The signal on 4.50 ppm is indicating CH₂ in benzyl bromide. If all the vanillin has been consumed, the intensity of the signal on 5.25 should be double as the intensity of the signal on 9.84.

The NMR of sample 1 (see figure 7) is hard to compare with the other three. The reason is this reaction processed differently as the other three since different processing methods were using. The method that was used was to precipitate the desired product by water. In the NMR for sample 3 (see figure 8), there was no trace of benzyl bromide. But the trace of vanillin has been founded. This indicates an excess of vanillin and this might because of some mistake on the weight scales. The NMR for sample 5 was not performed. This is because an unknown substance showed in the TLC, and no trace of **2** was found.

In the NMR of sample 2 (see figure 9), some vanillin was still left by the comparison of the intensity of the signal. On the contrary, in sample 4 (see figure 10) the intensity of the aldehyde signal is half of the intensity of the product signal. This indicates the vanillin in this sample has all consumed, which means this reaction gives the best result.

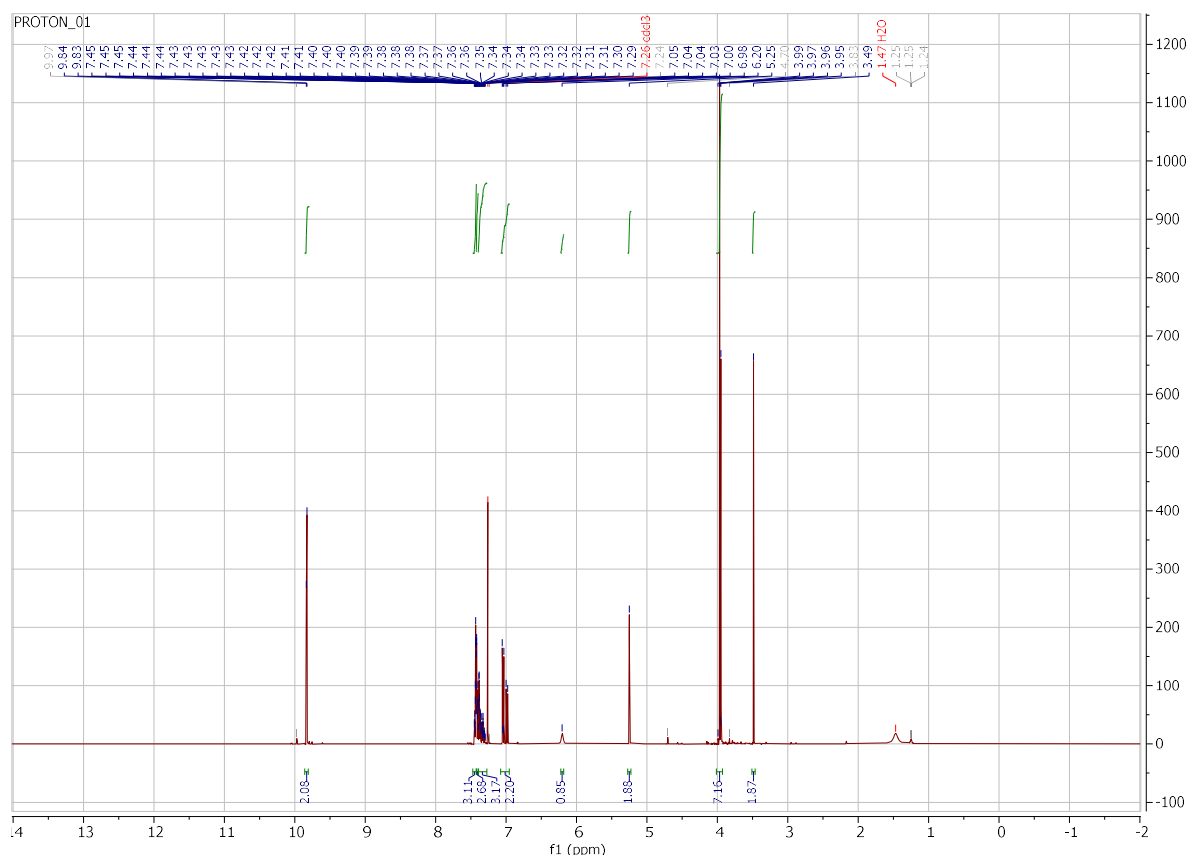


Figure 7. ¹H NMR for sample 1.

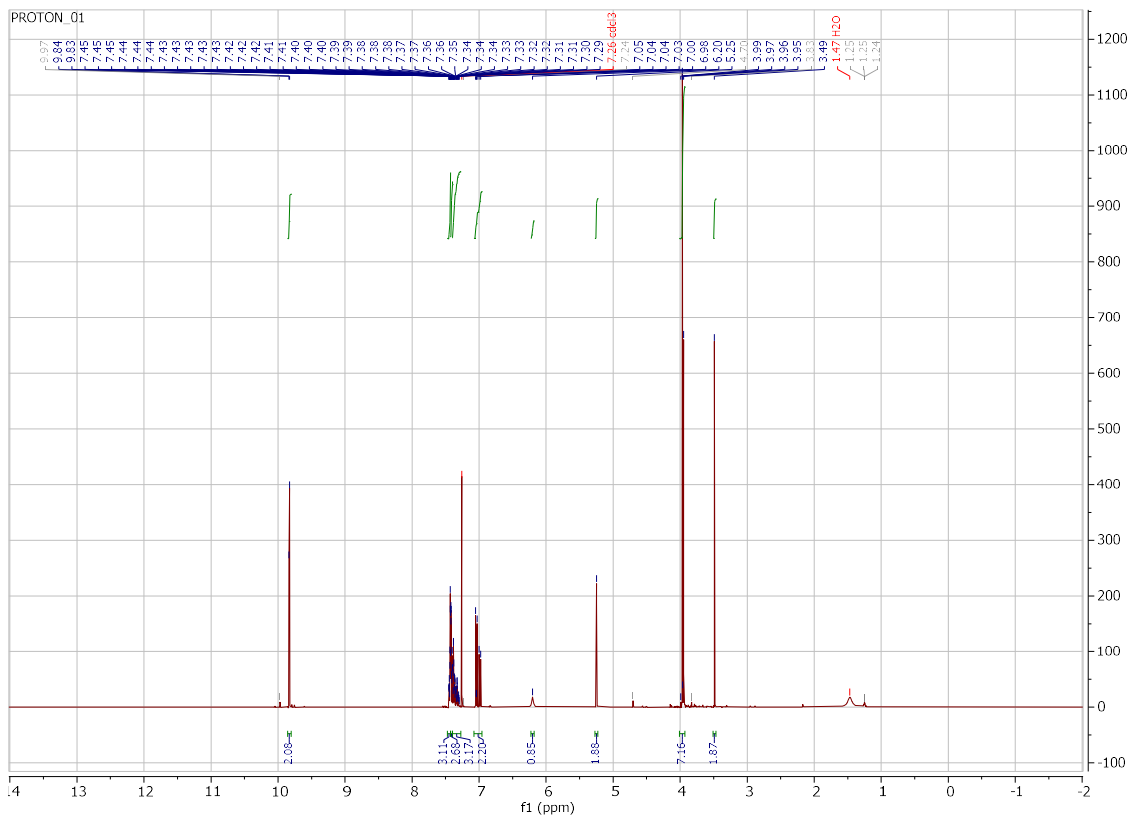


Figure 8. ¹H NMR for sample 2.

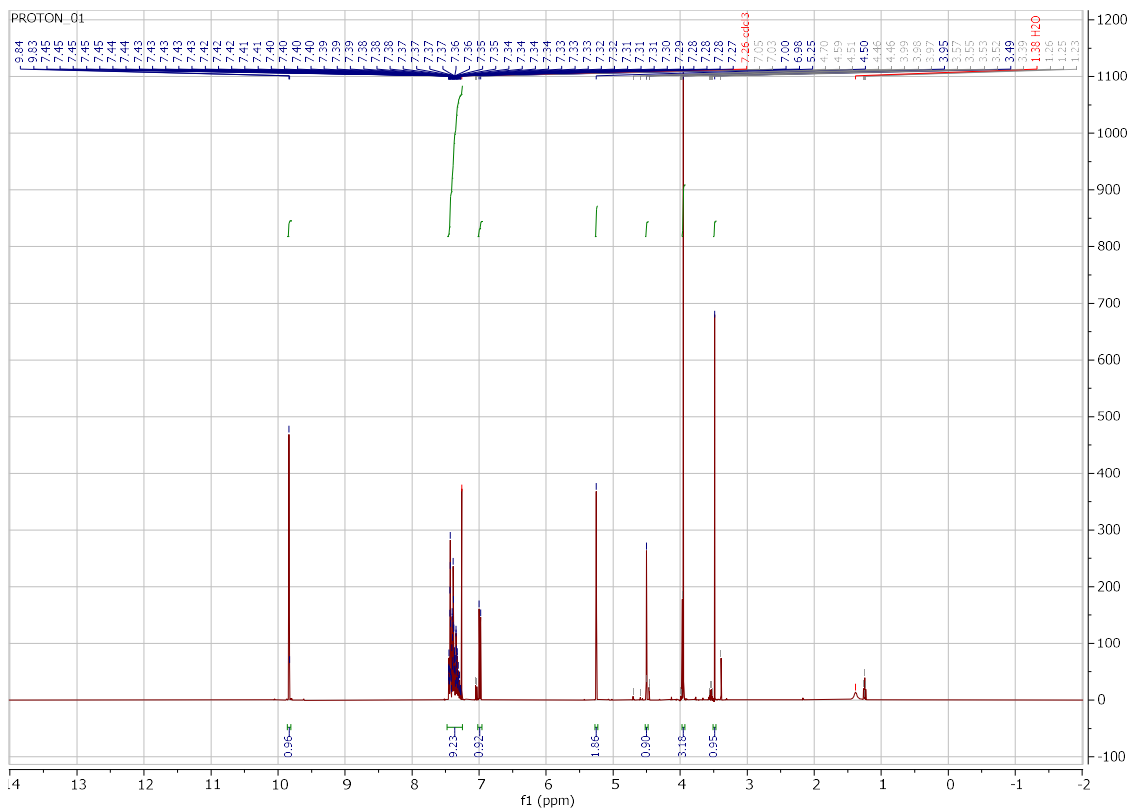


Figure 9. ¹H NMR for sample 3.

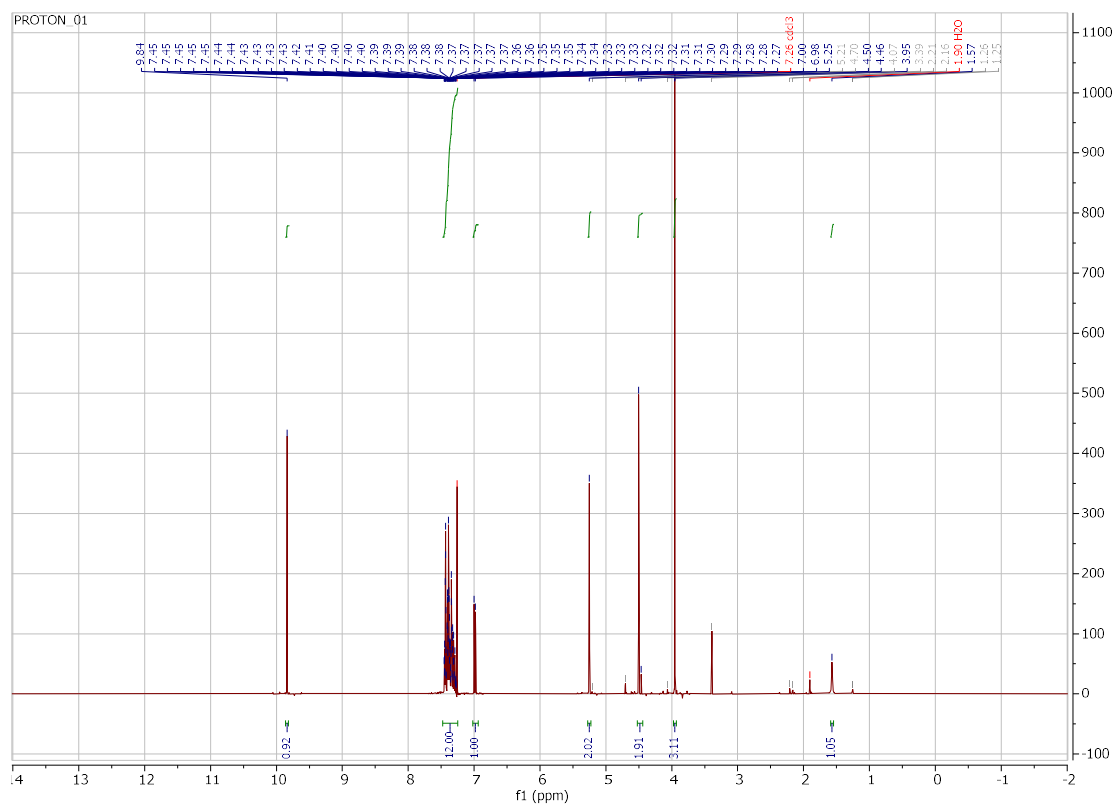


Figure 10. ¹H NMR for sample 3.

4.2 3-(4-(BENZYLOXY)-3-METHOXYPHENYL)ACRYLATE

Both Wittig reactions go as expected. But from the perspective of the time-efficiency and the environment-friendly, the one-pot Wittig reaction has taken advantage. This is because the one-pot Wittig reaction only took four hours to react and it uses water as the solvent. The yield of both reactions together was only 7%, which is very low. However, in Mukhtar et al.'s article [4], the total yield of non-one-pot Wittig reaction was 90%. By the NMR of one-pot reaction (see figure 12), no aldehyde peak was shown. But on the other hand, in the non-one-pot reaction, there is still an aldehyde peak left after the reaction (see figure 11). These indicate the one-pot reaction should have a better yield than the non-one pot reaction.

Another reason for choosing the one-pot reaction is because of the use of a greener solvent and reduced processing steps. In the non-one-pot reaction, the entire synthesis of **3** used ethyl acetate and ethanol as the solvents and extracted a total of seven times with diethyl ether. On the other hand, the one-pot reaction uses water as the solvent and extracted only three times.

In purification steps, column chromatography was used for the removal of triphenylphosphine oxide. The initial intention was to remove both triphenylphosphine oxide and **2**. But in the end, the **2** still mixed with **3**. Therefore, extra steps of removal of **2** were added, which are extraction with NaHSO₃ and

recrystallization with ethanol. The reason for the low yield might be because of unnecessary much purification step.

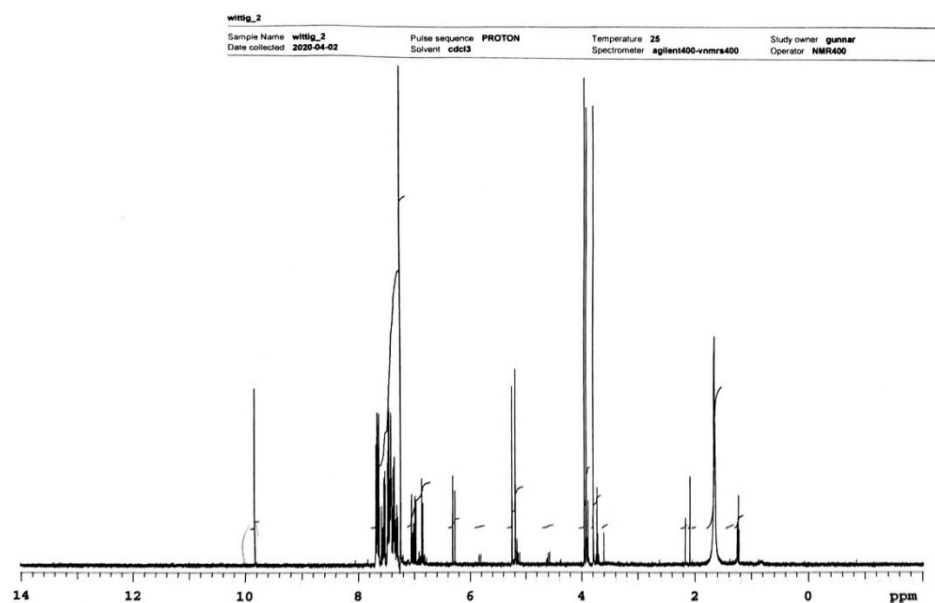


Figure 11. ¹H NMR for non-one-pot Wittig reaction.

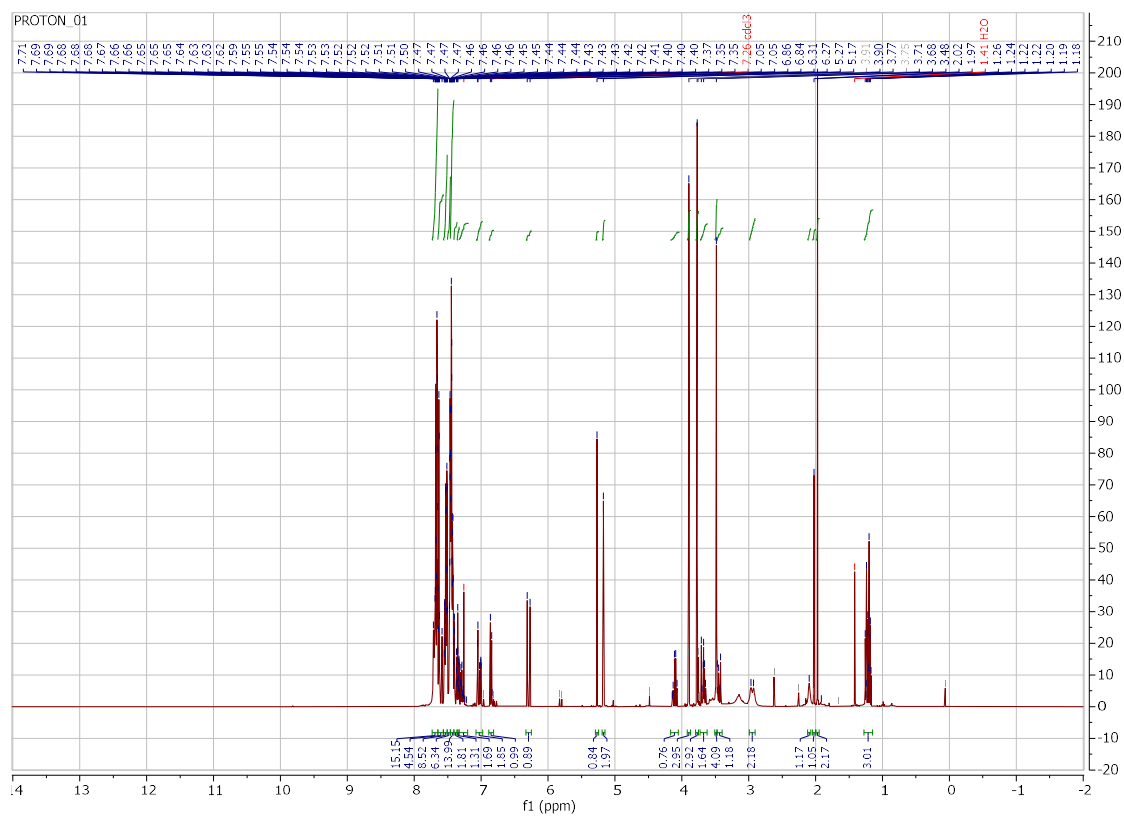


Figure 12. ¹H NMR for one-pot Wittig reaction.

4.3 TETRABUTYLAMMONIUM PEROXYDISULFATE

This reaction was completed without any problem. The NMR shows an indication of the desired product, **4** (see fig 13). But the NMR also shows some trace of DCM and water in the product. In the case when the product is completely purified, the intensity of the signals on 3.3, 1.6, 1.4 ppm should be equal. But in this NMR, the signal of water coincides with the signal in 1.6 ppm which makes the peak bigger. The signal in 7.2 and 5.5 are signals for DCM. The yield was not calculated since the weight was not recorded.

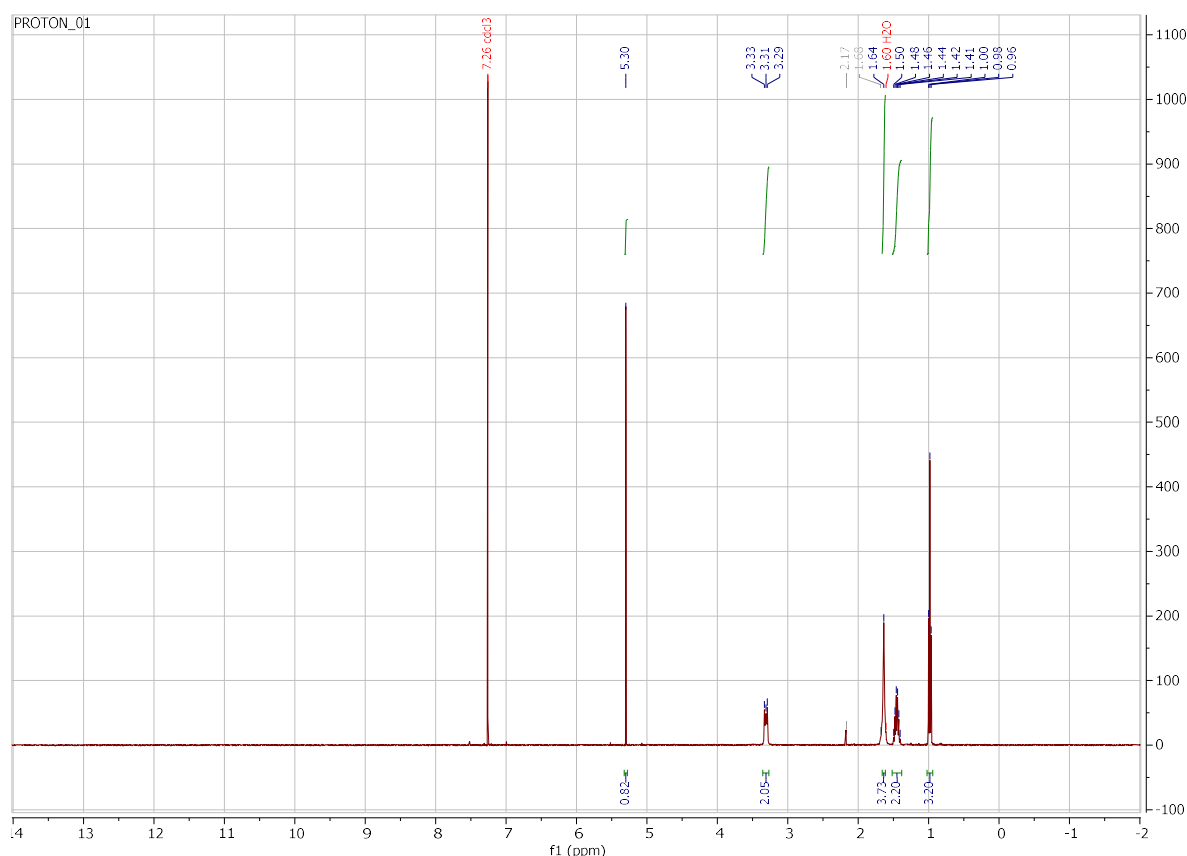


Figure 13. ¹H NMR for tetrabutylammonium peroxydisulfate.

4.4 METHYL 3-(4-(BENZYLOXY)-3-METHOXYPHENYL)OXIRANE-2-CARBOXYLATE

By a series of testing with trans-cinnamaldehyde, an α,β -unsaturated aldehyde, the possibility of epoxidizing **3** was been shown. However, in the epoxidizing of **3**, the reaction did not go as expected. The NMR did not show any trace of **5** (see figure 14). In the test by using trans-cinnamaldehyde, four different aldehyde peaks have been detected; benzaldehyde, trans-cinnamaldehyde, epoxide of cinnamaldehyde, and an unknown.

Benzaldehyde has a signal at 10.0 ppm (see figure 15). Due to the lack of time, the reason for the formation of benzaldehyde could not be investigated. But estimation is when the oxidation of **3**, both sides of the double bond formed a hydroxide group. This caused the cleavage of carbon bonds [15, 16] and formed benzaldehyde. The unknown peak has not been investigated due to the time limit. But guessing is it might have formed a cis-isomers of cinnamaldehyde.

Few indications show the reaction of cinnamaldehyde formed epoxide, according to Yang et al.'s article [9]. Firstly, the peak in 9.19 might be aldehyde peak for the epoxide (see figure 14). Secondly, the double on 4.16 and the doublet of doublets on 3.44 might indicates the protons on the epoxide carbon.

By studies, two possible reasons for why epoxidation of **3** did not work, have been assumed. Firstly, **3** that used was an α - β -unsaturated ester which differs in reactivity with trans-cinnamaldehyde. Secondly, the benzyl group in **3** may cause a steric hindrance to the reaction which makes it difficult to react. However, the real reason was not investigated due to the lack of time.

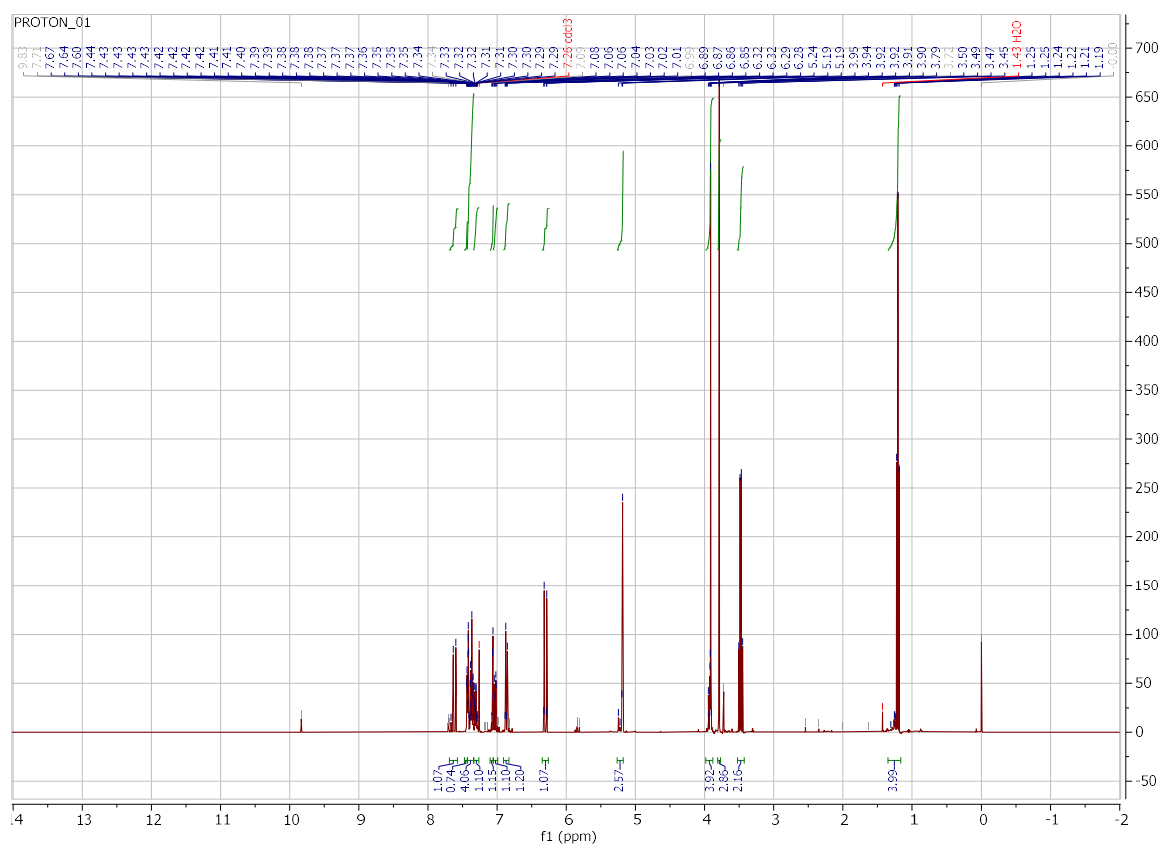


Figure 14. ¹H NMR of epoxidation of **3**.

5 CONCLUSION AND FUTURE OUTLOOK

Synthesis of the β -O-4 containing lignin model compound did not succeed due to the time lack. However, some steps have been successfully performed and improved.

By the tests, the combination of acetone and K_2CO_3 gives the best result at the synthesis of **2**. But since the recrystallization did not successively perform, the actual yield is unknown. However, in the TLC and NMR shows all vanillin consumed after the reaction. In the synthesis of **3**, the one-pot Wittig reaction took advantage in terms of time-efficiency, environmentally friendly, and yield. The synthesis of **5** did not succeed. The possible cause can be the protecting group, benzyl group, acted as a steric hindrance to the reaction and the reactivity of ester.

There are some parts in the syntheses that can be improved to give a better result. In the synthesis of benzyl vanillin, a step of column chromatography could be added. By a test of TLC, Hexane was confirmed to give motion to benzyl bromide and barely any movement to **3**. So, hexane could use for eluent to remove benzyl bromide. In the synthesis of the **3**, there were unnecessarily many purifications. If a more suitable eluent could be founded, the only purification will need is column chromatography. As earlier mentioned, the reason for failed epoxidizing may be the protecting group. In this case, the protecting group could be removed from **3** before epoxidizing or not use the protecting group at the start.

Finally, this study will give a deeper understanding to lignin model compound and will provide convenience to the future study of lignin.

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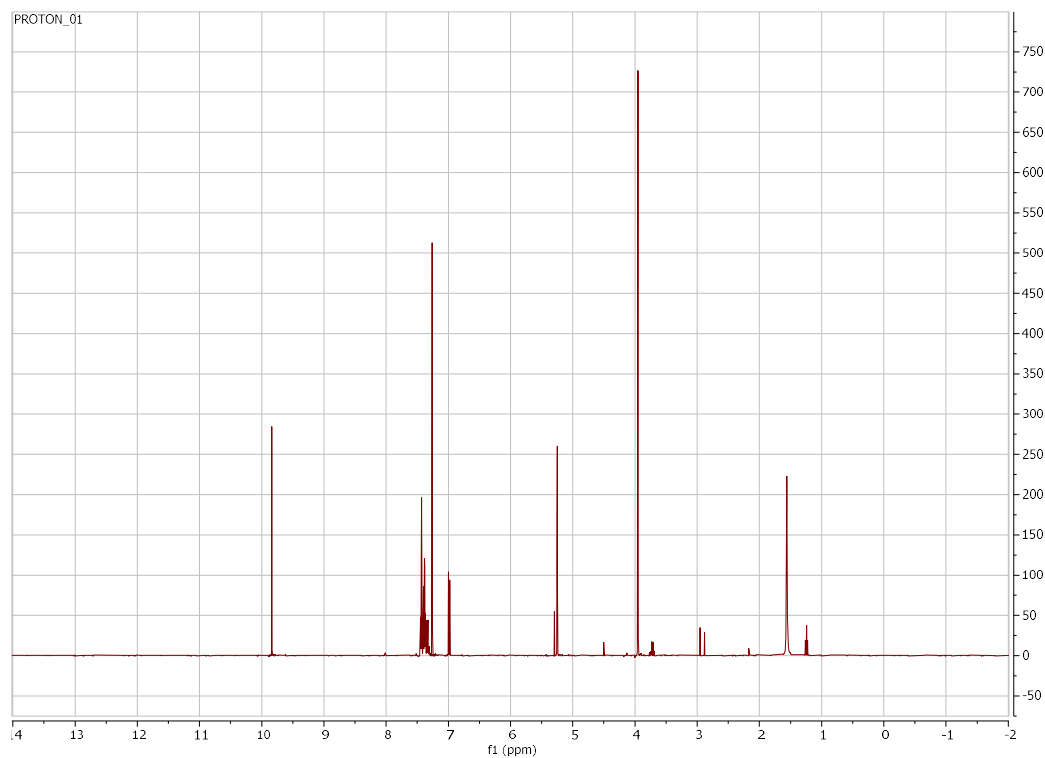
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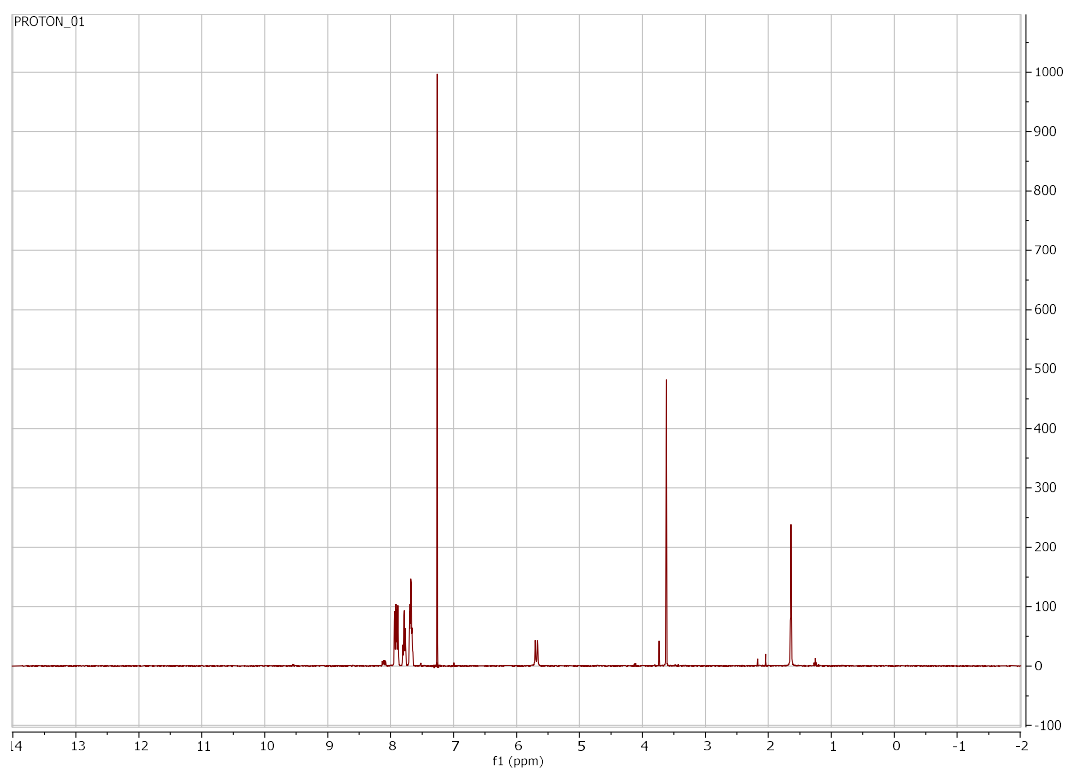
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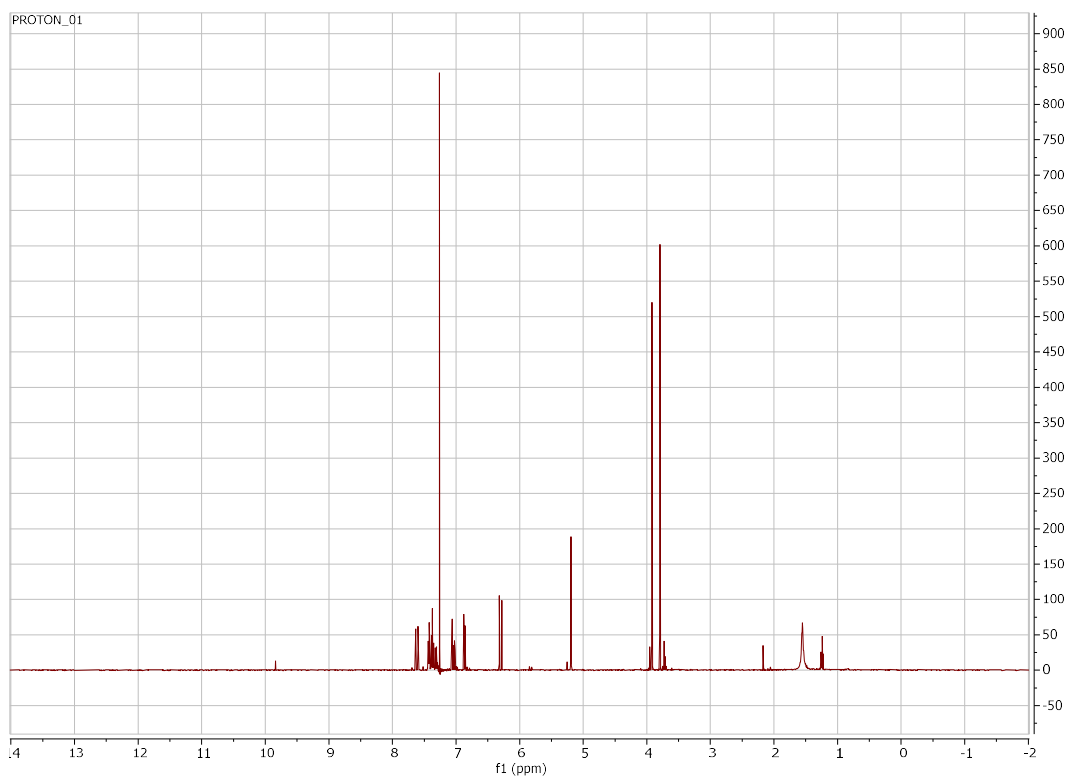
APPENDIX



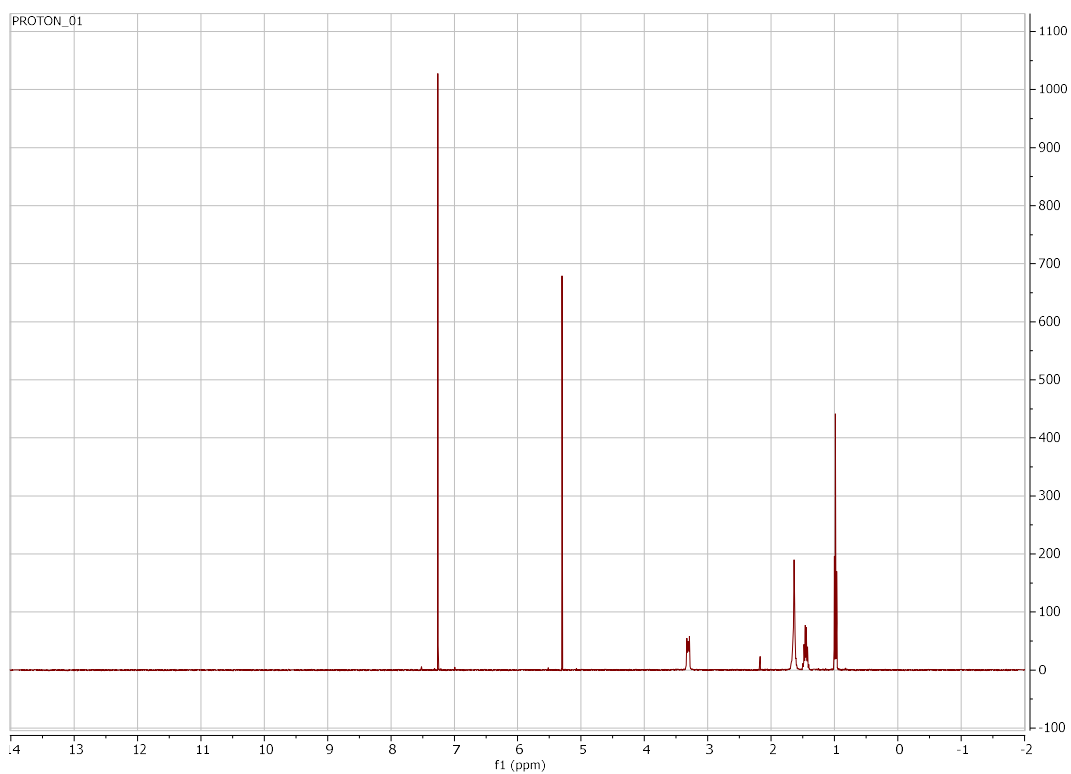
Appendix 1. NMR for benzyl vanillin (2).



Appendix 2. NMR for (2-methoxy-2-oxoethyl)triphenylphosphonium bromide.



Appendix 3. NMR for methyl 3-(4-(benzyloxy)-3-methoxyphenyl)acrylate (3).



Appendix 4. NMR for tetrabutylammonium hydrogensulfate (4).