university of groningen / faculty of science and engineering

Green epoxides and Their Reaction With CO_2 to Produce Cyclic Carbonates

Deniz Pot

University of Groningen

Green epoxides and their reaction with CO_2 to produce cyclic carbonates

BSc Research project

Deniz Pot (s3639525)

To fulfill the requirements for the bachelor degree of Chemical Engineering at the University of Groningen under the supervision of

Giulia Chiarioni
&
Prof. Dr. Paolo P. Pescarmona

Abstract

Starting from four green phenolic derivatives, the synthesis of four novel green cyclic carbonates has been explored. This was achieved through glycidylation of the phenolic derivatives with epichlorohydrin and NaOH which turns them into their respective glycidyl ethers which present an epoxy functionality. The resulting epoxides were then reacted with CO_2 to produce their corresponding cyclic carbonates. The chosen green phenolic derivatives are eugenol, isoeugenol, creosol and vanillyl alcohol. Bedsides vanillyl alcohol, all other substituted phenols were successfully converted fully into their respective glycidyl ethers and characterized with ^{1}H-NMR and ^{13}C-NMR. Complete conversion towards the epoxide was not achieved due to formation of the diol side product. The glycidyl ethers were then reacted with CO_2 in a high-throughput reactor using TBAI (Lewis base) and water (hydrogen bond donor) as catalytic system. The reaction was performed at 80 °C and 10 bar as these conditions were previously found to favor the formation of cyclic carbonates instead of polycarbonates. H-NMR's and FTIR's were used to characterize the products of the reaction for which full conversion of the epoxide and selectivity for the cyclic carbonate were reported. The following product masses and yields were obtained: eugenol cyclic carbonate (5.915g, 81.0%), isoeugenol cyclic carbonate (5.821g, 83.4%), creosol cyclic carbonate (5.316 g, 90.5%), and vanillyl alcohol cyclic carbonate (-). With the exception of the vanillyl alcohol cyclic carbonate, it was possible to successfully separate the TBAI catalyst for the cyclic carbonate samples by letting it precipitate in diethyl ether. Vanillyl alcohol cyclic carbonate this did not dissolve in diethyl ether so a different solvent has to be found in future research. it is also recommended to place the glycidyl ethers for more extended time inside the vacuum oven to ensure removal of all epichlorohydrin.

Acknowledgement

I would first like to thank my daily supervisor Gulia Chiarioni for helping and guiding me throughout the research project. She created a comfortable working environment in which any idea or need for help could be voiced. I also would not have been able to conduct the CO_2 reactor without her help.
I also want to thank the lab supervisors for ensuring safety while carrying out the experiments. Lastly I want to thank Prof. Dr. Paolo P. Pescarmona for providing feedback on how to carry on. He always pushed me to profoundly analyze the results and to make the most out of this interesting thesis topic. Lastly I want to thank the Faculty of Science and Engineering for using their lab spaces, chemicals and the CO_2 reactor.

List of Abbreviations & Nomenclature

Abbreviation	Terminology
FTIR	Fourier-transform infrared spectroscopy
NMR	Nuclear magnetic resonance
EGE	Eugenol glycidyl ether
CGE	Creosol glycidyl ether
IGE	Isoeugenol glycidyl ether
VAGE	Vanillyl alcohol glycidyl ether
ECC	Eugenol cyclic carbonate
CCC	Creosol cyclic carbonate
ICC	Isoeugenol cyclic carbonate
VACC	Vanillyl alcohol cyclic carbonate
NPD	Natural phenolic derivative
PTC	Phase transfer catalyst
HBD	Hydrogen bond donor

Contents

1.0 Introduction

An increase of global atmospheric temperature is one of the biggest threats to human society of the 21st century. An increase in heat waves, heavy precipitation, droughts and extreme weather are already observed and will increase as the temperature continues to rise. Of all greenhouse gasses, CO_2 is by far the biggest driver of the temperature rise and has seen a 47.3% increase in atmospheric levels between 1750-2019.[20] Since a near linear relation exists between atmospheric CO_2 and temperature achieving net-zero is a necessity. There are many mitigation strategies in place with wind and solar energy being the most effective ones. The chemical industry is another high emitting sector contributing a substantial 21% of total CO_2 emissions in the US. [18] Currently, improving mass and energy effiency and switching to non-fossil fuels in the current chemical processes have the most substantial potential in lowering emissions.[20] An upcoming industrial emission mitigation strategy is carbon capture & utilization (CCU). It is a process that will contribute to a human-made carbon cycle through capturing CO_2 from emitted gasses and converting it into valuable products. To further develop the contribution of CCU, this report will explore the cycloaddition reaction between CO_2 and bio-based epoxides yielding either cyclic carbonates or polycarbonates. This thesis will focus exclusively on the synthesis of cyclic carbonates.

Due to the low reactivity of CO_2, only 110 Mt of CO_2 are used as reactants in conversion processes.[19]The problem with CO_2 as a substrate is its high thermodynamic and kinetic stability. Epoxides are high energy substrates due to their ring strain. It is exactly this property that allow them to overcomes the thermodynamic stability of CO_2. In other words, the cyclic carbonate is substantially more stable than its derived epoxide. The kinetic stability can be overcome by using a suitable catalyst to render the cycloaddition. Further challenges in utilizing CO_2 come from the costs of capturing and transporting the gas from its sight of production. This is why the value of the produced product from the captured CO_2 is of great importance. This is what makes cyclic carbonates attractive as, mainly due to its solvent properties, their market share is expected to reach $7,1 Billion in 2030.[32] Polycarbonates are also of increasing value but, due to it being generally more researched, this thesis focusses on maximizing the selectivity towards the cyclic carbonate.

Currently, the main industrial production pathway of developing cyclic carbonates already uses this cycloadditon route. Important industrial advantages are the fact that this process is 100% atom economical and does not require a solvent. Although the utilization of CO_2 increases the greenness of the process, many of the used epoxides are still derived from fossil based starting molecules. Two of the most abundantly produced cyclic carbonates, propylene carbonate and ethylene carbonate, are reliant on propylene and ethylene feeds. A second obstacle in making this process green are the energy requirements. Most cycloadditions still require high temperatures and high CO_2 pressures for viable conversion rates.[23] This raises the energy demand and makes it less commercially viable due to energy costs. These problems increase the demand for bio-based epoxides and catalysts that are both green and active.

The bio-based epoxides that this project aims to convert into cyclic carbonates are derived from natural phenolic derivatives (NPD). The NPD's used in this thesis are eugenol, isoegeunol, vanillyl alcohol and creosol. Both eugenol and isoeugenol can be derived from natural oils and increasingly from lignin depolymerization. Vanillyl alcohol can be derived from vanillin, of which lignin depolymerization already provides 15% of its total production. Lastly, creosol is one of the main component of wood creosote and can also be derived from lignin depolymerization (although in small yields). The epoxidation of the NPD's involves a glycidylation step in which it is reacted with epichlorohydrin, in the presence of an alkyl ammonium phase transfer catalyst, to produce its respective bio-based epoxide. Subsequently, the resulting epoxide goes through cycloaddition, in which the epoxide is reacted with pressurized CO_2 in the presence of a Lewis acid/Lewis base catalytic

system. As an illustrative example, the generalized reaction scheme for this synthetic pathway for phenol is shown in figure 1. The used Epichlorohydrin is considered green as it can be synthesized from glycerol which is a waste product in the production of biofuel. It is already produced in this way by several companies such as Solvay using the Epicerol® process.[4] However, epichlorohydrin is not an ideal green reagent as hydrochloric acid is used as a chlorine source for tis production; a known pollutant.

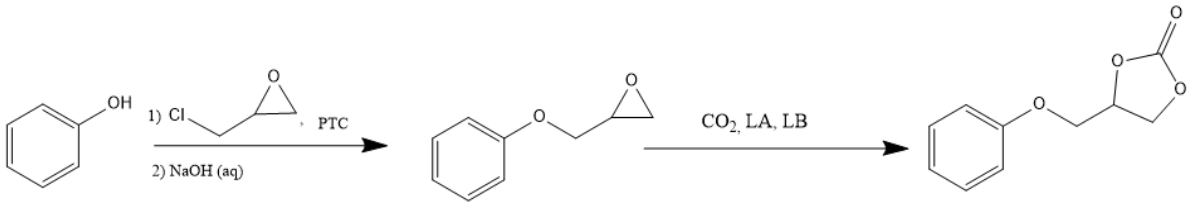


Figure 1: Example reaction scheme illustrating the glycidylation and cycloaddition step

The motivation for this specific aim comes from the gaps in research literature with respect to the conversion of NPD's into their respective cyclic carbonate. Independently, both the glycidylation and the cycloaddition step are well researched fields. However, the use of NPD's as starting materials, and to combine both steps is not. Papers exists, but are often limited to the glycidylation of the NPD's and don't involve the subsequent CO_2 cycloaddition. Instead, much of the research available in this area focusses on polymerizing the resulting bio-based epoxide into epoxy polymers.[22] This thesis intends to fill this gap through synthesizing novel aromatic cyclic carbonates from NPD's while maximizing the greenness of the process.

To fulfill this aim, both the glycidylation and cycloaddition reaction for each NPD were experimentally conducted. A catalytic system consisting of Tetrabutylammonium iodide (Bu_4NI) as the Lewis base and water as the Lewis acid was chosen to perform their cycloaddition with CO_2. Both the NPD's and epoxides conversion into their desired product (glycidyl ether and cyclic carbonate respectively) were calculated using ^{1}H-NMR and ^{13}C-NMR. The selectivity towards cyclic carbonates for the cycloaddition reaction was determined through FTIR.

2.0 Theory and Literature

This section will discuss and explain the most essential concepts behind the synthetic pathway. It will also talk through the literature and, when relevant, the industrial context behind it.

2.1 Glycidylation reactions

In order to make the synthetic route of aromatic cyclic carbonate green it must be ensured that the used epoxides are bio-based. A green epoxide that has already seen promising results when undergoing cycloaddition with CO_2 is epichlorohydrin itself.[24] Due to the electron-withdrawing chlorine, it facilitates the nucleophilic ring opening during the cycloaddition reaction. In the lab, this translates into a shorter reaction time making it a useful substrate for research. However, plentiful research on the cycloaddition of epichlorohydrin with CO_2 already exists.[1,24] Through glycidylation, epichlorohydrin can be easily turned into a wide range of aromatic epoxides. This reaction takes advantage of epichlorohydrine's chlorine atom, making it sensitive to nucleophilic attacks. In the presence of an alkyl ammonium phase transfer catalyst (PTC) and sodium hydroxide there are two plausible glycidylation mechanisms that are in competition with eachother.[2] Figure 2 and 3 shows both mechanisms using the conducted glycidylation of eugenol (section 3.1) experiment as an example.

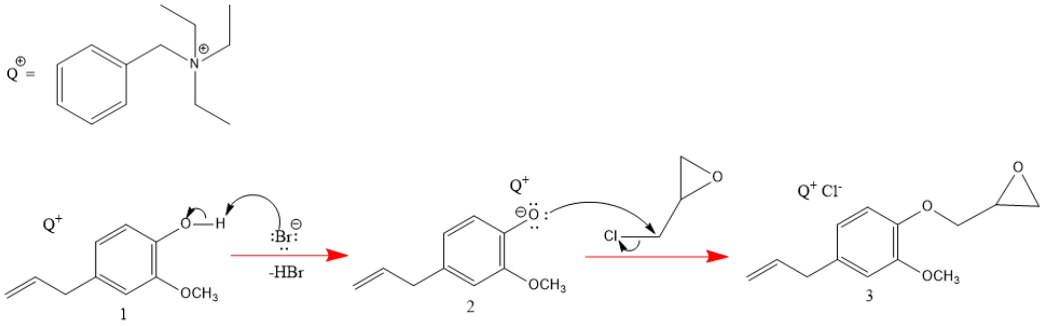


Figure 2: mechanism A of the glycidylation reaction. QBr represents the benzyltriethylammonium bromide PTC that was used in the experiments

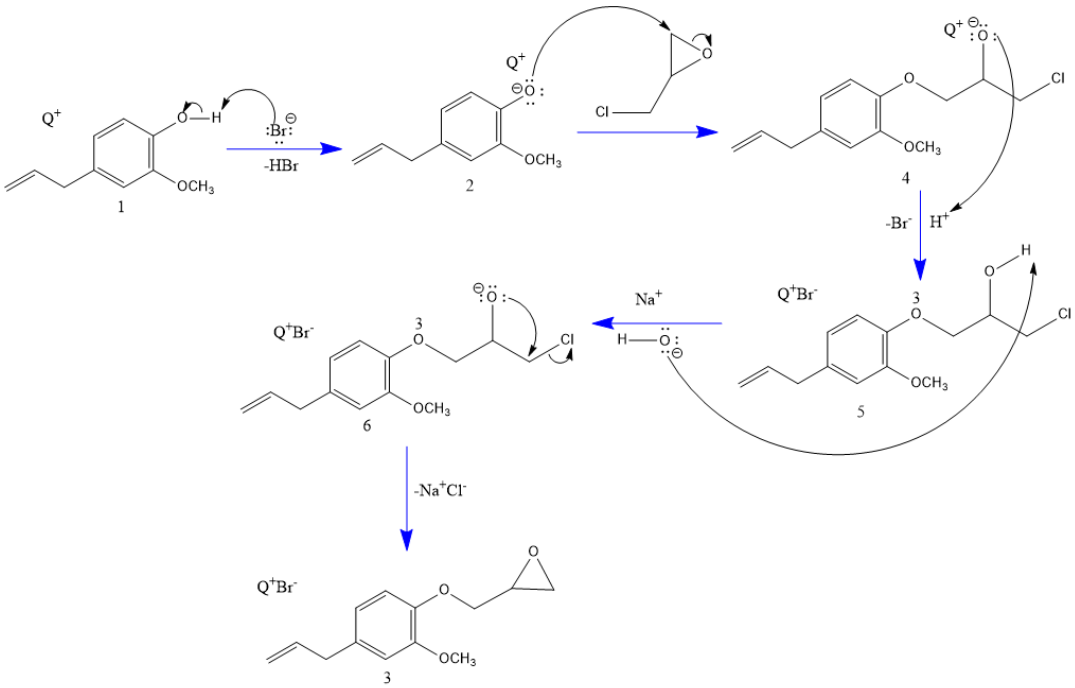


Figure 3: mechanism B of the glycidylation reaction

In both mechanisms, the PTC solubilizes the inorganic bromide ion in the epichlorohydrin (reactive solvent). This allows the bromide to act as a base and deprotonate the eugenol. The PTC used is benzyltriethylammonium bromide but other similar compounds such as benzyltrimethylammonium chloride can be used.[3] In mechanism A, the created phenolate ion attacks the epiclorohydrin directly with the simultaneous cleavage of the C-Cl bond. Because the phenolate ion is a strong nucleophile, and the chlorine is a good leaving group, this exemplifies a typical S_N2 mechanism. The product is the desired eugenol glycidyl ether (EGE). In mechanism B, the phenolate ion causes cyclic opening (4). In the absence of sodium hydroxide, the EGE is formed through subsequent ring closing (S_N1). Most of intermediate 4 is, however, protonated by the previously formed strong hydrobromic acid. The hydroxide group from the sodium hydroxide increases the S_N1 ring closing by reforming intermediate 4. The PTC and sodium chloride will be present as waste products in the final product mixture.

Glycidylation has the disadvantage of several side products. The most significant ones are the chlorinated and the diol derivatives. Figure 4 shows the possible side-product the glycidylation of eugenol could yield.

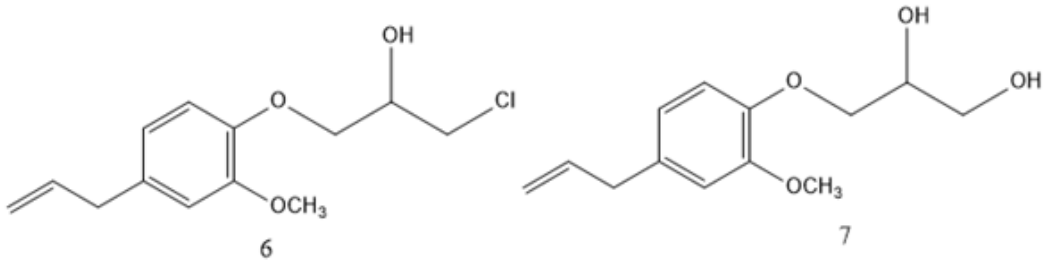


Figure 4: The chlorinated and diol derivatives of eugenol glycidylation

2.1.1 Eugenol

Eugenol is bio-based because it can be extracted from natural oils and lignin depolymerization. At present the majority of eugenol comes from producing clove oil from Indonesia and Thailand. However its production is likely to shift as lignin depolymerization as the technology improves, as this eliminates the need for specific climate conditions. Since lignin is such an abundant natural polymer the market price for Eugenol can be expected to decrease over time. This makes Eugenol not only green but also a cheap chemical. To get a significant yield of green eugenol from lignin research shows that ionic-liquid pretreatment works best. A recent study shows the 2.5g of eugenol was produced per kg of low sulfonate lignin.[5] However, the research on optimal lignin polymerization is still in its initial stages and this yield is likely to improve.

Some papers have already been published on the glycidylation of eugenol into EGE.[30] Not a single paper was found on the subsequent conversion of EGE into its respective cylic carbonate. Hence, choosing eugenol as one of the starting NPD will contribute to this research field. The reaction scheme of its glycidylation can be seen in figure 5

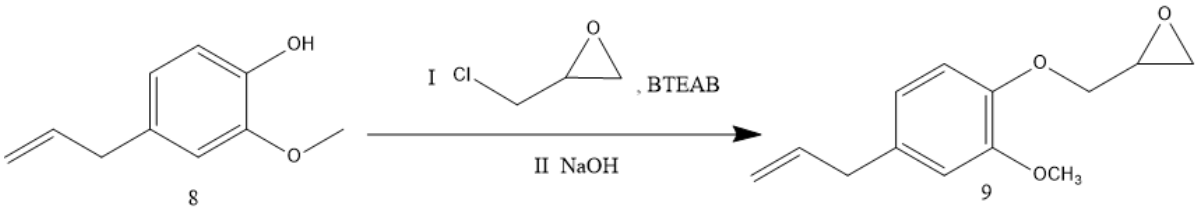


Figure 5: Glycidylation reaction scheme of eugenol

Possible side-products are the usual chlorinated and diol form of the glycidyl ether. The H-NMR result analysis includes checking whether these are formed.

2.1.2 Vanillyl alcohol

One of the only aromatics produced from lignin on an industrial scale is vanillin, which is one of the most important commercial flavor's. Although 85% of the vanillin is derived from petroleum, it can also be produced from lignin which accounts for 15% of the overall production.[25] This is done through oxidation of kraft-ligning or lignosulfonate. This technology too is likely to improve as the current technology is unselective and has a low vanillin yield. An example of such an improvement is the vanillin selective oxidation done in a phenol media with γ-Al_2O_3 supported RO_X particles. This process already shows a 95% selectivity and a 7.4 lignin wt% vanillin yield.[6]

The direct glycidylation of vanillin itself is not well documented in scientific literature. This is likely due to its reactive aldehyde group making it prone to side reactions. Instead research has focused on using vanillin derivatives.[33] One of these is known as vanillyl alcohol and its general reaction scheme used is shown in figure 6. Vanillyl alcohol can be readily prepared from the bio-based vanillin through reducing the aldehyde group. This ensures that the synthetic route is still bio-based. Like eugenol, a paper was found in which the two alcohol groups of the vanillyl alcohol were converted into epoxy rings.[31] No research has however been conducted on turning the vanillin-derived epoxy resin into a cyclic carbonate. Synthesizing this compound and determining its properties could therefore be of interest.

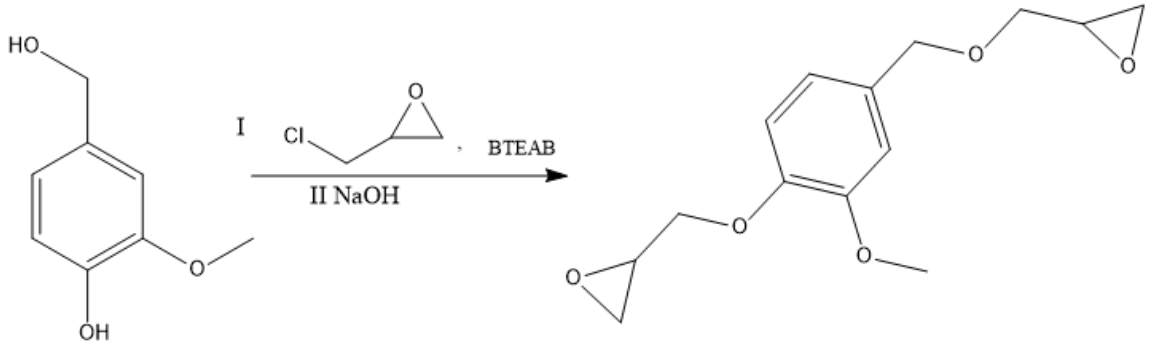


Figure 6: Glycidylation of vanillyl alcohol

2.1.3 Creosol

Another natural phenol derivative is creosol. Although it is not directly extracted from natural sources it is the main component of wood creosote. Creosote is a viscous oil that can either be derived from coal or wood pyrolysis. As industry is gradually moving away from coal it can be expected that creosote production is going to shift from oil to wood. In fact, the primary use of creosote is for wood preservation. Creosol the main components in wood creosote along with other natural phenols. The composition depends on the type of wood, but in typical beech-creosote it holds a 35% weight percentage.[21] Wood is becoming increasingly used as a sustainable material for building materials which will cause an increase in the need for wood preservatives. Creosol will therefore be an increasingly abundant natural feedstock. No published research paper is available on either the glycidylation of creosol nor its subsequent cycloaddition making it an interesting and relevant experiment. The reaction scheme is depicted in figure 7

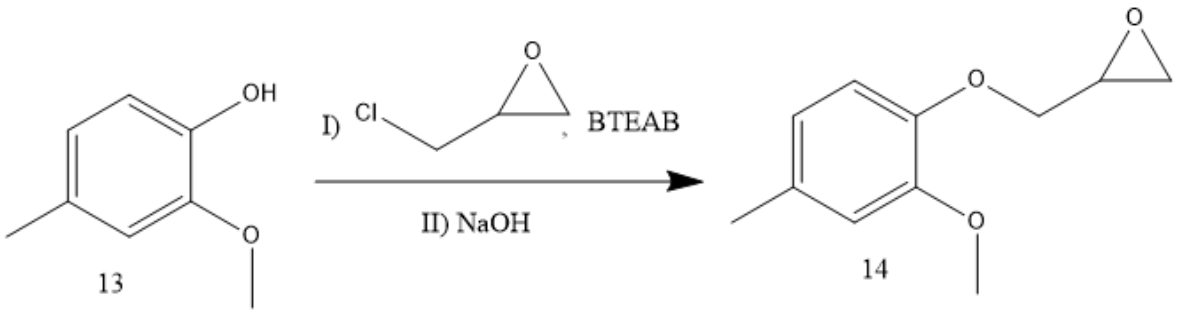


Figure 7: Glycidylation reaction scheme for creosol

2.1.4 Isoeugenol

Another NPD that has been converted is isoeugenol. This compound is a structural isomer of eugenol. The only difference is the location of the double bond. On industrial scale it is produced by isomerizing eugenol using a ruthenium catalyst reaching near 100% conversion rates.[34] Since eugenol is extracted from clove oil, the production for isoeugenol remains bio-based. Only one published reports has demonstrated isoeugenol's conversion into its glycidyl product, but it did not subsequently react it with CO_2.[35] Isoeugenol and eugenol have different physical and chemical properties so producing its respective cyclic carbonate is not redundant. The general reaction scheme of its glycidylation shown in figure 8. Note that commercially used isoeugenol is a mix between the trans and cis isomer. Due to increased thermodynamic stability the trans-isomer dominates.

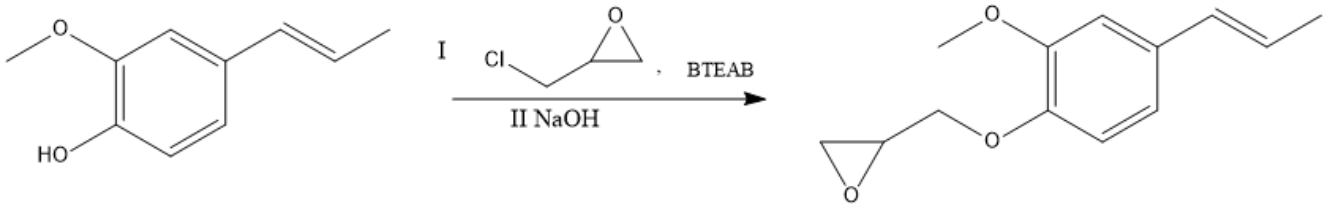


Figure 8: Glycidylation reaction scheme for isoeugenol

2.2 Cyclic carbonates

The commercialization for cyclic carbonates started in the 1950's due to its many applications. Out of many things it is most often used as solvent, electrolyte in lithium batteries and as reactants. Due to the polarity of cyclic carbonates, it makes a great aprotic polar solvent. With the *12 principles of green chemistry* gaining increasing importance they also make for a good substitution for the conventionally used toxic polar aprotic solvents such as dimethyl sulphoxide (DMSO) and acetonitrile. The reason cyclic carbonates are great solvents is because they have large dipolar moments, are generally liquids at room temperature, and are odorless and transparent. As a green solvent, the most used cyclic carbonate is propylene carbonate. Not all cyclic carbonates adhere to these properties. For example, the second most produced cyclic carbonate is ethylene carbonate, which is a solid a room temperature. However, ethylene carbonate is often utilized as an important electrolyte component in lithium batteries. Cyclic carbonates are also increasingly used for a wide range of synthetic routes. One with great potential is the formation of carbamate's and urethanes from the aminolysis of cyclic carbonates.[7] This is in ecofriendly alternative as carbamate's are conventionally synthesized with highly toxic reactants such as phosgene or isocyanate with an alcohol. Alkylated cyclic carbonates are also used to alkylate for aromatic phenols, amines and thiols.[7]

Although the industrial production of cyclic carbonates involves the use of supercritical CO_2 it is not a fully green process. This is because they often stem from epoxides produced from fossil based reactants. For example, the epoxide used for the production of propylene is propylene oxide which is produced from the oxidation of propylene. This keeps the production of cyclic carbonates dependent on the fossil industry. Hence, there is still a great need for synthesizing novel cyclic carbonates that start from green substrates. This research will help fill this void by creating cyclic carbonates with aromatic side groups. Not only are the applications and properties of these novel compounds of interest, but due to the used synthetic route they will also be green compounds.

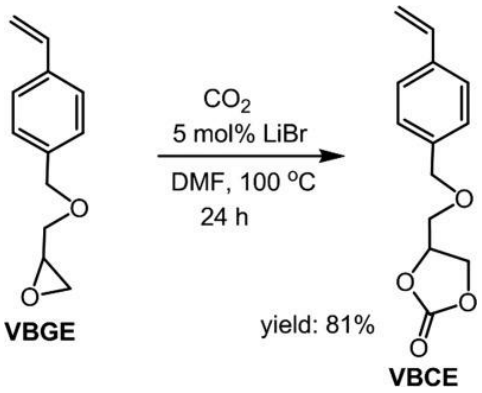


Figure 9: Example of aromatic cyclic carbonate

There are however a limited number of research papers that added aromatic rings to cyclic carbonates. This paper managed to include a styrene monomer to an epoxide which was covered into a cyclic carbonate using CO_2.[9] When polymerized the properties were quite different than regular polystyrene. For example, due to the addition of the large aromatic ring the T_g dropped significantly due to the large free volume around the main chain.

None of the glycidyl ethers synthesized in this research have been turned into their cyclic carbonates. The only comprehensive study found tested various glycidyl ethers for their conversion into cyclic carbonates.[8] However these were all linear glycidyl ethers which are not synthesized through a green method.

2.2.1 Reaction mechanism and selectivity

The reaction of CO_2 with epoxides can result in two possible products: cyclic carbonates or polycarbonates. This is because there are two possible mechanisms that couple the CO_2 with the epoxide. However, with the chosen conditions (see 2.2.3) the synthesis of polycarbonate has not been reported before. Figure 10 shows the reaction mechanism concerning only cyclic carbonate formation.[37] Initially, the epoxide is activated through coordination of the Lewis acid forming an intermolecular bond with the oxygen. This then lowers the activation energy required for a ring opening nucleophilic attack by a Lewis base. The formed alkoxide then performs a nucleophilic attack on the CO_2 resulting in its incorporation. What follows determines the selectivity between the cyclic carbonate and the polycarbonate. Either the carbonate goes through an intramolecular S_N2 ring closure occurs forming the cyclic carbonate, or the carbonate goes on to propagate with surrounding epoxides and CO_2 to form polycarbonate.

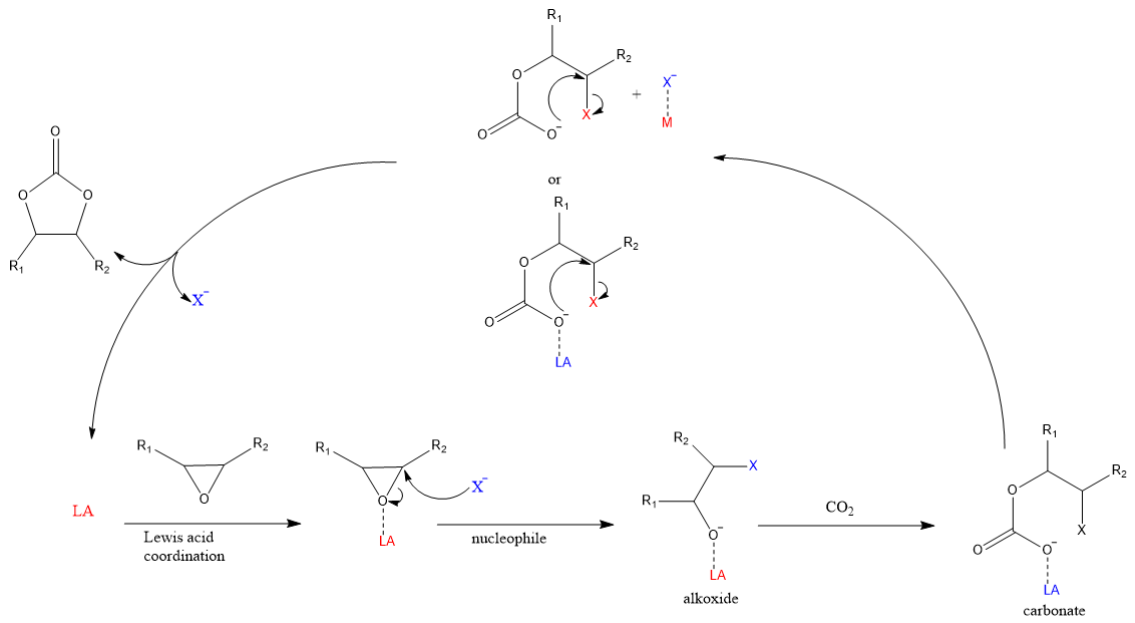


Figure 10: Cyclic carbonate reaction mechanism.[37]

The selectivity between is dependent on a few key variables. Most important is the catalyst used, the reaction conditions and the nature of the epoxide. As far as the catalyst goes, literature shows that the use of metal-free organocatalysts in combination with hydrogen bond donors (HBD) as Lewis acids are selective towards the cyclic carbonate.[27] The most extensively studies group of catalysts are, however, the homogenous metal catalysts. The use of metal complexes to coordinate the oxygen allows selectivity towards both products depending on other variables. One of these other variables is nature of the Lewis base which serves as the nucleophile. The intramolecular S_N2 ring closure for the cyclic carbonate is favored when the nucleophile is a good leaving group. Further selectivity for the cyclic carbonate is achieved by using an excess of nucleophile relative to the Lewis acid. This is because the nucleophile has the ability to displace the carbonate intermediate making it more prone to ring closure.

The epoxide itself also influences selectivity, mainly due to potential steric hindrance during ring closure. However, since all epoxides synthesized are terminal there should be no major geometric strain during the formation of their respective cyclic carbonates. One study found that the electron-withdrawing effect of the phenyl group of styrene oxide promotes cyclic carbonate formation.[38] All glycidyl products used in this research also have electron-withdrawing groups which promote cyclic carbonate selectivity. Lastly the selectivity is also influenced by the pressure of the CO_2 and temperature. The cyclic carbonate is more energetically stable than the polycarbonate making it the thermodynamic product. The polycarbonate requires a lower activation energy making it the kinetic product. In general, to synthesize the cyclic carbonate temperatures higher than 100 ℃ are used.[27] For cyclic carbonate selectivity the CO_2 pressure is kept low enough to prevent polymer growth and dilution of the reaction mixture while maintaining a sufficient rate of CO_2 insertion rate. Hence both the yield and selectivity of the cyclic carbonate are dependent on the reaction conditions.

2.2.3 Chosen catalyst system and reaction conditions

For industrial viability, it is important to ensure a high selectivity and yield for the cyclic carbonate. In principle using only a Lewis base can catalyze epoxide cycloadditions with CO_2, but the addition of a coordinating Lewis acid increases the reaction rate considerably.[23] The used catalyst system can be either be homogenous or heterogenous, the former being more active but harder to separate. Homogenous systems consist mainly of organocatalysts, metal salts and organometallic catalysts. Either the systems are bifunctional, or the Lewis acid and Lewis base are separate components. Generally, metal-free organic catalysts are more selective for the cyclic carbonate than metal complexes.[11] A considerable amount of research have tested multiple heterogeneous catalysts such a basic metal oxides, smectites, polymers, zeolites and recently metal organic frameworks (MOF).[15,16,17]. Although showing easy separation, most of these catalysts show relatively low activity and need relatively high temperatures for acceptable yields. They are also generally more expensive and harder to synthetize compared to, for example, metal-free organocatalysts. Hence, this research will focus on homogenous catalysts instead.

To adhere to the green principle's, it is important that this research uses a catalyst that is non-toxic and reusable. A new class of catalysts that is widely studied in this respect are binary catalytic systems consisting of an organic halide as the Lewis base and a hydrogen bond donor (HBD) as Lewis acid. Generally, the hydroxyl moiety of HBD's are less effective in coordinating the epoxy oxygen than metal complexes. Therefor it is important to consider the type of HBD used as a wide range of activity has been observed.[12] Halide salts such as Tetrabutyl-ammonium iodide (Bu_4NI) in combination with HBD's has shown to give high selectivity for the cyclic carbonate[13]. One study shows that using it in combination with water as the HBD full conversion of 1,2-epoxyhexane with 100% selectivity towards the cyclic carbonate was reached at a mild 60 ℃ and 10bar.[14] Since Bu_4NI precipitates in diethyl ether it is also easy to separate and recycle it on industrial scale.

This research could discover if this catalytic system shows similar activity for the glycidyl ethers derived from the chosen NPD's. Their respective reaction scheme can be seen in figure 11. The mild conditions combined with the low price and relative low toxicity of using a Bu_4NI/ H_2O catalyst system make it of interest for industrial upscaling. As mentioned before, to increase selectivity for the cyclic carbonate it is important to work at higher temperatures and low CO_2 pressure and use a high Lewis base:Lewis acid ratio. This is why the reaction is performed at 10 bar and 80℃.

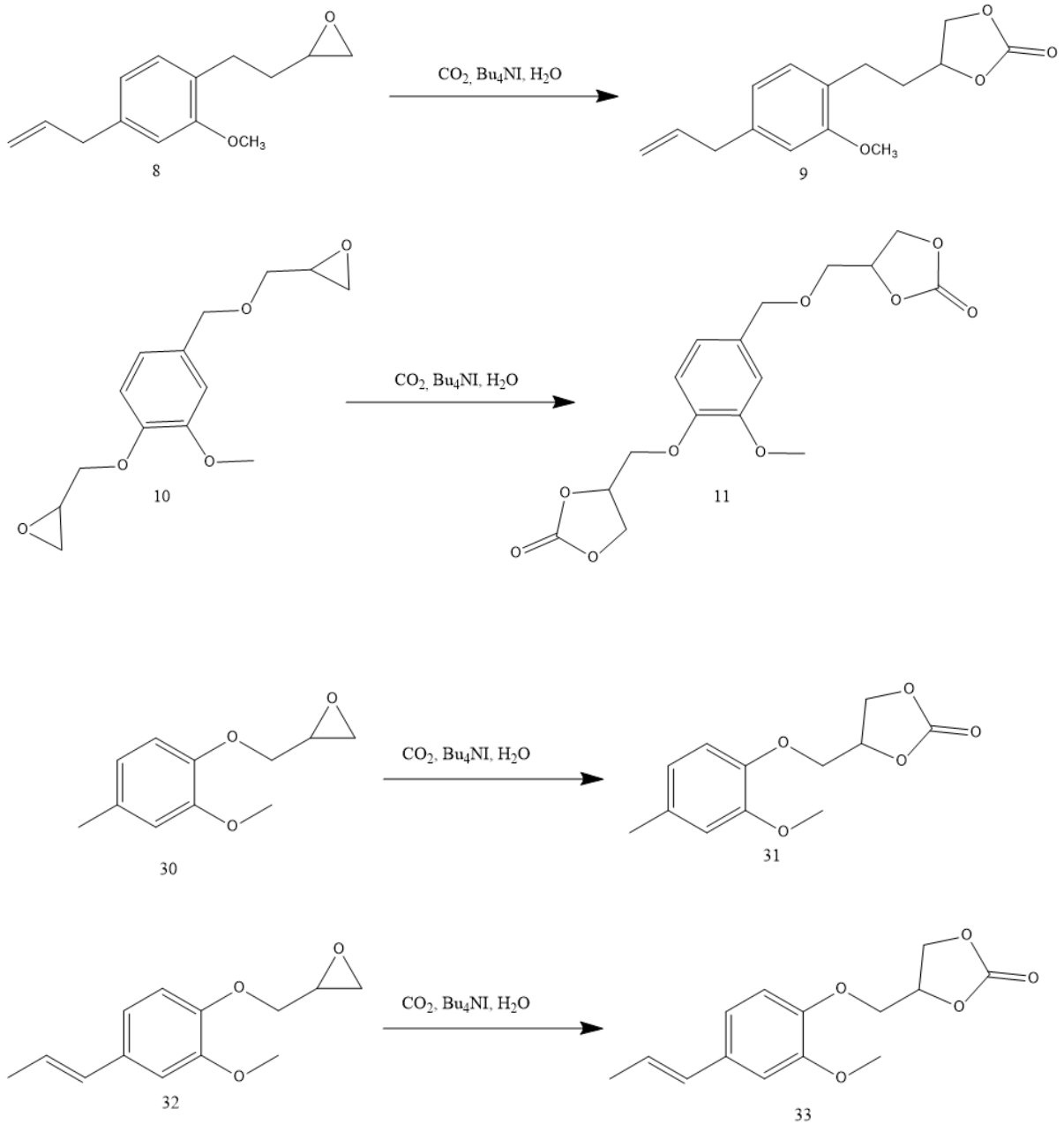


Figure 11: Cycloaddition reaction for all glycidyl ethers synthesized

3.0 Experimental

This section explains the materials and method used for the first step (glycidylation of chosen NPD's) and second step (reaction of the glycidyl ethers wit CO_2). The materials for both steps, and additional purification, are laid out in table 1. This followed by the experimental methods used to synthesize both the glycidyl ethers (section 3.2), cyclic carbonates (section 3.3) and how the cyclic carbonates were purified (section 3.4)

3.1 Materials

For 3.2	For 3.3	For 3.4
• NPD (120 mmol, 1 eq) • benzyl triethylammonium bromide (3.26g, 12mmol, 0.1eq) • Epichlorohydrin (118.43g. 1.2 mol, 10eq) • 40 wt% NaOH solution (42.30g, 426mmol, 3.5eq) • Chloroform (400mL) • Ethyl acetate (400mL) • Brine (200mL) • Buchner Funnel • Seperation funnel (500 mL) • Rotary evaporator	• 4x Vial (46mL, 30 mm external diameter) • 20 mmol epoxide • Bu_4NI (3mol% with respect to epoxide) • mesitylene (1.5mmol) • deionized water (0.05mL) • 10-block reactor	• 200 mL beaker • 100 mL diethyl ether • Buchner funnel • Rotary evaporator

Table 1: Materials for glycidylation (3.1.2), cycloaddition (3.2) and purification (3.2.1)

3.2 Glycidylation method

The first step involves the reaction between the chosen NPD, epichlorohydrin and NaOH in the presence of the PTC benzyltriethylammonium bromide. The procedure is roughly the same as the documented glycidylation procedure from a published paper.[36]

3.2.1 Synthesis of eugenol, isoeugenol and creosol glycidiyl ether

The NPD (120 mmol, 1 eq), benzyltriethylammonium bromide (12 mmol, 0.1 eq, 3.26g) and epichlorohydrin (1.2 mol, 10 eq, 100.36mL) were added to a three-necked flask. This mixture is heated to 80℃ for 5hr using a stirrer hotplate. The temperature of the reaction mixture is followed by a thermometer. The NaOH solution (426 mmol, 3.5eq, 42.6g) is added to the flask and the mixture is left to react for one more hour at 80℃. The NaOH solution can be prepared by mixing 40g NaOH with 60mL water. The product mixture was left to cool to room temperature. A Buchner funnel was used to filter the NaCl salts formed during the reaction. The mixture was put into a separating funnel. 200mL of Ethyl acetate and distilled water were added after which the organic and aqueous layers were separated. The aqueous layer was extracted three times with the remaining ethyl acetate. The organic mixtures were combined and rinsed with brine. MgSO4 is added to get the last bits of water out of the organic mixture. Ethyl acetate and most excess epichlorohydrin were removed using rotary evaporation. The remaining epichlorohydrin was removed in a vacuum oven running at 110℃ for 24 hours . Due to unavailability, isoeugenol and creosol glycidyl ether were not put in the oven and some remaining epichlorohydrin is expected. All four glycidyl ethers were collected as a yellow liquid. Both a ^{1}H-NMR and ^{13}C-NMR were taken to analyze the reaction mixture.

3.2 Synthesis of vanilyl alcohol glycidyl ether

This synthesis was done the same way as for the eugenol glycidyl ether (4.1.2). Important to note is that the initial vanillyl alcohol, benzyltriethylammonium bromide and epichlorohydrin mixture was not kept at a constant 80℃ by mistake. This was caused by the evaporation of most of the water in the water bath upon return to the lab. Hence, when using a smaller water bath it is important to refill with hot water to ensure thermal equilibrium for the reaction mixture is remained.

3.3 CO_2 cycloaddition procedure

For each glycidyl ether, a vial (46mL, 30 mm external diameter) was equipped with 20 mmol of the epoxide, Bu_4NI (3mol% with respect to epoxide), deionized water (0.05mL), and mesitylene (1.5mmol). The CO_2 can enter the vials through two needles going through a silicone/polytetrafluoroethylene septum that is closing the vials. The vials were put inside the 10-reactor block and were closed according to given procedure. The temperature and reaction temperature in the reactor were controlled with a computer program. The P_{CO_2} was increased to near the desired pressure after which the reactor is heated up to desired temperature. The P_{CO_2} was then adjusted to the desired pressure. When the chosen reaction condition was reached, the reactor was kept stirring for 24 hours. At that point, the reactor was cooled to room temperature and depressurized to 1 bar using the program. The vials were the removed from the reactor and ^{1}H-NMR and FTIR samples were taken.

3.4 Cyclic carbonate purification procedure

In none of the crude cyclic carbonate products a significant amount of diol was found that would require its removal. This is according to the previously taken ^{1}H-NMR and FTIR. To remove the catalyst the inside of the vials were emptied in 200 mL beakers and filled with 100mL diethyl ether. This was stirred for one hour after which white precipitation was observed. The vanillyl alcohol cyclic carbonate (VACC) did not dissolve in the diethyl ether and another solvent needs to be used in the future. The white precipitate (catalyst) is removed through filtering using a Buchner funnel. This procedure is repeated twice. Finally the diethyl ether is removed using the rotovap. A ^{1}H-NMR and ^{13}C-NMR were taken.

4.0 Results and Discussion

The first step was to synthesize the glycidyl ethers from epichlorohydrin and the chosen NPD's. Important is that these epoxides are first properly characterized through ^{1}H-NMR and ^{13}C-NMR (section 4.1) before continuing with the second step in which they are reacted with CO_2. Not only does the purity of the glycidyl ether has an effect on the reaction rate but side products could interfere with the cycloaddition reaction. First off, the used PTC ''benzyltriethylammonium bromide'' can serve as a second organohalide Lewis Base catalyst if found in significant amounts. It is also important to know if any diol has formed as this can serve as a HBD competing with H_2O during the cycloaddition reaction. The second step was the cycloaddition reaction with CO_2 for each glycidyl ether. Both H-NMR's and FTIR's were taken to fully analyze the achieved products (see section 4.2). FTIRs were taken from the crude cyclic carbonate products to confirm the production of cyclic carbonates and determine if there was significant diol formation. If the latter was the case, an extra purification step would have been required to remove the diol.

4.1 ^{1}H-NMR and ^{13}C-NMR analysis of glycidyl ethers

The ^{1}H-NMR and ^{13}C-NMR spectra's in the following section have characterized all synthesized glycidyl ethers (see figure 12,14,15,17,18,19,21,22). The only exception is that the primary alcohol of vanillyl alcohol was only converted 39% (see figure 18). The analysis was done though labelling the signals in the spectra's to the different moieties in the glycidyl ethers. Certain moieties such as that of the oxirane, benzyl ring and methoxy side group remained approximately constant with respect to their produced signal which simplified the analysis. The benzyl side group for eugenol, isoeugenol, creosol and vanillyl alcohol are of course different and analyzed separately. The spectra's also confirm significant epichlorohydrin traces and the formation of the diol side product. Epichlorohydrin was characterized with the help of predicted spectra's from *MestReNova* and through overlapping the remaining non-characterizable signals from the spectra's of each glycidyl ether product (see figure 13). The diols were characterized in section 4.2 with the help of the spectra's of the cyclic carbonates.

4.1.1 Creosol glycidyl ether (CGE)

^{1}H-NMR

In figure 12, the ^{1}H-NMR shows the signals that belong to Creosol. The most upfield peak is that from the methyl group at 2.27ppm. The peaks inbetween 2.65 and 3.37 ppm are the typical peaks of the oxirane moeities. The two H14 protons cannot rottate freely due to the oxirane ring. A triplet is seen at 2.87 ppm and a doublet of doublet at 2.72 ppm. One of the H14 protons is centered inbetween the other H14 proton and the H12 proton. Due to the symmetry, the coupling constant between from these two are equal producing the triplet. The other H14 proton is further away from the H12 proton. Due to the unsymmetry, unequal coupling constant with respect to its coupling with the H12 proton and with the other H14 proton are formed which explains the doublet of doublet. The singlet at 3.82 ppm shows the typical singlet singal of the methoxy attached to the benzene ring. The alkyl protons (H11) also couple to eachother and independetly to the H12 proton. This then forms the two doublet of doublet seen (3.96 and 4.18 ppm). The reason for their lack of symmetry also lies in the fact that they can't rotate freely because C12 is attached to two bulky groups. The multiplet at 6,67 ppm are from the protons of H6 and H4. Their signals are expected further upfield than that of the signal from the aromatic H1 proton (6.80 ppm) since they are next to electron withdrawing alkoxy groups.

The yet unassigned peaks can be explained by epichlorohydrin impurties that were not evaporated off (see bottom of figure 12) and diol side product. To confirm that some of these peaks correspond to epichlorhydyrin, the H-NMR's of all glycidyl products and epichlorohydrin were stacked (see figure 13). Epichlorohydrin's protons A,B,C and D should produce signals overlapping in all four spectra's. This is indeed the case. All four of these can be found in the spectra of each synthesized glycidyl ether. The proton "C" overlaps with the signal of one of the oxirane protons so can't be seen. Another argument for why these peaks belong to epichlorohyrine is that it explains why they are the biggest in the creosol glycidyl ether. Along with isoeugenol glycidyl ether it was not put in the vacuum oven so a bigger trace of epichlorohydrin is expected. ^{13}C-NMR further confirmed epichlorohdyrine traces.

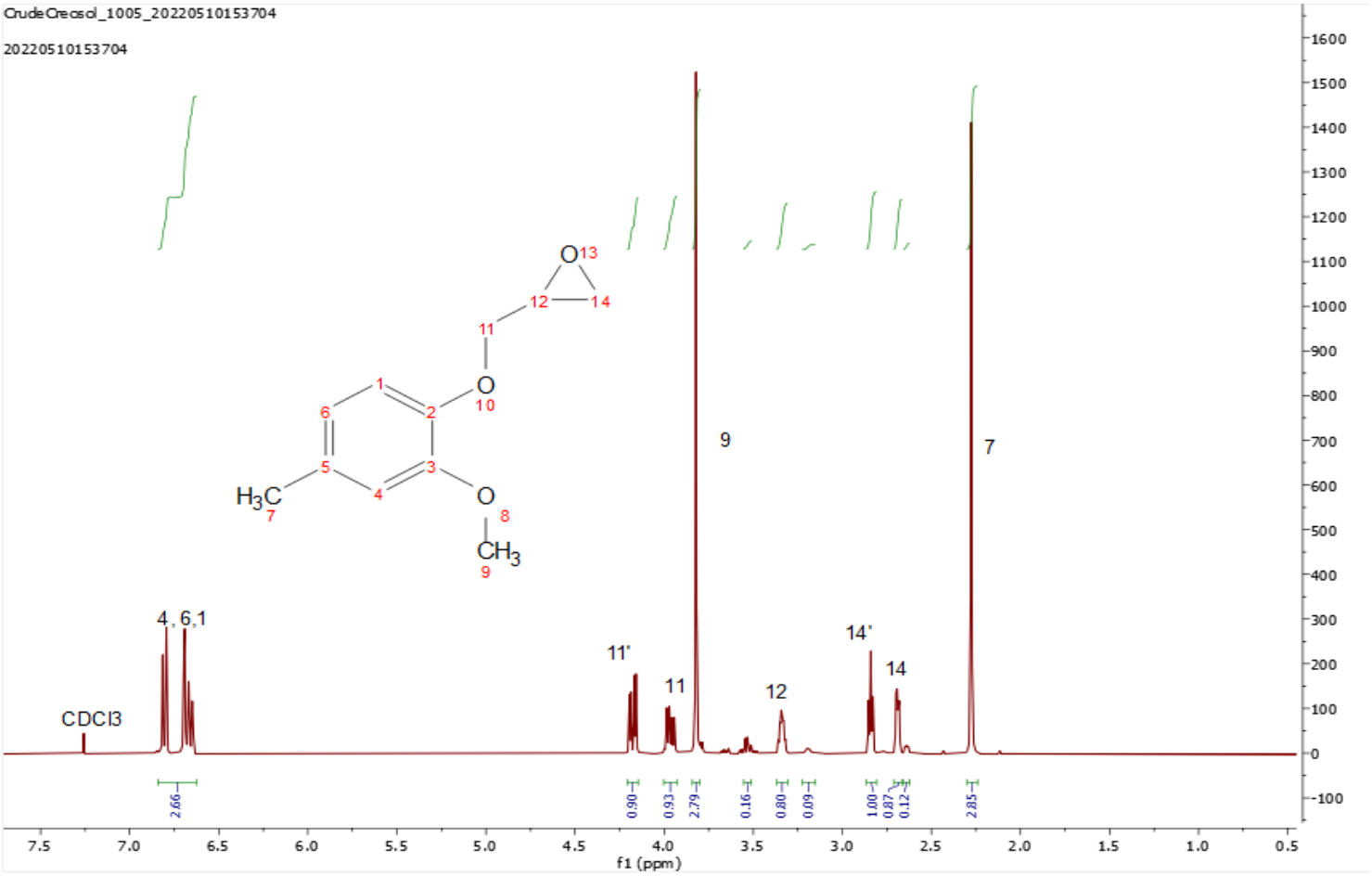
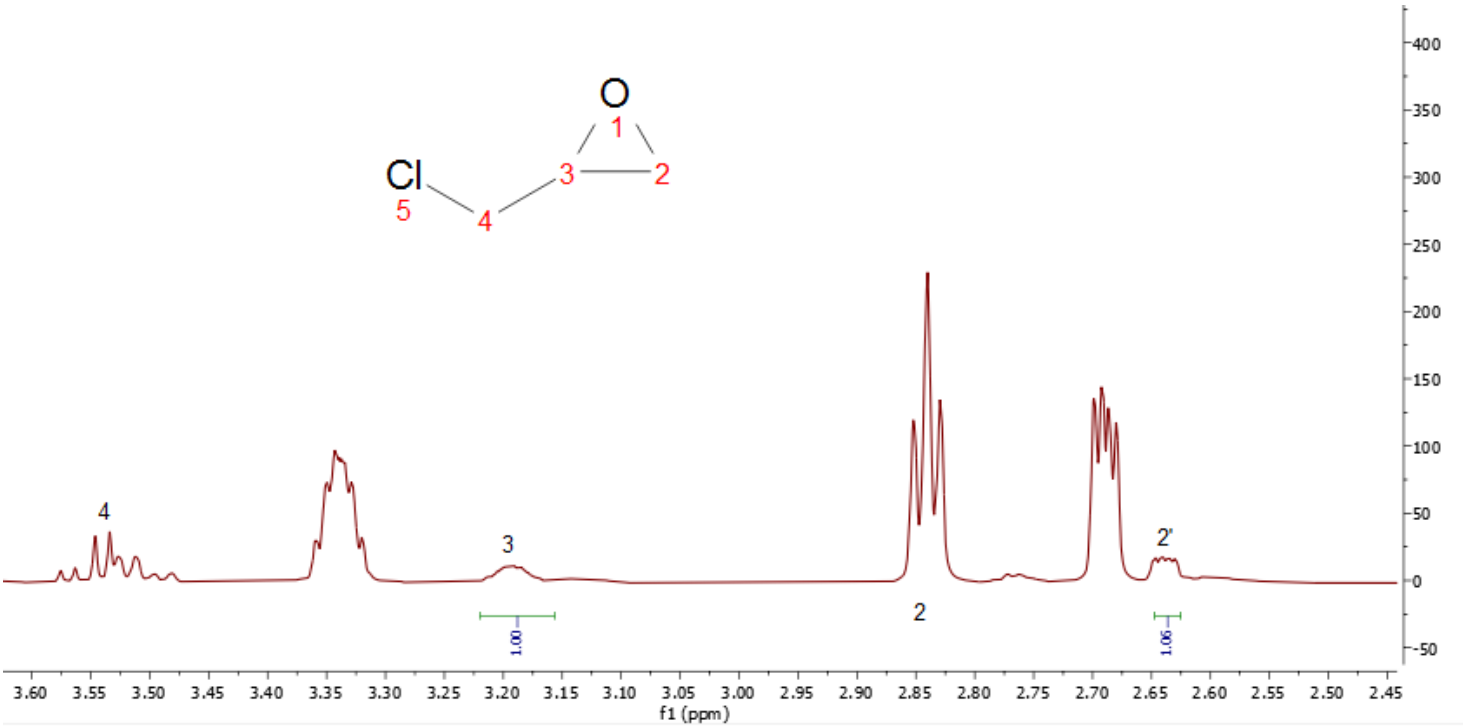


Figure 12: 1H-NMR spectra of creosol glycidyl ether. Left picture shows the main product peaks. Right picture shows a zoomed in fragment to display the epichlorohydrin impurity peaks



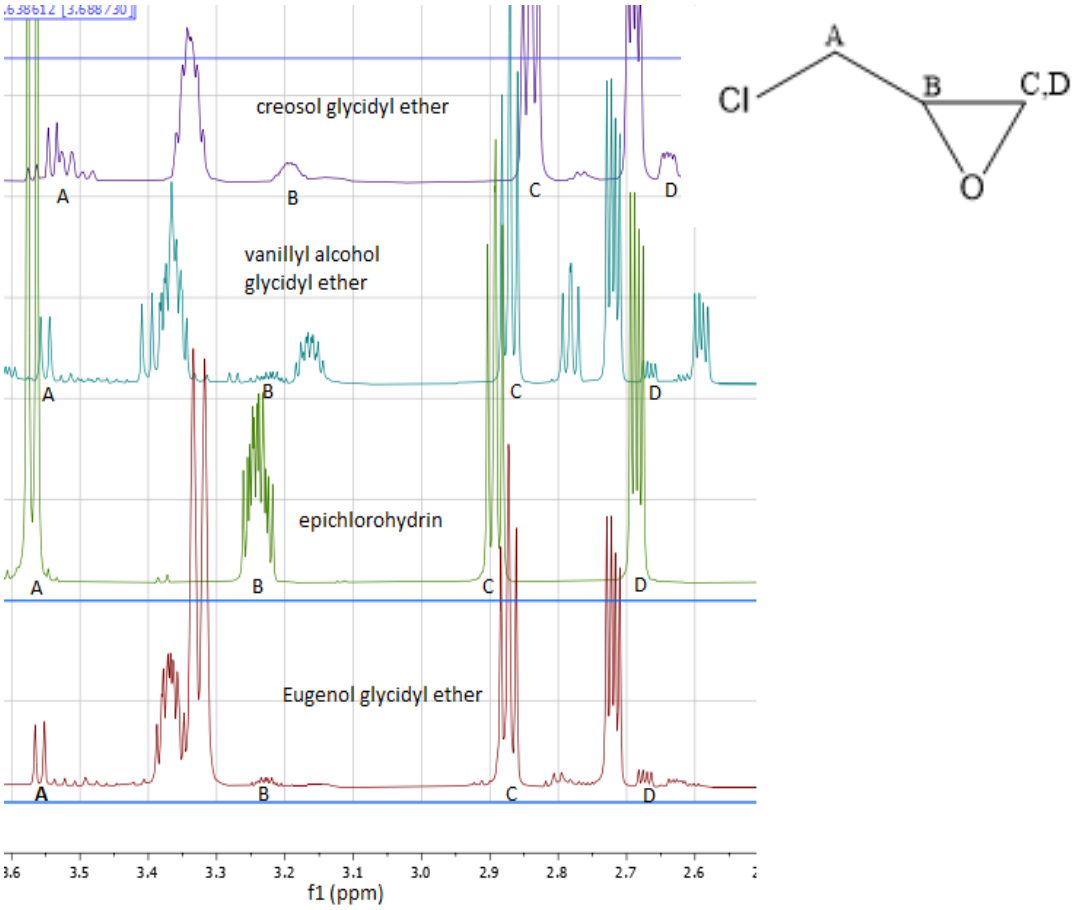


Figure 13: Epichlorohydrine peaks in all glycidyl ether products

Note, the epichlorohydrin peaks are present in every spectra, so won't be analysed seperately in the other ^{1}H-NMR spectra's. Table 2 shows the percentage of epichlorohydrin impurity (see 4.2.1 for method used). It is clear to see that the vacuum oven is necessary to get more epichlorohydrin out. Traces of the diol can also be found but this will be elaborated on later in the results section.

	% epichlorohydrine impurity	% diol
Creosol glicidyl ether	12	2.1
Vanilyl alcohol glycidyl ether (oven)	3.0	3,6
Eugenol glycidyl ether (oven)	7.0	7.3
Isoeugenol glycidyl ether	16	7.6

Table 2: % of epichlorohydrin and diol per glycidyl ether.

^{13}C-NMR

The spectra of creosol glycidyl ether is shown in figure 14. All expected signals can be seen on the spectra and are allocated accordingly. The peak at 20.71ppm (s,C1) is the most shielded carbon, hence, it corresponds to the methyl structure on the benzene ring. The peaks appearing at 43.71 ppm (s,C14) and 50.29 ppm (s,C12) are typical chemical shifts of the carbons in the oxirane ring. The structural

characteristic of the methoxy carbon correspond to the peak at 55.83 ppm. The $–CH_2$- carbon (s,C11) appears at 70.45ppm. The chloroform solvent peaks at 77.06 ppm ($CDCl_3$). The leftover peaks belong to the aromatic carbons comprising 112.90 ppm (s,C7), 114.38 ppm (s,C4), 120.63 ppm (s,C3), 131.42 ppm (s,C2), 145.61 ppm (s,C5), and 149.37 ppm (s,C6).

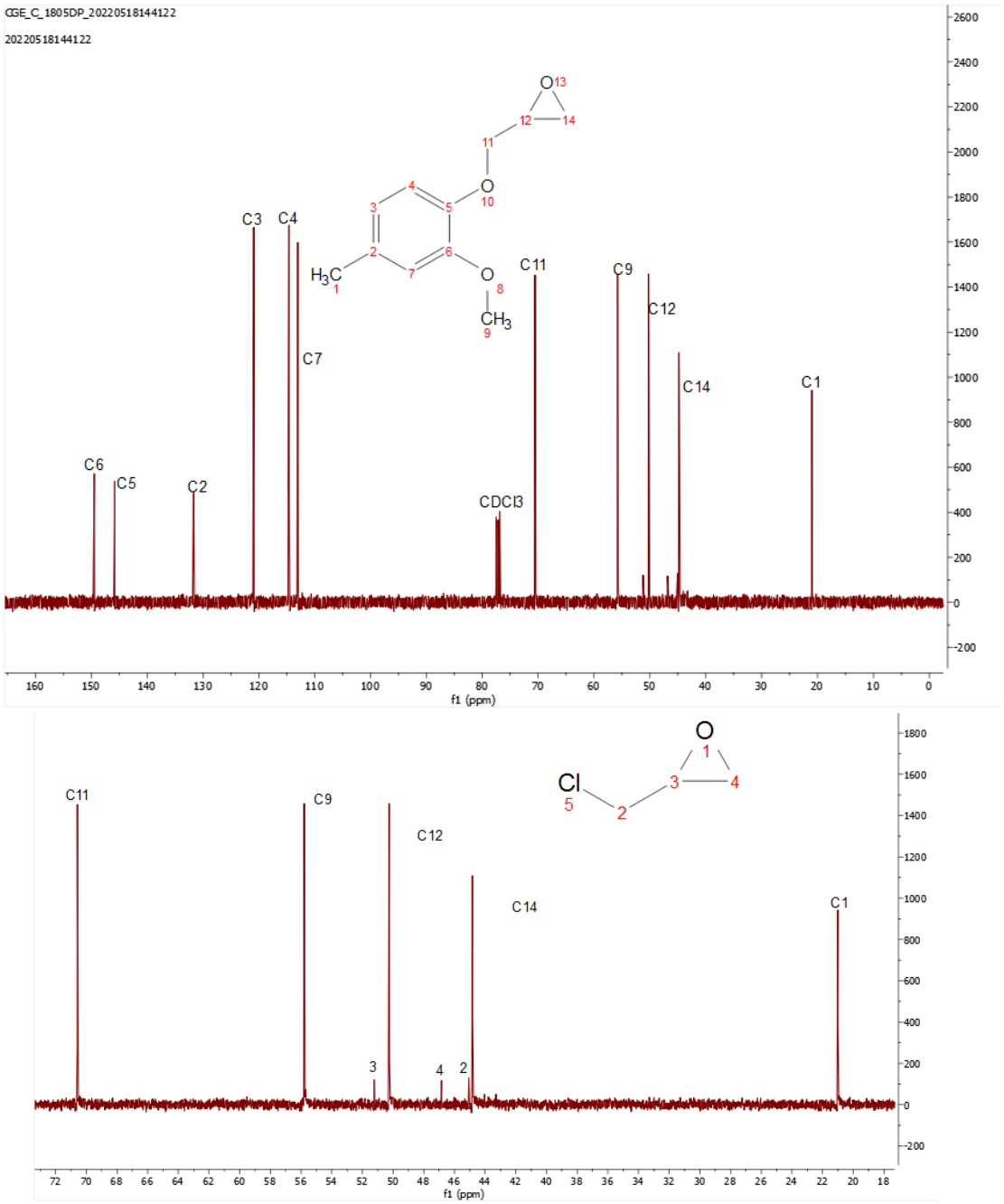


Figure 14: The ^{13}C NMR spectra of creosol glycidyl ether (top) and epichlorohydrin (bottom)

Just like the ^{1}H-NMR of creosol glycidyl ether there a few noteworhty impurity signals. These again corrospond to the epichlorohdyrine that was not removed. The botton part of figure 14 shows to which carbons on the epichlorohdyrine the impure signals between 40-55 ppm corrospond.

Note, the epichlorohydrin peaks are present in every spectra, so won't be analysed seperately in the other 13C-NMR spectra's.

4.1.2 Eugenol glycidyl ether (EGE)

^{1}H-NMR

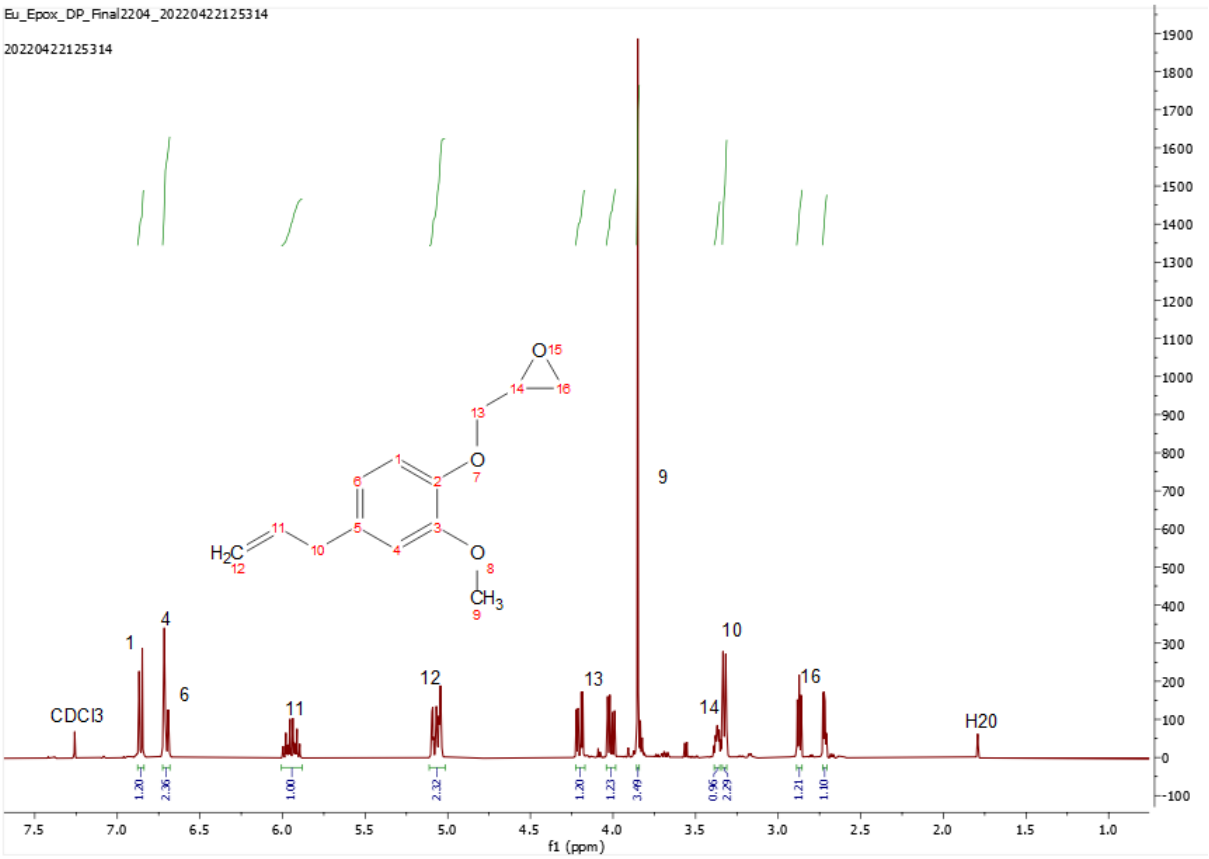


Figure 15: H-NMR spectra EGE

The H-NMR anylsis of the EGE is similar to that of the CGE since they share two side groups. Distinction is seen from the signals stemming from the protons of the alkyl side group including H10,H11,H12. The alkyl proton from H10 produce the expected doublet at 3.33 ppm. The protons of H12 can't rotate and therefor create a multiplet (5.07 ppm) as they interact with both eachother and the proton from H11. The proton of H11 is more downfield as it both part of a double bond and closer to the ring. The fact it produces a multipelt is because it couples with the proton from H10 and indepently with each of the two H12 protons. The usual epichlorohydrin peaks described in the previous section are present again. Another observation to make is that all eugenol has been converted. The ^{1}H-NMR of eugenol displays the peak of the alcohol group of eugenol at 5.5 ppm. This peak is absent in the EGE H-NMR spectrum. The usual epichlorohydrin peaks are present at 3.56, 3.22, 2.86, and 2.67ppm.

This spectra was also most suitable to display the peaks of the benzyltriethyl ammonium bromide used as PTC. Due to its relatively low molar percetnage and its partial solubility in the aqeous phase its signals on the spectra are of very low intensity. Due to spectra being noisy it can be found in Appendix D.

^{13}C-NMR

The ^{13}C spectra confirms the formation of eugenol glycidyl ether (see figure). The oxirane moeities can again be seen at 44.15 ppm (s,C17), 50.18 ppm (s,C15). The methoxycarbon is seen at 55.08

(s,C12) and the –CH_2- carbon next to the oxirane is seen at 70.65 ppm (s,C14). These are at almost identical shifts as for CGE. The alkyl sidegroup unique to eugenol can also be detected at 39.77 ppm (s,C8), 115.62 ppm (s,C10), 137.52 ppm (s,C9)., almost identical to its shift in CGE. What remains are again the aromatic carbons at 112.19 ppm (s,C1), 114.85 ppm (s,C4), 120.34 ppm (s,C3), 133.91 ppm (s,C2), 146.48 ppm (s, C5), 149.45 ppm (s, C6). The peaks of epichlorohdyrin are, as expected, smaller than in the ^{13}C NMR of CGE.

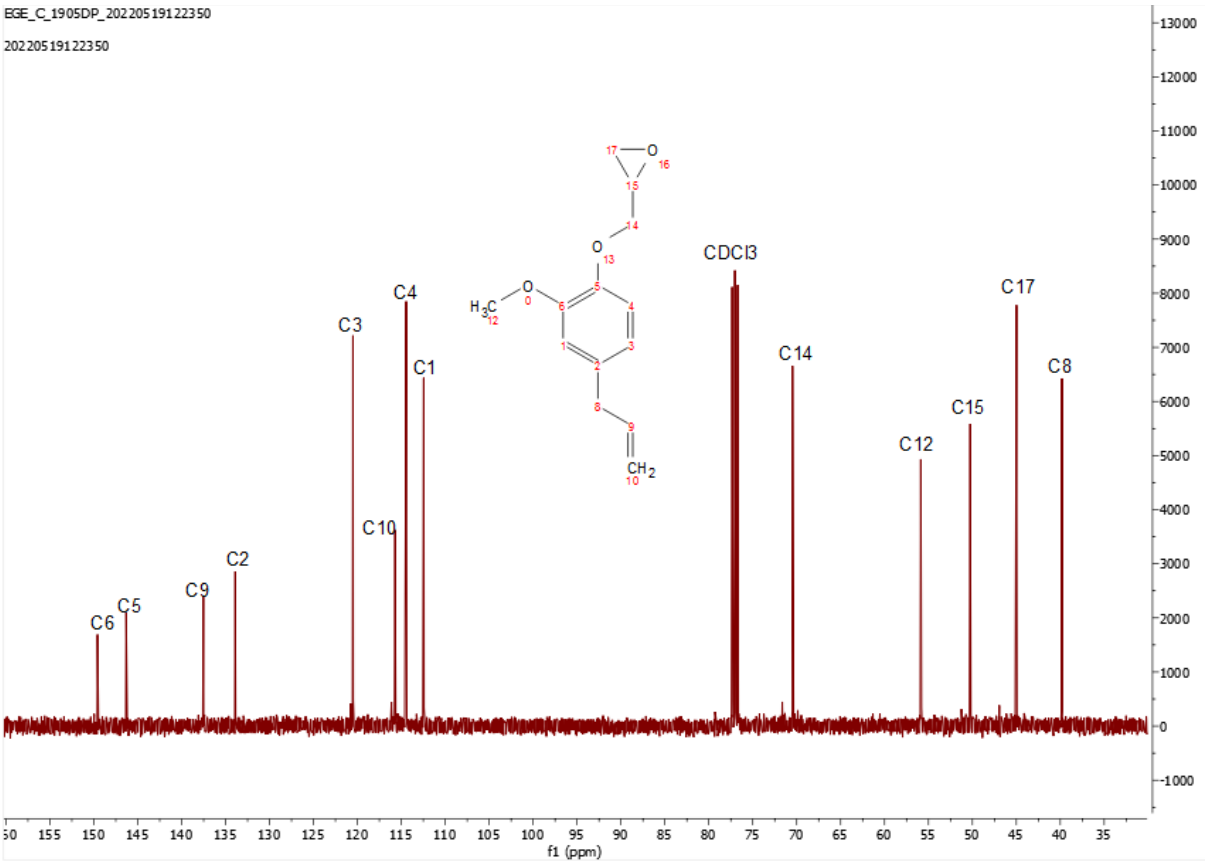


Figure 17: ^{13}C spectra of EGE

4.1.3 Vanillyl alcohol glycidyl ether (VAGE)

The H-NMR of the product shows that the glycidylation is incomplete for the primary alcohol of the vanilyl alcohol. The glycidylation of the seoncdary alcohol leads to the same benzyl side group as in the EGE so the peaks for H14, H15, and H17 stayed the same. On the contrary, the protons of the primary alcohol and its adjacent CH_2 group (H21,H20) can be seen on the spectrum and match predictive H-NMR's precisely. Besides chemical shift their splitting also shows the expected triplet for the alcohol and the expected doublet for the CH_2 group. The primary alcohol integrates to 0.61 indicating a 39% conversion of the primary alcohol side group of vanilyl alcohol. This is further reflected by the fact that protons belonging to the epoxidized primary lacohol (H9, H10, H11) all integrate to approximately 1/3 of their expected integration. The 39% conversion of the primary alcohol is further reflected in H20 integrating to 1.38 instead of 2 and H7 to 0.76 instead of 2. Furthermore, the usual epichlorohydrin peaks are present at 3.55, 3.25, 2.86, and 2.66 ppm.

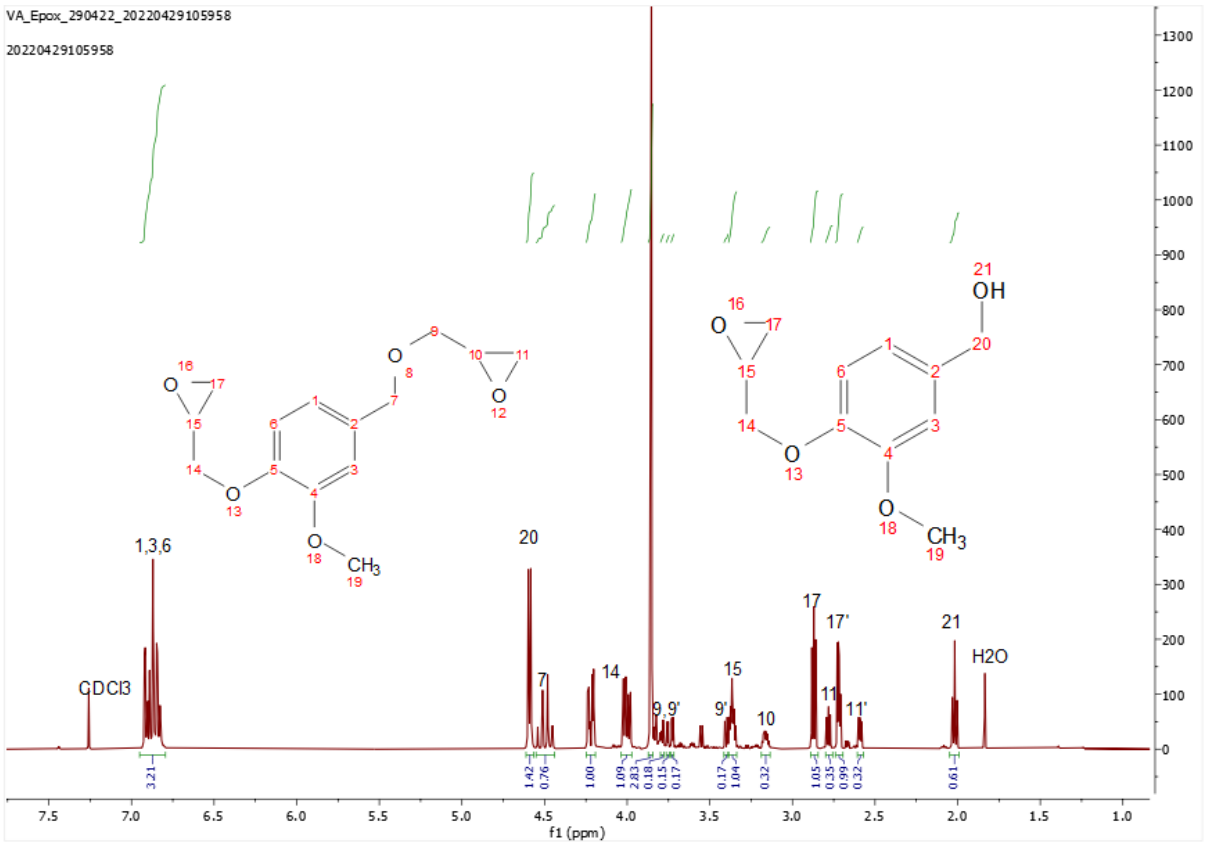


Figure 18: ^{1}H-NMR of VAGE and partially converted vanillyl alcohol

^{13}C-NMR

The ^{13}C-NMR confirms the incomplete conversion of the primary alcohol (see figure 20). Additional peaks from the unconverted structure can be seen at 65.19 ppm (s,C12),134.50 ppm (s,C23), 110.66 ppm (s,C22), 118.98 ppm (s,C21), and 114.01 (s,C20). As in the H-NMR these peaks are bigger then their counterparts in the fully converted product. For example the signal from C23 is bigger than the same positioned C2 from the fully converted product.

The question now is why the – CH_2OH group did not fully convert within the vanilyl alcohol. The answer lies in the relative reactivity of a –OH group vs a – CH_2OH group. In both mechanisms of glycidylation, the alcohol group gets deprotonated by the bromide. In the case of a phenol group, the alcohol and the bezene acts as a single function. Due to the pi-donation of the directly attached alcohol group, a serries of resonance structures manifest in which the oxygen is positively charged (see figure 21). This leaves the hydroxygroup a stronger Brønsted acid compared to the hydroxygroup in the benzyl alcohol. In the latter such a resonance structure is redundant as the negative charge on the $–CH_2-$ group is highly unfavorable. The rate of the glycidylation reaction is thus faster for the Ph-OH group than the Ph-CH_2OH group within the vanilyl alcohol.

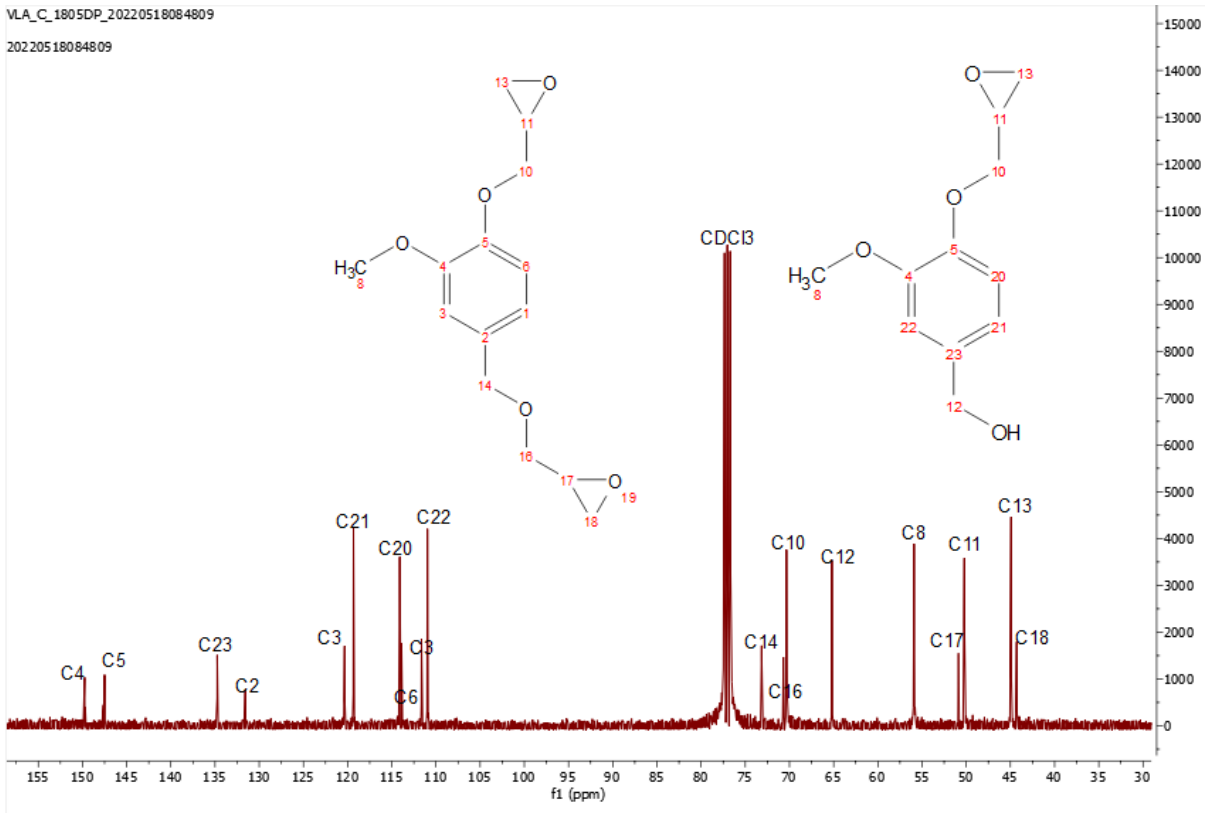


Figure 21: C-NMR for the VAGE

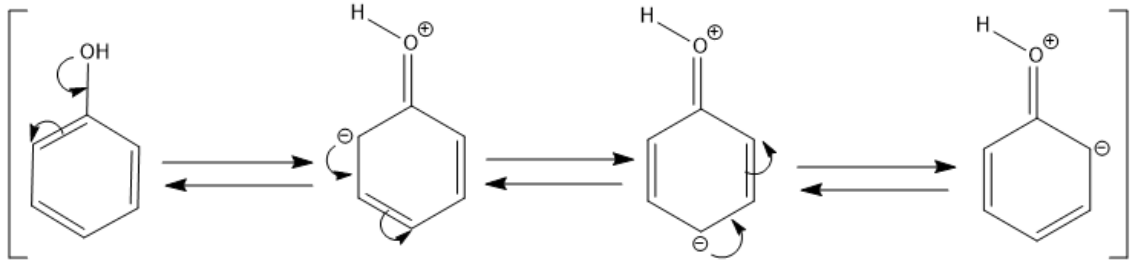


Figure 20: Resonance structures for the secondary alcohol

4.1.4 Isoeugenol glycidyl ether (IGE)

^{1}H-NMR

All expected peaks of IGE are seen on the spectrum (see figure 22). This is for most part the same spectrum as for the EGE. The distinctive peaks are the protons H12, H11, H10 due to the shift of the double bond. Note that this sample was also not put in the vacuum oven, which is why the epichlorohydrin peaks are of greater magnitude. These again include the signals at 3.56, 3.27, 2.87 and 2.66 ppm. Note that there is a quintet at 5.71 ppm and that there is a doublet next to peak 12. These two peaks represent the less favorable Cis-isomer. This explains not only why they have the same splitting pattern as their trans counterpart, but also why, for example, Cis-H11 is more upfield as it is further distanced from the benzene ring.

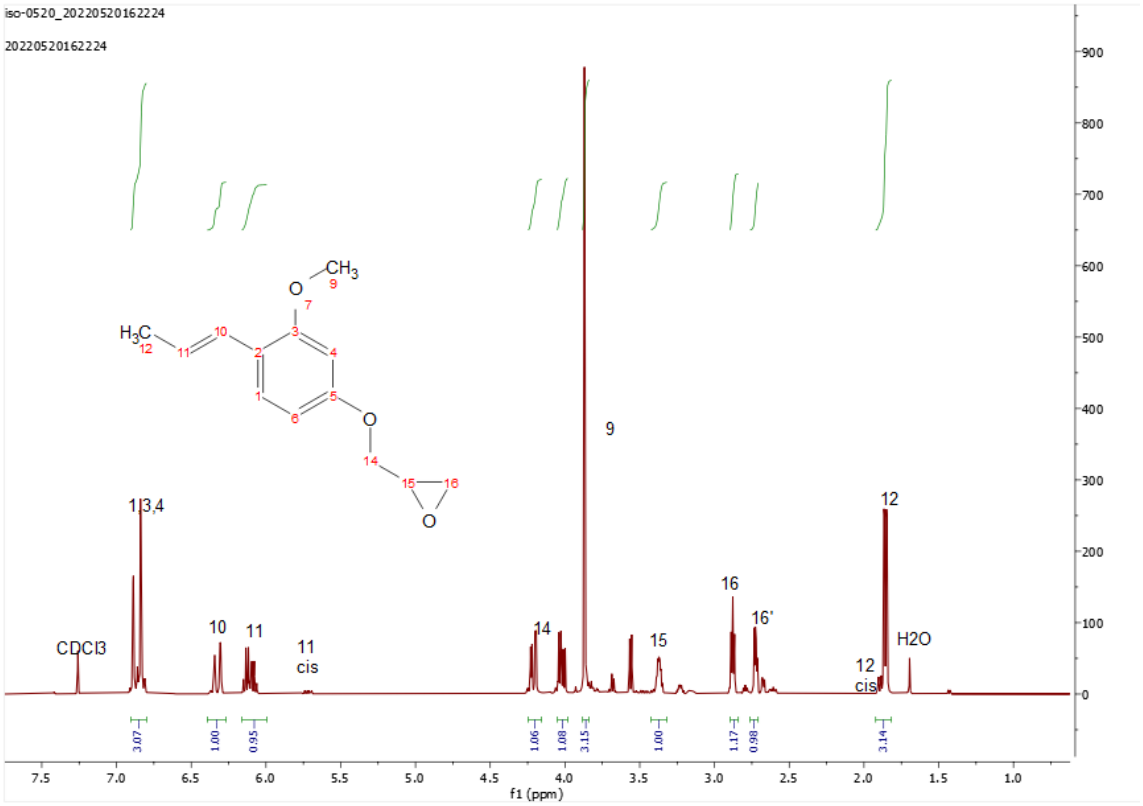


Figure 22: H-NMR of IGE

^{13}C-NMR

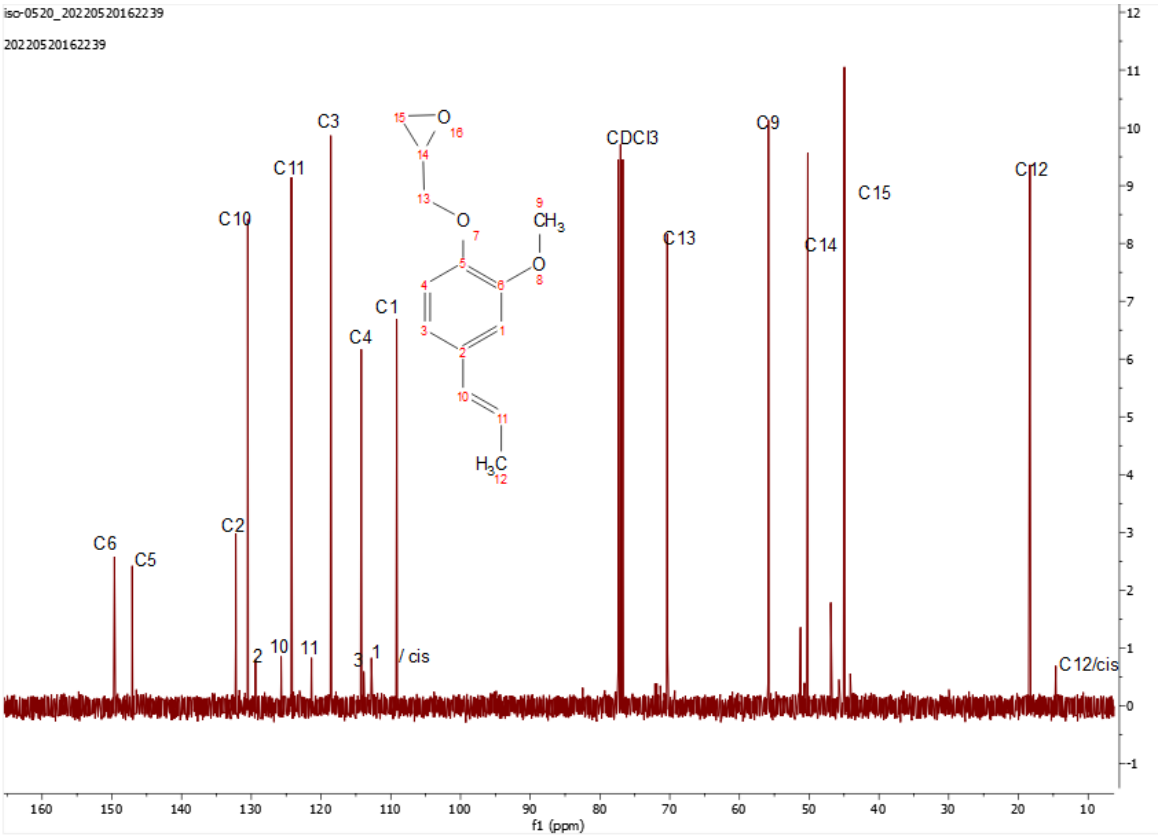


Figure 23: ^{13}C-NMR of IGE

4.2 ^{1}H-NMR and FTIR analysis of Cyclic carbonates

After the vials were taken out the reactor, both ^{1}H-NMR's and FTIR scans were taken. The FTIR analysis, section 4.2.3, shows successful synthesis of the cyclic carbonates which are mostly characterized by its peak around 1800 (1/cm) from the C=O bond (see figure 28, 29). No significant amount diol formation was seen on the FTIR spectra's which would have been characterized by a broad band between 3230-3550 (1/cm). As examples, section 4.2.1 and 4.2.2 discusses the ^{1}H-NMR spectra of ECC and VACC respectively. The ^{1}H-NMR spectra's of ICC and CCC can be found in appendix A. All glycidyl ethers were successfully turned into their respective carbonates (see figure 24,17 and appendix A) . The analysis was done through labelling the signals with their corresponding proton. Advantage is taken from the consistency of the signals from the pentagon, benzyl ring and the methoxy side group moiety. The results also show the Bu_4NI catalysts still present. Section 4.2.1 goes also goes more in depth on diol characterization. Section 4.2.3 shows how the catalyst was successfully separated reflected by the disappearance of its corresponding peaks.

4.2.1 Eugenol cyclic carbonate (ECC) & diol formation

^{1}H-NMR

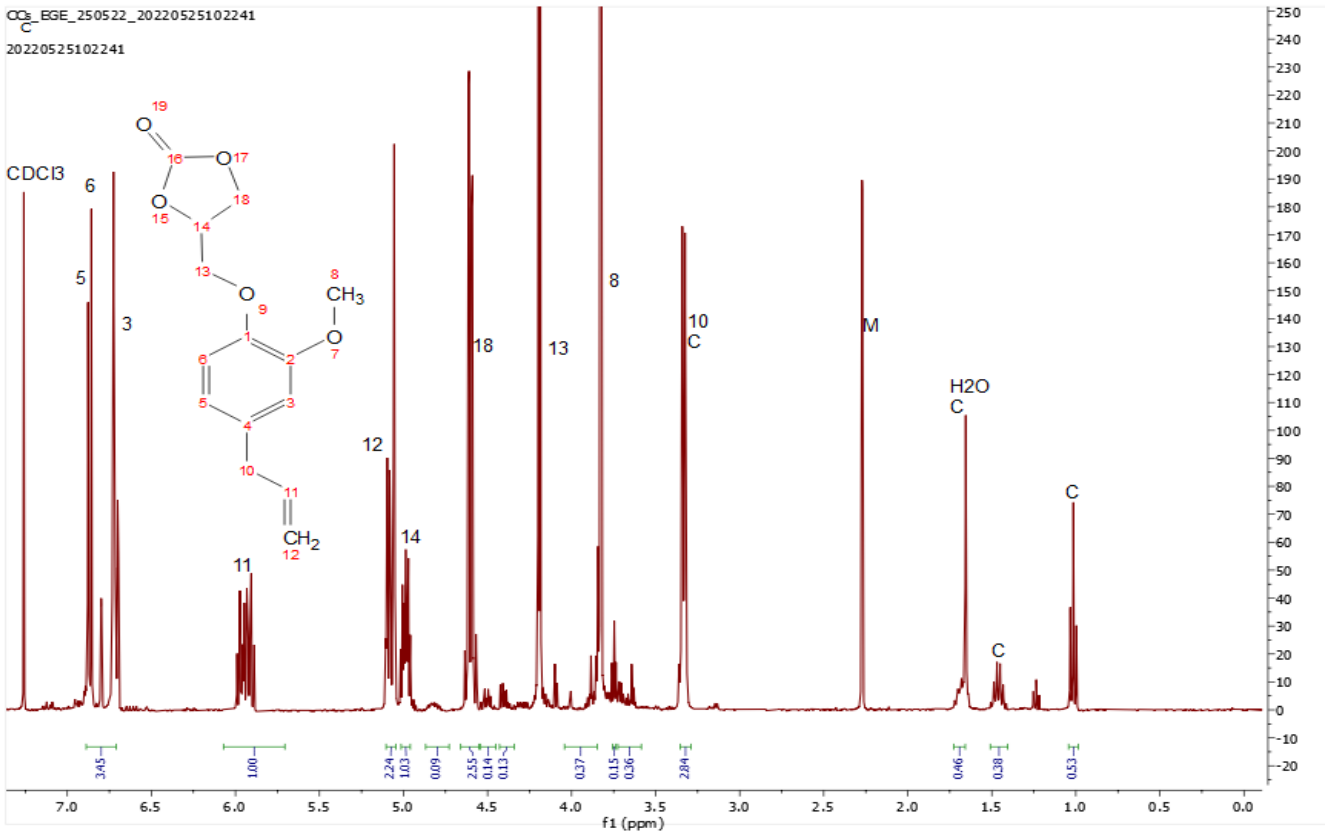


Figure 24: ^{1}H-NMR of ECC (C=Bu_4NI, M=mesistylene)

Figure 24 shows that the ECC has been successfully synthesized. All its characteristic peaks can be traced back in the spectrum. It also shows a 100% conversion of EGG as all peaks belonging to the oxirane moieties have disappeared (see fig 15). All peaks below O9 belong to the eugenol backbone and are exactly the same as in figure 15 so will not be discussed again. The peaks belonging to the cyclic carbonate moiety are novel. The most downfield signal belong to the proton H14 as it is closest to the eugenol backbone. This is followed by the two H18 protons which formed an expected doublet although distorted due to its position in the ring. The protons H13 are at a similar chemical shift as for the EGE but the complex splitting has resolved itself in a single peak. This due to the added symmetry

from the cyclic carbonate compared to the oxirane. The latter resembles the benzene ring less and the resulting asymmetry causes the unequal coupling constants.

The leftover signals belong to Bu_4NI, mesistylene, diol formation and epichlorohydrin cyclic carbonate. Starting with Bu_4NI, its corresponding peaks are the triplet at 1.01ppm, the heptet at 1.46ppm and the quintet at 1.67ppm. The latter overlaps with a water peak that was used as Lewis acid catalyst. The most downfield peak of Bu_4NI belongs to the protons next to the nitrogen but cannot be seen as it overlaps with peak H10. The mesitylene methyl group protons peak at 2.27ppm. Another interesting observation is that the epichlorohydrin signals have disappeared (see figure 13) which suggests that all of it has undergone cycloadditon. To identify which peaks belong to epichlorohydrin cyclic carbonate and which belong to the diol it is useful to overlap the EGE with the ECC spectra (see figure 25). The newly formed peaks are likely to come from epichlorohydrin cyclic carbonate whereas the peaks that remained likely belong to the diol derivative. This hypothesis is verified by a predicted ^{1}H-NMR spectra for epichlorohydrin cyclic carbonate which indeed overlaps the new peaks formed in between 3.5ppm and 5.2ppm.[29]A predicted spectra of the diol form of eugenol from *MestReNova* also overlap the labelled diol peaks. Figure 26 shows the labelled diol and epichlorohydrin cyclic carbonate peaks on the ECC predicted ^{1}H-NMR spectra.

Integration of the diol and epichlorohydrin cyclic carbonate reaffirm the assignment of their respective protons. It also yield information on the molar percentage of diol and epichlorohydrin cyclic carbonate formed. Starting with the diol, figure 26 shows that 3 protons from the diol correspond to 0.36H. Figure shows that a single proton from the ECC product corresponds to 1.00H.

$$\%diol = \frac{0.12}{1.00} \times 100 = 13\%$$

For epichlorohydrin cyclic carbonate one protons corresponds to 0.75H

$$\%Epi\ C.C = \frac{0.75}{1.12} \times 100 = 7.5\%$$

As can be seen there is quit a significant increase in the mole fraction of the diol. If the same method is applied to EGE spectrum only a 7.3% diol formation is found (see table 2). Part of the increase in diol happened due to the hydrolysis of the cyclic carbonate while in the reactor.

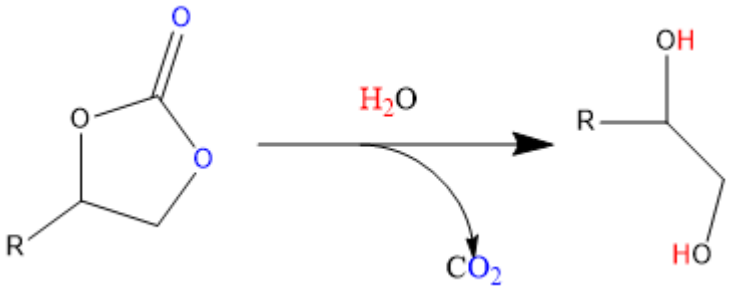


Figure 27: Cyclic opening due to hydrolysis

Note that this amount of diol could have competed with the water as a HBD. It is therefore not possible to attribute the catalytic activity solely to water with respect to the Lewis acid.

Table 3 shows the molar percentages of epichlorohydrin cyclic carbonate and of diol formation for the ECC,ICC and CCC. The ^{1}H-NMR spectra's of the last two can be found in the appendix. The ^{1}H-NMR of VACC will be further elaborated. The molar percentage of the Bu_4NI are around 3% which is expected as 3% relative to the epoxide was added. The fact that they are a bit higher is due to diol formation as shown in figure 27. The ratio of catalyst: cyclic carbonate increases as a result.

	Molar percentages			
	Cyclic Carbonate	Epi.CC	Diol	Bu_4NI
ECC	75%	7.5%	13%	4.2%
ICC	71%	17%	9.2%	3.1%
CCC	78%	12%	6.3%	3.3%

Table 3: Purity of cyclic carbonates before catalyst separation

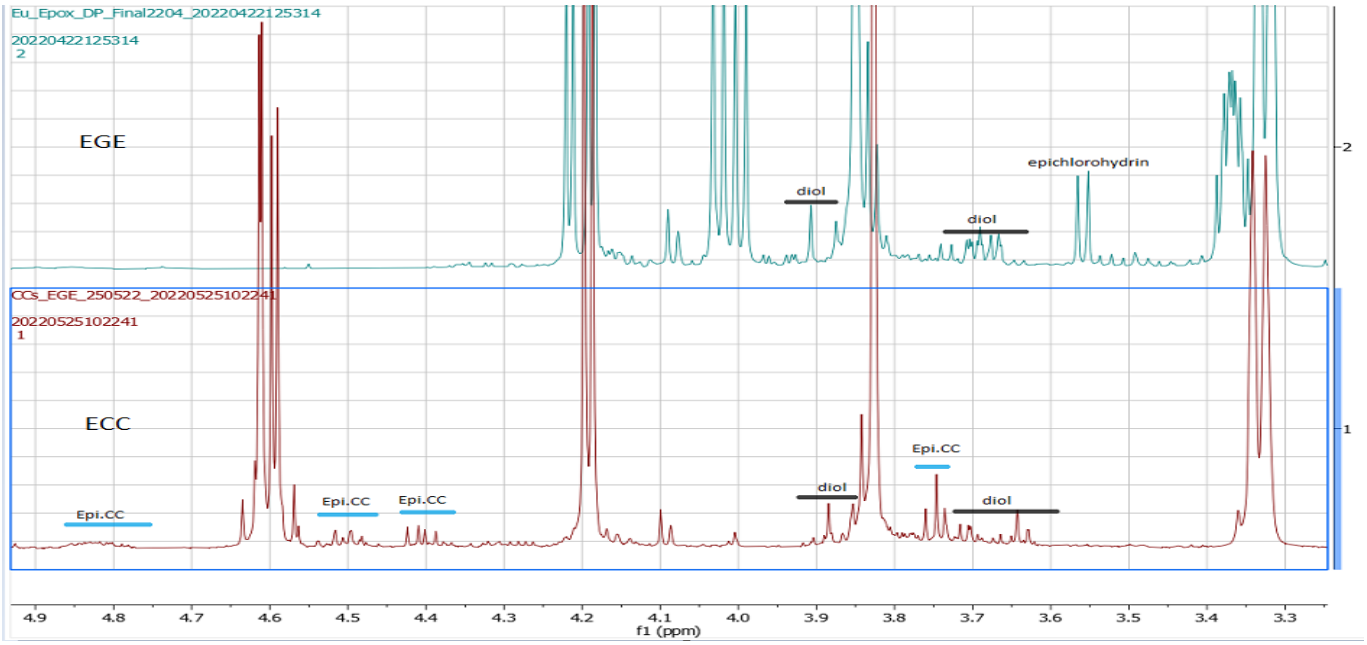


Figure 25: Part of the ^{1}H-NMR spectra of EGE (top) and ECC (bottom)

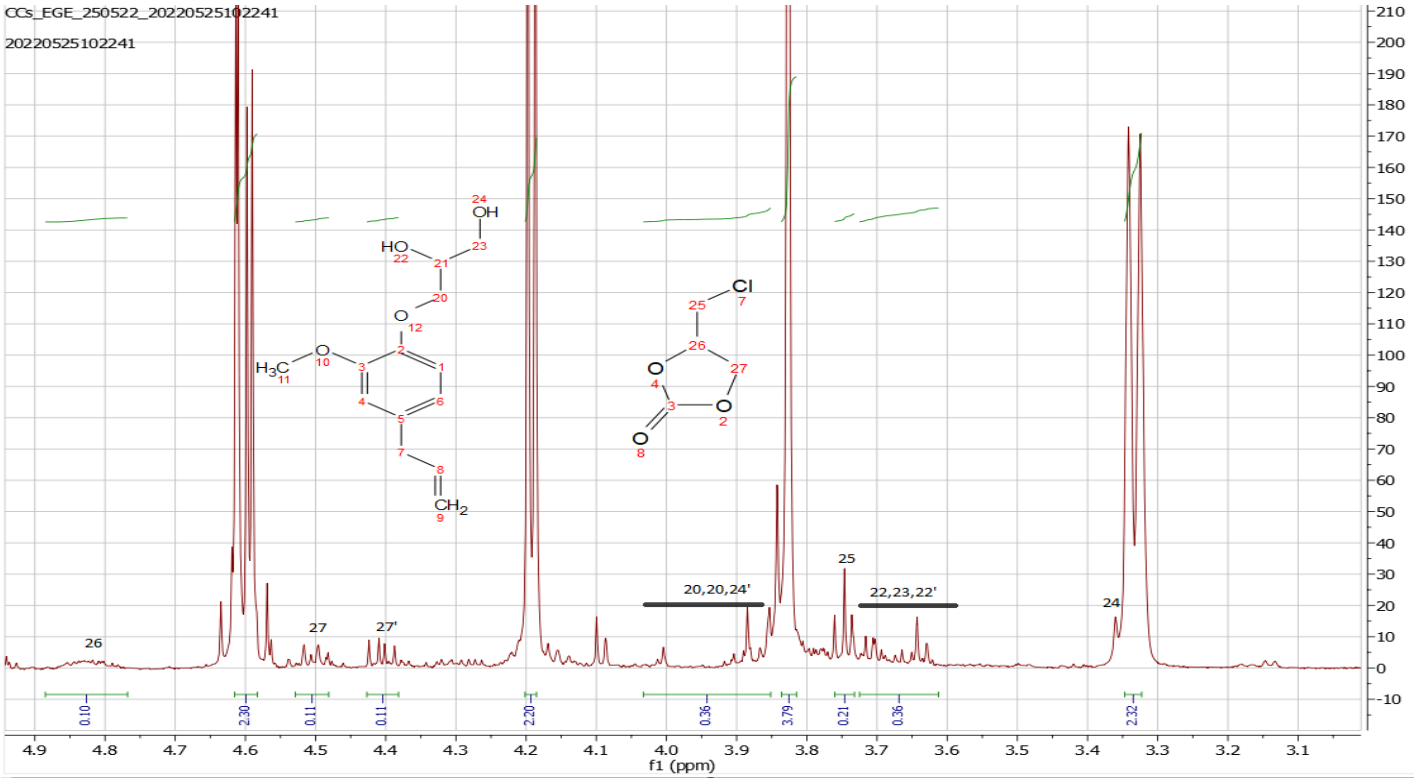


Figure 26: ^{1}H-NMR spectra of ECC with labelled diol and epichlorohydrin CC peaks

4.2.2 VACC

One cyclic carbonate that has to be elaborated on is that of vanillyl alcohol. As mentioned in section 4.1.3 the epoxidation of the –CH_2OH- group was only 39% complete. The hypothesis is therefor that for this group also only 39% has undergone cycloaddition. Indeed this turned out to be true (see figure 28). In the ^{1}H-NMR spectra, both the fully (A) and partially (B) carbonated product can be found. This is easily seen as the cyclic carbonate protons H9 and H19 produce their own quintet representing two cyclic carbonates with the latter being more distanced from the benzene ring (more upfield in spectra). Note that H9 representing two protons (A & B) has been integrated to 1.00 in *MestReNova*. The alcohol group, that was never epoxidized, is again present at 1.87ppm but this time displays as a broad peak. Furthermore the unique peaks of 16, 18 and 29 could also be identified with the help of integration. For the cyclic carbonate of vanillyl alcohol, the percentage ratio between product B and A is again roughly 61:39% suggesting full conversion of both epoxides. This is further backed by the fact that all epoxide moieties have disappeared. This is why, for example, the peak at 4.59 ppm integrates to 2.84 of which 2H come from the four H13 protons and 0.84 comes from the four protons of H16 and H20 (**0.39%** *2 = 0.78 ≈ 0.84). All epichlorohydrin has again be turned into epichlorohydrin cyclic carbonate. The diol was again seen but in both the VAE and VACC they shifted more downfield. This is due too there being more hydrogen bonds as the diol byproduct can form on both hydroxyl groups of the vanillyl alcohol. This can further deshield the protons of the diol product.

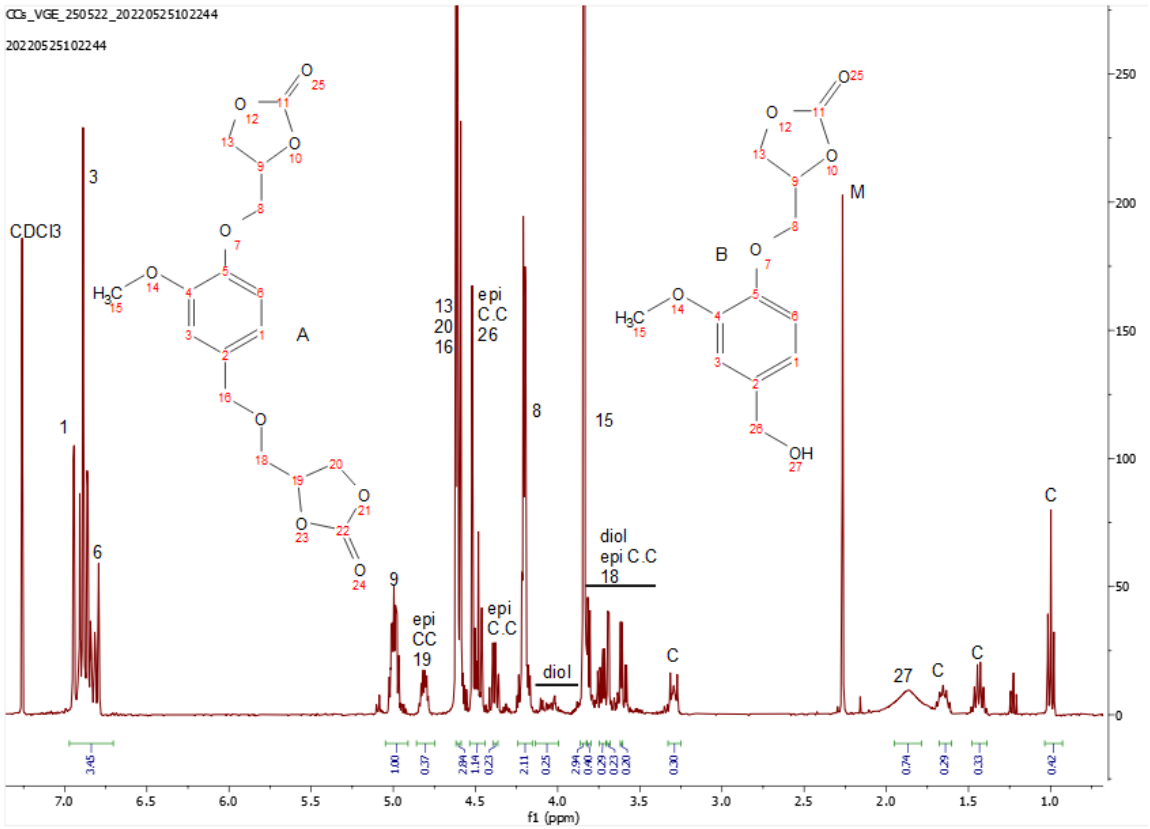


Figure 28: ^{1}H-NMR of VACC

4.2.3 FTIR of cyclic carbonates

Figure 29, shows the FTIR spectra of ECC and VACC. As can be seen, the cyclic carbonate of eugenol has been formed which is mostly characterized by the carbonyl group in the ring which peaks at 1787

[1/cm]. Complete selectivity towards the cyclic carbonate can also be derived from the spectra since the carbonyl group in polycarbonate usually peaks lower around 1750 [1/cm]. Furthermore the traditional carbon-carbon stretches of the aromatic rings can be found at 1595,1511 and 1468 [1/cm]. Lastly, both the alkyl (right of 3000 [1/cm]) and aromatic (left of 3000 [1/cm]) C-H vibrations can be found. The spectra of VACC can be seen to be highly similar. The noteworthy difference with the other cyclic carbonates is the increased intensity of the alcohol group signal (see figure 29). This is only to be expected as the -CH_2OH- of vanillyl alcohol only converted 39% into its respective epoxide. This is then combined with the diol side-product that was found in the ^{1}H-NMR and, in the case of fully converted vanillyl alcohol, accounts for four alcohol groups. The FTIR spectra's of ICC and CCC can be found in Appendix C as they are highly similar

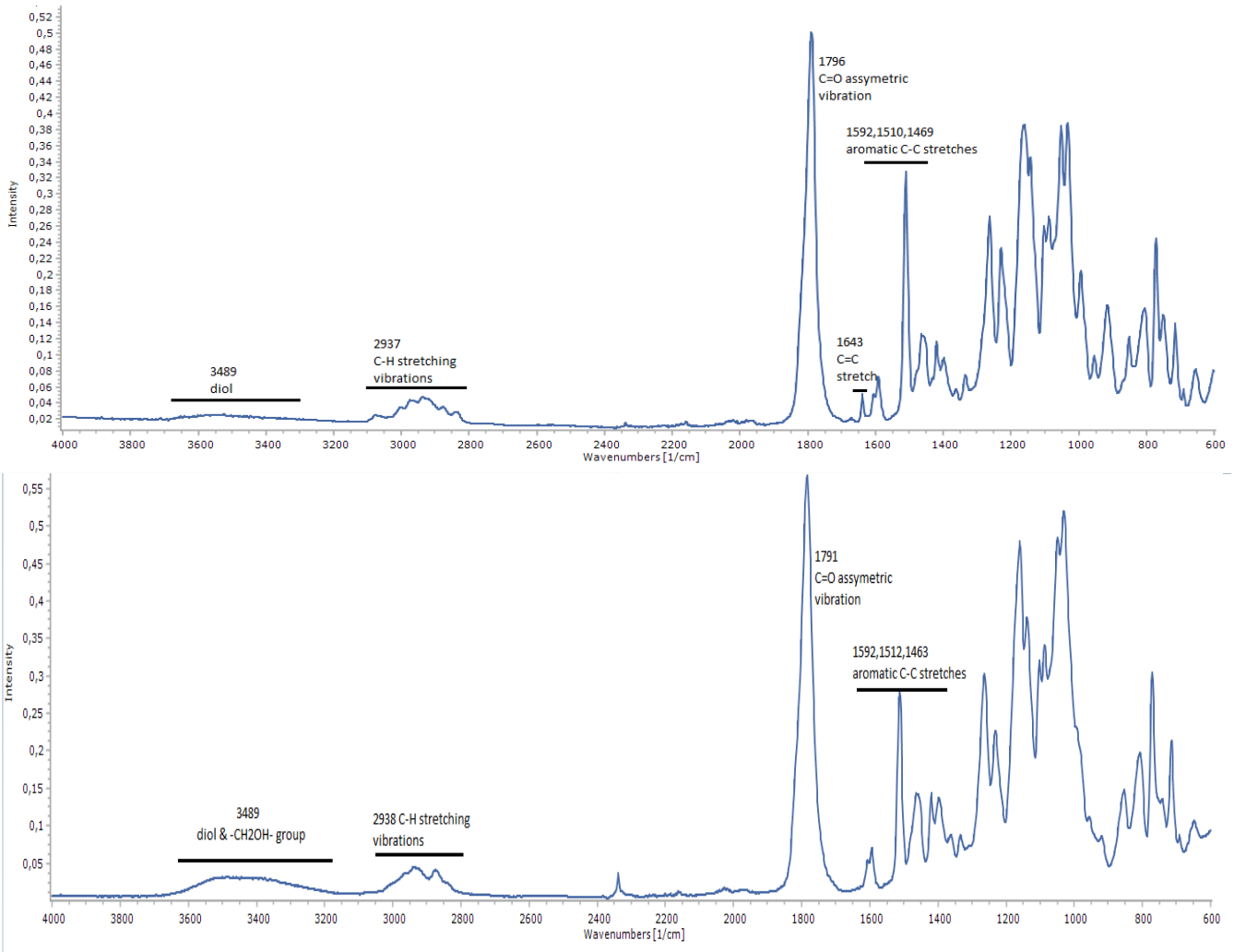


Figure 29: FTIR of ECC (above) and VACC (bottom) before purification.

4.3 Purification of cyclic carbonates

The spectra are expected to look the same but without the Bu_4NI catalyst. This is exactly what was found (see figure 30). The catalyst signals of 3.31, 1.67, 1.44 and 1.01 ppm have disappeared. Because the samples did not go into the vacuum oven at 70 °C there were still traces of diethyl ether left. These traces can be found at 3.47ppm and 1.20ppm. According to integration leftover diethyl ether makes up 1.5% of the product so removal before further use is advised. The water (used as HBD) produces a signal at 1.66 ppm. This too should and can be removed. The same results are available for the other epoxides listed in Appendix B.

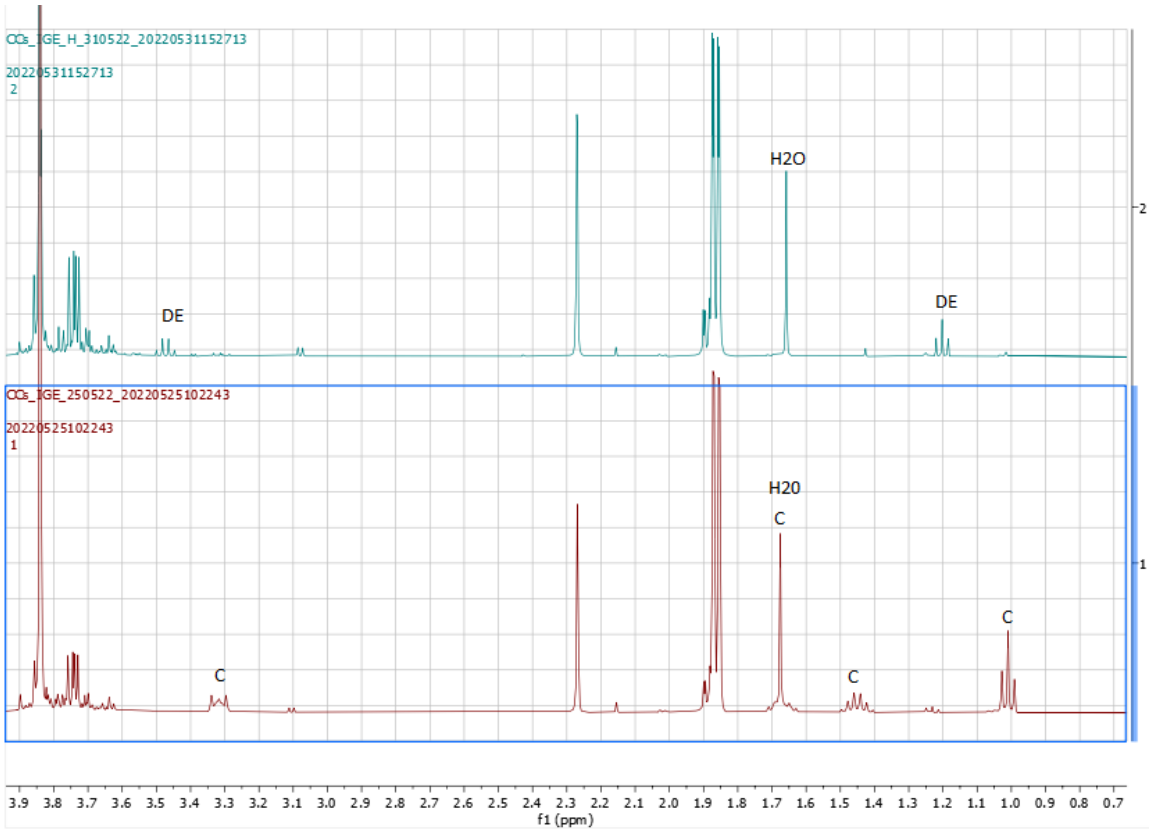


Figure 30: H-NMR spectra of IGE before purification (bottom) and after purification (up)

4.4 Conversion, yield and selectivity

Knowing the diol molar fraction for both the glycidylation and cycloaddition step it was possible to calculate the yield for both reactions (see table 4, and 5). This was done through calculating the mass percentages of both the diol and the product. Note, for the cyclic carbonate yield only the added diol during cycloaddition has been taken into account. . Appendix D shows an example of a calculations for the yield. The yields seen in table 4 and 5 are there for reflective for the amount of diol formed in each step. Both the NPD's and the epoxide converted 100% as a starting product as was already discussed in their respective H-NMR analysis. Vanillyl alcohol is excluded because it was not possible to successfully characterize the diol in the spectra. Also, it was earlier found that only 39% of the primary alcohol underwent both reactions.

NPD	conversion	epoxide yield	selectivity
Eugenol	100%	80.3%	80.3
Creosol	100%	86.4%	86.4%
Iso-eugenol	100%	79.2%	79.2%

Table 4: conversion, yields and selectivity for the glycidylation reactions

Epoxide	conversion	cyclic carbonate yield	selectivity
EGE	100%	81.0%	79.8%
CGE	100%	90.5%	81.6%
ICE	100%	83.4%	73.6%

Table 5: conversion, yields and selectivity for the cycloaddition reactions

5.0 Conclusion

This work has demonstrated that eugenol, isoeugenol, creosol and vanillyl alcohol can be successfully synthesized into their respective glycidyl ethers and cyclic carbonates. In the first part of the thesis, it was shown that the mild conditions for the glycidylation reaction (80°C, atm) proved to be sufficient for successful conversion of the natural phenolic derivatives (NPD's) into their respective glycidyl ethers. Conversions did not reach 100% due to the formation of the diol side product whose mole percentages range from (2.1% to 7.6%). The primary alcohol of vanillyl alcohol, however, only reached a 39% conversion. Although this alcohol group has lower reactivity, this was due to experimental error and further research is needed. Traces of remaining epichlorohydrin were also found so it is recommended to let the product sit in the vacuum oven at 110°C for at least 24 hours.

In the second part of thesis it was shown that all glycidyl ethers formed were successfully converted to their respective cyclic carbonate. The combination of water and tetrabutylammonium iodide (Bu_4NI) was sufficient to catalyze the reaction between the synthesized glycidyl ethers and CO_2. Water did not only, however, catalyze the reaction by serving as a hydrogen bond donor (HBD) but also led to the formation of more diol side product through cyclic carbonate hydrolysis. Taking into account the diol formation the final yields for the formed cyclic carbonated of eugenol, isoeugenol and creosol were 81.0, 83.4 and 90.5% respectively. The remaining epichlorohydrin has all undergone cycloadditon lowering the final product purity. In future research this can be avoided by ensuring removing of all epichlorohydrin beforehand.

Overall this thesis shows that cyclic carbonates stemming from green reagent can be synthesized at high yield at mild conditions. Further research should focus on finding their chemical and physical properties to determine their potential applications.

6.0 References

1. Huang, Kuan, et al. “Synthesis of Porous Polymeric Catalysts for the Conversion of Carbon Dioxide.” *ACS Catalysis*, vol. 8, no. 10, 2018, pp. 9079–9102., https://doi.org/10.1021/acscatal.8b02151.
2. Aouf, Chahinez, et al. “Study of the O-Glycidylation of Natural Phenolic Compounds. the Relationship between the Phenolic Structure and the Reaction Mechanism.” *Tetrahedron*, vol. 69, no. 4, 2013, pp. 1345–1353., https://doi.org/10.1016/j.tet.2012.11.079.
3. Webster, Dean C. *Epoxy Resin Derived from Vanillin and Thermosets Therefrom*. 27 Oct. 2016.
4. “Solvay Epicerol® Earns Roundtable on Sustainable Biomaterials Certification.” *Solvay*, 1 Dec. 2015, https://www.solvay.com/en/press-release/solvay-epicerol-earns-roundtable-sustainable-biomaterials-certification.
5. Varanasi, Patanjali, et al. “Survey of Renewable Chemicals Produced from Lignocellulosic Biomass during Ionic Liquid Pretreatment.” *Biotechnology for Biofuels*, vol. 6, no. 1, 2013, https://doi.org/10.1186/1754-6834-6-14.
6. Luo, Jizhong, et al. “Selective Lignin Oxidation towards Vanillin in Phenol Media.” *ChemistrySelect*, vol. 1, no. 15, 2016, pp. 4596–4601., https://doi.org/10.1002/slct.201600758.
7. Clements, John H. “Reactive Applications of Cyclic Alkylene Carbonates.” *Industrial & Engineering Chemistry Research*, vol. 42, no. 4, 2003, pp. 663–674., https://doi.org/10.1021/ie020678i.
8. Zhang, Qian, et al. “Efficient Solvent-Free Synthesis of Cyclic Carbonates from the Cycloaddition of Carbon Dioxide and Epoxides Catalyzed by New Imidazolinium Functionalized Metal Complexes under 0.1 MPA.” *Catalysis Letters*, vol. 150, no. 9, 2020, pp. 2537–2548., https://doi.org/10.1007/s10562-020-03163-6.
9. Miyata, Takahiro, et al. “Synthesis and Radical Polymerization of Styrene-Based Monomer Having a Five-Membered Cyclic Carbonate Structure.” *Journal of Polymer Science Part A: Polymer Chemistry*, vol. 50, no. 15, 2012, pp. 3046–3051., https://doi.org/10.1002/pola.26090.
10. Fache, M., et al. “Epoxy Thermosets from Model Mixtures of the Lignin-to-Vanillin Process.” *Green Chemistry*, vol. 18, no. 3, 2016, pp. 712–725., https://doi.org/10.1039/c5gc01070e.
11. Kamphuis, Aeilke J., et al. “Co2-Fixation into Cyclic and Polymeric Carbonates: Principles and Applications.” *Green Chemistry*, vol. 21, no. 3, 2019, pp. 406–448., https://doi.org/10.1039/c8gc03086c.
12. Alves, M., et al. “Organocatalytic Promoted Coupling of Carbon Dioxide with Epoxides: A Rational Investigation of the Cocatalytic Activity of Various Hydrogen Bond Donors.” *Catalysis Science & Technology*, vol. 5, no. 9, 2015, pp. 4636–4643., https://doi.org/10.1039/c5cy00891c.
13. Wang, Lin, et al. “An Efficient Metal- and Solvent-Free Organocatalytic System for Chemical Fixation of CO2 into Cyclic Carbonates under Mild Conditions.” *Green Chemistry*, vol. 18, no. 5, 2016, pp. 1229–1233., https://doi.org/10.1039/c5gc02697k.
14. Alassmy, Yasser A., and Paolo P. Pescarmona. “The Role of Water Revisited and Enhanced: A Sustainable Catalytic System for the Conversion of CO 2 into Cyclic Carbonates under Mild Conditions.” *ChemSusChem*, vol. 12, no. 16, 2019, pp. 3856–3863., https://doi.org/10.1002/cssc.201901124.
15. Bhanage, Bhalchandra M, et al. “Synthesis of Dimethyl Carbonate and Glycols from Carbon Dioxide, Epoxides, and Methanol Using Heterogeneous Basic Metal Oxide Catalysts with High Activity and Selectivity.” *Applied Catalysis A: General*, vol. 219, no. 1-2, 2001, pp. 259–266., https://doi.org/10.1016/s0926-860x(01)00698-6.
16. Fujita, Shin-ichiro, et al. “Chemical Fixation of Carbon Dioxide to Propylene Carbonate Using Smectite Catalysts with High Activity and Selectivity.” *Catalysis Letters*, vol. 79, no. 1/4, 2002, pp. 95–98., https://doi.org/10.1023/a:1015396318254.
17. Appaturi, Jimmy Nelson, et al. “Review on Carbon Dioxide Utilization for Cycloaddition of Epoxides by Ionic Liquid-Modified Hybrid Catalysts: Effect of Influential Parameters and Mechanisms Insight.” *Catalysts*, vol. 11, no. 1, 2020, p. 4., https://doi.org/10.3390/catal11010004.
18. “Sources of Greenhouse Gas Emissions.” *EPA*, Environmental Protection Agency, https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions.
19. Bhanage, Bhalchandra M, et al. “Synthesis of Dimethyl Carbonate and Glycols from Carbon Dioxide, Epoxides, and Methanol Using Heterogeneous Basic Metal Oxide Catalysts with High

Activity and Selectivity." *Applied Catalysis A: General*, vol. 219, no. 1-2, 2001, pp. 259–266., https://doi.org/10.1016/s0926-860x(01)00698-6.
20. IPCC, 2022: Summary for Policymakers. In: Climate Change 2022: Mitigation of Climate Change. Contribution of Working Group III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [P.R. Shukla, J. Skea, R. Slade, A. Al Khourdajie, R. van Diemen, (eds.)]. Cambridge University Press, Cambridge, UK and New York, NY, USA. doi: 10.1017/9781009157926.001
21. "Antioxidant Activity and Characterization of Volatile Constituents of Beechwood Creosote." *Journal of the Science of Food and Agriculture*, vol. 85, no. 9, July 2005, pp. 1580–1588.
22. Fache, M., et al. "Epoxy Thermosets from Model Mixtures of the Lignin-to-Vanillin Process." *Green Chemistry*, vol. 18, no. 3, 2016, pp. 712–725., https://doi.org/10.1039/c5gc01070e.
23. North, Michael, et al. "Synthesis of Cyclic Carbonates from Epoxides and CO2." *Green Chemistry*, vol. 12, no. 9, 2010, p. 1514., https://doi.org/10.1039/c0gc00065e.
24. Macias, Eugenia E., et al. "Catalytic Activity of Metal Organic Framework CU3(BTC)2 in the Cycloaddition of CO2 to Epichlorohydrin Reaction." *Catalysis Today*, vol. 198, no. 1, 30 Dec. 2012, pp. 215–218., https://doi.org/10.1016/j.cattod.2012.03.034.
25. Fache, Maxence, et al. "Vanillin Production from Lignin and Its Use as a Renewable Chemical." *ACS Sustainable Chemistry & Engineering*, vol. 4, no. 1, 2015, pp. 35–46., https://doi.org/10.1021/acssuschemeng.5b01344.
26. Gandilhon, Pierre. *Process for the Isomerization of Aromatic Alkenyl Compounds*. 6 Feb. 1979.
27. Taherimehr, Masoumeh, and Paolo P. Pescarmona. "Green Polycarbonates Prepared by the Copolymerization of CO2with Epoxides." *Journal of Applied Polymer Science*, vol. 131, no. 21, 2014, https://doi.org/10.1002/app.41141.
28. scraped
29. LI, HONGCHUN. "Synthesis of Cyclic Chloropropylene Carbonate from Carbon Dioxide with Epichlorohydrin." *Asian Journal of Chemistry*, vol. 23, ser. 8, 11 Apr. 2011, pp. 3344–3346. *8*.
30. Simon Le Luyer, Baptiste Quienne, Matthieu Bouzaid, Philippe Guégan, Sylvain Caillol, et al.. Biobased poly(ester- alt -thioether)s synthesized by organo-catalyzed ring-opening copolymerizations of eugenol-based epoxides and N -acetyl homocysteine thiolactone. Green Chemistry, Royal Society of Chemistry, 2021, 23 (19), pp.7743-7750.
31. Wang, Zhenyu, et al. "Curing Behavior and Thermomechanical Performance of Bioepoxy Resin Synthesized from Vanillyl Alcohol: Effects of the Curing Agent." *Polymers*, vol. 13, no. 17, 2021, p. 2891., https://doi.org/10.3390/polym13172891.
32. "Carbonate Market Statistics, Trends: Industry Analysis 2030." *Allied Market Research*, https://www.alliedmarketresearch.com/carbonates-market.
33. Aouf, Chahinez, et al. "Study of the O-Glycidylation of Natural Phenolic Compounds. the Relationship between the Phenolic Structure and the Reaction Mechanism." *Tetrahedron*, vol. 69, no. 4, 2013, pp. 1345–1353., https://doi.org/10.1016/j.tet.2012.11.079.
34. Lastra-Barreira, Beatriz, et al. "Eugenol Isomerization Promoted by Arene–Ruthenium(II) Complexes in Aqueous Media: Influence of the Ph on the Catalytic Activity." *RSC Advances*, vol. 3, no. 43, 2013, p. 19985., https://doi.org/10.1039/c3ra43030h.
35. Caillol, S., Boutevin, B., & Auvergne, R. (2021). Eugenol, a developing asset in biobased epoxy resins. *Polymer*, *223*, 123663.
36. Le Luyer, Simon, et al. "Bio-Based Poly(Ester-*Alt*-Thioether)s Synthesized by Organo-Catalyzed Ring-Opening Copolymerizations of Eugenol-Based Epoxides and *n*-Acetyl Homocysteine Thiolactone." *Green Chemistry*, vol. 23, no. 19, 2021, pp. 7743–7750., https://doi.org/10.1039/d1gc02138a.
37. Kamphuis, Aeilke J., et al. "Co2-Fixation into Cyclic and Polymeric Carbonates: Principles and Applications." *Green Chemistry*, vol. 21, no. 3, 2019, pp. 406–448., https://doi.org/10.1039/c8gc03086c.
38. Wu, Guang-Peng, et al. "Perfectly Alternating Copolymerization of CO2 and Epichlorohydrin Using Cobalt(Iii)-Based Catalyst Systems." *Journal of the American Chemical Society*, vol. 133, no. 38, 2011, pp. 15191–15199., https://doi.org/10.1021/ja206425j.

7.0 Appendix

Appendix A: ^{1}H-NMR for cyclic carbonates

^{1}H-NMR creosol cyclic carbonate

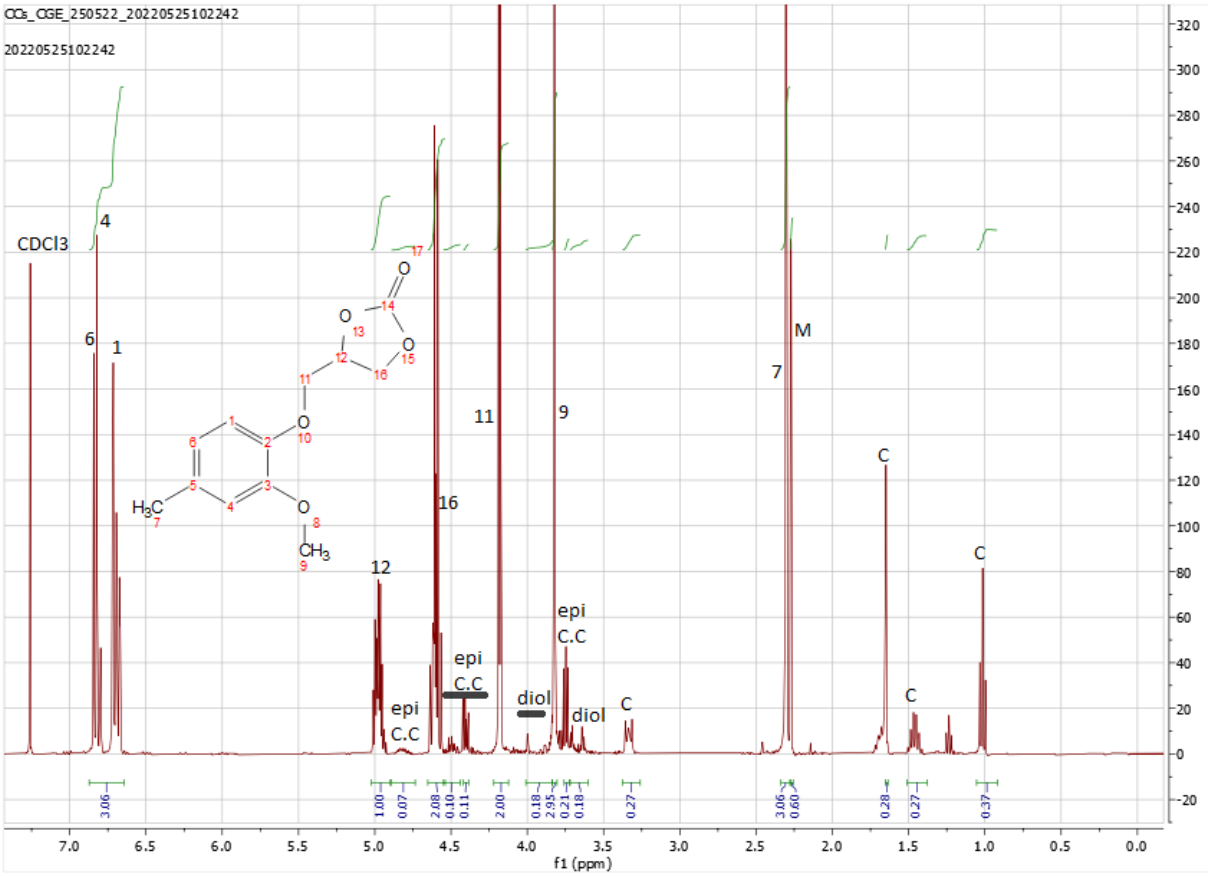


Figure S1: ^{1}H-NMR of CCC

^{1}H-NMR Isoeugenol cyclic carbonate

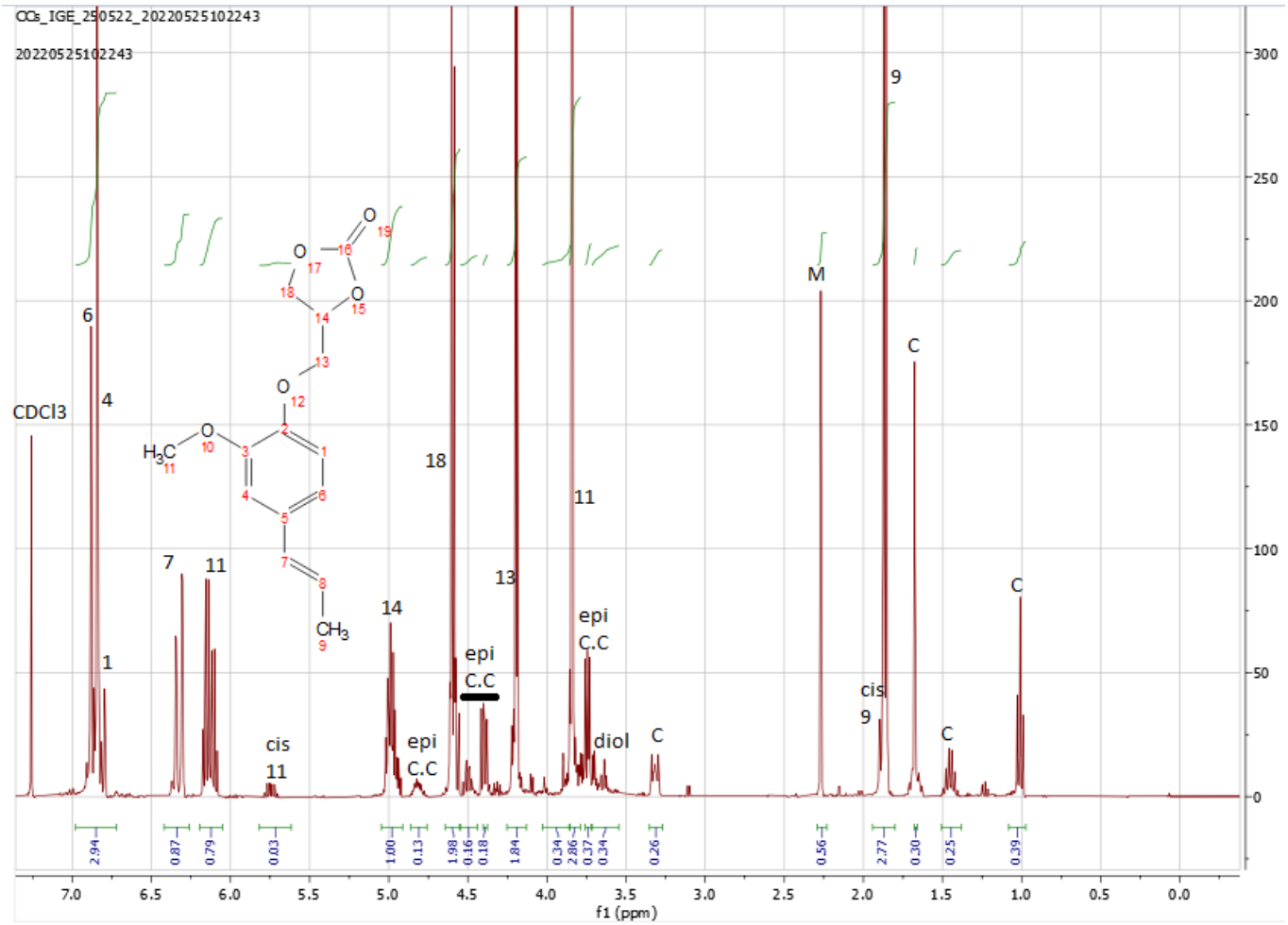


Figure S2: ^{1}H-NMR of ICC

Appendix B: ^{1}H-NMR of purified cyclic ECC and CCC

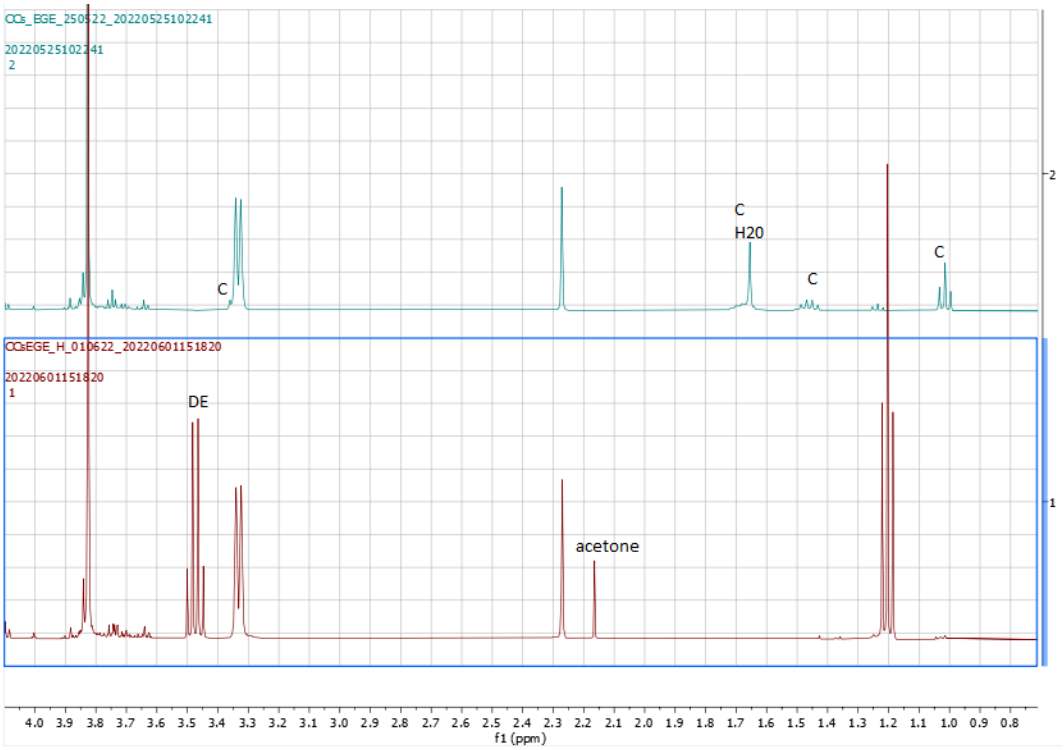


Figure S3: ECC H-NMR spectra before purification (above) and after purification (below).

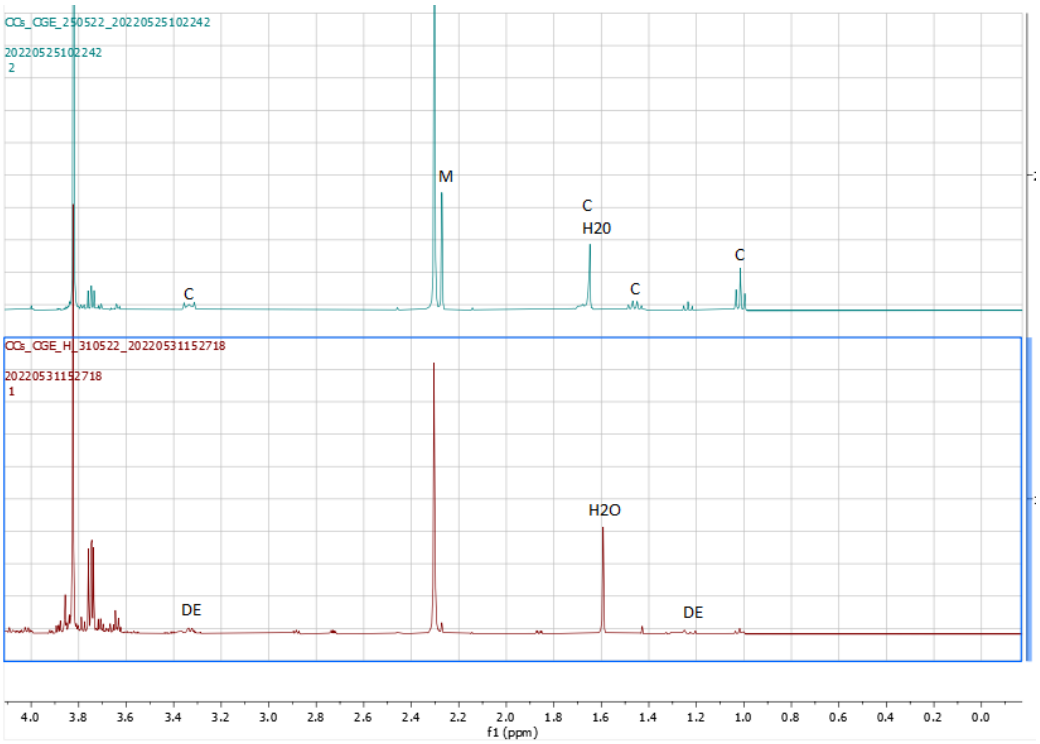


Figure S4: H-NMR spectra of CCC before purification (above) and after purification (below).

Appendix C: FTIR of CCC, IGC

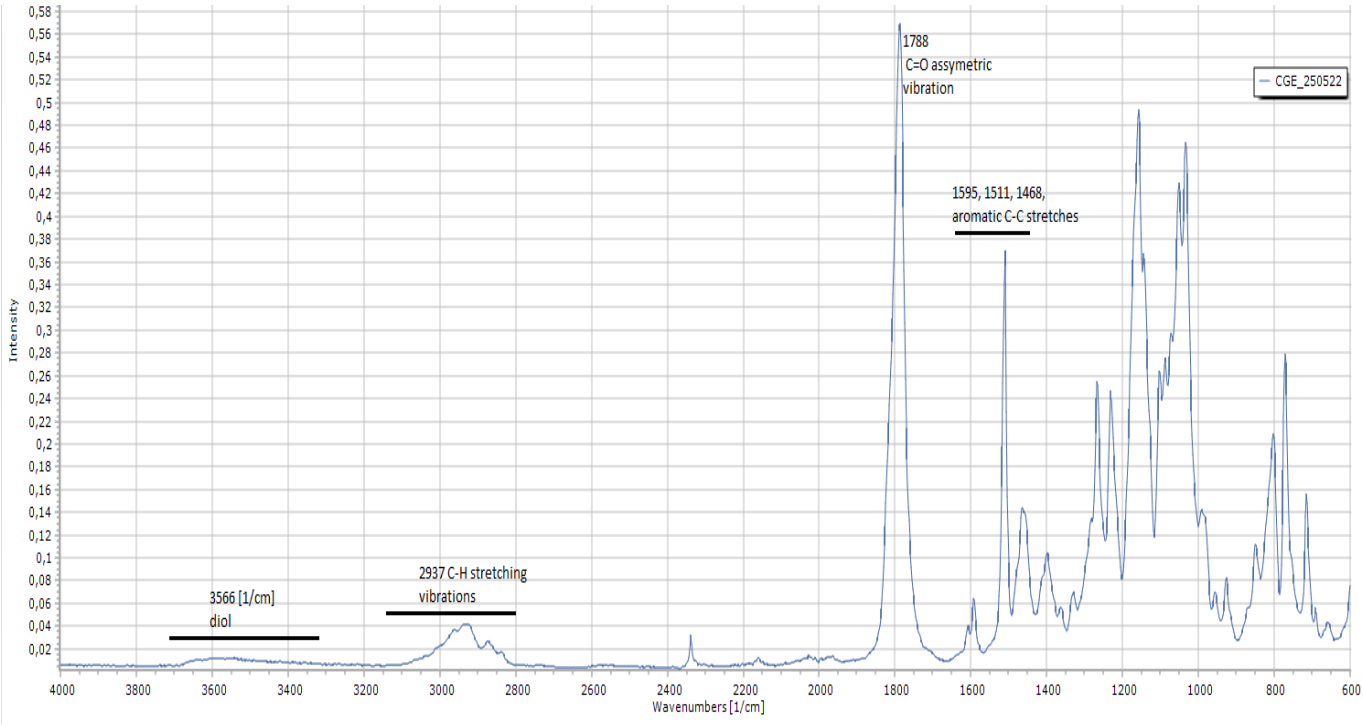


Figure S5: FTIR of CCC before purification

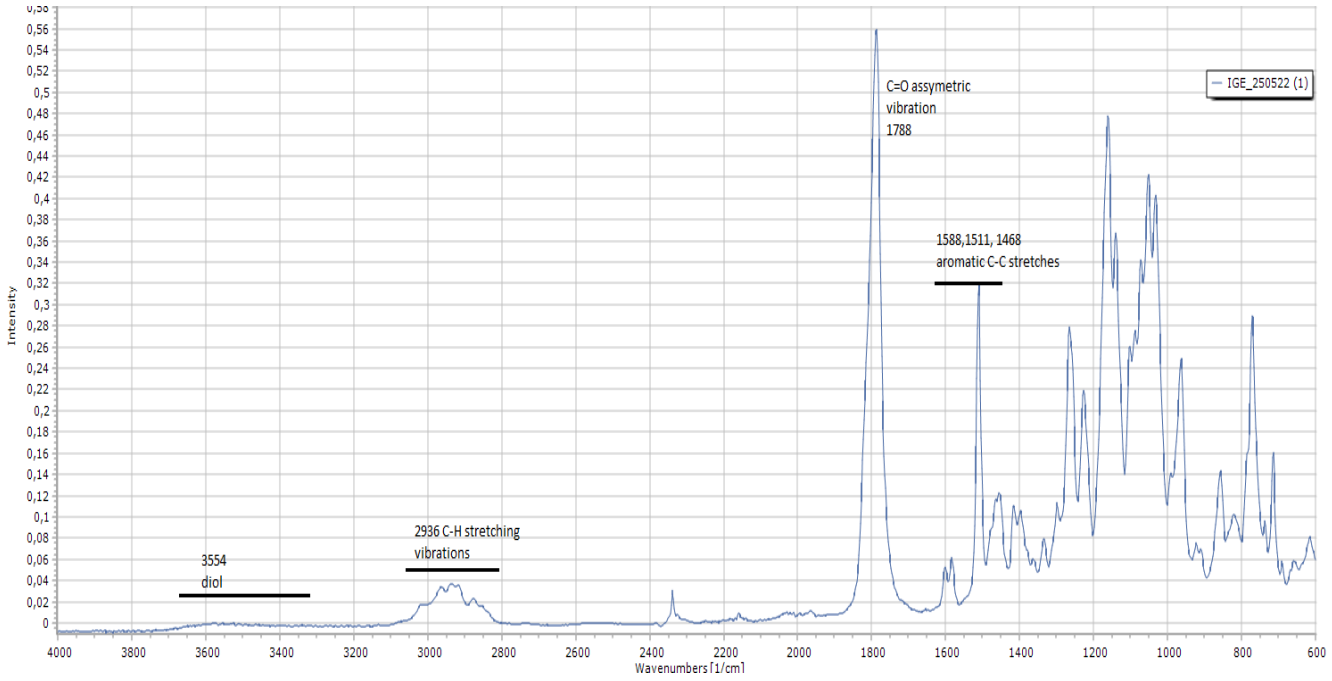


Figure S6: FTIR of ICC before purification

Appendix D: Yield calculation

Example Eugenol

Actual yield

$$mass\ C.C = mass\ of\ product - (mass\ of\ diol + mass\ of\ mesistylene + mass\ of\ epichlorodrin\ cyclic\ carbonate)$$

Mass of product = 5.915g

1 mole of product will consist of the follow masses according to the mole fractions derived from ^{1}H-NMR integration (see table 3):

Mass of C.C = 0.7556 * 164.10 g/mol = 124.0g

Mass of diol =0.127 molar *238.12 g/mol = 30.24g

Mass of epichlorohydrin cyclic carbonate = 0.075* 135.99 g/mol = 10.20g

	Wt%	Mass in product (g)
ECC	75.4	4.460
Diol	18.4	1.088
Epichlorohydrin C.C	6.2	0.367

Mass C.C = 5.915g – (1.088g+0.180g+0.367g) = 4.280g

Theoretical yield

4.400 g EGE (20mmol) → 5.282 g ECC (20mmol)

$$\boldsymbol{Yield = \frac{4.280g}{5.282g} * 100 = 81\%}$$

Appendix D: Benzyltriethylammonium bromide

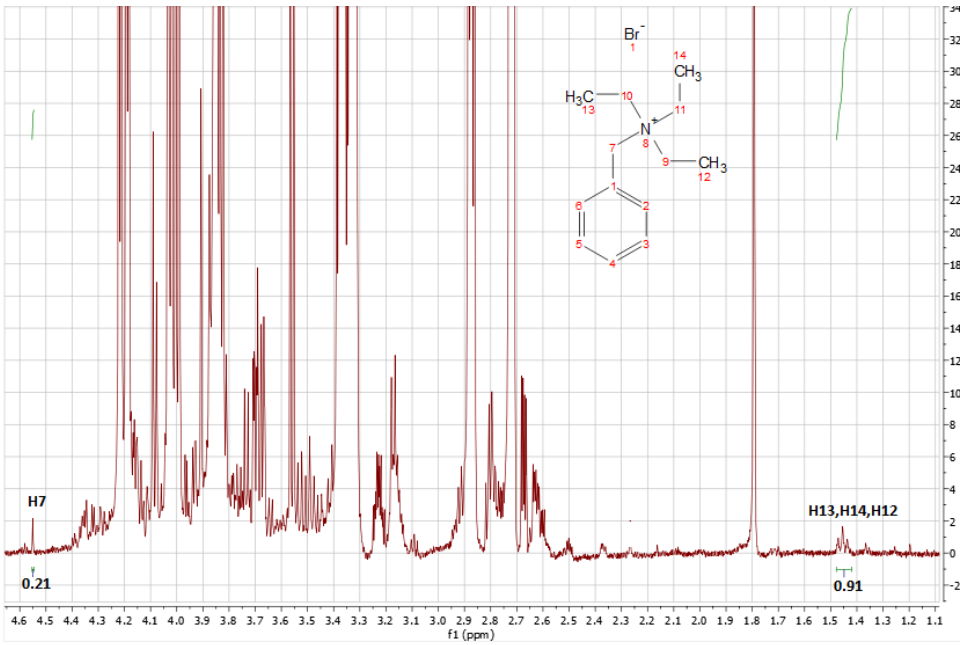


Figure S7: Zoomed in image of figure 15 to highlight benzyltriethyl ammonium bromide's peaks