

# Production and optimization of Azetidiniumsalts

Bachelor's Thesis in Chemical Engineering

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# Abstract

Biobased materials are heavily researched and have been increasingly alerted by the pollution of fossil based materials to reduce environmental impact. The situation has led to further improvement of cellulosic materials as well as modification of cellulose nanocrystalline with its natural abundance and great biocompatibility to keep the planet green again. Nanocellulose materials can be produced by functionalizing nanocrystalline with sulphate and carboxyl groups that can be used as a benefit in production of biobased materials. Modification of nanocellulose crystalline can also be acquired by the usage of azetidiniumsalts that can eventually be used in improved and modified biocomposites. Azetidiniumsalts have an end group as well which can be varied and substituted with other types of groups such as carboxylic acid and sulphate groups depending on the application areas to obtain further improved properties of a material.

The aim of this project was focused on production of symmetrical azetidiniumsalts with various dialkylamine groups that were produced under different reaction circumstances as well as timeframes. Circumstances that were evaluated included changes in solvents and temperature conditions to optimize the salts. Optimization is mostly based on each of the salts properties and structure, Di-n-Hexylamine was preferred as an alkylamine during optimization for its complexibility and unique form of structure. There is however no indication that different reaction conditions are only applied for this particular salt, but are rather applied for each azetidiniumsalt depending on its design and proposed change in condition. The azetidiniumsalts were analyzed with H-NMR and FTIR. Production of the salts were achieved and verified according to spectras and peaks evaluated. By synthesizing these azetidiniumsalts, modified improvements could be applied and used in biocomposites as well as biobased materials in the near future to help minimize fossil fuels emissions. A deeper knowledge of the salts attributes can also play a great factor for the environmental aspects in the next upcoming years.

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# Introduction

Fossil fuels have impacted society to a great extent in the last 20 years and awareness of resources has been increased. To reduce the environmental impact, different aspects of developing and utilizing materials from renewable sources in more productive ways has been prioritized. The impacts and effects on the environment has led to research on development and also establishing new biobased materials such as biocomposites that can be used in more non-polluted areas. A major difference between biopolymers and fossil fuel based polymers is the higher amount of oxygen in biobased polymers/materials which is dependent on the heat value and has a great contribution to the environmental consequences. Number of practical applications of hemicellulose have increased significantly in the 21st century, especially towards materials that do not dissolve in water. The main properties of hemicelluloses depend on the chemical structure of their carbohydrate and the structure of added substituents. Hemicellulose usually represents 20-30 % of the biomass and is relatively shorter than cellulose.

Azetidiniumsalts works as new reagents that can be used for functionalization of hemicelluloses. Azetidines are typically found in natural products and provide a basement for other structural classes. The azetidine-ring can be converted as an amine to an azetidinium ion and in combination with the ring strain, it can work as a suitable reagent due to its high reactivity. The ions can easily be synthesized from epichlorohydrin and secondary amines. Branching of hemicelluloses through azetidinium salts gives various possibilities to attach different functional groups such as carboxylic acid and sulphate groups that give new properties to the material depending on how the branching is structured and designed.

Chemical modification of cellulose nanocrystalline has a dominant role of its natural affluence on this planet with great biocompatibility and the attractive compatibility of undergoing surface chemical modifications. The modifications are mainly performed to introduce either charged or hydrophobic moieties that can include oxidation, carboxymethylation, epoxidation as well as sulfonation. The modification can be applied in the main areas of nanocellulose research, such as drug delivery, tissue regeneration and biosensing. The approach for surface modification greatly relies on the reactivity of the hydroxyl groups and has in recent years gained a lot of attention in studies to further improve and develop biomedical applications.

This thesis studied and investigated the synthesis of azetidiniumsalts under different reaction circumstances regarding the amount of solvents used, temperature variations as well as reacting azetidiniumsalts with different types of side groups. Strive for better biobased materials and resources was also studied by modification of cellulose nanocrystalline with the produced azetidiniumsalts. The choice of side groups can be efficient and improve the interaction of modified hemicellulose and also the materials in biocomposites which can eventually have a great positive impact on the environment as well as further improvements that need to be investigated on biobased materials. [1, 2]

# Aims and Observations

The aim of this project was solely focused on the synthesis of symmetrical azetidiniumsalts, from open-form to the ring-closed molecule with isopropanol and water alone as solvents. To take in consideration is that each of the salt's side group substitution as well as modification of CNC was theoretically researched and evaluated as application areas to azetidiniumsalts.

# Theory

## Dialkylamine

Dialkylamine is an amine containing two alkyl groups paired to the amino nitrogen and is used to produce natural products such as salt. Azetidiniumsalt is synthesized with the reaction of an dialkylamine with epichlorohydrin that is stirred at a certain temperature. When the reaction is stirred and completed a ring-open structure is obtained. Water is a deciding factor to either obtain a ring-open or ring-closed structure of the molecule, when the reaction is repeated and water is added to the solution, a ring-closed structure is obtained and the azetidiniumsalt is produced, which can eventually be analyzed by NMR data and further analysis. [3]

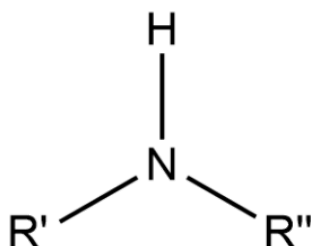


Figure 1: Structure of dialkylamine

## Epichlorohydrin

Epichlorohydrin is a chlorinated epoxy compound that is mainly used in synthesis of glycerol and epoxy resins and is applied in materials such as air ducts, emissions tubing and fuel hoses. It contains a triangle shaped form with an oxygen atom attached to the bottom as well as a carbon chain attached with an chlorine atom at the end of the chain. Epichlorohydrin is used as a reagent with an dialkylamine when producing azetidiniumsalts. This particular reagent is necessary for a reaction to occur between the solution and the reagent which eventually works as a reactive group to produce the salts. Epichlorohydrin works as of today as the most effective reagent to produce either a ring-open or a ring-closed form of azetidiniumsalt. [4, 5]

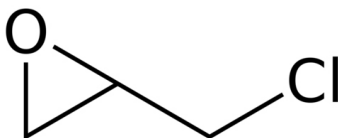


Figure 2: Structure of epichlorohydrin

## Azetidiniumsalts

Azetidiniumsalts are primarily divided into two different groups, symmetrical and asymmetrical salts, which is dependent on the structure of their respective end groups R' and R''.

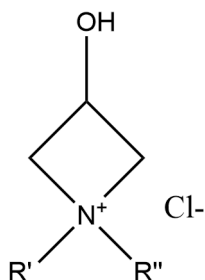


Figure 3: Structure of Azetidiniumsalt

Synthesis of symmetrical azetidiniumsalts are more common and consists of carbon atoms in a square with an hydroxylgroup attached to the third atom as well as two R' and R'' groups attached to a nitrogen atom with a positive charge. The negative charged chlorine atom works as an opposite ion.

Azetidiniumsalts usually have a couple of areas on its ring that are sensitive to nucleophilic attacks due to the positive charge of the nitrogen which eventually opens up with a SN2 reaction into a ring opened product. Production of the salts can either form the ring-open product or the ring-closed product depending on the solvents used. Isopropanol as a solvent gives the ring-open structure and addition of water typically gives the ring-closed structure. To receive the ring-closed salt some impacting factors need to be noted such as temperature degree and the amount of solvent (Isopropanol/water) used. [8, 9]

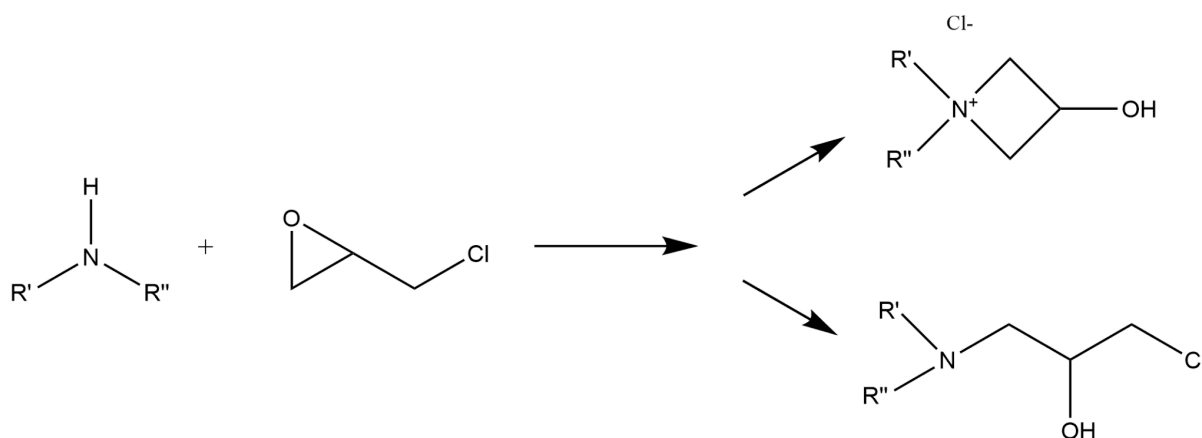


Figure 4: Dialkylamine and epichlorohydrin gives either the ring-closed product (top product) or the ring-open product (bottom product)

Asymmetrical azetidiniumsalts are produced from secondary amines in reaction with epichlorohydrin. These types of amines usually have different kinds of functional groups of the R' and R'' structure. The secondary amines can be produced by amination of aldehydes with primary amines under the influence of a reducing agent. This mechanism gives a large variation of asymmetrical secondary amines by differentiation of primary amines and aldehydes used. The change in side groups gives the azetidiniumsalt different structure as well as properties. [10]

## Nanocrystalline cellulose modification (CNC)

Nanocrystalline cellulose is a renewable nanomaterial that has received a huge amount of attention for its use in various applications from food packaging material to advanced biomedical material. Depending on the desired application, chemical modification of CNC can be carried out at the hydroxyl groups of the glucose units on the crystalline backbone structure. The cellulose fibers are semi-crystalline, consisting of both crystalline and amorphous regions. Amorphous areas are known for being hydrolyzed due to its sensitive acid attack that leads to production of single crystallites.

Molecules with low molecular weight can be covalently attached to nanocellulose surfaces through various chemical reactions such as esterification and etherification. Esterification is the most commonly used reaction for the hydrophobization of cellulose. During the process, the reaction either occurs on the whole cellulose polymer chains to form conventional cellulose esters or occurs at the outer of cellulose fibers leaving the cellulose crystalline structure in the interior intact. Both homogenous and heterogeneous esterification can be applied for the synthesis of a vast number of cellulose esters, however the reactions under heterogeneous conditions can be carried out almost exclusively for the surface modification of native cellulose, which also represents one of the main strategies for the isolation and chemical modification of nanocelluloses.

The amount of crystallinity in CNC can be estimated with X-ray diffraction and the percentage (%Cr) can be calculated in regards to the diffraction intensity for the amorphous as well as the angle taken where the intensity is at the minima. [6, 7]

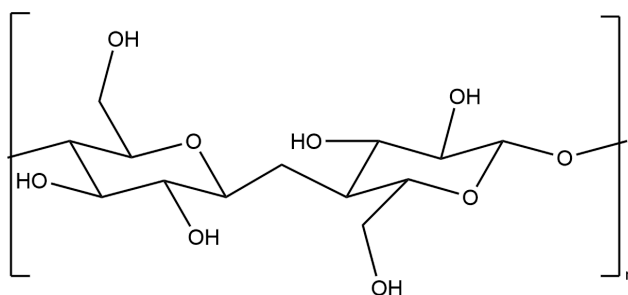


Figure 5: Structure of cellulose

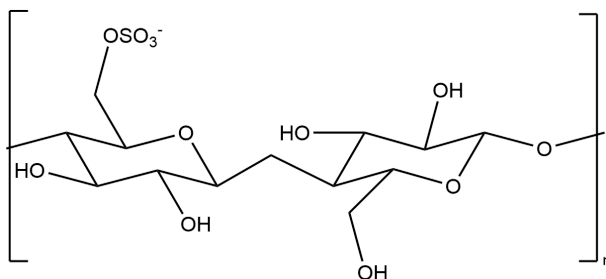


Figure 6: Structure of Nanocrystalline cellulose (CNC)



## Modification of Nanocrystalline cellulose with azetidiniumsalts

The materials of nanocrystalline cellulose are an interesting aspect in regards to their combination of properties and features such as being biodegradable, light in terms of weight as well as having a large surface area with mechanical properties. CNC can be obtained by acid hydrolysis of cellulosic fibres to remove the amorphous parts of the cellulosic materials. Sulphuric acid is commonly used for hydrolysis to convert some of the surface hydroxyl groups on the CNC to negatively charged sulphate ester units. Groups that are charged usually contribute to the stability of the CNC dispersion by reducing the tendency for particle aggregation. However, the thermal stability of the CNC can be improved by reacting the sulphate groups with a suitable compound or desulphation. The use of azetidiniumsalt as a reagent for modification is still something that is being explored, but the salt is most probably a reactive group together with epichlorohydrin in the wet-strength agent polyamideamine-epichlorohydrin (PAE). Attaching the salts to CNC will improve its properties and stability which prevents degradation at the polymers melting temperature. Therefore different CNC applications are suitable for different types of azetidiniumsalts that can be achieved by synthesis optimization of the salts. [11]

## NMR

NMR is a physical phenomenon of resonance transfer properties between magnetic energizers that occurs when an atom nucleus gets exposed to an external magnetic field and a specific electromagnetic radiation. Only atomic nuclei that have a property which is called "spin" can be analysed with the help of NMR spectroscopy, this is called NMR activity. For a nucleus to be active the atom must be at least one proton and / or one neutron number. Usually it is the 1-H and 13-C that gets examined in NMR. The main difference is that the Hydrogen NMR data show the hydrogen and their positions and 13-C show the amount and positions of the carbon atoms.

The peaks that appear in the spectra can appear in different amounts of divided peaks. The resonance will remain a single peak, a singlet, if there are no hydrogens in the neighboring atoms. If the peak is divided into two peaks, forming a doublet there is an adjacent atom that has hydrogen. Furthermore, if there is a neighboring group that contains two hydrogens, a triplet of a peak will appear. Analysing the visual appearance and the position of the peaks will give a general outlook over the molecule and its relations between the various hydrogens and therefore makes NMR-spectra an efficient way to get a greater overview of a product. [12]

NMR is very useful to detect if either the right salt is produced or if another reaction has taken place during the procedure. Information about the startmaterial can also be known by studying the peaks. If the startmaterial is obtained, other reactions can be performed as well as error of margins can be noted, otherwise the goal to produce a certain kind of azetidiniumsalt should be completed if no peaks indicate a sign of the startmaterial.

## **TLC**

Thin layer chromatography is a separation process that contains two phases, a stationary phase as well as a mobile phase, similar to other chromatography approaches. The stationary phase is usually the silica gel coated on the TLC plate and the mobile phase is a solvent chosen based on the properties of the mixture. TLC is a typical process for distinguishing compounds in a solution and assessing their purity which is based on the relative affinity of the compounds to the mobile and stationary phases.

A drop of the sample solution is placed on a TLC plate and any reference is placed next to it. The plate is then placed in a special beaker with enough solvent to cover the lower part of the plate by a small margin. The solvent or mobile phase flows upwards through the stationary phase due to capillary forces. The various components of the sample solution are separated according to the distribution equilibrium between the polar stationary phase and the non-polar mobile phase of the various components. The migration and distribution of the analytes can later be visible under UV light. [13]

## **Column chromatography**

Column chromatography is the most popular separation and purification technique. Both solid and liquid samples can be separated and purified by column chromatography. This particular method consists of a stationary solid phase that adsorbs and separates the compounds passing through it with the help of a liquid mobile phase. On the basis of their chemical properties and nature, compounds get adsorbed and elution is based on differential adsorption of a substance by the adsorbent. Various stationary phases, such as silica, alumina, calcium phosphate as well as other different solvent compositions based on the nature of compounds to be separated and isolated, are used in column chromatography.

Samples to be separated are mixed with silica and introduced at the top of the column and allowed to move with the solvent. With polarity differences, compounds are adsorbed at different regions and desorbed with suitable solvent polarity. The compound of higher adsorption ability will be adsorbed at the top and that with the lower one will be at the bottom. By adding the solvent at the top, compounds get desorbed and pass through the column and this process is called elution that needs to be performed to complete the separation. [14]

# Methods

To produce the azetidinium compounds there are several different methods to get the wanted product. The method we've chosen has previously been studied to produce azetidinium salts with various dialkylamines. Dialkylamine is the startmaterial that synthesis with the reagent epichlorohydrin. For this synthesis four different dialkylamines were used to determine the accuracy of the experiment. Following this paragraph is a table containing the molecular weight of each dialkylamine and the amount used for each of the individual synthesis.

Dialkylamine	Molecular mass (g/mol)	Amount used (g)
<u>Diallylamine</u>	97,16	0,97
<u>Di-n-Hexylamine</u>	185,35	1,85
<u>Bis(2-ethylhexyl)amine</u>	241,46	2,41
<u>Bis(2-methoxyethyl)amine</u>	133,19	1,33

Table 1: The amount and the different secondary amines used.

Each of the dialkylamines was prepared in individual batches and combined with 1ml of epichlorohydrin. 10ml Isopropanol was also added to dissolve the compounds. The solution was later stirred at room temperature for 12 h. The solvent was evaporated on a rotary evaporator to remove the solvent used. When this process is completed the ring open intermediar should be formed. To close the ring open structure and finalise the Azetidinium salt, water was added. When water is added the solution is once again stirred at 100 C to react. Since the solution is water based it went through distillate to remove the miscellaneous liquids.

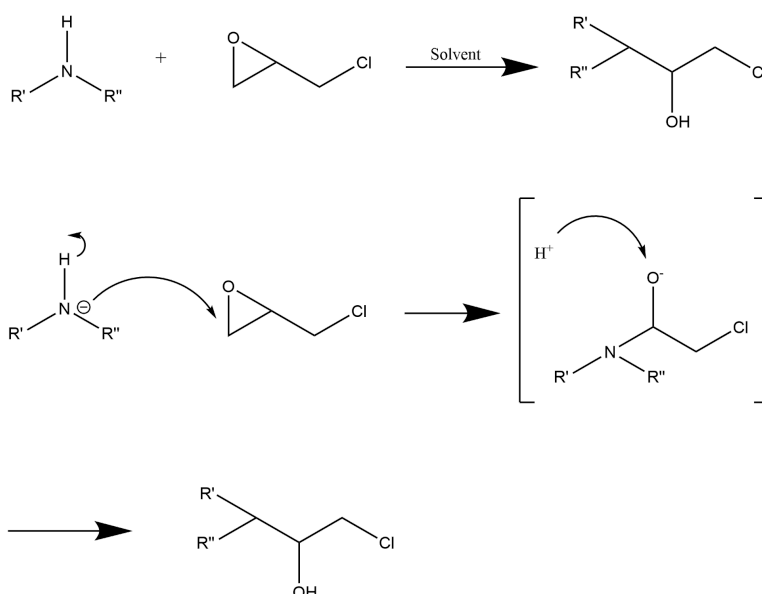


Figure 7: Reaction mechanism for the ring open molecule

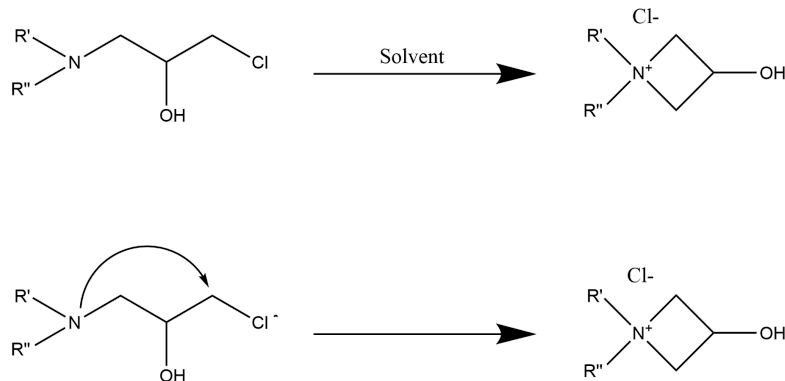


Figure 8: Reaction mechanism for Azetidinium synthesis

This procedure is divided into two steps. First to create the ringopen molecule, and later on add water to create the ring-closed molecule which is the azetidinium ion.

The procedure can also be reduced into one step by performing the synthesis with isopropanol and water as solvent from start and later stirring the solution in 100 C to obtain the salt. When the azetidiniumsalts are produced, optimization and evaluation can be made to make the production a lot smoother and more efficient in terms of time as well as the material impact on the environment.

To illustrate a brief idea how the azetidiniumsalts can react with CNC, a molecule model would be synthesized as a reference.

### Sulphate glucoside (Molecule model)

To perform modifications of nanocrystalline cellulose, an alternative molecule model with a sulphate group was produced with similar identity and structure regards to CNC. This makes it easier to react azetidiniumsalts with the molecule model as well as further applications of CNC.

Solvents used	Amount used
Anhydrous D-glucopyranose	2.7 g
P-TsOH	0.32 g
BnOH	22 ml

Table 2: Table displaying the compounds used for the first step of the synthesis of Sulphate glucoside.

The solvents used were mixed together in a beaker and distillation was performed with a gradually growing temperature between 75 - 95 degrees C. After 4 hours of distillation, enough benzyl alcohol could be extracted, around (90%) to obtain the glucopyranoside and H-NMR indicated that signals of the sugar unit could be seen in the product which completed the synthesis.

Solvents used	Amount used
D-glucopyranoside	0,77 g
Dimethylformamide (DMF)	9 + 1 ml
SO3 trimethylamine complex	0.5 g

Table 3: Table displaying the compounds used for the second step of the synthesis of Sulphate glucoside.

The D-glucopyranoside solution was mixed with 9 ml DMF in a beaker which was placed in a water bath containing ice as well as sodium chloride. The water bath was used to cool down the solution to a temperature of - 20 degrees C. When the cool down was completed a mixture of SO3 trimethylamine with 1 ml DMF was added to the initial mixture and taken out of the water bath to let the solution stir at room temperature for approximately 12 h. Distillation was once again performed to extract DMF from the solution with a temperature range from 50 - 85 degrees C during a span of 2-3 hours. When distillation was completed the sulphate glucoside was obtained.

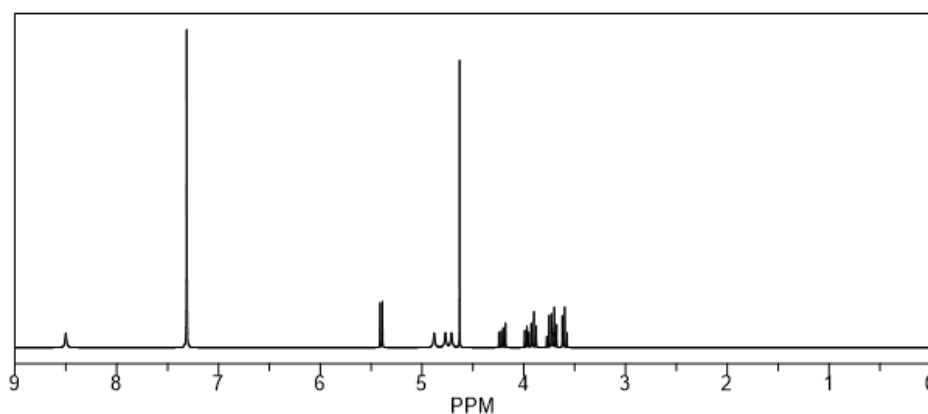


Figure 9: <sup>1</sup>H-NMR spectra of expected peaks for sulphate glucoside

To purify the sulphate glucoside, thin liquid chromatography (TLC) was performed. TLC was performed with silica gel coated plates as a stationary phase, which has a high polarity. Two alternate eluent systems were used, EtOAc:MeOH = 50:6 ml and EtOAc:MeOH:H<sub>2</sub>O = 10:1,7:1,4 ml with ethyl acetate as a mobile phase. The second eluent system gave a clearer migration and distribution of the analytes as opposed to the first one due to different polarities in each system as well as the tendency for the D-glucopyranoside and sulphate glucoside to react with the mobile phase.

***TLC - (EtOAc:MeOH:H<sub>2</sub>O) results***

***Stained***



***RP      FP***

***UV-visible spots***



***RP      FP***

*Rp - Reference Product*

*Fp - Final Product*

Following TLC results indicated that there still is a good amount of benzyl alcohol and DMF left in the sulphate glucoside solution. To extract the remaining parts of benzyl alcohol as well as obtaining a pure compound, column chromatography was performed.

To receive the product a column chromatography was done using ethyl acetate, methanol and water as eluent or mobile phase as well as silica sand as a stationary phase. After the completion of chromatography, solvents were evaporated through the rotary evaporator for approximately 15 min. TLC and H-NMR was once again performed for product confirmation and the final product (sulphate glucoside) should be obtained.

## Sulphate glucoside - Significance and Applications

Sulphate glucoside was made as a model compound for CNC and contains a sulphate group that can now be reacted with azetidiniumsalts through different types of reactions such as hydrophobization. Hydrophobization is a process of making the surfaces hydrophobic. When azetidiniumsalts is reacted with a sulphate group, improvements of properties and different application areas is obtained such as renewable biobased materials and benefits in nanocomposite manufacturing. Furthermore CNC modifications such as thermal stability can then be improved by reacting the sulphate group with azetidiniumsalts. In this manner sulphate glucoside basically works as a model compound for CNC modification.

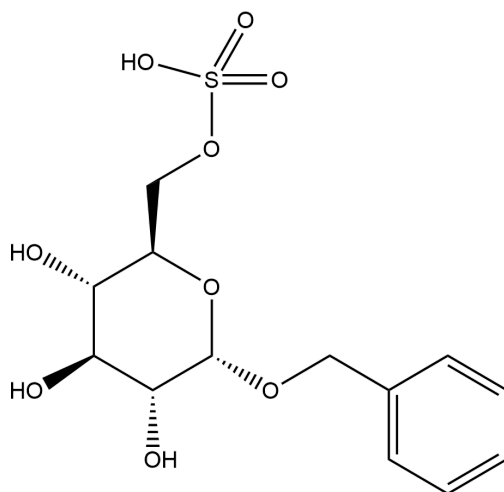


Figure 10: Molecule structure of Phenyl alpha-D-glucopyranoside pyridine (molecule model)

## Results and discussion

During the Azetidinium synthesis, various dialkylamines were used and also the circumstances varied depending on the solvent.

<i>Side groups</i>	<i>Solvent</i>	<i>Temperature (C)</i>
Allyl	Isopropanol	20
Allyl	Isopropanol/water	100
Hexyl	Isopropanol	20
Hexyl	Isopropanol/water	100
Hexyl	Isopropanol/water	100
Ethylhexyl	Isopropanol	20
Methoxyethyl	Isopropanol	20

*Table 4: A table of the different azetidiniumsalts synthesized under different reaction circumstances*

A product was obtained with each of the four side groups chosen, but the results varied due to differences in properties and characterization. Reaction conditions also varied with change in solvent as well as temperature. Allyl as an dialkylamine with only isopropanol as a solvent gave the more effective production in terms of quality and quantity, but timewise the solvent with isopropanol and water together worked best. Combination of isopropanol and water can work in the majority of the dialkylamines but preferable in dialkylamines that are more complex, such as di-n-hexylamine for instance. Solvents with the majority of the solution consisting of water were not efficient based on H-NMR results, but in terms of economical and environmental aspects it could be a favourable idea.



## H-NMR analysis

This is the H-NMR spectra for Diallylazetidiniumsalt. A positive nitrogen and a negative chlorine atom is obtained when the salt is ring-closed. The peak for hydroxyl should be around 5 - 7 ppm and methylene chains around 2 - 3 ppm. Signals from the protons on carbon 6,7,8 and 9 are usually visible between 3 - 4 ppm and protons from carbon 1,2,3 and 4 which is also the main azetidinium should appear around 4 - 5 ppm. [12]

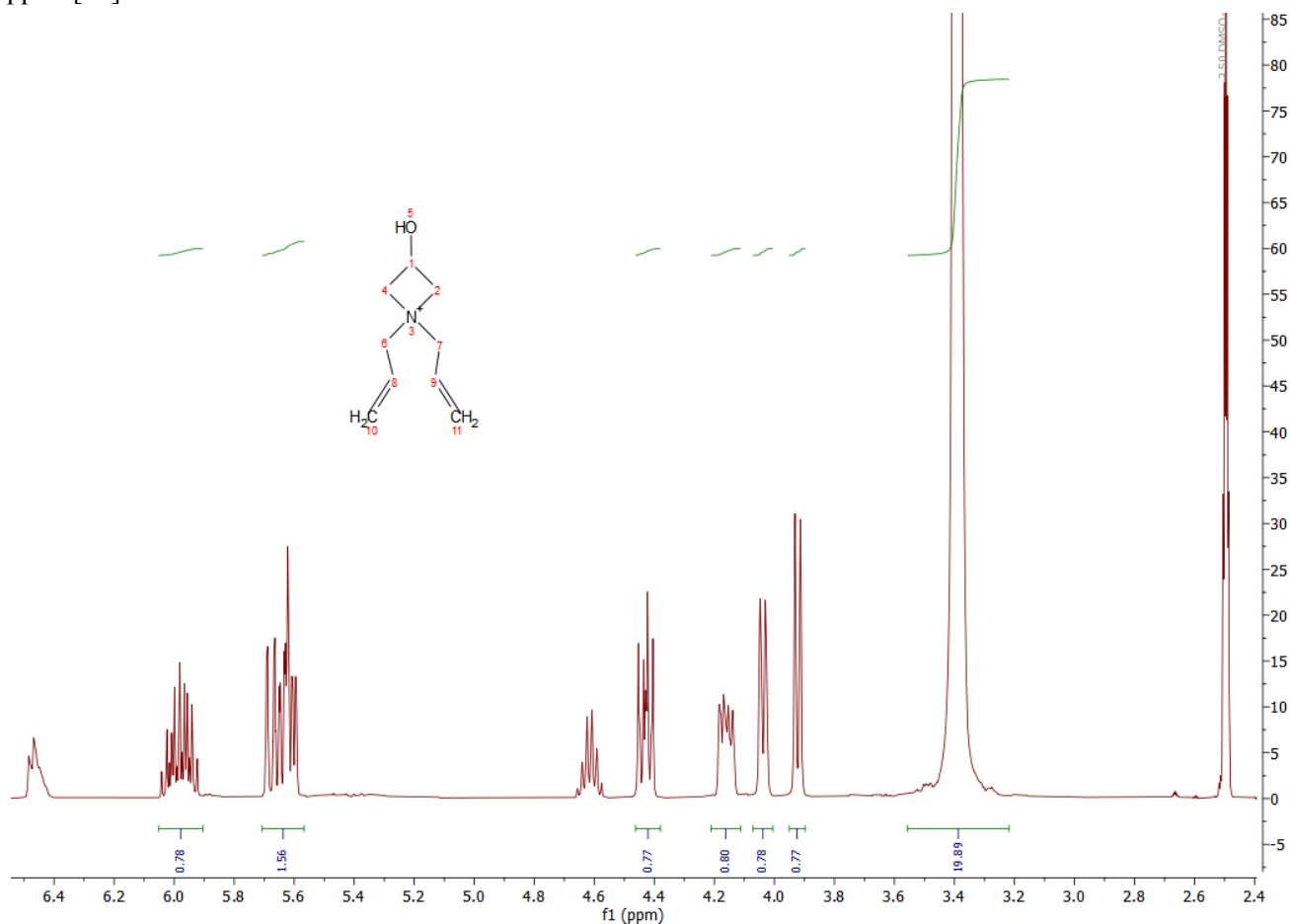


Figure 11: H-NMR for diallylazetidiniumsalt

## FTIR analysis

Following spectras represent both Bis(2-methoxyethyl)azetidinium salt and the ring open molecule. This is a second method to verify which products have been obtained during the reaction. The characteristics for both the ring open molecules are the OH- group that is present in both molecules. According to the spectras from the research there are absorption signals between 3200-3500 which is the common frequency range for OH-groups. Ranges between 400 - 1500 usually represent a fingerprint region that contains a number of complicated absorptions and the wavelength range, 2800 - 3000 represents saturated protons. The difference between open and closed signals are relatively small, due to the same amount of molecules in both spectras. A difference is the higher amount of transmittance in the ring-closed molecules because of the positive and negative ions in azetidiniumsalt. A wide range of signals is typical for ring-closed molecules and short signals are typical for ring-open molecules. [15]

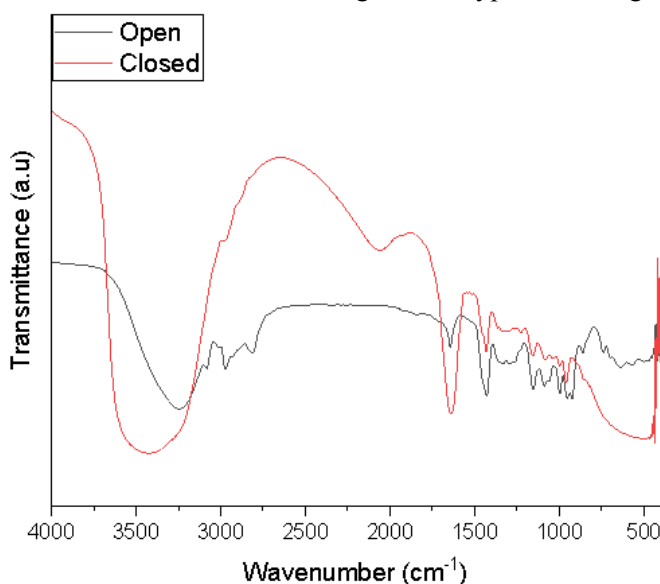


Figure 12: FT-IR for both the ring open molecule (*Open*), and diallylazetidiniumsalt (*Closed*).

IR bands (cm <sup>-1</sup> )	Assignment
3600-3200 (3215)	O-H stretching
2924	CH <sub>2</sub> asymmetrical stretching
2854	CH <sub>2</sub> symmetrical stretching
1745-1730	-CF=CF- internal double bonds
1640	-CRR'=CH <sub>2</sub> terminal stretching
1445-1430	CH <sub>2</sub> scissoring
1205	CF <sub>2</sub> symmetric stretching
1152	CF <sub>2</sub> asymmetric stretching
1086	C-O hydroxyl stretching
1050	
1035	
1009	=CH <sub>2</sub> out-of-plane bending (terminal methylene)
982	=CHR out-of-plane bending (terminal partially substituted methylene)
880	

Table 4: A table for the expected signal ranges in FT-IR spectras.

# Conclusions

The synthesis of symmetrical azetidiniumsalts were successful by verification of H-NMR data and FTIR. Table 1 showed the various reaction circumstances performed and each condition gave different results depending on the alkylamine or solvent used. Isopropanol alone as a solvent worked great at room temperature, however when water was partially added as a solvent reaction worked optimally at higher temperature. The increase of water in the solution can be good in terms of economical aspects and time, but isopropanol as solvent gives the more accurate H-NMR spectra for the product. The solvents for each particular salt were optimized depending on the properties of their side groups, Di-n-Hexylamine was preferable when undergoing optimization due to its complex structure and design which would give clearer results as well as observations opposed to a salt with less properties.

An alternative way of nanocrystalline cellulose modification was researched by producing a molecule model (Sulphate Glucoside) that is identical in structure and characteristics. This particular molecule could be used for modifying CNC without the synthesization of pure cellulose, by measuring the sulphate content and reacting the azetidiniumsalts with the molecule to eventually complete the modification of CNC.

The reaction of different compounds with azetidiniumsalt is still an area that is being explored and new applications can be obtained by further analysis and optimization of the salts. New methods of nanocrystalline cellulose modifications can be achieved by several reaction conditions that work for a specific compound or side group in azetidiniumsalts. These investigation areas may have a great impact on mechanical, thermal and biodegradable properties on composites, which can eventually have a utility in future pharmaceutical industries as well as benefits in medical applications.

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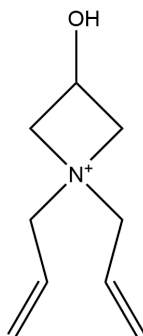
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# Appendix

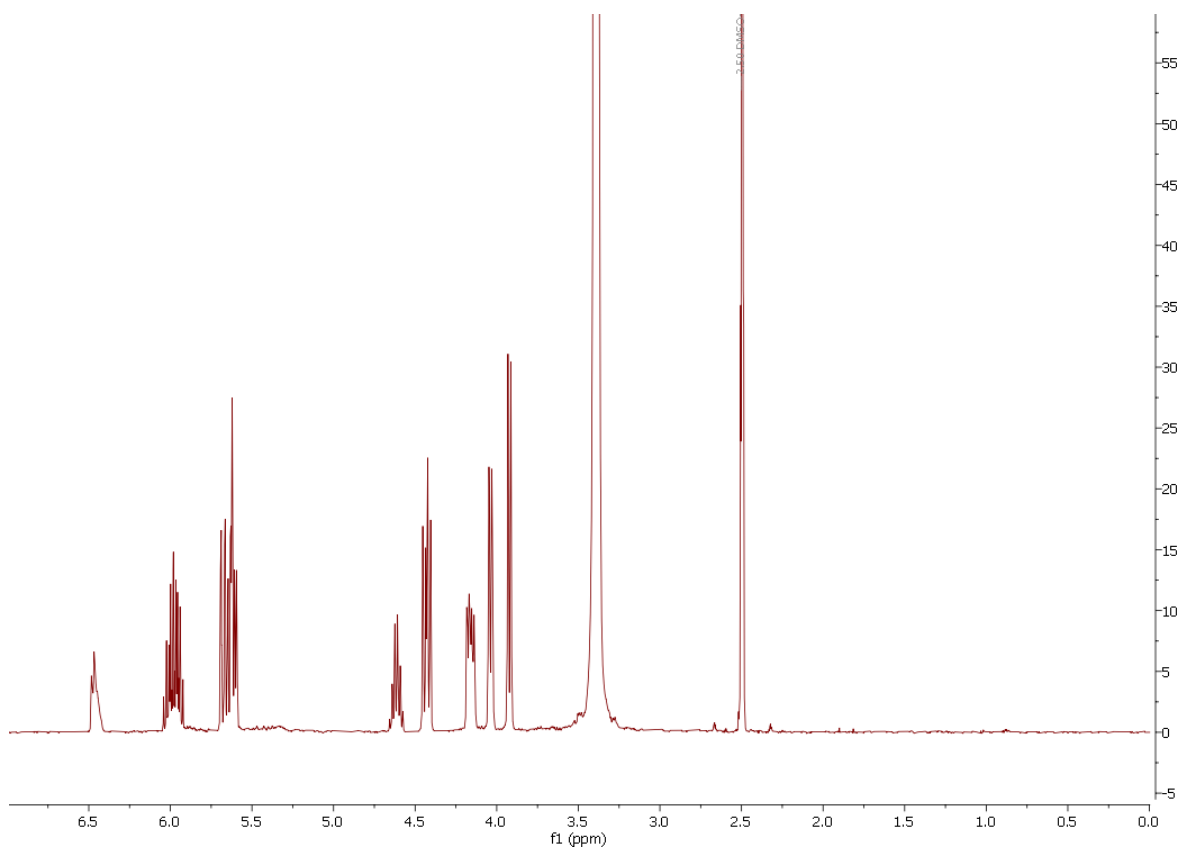
## A. *H-NMR Ring-closed Structure*

H-NMR spectras & FTIR for produced:

**Diallylazetidinium salt**



*Figure 13: Structure for Diallylazetidinium salt*



*Figure 14: <sup>1</sup>H-NMR for Diallylazetidinium salt*

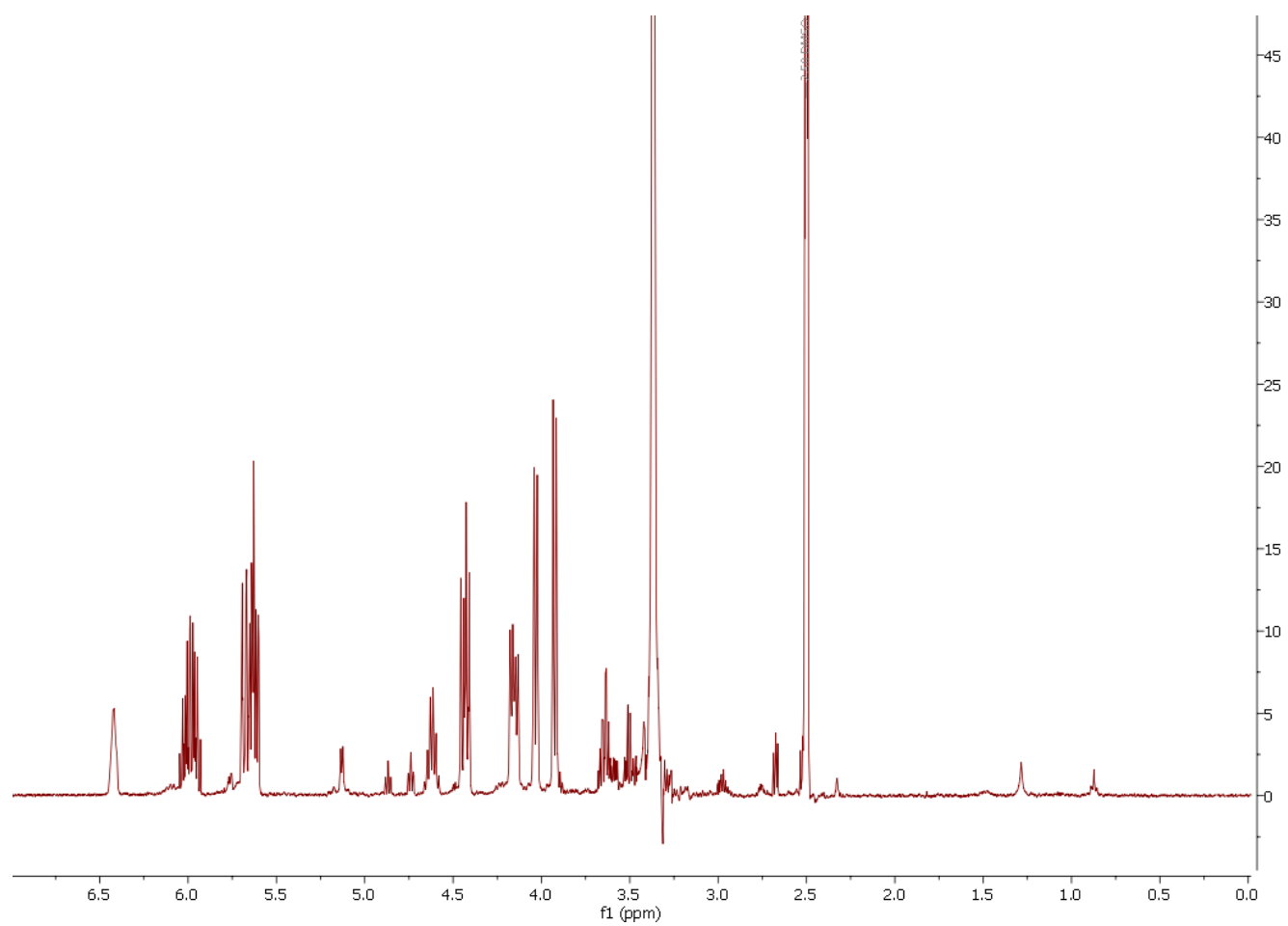


Figure 15:  $^1\text{H}$ -NMR for Diallylazetidinium salt with solvent  $\text{H}_2\text{O}$ :isopropanol = 9:1

## FTIR

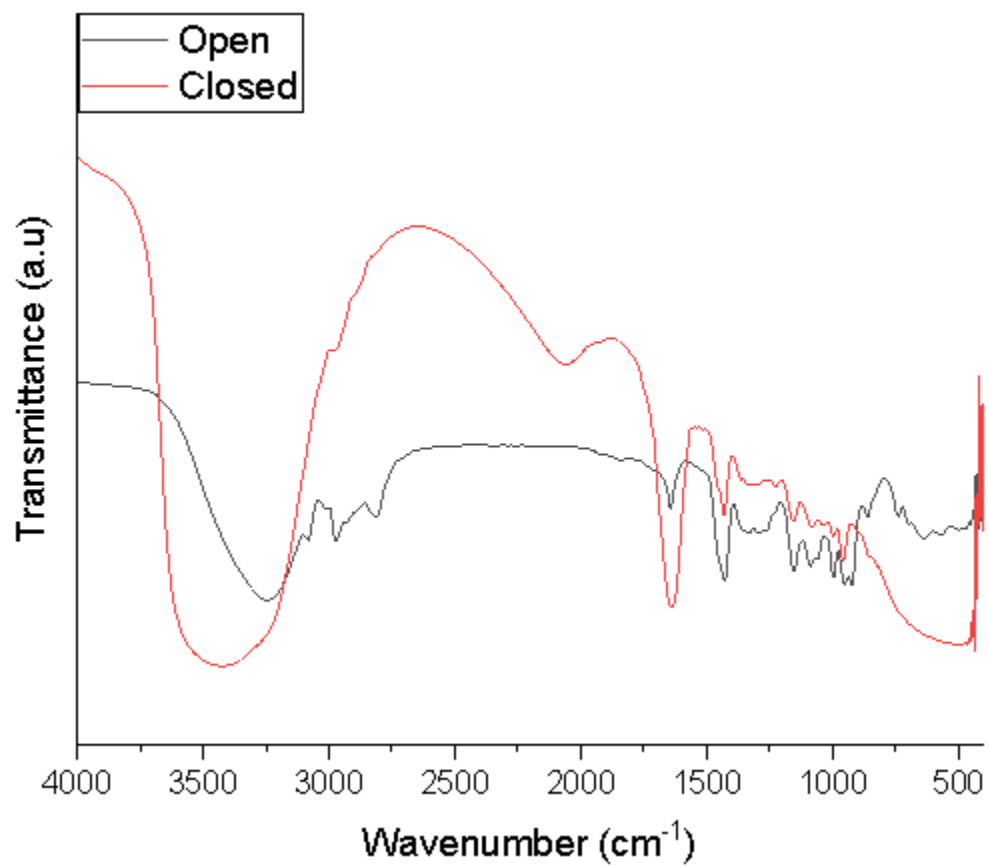


Figure 16: FT-IR spectra for Diallylazetidinium salt (Closed), and Ring open molecule (Open)

### Di-n-Hexylazetidinium salt

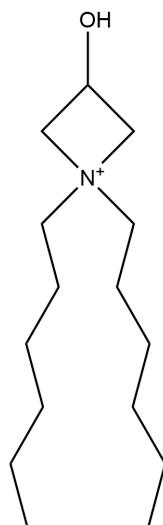


Figure 17: Structure for Di-n-hexylazetidinium salt

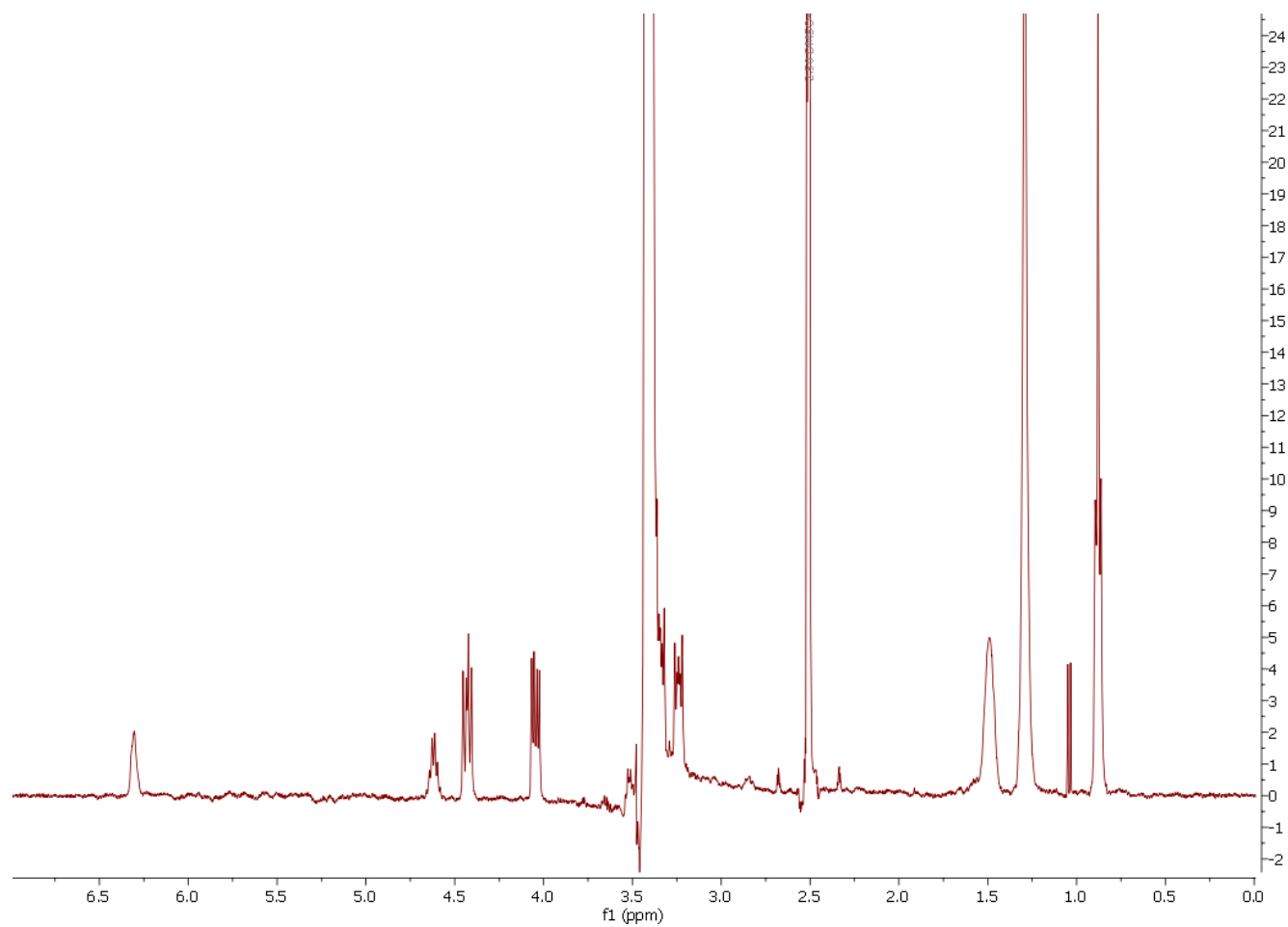


Figure 18: <sup>1</sup>H-NMR for Di-n-hexylazetidinium salt



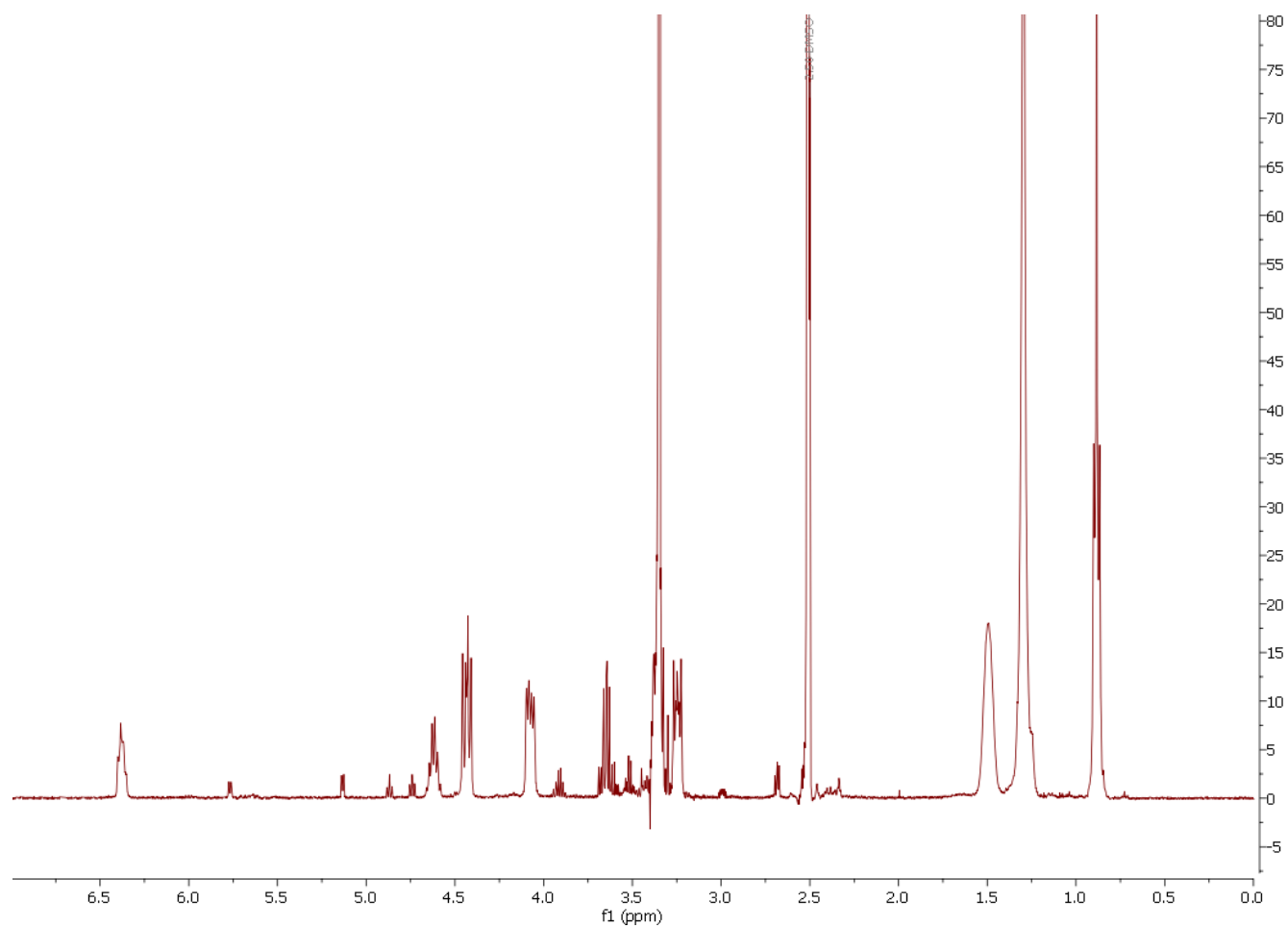


Figure 19:  $^1\text{H}$ -NMR for Di-*n*-hexylazetidinium salt with solvent  $\text{H}_2\text{O}$ :isopropanol = 9:1

## FTIR

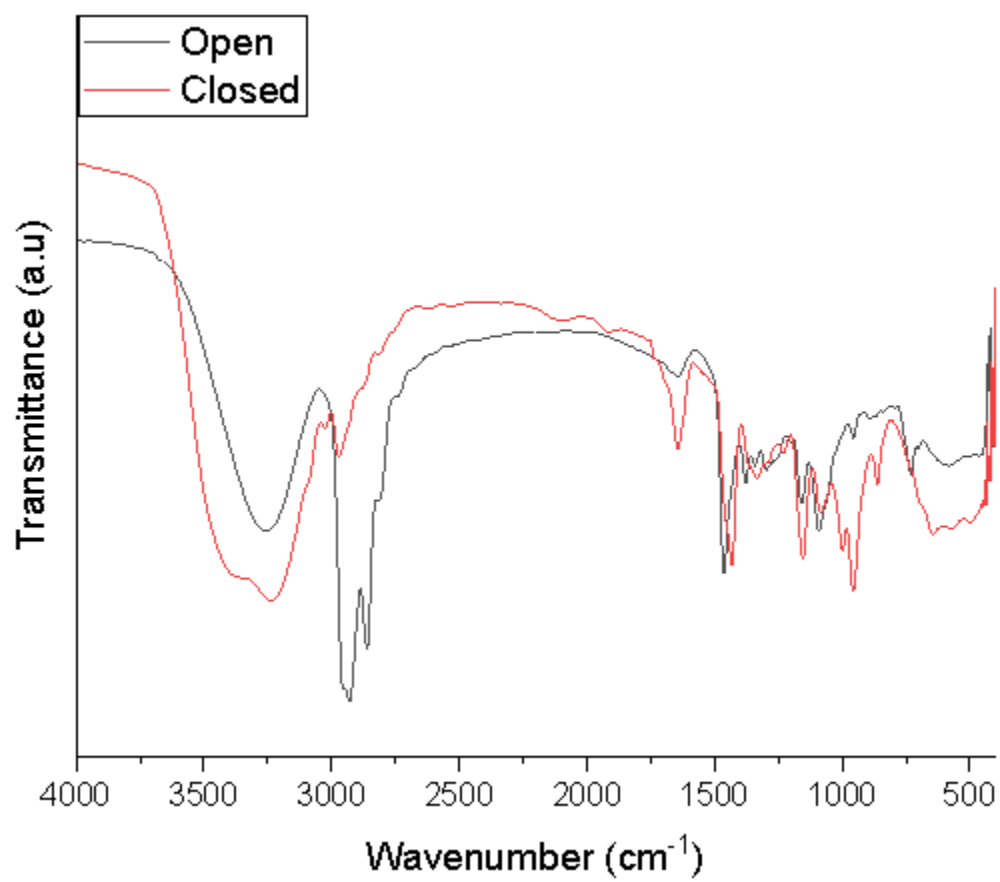
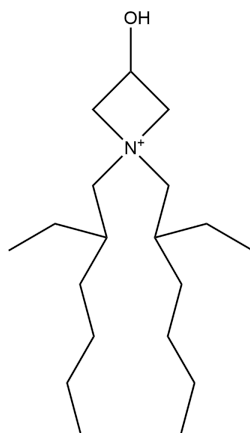
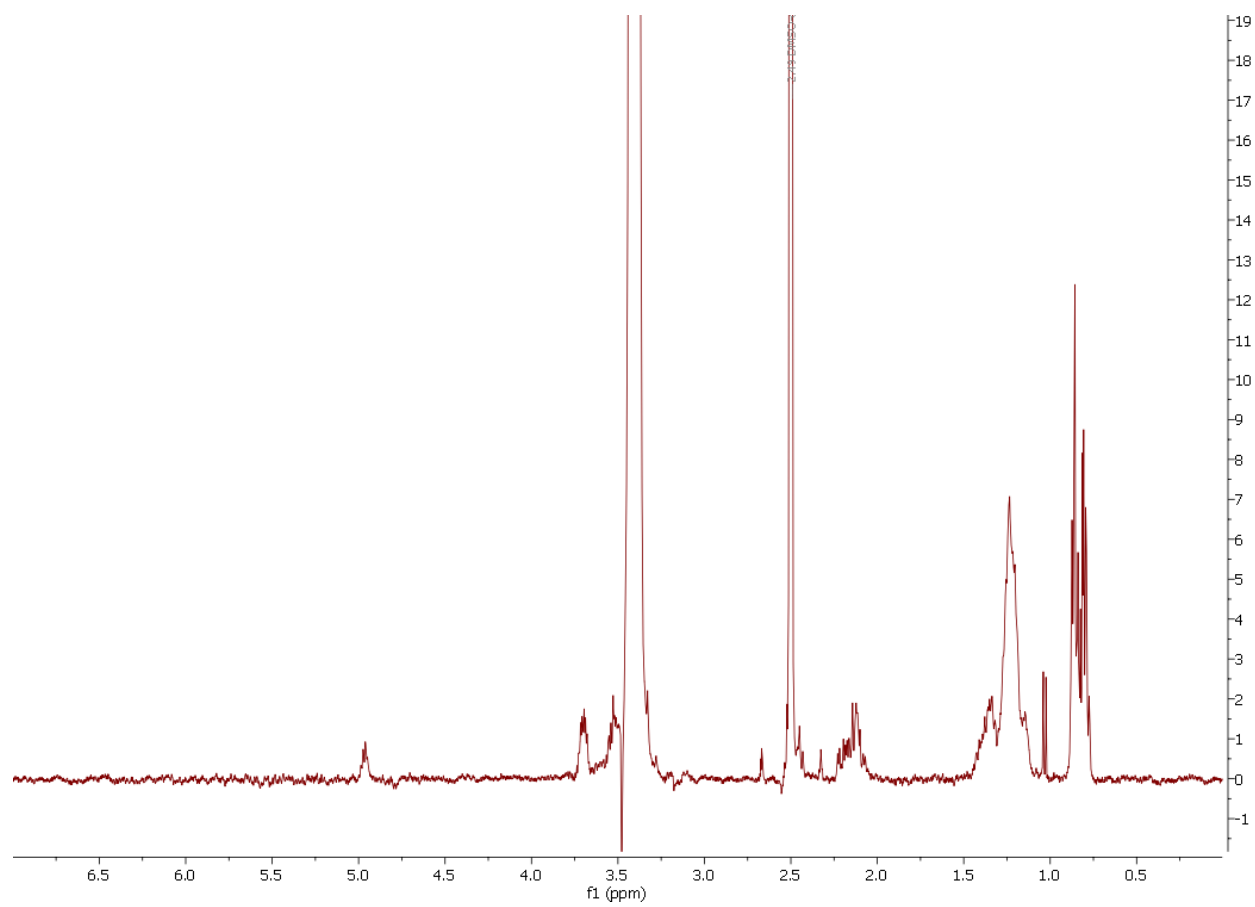


Figure 20: FT-IR spectra for Di-*n*-hexylazetidinium salt (Closed), and Ring open molecule (Open)

**Bis(2-ethylhexyl)azetidinium salt**



*Figure 21: Structure for Bis(2-ethylhexyl)azetidinium salt*



*Figure 22: <sup>1</sup>H-NMR for Bis(2-ethylhexyl)azetidinium salt*

## FTIR

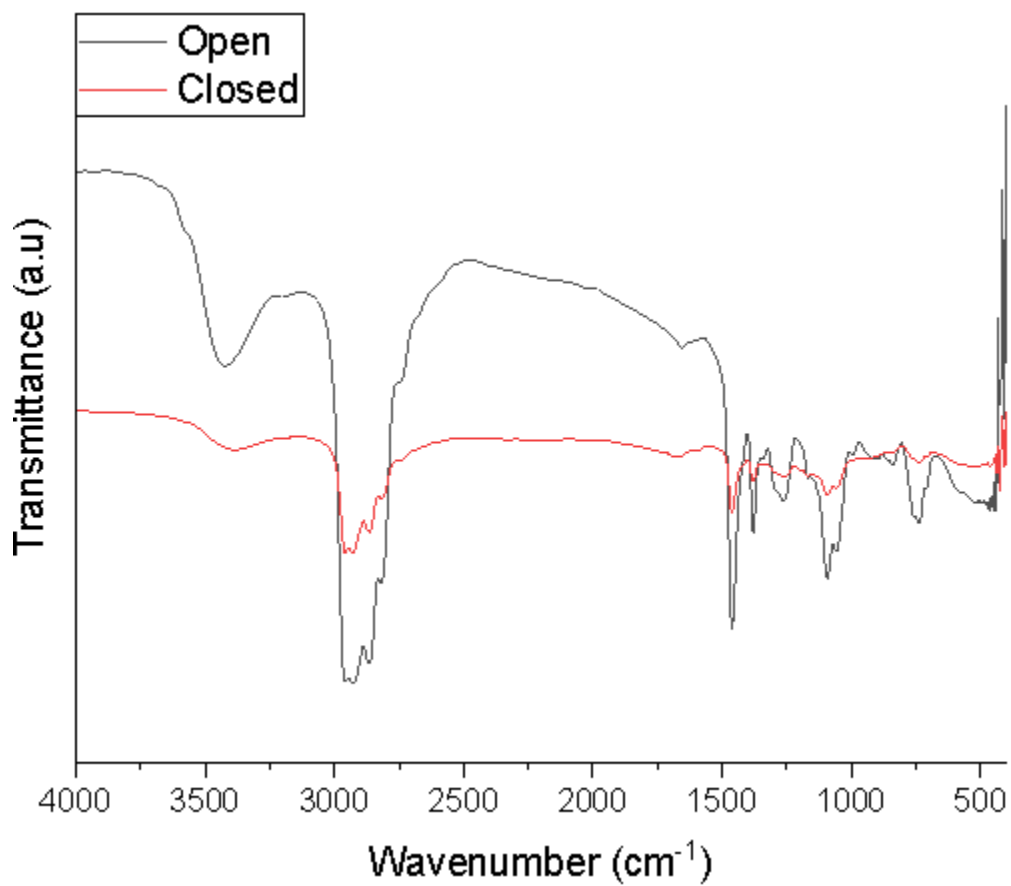
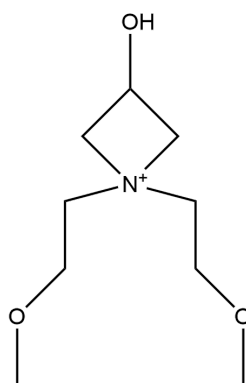
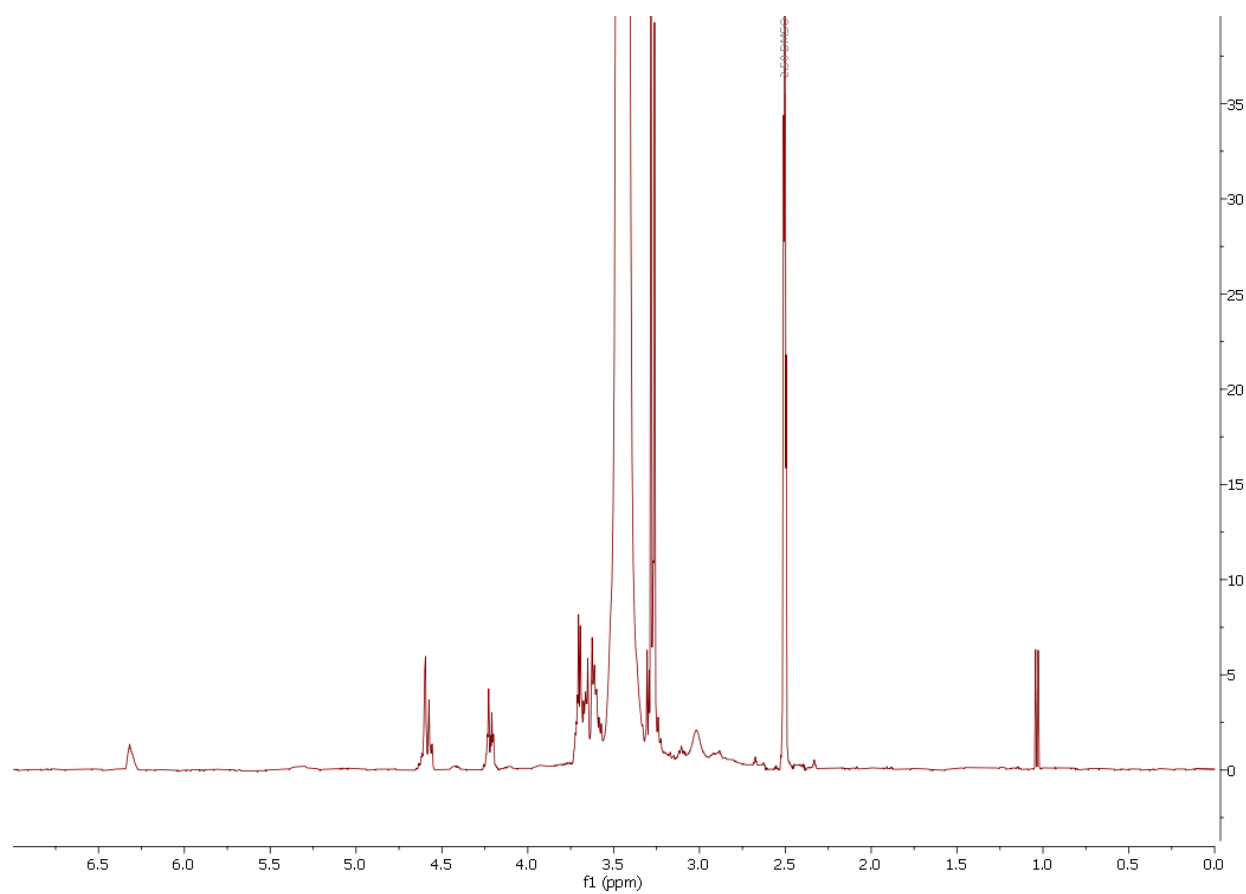


Figure 23: FT-IR spectra for Bis(2-ethylhexyl)azetidinium salt (Closed), and Ring open molecule (Open)

**Bis(2-methoxyethyl)azetidinium salt**



*Figure 24: Structure for Bis(2-methoxyethyl)azetidinium salt*



*Figure 25: <sup>1</sup>H-NMR for Bis(2-methoxyethyl)azetidinium salt*

## FTIR

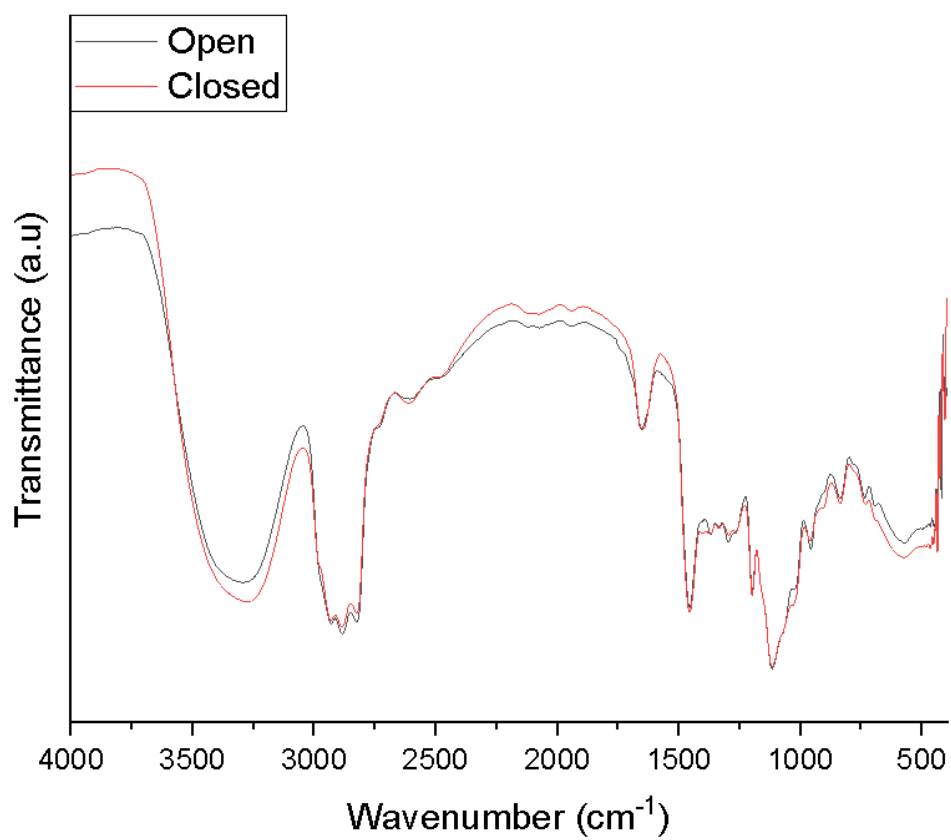
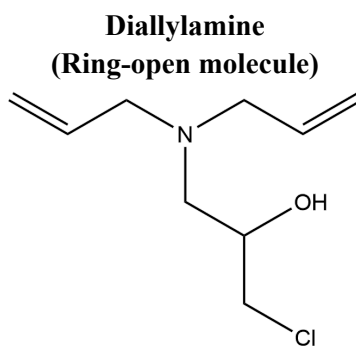


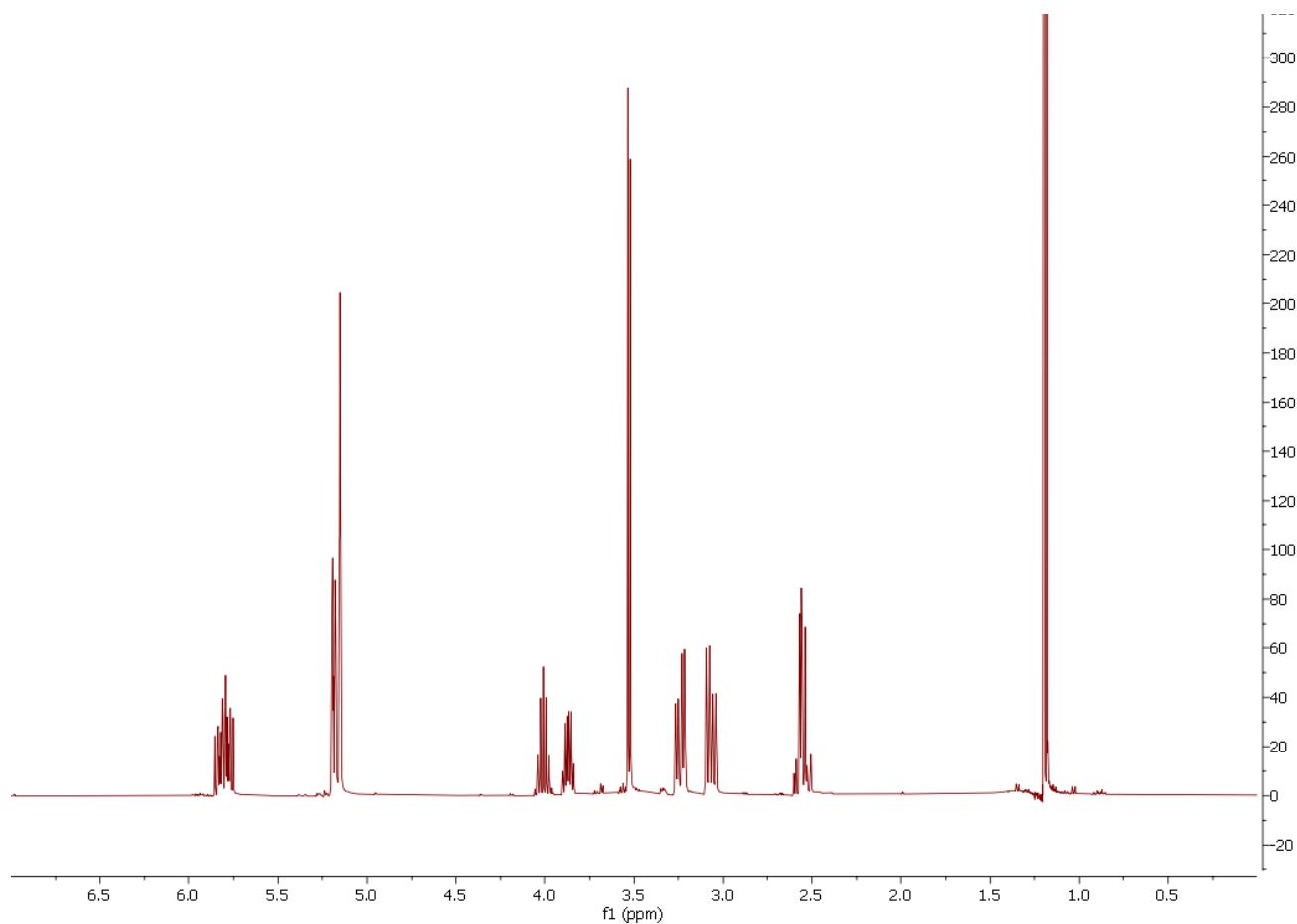
Figure 26: FT-IR spectra for Bis(2-methoxyethyl)azetidinium salt (Closed), and Ring open molecule (Open)

## ***B. <sup>1</sup>H-NMR - Ring-Open Structure***

<sup>1</sup>H-NMR spectras & FTIR for produced:



*Figure 27: Chemical structure of Diallylamine (Ring-open molecule)*



*Figure 28: <sup>1</sup>H-NMR for Diallylamine (Ring-open molecule)*

**Bis(2-ethylhexyl)amine  
(Ring-open molecule)**

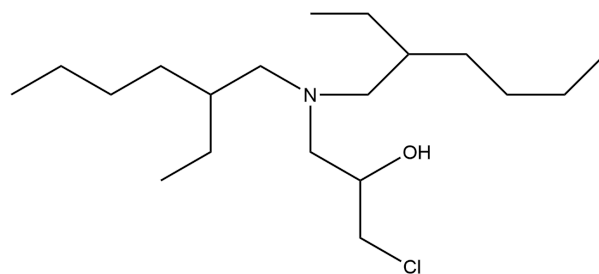


Figure 29: Chemical structure of Bis(2-ethylhexyl)amine (Ring-open molecule)

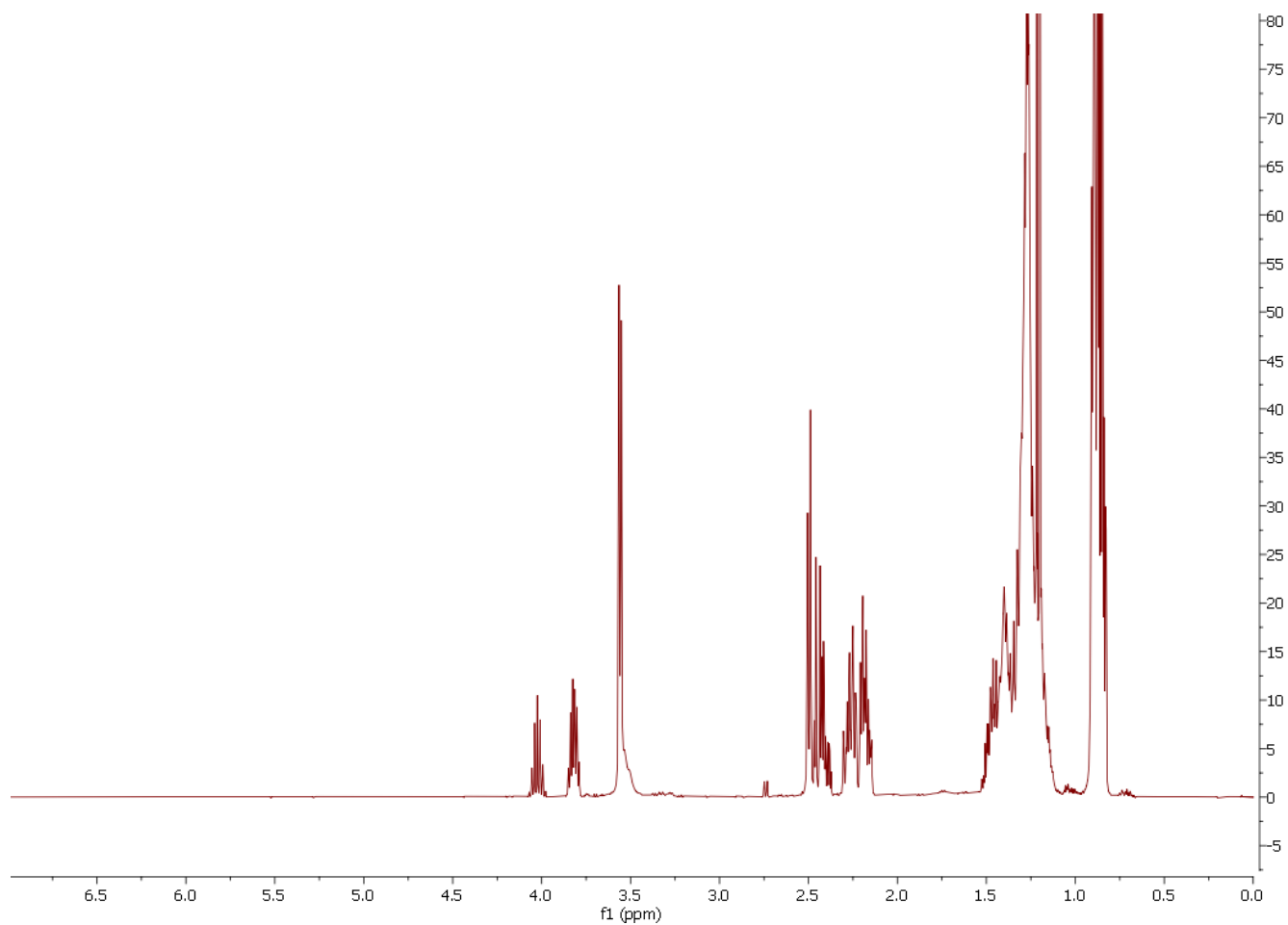


Figure 30:  $^1\text{H}$ -NMR for Bis(2-ethylhexyl)amine (Ring-open molecule)



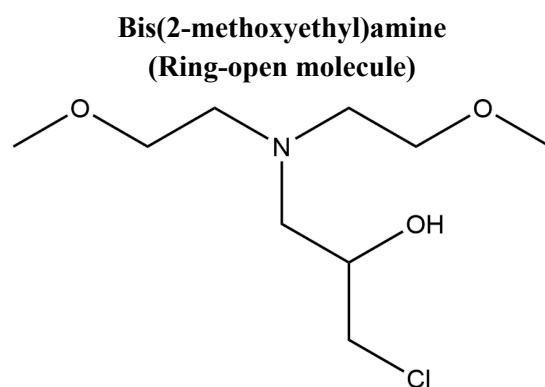


Figure 31: Chemical structure of Bis(2-methoxyethyl)amine (Ring-open molecule)

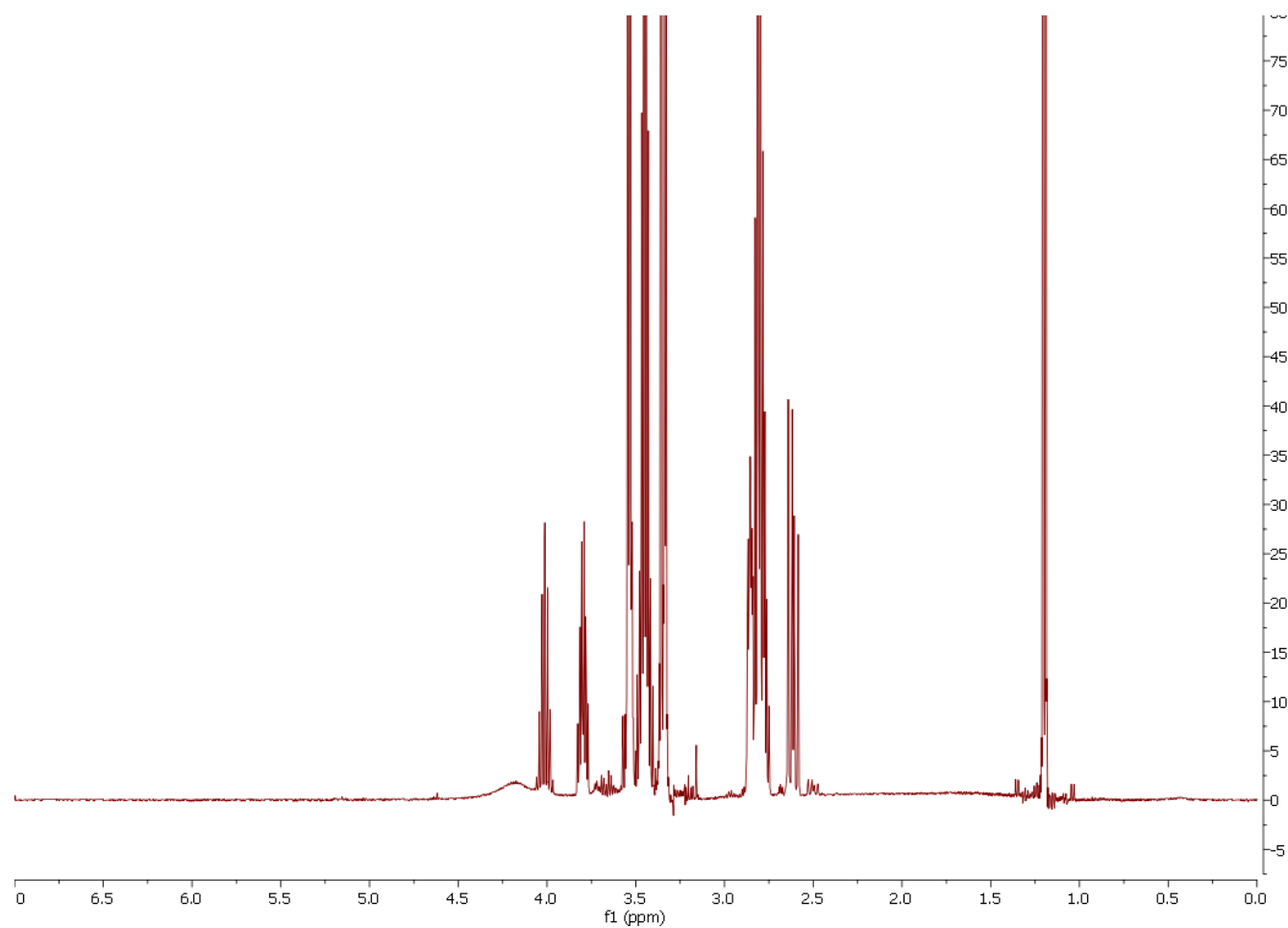
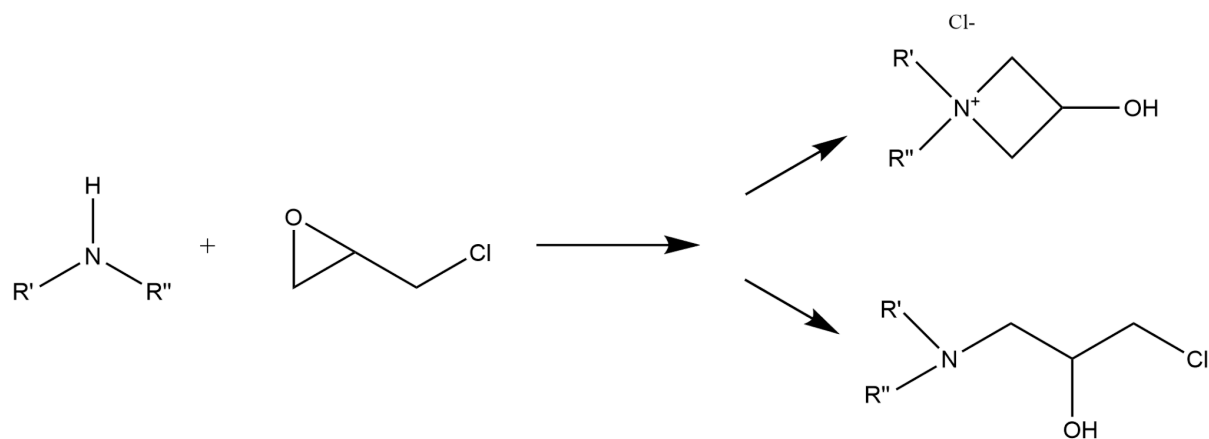


Figure 32: <sup>1</sup>H-NMR for Bis(2-methoxyethyl)amine (Ring-open molecule)

## Process for synthesis of dialkylazetidiniumsalt



*Dialkylamine mixed with epichlorohydrin produces the ring-closed product (top product) or ring-open product (bottom product)*

1. 10 mmol of dialkylamine was mixed with 10 ml solvent (Isopropanol)
2. A reagent of 13 mmol epichlorohydrin was added into the mixed solution
3. The solution was stirred at room temperature for approximately 24 h
4. Isopropanol solvent is finally extracted from the solution by a rotary evaporator
5. The final product (Azetidiniumsalt) is obtained