**University of Alberta**

# Synthesis and Characterization of Novel Polyols and Polyacids from Vegetable Oils for Use in Polymer Manufacture

by
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# ABSTRACT

Methodology for the synthesis of aliphatic and aromatic polyols, polyacids from vegetable oils and its derivatives have been described. First generation aliphatic polyols containing terminal hydroxyl functionalities were produced *via* ozonolysis of canola oil followed by catalytic hydrogenation of the ozonolysis product. The polyols are comprised of saturated triacylglycerols (TAGs), mono-ols, diols and triols, which were separated and purified by flash chromatography and identified by IR, $^1$H-NMR, $^{13}$C-NMR, and Mass Spectroscopy. An HPLC-ELSD method was developed to separate and quantify the four components in the polyols. Second generation polyols containing a significantly higher triol content and higher hydroxyl value were synthesized from canola oil by utilizing a milder solvent (ethyl acetate) and a more efficient reductive reagent (zinc) compared to the previous synthetic procedure.

Hexasubstituted benzene derivatives such as aromatic triols and triacids have been synthesized from oleic and erucic acid derivatives *via* a cyclotrimerization step catalyzed by palladium-on-carbon (Pd/C) and chlorotrimethylsilane (TMSCl). The asymmetric isomer, which is the main product, was isolated from its symmetric isomer by silica flash chromatography. All the products were fully characterized by IR, $^1$H-NMR, $^{13}$C-NMR and Mass Spectroscopy. These aromatic products are potentially useful monomers for the production of polyurethanes, polyesters and polyamides. It has been confirmed that the same pure fatty alkyne as derived from pure oleic acid, which is the precursor to the final hexasubstituted benzene derivatives, can be obtained.from the mixture of fatty acids derived from the saponification of canola oil. Therefore, it is

predicted that the same aromatic triol and triacid products can be obtained from canola oil as from pure oleic acid.

# ACKNOWLEDGEMENTS

This thesis is the result of four years of work whereby I have been accompanied and supported by many people. It is a pleasant aspect that I now have the opportunity to express my gratitude to all of them.

It is difficult to overstate my gratitude to my Ph.D. supervisor, Dr. Suresh S. Narine. His enthusiasm, his inspiration, and his guidance have provided a good basis for the present thesis. I am greatly thankful to Dr. Narine for suggesting and persuading me to transfer back to the PhD program, otherwise this thesis would not be possible. Besides being an excellent academic supervisor, Dr. Narine has provided great help to my family. Thank you, Dr. Narine. I am also grateful to my supervisory committee members: Dr. Peter Sporns, Dr. David Bressler, and Dr. Lech Ozimek.

I wish to express my warm and sincere thanks to Dr. Wan and Dr. Bouzidi for their proof reading of this whole thesis and each of my papers. Gratitude is also due to Dr. Kong, who provided valuable advice on my research and family life. I would like to thank Ereddad Kharraz for his technical support. I am grateful to all colleagues at ALUP.

I feel a deep sense of gratitude to my parents who always support and encourage me. However, I also feel very sorry for not being able to accompany and take care of them when they are sick. Although they are living far away, their nice smiles through the webcam made me feel warm, calm, and confident.

To Dong for sharing your knowledge of chemistry and lab techniques, for helping me with this thesis, for being my driver, for the warm embrace when I was at my low points, for the patience when I was fretful, most of all for your unwavering love and support. One of the best experiences that we lived through during my PhD period was the birth of our son, Weihan, who provided an additional and joyful dimension to our life mission.

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| ASTM | American Society for Testing and Materials |
| Bn | Benzyl |
| Calcd. | Calculated |
| Cat. | Catalyst |
| d | Doublet |
| DCM | Dichloromethane |
| dd | Doublets of Doublets |
| DMA | Dynamic Mechanical Analysis |
| DMF | Dimethylformamide |
| DMSO | Dimethyl Sulfoxide |
| DSC | Differential Scanning Calorimetry |
| EANC | Elastically Active Network Chain(s) |
| Et | Ethyl |
| EI | Electron Impact |
| ELSD | Evaporative Light Scattering Detection |
| Equiv | Equivalent(s) |
| ESI | Electospray Ionization |
| FID | Flame Ionization Detector |
| FTIR | Fourier-Transform Infrared |
| FWHM | Full Width at Half Maximum |
| GC | Gas Chromatography |

| | |
|---|---|
| GPC | Gel Permeation Chromatography |
| h | Hour(s) |
| HDI | 1,6-Hexamethylene Diisocyanate |
| HPLC | High Performance Liquid Chromatography |
| Hz | Hertz |
| IPA | Isopropyl Alcohol |
| IR | Infrared |
| LRMS | Low Resolution Mass Spectrometry |
| MDSC | Modulated Differential Scanning Calorimetry |
| Me | Methyl |
| mg | Milligram(s) |
| min | Minute(s) |
| mL | Millilitre(s) |
| mmol | Millimole(s) |
| MeOH | Methanol |
| m.p. | Melting Point |
| MS | Mass Spectrometry |
| mV | Millivolt |
| NMR | Nuclear Magnetic Resonance |
| PET | Polyalkylene terephthalate |
| Ph | Phenyl |
| ppm | Parts Per Million |
| PTMEG | Polytetramethyleneetherglycol |

| | |
|---|---|
| psi | Pounds Per Square Inch |
| PUR | Polyurethane(s) |
| R | Generic Alkyl Group |
| RA-Ni | Raney Nickel |
| $R_f$ | Retention Factor |
| rt | Room Temperature |
| s | Singlet |
| $scCO_2$ | Supercritical Carbon Dioxide |
| t | Triplet |
| TAG | Triacylglycerol or Triglyceride |
| THF | Tetrahydrofuran |
| TLC | Thin Layer Chromatography |
| TMSCl | Trimethylsilyl Chloride |
| µm | Micro Meter |
| UV | Ultraviolet |

# 1 Introduction and Background Information

## 1.1. Introduction

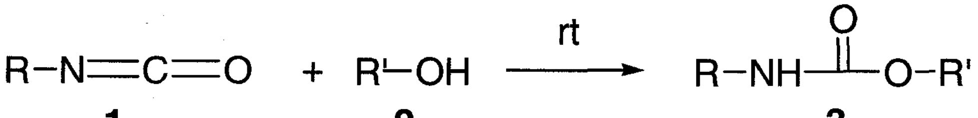
Recently, many environmental issues and concerns have been raised about petroleum-based polymeric materials. Production of biodegradable polymeric materials, especially from inexpensive and readily available renewable resources such as starch, carbohydrates and proteins, etc. have recently become more important (Smith, 2005). In this context, the research detailed in this thesis was targeted at the development of methodologies for chemically modifying vegetable oils and their derivatives to produce value-added compounds for making polymers. In particular, the production of polyols and polyacids from triacylglyceride (TAG) oils were attempted, as well as the production of polyurethanes from the polyols produced. It should be noted here that the work performed for this thesis mostly concentrated on the synthesis of polyols and polyacids, and that the work to produce polyurethanes was done by collaborating peers within the same research group. However, some amount of polyurethane synthesis and physical properties is reported in this thesis, so as to highlight the relative performance of various grades of polyols produced under the rubric of the author's Ph.D. project.

This thesis begins with a review (Chapter 1) of polyols and the reactions used to produce them in this work (ozonolysis and hydrogenation), as well as intermolecular cyclotrimerization reactions of fatty acid alkynes for the production of aromatic triols and triacids.

A methodology that uses ozonolysis followed by hydrogenation to produce aliphatic polyols containing terminal hydroxyl groups was successfully developed and is summarized in Chapter 2. Identification of the structures of the components in the polyols has also been studied, and is summarized in Chapter 2. An HPLC-ELSD method to quantitatively analyze the polyols was developed and is discussed in Chapter 3. Production of polyols with the same structure as described in Chapter 2 and 3 but with varying hydroxyl numbers was also studied and is presented in Chapter 4. The physical properties of polyurethanes produced using the various grades of polyols produced are also presented in Chapter 4, so as to highlight the potential differences in physical properties of polyurethanes achievable. The polyurethanes were synthesized by a collaborating peer within the research group, Dr. Xiaohua Kong, who also performed the physical measurements. A methodology for producing aromatic triols and triacids from mono-unsaturated fatty acids or vegetable oils has also been developed and the results discussed in Chapter 5. Chapter 6 of this thesis provides summary conclusions of the work performed, and proposes future work in the area.

## 1.2. Polyols

Polyols refer to a class of compounds containing more than one hydroxyl group, which in some cases can be used to prepare polyurethanes. Polyurethanes are polymers containing urethane linkages, -NH-C(=O)-O-, **3**, which can be formed by reaction of an organic isocyanate group (-CNO) **1** with a hydroxyl group (-OH) **2**, as shown in **Scheme 1-1**. When polyfunctional isocyanates react with molecules containing more than one hydroxyl group in the proper ratios, many different kinds of polyurethane materials can be produced, for example, rigid or flexible foams, elastomers, coatings, adhesives and sealants. Different polyols have varying effects on the properties of the polyurethanes produced.



**1** **2** **3**

**Scheme 1-1:** Formation of a Urethane Linkage

### 1.2.1. Petroleum Based Polyols

Polyols are traditionally derived from petroleum. Polyether polyols, and polyester polyols are the two main classes of petroleum based polyols.

#### 1.2.1.1 Polyether Polyols

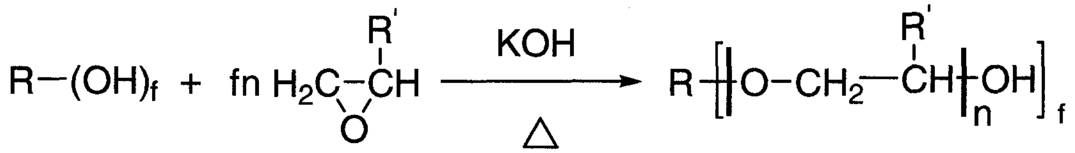
Conventional polyether polyols contain the repeating ether linkage –R-O-R- and are suitable for the production of high quality polyurethane elastomers and foams. They are generally divided into three classes (Ashida, 2006; Szycher, 1999): polyoxyalkylene polyols, graft polyols and polytetramethyleneetherglycol.

##### 1.2.1.1.1 Polyoxyalkylene Polyols

Polyoxyalkylene polyols **6** are prepared from the polymerization of alkylene oxide **5** initiated by a hydroxyl-containing compound **4** as shown in **Scheme 1-2**. The initiator can be water, glycols or polyols, which all contain hydroxyl groups. The functionality of the produced polyether polyol depends on the functionality of the initiator, f. Potassium hydroxide (KOH) is the traditional catalyst for this reaction. The most frequently used alkylene oxides, by far, are propylene oxide and ethylene oxide. Polyoxyalkylene polyols are representative polyols for producing various polyurethane foams.

##### 1.2.1.1.2 Graft Polyols (Polymer Polyols)

Polymer polyols contain a grafted polymer in the polyether polyol framework. The polymers are composed of acrylonitrile, styrene or the copolymers and terpolymers of such monomers. Polymer polyols are typically blended with other highly reactive



**4** **5** **6**

**Scheme 1-2:** Polymerization of Alkylene Oxide for the Preparation of Polyether Polyols

polyols to produce high-resilience flexible foams. **Figure 1–1** shows the chemical structure of an acrylonitrile-styrene-grafted polyether polyol **7**.

#### 1.2.1.1.3 Polytetramethyleneetherglycol (PTMEG)

PTMEGs **9** are prepared by ring-opening polymerization of cyclic ethers such as tetrahydrofuran (THF) **8** as shown in **Scheme 1-3**. Polyurethanes derived from PTMEGs are suitable for thermoplastics, hydrolysis-resistant elastomers, fibers and foams.

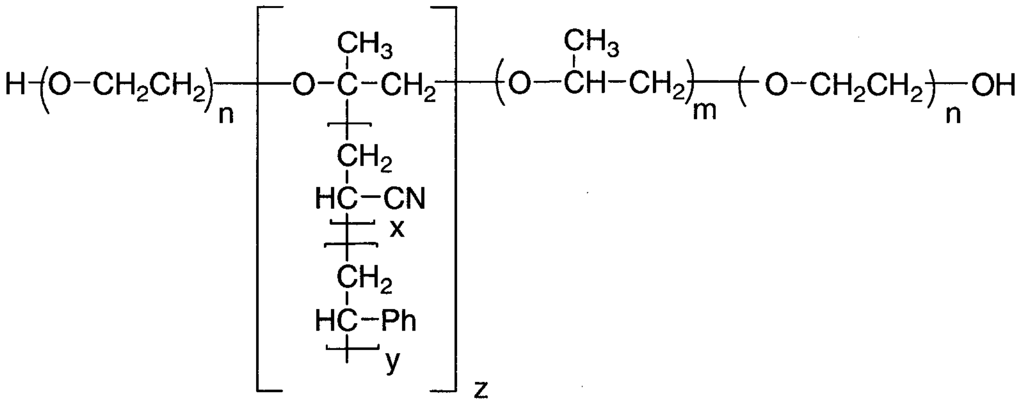
### 1.2.1.2 Polyester Polyols

Polyester polyols are used as the soft segment in polyurethane products. In comparison to polyurethanes made from polyethers, polyester polyol derived polyurethanes are more likely to hydrolyze and therefore have reduced elasticity. One advantage though is that they often have improved mechanical properties such as tear strength. Polyester polyols can be classified into aliphatic and aromatic polyester polyols (Ashida, 2006; Szycher, 1999).

#### 1.2.1.2.1 Aliphatic Polyester Polyols

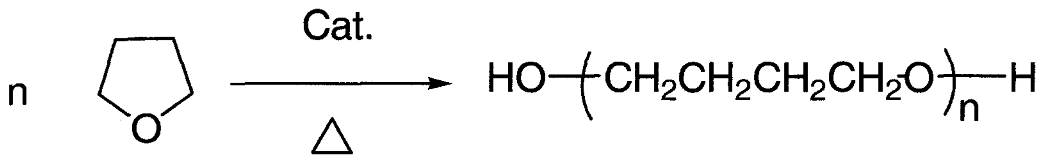
There are two methods to produce aliphatic polyester polyols. One method is the polycondensation of diacids e.g. adipic acid, phthalic acid or sebacic acid with a glycol e.g. ethylene glycol, propylene glycol, diethylene glycol, 1,4-butanediol or 1,6-hexanediol. **Scheme 1-4** shows an example of an aliphatic polyester polyol **12** prepared from ethylene glycol **10** and adipic acid **11**.

Another method for the production of aliphatic polyester polyols **14** is to carry out ring-opening polymerization on lactone starting materials, such as ε-caprolactone **13** (**Scheme 1-5**).



**7**

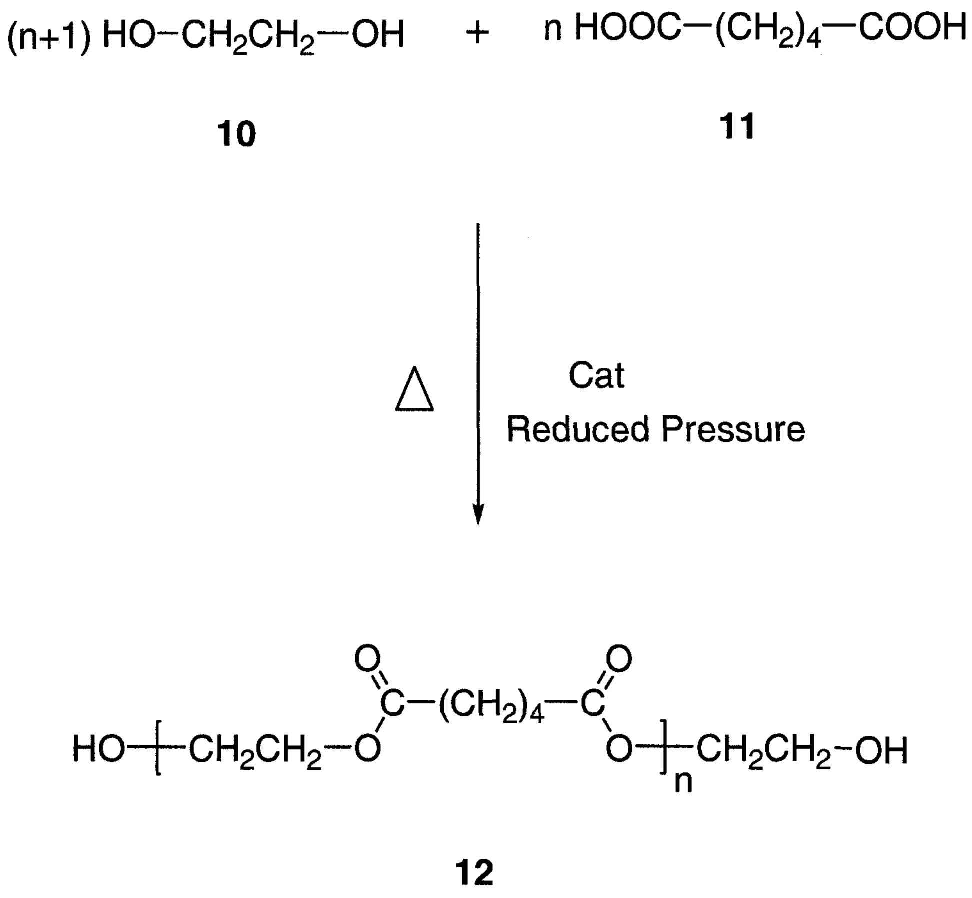
**Figure 1-1:** Graft Polyols



**8** **9**

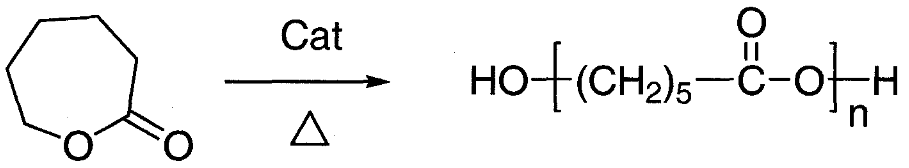
Cat = $FSO_3H$, $ClSO_3H$, $H_2SO_4/SO_3$, etc

**Scheme 1-3:** Production of Polytetramethyleneetherglycol (PTMEG) from Tetrahydrofuran (THF)



Cat = Fe, Co, Pb, etc and their oxides and salts

**Scheme 1-4:** Preparation of Aliphatic Polyester Polyols by Polycondensation



**13** **14**

Cat = Sn, Zn, Co, etc and their complexes or lipase

**Scheme 1-5:** Preparation of Aliphatic Polyester Polyols by Ring-Opening Polymerization of ε-Caprolactone

#### 1.2.1.2.2 Aromatic Polyester Polyols

Aromatic polyester polyols **17** are produced by trans-esterification of polyalkylene terephthalate **15** with a low molecular weight polyol, for example diethylene glycol **16 (Scheme 1-6)** (George and Michael, 1984).

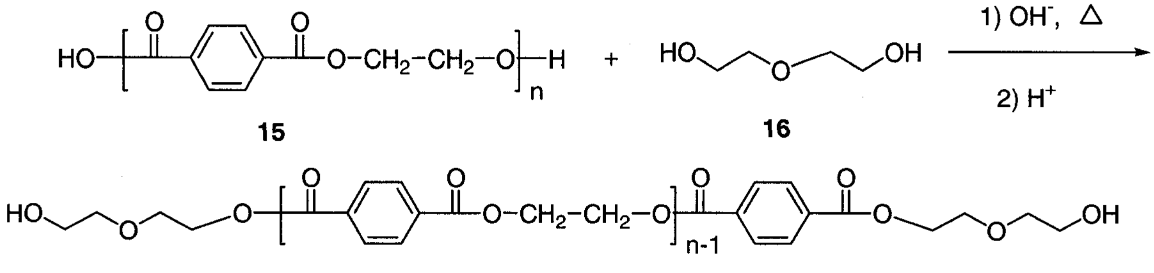
Due to their lower compatibility, aromatic polyester polyols are usually used for blending with aliphatic polyether polyols to obtain rigid PUR foams.

### 1.2.2. Vegetable Oil Based Polyols

Triacylglycerols (TAGs) are the most common components of vegetable oil. A general structure for a TAG molecule **18** can be represented in the solid and broken wedge form as shown in **Figure 1-2**. The three carbon atoms of the glycerol backbone are designated by the stereospecific numbering *sn*-1 from the top to *sn*-3 at the bottom.

Among the naturally occurring vegetable oils, castor oil and lesquerella oil are natural polyols containing hydroxyl fatty acid. Castor oil contains 87 % of ricinoleic acid (12-hydroxy-*cis*-9-octadecenoic acid) **19**, and lesquerella oil contains 55 % of lesquerolic acid (14-hydroxy-cis-11- eicosenoic acid) **20** (Firestone, 1999), the structures of which are shown in **Figure 1-3**. However, castor oil as a large-scale commercial product has been given much more attention in this regard (Sperling et al., 1991).

Castor oil has been extensively explored as a raw material for the preparation of rigid polyurethane foam (Baser and Khakhar, 1993), polyurethane elastomers (Petrovic and Fajnik, 1984; Yeganeh and Hojati-Talemi, 2007; Yeganeh and Mehdizadeh, 2004), polyurethane nanoparticles (Zanetti-Ramos et al., 2006; Zanetti-Ramos et al., 2005), polyurethane-polystyrene interpenetrating networks (Singh *et al.*, 2005), poly

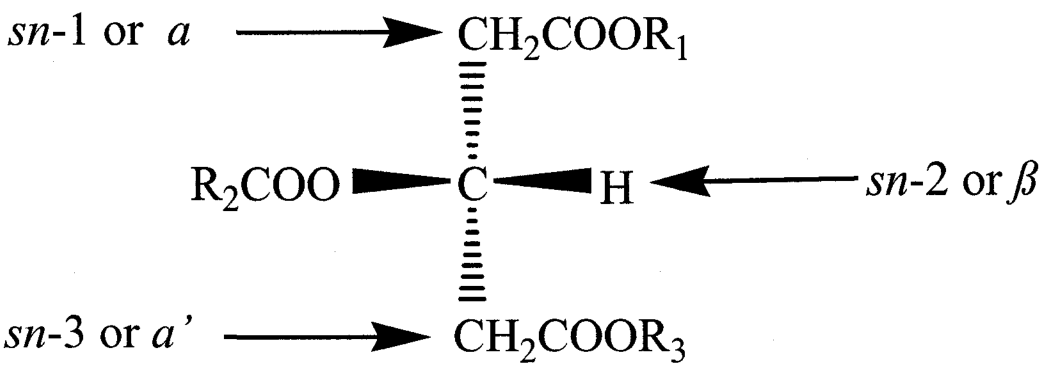


15

16

17

**Scheme 1-6**: Transesterification of polyalkylene terephthalate (PET) with Diethylene Glycol

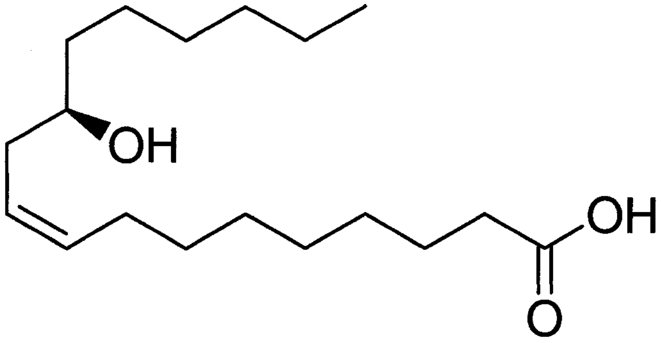


**18**

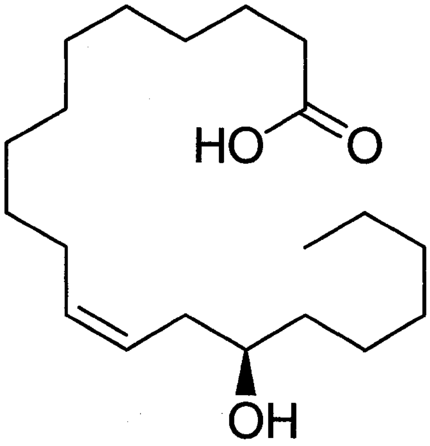
**Figure 1-2:** Stereospecific Numbering of the Carbons of the Triacylglycerol (TAG) Molecule

The solid wedge indicates a substituent comes out of the plane toward the observer

The broken wedge indicates a substituent going into the plane away from the observer



**19**



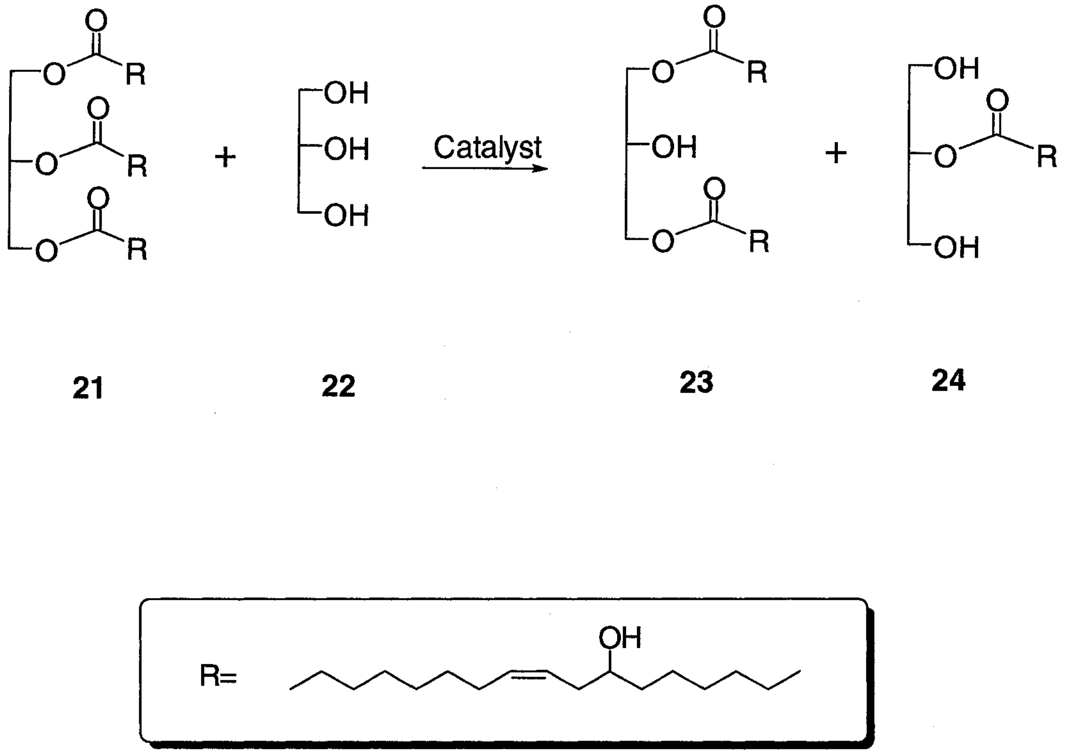
**20**

**Figure 1-3:** Structures of Ricinoleic Acid and Lesquerolic Acid (ethylene terephthalate)-triglyceride oil semi-interpenetrating networks (Barrett et al., 1993a; Barrett et al., 1993b), polyurethane resins (Melo and Pasa, 2003), and polyurethane potting compounds (Jayabalan and Lizymol, 1997) without any further modification.

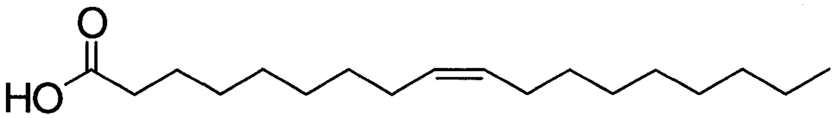
However, due to the structure of castor oil and its low hydroxyl number, there are some disadvantages in using this natural polyol to produce polymeric materials. For example, the secondary hydroxyl groups make curing sluggish and the polymer produced has low tear strength due to the steric hindrance caused by the long pendant fatty acids. Castor oil also has low resistance to oxidation. To overcome these disadvantages, modified castor oil has been developed. One commonly utilized method to modify castor oil is transesterification of castor oil **21** with glycerol **22** (Athawale and Kolekar, 1998; Prashantha *et al.*, 2001; Sanmathi *et al.*, 2004) as shown in **Scheme 1-7.** Other alcohols such as trimethylol propane (Kaushik and Singh, 2005), pentaerythritol and the aromatic triol, bisphenol A propoxylate (Can *et al.*, 2006) have also been used to transesterify castor oil.

Physical blending of castor oil with glycerol (Baser and Khakhar, 1993), triisopropanolamine or triethanolamine (Lyon *et al.*, 1974; Lyon *et al.*, 1962) is another method of modifying castor oil.

Most of the vegetable oils consist of TAGs composed of three dominant unsaturated fatty acids: oleic (octadec-11-enoic) acid **25**, linoleic (octadec-9:12-dienoic) acid **26** and linolenic (octadec-9:12:15-trienoic) acid **27** (**Figure 1-4**). All of them contain at least one internal double bond (potential sites for introduction of hydroxyl



Scheme 1-7: Modification of Castor Oil by Transesterification with Glycol



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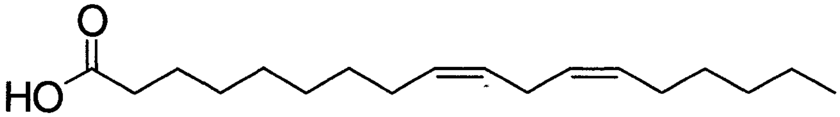

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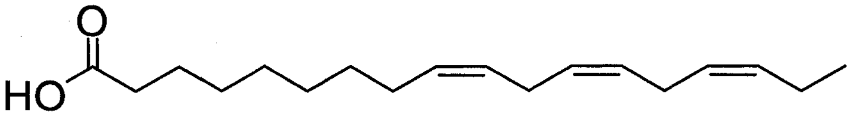


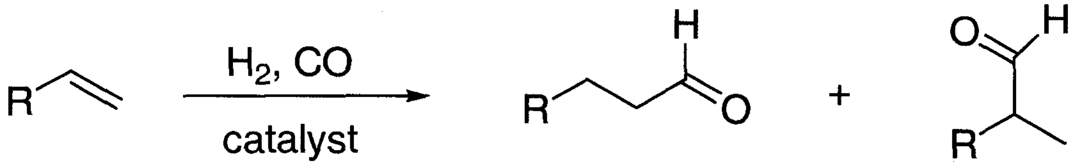
**27**

**Figure 1-4:** Structures of Oleic Acid, Linoleic Acid and Linolenic Acid groups), which makes these vegetable oils suitable candidates in the preparation of polyols. Vegetable oils are abundant in the world and can be easily replenished annually; therefore they have the potential to partly replace petroleum starting materials in the production of polyols. Due to the hydrophobic character of the TAGs, polyurethanes based on vegetable oil polyols have excellent physical and chemical properties such as improved thermal and hydrolytic stability (Javni et al., 2003; Zlatanic et al., 2004).

Until now, four chemical methods have been reported for the modification of vegetable oils into polyols: 1) hydroformylation followed by reduction of the aldehyde; 2) epoxidation followed by ring-opening of the epoxides; 3) reductive ozonolysis and 4) transesterification.

### 1.2.2.1 Hydroformylation

Hydroformylation, also known as oxo synthesis, is an important industrial process for the production of aldehydes from alkenes. This was discovered accidentally in 1938 by Otto Roelen and co-workers (Cornils *et al.*, 1994a; Cornils *et al.*, 1994b). Hydroformylation is the simultaneous addition, in the presence of catalyst, of one mole of hydrogen and one mole of carbon monoxide (known as *syngas*) across a carbon–carbon double bond **28** to produce linear **29** and branched **30** aldehydes with one more carbon atom than the original compound (**Scheme 1-8**). Usually linear aldehydes are the main product due to steric and electronic effects. Hydroformylation is a mild, clean procedure and is compatible with many functional groups such as esters, amides and nitriles. The reaction is 100 % atom economical since all the atoms in the reactants end up in the product, leading to minimal production of chemical waste.



**28** **29** **30**

**Scheme 1-8:** Hydroformylation Reaction

The aldehyde produced by hydroformylation can be simply transformed into an alcohol *via* a hydrogenation reaction catalyzed by Raney Nickel. Applying this technology (hydroformylation followed by hydrogenation) to vegetable oils allows for polyols to be produced (Lyon *et al.*, 1974; Lyon *et al.*, 1962; Petrovic and Fajnik, 1984).

There are three types of catalysts that are commonly used in hydroformylation of vegetable oils and their derivatives: 1) simple cobalt carbonyl complexes (Frankel *et al.*, 1969); 2) rhodium catalyst in the presence of tertiary phosphine/phosphite ligands (Frankel and Thomas, 1971; Frankel and Thomas, 1972), and 3) bulky phosphite-modified rhodium catalysts (Kandanarachchi et al., 2002; Muilwijk et al., 1997).

Cobalt carbonyl [$Co_2(CO)_8$] is a conventional and economical catalyst used in hydroformylation. However, using this catalyst requires high temperatures (140-180 ºC) and high pressures (3000-4000 psi). At temperatures higher than 160 ºC, cobalt carbonyl is able to catalyze the hydrogenation of the produced aldehyde to alcohol, so that when vegetable oil is hydroformylated in the presence of cobalt carbonyl, polyols can be obtained directly. The high temperature also yields other side reactions including transformation of *cis* alkenes into *trans* alkenes, alkene isomerization, aldol additions to aldehydes to give aldehyde dimers and ester triols, hydroformylation of aldehydes to formate esters and reaction of aldehydes with the side-product alcohol to give acetals (Frankel *et al.*, 1969). When polyunsaturated substrates such as methyl linoleate and linolenate are subjected to similar treatment, only one double bond is hydroformylated and any remaining unsaturation is hydrogenated to saturation. Polyurethanes derived from the cobalt catalyzed hydroformylation of soy bean oil have properties similar to a hard rubber due to the low conversion of olefins (A. Guo et al., 2002).

Compared to cobalt carbonyl, the rhodium/triphenylphosphine system has been found to be a much more active catalyst for hydroformylation. The rhodium can be supported on charcoal, calcium carbonate or alumina. Under hydroformylation conditions, the rhodium is solubilized in the reaction mixture to form a homogenous rhodium carbonyl/triphenylphosphine complex, which is the active catalytic complex (Frankel, 1971). Due to its high reactivity, the phosphine modified rhodium catalyst presented new possibilities for the commercial hydroformylation of vegetable oils and their derivatives. It was also found that when methyl oleate was hydroformylated, high yields (90–99 %) of methyl formylstearate were obtained at lower temperatures (95-110 °C ) and lower pressures (500-2000 psi) with or without toluene as the solvent (Frankel and Pryde, 1977). Another advantage of using rhodium catalyst was that all the unsaturation on the polyunsaturated fatty material can be hydroformylated (Frankel *et al.*, 1973). However, even under high temperatures, reduction of the double bonds or the aldehyde product did not occur and in order to make polyols, another catalyst has to be introduced to hydrogenate the aldehyde into alcohol. Some researches have produced rigid polyurethane plastics from hydroformylation of soybean oil by this rhodium process (A. Guo et al., 2002).

In 1983, some researchers (Vanleeuwen and Roobeek, 1983) developed a series of new bulky phosphite-modified rhodium catalysts with which unreactive olefins such as internal, branched or cyclic olefins can be hydroformylated under mild conditions. In 1997, they reported on the hydroformylation of methyl oleate using a rhodium catalyst modified by the bulky tris(2-*tert*-butyl-4-methylphenyl) phosphate **31** (structure shown in

**Figure 1-5**). The reaction was carried out at 80-100 °C and 290 psi resulting in 95 % conversion within 3 hours.

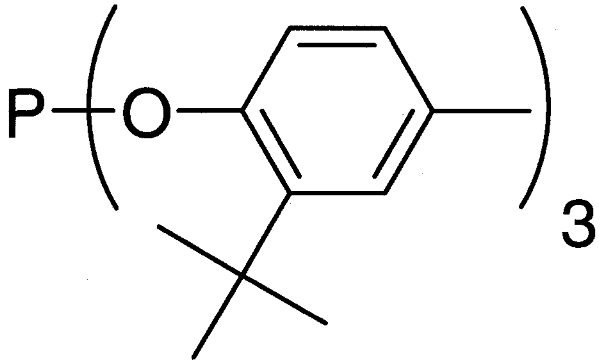
Some researches (Kandanarachchi *et al.*, 2002) reported their work on the use of $Rh(CO)_2(acac)$ ((acetylacetonato)dicarbonylrhodium) as the catalyst precursor in the presence of triphenylphosphine or triphenylphosphite to hydroformylate vegetable oils (soybean, high oleic safflower, safflower, and linseed) as neat liquids or in toluene solutions. The reactions were conducted at 70-130 °C and 600-1300 psi of gas. This resulted in the unsaturated vegetable oils being converted quantitatively into the desired aldehydes within 2 to 5 hours.

Although much attention has been paid to the regioselectivity of the hydroformylation reaction of various olefins, it is not a concern for the preparation of vegetable oil based polyols.

#### 1.2.2.2 Epoxidation

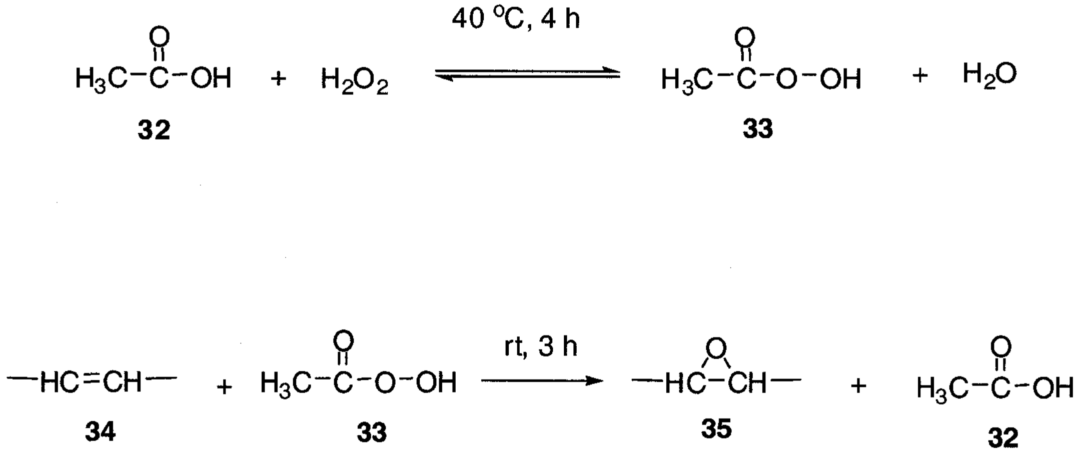
Epoxidation of alkenes followed by ring opening of the epoxide is another practical method for the production of vegetable oil based polyols. Peracetic acid is commonly used for the epoxidation of unsaturated TAGs; this was first proposed by Swern and coworkers (1945). In this process, peracetic acid **33**, which is formed *in situ* from glacial acetic acid **32** and hydrogen peroxide, oxidizes the alkene **34** to form the epoxide **35** and regenerates acetic acid at the same time (**Scheme 1-9**).

The conversion of epoxidized oil into hydroxylated oils in order to produce polyols has been achieved by: *a.* catalytic hydrogenaton (A. Guo et al., 2000a);



**31**

**Figure 1-5**: Structure of the Tris(2-*tert*-butyl-4-methylphenyl)phosphate Ligand

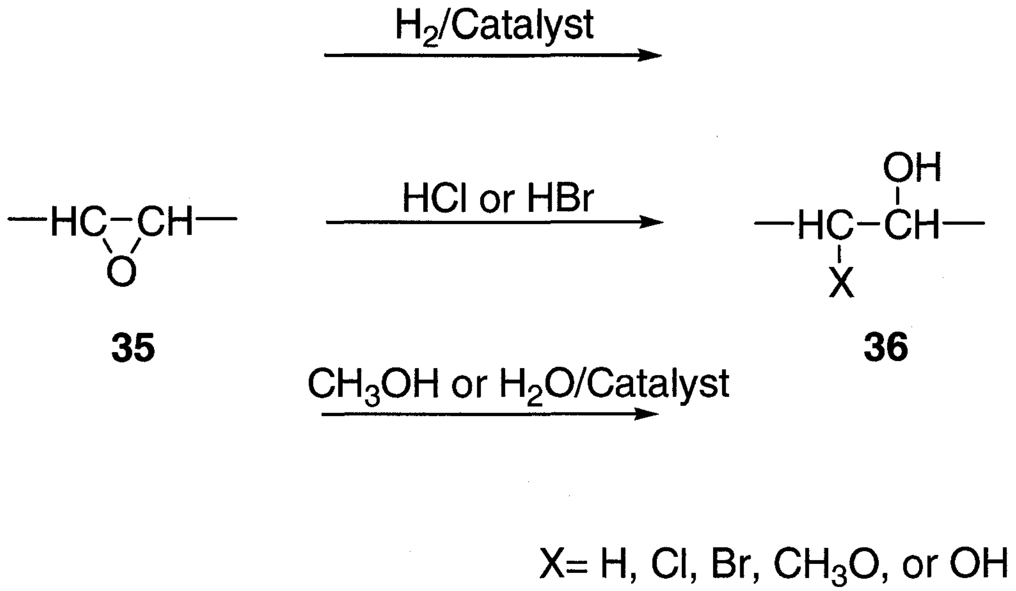


**Scheme 1-9:** Epoxidation of Olefins by Peracetic Acid

*b*. reaction with hydrochloric or hydrobromic acid yielding halogenated polyols (Petrovic et al., 2000); *c*. acid catalyzed ring opening with methanol or water resulting in methoxylated polyols or vicinal hydroxyl groups (A. Guo et al., 2000b; Zlatanic et al., 2004). General methods for the ring opening of epoxides **35** into an alcohol **36** are shown in **Scheme 1-10**.

Hydrogenation of epoxides was catalyzed by Raney Nickel and the product obtained from the hydrogenation of epoxidized oil was semi-solid with a melting range between 40 and 60 °C (A. Guo et al., 2000a). The reactions of epoxides with hydrochloric and hydrobromic acid were self-catalyzed and gave a good conversion, but the products obtained were highly viscous greases at ambient conditions (A. Guo et al., 2000a; Petrovic et al., 2000). Guo *et al* studied the ring opening of epoxidized soybean oil with hydrochloric acid and hydrobromic acid. 94 % and 100 % yields were obtained, respectively (A. Guo et al., 2000a). Polar solvents such as dioxane, acetone or *t*-butyl alcohol were required to dissolve these inorganic acids in order to facilitate the reactions with the epoxides. Hydrolysis yielded a viscous product and caused some side reactions giving the product a much lower hydroxyl number than the expected theoretical value (Andrew Guo and Petrovic, 2005).

Alcoholysis was found to be the most practical method to prepare oil based polyols. This was catalyzed by acid (usually fluoroboric acid) and the obtained polyols have low viscosities and almost the expected theoretical hydroxyl values (A. Guo et al., 2000a; A. Guo et al., 2002; Petrovic et al., 2000). However, side reactions were noticeable after a certain period of time. The main side reaction in the ring opening reaction was polymerization of the formed hydroxyl functionality with unreacted



**Scheme 1-10**: General Methods for the Ring Opening of Epoxidized Oils

epoxides to form dimers or trimers.

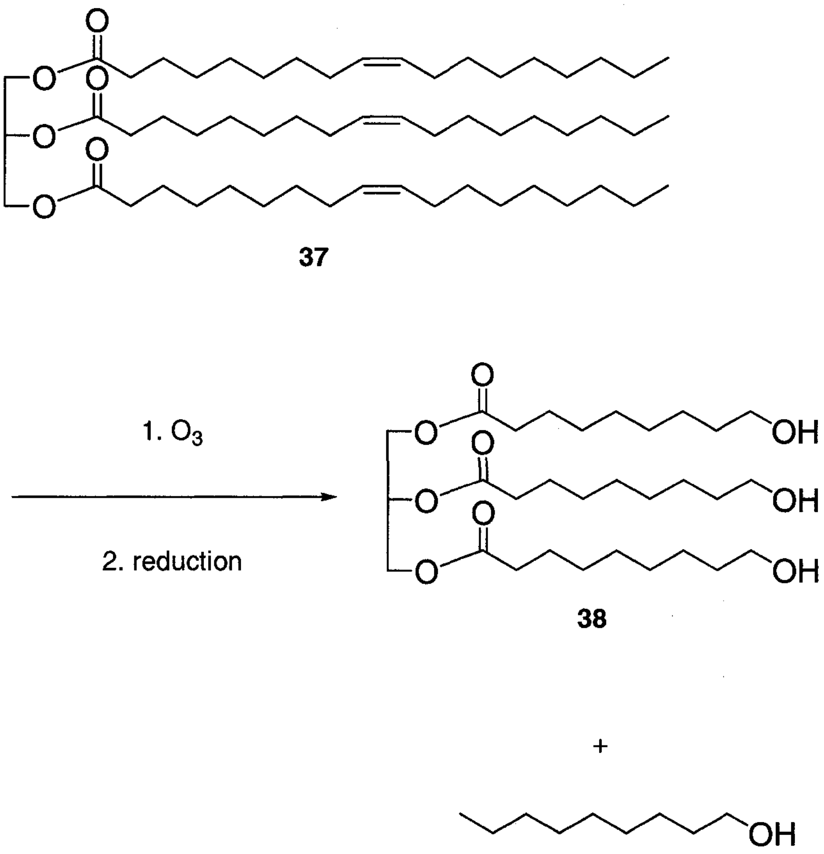
### 1.2.2.3 Reductive Ozonolysis

The above two discussed methods for the preparation of polyols from vegetable oil produced polyols with hydroxyl groups located in the middle of the fatty acid chains, typically at the 9th or 10th carbon in the oleic fatty acid and at the 12th or 13th carbon in the linoleic fatty acid, leaving the rest of the chain (up to 18 carbons) pendent on the molecule. These act as dangling chains in polyurethane networks. The dangling chains do not support stress when the material is loaded and also act as plasticizers which reduce the polymer rigidity.

The polyols made by ozonolysis of vegetable oils contain terminal hydroxyl functionalities and therefore do not have dangling chains. However, there is always a finite percentage of saturated fatty acids in the vegetable oils, which do not undergo any changes through ozonolysis and act as dangling chains in a polyurethane network.

Taking triolein **37** as an example, **Scheme 1-11** shows the production of polyols from vegetable oils using reductive ozonolysis. The product **38** obtained has terminal primary hydroxyl groups and a maximal functionality of 3. Nonanol **38'** is also produced as a side product.

Petrovic and coworkers (2005) used soybean oil and low-saturation canola oil as the feedstock to produce polyols *via* ozonolysis and reduction of the ozonide with sodium borohydride. Sodium borohydride was an effective reducing reagent, however, this reduction step required an alkaline medium in order to cause hydrolysis of the TAG linkage (A. Guo et al., 2000a).



**Scheme 1-11**: Ozonolysis of Vegetable Oil to Produce Polyols

In the Narine group, polyols were produced from canola oil *via* ozonolysis followed by a hydrogenation reaction catalyzed by Raney nickel (Narine et al., 2007). This work is detailed introduced and discussed in Chapters 2, 3 and 4.

#### 1.2.2.4 Transesterification

A polyol can be produced by transesterification of vegetable oils with glycerin. This method is the same as for the modification of castor oil which was introduced in Section **1.1.2**. The polyols produced by this method created fatty acid dangling chains in the product and thus may not contribute mechanical strength to the polymer material.

### 1.2.3. Summary

Modification of vegetable oil instead of petro-chemicals to make polyols has generated a great deal of interest from the scientific community. Four chemical methods have been reported: 1) hydroformylation followed by reduction of the aldehyde; 2) epoxidation followed by ring-opening of the epoxides; 3) reductive ozonolysis and 4) transesterification. However, ozonolysis of vegetable oils followed by catalytic hydrogenation to make polyols with terminal hydroxyl functionalities has not been reported.

## 1.3. Ozonolysis

Ozone ($O_3$) is an allotropic form of oxygen and is much more reactive than the diatomic species, $O_2$. Ozone has been shown to have four resonant hybrid structures **(Figure 1-6)** as shown by physical measurements such as microwave spectroscopy (Trambarulo *et al.*, 1953a; Trambarulo *et al.*, 1953b). Structures **39** and **40** are ground state structures of ozone and structures **41** and **42** show the reactive states of ozone.

Alkenes are very susceptible to attack by ozone and cleavage of the double bond occurs. Ozonolysis usually takes places with high rates and low activation energies.

### 1.3.1. Mechanism

The mechanism of ozonolysis has been examined and proposed by many researchers (Criegee, 1957; Harries, 1905; Harries and de Osa, 1904; Staudinger, 1925). Among those, the Criegee mechanism was considered to be a completely satisfactory means of explaining all manifestations including the stereochemical outcome. The mechanism is outlined in **Scheme 1-12**.

Ozone reacts with C=C double bond to form a primary ozonide **44**, which is unstable and cleaves to produce a zwitterion, **47,** and an aldehyde or ketone **46,** presumably *via* the unstable intermediate, **45.** There are at least four ways that the zwitterion **47** can stabilize itself: *a.* react with **46** to form an ozonide **48** or polymeric ozonide; *b.* react with the another zwitterion to yield the dimer **49** or polymeric peroxides; *c.* react with the solvent of type HG to produce hydroperoxide **50**; *d.* undergo a rearrangement. One rearrangement is shown in **Scheme 1-13.** The carbonyl **46** reduces zwitterion **47** through hydrogen migration to produce an acid **52** and the other carbonyl **53** (Diaper, 1973).

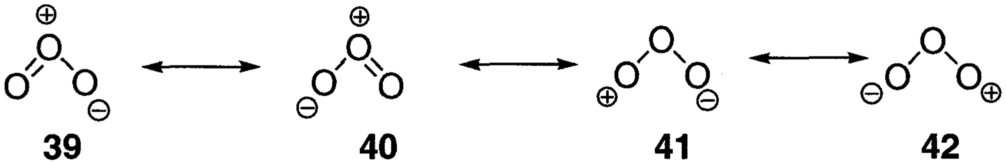
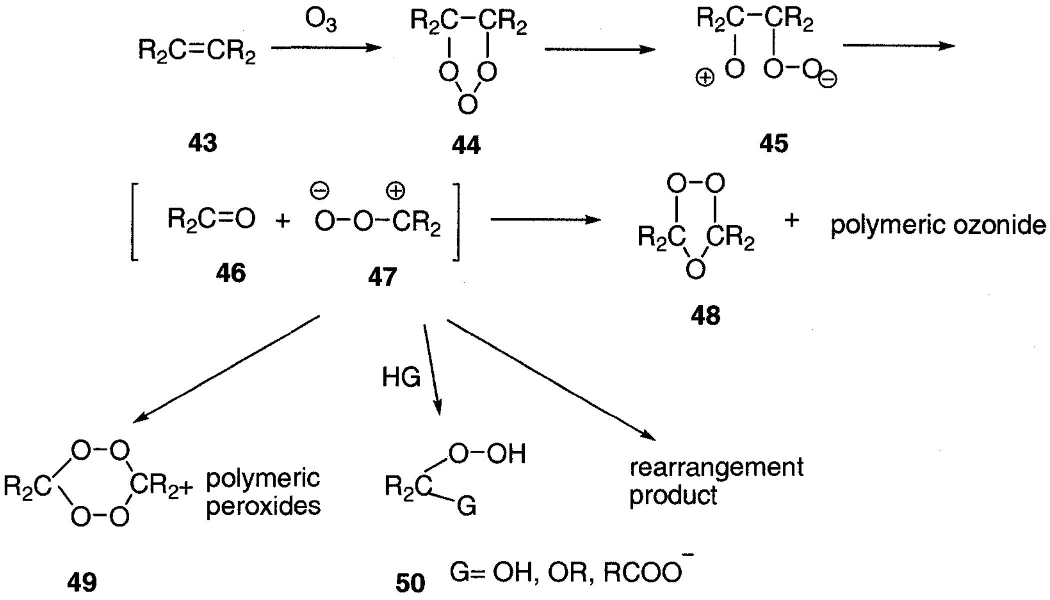
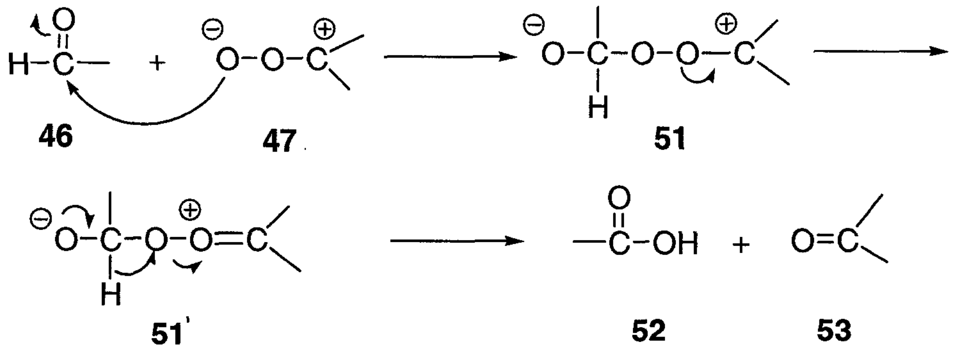


**Figure 1-6:** Resonant Hybrid Structures of Ozone



**Scheme 1-12**: Criegee Mechanism of Ozonolysis



**Scheme 1-13:** Mechanism of Rearrangement of the Zwitterion

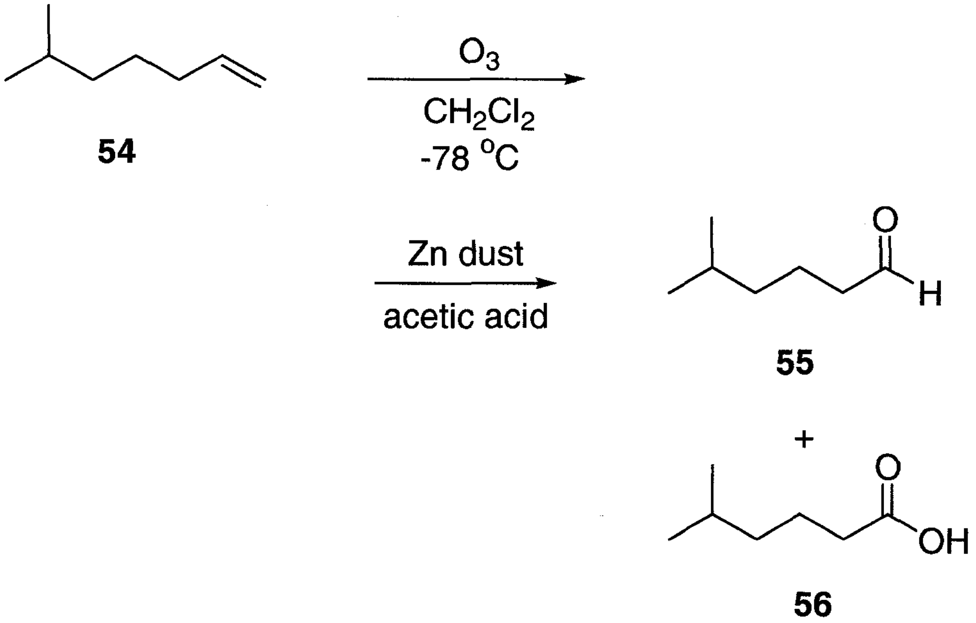
The fate of the primary ozonide **44** is dependent partly on itself, but mostly on its environment (Bailey, 1958). When the reaction takes place in a participating solvent such as water, alcohol, or carboxylic acid, **50** is produced in high yield. If the solvent is inert and acts as a nonparticipating solvent such as alkanes, benzene, chloroform, methylene chloride, tetrahydrofuran, acetone or ethyl acetate etc, **47** has to react with itself or with **46**. Since the carbonyl functionality of aldehydes is more reactive than ketones, if **46** is an aldehyde, the predominant reaction leads to product **48** and small amounts of polymeric ozonide; if **46** is a ketone, **47** has the potential to react with itself and **49** is obtained as the major product.

## 1.3.2. Decomposition of the Ozonide

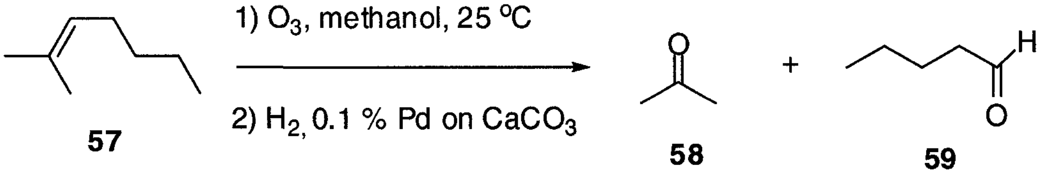
### 1.3.2.1 Reduction

Ozonolysis products can be reduced to aldehydes and ketones using different reducing reagents. One of the most widely employed methods is the use of zinc and acetic acid. Henne and Hill (Henne and Hill, 1943) reported that an alkene **54** underwent ozonolysis followed by a reduction by zinc dust in acetic acid, an aldehyde **55** was produced in a yield of 62 %. In addition, acid **56** is produced as a side product in a yield of 5 % (as shown in **Scheme 1-14)**. The over-reduction of ozonides to alcohols was not observed.

Catalytic reduction has been popular in large scale work as it is an economical method. Henne and Perilstein (Henne and Perilstein, 1943) reported their work on the catalytic hydrogenation of ozonides to produce ketones and aldehydes. 0.1 % of palladium on calcium carbonate was used and the yield of pentanal **59** was 49 % **(Scheme 1-15)**. They also reported that the yields were not affected by variation of the



**Scheme 1-14:** Reduction of Ozonide by Zinc Dust



**Scheme 1-15**: Hydrogenation of the Ozonolysis Product in Presence of Palladium

reaction temperature between the range of -78 and 55 °C, and methylene chloride should be avoided in this reaction because it prevented catalytic hydrogenation. Methanol was discovered to be the best participating solvent.

It was found that ozonides vigorously reacted with Raney Nickel at 35 °C in a pentane solution and the products obtained were aldehydes or ketones and nickel oxide (Cook and Whitmore, 1941).

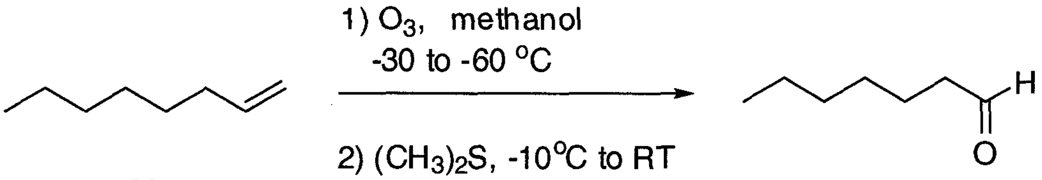
Dimethyl sulfide reduction of ozonide into aldehyde or ketone was also reported (Pappas *et al.*, 1966). The reaction was carried out under mild conditions using methanol and was highly selective, e.g., nitro groups or carbonyl groups were not reduced further. For example, the ozonolysis product of 1-octene **60** was reduced by dimethyl sulfide and heptanal **61** was produced with a yield of 75 % (**Scheme 1-16**).

Preparative reduction of ozonides to alcohols was successfully carried out in many ways. Treatment of ozonide by lithium aluminium hydride is a vigorous reaction but with proper cooling and agitating of the reactants, the reaction could be well controlled (Greenwood, 1955). The solvents that are compatible with lithium aluminium hydride are limited to ether and hydrocarbons (Sousa and Bluhm, 1960).

Sodium borohydride was a mild reagent that selectively reduced ozonides into alcohols, but left the carboxylic acid and ester functionalities untouched. The reduction can be carried out in most common organic solvents such as alcohols, chloroform, ether, and hydrocarbons (Paukstel and Macharia, 1973; Sousa and Bluhm, 1960).

### 1.3.2.2 Oxidation

Hydrogen peroxide was usually used to oxidatively decompose the ozonides into the corresponding acids. The reaction was generally performed in an acid solution and



**60**

**61**

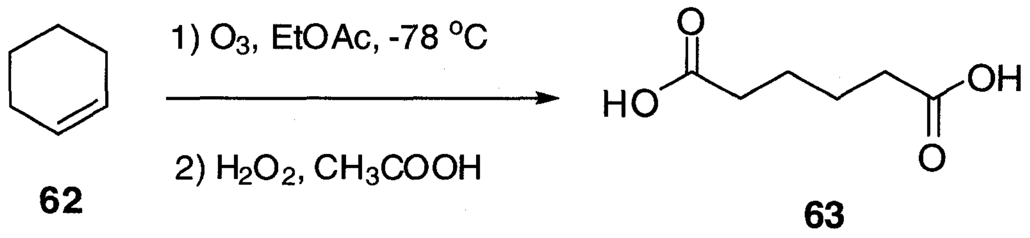
**Scheme 1-16**: Reduction of the Ozonolysis Product by Dimethyl Sulfide provided high yields (Henne and Hill, 1943). For example, as shown in **Scheme 1-17** cyclohexene **62** was ozonized in ethyl acetate at -78 °C followed by treatment with hydrogen peroxide in acetic acid. The major product was adipic acid **63** obtained in a yield of 60 %.

Marshall and Garofalo (1993) have found that certain olefins can be directly converted to methyl esters by treatment with ozone in a methanolic solution of sodium hydroxide and methylene chloride as a cosolvent.

### 1.3.3. Application of Ozonolysis on Vegetable Oils and Derivatives

Ozonolysis has been used to determine the position of the double bond functionality in long-chain fatty acids. Ackman and coworkers (1961) converted oleic acid into dicarboxylic acid *via* ozonolysis in methanol followed by oxidative decomposition of the ozonide product with hydrogen peroxide. Reductive ozonolysis was applied to oleic acid by Privett and Nickell (1962). The ozonolysis was carried out in pentane at temperatures between -60 and -70 °C and the ozonide was reduced to an aldehyde by Lindlars catalyst. In these two studies, the products were identified by gas-liquid chromatography.

Ozonolysis of methyl oleate has been intensively studied by Pryde and coworkers. Chemical and catalytic reductions of ozonolysis products as well as solvent effect have been studied. It was found that application of methanol or a similar alcohol, as a participating solvent in the ozonolysis reaction resulted in a significant improvement of the yield for the corresponding acids, aldehydes or alcohols (Pryde et al., 1960). It was also found that chemical reduction of ozonolysis products with zinc and acetic acid in methanol is superior to catalytic hydrogenation for the preparation of aldehydes from



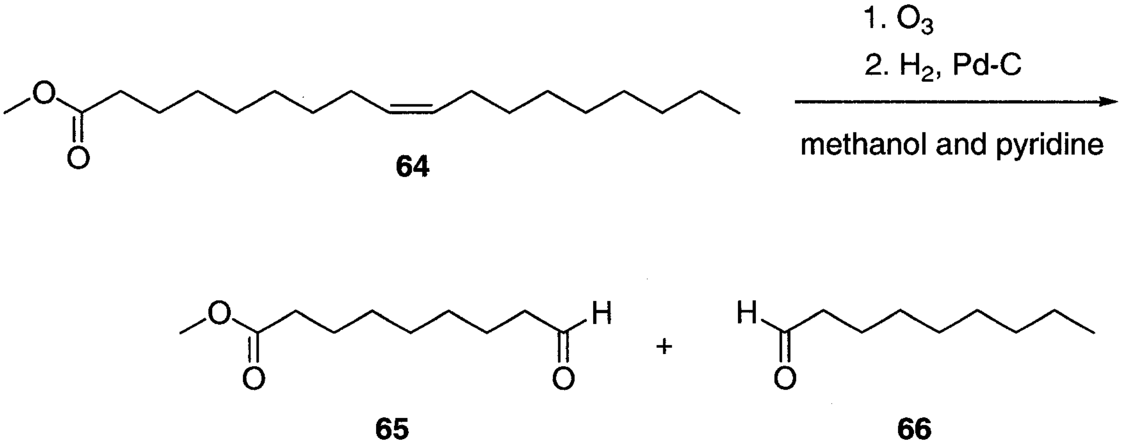
**Scheme 1-17:** Oxidation of the Ozonolysis Product by Hydrogen Peroxide

methyl oleate . Using activated zinc in the absence of acid or water, side reactions such as acetylation and aldehyde condensation could be conveniently avoided (Awl and Pryde, 1966). When the catalytic hydrogenation technique was used to decompose the ozonolysis products, the presence of pyridine in methanol reduced the amount of dimethyl azelate and other undesired by-products and prevented hydrogenation of the olefins (Pryde et al., 1962). Therefore, decomposition of the ozonolysis product formed from methyl oleate **64** gave methyl 8-formyloctanoate **65** as the major product with a yield of 74 % when hydrogenation was carried out with palladium on charcoal at room temperature and atmospheric pressure (**Scheme 1-18**).

Reductive ozonolysis of soybean oil to a polyaldehydic product, named aldehyde oil, was also studied by Pryde and coworkers. They found that ozonolysis of soybean oil followed by reductive decomposition gave a higher yield of carbonyls in the aldehyde oil than using catalytic reduction (Pryde and Anders, 1961). Methanol was not a good solvent for ozonolysis of vegetable oil but the combination of methanol and a co-solvent such as methylene chloride or ethyl acetate gave good results (Pryde and Cowan, 1962). Ozonolysis of soybean oil in methanol and reductive decomposition with zinc and acetic acid provided the aldehydes in a yield of 77 %. When methylene chloride – methanol (55 : 45) and ethyl acetate – methanol (80 : 20) were used instead of methanol, the yields were 91 % and 92 %, respectively.

### 1.3.4. Summary

Ozonolysis as a developed and economic technique has been widely used to cleave carbon-carbon double bonds and produce ketone, aldehyde, carboxylic acid and



**Scheme 1-18:** Ozonolysis of Methyl Oleate

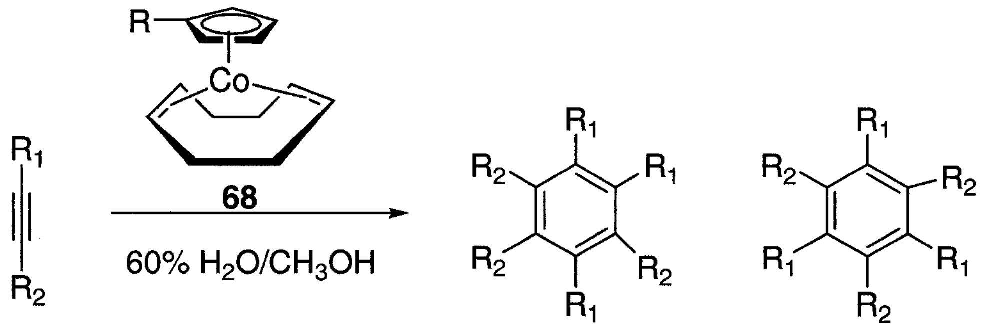
alcohol intermediates *via* the stoichiometric or catalytic decomposition of ozonolysis products.

Ozonolysis has also been applied on vegetable oils and their derivatives. Hydrogenation of ozonolysis products is usually performed at room temperature and atmospheric pressure to produce the corresponding aldehydes. However, production of polyols through hydrogenation of ozonolysis products formed by ozonolysis of vegetable oil has not yet been reported.

## 1.4. Intermolecular Cyclotrimerization of Alkynes

Benzene derivatives are a unique group of organic compounds due to their delocalized electronic character, rigid geometric structure, as well as high thermal, chemical, and photochemical inertness. They are very important precursors in the production of many biological and pharmaceutical based polymeric materials. The principal sources of benzene derivatives are crude oil, coal and oil shale. Benzene was first artificially synthesized in 1866 when Bertholet discovered that acetylene thermally trimerized into benzene in low yield at temperatures above 400 °C (Reikhsfeld and Makovetskii, 1966). In 1948, Reppe and coworkers reported that acetylene cyclized to form benzene in the presence of nickel (1948). This work stimulated an intensive investigation of various metal and non-metal catalysts in the cyclotrimerization of alkynes to obtain benzene derivatives (Chini *et al.*, 1967; Dietl and Maitlis, 1968; Donda and Moretti, 1966; Schlogl and Soukup, 1967; Strohmeier and Barbeau, 1964).

Alkyne cyclotrimerization is an exothermal process that usually involves high temperatures or a catalyst and in some cases both. These types of reactions require kinetic and entropic factors to be considered (Kotha *et al.*, 2005). Recently, with the development of "green" chemistry, cyclotrimerization of alkynes in aqueous media has been reported. It was found that with cyclotrimerization reactions carried out in aqueous media, the protection of other functional groups including amine, hydroxyl, ketone, ester, and carboxylic was not necessary. For example, a water soluble cobalt catalyst, CpCo-$\eta^4$-cyclooctadiene **68**, was used to catalyze an alkyne cyclotrimerization reaction carried out in water at elevated temperature **(Scheme 1-19)** (Sigman *et al.*, 1998). The highest yield (85 %) was obtained when $R_2$ was an alcohol functionality **67c**. In most cases,



**67a-e** R = $CO(CH_2)_2CH_2OH$ **69a-e** **70a-e**

| | $R_1$ | $R_2$ | Yield (%) | *69/70* |
|---|---|---|---|---|
| **a** | H | $CH_2OH$ | 85 | 62/23 |
| **b** | H | $CH_2NHCH_3$ | 73 | 47/26 |
| **c** | H | $(CH_2)_2COOH$ | 56 | 36/20 |
| **d** | H | COMe | 44 | 0/44 |
| **e** | H | COOMe | 67 | 47/20 |

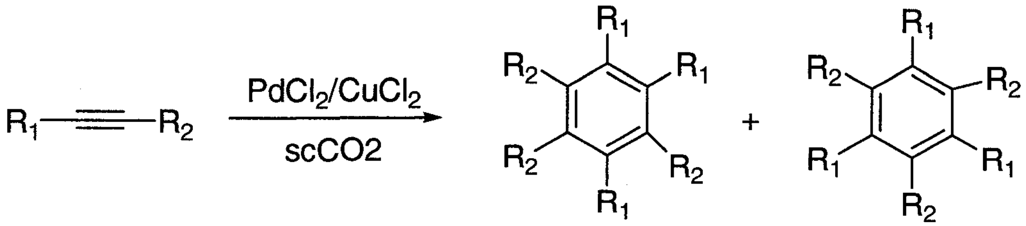
**Scheme 1-19**: Cyclotrimerization of Alkynes in Aqueous Media Catalyzed by CpCo-$\eta^4$-cyclooctadiene (Sigman et al., 1998)

symmetric isomers **69b-e** were the major product, except in the case where $R_2$ was a carbonyl **67a**, the only symmetric isomer produced was **70a**.

Cheng *et al.* (2004) reported their work on the cyclotrimerization of different substituted alkynes in "environmentally friendly" supercritical carbon dioxide ($scCO_2$) in the presence of $PdCl_2$/ $CuCl_2$ with MeOH as a co-solvent (**Scheme 1-20**). The reaction was found to be regioselective and good yields were obtained. In most cases, the asymmetric isomer e.g. **72a-c & e**, was the major product. In the case of **73d**, the symmetric isomer was the major product. When **71f** & **g** were cyclotrimerized in $scCO_2$, a low yield or only trace amounts of products were detected and the structures of the products were not reported.

Cyclotrimerization of alkynes is generally performed in organic solvents such as ethers, alcohols or methylene chloride etc. Various transition metals including Ni, Co, Pd, Fe, Rh, Cr, Zr, Nb, Ir, Ta and their complexes have been found to be effective in catalyzing these reactions. A common mechanism (Collman *et al.*, 1968; Schore, 1988; Winter, 1985) is shown in **Scheme 1-21**.

The initial step involves the loss of two ligands and the coordination of two alkyne molecules to a single metal center. In cases where the ligands are firmly bound to the metal center, for example, $PMe_3$ or $PEt_3$, the ligands do not leave (Winter, 1985). The bis-alkyne **76** then undergoes an oxidative coupling to form a metallacyclopentadiene **77**, and a carbon-carbon bond is simultaneously formed. **77** has an open coordination site that is able to trap another alkyne molecule, as shown in intermediate **78**. This alkyne can insert to form a metallacycloheptatriene intermediate **79**. The rate determining step in these cyclotrimerization reactions is the last step, in which a benzene ring **80** is

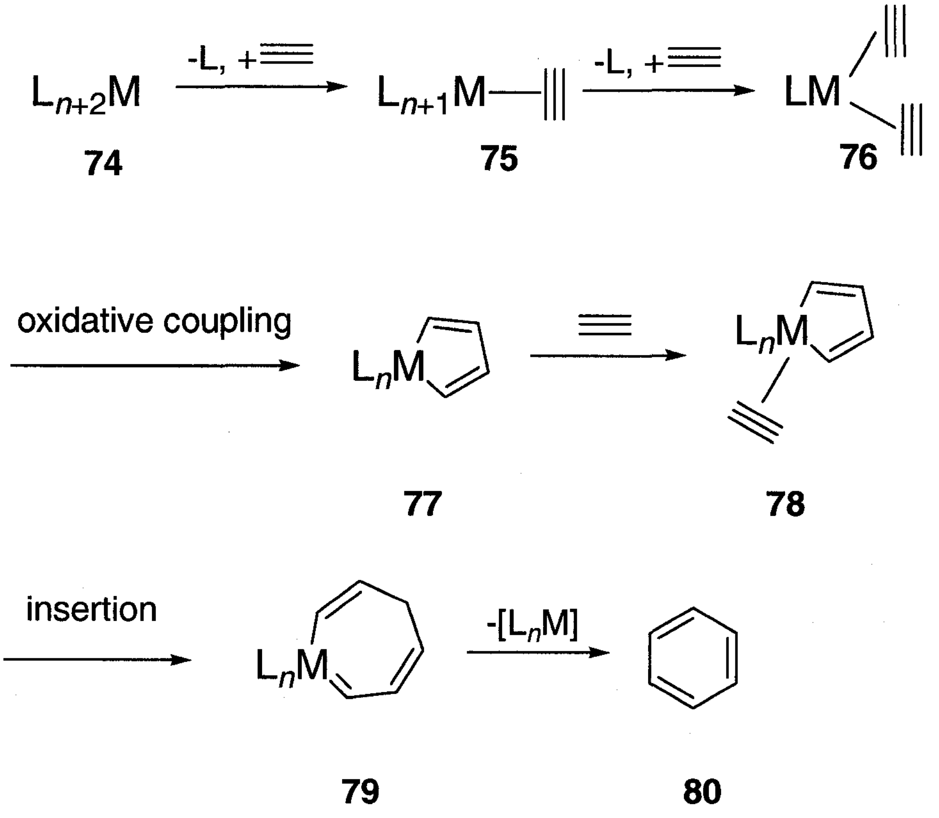


**71a-h** **72a-h** **73a-h**

**a** $R_1 = Ph, R_2 = CH_3$
**b** $R_1 = C_3H_7, R_2 = C_3H_7$
**c** $R_1 = tBu, R_2 = H$
**d** $R_1 = H, R_2 = COOEt$
**e** $R_1 = H, R_2 = H$
**f** $R_1 = H, R_2 = CH_2OCH_3$
**g** $R_1 = COOMe, R_2 = COOMe$

| **Alkyne** | ***t*** **(h)** | ***Product*** | *Isolated Yield (%)* |
|---|---|---|---|
| $\mathrm{PhC{\equiv}CMe}$ | 8 | **72a** | 92 |
| $\mathrm{C_3H_7C{\equiv}CC_3H_7}$ | 8 | **72b** | 92 |
| $\mathrm{tBuC{\equiv}CH}$ | 8 | **72c** | 97 |
| $\mathrm{HC{\equiv}COOEt}$ | 12 | **73d** | 96 |
| $\mathrm{HC{\equiv}CH}$ | 8 | **72e** | 97 |
| $\mathrm{HC{\equiv}CCH_2OMe}$ | 8 | - | trace |
| $\mathrm{MeOOCC{\equiv}CCOOMe}$ | 8 | - | 11 |

**Scheme 1-20**: Cyclotrimerization of Alkynes in Supercritical Carbon Dioxide ($scCO_2$) in the Presence of $PdCl_2/CuCl_2$ and MeOH (Cheng and Jiang, 2004)



**Scheme 1-21**: Mechanism for Transition Metal Catalyzed Cyclotrimerization of Alkynes

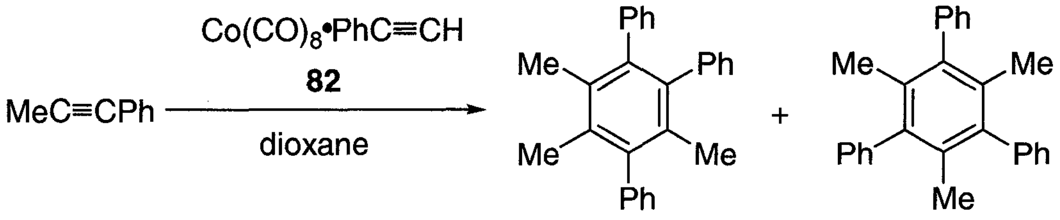
generated and a new catalyst which has free coordination sites is regenerated. In the oxidative coupling step, the metal center prefers to coordinate to the least hindered alkyne carbon. Therefore, when an unsymmetrically substituted alkyne undergoes cyclotrimerization, usually it gives a benzene derivative with the larger substituents at positions 1, 2 and 4 as the main product. **Scheme 1-22** shows an unsymmetically substituted alkyne **81** undergoing a cyclotrimerization reaction in the presence of a cobalt catalyst **82** to give the asymmetric isomer **83** in 87 % yield and the symmetric isomer **84** in 3 % yield (Schore, 1988).

Typical catalysts used for alkyne cyclotrimerizations can be classified into the following types: metal carbonyl, Ziegler Natta catalyst, other transiton metal and their complexes and metal free catalyst.

### 1.4.1. Metal Carbonyls

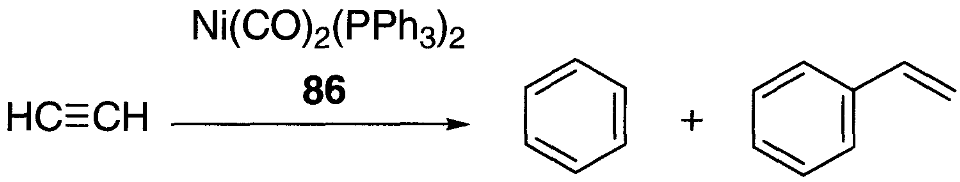
Nickel-carbonylphosphine [$Ni(CO)_2(PPh_3)_2$] **86**, as discovered by Reppe (Reppe *et al.*, 1948), was one of the first catalysts utilized for the cyclotrimerization of acetylene **85**. The products obtained from this reaction were benzene **87** in 88 % yield and styrene **88** in 12 % yield (**Scheme 1-23**). It was also found that with the same catalyst, monosubstituted acetylenes formed a mixture of 1,3,5- and 1,2,4-trisubstituted benzenes in quantitative yield. Unfortunately, most of the disubstituted acetylenes did not react.

However, in later work, hexa-substituted benzene was synthesized utilizing the same catalyst (Meriwether et al., 1961; Rose and Statham, 1950). In most of these reactions, a mixture of the two benzene derivative isomers and linear polymers **89** and **90,** shown in **Figure 1-7**, were produced. A detailed study (Meriwether et al., 1962)



**81** **83** **84**

**Scheme 1-22:** Cyclotrimerization of Unsymmetrically Substituted Alkynes Using a Cobalt Metal as the Catalyst



**85** **87** **88**

**Scheme 1-23:** Cyclotrimerization of Acetylene Catalyzed by $[Ni(CO)_2(PPh_3)_2]$

$$\mathrm{R{-}C{\equiv}C{-}\!\left(CR{=}CH\right)_{n}CH{=}CHR}$$

**89**

or

$$\mathrm{R{-}C{\equiv}C{-}\!\left(CR{=}CH\right)_{n}CR{=}CH_2}$$

**90**

$n = 0 - 10$

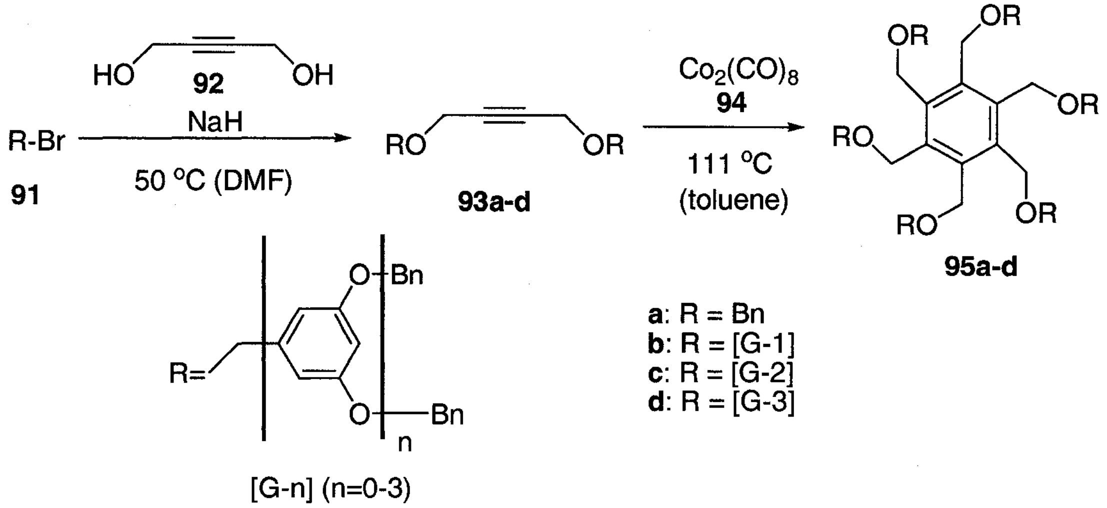
**Figure 1-7:** General Structures of Linear Polymers showed that more reactive monomers, such as acetylenes with electron-withdrawing substituents, mainly yielded aromatic products, while less reactive monomers such as acetylenes with larger substituents had the tendency to form linear polymers. This was due to a steric hindrance issue. Other nickel catalysts with different ligands have also been studied. It has been shown that $[Ni(CO)_3PPh_3]$ was an effective catalyst while $[Ni(CO)(PPh_3)_3]$ and $[Ni(PPh_3)_4]$ were inactive for catalyzing the trimerization of 1-heptyne.

Cobalt carbonyl complexes, such as $Co_2(CO)_8$, $MgCo_2(CO)_8$, $Hg[Co(CO)_4]_2$, $Co_2(CO)_6RC_2R'$ or $Co_4(CO)_{10}RC_2R'$ were shown to have very high catalytic activity in the cyclotrimerization of alkynes. They gave high yields and good selectivity, especially when dioxane was used as a solvent (Hubel and Hoogzand, 1960; Mills and Robinson, 1964; Schore *et al.*, 1984). In 1999, Hecht *et al.* reported their interesting study on the convergent synthesis of dendrimers **95a-d**, in which the dendrimer core was generated by an alkyne cyclotrimerization reaction using $Co_2(CO)_8$ **94** as a catalyst (Hecht and Frechet, 1999) **(Scheme 1-24)**. As the size of the benzene substitutuents increased, the reaction times also increased but the yield decreased.

Alkyne cyclotrimerization also took place in the presence of some other metal carbonyl complexes including iron, manganese, molybdenum, tungsten, chromium and rhodium (Hubel and Hoogzand, 1960; Kruerke and Hubel, 1961; Maitlis and McVey, 1965; Strohmeier and Barbeau, 1964; Tate *et al.*, 1964).

### 1.4.2. Ziegler-Natta Catalysts

A Ziegler-Natta catalyst is typically composed of two parts: a transition metal component, usually either titanium or vanadium, and a main group metal alkyl compound,



| **Compound** | **R** | **Time 93→95** | **Yield of 93** | *Yield of 95* |
|---|---|---|---|---|
| **a** | Bn | 0.5 h | 62 % | 83 % |
| **b** | [G-1] | 2 h | 62 % | 80 % |
| **c** | [G-2] | 20 h | 50 % | 50 % |
| **d** | [G-3] | 48 h | 41 % | 36 % |

**Scheme 1-24**: Synthesis of Benzene-Cored Dendrimers via the Cyclotrimerization of Alkynes (Hecht and Frechet, 1999)

usually an aluminum alkyl. The Ziegler-Natta catalyst was first used in the cyclotrimerization of alkynes in 1959, when Franzus and coworkers found that hexasubstituted benzenes could be obtained from disubstituted acetylenes in the presence of Al $(iso\text{-}C_4H_9)_3 + TiCl_4$ (Franzus *et al.*, 1959).

With the same catalyst, monosubstituted acetylene can be trimerized into a mixture of 1, 3, 5- and 1, 2, 4-trisubstituted benzene derivatives (Schlogl and Soukup, 1967), although it was suggested that the catalyst was being decomposed by the "acidic" acetylene. In some cases, a linear polymer was also found in the mixture. Donda and coworkers found that the Al/Ti ratio determined the relative yield of cyclic and linear products (1962). When the ratio was less than 4, only cyclic benzene derivatives were obtained but when the ratio was between 2 and 4, the linear compound reached the highest yield (75 %).

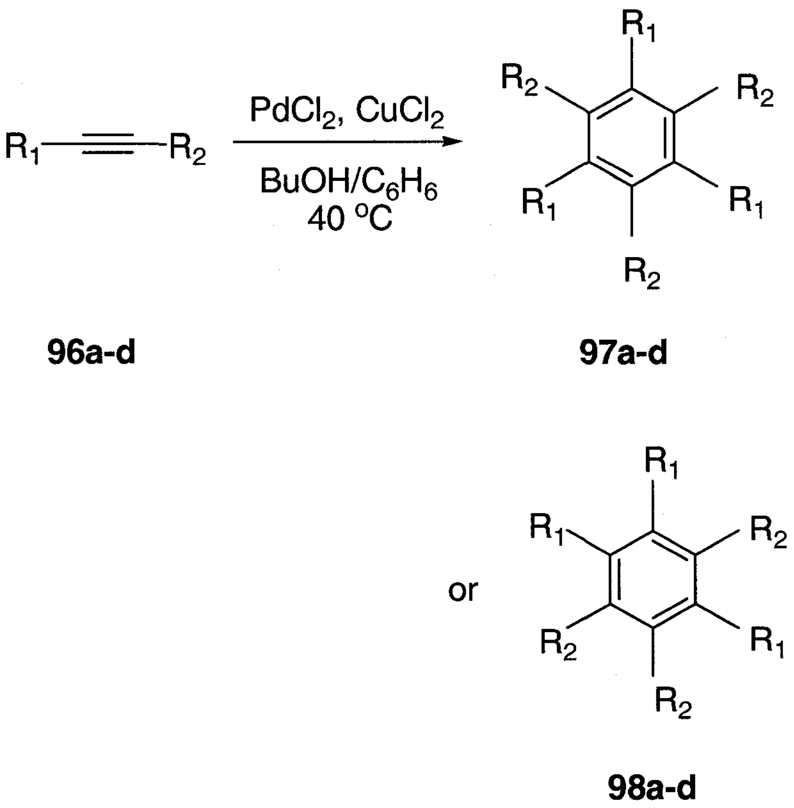
Some other Ziegler-Natta catalysts displayed good catalytic activities, for example, $Al(C_2H_5)_3 + TiCl_4$. Lutz cyclotrimerized a number of mono- and di-substituted acetylenes in the presence of this catalyst system (1961). He reported that the use of a large volume of solvent was optimal for successful cyclotrimerization. The best yield (80.2 % of the trimers) was obtained when dimethylacetylene was used in the reaction at ambient temperature.

### 1.4.3. Other Transition Metal and their Complexes

Various palladium complexes have been used in the cyclotrimerization of alkynes. Bis(benzonitrile) palladium chloride and uncomplexed $PdCl_2$ were found to be suitable catalysts (Blomquist and Maitlis, 1962; Dietl and Maitlis, 1968; Maitlis *et al.*, 1965; Pollock and Maitlis, 1971). Li and coworkers reported that $PdCl_2$ catalyzed these types of reactions in the presence of $CuCl_2$ and benzene derivatives were produced in high yield and high chemo- and regio-selectivity (Li *et al.*, 2001). Under these conditions, a monosubstituted alkyne **96a-c** yielded 1, 3, 5- trisubstituted benzene derivatives **97a-c** as products, while asymmetric hexasubstituted benzene derivative **98d** was obtained as the main product when 1-phenyl-1-propyne **96d** was trimerized (**Scheme 1-25**).

Jhingan and coworkers studied the cyclotrimerization of alkynes catalyzed by palladium on carbon in the presence of trimethylsilyl chloride (1987). After a detailed inspection, this apparently heterogeneously catalyzed cyclization was actually found to be homogenous. This catalytic system was then applied by Renga (1990) and Lligadas (2007) in the cyclotrimerization of fatty alkynes to produce tri-functional benzene derivatives such as aromatic triols **99** and triacids **100 (Figure 1-8)**. Abbet and coworkers reported that a MgO (100)-film-supported single palladium atom can catalyze the production of benzene from acetylene at ambient temperature but the yield was not reported (Abbet *et al.*, 2000).

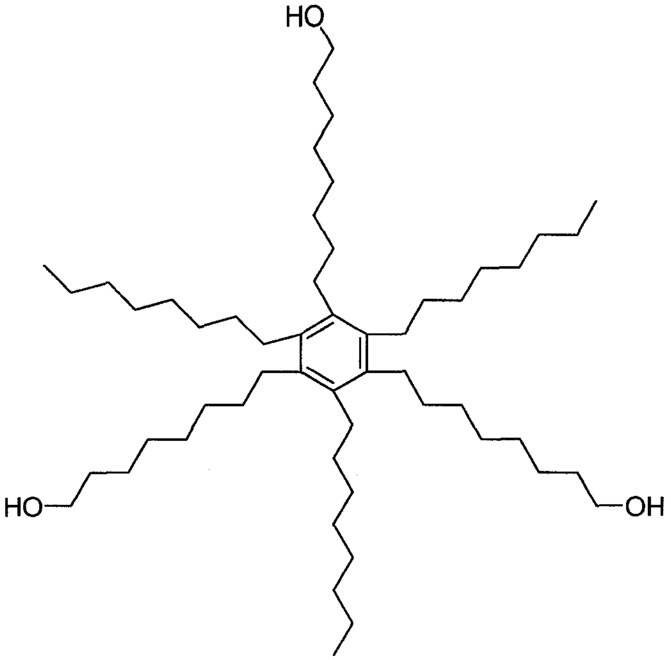
An interesting catalytic system comprising of Group VIII transition metal salts and a hydride reducing agent, for example $NiCl_2$-$NaBH_4$ and $(Ph_3P)_2NiCl_2$-$NaBH_4$, was proposed to be suitable for the cyclotrimerization of alkynes (Donda and Moretti, 1966; Kern, 1969; Luttinger, 1962; Luttinger and Colthup, 1962). Alphonse and coworkers reported that the catalytic cyclotrimerization of acetylenic compounds **101** by transient complexes formed in the reduction of nickel halides by magnesium occurs with many alkynes (Alphonse *et al.*, 1988). 1, 3, 5-trisubstituted benzene derivative **102** was the major product with a yield of 65 % **(Scheme 1-26)**. However, it was found that this



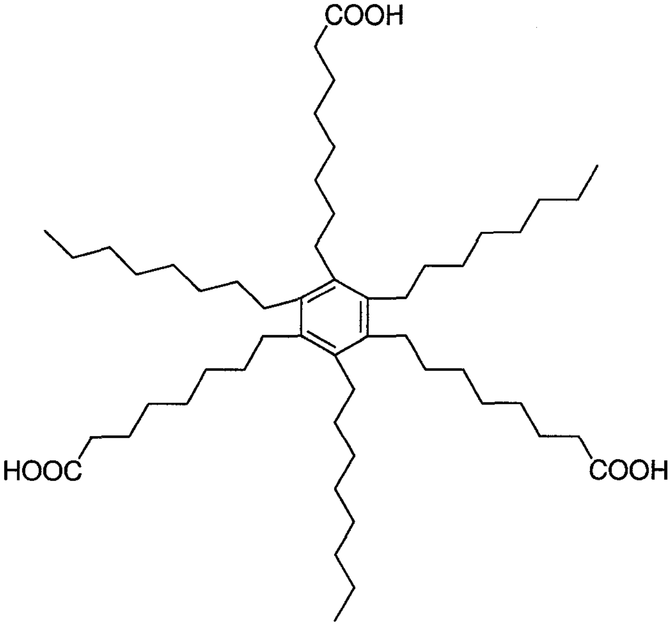
**96a-d** **97a-d** **98a-d**

| Compound | R1 | R2 | Time (h) | Product | *Yield (%)* |
|---|---|---|---|---|---|
| **a** | *p*-MePh | H | 15 | **97a** | 95 |
| **b** | $C_5H_{11}$ | H | 12 | **97b** | 78 |
| **c** | *t*-Bu | H | 12 | **97c** | 100 |
| **d** | Ph | Me | 12 | **98d** | 80 |

**Scheme 1-25**: $PdCl_2$ Catalyzed Cyclotrimerization of Alkynes in the Presence of $CuCl_2$ (Li et al., 2001)

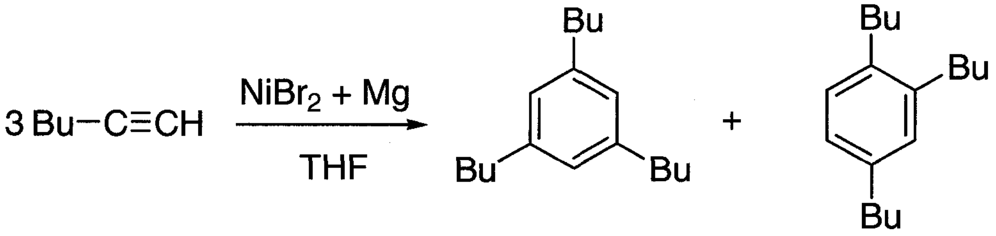


**99**



**100**

**Figure 1-8**: Aromatic Triol and Triacids Derived from Fatty Alkynes



**101** **102** **103**

**Scheme 1-26:** Catalytic Cyclotrimerization of Alkynes by Nickel-Complexes Formed *in situ.*

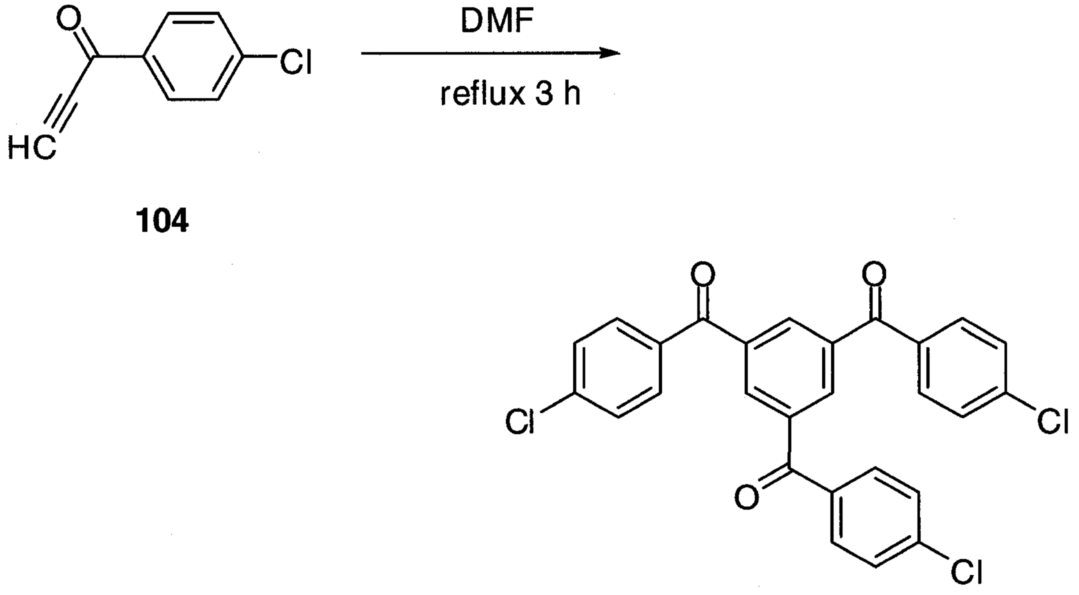
cyclization was hindered when the substituents were bulky groups such as butyne 1, 4-diol.

### 1.4.4. Metal-free Catalysts

In 1980, it was discovered that refluxing a solution of aryl ethynyl ketone **104** in dimethylformamide (DMF) provided the corresponding 1,3,5-substituted benzene trimer **105** in 80 % yield **(Scheme 1-27)** (Balasubramanian *et al.*, 1980). This reaction is simple, efficient and regio-selective.

### 1.4.5. Summary

Cyclotrimerization of alkynes is usually carried in organic solvents and catalyzed by transitional metals and their complexes. Among those catalysts, palladium on carbon with trimethylsilyl chloride as a co-catalyst is a simple and efficient system (Jhingan and Maier, 1987). This catalyst system has been used in the cyclotrimerization of fatty alkynes to produce aromatic triols and triacids (Lligadas *et al.*, 2007; Renga *et al.*, 1990). However, successful separation of the symmetric and asymmetric isomers of these aromatic triols and triacids has not been reported. Therefore, the structure confirmation and yield of each isomer are still unknown.



**104**

**105**

**Scheme 1-27**: Cyclotrimerization of Aryl Ethynyl Ketone in Dimethylformamide (DMF)

## 1.5. Hypotheses

The concrete objectives of the research described in this thesis are to test the hypotheses stated below:

1. The double bonds in TAGs will be cleaved when exposed to ozone.
2. The ozonide formed can be hydrogenated using a catalyst to produce polyols from TAGs.
3. The produced polyols will comprise mono-ol, diol and triol as well as small amounts of saturated TAGs.
4. The components of polyols can be separated by HPLC with a polar column. Using proper standards, the polyols can be quantitatively analyzed.
5. Unsaturated fatty acids can be converted into fatty alkynes containing hydroxyl or acid functionalities. *Via* a cyclotrimerization reaction, the fatty alkynes can produce an aromatic compound containing the same hydroxyl or acid functionalities.
6. The same aromatic compounds can be synthesized from saponified vegetable oil.

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# 2 Production of Polyols from Seed Oils and their Chemical Identification and Physical Properties*

## 2.1. Introduction

Polymeric materials, such as polyurethanes (PURs) are traditionally derived from petrochemical polyols (Szycher, 1999), but as oil reserves are depleting and prices continue to rise, the development of alternatives is becoming necessary (Guo et al., 2002; Khoe et al., 1972; Lyon et al., 1974). Worldwide economic and scientific interest in vegetable oils as an inexpensive, readily available renewable resource is growing and has already been the subject of significant attention (John *et al.*, 2002). Native North American vegetable oils are mainly constituted of triacylglycerols (TAGs) containing predominantly unsaturated fatty acids, which are chemically relatively unreactive. In order to produce reactive materials which then can be utilized in producing valuable polymeric materials, functional groups such as hydroxyl, epoxy, or carboxyl groups have to be introduced at the positions of the double bonds of the unsaturated TAGs (Gryglewicz et al., 2003; Guo et al., 2000; Petrovic et al., 2000; Petrovic et al., 2005).

As a low-cost and easily produced reagent, ozone is widely used to oxidatively cleave the double bond of alkenes (Bailey, 1958). In the 1960's and 1970's, Pryde's group (Pryde et al., 1960; Pryde et al., 1962; Pryde et al., 1976) successfully applied ozonolysis on methyl oleate to produce alcohol and aldehyde products. Employing a similar procedure, soybean oil was also used as feedstock to make aldehyde oils (Pryde et

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al., 1963; Pryde et al., 1961; Pryde and Cowan, 1962). More recently, Petrovic *et al.* (Petrovic et al., 2005) used ozonolysis followed by reduction to make a triol product from triolein, soybean oil and canola oil.

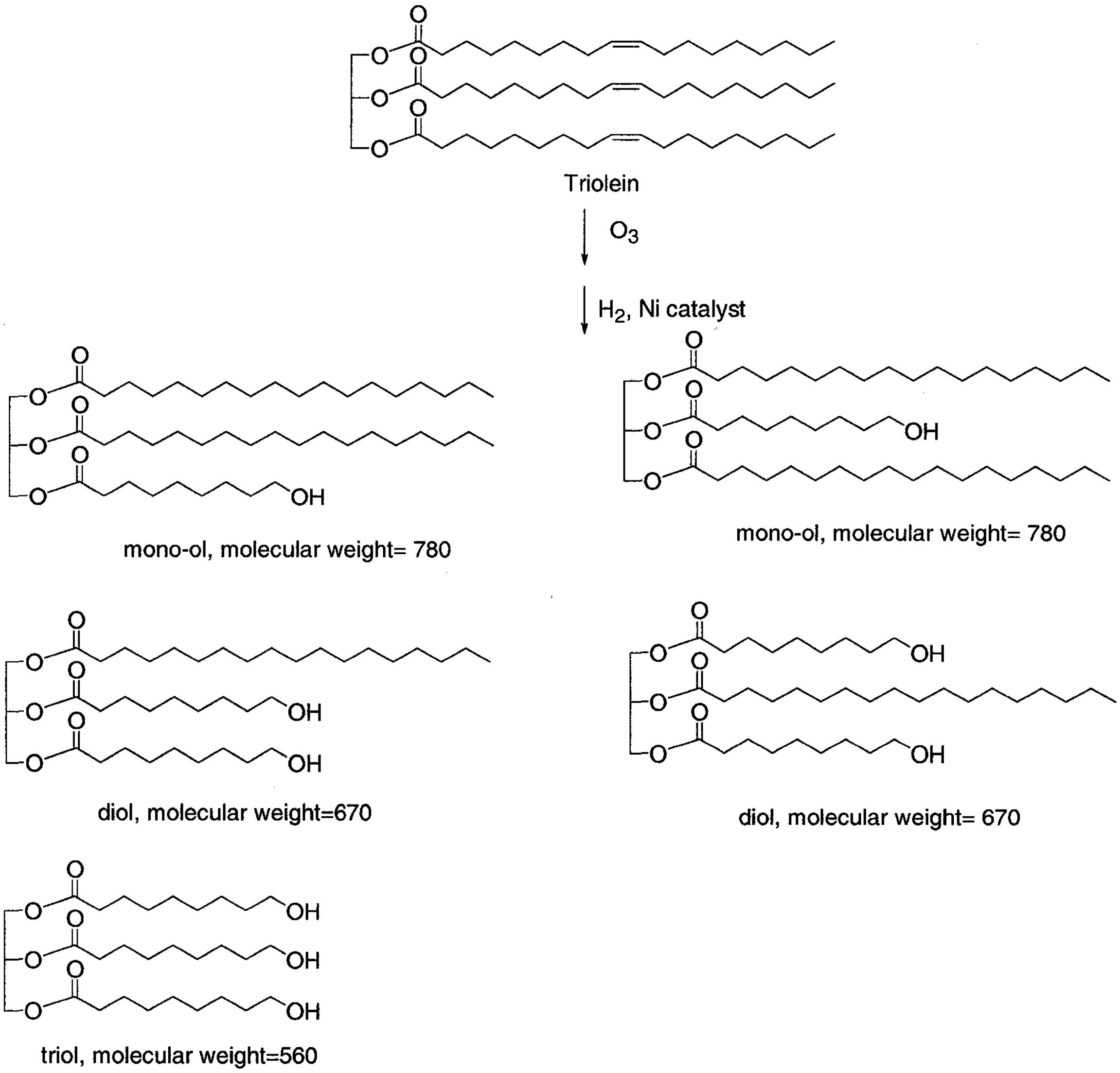
Canola vegetable oil is a good candidate for the production of polyols using ozonolysis and hydrogenation reactions. It contains more than 90 % of unsaturated fatty acids, including oleic acid, linoleic acid, and linolenic acid (Firestone, 1999), which all have a double bond at carbon nine that could be easily cleaved and the cleavage products hydrogenated to provide terminal functional groups. The probability of forming a single alcohol group (which is a chain terminator) on a triacylglycerol would be in this case very low. Triolein has been used as an example, the mechanism leading to the production of polyols from unsaturated TAG is illustrated by the reaction shown in **Scheme 2-1**. In this study, ozonolysis and hydrogenation technology was used to produce polyol from canola oil. Identification of the polyol and the valuable side-products are presented. The physical properties of the polyol are also reported.

## 2.2. Experimental Procedures

### 2.2.1. Materials

The canola vegetable oil used in this study was a "100% Pure Canola" supplied by Canbra Foods Limited, Lethbridge, AB, Canada. Raney nickel 2800 (slurry in water) catalyst was obtained from Sigma-Aldrich Co., USA. Pentane, Celite, dichloromethane (HPLC grade), heptane (HPLC grade), 2-propanol (isopropanol, HPLC grade), ethyl acetate, hexane and 1-nonanol were obtained from Fisher Scientific, USA.

Tetrahydrofuran (THF) was obtained from Caledon Laboratories Limited, ON, Canada. Silica gel (230-400 mesh) was obtained from Rose Scientific Ltd, AB, Canada.



**Scheme 2-1:** Polyol Production after Ozonolysis and Hydrogenation of Triolein

Si-Diol Silica Gel (230-400) mesh was obtained from Silicycle Chemistry Division, QC, Canada. All chemicals were reagent grade or better.

### 2.2.2. Ozonolysis

An ozonolysis batch consisted of about 100 g of canola oil and 400 g of deionized water. The mixture was poured into a specially designed reactor (**Figure 2-1**), fed with a Direct Current Permanent Magnet 1 HP Motor from Leeson electric-corporation, USA. Ozone was produced in an ozone generator (Azcozon Model RMV16-16 from Azco Industries Ltd, Canada) with oxygen or air as the feed gas. The reaction was performed at 0 °C, at 5 L/min air or oxygen flow rate and 500 rpm agitation rate for 8 hours. The concentration of ozone was 62 $g/m^3$ when oxygen was used and 29 $g/m^3$ when air was used. After 8 hours, the ozone generator was stopped and the reaction vessel was purged with $N_2$ for 10 minutes to remove the unreacted ozone in the vessel. The product of ozonolysis was dissolved in 400 mL of THF and transferred to a separatory funnel where the organic portion was separated from the aqueous portion and collected for hydrogenation.

### 2.2.3. Hydrogenation

15 g of Raney nickel catalyst (RA-Ni) (slurry in water) was added to the ozonolysis product in a hydrogenation vessel (2 L, Parr Instrument Co, USA) fitted with a magnetic drive. The reaction vessel was charged with hydrogen gas at 350 psi at room temperature. The temperature was then increased to 130 °C. After 8 hours, the temperature was reduced to room temperature. The reaction vessel was finally purged with nitrogen gas to remove unreacted hydrogen gas. The resulting mixture was filtered over Celite and the aqueous layer was removed. The solvent was then removed from the

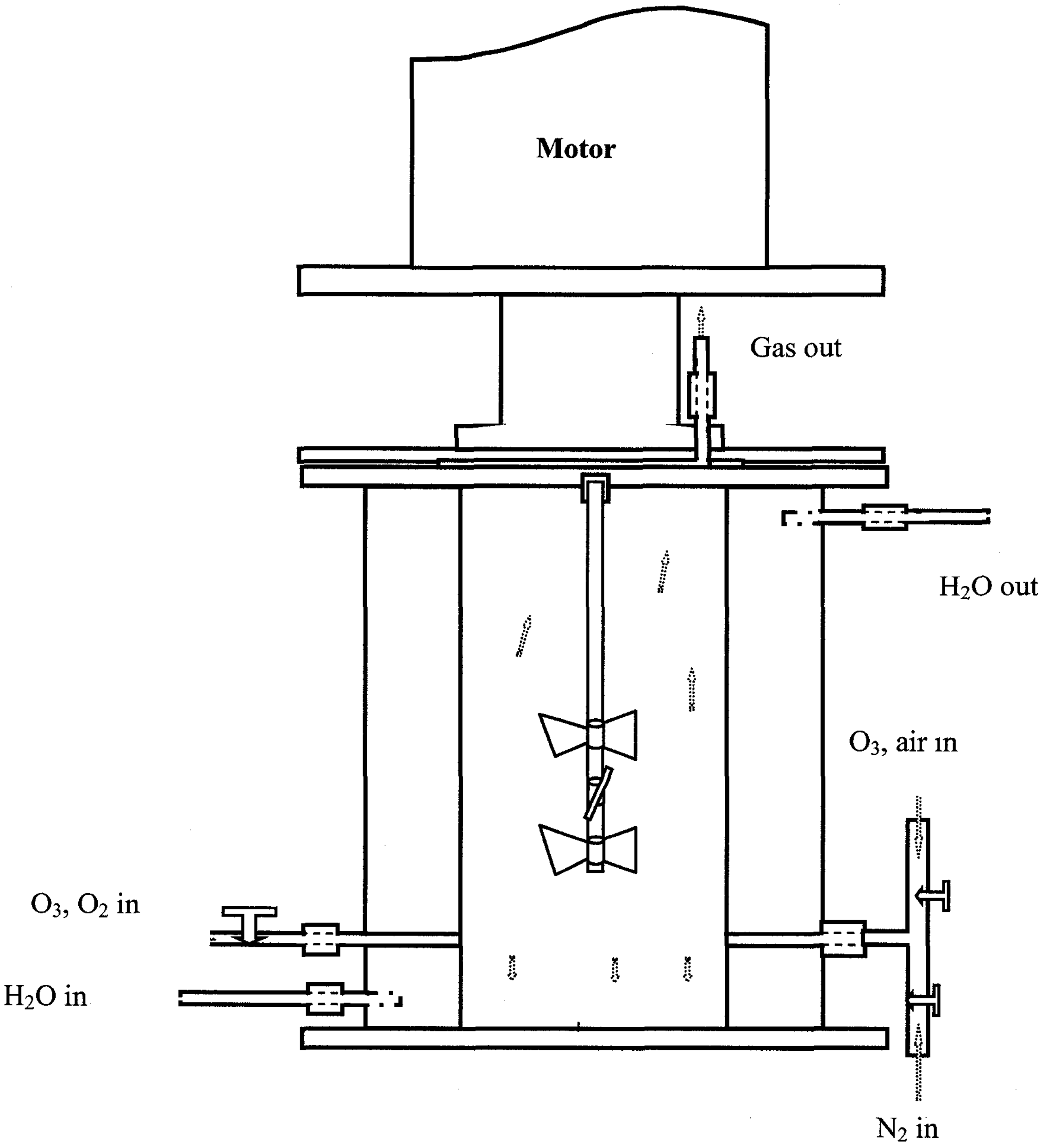


**Figure 2-1:** Schematic of the Ozonolysis Reaction Vessel

organic layer by rotary evaporation and the final product was kept for distillation.

The presence of nonanal, easily identified by GC, was used as an indicator for the completion of hydrogenation.

### 2.2.4. Wiped-Blade Molecular Distillation

The unit (Model VKL 70/ICL-04, from Incon Processing, IL, USA) was set up at a jacket temperature of 115 °C and condenser temperature of 30 °C. The pressure of the distillation system was reduced to 20 mTorr and the final hydrogenation product added into the distillation system through an addition funnel at a rate of 1 mL/min. The polyol was collected in the residue part because of its high boiling point, and the short-chain molecules cleaved from the fatty acid chain were distilled and condensed in the distillate part.

The polyol obtained when using oxygen is referred to as Canola-Oxygen Polyol, and the polyol obtained when using air is referred to as Canola-Air Polyol.

### 2.2.5. High Performance Liquid Chromatography (HPLC) System

The HPLC analysis protocol used was a modification of the procedure developed by Elfman-Borjesson and Harrod (Elfman-Borjesson and Harrod, 1997) for analysis of lipid derivatives. The HPLC system consisted of a dual Milton Roy pump with a 20 μL auto-injector. The column was packed by Betasil Diol-100 (5 μm particle size) 250 mm × 4 mm produced by Thermo Hypersi-Keytone and maintained at 50 °C with a Biorad column heater. The detector was an Alltech ELSD 2000 evaporative light scattering system maintained at 100 °C with a gain setting of 10 (on the 12 unit scale) and a nitrogen pressure of 2 bar. Two solvents ($A$ and $B$) were connected to the pump as the mobile phase. *A* was 100% heptane and *B* was 50% heptane with 50% isopropyl alcohol (IPA). A run consisted of a linear gradient of 100% *A* to 83% *A* and 17% *B* in 30 min; then back to 100% *A* in 1 minute at a flow rate of 3 mL/min.

### 2.2.6. Flash Chromatography

4.3 g of Canola-Oxygen Polyol components were separated in a column of dimension 3 cm × 30 cm packed with silica gel (230 - 400 mesh). The column was eluted with gradient flow phase composed of hexane and ethyl acetate. The final collected pure fractions, i.e. saturated TAGs, mono-ol, diol and triol, were analyzed by HPLC, FTIR, $^{1}$H-NMR, $^{13}$C-NMR and Mass spectrometry.

### 2.2.7. Gas Chromatography (GC) System

Varian 3500 Capillary GC equipped with a Flame Ionization Detector (GC-FID), Varian 8200 Auto Sampler and a BP20025 column (30m × 0.25mm i.d., 0.25-µm) was used to identify and quantify the short chain compounds present as by-products of the hydrogenation reaction. The injector and the detector temperature were fixed at 250 °C. The temperature of the column initially set at 50 °C was increased to 250 °C in two successive steps: from 50 °C to 90 °C at a rate of 25 °C/min and from 90 °C to 250 °C at a rate of 10 °C/min.

### 2.2.8. FTIR, $^{1}$H-NMR and Mass Spectrometry

FTIR spectra were measured with a Mattson Galaxy Series FT-IR 3000 spectrophotometer. $^{1}$H NMR and $^{13}$C-NMR were recorded at 500 MHz using Varian 500 MHz or 400 MHz spectrometers (Varian, Inc., CA, USA) with $CDCl_3$ as a solvent. Mass spectra were acquired on a Mariner Biospectrometry Workstation (PerSeptive Biosystems, Inc., MA, USA).

*Saturated TAGs:* $^1$H-NMR ($CDCl_3$ 500 MHz): δ 5.26 (m, 1H, CHOCOR), 4.29 (dd, $J$ = 4.0 Hz, 12.0 Hz, 2H, $CH_2OCOR$), 4.14 (dd, $J$ = 5.5 Hz, 11.5 Hz, 2H, $CH_2OCOR$), 2.30 (t, $J$ = 7.5 Hz, 6H, $CH_2CO$), 1.60 (m, 6H, $C\underline{H_2}CH_2CO$) 1.20 (m, $C\underline{H_2}$), 0.88 (t, $J$ = 7.0 Hz, 9H, $CH_3$). $^{13}$C-NMR ($CDCl_3$ 125 MHz): δ 173.3 (COR, *sn*-1, 3), 172.92 (COR, *sn*-2), 172.86 (COR, *sn*-2), 68.94 ($\underline{C}$HOCOR), 62.16 ($\underline{C}H_2OCOR$), 34.28, 34.12, 31.98, 29.76, 29.72, 29.68, 29.54, 29.42, 29.35, 29.33, 29.18, 29.15, 24.97, 24.93, 22.74, 14.58 ($CH_3$).

*Mono-ol:* $^1$H-NMR ($CDCl_3$ 500 MHz): δ 5.26 (m, 1H, CHOCOR), 4.29 (dd, $J$ = 4.5 Hz, 12.0 Hz, 2H, $CH_2OCOR$), 4.14 (dd, $J$ = 6.0 Hz, 11.5 Hz, 2H, $CH_2OCOR$), 3.62 (t, $J$ = 6.5 2H, $CH_2OH$), 2.30 (t, $J$ = 7.5 Hz, 6H, $CH_2CO$), 1.60 (m, 8H, $C\underline{H_2}CH_2CO$ and $C\underline{H_2}CH_2OH$), 1.20 (m, 64H, $CH_2$), 0.88 (t, $J$ = 6.5 Hz, 6H, $CH_3$). $^{13}$C-NMR ($CDCl_3$ 125 MHz): δ 173.34 (COR, *sn*-1, 3), 173.32 (COR, *sn*-1, 3), 173.26 (COR, *sn*-1, 3), 172.91, (COR, *sn*-2), 172.84 (COR, *sn*-2), 68.94 ($\underline{C}$HOCOR), 68.93 ($\underline{C}$HOCOR), 62.98 ($\underline{C}H_2OCOR$), 62.15 ($CH_2OH$), 62.11 ($CH_2OH$), 34.25, 34.20, 34.09, 34.03, 32.77, 32.76, 31.96, 29.73, 29.71, 29.69, 29.68, 29.65, 29.53, 29.51, 29.39, 29.33, 29.30, 29.23, 29.21, 29.20, 29.19, 29.15, 29.11, 29.01, 28.98, 25.70, 25.68, 24.94, 24.90, 24.86, 24.83, 22.72, 14.13 ($CH_3$). CI-MS: *m/z* 803.7 ($[M+Na]^+$).

*Diol:* $^1$H-NMR ($CDCl_3$ 400 MHz): δ 5.26 (m, 1H, CHOCOR), 4.29 (dd, $J$ = 4.5 Hz, 12.0 Hz, 2H, $CH_2OCOR$), 4.14 (dd, $J$ = 6.0 Hz, 12 Hz, 2H, $CH_2OCOR$), 3.62 (t, $J$ = 6.5 4H, $CH_2OH$), 2.30 (t, $J$ = 7.5 Hz, 6H, $CH_2CO$), 1.60 (m, 10H, $C\underline{H_2}CH_2CO$ and $C\underline{H_2}CH_2OH$), 1.20 (m, 44H, $CH_2$), 0.88 (t, $J$ = 6.5 Hz, 3H, $CH_3$). $^{13}$C-NMR ($CDCl_3$ 100 MHz): δ 173.09 (COR, *sn*-1, 3), 173.01 (COR, *sn*-1, 3), 172.59 (COR, *sn*-2), 68.94 ($\underline{C}$HOCOR), 62.90 ($\underline{C}H_2OCOR$), 62.14 ($CH_2OH$), 34.29, 34.16, 34.13, 32.81, 32.04, 29.82, 29.78, 29.74, 29.60, 29.48, 29.39, 29.31, 29.23, 29.10, 29.07, 28.96, 25.82, 25.80, 24.99, 24.94, 22.83, 14.27 ($CH_3$). CI-MS: *m/z* 693.6 ($[M+Na]^+$).

*Triol:* $^1$H-NMR ($CDCl_3$ 500 MHz): δ 5.26 (m, 1H, CHOCOR), 4.29 (dd, $J$ = 4.5 Hz, 12.0 Hz, 2H, $CH_2OCOR$), 4.14 (dd, $J$ = 6.0 Hz, 12 Hz, 2H, $CH_2OCOR$), 3.62 (t, $J$ = 6.5 6H, $CH_2OH$), 2.30 (t, $J$ = 7.5 Hz, 6H, $CH_2CO$), 1.60 (m, 12H, $C\underline{H}_2CH_2CO$ and $C\underline{H}_2CH_2OH$), 1.20 (m, 24H, $CH_2$). $^{13}$C-NMR ($CDCl_3$ 125 MHz): δ 173.31 (COR, *sn*-1, 3), 172.89 (COR, *sn*-2), 68.93 ($\underline{C}HOCOR$), 62.86 ($\underline{C}H_2OCOR$), 62.85 ($\underline{C}H_2OCOR$), 62.12 ($CH_2OH$), 34.19, 34.03, 32.69, 29.22, 29.19, 29.18, 29.16, 28.97, 28.95, 25.69, 25.66, 24.85, 24.81. CI-MS: *m/z* 583.4 ($[M+Na]^+$).

### 2.2.9. Rheometeric measurements

The viscosities of the polyol samples were measured in shearing mode with the Universal Dynamic Rheometer PHYSICA UDS 200 (Paar Physica USA) with a constant shearing rate of 51.6 $s^{-1}$. The results are listed in **Table 2-1**.

### 2.2.10. DSC

The "TA 2920 Modulated DSC" system from TA Instruments was used to study the thermal transitions of the polyols. The procedure to record the crystallization and melting curves was as follows: Initially the sample was kept at 20 °C for 5 min to reach its equilibrium state and then was heated to 80 °C with a rate of 5 °C/min to erase its thermal history. To record the crystallization curve, the sample was cooled down to -50 °C at a constant rate of 5 °C/min and kept at this temperature for 5 min to allow for the completion of the crystallization. The sample was then heated to 80 °C at a constant rate of 5 °C/min to record the melting curve.

### 2.2.11. Refractometry

The refractive index of the materials was determined according to the ASTM D1747– 99, using a CARL Zeiss (Germany) refractometer. The results are reported in **Table 2-1**.

### 2.2.12. Hydroxyl and acidity values

The hydroxyl numbers of the polyols were determined according to the ASTM D1957-86 and the acidity values were determined according to the ASTM D4662-98. The average values and standard deviations of triplicate measurements are reported in **Table 2-1**.

## 2.3. Results and Discussion

### 2.3.1. Polyols from Seed Oils and their Chemical Identification

In all the FTIR spectra of the collected pure fractions (**Figure 2-2**), i.e. saturated TAG, mono-ol, diol and triol, the 1650 cm-1 characteristic C=C double bond stretch is reduced to very small bumps, confirming that almost all the double bonds in the canola oil have been reduced. The absorption band centered at 3300 $cm^{-1}$, characteristic of hydroxyl groups, is missing in the saturated TAG, but appears in the other three samples with a tendency to grow bigger and broader from mono-ol to diol to triol.

The FTIR indications were confirmed by $^{1}H$-NMR and $^{13}C$-NMR. For the triol, the methyl protons and carbon were not observed and for saturated TAG, the methylene protons and carbon adjacent to hydroxyl group were not observed. As for the integration

| **Polyol** | **Hydroxyl number (mg KOH/g)** | **Acidity number (mg KOH/g)** | **Viscosity at 25°C ± $5\times10^{-4}$ (Pa.s)** | **$n_D^{35}$ ± $5\times10^{-4}$** |
|---|---|---|---|---|
| Canola-Air | 152.4 ± 0.3 | 22.9 ± 0.3 | 0.4527 | 1.4663 |
| Canola-Oxygen | 176.4 ± 0.5 | 51.7 ± 0.1 | 0.9067 | 1.4658 |

**Table 2-1:** Hydroxyl Number, Acidity Number, Viscosity, and Refractive Index of Canola Polyols. (Errors are standard deviations, n=3)

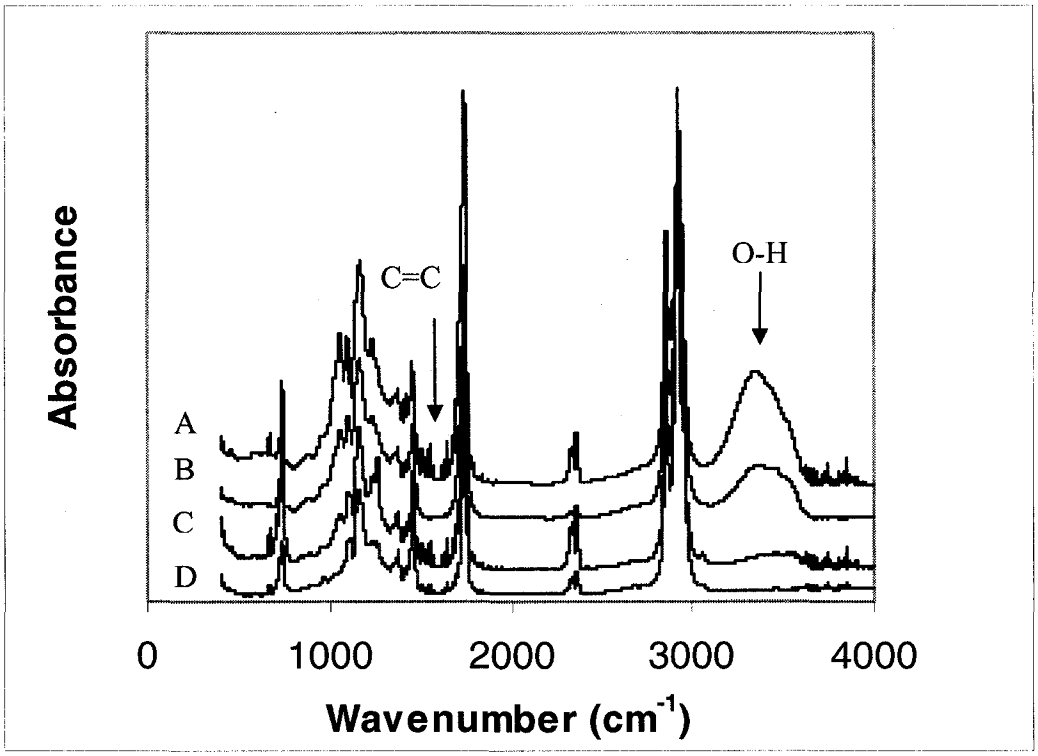


**Figure 2-2:** FTIR Spectrum of Saturated Triacylglycerol (TAG) (D), Mono-ol (C), Diol (B) and Triol (A)

of the triplet at 0.88 ppm (representing the terminal methyl groups of the fatty acids), mono-ol was 6, and diol was 3. For the integration of the triplet at 3.62 ppm (representing the methylene protons adjacent to hydroxyl group), mono-ol was 2 and diol was 4. This indicated that saturated TAG has three fatty acid chains with a methyl group at the end of each chain and that the triol has three chains with a hydroxyl group at the end of each chain. It also indicated that the mono-ol has two fatty acid chains and one alcohol chain and that the diol has one fatty acid chain and two alcohol chains.

Samples of saturated TAG, mono-ol, diol and triol were analyzed using HPLC. Each of them demonstrated a single peak with the retention times of 4.04 min, 5.86 min, 15.94 min, and 30.92 min, respectively (**Figure 2-3**). The HPLC (**Figure 2-4**) of the polyol mixture obtained directly after distillation demonstrated four main peaks, with retention times matching those of saturated TAG, mono-ol, diol and triol separately.

Apart from the polyol, some short-chain molecules were also produced as side products. **Figure 2-5** shows the three possible unsaturated fatty acids in canola (linoleic, linolenic and oleic acids) and the potential short chain alcohols that can be produced from these materials.

Conveniently, the shorter chain products were all removed by a single pass in the wiped blade molecular distillation process. GC chromatographs **(Figure 2-6)** recorded before and after distillation demonstrated that the end-product polyols were practically free of short-chain by products except of a small amount of nonanol (<1%). Their separation from the polyols by wiped blade molecular distillation is desired because, on one hand, all these small side-products are very valuable materials for the chemical industry and on the other hand, mono-alcohols are potential chain terminators to the

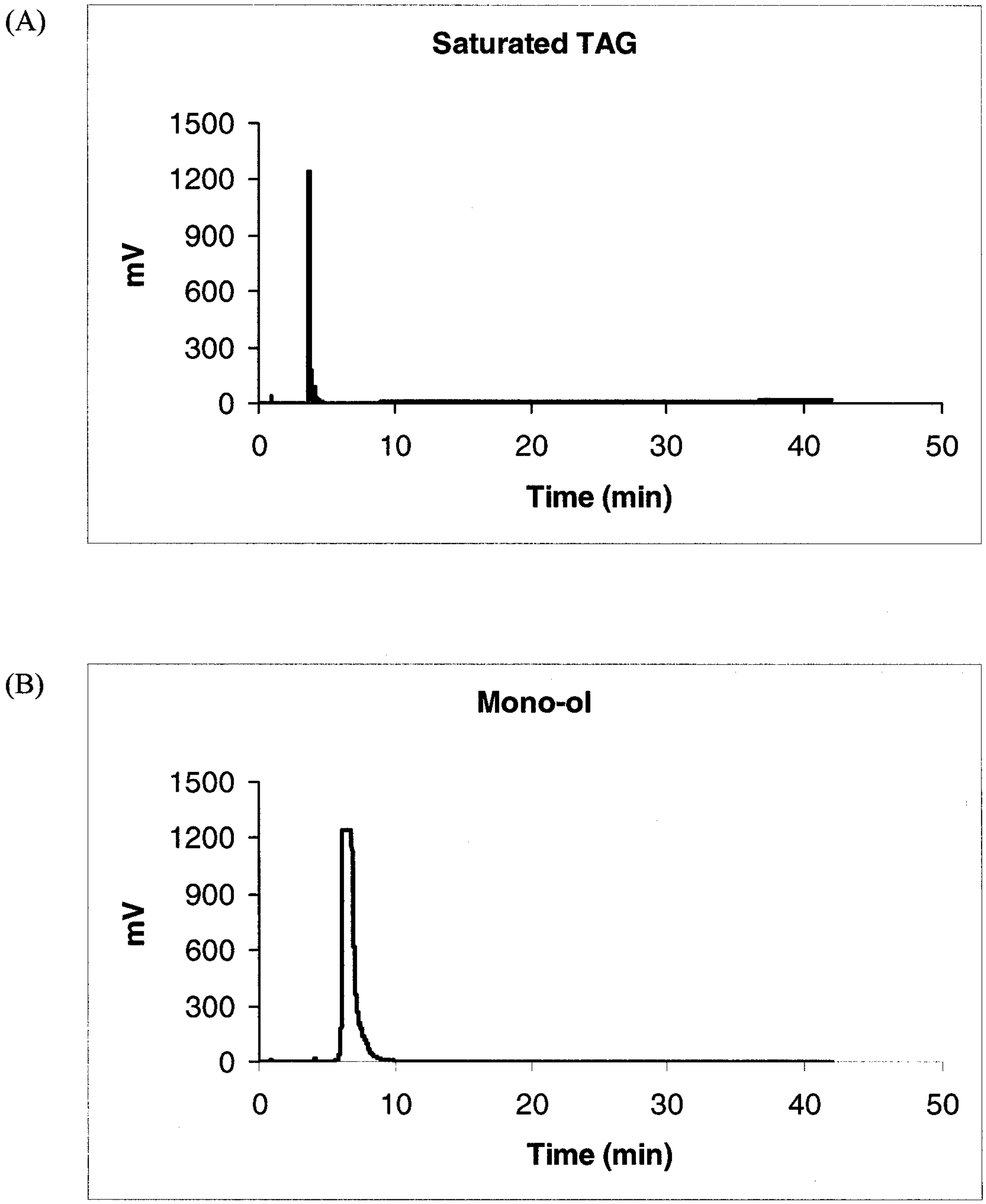


**Figure 2-3:** High Performance Liquid Chromatography (HPLC) of (A) Saturated Triacylglycerol (TAG), (B) Mono-ol

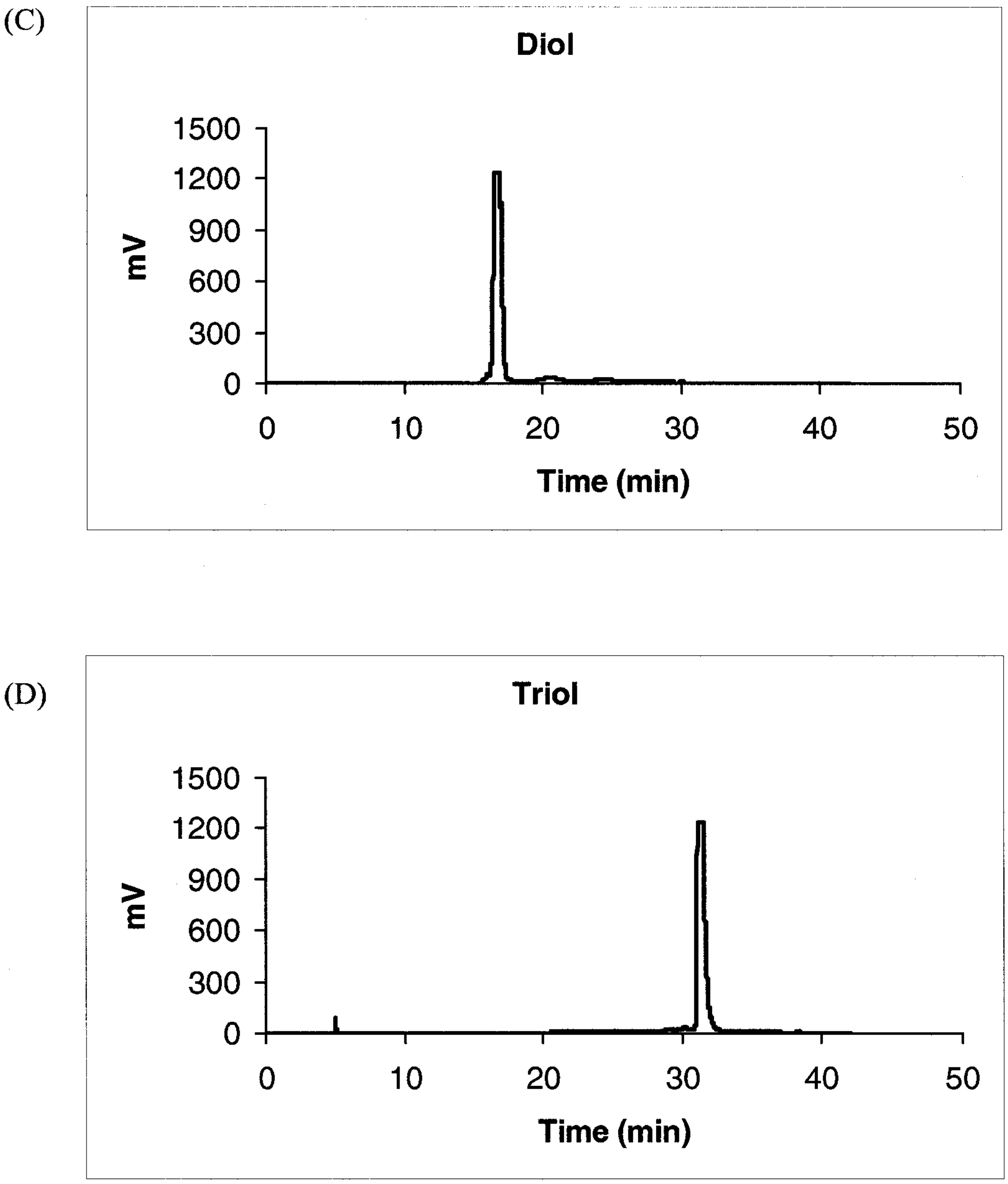


**Figure 2-3:** High Performance Liquid Chromatography (HPLC) of (C) Diol and (D) Triol

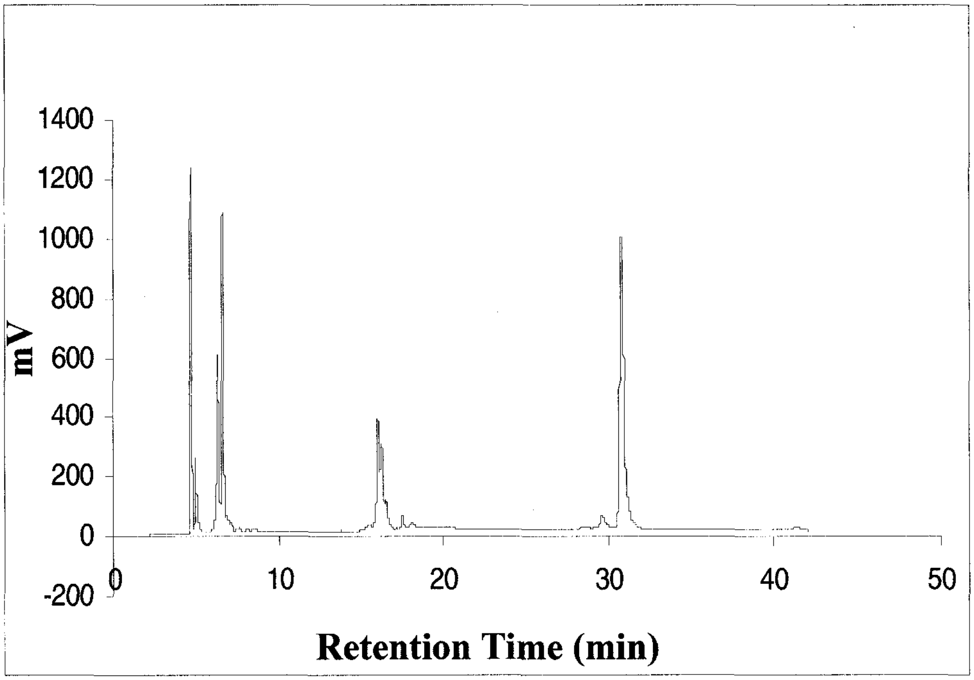


**Figure 2-4:** High Performance Liquid Chromatography (HPLC) of Crude Polyols Product

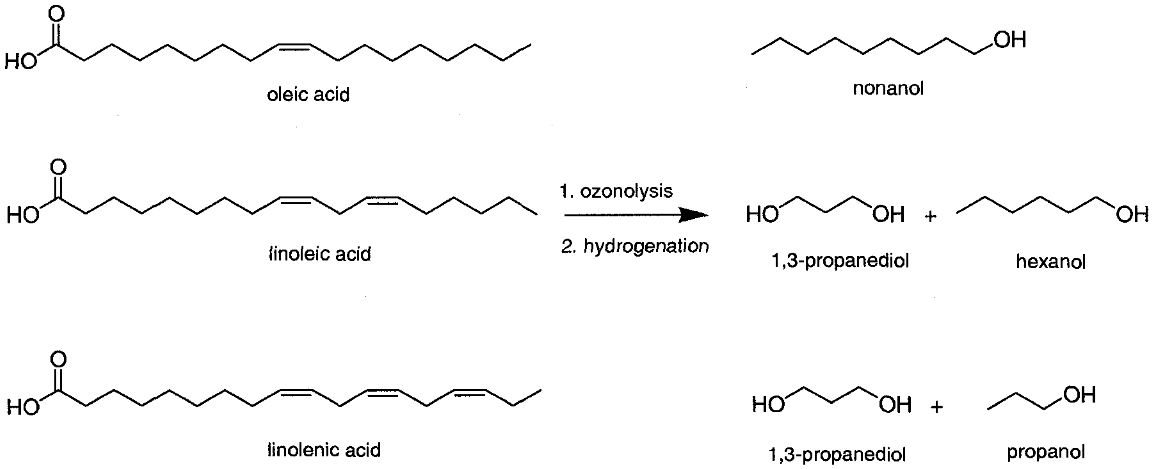


**Figure 2-5:** Production of Potential Short Chain Alcohols by Ozonolysis and Hydrogenation from Possible Unsaturated Fatty Acids (Linoleic, Linolenic And Oleic Acids) in Canola Oil

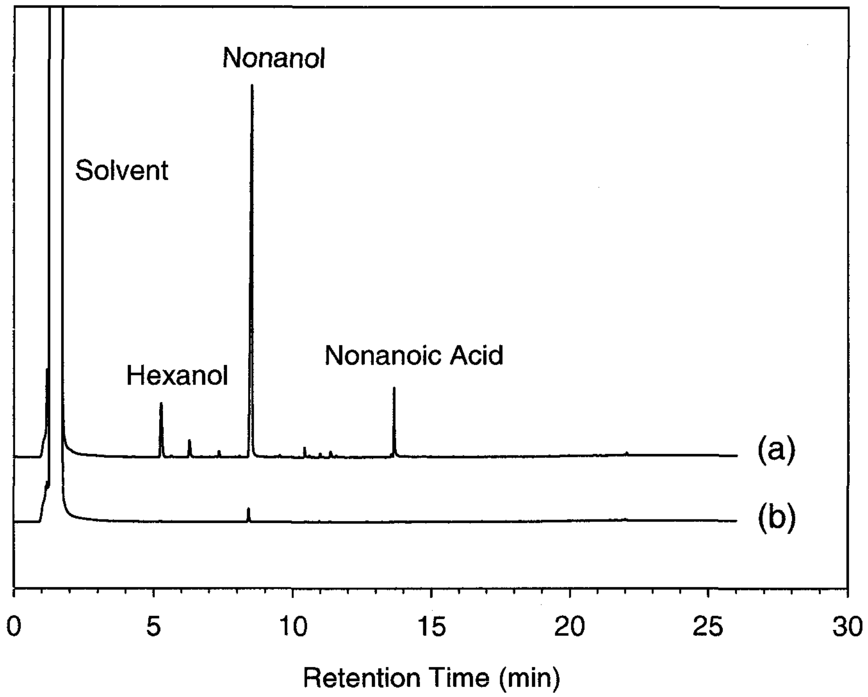


**Figure 2-6**: Gas Choromatography (GC) of Products before and After Distillation

(a) Product before distillation

(b) Product after distillation

cross-linking reaction in the production of polyurethanes and short chain di-alcohols do not add any benefits to polyurethane formation in the heavier polyol mixture (beyond minimal utility as chain extenders). **Table 2-2** gives their theoretical and experimental amounts in grams as well as those of the polyols, produced from 100 g of canola oil. The theoretical values were calculated based on the amount of TAGs compiled by Neff *et al.* (Neff *et al.*, 1994) for 100 g of canola oil and by considering that all the double bonds are cleaved.

### 2.3.2. Physical Properties of the Polyols from Seed Oils

The hydroxyl and acidity numbers and the refractive indices of the Canola-Oxygen Polyol and Canola-Air Polyol are shown in **Table 2-1**. Both polyols ended up with relatively high acidity number because the ozonide, the product of ozonolysis, tends to hydrolyze and produce carboxylic acid (Bailey, 1958) that cannot be hydrogenated under the conditions employed in our reactions. As expected, since more oxygen is readily available to cleave double bonds during the ozonolysis reaction, the polyol obtained with oxygen as a supply gas had higher hydroxyl and acidity numbers than the polyol obtained when using air. The polyols produced here had relatively lower hydroxyl values than those produced using other technologies such as epoxidation and hydroformylation, because it produces only primary hydroxyl groups rather than secondary hydroxyl groups which have the possibility of more than one available position on each carbon chain. Theoretically, there is a maximum hydroxyl value of 251 mg KOH/g for canola that can be obtained when producing polyol from canola oil by assuming that all of the double bonds are cleaved (Firestone, 1999; Neff *et al.*, 1994). The lower than theoretical hydroxyl values obtained for the polyols produced here are

|  | Polyol | Propanol Equivalent | Hexanol Equivalent | Nonanol Equivalent | 1,3 propanediol |
|---|---|---|---|---|---|
| **Theoretical Values** | 65.3 | 1.70 | 7.46 | 28.60 | 10.00 |
| **Canola–Air** | 76.9 | 0.44 ± 0.19 | 2.59 ± 0.29 | 11.85 ± 1.09 | 0.72 ± 0.21 |
| **Canola–Oxygen** | 56.3 | 0.28 ± 0.06 | 4.09 ± 0.18 | 23.53 ± 0.32 | 0.59 ± 0.04 |

**Table 2-2:** Calculated and Experimental Amounts in Grams of Polyol and Short Chain By-Product from 100g Canola. (Errors are standard deviations, N=3)

Polyol Includes Saturated TAGs, Mono-ol, Diol and Triol;

Propanol Equivalent Includes the 3-Carbon Derivatives (Propanol and Propionic Acid);

Hexanol Equivalent Includes the 6-Carbon Derivatives (Hexanol and Hexanoic Acid);

Nonanol Equivalent Includes the 9-Carbon Derivatives (Nonanol and Nonanoic Acid).

due to the molecular diversity of the starting materials as well as to possible incomplete reactions. Mono-ol and diol are produced because the starting TAGs are not constituted only of three unsaturated fatty acids but contain a mixture of saturated and unsaturated fatty acids. They can also be produced if the ozonolysis reaction does not cleave all the double bonds on all the fatty acids. This was evident in the case of ozonolysis with air as the feed gas where the extra saturated fatty acids resulted in a mass of the Canola-Air Polyol higher than the theoretical value (see **Table 2-2**).

**Table 2-3** summarizes the crystallization and melting temperatures of the polyol samples. Various levels of crystallinity are present, suggesting a promising suitability to processing within current standard polyurethane-forming capital equipment. In the case of Canola-Oxygen Polyol, a higher crystallization peak (29.6 °C) combined with a higher hydroxyl number resulted in a greater viscosity at the same temperature than that of Canola-Air Polyol (**Figure 2-7**). Because it could be a barrier to mass transfer of crosslinkers, the presence of crystals at the processing temperature can be either a problem or a benefit, depending on what type of polyurethane is being produced. It affected the viscosity which obviously would result in increased requirements on the shear and pumping systems etc. of a processing plant. However, these variances in crystallinity and viscosity can be manipulated well within the plant environment to create polyurethanes with desirable properties. Compared to commercially available polyols, the polyols synthesized here, were well within acceptable tolerances for standard capital equipment.

| | Crystallization temperature (°C) | | | Melting temperature (°C) | | |
|---|---|---|---|---|---|---|
| | $T_{1C}$ | $T_{2C}$ | $T_{3C}$ | $T_{1M}$ | $T_{2M}$ | $T_{3M}$ |
| Canola-Air Polyol | -9.6 | 2.3 | | -8.7 | -0.7 | 8.2 |
| Canola-Oxygen Polyol | -25.4 | 16.8 | 29.6 | -4.5 | 23.2 | 39.7 |

**Table 2-3:** Crystallization and Melting Temperatures Tested from Differential Scanning Calorimetry (DSC) of Canola Polyols

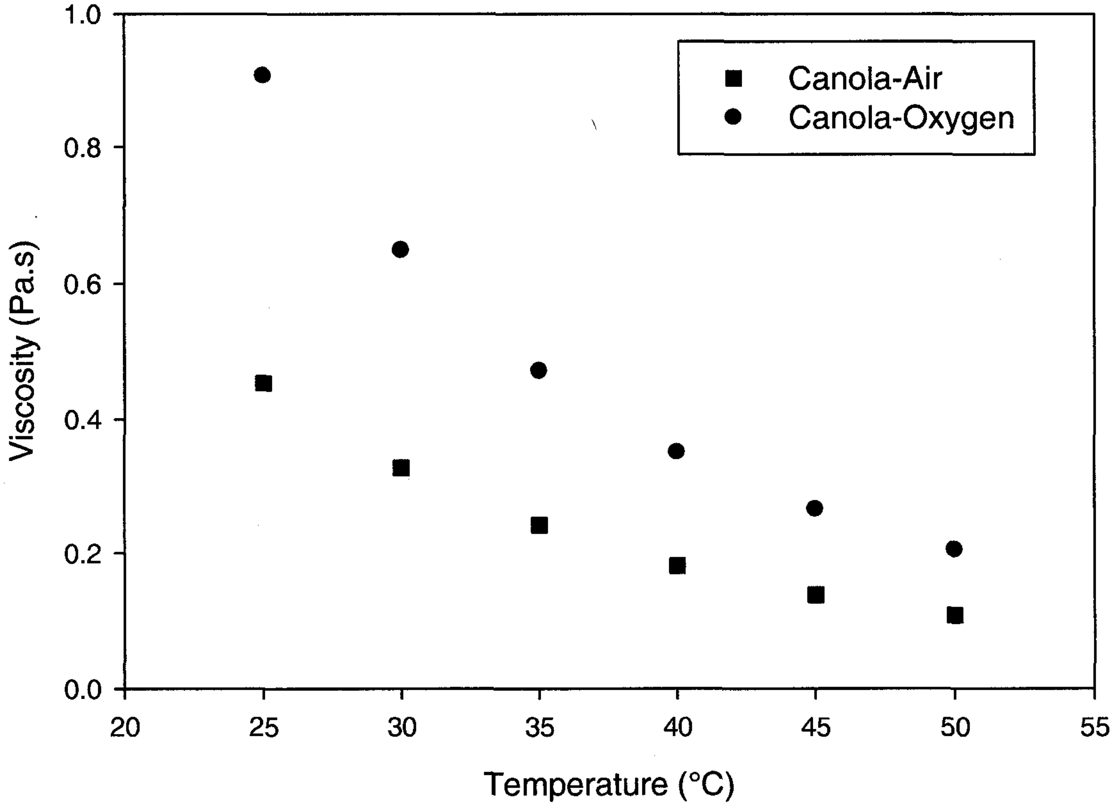


**Figure 2-7:** Vicosity vs. Temperature of Canola-Air Polyol and Canola-Oxygen Polyol

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## 2.5. Appendix I: Standard Test Methods for Testing Polyurethane Raw Material: Determination of Hydroxyl Numbers of Polyols (ASTM D 4274-99)

**Reagent:**

Acetic Anhydride

Acetylation Reagent – Mix 127 mL of acetic anhydride with 1000 mL of pyridine. Prepare the reagent fresh daily and keep it in a dark bottle.

Hydrochloric Acid (0.5 N)

Phenolphthalein Indicator Solution –Dissolve 1 g of phenolphthalein in 100 mL of pyridine.

Pyridine

Sodium Hydroxide Solution (0.5 N)

**Procedure and Theory:**

Pipet 20.0 mL of the acetylation reagent to four pressure bottles for the blank and sample determinations.

Reserve two of the bottles for the blank determinations; weigh samples into the other bottle.

Stopper the bottle and swirl it until the sample is completely dissolved. Place all bottles in the water bath at 98 ± 2 °C for 2 h.

Remove the bottle from the water bath and allow them to cool to room temperature.

Add 1 mL of the phenolphthalein indicator solution and titrate immediately with the 0.5 N NaOH solution to the first faint pink end point that persists for 15 s. Record the volume of titrant. With the help of pyridine, the hydroxyl groups react with acetic anhydride to give acetylation product, as well as acetic acid, which then titrated by NaOH.

Acidity Correction – If the sample contains significant acidity, correct the result as follows. Weigh into a 400 mL Erlenmeyer flask the same amount of sample used before for the hydroxyl determination. Add to the flask 75 mL of the redistilled pyridine, 75 mL of distilled water, and 0.5 mL of phenolphthalein indicator solution. If the solution is colorless, titrate with standard 0.1 N NaOH to a pink end point that persists for at least 15 s. Under this condition, only acid group can be titrated by NaOH.

The acidity correction, mg KOH/g, is calculated as follows:

Acidity correction = $[(A - B)N * 56.1]/ W$

Where:

A = NaOH solution required for titration of the sample, mL

B = NaOH solution required for titration of the blank, mL

N = normality of the NaOH solution, and

W = sample used, g

**Calculation:**

Hydroxyl number = $[(B - A)N * 56.1]/ W$

A = NaOH solution required for titration of the sample, mL

B = NaOH solution required for titration of the blank, mL

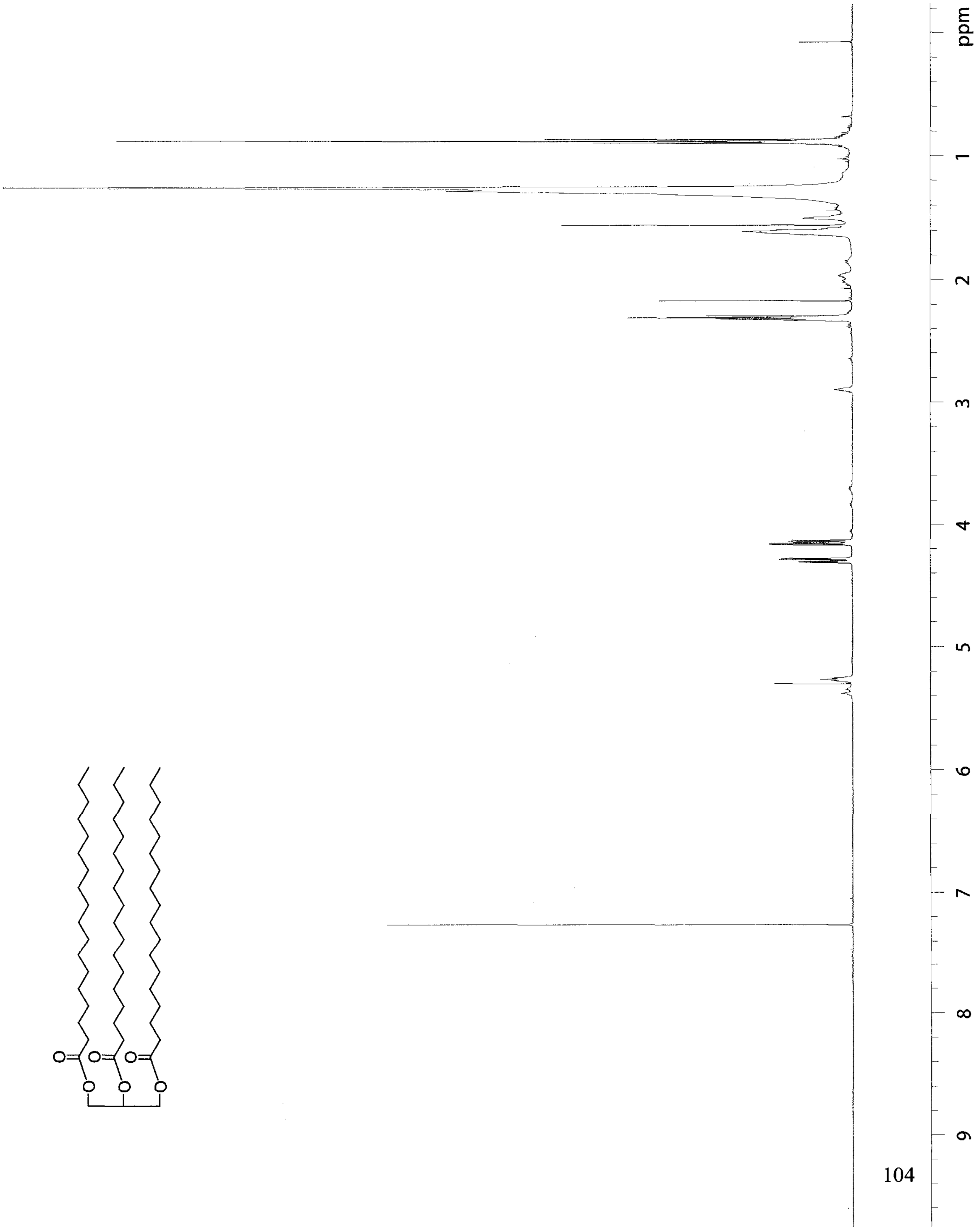
N = normality of the NaOH solution, and

W = sample used, g

If the sample contains free acidity, the result must be corrected as follows:

Hydroxyl number (corrected) = hydroxyl number + acidity

## 2.6. Appendix II: Chapter 2 NMR Spectra



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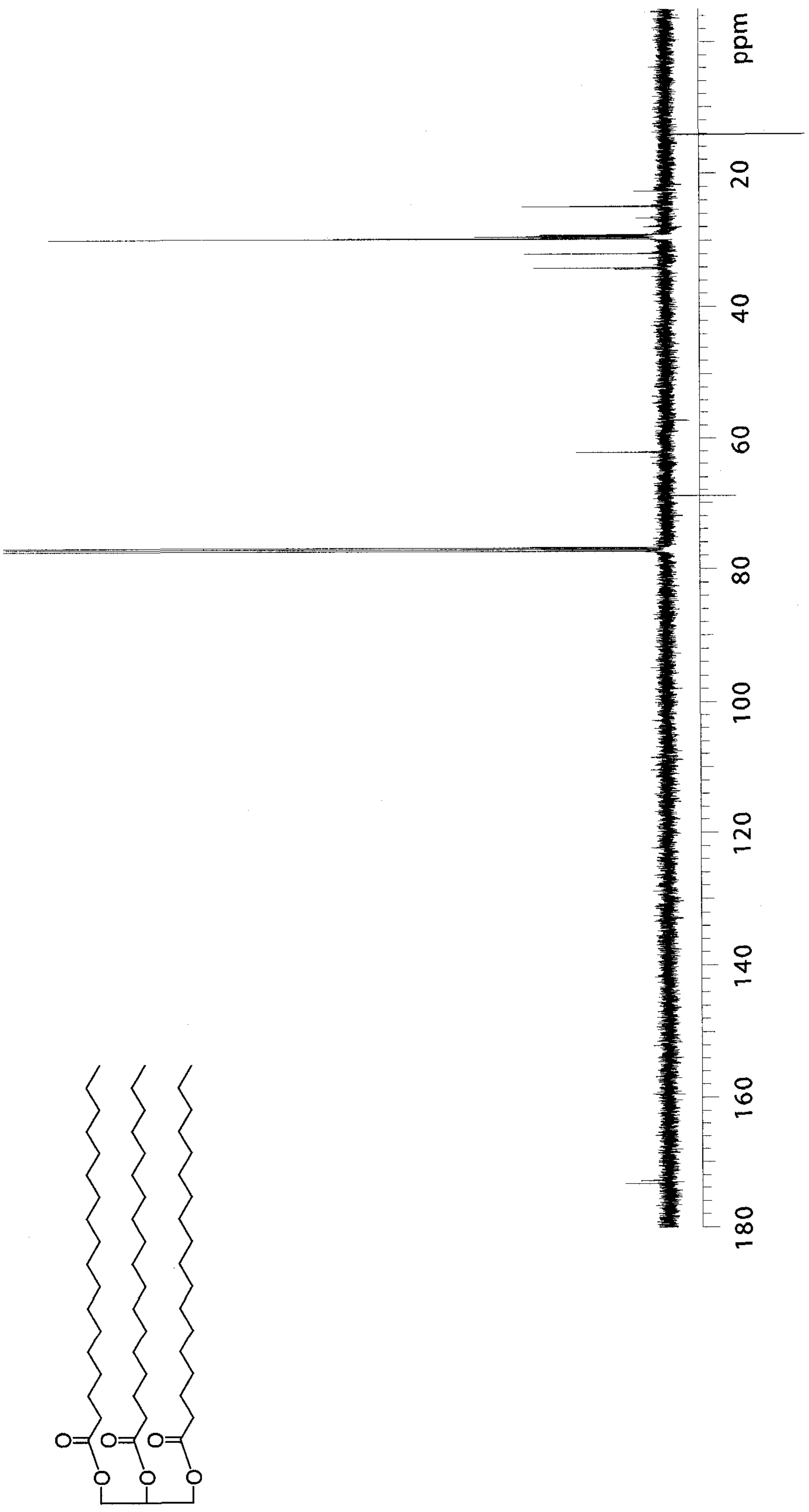
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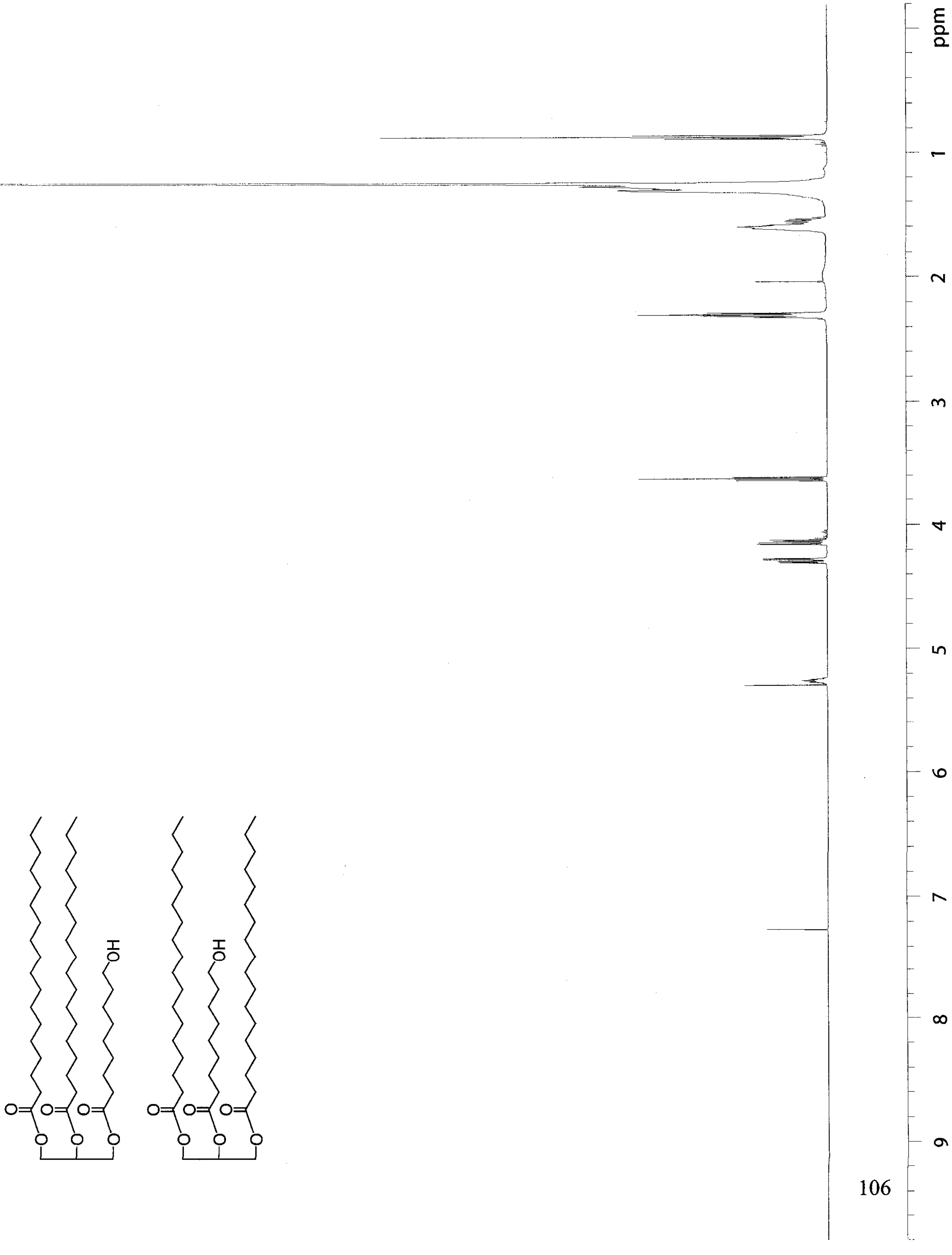
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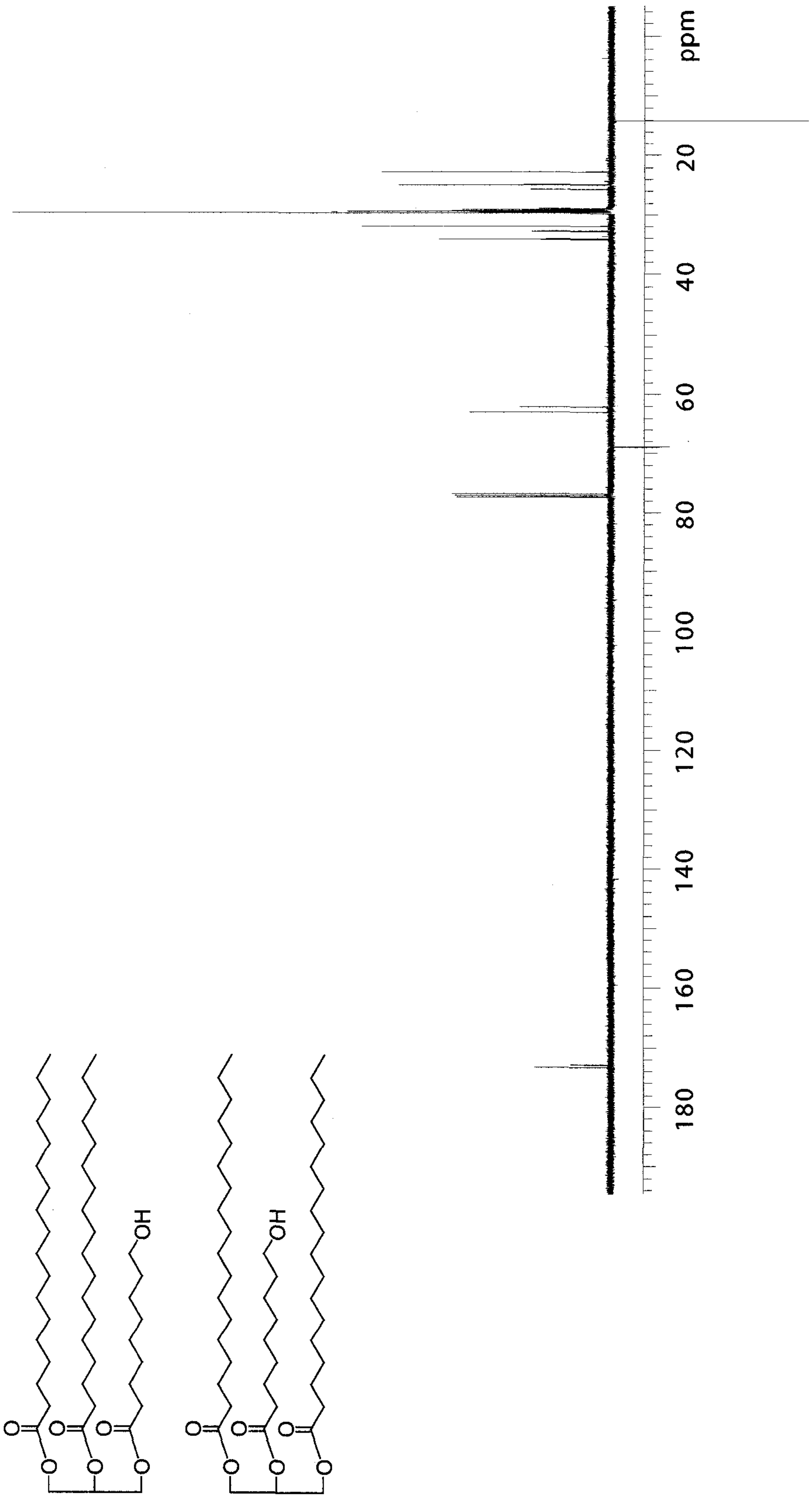
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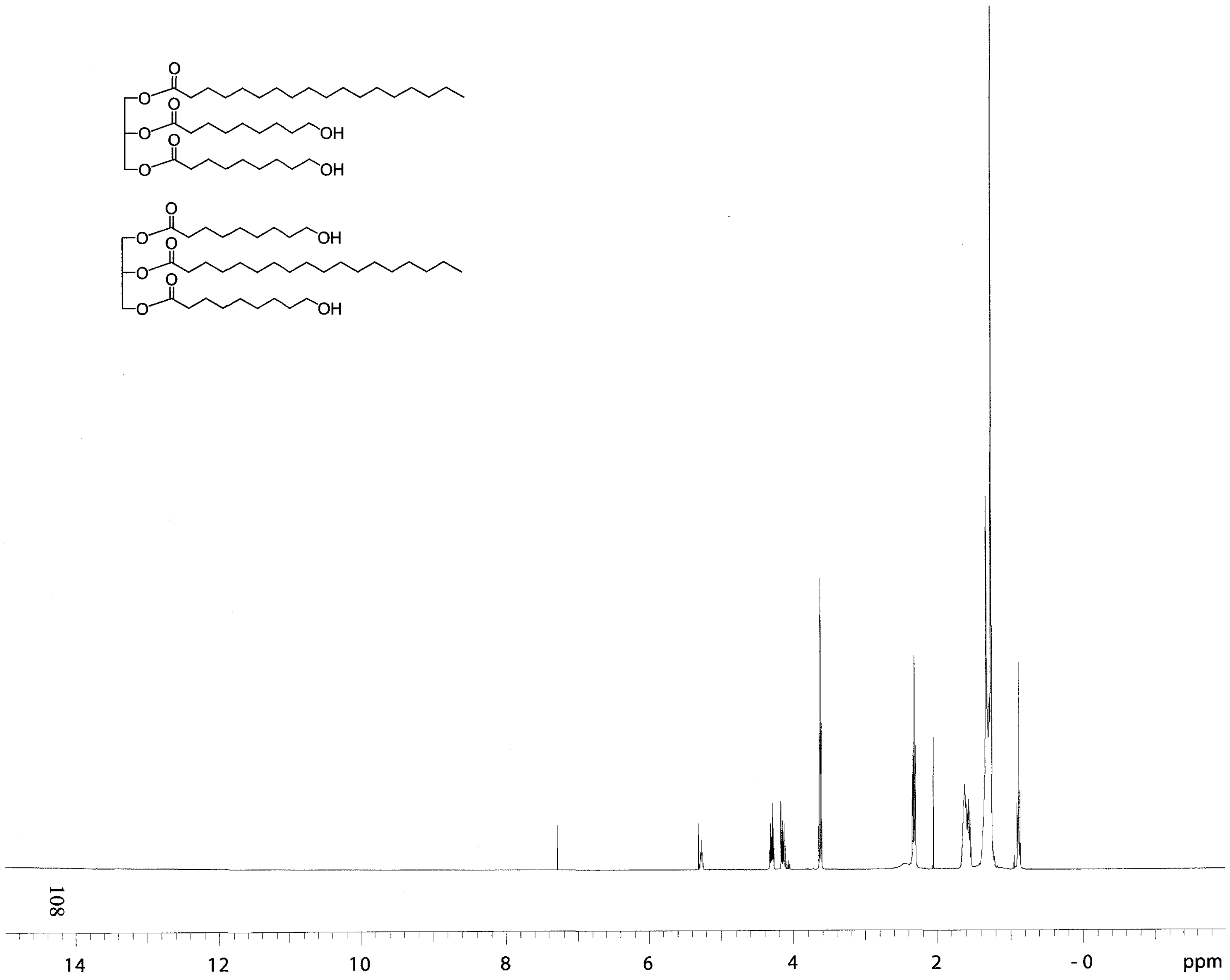
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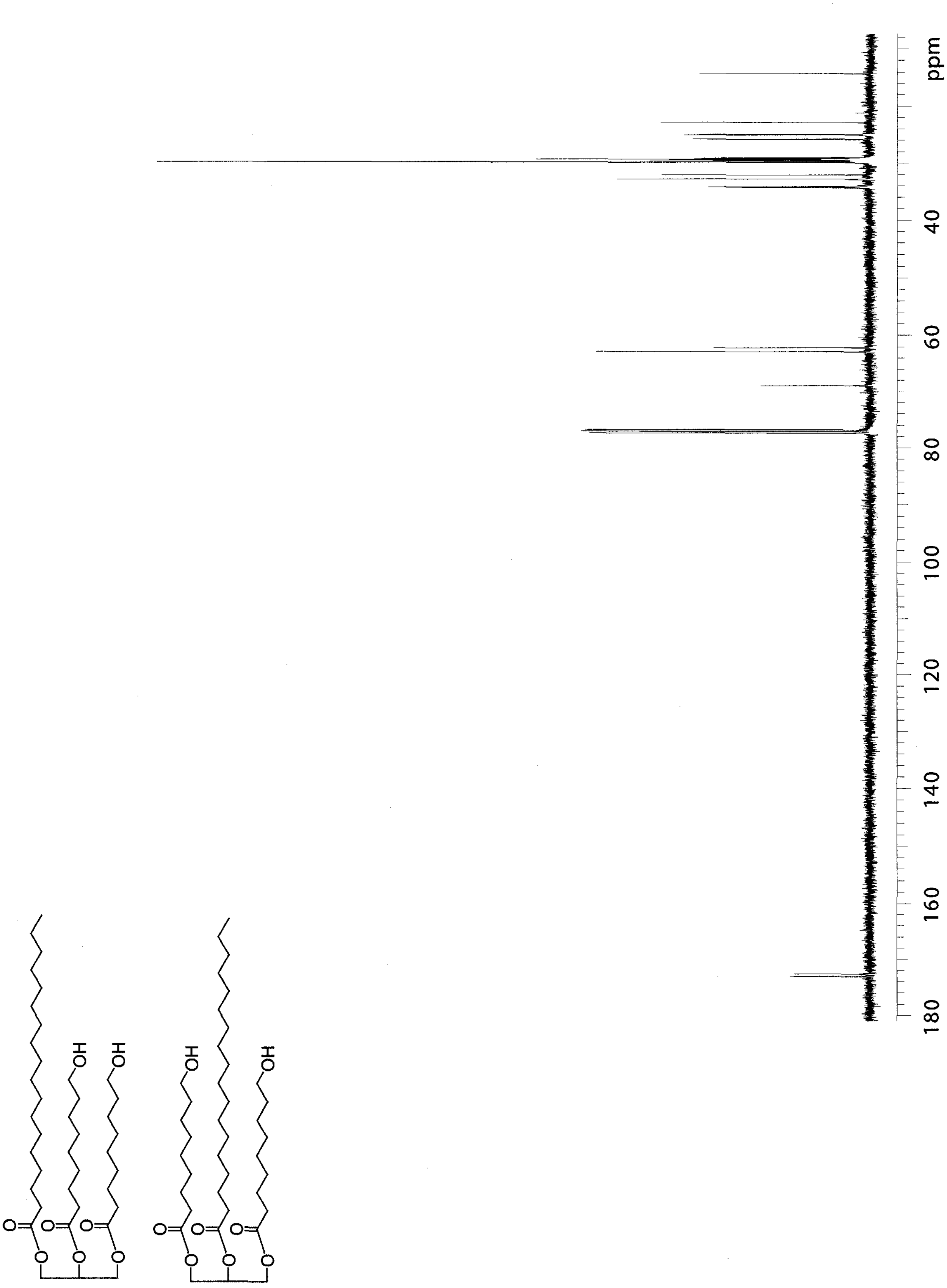
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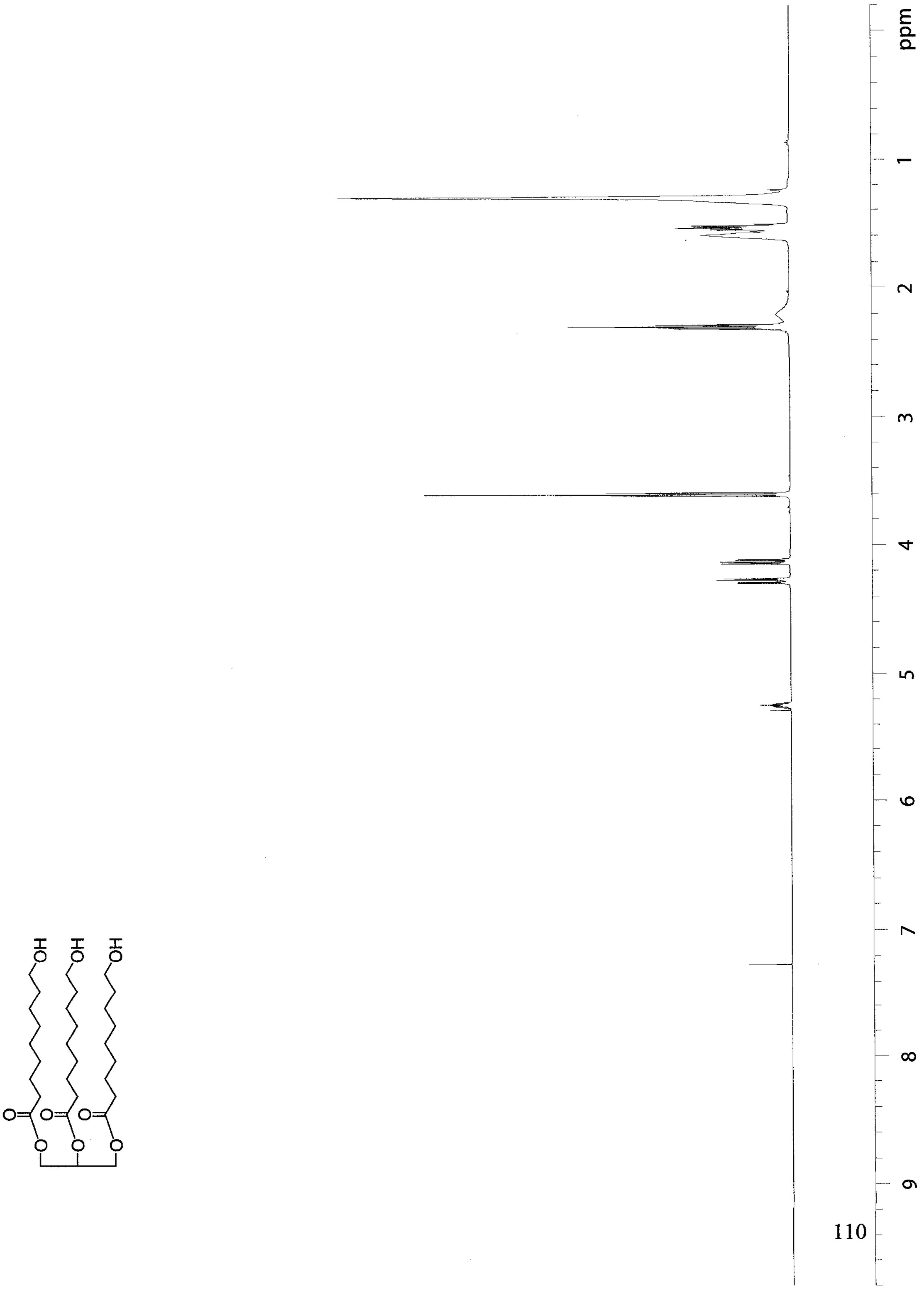
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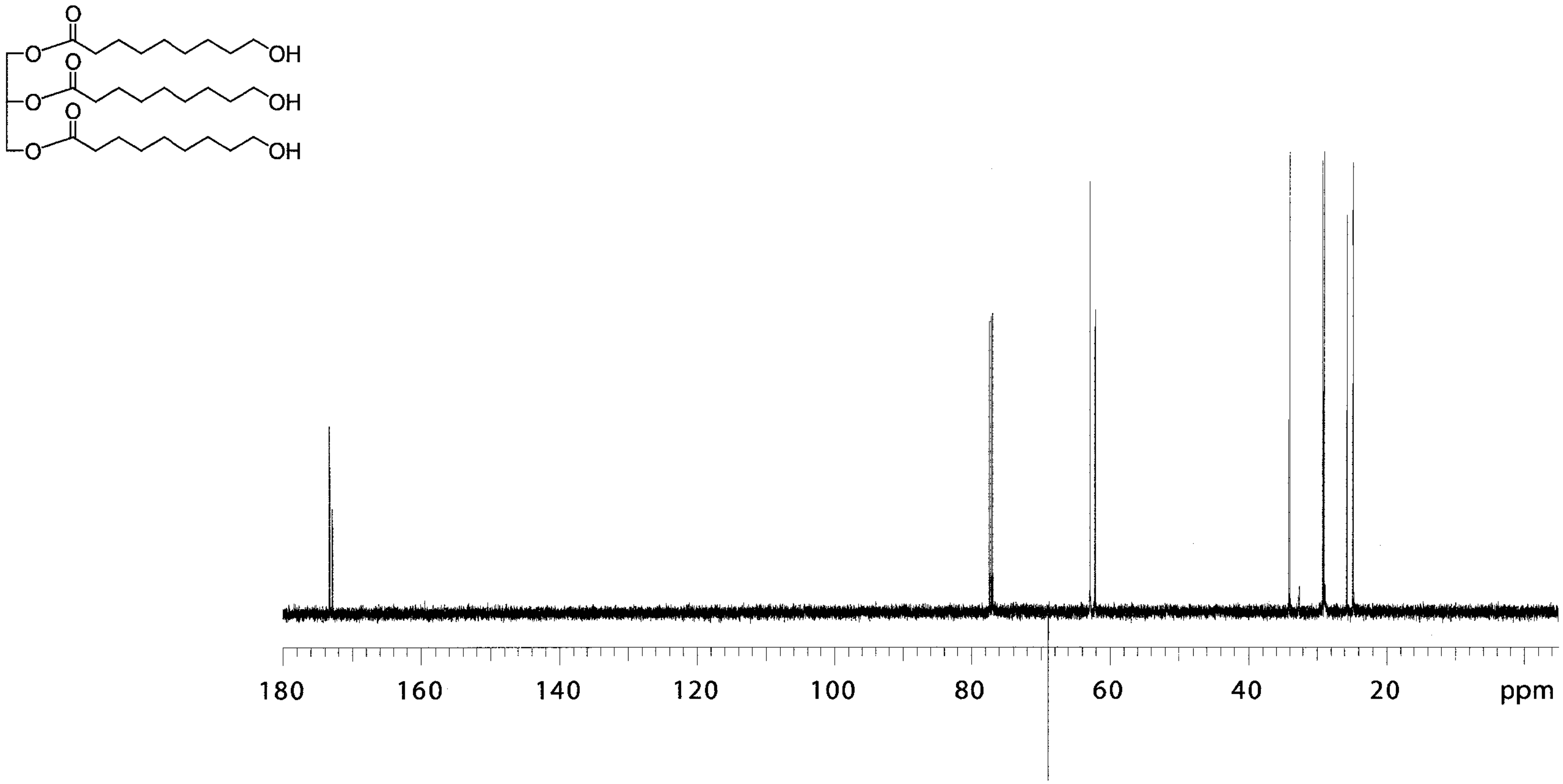
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# 3 Separation and Quantification of Vegetable Oil Based Polyols by High Performance Liquid Chromatography with Evaporative Light Scattering Detection[*]

## 3.1. Introduction

Vegetable oil is an abundant renewable source that can be used for the manufacture of polyurethanes (PURs) so long as it comprises double bonds in its structure which can be converted to alcohol functionalities to make polyols, the monomers for polyurethane production. There are many ways to synthesize polyols from various vegetable oils. Some research groups have sought to introduce alcohol functionality by hydroformylation of double bonds (Lyon et al., 1974) followed by hydrogenation or epoxidation then ring opening (Hu et al., 2002; Lyon et al., 1974). The above mentioned methodologies have produced TAG polyols with hydroxyl functionality situated in the middle of the fatty acid chains. For the synthesis of polyols with terminal hydroxyl groups from vegetable oils, the process of ozonolysis is generally adopted (Petrovic et al., 2005; Tran et al., 2005). In our research group, a process of ozonolysis followed by hydrogenation has been successfully utilized with canola oil to make polyols with terminal hydroxyl groups (Narine et al., 2007c). These polyols are capable of producing high-quality PUR foams and elastomers (Narine et al., 2007a; Narine et al., 2007b).

Gel permeation chromatography (GPC) and FTIR methods were used in Petrovic's

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[*] A version of this chapter has been published:
Yue J. and Narine S.S., 2007. *Separation and Quantification of Vegetable Oil Based Polyols by High Performance Liquid Chormatography with Evaporatvie Light Scattering Detection,* Journal of the American Oil Chemists Society. *84*, 803-807

work to characterize terminal hydroxyl polyols (Petrovic et al., 2005); FTIR and $^{13}$C-NMR were adopted in Tran's research for characterization of similar structures (Tran et al., 2005). Neither of these analytical methods allowed for quantification of the components of the polyols. Currently, there is no literature published on the separation and quantification of different components in polyol products from vegetable oils. In this paper, we report a methodology for the separation and quantification of different components in polyols, including saturated triacylglycerols (TAGs), mono-ols, diols and a triol, utilizing high performance liquid chromatography (HPLC) and an evaporative light scattering detector (ELSD).

Evaporative light scattering detection for HPLC has been widely used for the separation and quantification of lipid classes (Beermann et al., 2003; Breton et al., 1989; Christie, 1985; Christie, 1986; Grizard et al., 2000; Homan and Anderson, 1998; Neff et al., 1999; Silversand and Haux, 1997; Stith et al., 2000) using stationary phases of silica (Murphy *et al.*, 1996), diol (Perona and Ruiz-Gutierrez, 2004), cyanopropyl (Elhamdy and Christie, 1993), or bonded polyvinyl alcohol (Christie and Urwin, 1995). The use of ELSD has some advantages in the area of lipid analysis: 1) it is not sensitive to the solvent flow rate and ambient temperature (Christie, 1992); 2) it eliminates the need for lipid derivatization; and 3) it allows for the use of solvents that are usually not suitable for UV detection such as chloroform, which has a similar absorbance region to the lipids (Becart *et al.*, 1990).

## 3.2. Experimental

### 3.2.1. Materials

100% pure canola oil was supplied by Canbra Foods Limited, Lethbridge, AB, Canada. Raney nickel 2800 (slurry in water) catalyst was purchased from Sigma-Aldrich Co., USA. The ozone generator (Azcozon Model RMV16-16) was purchased from Azco Industries Ltd, Canada. The hydrogenation vessel (2 L) was purchased from Parr Instrument Co, USA. The Wiped-Blade Molecular Distillation apparatus (Model VKL 70/ICL-04) was purchased from Incon Processing, IL, USA.

## 3.3. Methods

### 3.3.1. Synthesis and Characterization of Polyols from Canola Oil

Canola oil (100 g) was dissolved in ethyl acetate (400 mL) and ozonized at room temperature for 1 h (or 30 min, 40 min, 50 min and 60 min in different batches). An oxygen flow rate of 5 L/min was passed through the ozone generator allowing for an ozone concentration of 62 g/cm$^3$. The ozonolysis crude product was then hydrogenated for 3 hrs at 135 °C and 100 Psi using Raney Ni (10 % weight of ozonolysis crude product) as a catalyst. Ethyl acetate was removed by rotary evaporation and wiped blade molecular distillation was used to remove low molecular weight by-products to obtain polyols products.

### 3.3.2. HPLC System

The HPLC system consisted of a dual Milton Roy pump with a 20 μL auto-injector. A 250×4 mm Betasil Diol-100 (5 μm particle size) column was used (purchased from Thermo Hypersil-Keytone) and maintained at 50°C with a Biorad column heater. The detector was an Alltech ELSD 2000 evaporative light scattering system maintained at 100°C with a gain setting of 16 (on the 16 unit scale) and a nitrogen flow rate of 3 L/min. The mobile phase comprised of two solvents, *A* and *B*. *A* was 100% heptane and *B* was 50% heptane with 50% isopropyl alcohol (IPA). A run consisted of a linear gradient of 100% *A* to 70% *A* and 30% *B* over 30 min with a flow rate of 2 mL/min.

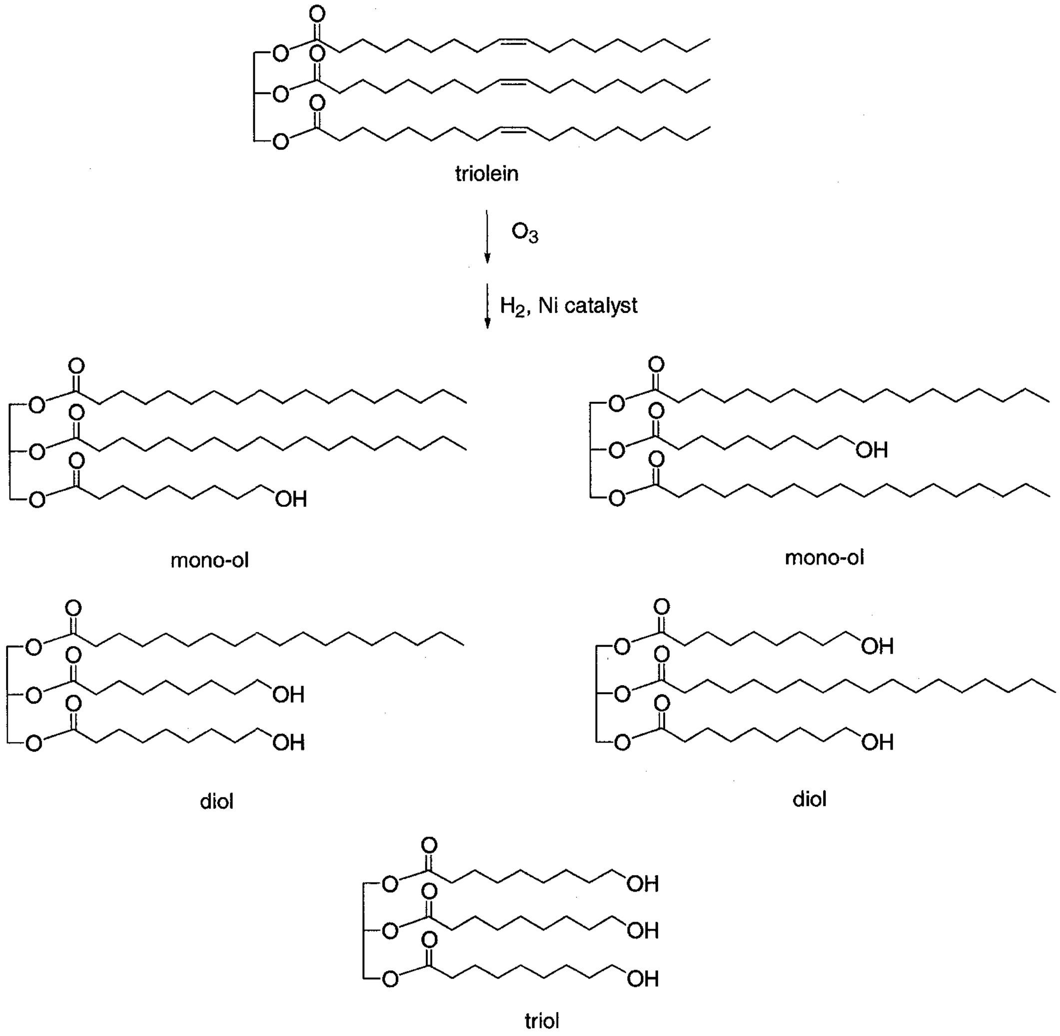
### 3.3.3. HPLC Standard Curves

Pure mono-ol, diol and triol standards were obtained by isolating polyol products by flash silica chromatography. The purification process, chromatographic data and compound characterization are reported in detail in Chapter 2. Dichloromethane (DCM) solutions of known concentrations of each standard were injected separately. Each concentration of the standard solution was injected three times and the average peak area was plotted against the concentration to obtain the standard curve. Correlation ($r^2$) was determined for all curves by linear regression analysis.

## 3.4. Results and Discussion

Polyols were obtained by ozonolysis of canola oil in ethyl acetate followed by hydrogenation. Canola vegetable oil contains more than 90 % of unsaturated fatty acids (Firestone, 1999), including oleic acid, linoleic acid, and linolenic acid, all of which have a double bond at carbon nine that can be cleaved by reductive ozonolysis to provide terminal hydroxyl polyols. The polyol products obtained are a mixture of saturated TAGs along with mono-ols, diols and triols. The presence of saturated alkyl chains in the TAG products is due to two main reasons: 1) In addition to unsaturated fatty acids being present in canola oil, there are also small amounts of saturated fatty acids (mainly palmitic and stearic acid); 2) Ozone may not have reacted with all of the double bonds and hydrogenation of the unreacted double bonds produces TAGs containing saturated alkyl chains. Using triolein as an example, **Scheme 3-1** illustrates the mechanism of polyol production from unsaturated TAGs and the structures of these products.

In our study, an HPLC-ELSD method was developed to separate and quantify the components in the polyol mixture. A diol-based column and gradient elution system provided good separation of saturated TAGs, mono-ols, diols and triols within a relatively short run time. **Figure 3-1** shows a typical HPLC chromatogram of polyol products (after ozonolysis for 1 hr) in canola oil. As four main peaks were observed by HPLC using the diol-based column, it was logical to assign them according to the polarities of those components in the polyols. Beginning with the first peak which has the shortest retention time, the peaks were assigned to the saturated TAGs (the least polar components), followed by TAGs with a single alcohol group (mono-ols) then TAGs with two alcohol groups (diols) and finally TAGs with three alcohol groups (triol), the most polar component. The peak of mono-ols (seen clearly in the insert of **Figure 3-1**) was very small due to the relatively small amount of mono-ol in the polyol product. A small peak was always observed at 24.5 minutes. This could be due to a transesterification product also containing three hydroxyl groups, which would have similar polarity to the main triol product. The transesterification mechanism is shown in **Scheme 3-2.** Due to the high temperatures used during distillation to remove unwanted byproducts and also high pressures used in the hydrogenation steps, transesterification could have occurred between the triol and the alcohol by-product.



**Scheme 3-1**: Production of Polyols from Triolein

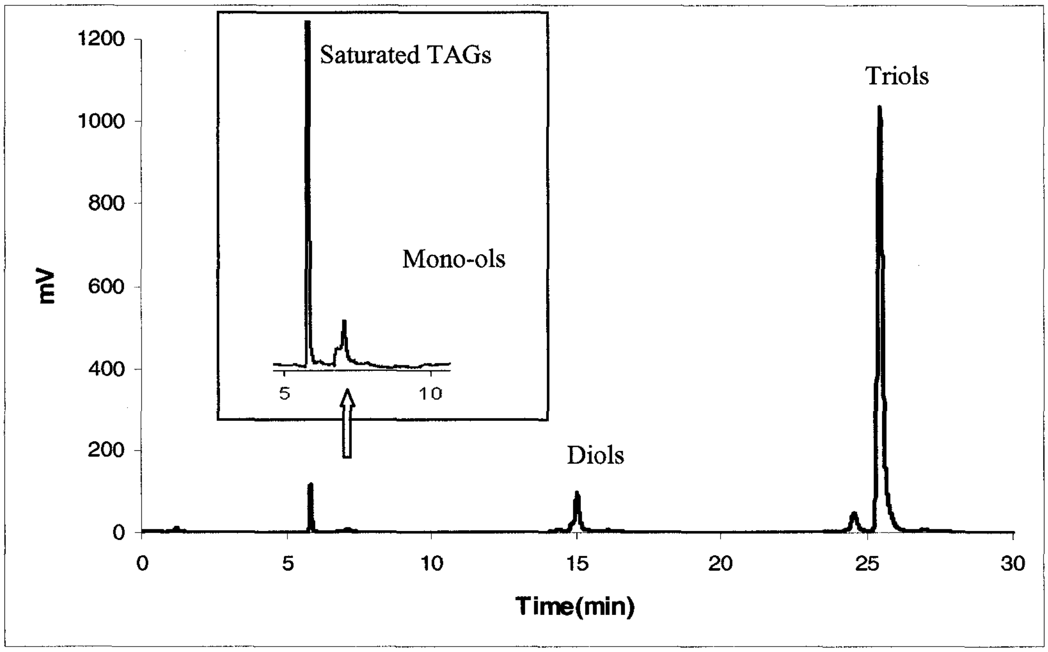
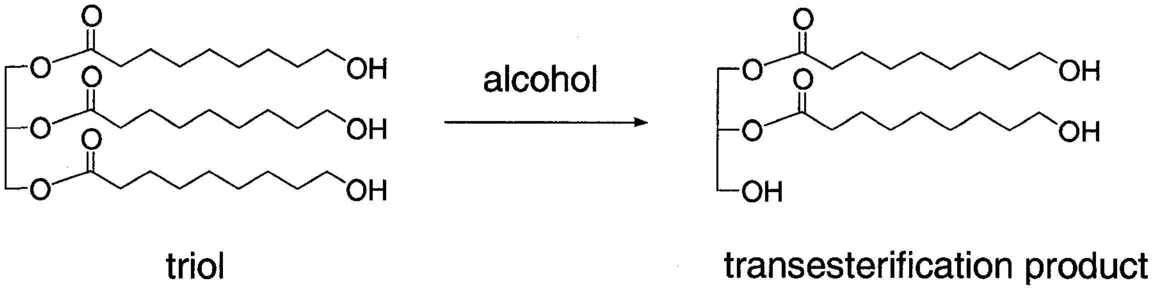


**Figure 3-1:** High Performance Liquid Chromatography (HPLC) of Polyol Products from Canola Oil



**Scheme 3-2:** Transesterification between Triol and the Other Alcohol

Purified mono-ol, diol and triol samples were analyzed individually on the same HPLC system and the results are shown in **Figure 3-2**. The retention times of the mono-ol, diol and triol components were 7.3 min, 14.9 min and 25.3 min respectively, which correlates to the previous HPLC chromatogram shown in **Figure 3-1**. Expansion of the mono-ol and diol peaks of the HPLC revealed some peak splitting as shown in **Figure 3-2**. This is due to different hydroxyl and alkyl group substitutions in the *sn*-1(3) or *sn*-2 positions of the mono-ols and diols *i.e.* mono-ol and diol isomers. The retention times and peak resolution for the mono-ol, diol and triol components were highly reproducible.

Calibration curves for the mono-ol, diol and triol are shown in **Figure 3-3**. The peak area increased linearly with increasing standard concentration within a certain range: mono-ols, 193 -650 $\mu$g mL$^{-1}$; diols, 288-1370 $\mu$g mL$^{-1}$, and triols 268-671 $\mu$g mL$^{-1}$. When the standard concentration was below this range, the response deteriorated; above this range, the peaks reached the upper detection limit. The $r^2$ for a linear curve fitting for the mono-ol and diol was above 0.99, but the $r^2$ for the triol was 0.98. To quantify the polyol products from one reaction batch, the batch was either concentrated or diluted to obtain the concentration of each component within the range. Peak area of each component was obtained from the chromatogram and the concentration of each component was calculated according to the calibration curve equation. After comparison with the total sample concentration, the content of each component was obtained.

**Table 3-1** shows the content of mono-ol, diol and triol in the polyol products. The rests are saturated TAGs. It can be seen that with increasing ozonolysis time, the content of mono-ol decreased while that of triol increased. The reason is that over time

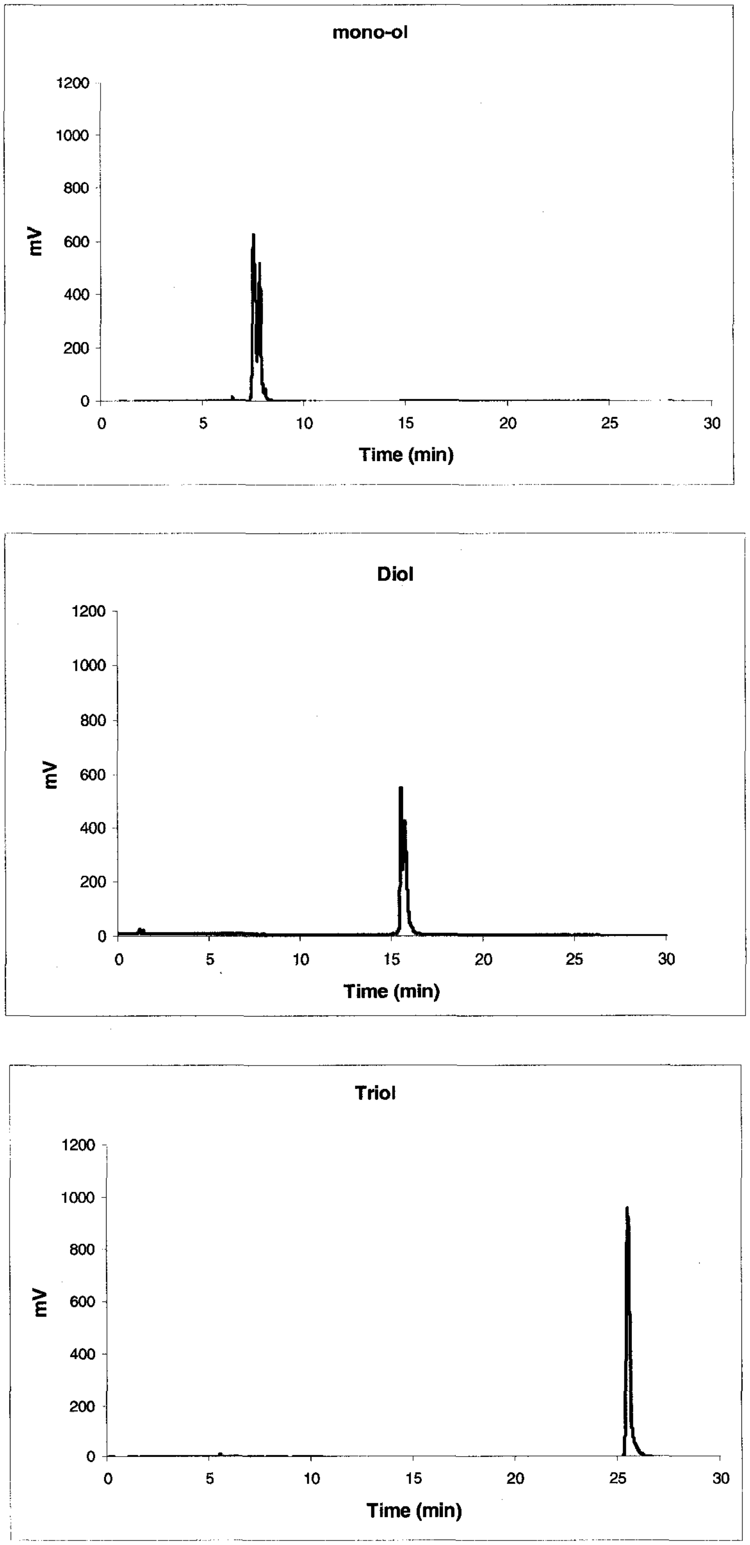


**Figure 3-2**: High Performance Liquid Chromatography (HPLC) of Pure Mono-ol, Diol and Triol

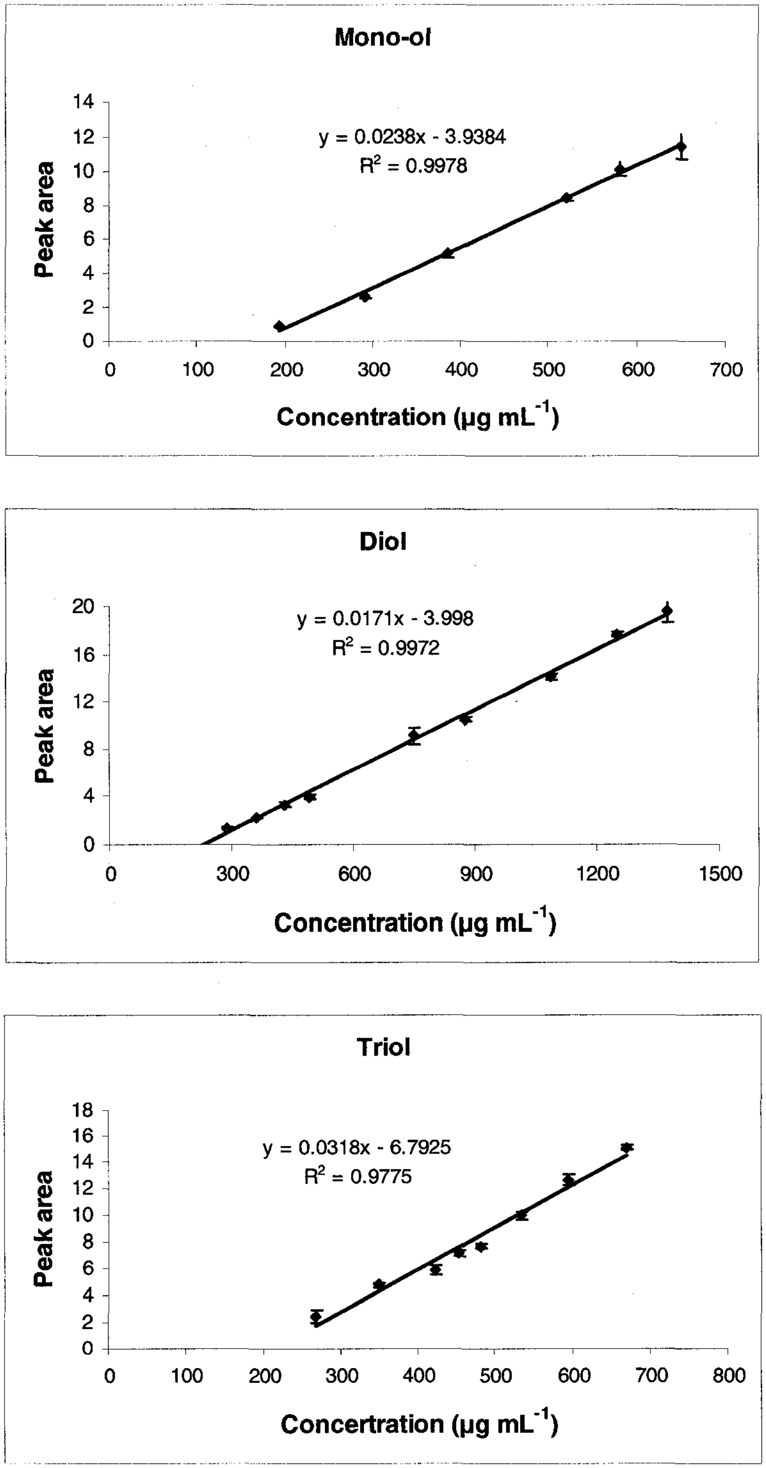


**Figure 3-3:** High Performance Liquid Chromatography (HPLC) Calibration Curves for Mono-ol, Diol and Triol Products

| **Ozonolysis Time (min)** | | **30** | **40** | **50** | *60* |
|---|---|---|---|---|---|
| **Content (%)** | **Mono-ol** | 20.29 ± 1.05 | 14.11 ± 0.72 | 8.39 ± 0.04 | 4.72 ± 0.03 |
| | **Diol** | 45.78 ± 0.84 | 46.77 ± 1.30 | 34.52 ± 1.08 | 26.00 ± 0.48 |
| | **Triol** | 16.79 ± 0.23 | 30.17 ± 0.84 | 50.54 ± 0.32 | 60.18 ± 1.16 |

**Table 3-1:** Content of Mono-ol, Diol and Triol in the Polyol Products from Varying Ozonolysis Time

more double bonds can react with ozone and following hydrogenation, more hydroxyl groups are obtained.

It was also found that the detector response was different for mono-ols, diols and triols therefore, in order to accurately quantify the components of the polyol mixture, individual calibration curves for each component was necessary. Unlike UV-detection, ELSD response is independent of the chain length and degree of unsaturation of the fatty acid chain (Christie, 1992; Silversand and Haux, 1997), therefore the calibration curves reported in this paper are also applicable to other polyols with similar terminal primary alcohol functionalities.

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# 4 Physical Properties of Canola Oil Based Polyurethane Networks*

## 4.1. Introduction

Polyurethanes (PURs) form a large family of polymeric materials with versatile chemical compositions and properties. They have wide applications: automotive parts, furnishing, construction, paints and coatings for appliances, etc (Szycher, 1999). In general, PURs are industrially produced by reacting petroleum based polyols with isocyanates. The traditional process to produce suitable polyols from petroleum is costly and the resulting products may cause serious environmental issues. In order to reduce the dependence on petroleum which is being exhausted at a fast rate, it is necessary to find more versatile, renewable, and more environmentally friendly resources. Vegetable oils, an abundant renewable resource, can be used to produce PURs through the introduction of hydroxyl functional groups into their structures. This process involves a number of approaches and has been extensively investigated by several researchers (Erhan, 2005; Guo et al., 2000; Guo et al., 2002; Hu et al., 2002; Javni et al., 2003; Khoe et al., 1972; Kong and Narine, 2007; Lyon et al., 1974; Narine et al., 2007a; Narine et al., 2007b; Narine et al., 2007c; Petrovic et al., 2005; Tran et al., 2005).

One of the methods developed to prepare polyols from vegetable oils is to introduce epoxides onto the double bonds which later can be opened in various ways to produce polyols with secondary hydroxyl groups (Erhan, 2005; Guo et al., 2000; Hu et al., 2002). Another method is based on hydroformylating fatty acid double bonds to form

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*A version of this chapter is in Press:
Kong, X., Yue, J. and Narine S.S., *Physical Properties of Canola Oil Based Polyurethane Networks.* Biomacromolecues.

aldehyde first, which is then hydrogenated to produce polyols.(Erhan, 2005; Guo et al., 2002; Khoe et al., 1972; Lyon et al., 1974) However, both technologies yield heterogeneous polyols with hydroxyl functionality situated in the middle of the fatty acid chains, causing significant steric hindrance during cross-linking reactions in the production of polymers. Recently, an alternative method using ozone to cleave and oxidize the double bonds in the vegetable oil and then using various reducing catalyst to reduce the ozonides to polyols has been developed. Polyols prepared by this method have terminal primary hydroxyl groups, which reduce plasticizing effect in the subsequent PUR networks (Kong and Narine, 2007; Narine et al., 2007a; Narine et al., 2007b; Narine et al., 2007c; Petrovic et al., 2005; Tran et al., 2005).

Ozonolysis technology was first industrially established and used to produce azelaic acid and pelargonic acid from commercial-grade oleic acid (Goebel *et al.*, 1957). In our previous work, this technology was applied to vegetable oil to produce polyols with primary alcohol functional groups at position nine of the fatty acid ester (Narine et al., 2007c). This type of polyol is capable of producing high-quality PUR elastomers and foams which had very good thermo-mechanical and mechanical properties (Narine et al., 2007a; Narine et al., 2007b). However, the procedure to synthesize polyol involved toxic solvent, high temperatures and high pressure which would limit performance at an industrial scale. The yield of triols was 22 % (mass content) which is also relatively low (Narine et al., 2007c).

In this paper, generation-II polyol with higher hydroxyl value was synthesized from canola oil by introducing a mild solvent (ethyl acetate) and a more efficient reductive reagent (zinc) to the polyol preparation procedure. Generation-II PUR elastomers were prepared by reacting this polyol with aliphatic diisocyanates. The physical and thermal properties of the PUR elastomers were studied using dynamic mechanical analysis (DMA) and modulated differential scanning calorimetry (MDSC) and compared to the elastomers made from generation-I polyols. The difference in structure of the starting materials (polyol), i.e. higher triol and less mono-ol content in generation-II polyol, provided the opportunity to evaluate the effect of dangling chain on the properties of the elastomers.

## 4.2. Materials and Methods

### 4.2.1. Materials

The canola vegetable oil used in this study was a "100% pure Canola" supplied by Canbra Foods Limited, Lethbridge, AB, Canada. Raney nickel 2800 (slurry in water) catalyst was obtained from Sigma-Aldrich Co., USA. Ethyl acetate (reagent grade) and zinc (30 meshes, granular) were obtained from Fisher Scientific, USA. Aliphatic 1,6-hexamethylene diisocyanate (HDI, Desmodur N-3200) was sourced from Bayer Corporation, Pittsburgh, PA, USA. The relevant parameters of the polyols and diisocyanates used in this study are listed in **Table 4-1**.

### 4.2.2. Synthesis of Polyol

Generation–I polyol used in this study was synthesized in our laboratory using ozonolysis and hydrogenation based technology. Canola oil was reacted with ozone in water to produce ozonide then hydrogenated in tetrahydrofuran (THF) with Raney nickel as catalyst. The detail procedures have been described in Chapter 2. This grade of polyol is referred as Polyol-I.

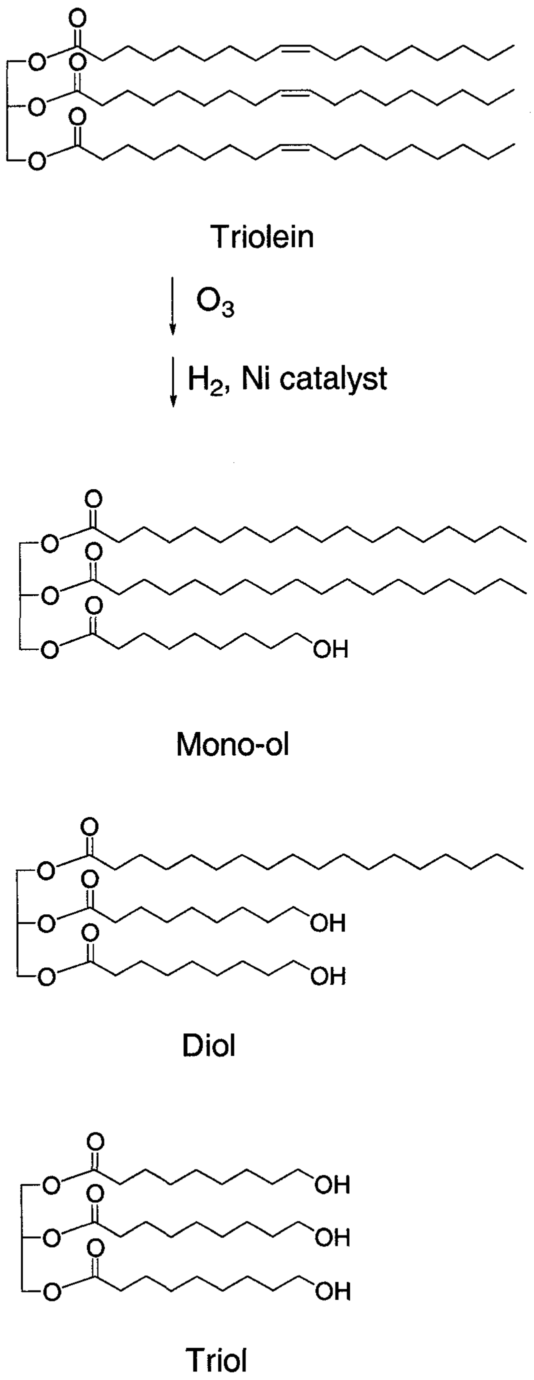
Generation-II polyol was synthesized by the following procedure: Canola oil in the ethyl acetate (volume of 1:4) was ozonized (20% volume solution) at 10 ℃, 5 L/min $O_2$ flow rate (with the concentration of ozone of 62 $g/m^3$) for 1 hour. The ozonolysis product was reduced by zinc (molar ratio of 1:1.2 of equivalent weight) at room temperature, followed by hydrogenation at 70 ℃, 100 psi with Raney nickel as catalyst. Finally, the solvent was removed by rotary evaporation and the low molecular weight by-products were removed by wiped blade molecular distillation. This grade of polyol is referred as Polyol-II. **Scheme 4-1** illustrated the reaction scheme using triolein as an example and the representative structure of the main component in polyol.

### 4.2.3. Preparation of the Polyurethane Elastomers

PUR elastomers were prepared by reacting polyols with diisocyanates and the detailed procedures have been described elsewhere (Narine et al., 2007a). The OH/NCO molar ratio was controlled as 1.0/1.2. A suitable amount of polyol mixture and HDI were weighed in a plastic container, mixed thoroughly, poured in a metallic mould previously greased with silicone release agent, and placed in a vacuum oven at 45°C for 10 to 20 min to degas the $CO_2$ released during the side reaction of isocyanate with moisture or carboxylic acids and the air trapped during mixing. Air was then introduced to the oven to avoid the deformation of the sample under vacuum and the sample was post-cured at 40°C — 45°C for about 48 hours. The sample was 2 mm thick and ready for mechanical and thermal mechanical properties tests. Based on different polyol used, i.e. Polyol-I or Polyol-II, the PUR samples are referred as PUR-I and PUR-II, respectively.

| | **Equivalent weight (g/mole)** | **OH number (mg KOH/g)** | **Acidity number (mg KOH/g)** | **Viscosity at 25°C (Pa.s) ± $5\times10^{-4}$** |
|---|---|---|---|---|
| **Polyol-I** | 368 | 152.4 ± 0.3 | 22.9 ± 0.3 | 0.4527 |
| **Polyol-II** | 239 | 235.2 ± 4.6 | 15.8 ± 2.1 | 0.9860 |
| **HDI** | 183 | | | |

**Table 4-1:** Parameters of the Polyols and Diisocyanate Used in the Formulations to Prepare Polyurethanes. Errors are standard deviations; n=3



**Scheme 4-1**: Reaction Scheme Using Triolein as an Example and Representative Structure of Main Component in Polyol

### 4.2.4. Hydroxyl and Acidity Values

Hydroxyl and acidity values of the polyols were determined according to ASTM titration method D1957-86 and ASTM D4662-98, respectively. All the samples were run in triplicate. The average values and standard deviations are reported.

### 4.2.5. Rheometeric Measurements

Viscosity of the polyols was measured in shearing mode with the TA Advanced Rheometer AR 2000 using a constant shearing rate of 51.6 $s^{-1}$ at 25 °C.

### 4.2.6. Density Tests

The density of the PUR elastomers was determined according to ASTM D 792-00 standards.

### 4.2.7. Thermal Properties

DSC measurements were carried out on a DSC Q100 (TA Instruments), equipped with a refrigerated cooling system. All the DSC measurements were performed following the ASTM E1356-03 standard. About 10mg of samples were heated at a rate of 10 °C/min from +25 °C to +100 °C to eliminate the thermal history, cooled down to − 50 °C at a cooling rate of 5 °C/min then heated again to +100 °C at a rate of 10 °C/min. Only the second heating step was selected for data analysis. All the procedures were performed under a dry nitrogen gas atmosphere.

DMA measurements were carried out on a DMA Q800 (TA Instruments) equipped with a liquid nitrogen cooling apparatus in the single cantilever clamp with a constant heating rate of 1 °C/min from –120 °C to 100 °C. The size of the samples was

18 × 7 × 2 mm. The measurements were performed following ASTM E1640-99 standard at a fixed frequency of 1 Hz and a fixed oscillation displacement of 0.015 mm. In the case of multiple isothermal oscillation experiments, the isothermal evolution of rheological parameters was recorded as a function of frequency ranging from 0.1 to 100 Hz. The isothermal oscillation was made, every 5 °C, 30 °C below and above glass transition temperature.

Stress relaxation experiment was performed at 50 °C above glass transition temperature ( $T_g$ ) with a shear clamp. A 0.2% strain was applied to each sample immediately prior to the collection of the relaxation spectrum. The relaxation modulus was monitored for approximately 10 min.

All the samples were run in triplicate for thermal property measurements. The reported errors are the subsequent standard deviations.

### 4.2.8. Mechanical Properties

Specimens for tensile measurements were cut out from the PUR samples using an ASTM D638 Type V cutter. The tests were performed at room temperature using an Instron (MA, USA) tensile testing machine (model 4202) equipped with a 50 Kgf load cell and activated grips which prevented slippage of the sample before break. The cross-head speed was 50 mm/min as suggested by the above mentioned ASTM standard. At least five identical dumbbell-shaped specimens for each sample were tested and their average mechanical properties are reported. The reported errors are the subsequent standard deviations.

## 4.3. Results and Discussion

### 4.3.1. Characterization of Polyols

The average values and standard deviations of hydroxyl and acidity of the polyols are reported in **Table 4-1**. The hydroxyl number of Polyol-II (235 mg KOH/g) is very close to the theoretical maximum value (251 mg KOH/g) which was calculated based on the data of triacylglycerols (TAGs) composition and structure of canola oil (Neff et al., 1994). It is much higher than that of Polyol-I (152 mg KOH/g). The composition of the polyols was determined by an analysis protocol developed in our laboratory based on the HPLC procedure developed by Elfman-Borjesson and Harrod (Elfman-Borjesson and Harrod, 1997) for the analysis of lipid derivatives. The mass content of triol, diol, mono-ol and saturated TAGs of Polyol-II was 60%, 26%, 5% and 9%, respectively, whereas those of Polyol-I was 22%, 38%, 26% and 14%, respectively. The saturated fatty acid chains in diol and mono-ol would act as dangling chains in the PUR networks. The lower hydroxyl value and amount of triol of the Polyol-I could be explained by the difficulty to completely convert the reactant in the presence of a medium for ozonolysis such as water which is immiscible with the oil nor with the ozonide. With the introducction of ethyl acetate as a solvent for ozonolysis and reduction, it can efficiently dissolve the starting material, the intermediate product and the final product to increase the reaction and the conversion rate.

It is noticed that both generations polyol were ended up with relatively high acid number, which resulted from oxidation, either during or after ozonolysis. Part of the ozonide was oxidized to carboxylic acid which couldn't be hydrogenated(Bailey, 1958). In order to compensate for the detrimental effect of the acid, a relatively higher isocyanate content was used in the formulation to produce PUR elastomers. To minimize the acid content, the following precautions could be taken: 1) dry the solvent (ethyl acetate) by using for example molecular sieve to get rid of the moisture; 2) perform ozonolysis reaction at lower temperature.

### 4.3.2. Characterization of PUR Networks

The concentration of elastically active network chains (EANCs), $\nu_e$ , were determined by measuring equilibrium modulus of networks based on rubber-elasticity theory by the following equation (Flory, 1976):

$$G' = \frac{E'}{3} = a\nu_e RT = \frac{a\rho RT}{M_c} \qquad (1)$$

where $a$ is a prefactor that depends on the assumptions of the model, $R$ is the gas constant, $T$ the absolute temperature, $M_c$ the number-average molecule weight between cross-links, and $\rho$ the density of the PUR networks.

Generally, the elastic behavior of polymer networks is described by either the phantom or the affine network model. For the phantom model, $a$ depends on the functionality of the cross-links (f): $a = 1 - (2/f)$, while for affinely deforming networks $a = 1$. Phantom networks (James and Guth, 1947) are defined as perfect networks, no interactions between network chains exist, the cross-links are fully mobile. However, in real networks, the network chains do interact. The molecular chains will also interact with each other and reduce the junction fluctuations. For example, non-idealities in the networks, such as dangling chains will decrease $\nu_e$ and entrapped entanglements will increase it, inversely. Because of the strong interactions between molecular chains in the PUR network, the junctions are assumed immobile, and the storage molulus G′ of the PUR network could be related to $\nu_e$ using the affine network model.

The equilibrium modulus of networks was investigated by creating master curves of the storage modulus vs. frequency following the time-temperature superposition principle (Ferry, 1980) using $T_g$ + 5°C as the reference temperature. **Figure 4-1** shows the master curve of E′ at a reference temperature of 20°C for PUR-II elastomers as an example. The extended frequency range obtained by the superposition is $10^{-7}$ to $10^{8}$ Hz. The pseudo-equilibrium modulus of the cross-linking network, $G'$ ($G' = E'/3$), is related to $\nu_e$ through Eq. (1). When the $M_c$ was calculated, $\rho$ was determined according to ASTM D 792-00 standards and assumed to be a constant. The results are listed in **Table 4-2**.

PUR-II elastomers have larger $\nu_e$ and smaller $M_c$ confirming that polyols with higher functionality are more efficient at building network structure than those with lower functionality. Furthermore, the large amount of saturated fatty acids in Polyol-I act as dangling chains, causing significant steric hindrance to cross-linking which resulted in lower $\nu_e$ in the produced PUR. As will be discussed later, the concentrations of elastically active network chains play an important role in the physical and mechanical properties of the PUR networks.

Note that the $\nu_e$ measured using the above mentioned procedure is composed of contributions from both chemical cross-links and trapped entanglements. In order to

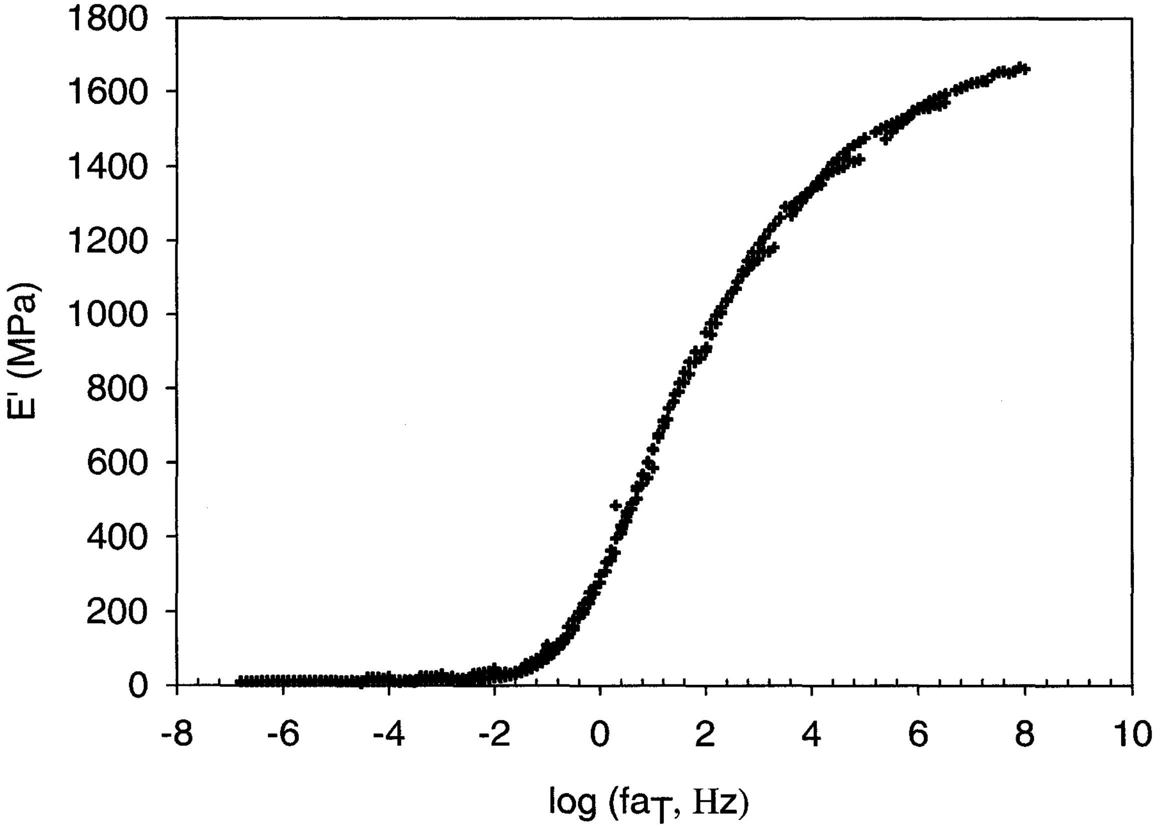


**Figure 4-1:** Master Curve of E′ at a Reference Temperature of $T_g$ + 5°C for PUR-II Elastomers

| | $T_g$ (°C) from DSC | $T_g$ (°C) from DMA | E′ (MPa)* | ρ at 23 °C (g/cm$^3$) | $\nu_e$ (mol/cm$^3$) | M$_c$ (g/mol) |
|---|---|---|---|---|---|---|
| **PU-I elastomers** | -9.6 ± 1.0 | -5.3 ± 0.6 | 8.0 | 1.112 | $1.0 \times 10^{-3}$ | 1066 |
| **PU-II elastomers** | 8.3 ± 0.6 | 15.0 ± 0 | 10.1 | 1.110 | $1.4 \times 10^{-3}$ | 803 |

* E′ at rubbery plateau from master curve

**Table 4-2:** $T_g$ (°C) Obtained by DSC and DMA, Density and Parameters of Cross-linking Networks of the Polyurethane Elastomers evaluate the amount of trapped entanglements in the PUR networks, relaxation of the shear modulus was measured as a function of time for each polymer in its rubbery state. To ensure that each material was in its rubbery region, each sample was tested at a temperature 50 °C above its $T_g$. It is evident from the relaxation spectra presented in **Figure 4-2** that PUR-II elastomers appeared to have an initial equilibrium value of the relaxation modulus at 2 min, while PUR-I elastomers underwent a relaxation process at longer time. PUR-I elastomers have a much higher fraction of "inert" material (dangling chains and saturated TAGs), which disrupt the network formation, and therefore "dilute" the elastically active network chains backbones. Alternatively, one can say that the dangling chains make the elastically active network chains more bulkly and the network structure loose. It is hypothesized that PUR-I elastomers may contain very loose networks of chemical cross-links augmented by physical cross-links that are caused by those "inert" materials. Thus, on short time scale these materials behave as though they are well cross-linked. But as the physical interactions are overcome on larger time scales, they begin to display the flow characteristics and long range relaxation ability of a loose network. This trend is consistent with what has been reported for lightly cross-linked natural rubber which can take hundreds of hours to equilibrate in a stress relaxation or creep experiment (Plazek, 1966) .

### 4.3.3. The Sol Fraction and Concentration of PUR Networks

The swelling of PUR-I elastomers in toluene at room temperature is 66%, which is higher than that of PUR-II elastomers (39%). The sol fraction for each sample was determined by multiple extractions with toluene. The content of soluble part of PUR-I elastomers is 8.6 % and that of PUR-II elastomers is only 0.8 %. By considering the

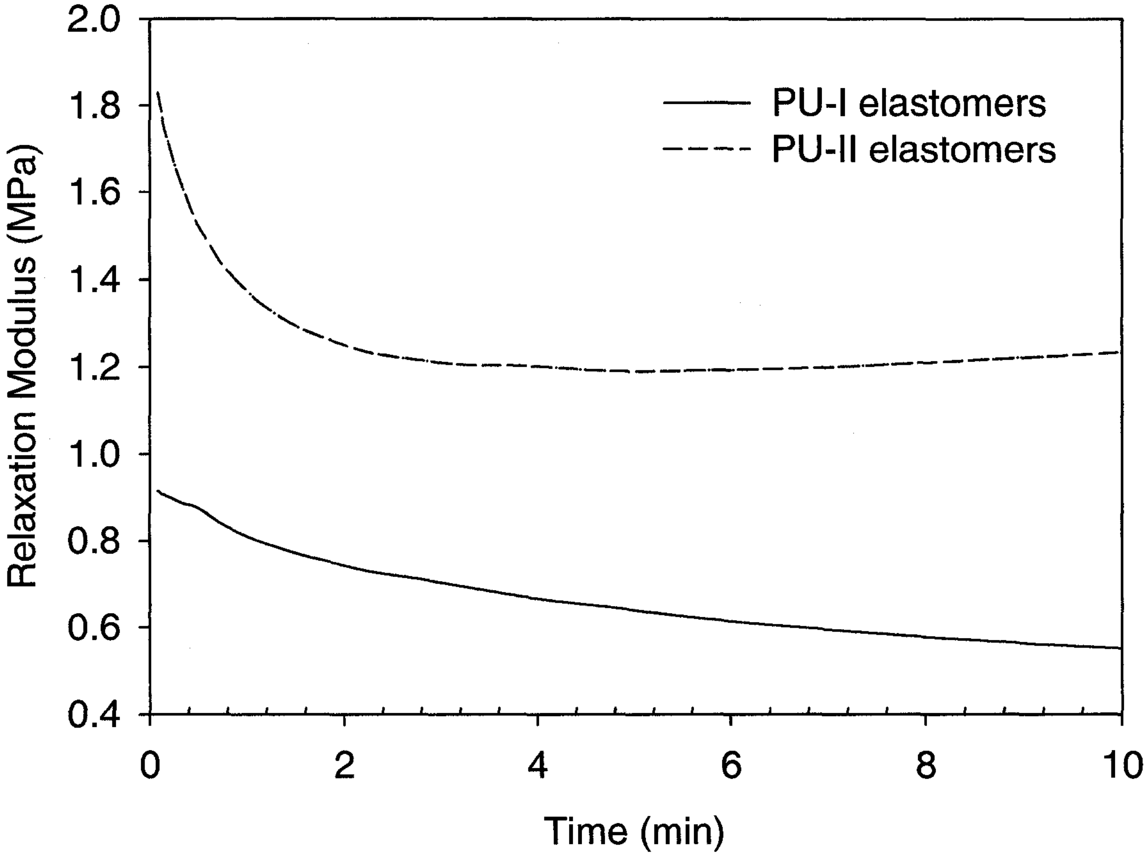


**Figure 4-2:** Response of the Relaxation Modulus during the Stress Relaxation Experiments Performed at 50 °C above $T_g$

mono-ol and saturated TAGs contents in the polyols, it was expected that PUR-I elastomers would have considerable sol fractions, whereas PUR-II elastomers would have low sol fractions. The existence of sol in these materials might have a substantial impact on various properties.

$\nu_e$ and $M_c$ of the PUR networks were also determined by applying the equilibrium degree of swelling to Eq (2) according to Flory-Rehner theory.(Flory and Rehner, 1943)

$$1/\nu_e = M_c/\rho_2 = \frac{[-V_1(A\phi_2^{1/3} - 2B\phi_2/f)]}{[\ln(1-\phi_2)+\phi_2+\chi_{12}\phi_2^2]} \qquad (2)$$

where $\rho_2$ is the density of the dry polymer, $V_1$ is the molar volume of the solvent, $\phi_2$ is the volume fraction of the polymer in the swollen sample, $f$ is the functionality of the network branch points, and $\chi_{12}$ is the polymer-solvent interaction parameter. A and B within the junction-fluctuation theory of Flory (JFF theory) (Flory, 1976) have the following limits: $A = (f-2)/f$, $B = 0$ (phantom model); $A = 1$, $B = 1$ (affine model).

The polymer-solvent interaction parameter, $\chi_{12}$, was calculated from the solubility parameters of the solvent, $\delta_1$, and the polymer network, $\delta_2$:

$$\chi_{12} = \frac{(\delta_1 - \delta_2)^2 V_1}{RT} \qquad (3)$$

The solubility parameter of toluene, $\delta_1 = 18.2\ (\mathrm{J/cm^3})^{1/2}$, was obtained from polymer handbook (Brandrup et al., 1999), the solubility parameter of PUR, $\delta_2$, can be calculated from cohesive energy densities and the volume contribution of atomic groups using group contributions theory (Krevelen, 1997).

Notice that $M_c$ calculated from Eq (2) is 210 g/mol for PUR-I elastomers and 150 g/mol for PUR-II elastomers by applying the affine model. These values are unrealistically low which can be due to the contribution of trapped entanglements. It might be also due to the inaccurate calculation of $\delta_2$ which was obtained by assuming a perfect network structure. In reality, impurity of the starting products, the presence of material with lower functionality, and competing side reactions can all lead to an influence on the network structure. It is therefore difficult to evaluate the exact network parameters calculated from swelling experiments. However, by comparing with the results described previously from equilibrium modulus, the trends are the same: PUR-II elastomers have larger $\nu_e$ and smaller $M_c$ than PUR-I elastomers.

### 4.3.4. Thermal Mechanical Properties of PUR Networks

The dynamic mechanical properties of both PUR elastomers were investigated as a function of temperature starting in the glassy state, through glass transition, and well into the rubbery plateau of each material. The storage modulus measured at frequency of 1Hz for PUR elastomers with different polyols are shown in **Figure 4-3**. For both elastomers, the storage modulus drops first gradually then exhibits a relatively rapid drop around -90°C to -70°C ($\beta-$transition) as indicated by the arrows in the figures, followed by another large drop during the transition from glassy to rubbery states (glass transition). The storage moduli of the PUR-I elastomers decrease slightly with increasing temperature, while that of PUR-II elastomers drop abruptly in the glass transition region. In the glassy state, stiffness is related to changes in the stored elastic energy upon small deformation as the molecular segments resist motion. The PUR-I elastomers with lower $\nu_e$ appear less able to resist segmental motion and thus are not capable of storing elastic energy, resulting in a lower glass modulus than those of PUR-II elastomers.

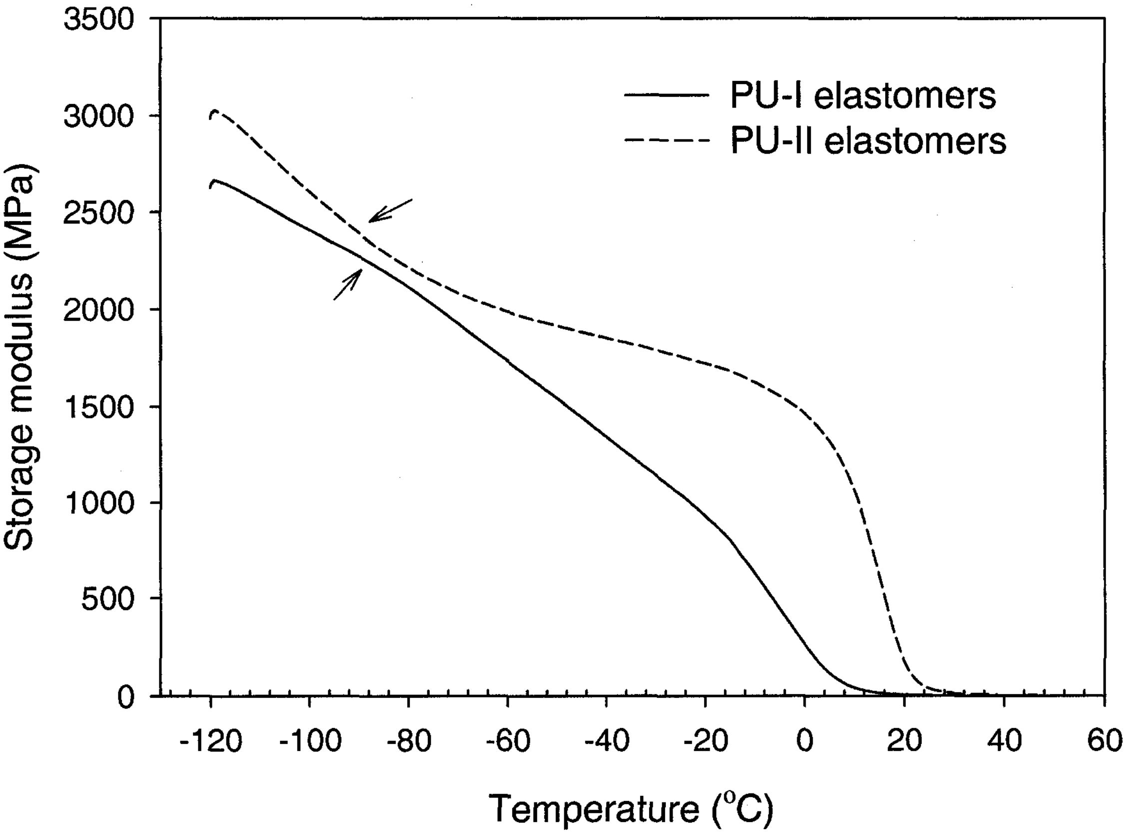


**Figure 4-3:** Storage Moduli vs. Temperature, Obtained from Dynamic Mechanical Analysis (DMA) Carried out at a Frequency of 1Hz

$T_g$ values for both elastomers determined from the inflection point of $E'$ vs temperature from DMA measurements are listed in**Table 4-2**. The $T_g$ s of the PUR elastomers were also determined from the shift of heat capacity with temperature of the DSC curves (see **Figure 4-4**) and listed in **Table 4-2** as well. The $T_g$ values determined by DSC and DMA showed the same trend: the $T_g$ s of PUR-II elastomers are about 20°C higher than those of PUR-I elastomers. However, the values obtained from DMA are somewhat higher than those obtained by DSC which is due to the frequency effect (Javni et al., 2003).

The glass transition of a polymer network is affected by cross-linking density and chemical structure as well. The increase of $T_g$ (~ 20°C) indicated that the flexibility of the polymer chains was reduced for the higher cross-linked networks shifting the rubbery state to higher temperatures. This could be explained by the high $\nu_e$ value for the PUR-II sample as mentioned earlier. In addition, the large amount of dangling chains in PUR-I sample act as plasticizers which reduce the polymer rigidity and increase the flexibility, resulting in lower $T_g$ as well.

Plots of loss modulus ($E''$) vs. temperature for both PUR elastomers are given in **Figure 4-5**. A weak $\beta-$transition in the range -90°C to -70°C was observed for both samples, which may be related to the movements of a chain part containing the urethane group attached to cross-linker (Czech et al., 2005) or to the motion of the backbone chain of the short groups in the fatty acid chains (Nielsen, 1994). The $\beta-$transition has also been detected in other PURs (Narine et al., 2007a; Narine et al., 2007b; Petrovic et al., 2005) as well. In the case of PUR-II elastomers, the strong peak in the loss modulus

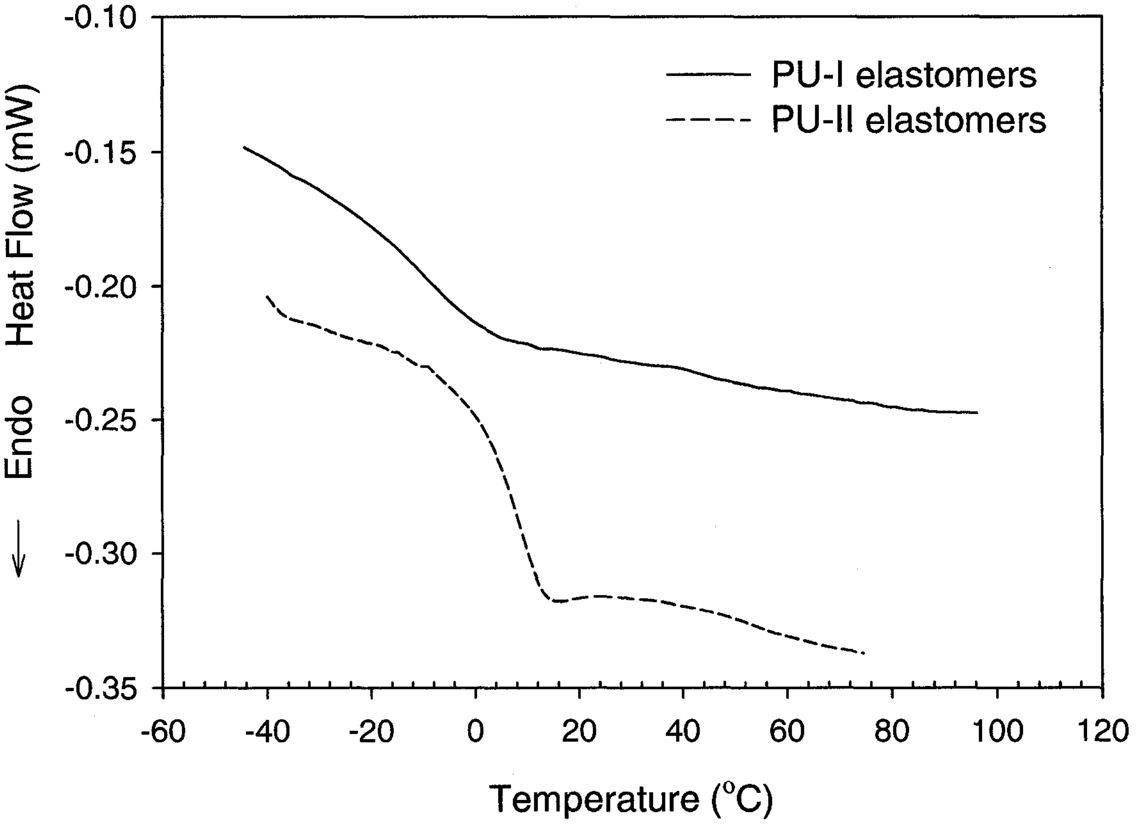


**Figure 4-4:** Differential Scanning Calorimetry (DSC) Curves of the Polyurethane (PUR) Elastomers

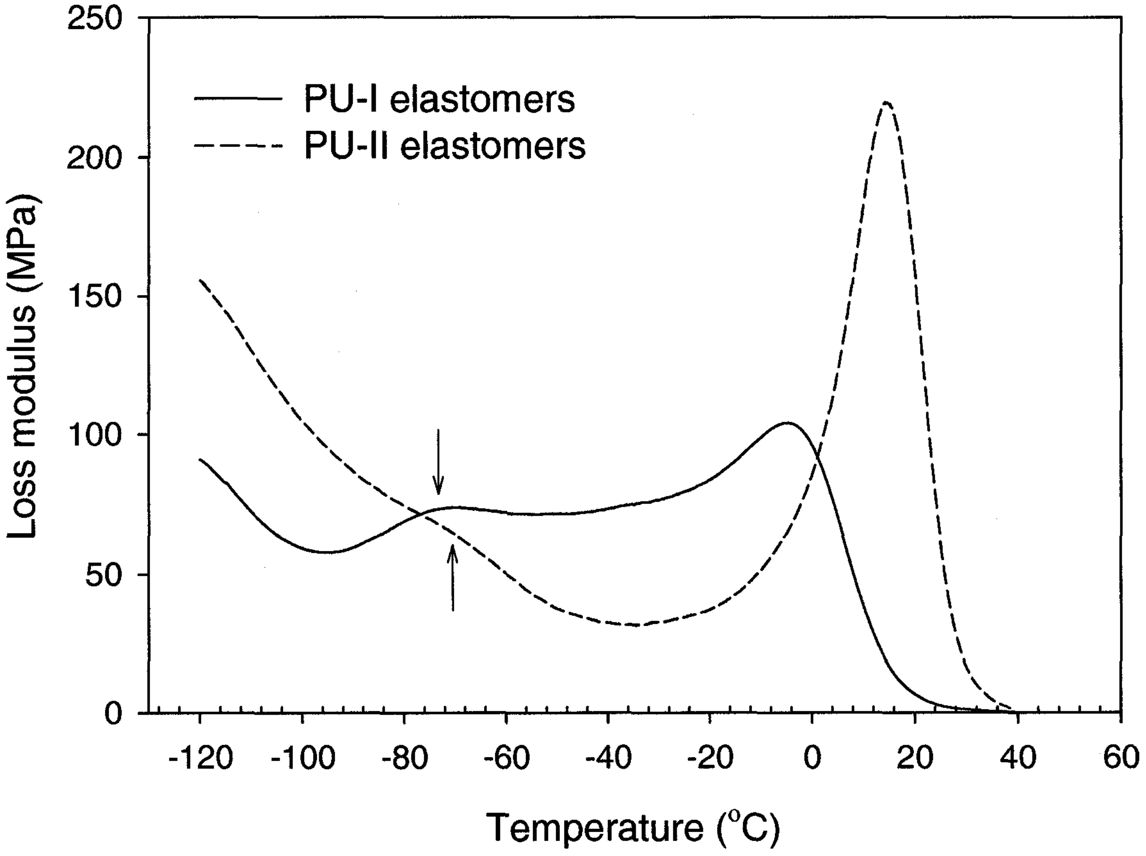


**Figure 4-5:** Changes in the Loss (E″) Moduli with Temperature, Obtained from Dynamic Mechanical Analysis (DMA) Carried out at Frequency of 1Hz

curve, which is associated with glass transition, appears to be narrower, indicating a narrower distribution of network structures.

The network homogeneity for each PUR may also be analyzed from the width of glass transition peaks in tangent δ (tan δ) curves (Son et al., 1999). The temperature dependence of tan δ from DMA for PUR elastomers is shown in **Figure 4-6**. The full width at half maximum (FWHM) of tan δ peak for PUR-II elastomers, around 16°C, is much less than that of PUR-I elastomers, around 28°C. The broader peak width at half-height of tan δ peak for PUR-I elastomers indicate a wider distribution of network structures, which is due to the heterogeneities in the molecular weight between cross-link joints resulting from the heterogeneous nature of Polyol-I as described previously.

### 4.3.5. Mechanical Properties of PUR Networks

The stress vs. strain curves for PUR elastomers are shown in **Figure 4-7**. PUR-II elastomers displayed a higher Young's modulus, higher tensile strength and larger elongation at break (9.9 ± 0.3 MPa, 6.9 ± 0.1 MPa and 69 ± 4%, respectively) than those of PUR-I elastomers (5.7 ± 0.2 MPa, 2.1 ± 0.2 MPa and 44 ± 3%, respectively). Both impurity of the starting products and the presence of material with lower functionality can affect the network structure, thus the mechanical properties. PUR-II elastomers exhibited better mechanical properties, which is due to the relatively homogeneous nature of PUR-II polyols and therefore, the higher $\nu_e$ and narrower distribution of polymer network. Whereas the poorer mechanical properties of PUR-I elastomers is a result of higher sol fraction, loose network structure and large amount of dangling chains which are imperfections in the final polymer network and do not support stress when the network is under load.

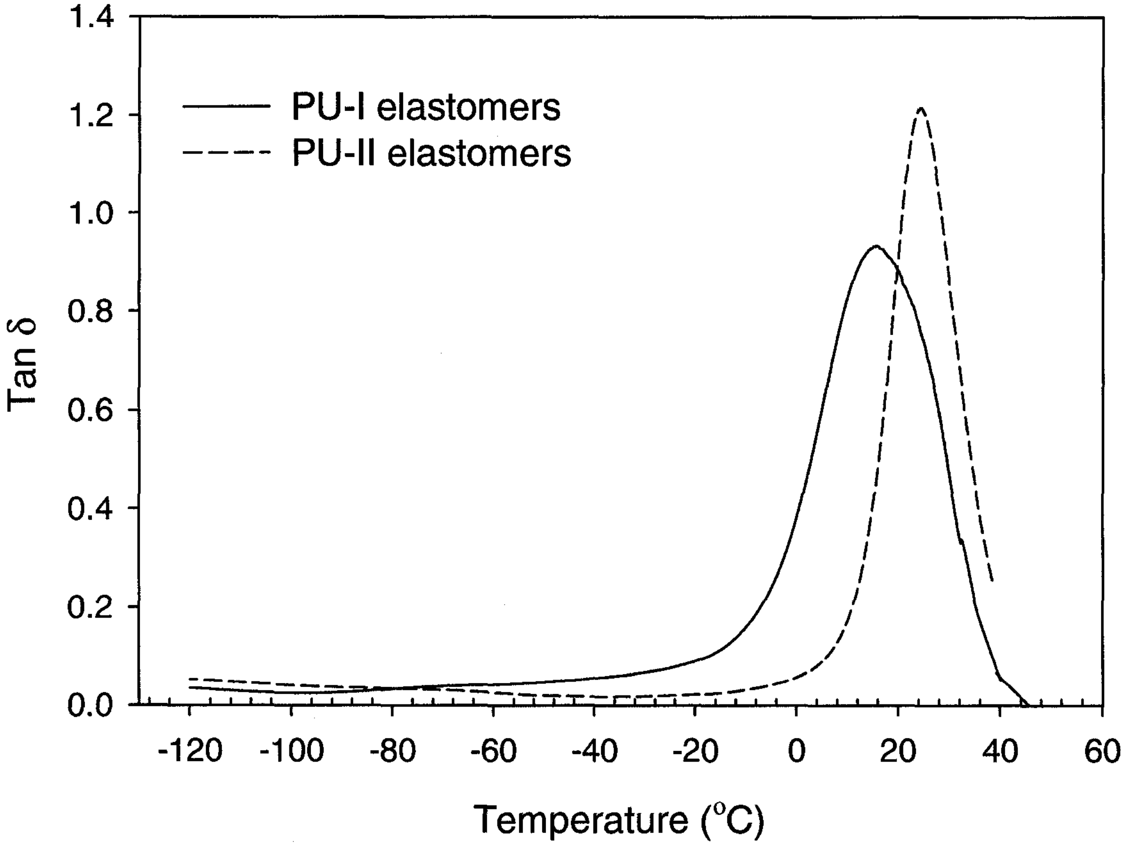


**Figure 4-6:** Temperature Dependence of Tangent δ (tan δ) of Polyurethane (PUR) Elastomers Measured by DMA

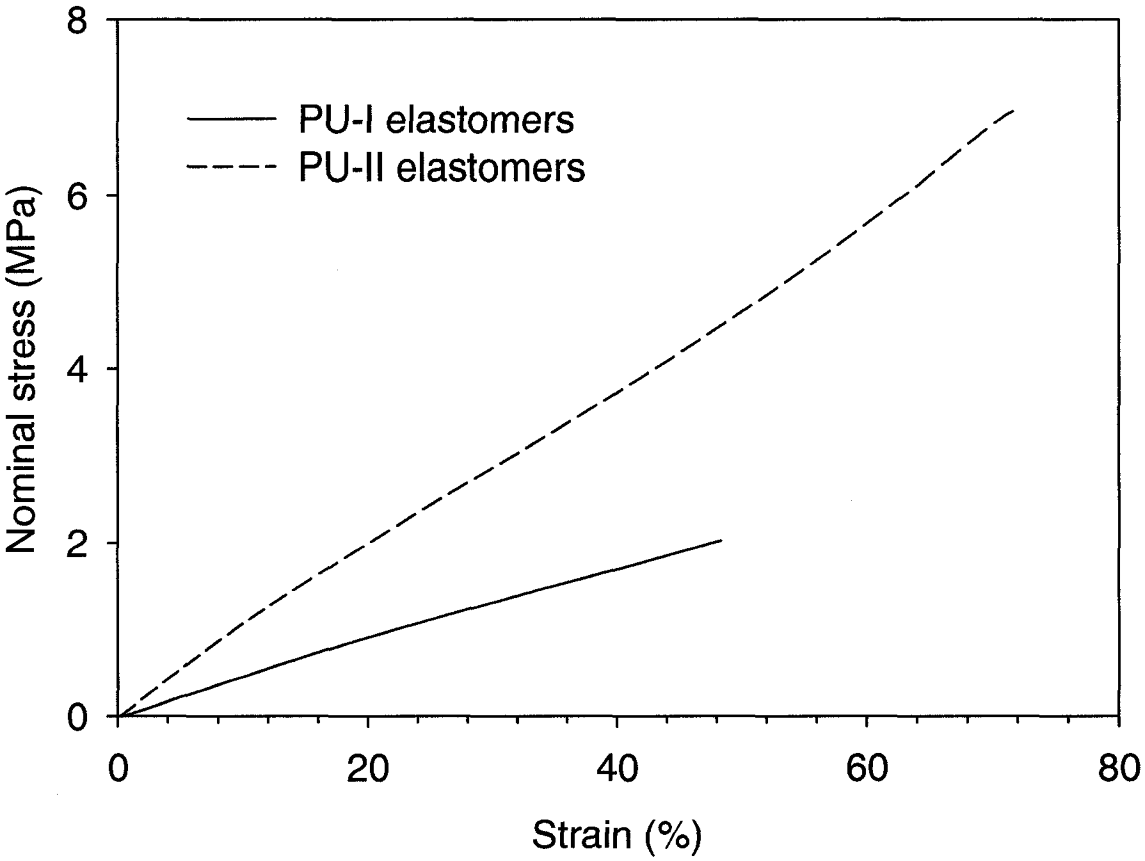


**Figure 4-7:** Stress vs. Strain Curves for the PUR Elastomers

It is worth pointing out that the strength and strain values of the vegetable oil based PUR elastomers, are lower than those of the commercial PUR elastomers currently used in the market (Vermette *et al.*, 2001). The poor performances of the vegetable oil based PUR elastomers can be attributed mainly to the structure of the polyols and the type of diisocyanate used. Vegetable oils offer sites for functionality mainly located at carbon 9 and hence produce polyols with functional groups (i.e. hydroxyl groups) located at carbon 9 which limits the length of the chain between two cross-links of their subsequent polyurethane. The use of the aliphatic diisocyanate (HDI), which is not as rigid as aromatic diisocyanates such as diphenylmethane diisocyanate, also limits the strength and elongation at break. However, the properties could be enhanced with addition of various ingredients in the formulation such as chain extenders or the use of specific types of isocyanate. In addition, it should be indicated that the present study focuses on the development of green PUR based on the proposed novel synthesis method; which could be a potential candidate to replace or partially replace petroleum based PUR in the market. To this end, further study on their various properties and functionalities, in particular, comparing them with those of petroleum based PUR, are underway in our laboratory.

## 4.4. Conclusions

Generation-II polyol with higher hydroxyl value and triol content was synthesized, and the corresponding PUR elastomers were prepared by reacting this type of polyol with HDI. By comparing with the PUR elastomers prepared from generation-I polyol, this PUR elastomers displayed a higher $T_g$, a larger $\nu_e$, a smaller $M_c$, a higher tensile strength and a longer elongation at break. The relatively faster relaxation at higher temperature for the generation-II PUR elastomers, suggests a tighter cross-linked network structure with narrower distribution by lowering dangling chains effect.

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# 5 Synthesis of Aromatic Triols and Triacids from Oleic and Erucic Acid: Separation and Characterization of the Asymmetric and Symmetric Isomers*

## 5.1. Introduction

As oil reserves are depleting and prices continue to rise, there is a growing worldwide interest in the development of renewable raw materials which are economical and environmentally friendly. Vegetable oils and fats are one of the most important sources of renewable raw materials for the chemical industry, since they are inexpensive, abundant, and provide versatile opportunities for transformation to meet specific applications. Twenty years ago, more than 90% of oleochemical reactions were performed on the fatty acid carboxyl group (Baumann et al., 1988), these include hydrolysis of fats to make soaps (Sonntag, 1982), and synthesis of fatty amines from fatty acids (Billenstein and Blaschke, 1984). Recently, increasing interest in industrial and academic research has been focused towards reactions on the hydrocarbon chains of fatty acids, especially on the double bonds of unsaturated fatty acids. An example being the epoxidation of the double bonds of fatty acids, followed by nucleophilic ring opening of the epoxide to make polyols for polyurethanes based on renewable raw materials (Guo et al., 2000). In our research group, a new method of producing polyols with terminated primary hydroxyl groups from vegetable oils has been developed (Narine et al., 2007c)

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and polyurethane elastomers and foams have been synthesized from these polyols (Narine et al., 2007a; Narine et al., 2007b).

Cyclotrimerization of alkynes to make benzene derivatives has been intensively investigated since 1948, when Reppe and coworkers reported that acetylene cyclized to form benzene in the presence of nickel (Reppe et al., 1948). A large number of transition metals and their complexes have been applied as catalysts in these types of reactions (Alphonse et al., 1988; Breschi et al., 2000; Chio et al., 1998; Fehlner, 1980; Ladipo et al., 2004). Among these catalysts, palladium or palladium chloride are the most economical and convenient. In Li's studies, under the induction of copper chloride, palladium chloride was utilized to catalyze the cyclotrimerization of terminal and substituted alkynes in the presence and absence of carbon dioxide (Li et al., 2001; Li et al., 2004; Li and Xie, 2004). In Jhingan's study, substituted benzenes were synthesized from alkynes with high yield in the presence of palladium on carbon (Jhingan and Maier, 1987).

Of all the reported studies, cyclotrimerization has only been performed on short chain alkynes. A review paper (Biermann et al., 2000) reported that Austin did some work on making some aromatic polyol compounds from fatty materials in his PhD thesis. A US patent (Renga et al., 1990) in 1990 claimed that polyfunctional hexasubstituted benzene derivatives could be obtained from fatty disubstituted alkynes, including fatty alcohols, fatty acids and fatty esters, but the end products were a mixture of symmetric and asymmetric benzene derivatives. Recently, Galia and coworkers reported the synthesis and characterization of fatty acid based aromatic triols (Lligadas et al., 2007). In this paper, they report the synthesis of aromatic triols from the esters of oleic and 10-undecenoic acid and their uses, without separation of the asymmetric and symmetric products, in the formation of polyurethane networks. This work highlights the potential importance of aromatic compounds synthesized from fatty acids which can function as monomers to create new polymers. Given the successful demonstration of the syntheses of polyurethanes from aromatic triols reported in the work of Galia and co-workers, we report here our work based on the cyclotrimerization of oleic and erucic acid to form ***both*** the corresponding asymmetric and symmetric aromatic triols and triacids. These triols and triacids are potentially versatile monomers to many polymer molecules, such as, polyurethanes, polyesters and polyamides. Our group has successfully separated and characterized the corresponding asymmetric and symmetric aromatic triols and triacids, which previously have not been reported.

## 5.2. Experimental

Oleic acid (90 %), erucic acid (90 %), and all other chemicals and reagents were purchased from Sigma-Aldrich Co. USA. Silica gel (230-400 mesh) was obtained from Rose Scientific Ltd, AB, Canada. TLC plate (250 μm) was obtained from Silicycle Chemistry Division, QC, Canada. FTIR spectra were measured with a Mattson Galaxy Series FT-IR 3000 spectrophotometer. $^1$H NMR and $^{13}$C-NMR were recorded on Varian 500 MHz or 400 MHz spectrometers (Varian, Inc., CA, USA) with $CDCl_3$ or $C_6H_6$ as solvent. Mass spectra were acquired on a Mariner Biospectrometry ESI system (PerSeptive Biosystems, Inc., MA, USA) or Kratos Analytical MS-50 (Kratos Analytical Ltd., Manchester, UK) EI high resolution spectrometer.

### 5.2.1. Synthesis of Aromatic Triol 4 and Triacid 5 from Oleic Acid

#### 5.2.1.1 Stearolic Acid 2

Stearolic acid **2** was prepared according to the literature (Silbert, 1984). A solution of oleic acid (10.6 g, 90% purity, 33.6 mmol) in diethyl ether (50 mL) was cooled to 0 °C in an ice-water bath. Bromine (2.7 mL, 52.3 mmol) was added dropwise (30 min for addition). The ice-water bath was then removed and the solution was stirred for another 30 min at RT. Saturated $Na_2S_2O_3$ solution (10 mL) was added to reduce the excess bromine. The organic layer was separated, washed with brine (20 mL) and dried over $MgSO_4$. The solvent was evaporated by reduced pressure to give a pale yellow oil (**1**). The dibromo intermediate (**1**) was then dissolved in 1-propanol (150 mL). KOH (20 g, 0.36 mol) and DMSO (18 mL, 0.25 mol) were added. The mixture was heated under reflux for 1 hr. The mixture was cooled to RT, poured into ice-cold 2N HCl (190 mL) containing ice chips, filtered and washed in the cold mixture. After drying, a white powder, **2**, was obtained (8.2 g, 29.2 mmol, 86.9 %). IR (thin film) 2750-3050 (OH), 1690 (C=O); 918 (OH) $cm^{-1}$; $^1$H-NMR ($CDCl_3$, 400 MHz) δ 11.2 (br s, 1H, COOH), 2.35 (t, *J* = 7.6 Hz, 2H, $CH_2CO$), 2.14 (t, *J* = 6.4 Hz, 4H, $C\underline{H}_2CC$), 1.64 (q, *J* = 7.2 Hz, 2H, $C\underline{H}_2CH_2CO$), 1.48 (q, *J* = 6.8 Hz, 4H, $C\underline{H}_2CH_2CC$), 1.24-1.43 (m, 16H, $CH_2$), 0.89 (t, *J* = 6.8, 3H, $CH_3$); $^{13}$C-NMR ($CDCl_3$ 100 MHz): δ 179.787 (COOH), 80.254 ($\underline{C}C$), 79.951 ($C\underline{C}$), 33.887, 31.745, 29.120, 29.067, 29.026, 28.956, 28.854, 28.772, 28.657, 28.505, 24.520, 22.559, 18.655, 18.618, 13.986 ($CH_3$); LRMS (ESI) calcd for $C_{18}H_{32}O_2Na$ ($[M+Na]^+$) 303.2, found 303.2.

### 5.2.1.2 Stearolyl Alcohol 3

Stearolic acid, **2**, (1.2 g, 4.3 mmol) was dissolved in 20 mL diethyl ether. $LiAlH_4$ (0.2 g, 5.1 mmol) was then added. The mixture was stirred at RT for 1 hr. Distilled water (10 mL) was added followed by 2 N HCl (20 mL). The organic layer was separated, washed with brine (20 mL) and dried over $MgSO_4$. The solvent was evaporated by reduced pressure to give an oil, which was purified by flash chromatography (silica gel; hexane/EtOAc 6:1) to afford 1.1 g (4.0 mmol, 93 %) of stearolyl alcohol, **3**, as a pale yellow oil. IR (thin film) 3156 (OH), 2850-3000 (CH), 1052 (C-O) $cm^{-1}$; $^1$H-NMR ($CDCl_3$, 500 MHz) δ 3.64 (t, *J* = 6.5 Hz, 2H, $C\underline{H}_2OH$), 2.14 (t, *J* = 7.0 Hz, 4H, $C\underline{H}_2CC$), 1.56 (q, *J* = 7.0 Hz, 2H, $C\underline{H}_2CH_2OH$), 1.48 (q, *J* = 6.5 Hz, 4H, $C\underline{H}_2CH_2CC$), 1.24-1.41 (m, 18H, $CH_2$), 0.88 (t, *J* = 7.0, 3H, $CH_3$); $^{13}$C-NMR ($CDCl_3$ 125.3 MHz): δ 80.286 ($\underline{C}C$), 80.150 ($\underline{C}C$); 63.042 ($CH_2OH$), 32.789, 31.846, 29.320, 29.221, 29.176, 29.139, 29.131, 29.118. 28.871, 28.780, 25.702, 22.657, 18.747, 14.091 ($CH_3$); LRMS (ESI) calcd for $C_{18}H_{34}ONa$ ($[M+Na]^+$) 289.3, found 289.3.

### 5.2.1.3 Aromatic Triols 4(a) and 4(b)

Stearoyl alcohol, **3**, (1.05g, 4.0 mmol) was dissolved in THF (20 mL). 0.25 g of Pd/C (10%) and TMSCl (0.75 mL, 6.0 mmol) were then added. The mixture was refluxed for 8 hrs then cooled to RT. The mixture was filtered to remove the Pd/C. Distilled water (20 mL) was then added. The resulting mixture was further extracted with diethyl ether and the organic layer was washed with brine (20 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue purified by flash chromatography (silica gel; hexane/EtOAc 5:1, 3:1, 2:1, 1:1) to afford yellow oils **4a** (178.5 mg, 0.22 mmol, 17.0 % ) and **4b** (635.3 mg, 0.80 mmol, 60.5 %).

**4a**: IR (thin film) 3328 (OH), 2850-3000 (CH), 1465 (C=C of benzene), 1057 (C-O) cm$^{-1}$; $^1$H-NMR ($CDCl_3$, 500 MHz) δ 3.63 (t, *J* = 6.5 Hz, 6H, C<u>H</u>$_2$OH), 2.46 (t, *J* = 7.5 Hz, 12H, $CH_2$Ph), 1.28-1.58 (m, 72H, $CH_2$), 0.88 (t, *J* = 6.5, 9H, $CH_3$); $^{13}$C-NMR ($CDCl_3$ 125.3 MHz): δ 136.840 ($CH_2$Ph), 136.810 ($CH_2$Ph), 136.686 ($CH_2$Ph), 136.642 ($CH_2$Ph), 63.118 ($CH_2$OH), 32.884, 32.015, 31.545, 30.747, 30.654, 29.833, 29.516, 29.412, 25.854, 22.769, 14.202 ($CH_3$); HRMS (EI) calcd for $C_{54}H_{102}O_3$ 798.7829, found m/z 798.7852.

$^1$H-NMR ($C_6D_6$, 500MHz) δ 3.36 (t, *J* = 6.5 Hz, 6H, C<u>H</u>$_2$OH), 2.86 (t, *J* = 6.5 Hz, 12H, C<u>H</u>$_2$Ph), 1.80-1.72 (m, 12H, C<u>H</u>$_2$$CH_2$Ph), 1.60-1.50 (m, 12H, C<u>H</u>$_2$$CH_2CH_2$Ph), 1.45-1.24 (m, 38H, C<u>H</u>$_2$), 0.55 (t, *J* = 7.0 Hz, $CH_3$); $^{13}$C-NMR ($C_6D_6$, 125 MHz) δ 137.081, 137.049, 62.682, 33.206, 32.538, 32.323, 31.137, 31.025, 30.451, 30.415, 29.872, 29.858, 29.854, 29.820, 29.774, 26.180, 23.068, 14.340.

**4b**: IR (thin film) 3333 (O-H), 2850-3000 (CH), 1465 (C=C of benzene), 1057 (C-O) cm$^{-1}$; $^1$H-NMR ($CDCl_3$, 500 MHz) δ 3.63 (t, *J* = 6.5 Hz, 6H, C<u>H</u>$_2$OH), 2.46 (t, *J* = 7.5 Hz, 12H, $CH_2$Ph), 1.25-1.58 (m, 72H, $CH_2$), 0.88 (t, *J* = 7.0, 9H, $CH_3$); $^{13}$C-NMR ($CDCl_3$ 125.3 MHz): δ136.798 ($CH_2$Ph), 136.783 ($CH_2$Ph), 136.745 ($CH_2$Ph), 136.731 ($CH_2$Ph), 136.693 ($CH_2$Ph), 136.673 ($CH_2$Ph), 63.148 ($CH_2$OH), 63.116 ($CH_2$OH), 32.897, 32.884, 32.008, 31.568, 30.743, 30.671, 30.654, 29.848, 29.527, 29.514, 29.505, 29.438, 29.414, 29.403, 25.846, 25.831, 22.754, 14.189 ($CH_3$); 14.181 ($CH_3$); HRMS (EI) calcd for $C_{54}H_{102}O_3$ 798.7829, found m/z 798.7830.

$^1$H-NMR ($C_6D_6$, 500MHz) δ 3.45 (t, *J* = 6.5 Hz, 2H, C<u>H</u>$_2$OH), 3.45 (t, *J* = 6.5 Hz, 2H, C<u>H</u>$_2$OH), 3.40 (t, *J* = 6.5 Hz, 2H, C<u>H</u>$_2$OH), 2.88-2.78 (m, 12H, C<u>H</u>$_2$Ph), 1.80-1.70 (m, 12H, C<u>H</u>$_2$$CH_2$Ph), 1.59-1.50 (m, 12H, C<u>H</u>$_2$$CH_2CH_2$Ph), 1.49-1.24 (m, 38H, $CH_2$), 0.55 (t,

$J$ = 7.0 Hz, 9H, $CH_3$); $^{13}$C-NMR ($C_6D_6$, 125 MHz) δ 137.074, 137.066, 137.040, 137.027, 62.675, 62.650, 33.213, 33.206, 32.524, 32.451, 32.435, 32.333, 31.135, 31.068, 31.020, 30.432, 30.389, 29.966, 29.944, 29.902, 29.882, 29.859, 29.852, 29.848, 29.809, 29.796, 29.788, 29.780, 26.271, 26.264, 26.219, 23.076, 14.358, 14.350.

### 5.2.1.4 Aromatic Triacids 5(a) and 5(b)

Stearolic acid, **2**, (1.91 g, 6.8 mmol) was dissolved in THF (20 mL). 0.35 g of Pd/C (10%) and TMSCl (1.1 mL, 8.7 mmol) were then added. The mixture was refluxed for 8 hrs and cooled to RT. The mixture was filtered to remove the Pd/C. Distilled water (20 mL) was then added. The resulting mixture was further extracted with diethyl ether and the organic layer was washed with brine (20 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue purified by flash chromatography (silica gel; hexane/EtOAc 6:1, 5:1, 3:1, 2:1) to afford orange oils **5a** (240 mg, 0.29 mmol, 12.6 %) and **5b** (1.23 g, 1.46 mmol, 64.4 %).

**5a**: IR (microscope) 2700-3200 (OH), 1710 (C=O), 1465 (C=C of benzene) cm$^{-1}$; $^1$H-NMR ($CDCl_3$, 500 MHz) δ 11.2 (br s, 1H, COOH), 2.46-2.49 (m, 12H, $CH_2Ph$), 2.35-2.39 (m, 6H, $CH_2CO$), 1.65 (q, $J$ = 6.5 Hz, 6H, $\underline{CH_2}CH_2CO$), 1.26-1.50 (m, 60H, $CH_2$), 0.89 (t, $J$ = 7.0, 9H, $CH_3$); $^{13}$C-NMR ($CDCl_3$ 100 MHz): δ 180.276 (COOH), 136.863 ($CH_2Ph$), 136.827 ($CH_2Ph$), 136.641 ($CH_2Ph$), 136.620 ($CH_2Ph$), 34.159, 34.034, 32.003, 31.534, 30.982, 30.738, 30.511, 29.968, 29.838, 29.751, 29.397, 29.175, 28.982, 28.715, 28.538, 24.723, 24.520, 22.752, 14.179 ($CH_3$); LRMS (ESI) calcd for $C_{54}H_{95}O_6$ ([M-H]$^-$) 839.7, found 839.7.

**5b**: IR (microscope) 2700-3200 (OH), 1710 (C=O),1465 (C=C of benzene) cm$^{-1}$; $^1$H-NMR ($CDCl_3$, 500 MHz) δ 11.2 (br s, 1H, COOH), 2.46-2.49 (m, 12H, $CH_2Ph$), 2.35-

2.39 (m, 6H, $CH_2CO$), 1.65 (q, *J* = 6.5 Hz, 6H, $\underline{CH_2}CH_2CO$), 1.27-1.51 (m, 60H, $CH_2$), 0.89 (m, 9H, $CH_3$); $^{13}$C-NMR ($CDCl_3$ 100 MHz): δ 180.461 (COOH), 180.383 (COOH), 180.265 (COOH), 179.897 (COOH),179.902 (COOH), 136.813 ($CH_2Ph$), 136.799 ($CH_2Ph$), 136.688 ($CH_2Ph$), 136.626 ($CH_2Ph$), 136.616 ($CH_2Ph$), 34.186, 34.151, 34.061, 32.001, 31.587, 31.544, 31.514, 31.502, 31.066, 30.737, 30.691, 30.525, 30.049, 30.007, 29.841, 29.829, 29.798, 29.400, 29.391, 29.374, 29.144, 29.064, 28.812, 28.771, 28.611, 28.599, 24.741, 24.536, 22.747, 14.183 ($CH_3$), 14.176 ($CH_3$); LRMS (ESI) calcd for $C_{54}H_{95}O_6$ ([M-H]$^-$) 839.7, found 839.7.

### 5.2.2. Synthesis of Aromatic Triol 9 and Triacid 10 from Erucic Acid

#### 5.2.2.1 Behenolic Acid 7

A solution of erucic acid (10.1 g, 90% purity, 26.8 mmol) in diethyl ether (20 mL) was cooled to 0 °C in the ice-water bath. Bromine (1.9 mL, 36.8 mmol) was added dropwise over 30 mins. The ice-water bath was removed and the solution was stirred for another 30 min at RT. Saturated $Na_2S_2O_3$ solution (10 mL) was added to reduce the excess bromine. The organic layer was separated, washed with brine (20 mL) and dried over $MgSO_4$. The solvent was evaporated by reduced pressure to give a pale yellow oil (**6**). The dibromo intermediate (**6**) was then dissolved in 1-propanol (100 mL). KOH (12.1 g, 0.22 mol) and DMSO (10.6 mL, 0.15 mol) were added. The mixture was heated under the reflux for 1 hr. The mixture was cooled to RT, poured into ice-cold 2N HCl (150 mL) containing ice chips, filtered and washed in the cold mixture. After drying, a white powder, **7**, was obtained (7.8 g, 23.2mmol, 86.6%): m.p. 52.5-53.1°C; IR (microscope)

2750-3050 (OH), 1713 (C=O), 916 (OH) cm$^{-1}$; $^1$H-NMR ($CDCl_3$, 400 MHz) δ 11.2 (br s, 1H, COOH), 2.35 (t, *J* = 7.6 Hz, 2H, $CH_2CO$), 2.14 (m, 4H, $C\underline{H}_2CC$), 1.64 (q, *J* = 7.2 Hz, 2H, $C\underline{H}_2CH_2CO$), 1.48 (q, *J* = 7.2 Hz, 4H, $C\underline{H}_2CH_2CC$), 1.26-1.39 (m, 24H, $CH_2$), 0.89 (t, *J* = 6.8, 3H, $CH_3$); $^{13}$C-NMR ($CDCl_3$ 100 MHz): δ 178.756 (COOH), 80.314 ($\underline{C}C$), 80.288 ($\underline{C}C$), 33.845; 31.909, 29.754, 29.592, 29.571, 29.473, 29.286, 29.232, 29.216, 29.194, 29.118, 28.931, 28.916, 24.744, 22.722, 18.820, 14.156 ($CH_3$); LRMS (ESI) calcd for $C_{22}H_{39}O_2$ ([M-H]$^-$) 335.3, found 335.3.

#### 5.2.2.2 Behenolyl Alcohol 8

Behenolic acid, **7**, (1.7 g, 5.1 mmol) was dissolved in 20 mL diethyl ether. $LiAlH_4$ (0.24 g, 6.3 mmol) was then added. The mixture was stirred at RT for 1 hr. Distilled water (10 mL) was added followed by 2 N HCl (20 mL). The organic layer was separated, washed with brine (20 mL) and dried over $MgSO_4$. The solvent was evaporated by reduced pressure to give a solid, which was purified by recrystallization from petroleum ether to afford 1.5 g (4.7 mmol, 91.3 %) of behenolyl alcohol, **8**, as a white power. m.p. 43.9-44.5 °C; IR (thin film) 3160 (OH), 2840-3000 (C-H), 1055 (OH) cm$^{-1}$; $^1$H-NMR ($CDCl_3$, 500 MHz) δ 3.64 (t, *J* = 6.5 Hz, 2H, $C\underline{H}_2OH$), 2.14 (m, 4H, $C\underline{H}_2CC$), 1.57 (q, *J* = 7.0 Hz, 2H, $C\underline{H}_2CH_2OH$), 1.47 (q, *J* = 7.0 Hz, 4H, $C\underline{H}_2CH_2CC$), 1.26-1.38 (m, 26H, $CH_2$), 0.88 (t, *J* = 7.0, 3H, $CH_3$); $^{13}$C-NMR ($CDCl_3$ 125.7 MHz): δ 80.311 ($\underline{C}C$), 80.298 ($\underline{C}C$), 63.173 ($CH_2OH$), 32.884, 31.911, 29.665, 29.660, 29.636, 29.607, 29.492, 29.285, 29.237, 29.230, 29.195, 28.932, 28.927, 25.796, 22.723, 18.823, 14.159 ($CH_3$); LRMS (ESI) calcd for $C_{22}H_{42}ONa$ ([M+Na]$^+$) 345.3, found 345.3.

### 5.2.2.3 Aromatic Triols 9(a) and 9(b)

Behenolyl alcohol, **8**, (1.0g, 3.1 mmol) was dissolved in THF (20 mL). 0.20 g of Pd/C (10%) and TMSCl (0.59 mL, 4.6 mmol) were then added. The mixture was refluxed for 8 hrs and cooled to RT. The mixture was filtered to remove the Pd/C. Distilled water (20 mL) was then added. The resulting mixture was further extracted with diethyl ether and the organic layer was washed with brine (20 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue purified by flash chromatography (silica gel; hexane/EtOAc 5:1, 3:1, 2:1) to afford yellow oils **9a** (90.0 mg, 0.09 mmol, 9.0 % ) and **9b** (720.0 mg, 74.5 mmol, 72.0 %).

**9a**: IR (microscope) 3330 (OH), 2850-3000 (C-H), 1466 (C=C of benzene), 1057 (OH) $cm^{-1}$; $^1$H-NMR ($CDCl_3$, 500 MHz) δ 3.63 (t, *J* = 6.5 Hz, 6H, C<u>H</u>$_2$OH), 2.48 (m, 12H, $CH_2Ph$), 1.30-1.59 (m, 96H, $CH_2$), 0.88 (t, *J* = 7.0, 9H, $CH_3$); $^{13}$C-NMR ($CDCl_3$ 125.7 MHz): δ136.777 ($CH_2Ph$), 136.755 ($CH_2Ph$), 136.742 ($CH_2Ph$), 63.137 ($CH_2OH$), 63.116 ($CH_2OH$), 63.102 ($CH_2OH$), 32.877, 32.000, 31.537, 30.729, 29.832, 29.774, 29.766, 29.756, 29.741, 29.707, 29.702, 29.526, 29.517, 29.508, 29.447, 29.398, 25.833, 25.820, 25.807, 22.751, 14.184 ($CH_3$), 14.176 ($CH_3$), 14.171 ($CH_3$); LRMS (ESI) calcd for $C_{66}H_{126}O_3Na$ ($[M+Na]^+$) 990.0, found 990.0.

**9b**: IR (microscope) 3330 (OH), 2850-3000 (C-H), 1466 (C=C of benzene), 1056 (OH) $cm^{-1}$; $^1$H-NMR ($CDCl_3$, 500 MHz) δ 3.64 (t, *J* = 6.5 Hz, 6H, C<u>H</u>$_2$OH), 2.49 (m, 12H, $CH_2Ph$), 1.30-1.60 (m, 72H, $CH_2$), 0.90 (t, *J* = 7.0, 9H, $CH_3$); $^{13}$C-NMR ($CDCl_3$ 125.3 MHz): δ 136.758 ($CH_2Ph$), 136.749 ($CH_2Ph$), 136.744 ($CH_2Ph$), 63.097 ($CH_2OH$), 63.090 ($CH_2OH$), 63.078 ($CH_2OH$), 63.074 ($CH_2OH$), 32.856, 31.991. 31.527, 30.718, 29.822, 29.756, 29.746, 29.737, 29.730, 29.722, 29.698, 29.687, 29.511, 29.500, 29.445, 29.434, 29.386, 25.815, 25.800, 22.742, 14.173 ($CH_3$), 14.167 ($CH_3$); LRMS (ESI) calcd for $C_{66}H_{126}O_3Na$ ($[M+Na]^+$) 990.0, found 990.0.

### 5.2.2.4 Aromatic Triacids 10(a) and 10(b)

Behenolic acid, **7**, (1.0 g, 3.0 mmol) was dissolved in THF (20 mL). 0.20 g of Pd/C (10%) and TMSCl (0.5 mL, 4.2 mmol) were then added. The mixture was refluxed for 8 hrs and cooled to RT. The mixture was filtered to remove the Pd/C. Distilled water (20 mL) was then added. The resulting mixture was further extracted with diethyl ether and the organic layer was washed with brine (20 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue purified by flash chromatography (silica gel; hexane/EtOAc 8:1, 7:1, 6:1) to afford orange oils **10a** (70 mg, 0.07mmol, 7.0 %) and **10b** (800 mg, 0.8 mmol, 80.0 %).

**10a**: IR (microscope) 2700-3200 (OH), 1710 (C=O), 1466 (C=C of benzene) $cm^{-1}$; $^1H$-NMR ($CDCl_3$, 500 MHz) δ 2.47-2.50 (m, 12H, $CH_2Ph$), 2.36 (t, 6H, *J* = 7.5 Hz, $CH_2CO$), 1.64 (q, *J* = 7.0 Hz, 6H, $\underline{CH_2}CH_2CO$), 1.26-1.51 (m, 60H, $CH_2$), 0.89 (t, *J* = 7.0, 9H, $CH_3$); $^{13}C$-NMR ($CDCl_3$ 100 MHz): δ 180.279 (COOH), 136.767 ($CH_2Ph$), 136.748 ($CH_2Ph$), 34.111, 32.008, 31.535, 30.738, 29.845, 29.740, 29.604, 29.594, 29.568, 29.458, 29.401, 29.391,29.354, 29.269, 29.239, 29.038, 29.013, 24.716, 22.757, 14.183 ($CH_3$); LRMS (ESI) calcd for $C_{66}H_{119}O_6$ ($[M-H]^-$) 1007.9, found 1007.9.

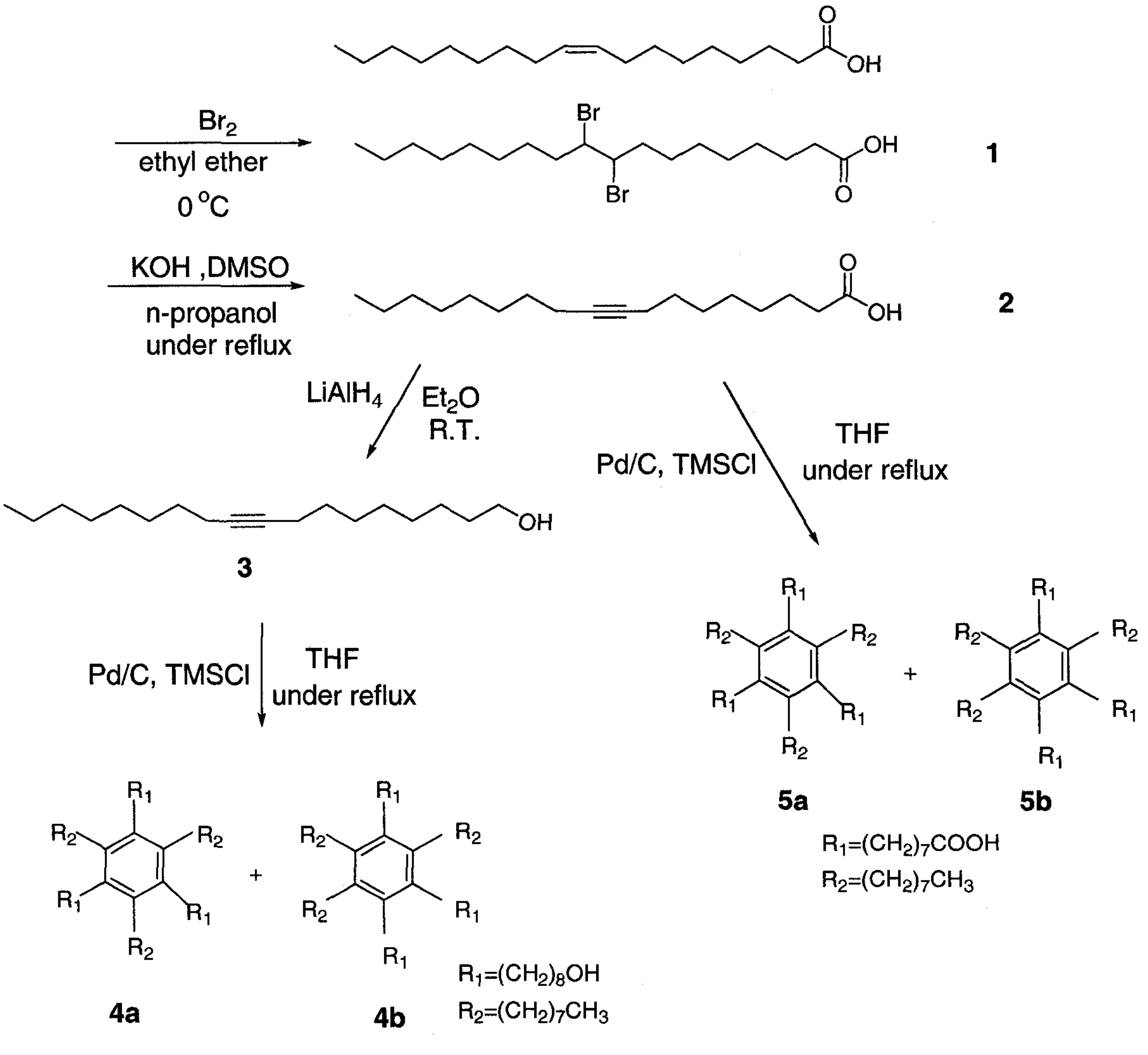
**10b**: IR (microscope) 2700-3200 (OH), 1711(C=O), 1466 (C=C of benzene ring) $cm^{-1}$; $^1H$-NMR ($CDCl_3$, 500 MHz) δ 2.49 (t, *J* = 8.0 Hz, 12H, $CH_2Ph$), 2.36 (t, 6H, *J* = 7.5 Hz, $CH_2CO$), 1.64 (q, *J* = 7.0 Hz, 6H, $\underline{CH_2}CH_2CO$), 1.31-1.51 (m, 60H, $CH_2$), 0.89 (t, *J* = 7.0, 9H, $CH_3$); $^{13}C$-NMR ($CDCl_3$ 100 MHz): δ 180.419 (COOH), 180.292 (COOH), 180.191 (COOH), 136.762 ($CH_2Ph$), 136.749 ($CH_2Ph$), 34.157, 34.141, 34.107, 32.005, 31.552, 30.732, 29.843, 29.691, 29.676, 29.655, 29.647, 29.613, 29.592, 29.503, 29.461, 29.451, 29.432, 29.400, 29.318, 29.299, 29.116, 29.101, 29.078, 24.731, 24.723, 24.717, 22.754, 14.180($CH_3$); LRMS (ESI) calcd for $C_{66}H_{119}O_6$ ($[M-H]^-$) 1007.9, found 1007.9.

## 5.3. Results and Discussion

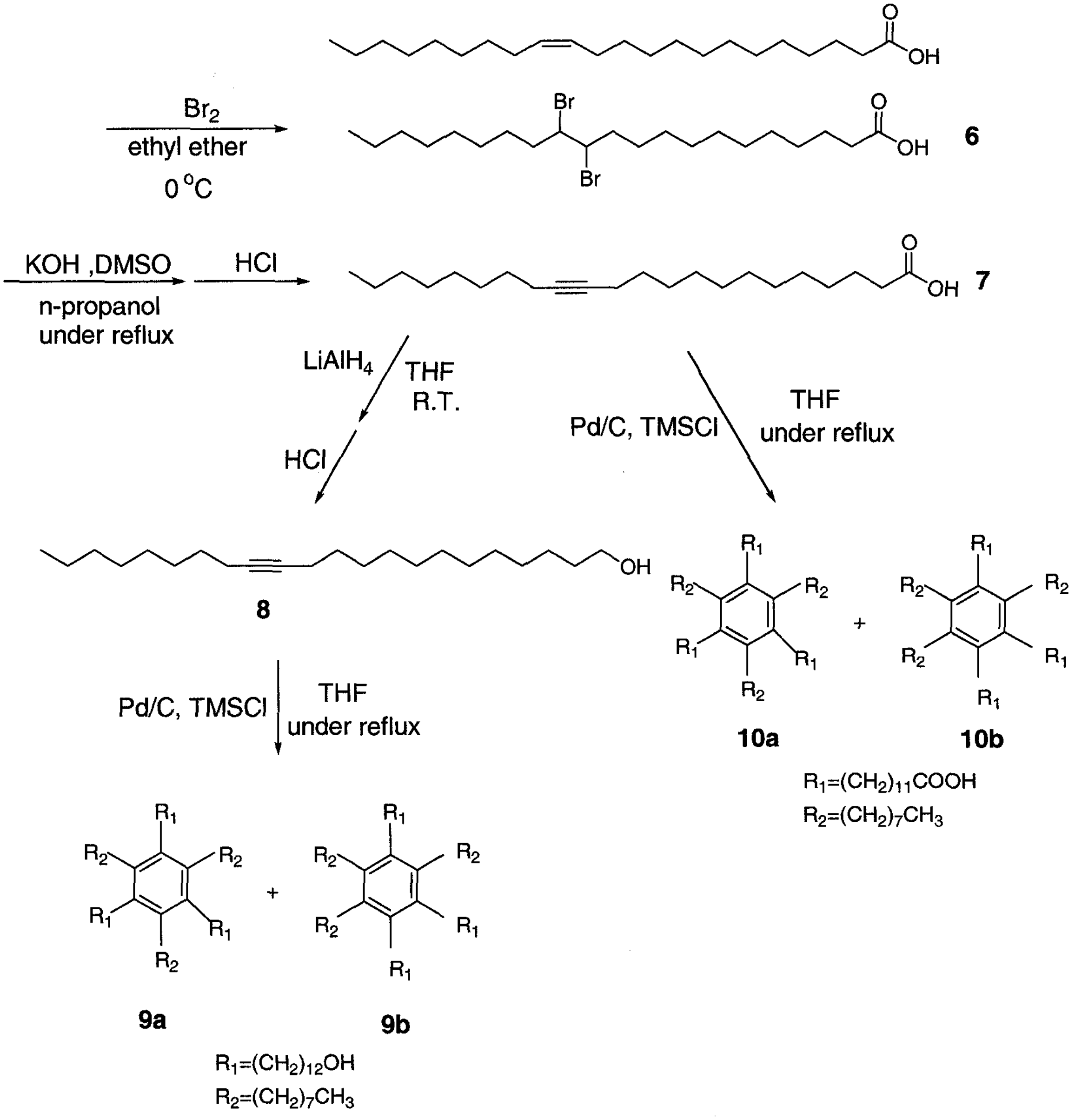
A similar method as reported by Galia and coworkers has been applied for the cyclotrimerization of fatty alkynes to produce hexasubstituted benzene derivatives. The symmetric and asymmetric isomers of the triols and triacids shown above **(Scheme 1 and 2)** have been isolated and fully characterized. The asymmetric isomer, a less stable compound, is the main product. Under the conditions discussed, this indicates that cyclotrimerization is kinetically controlled (Jhingan and Maier, 1987; Lligadas et al., 2007).

The symmetric and asymmetric isomers, such as aromatic triols **4(a)** and **4(b),** have almost identical IR or $^1$H-NMR spectra, but their $^{13}$C-NMR spectra show some visible differences, which confirm the identity of each isomer. **Figure 5-1**. shows the expanded $^{13}$C-NMR spectra including the chemical shifts for the aromatic carbons of triols **4(a)** and **4(b)**. Looking at the planar structure of triol **4(a)** **(Figure 5-2)**, two chemically different carbons on the benzene ring were expected due to the symmetry of the molecule; this would produce two signals at approximately 140 ppm in the $^{13}$C-NMR spectrum.

In reality, the long saturated carbon side chains are freely rotating which causes the six aromatic carbons to be chemically different from each other. It was observed that there was only a slight chemical shift difference between the six aromatic carbons, hence the $^{13}$C-NMR spectrum for triol **4a** **(Figure 5-1)** shows an overlap of some signals result



**Scheme 5-1:** Synthesis of Aromatic Triols 4 and Triacids 5 from Oleic Acid



**Scheme 5-2:** Synthesis of Aromatic Triols 9 and Triacids 10 from Erucic Acid

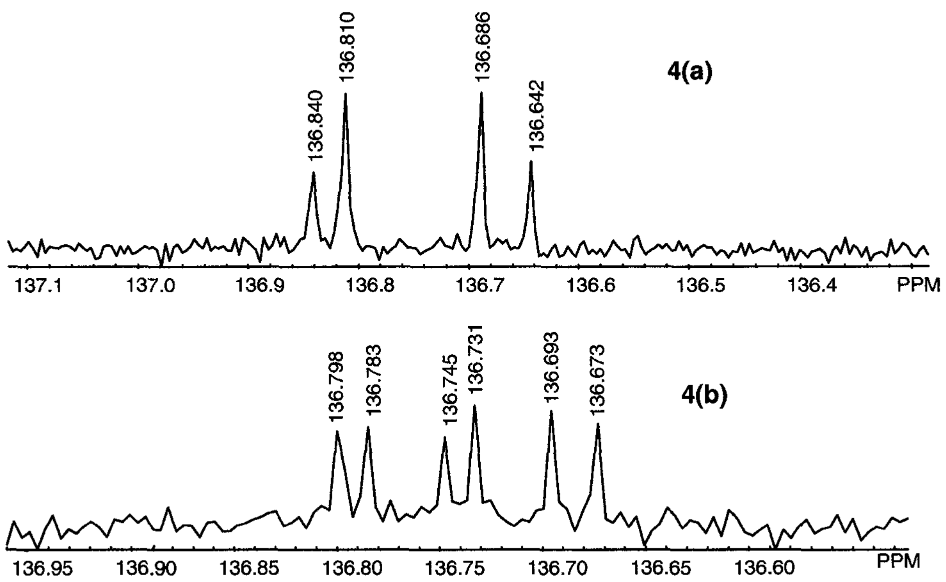
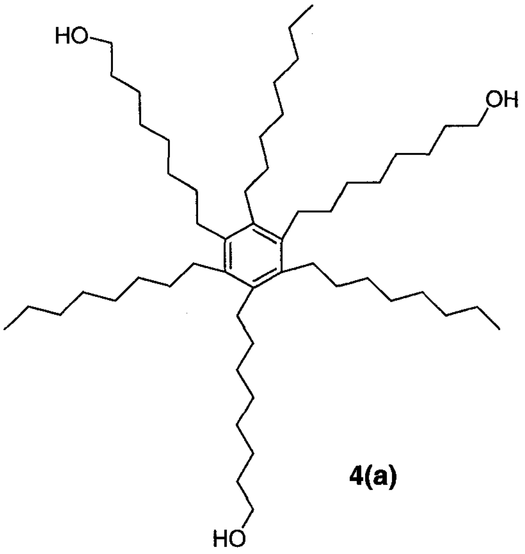
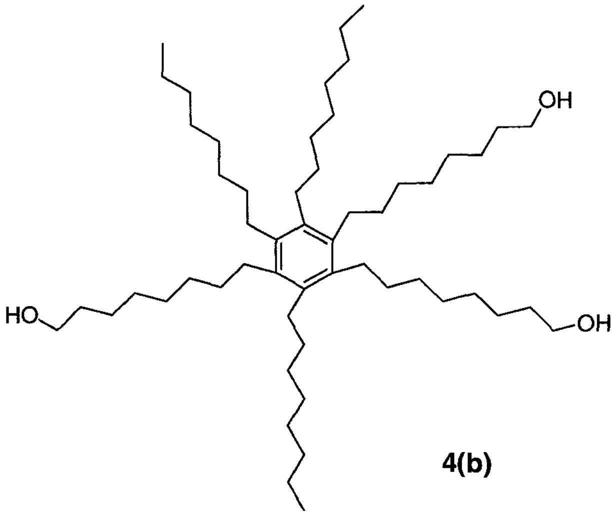


**Figure 5-1:** Chemical Shifts of Aromatic Carbons on Aromatic Triols 4(a) and 4(b) in $CDCl_3$



**4(a)**



**4(b)**

**Figure 5-2:** Structures of Aromatic Triols 4(a) and 4(b) in only four peaks being observed. Although a decoupled $^{13}$C-NMR experiment is not quantitative, it is visible from the first spectrum in **Figure 5-1** that the ratio (intensities) of the four peaks of **4(a)** is 1:2:2:1 indicating that the peaks at 136.69 and 136.81 ppm represent two carbons each. Triol **4(b)**, because of its unsymmetrical structure, produces a spectrum that shows the six aromatic carbons to be all chemically different from each other resulting in six peaks within the range 136-137 ppm and approximately the same peak intensities.

In order to solidify our arguments, a $^{1}$H-NMR experiment in $C_6D_6$ was carried out. The signals for the methylene protons adjacent to the hydroxyl group occur between 3.30 and 3.50 ppm, as expected (**Figure 5-3**). It can be seen in that $C_6D_6$, the three different methylene protons in the asymmetric triol **4(b)** occur in the $^{1}$H-NMR spectrum as three triplet peaks. Also from $^{13}$C-NMR of the aromatic carbons in **4(a)** and **4(b)** (**Figure 5-4**), only two separate peaks were observed for the symmetric triol **4(a)** in a 1:1 intensity ratio, whereas four distinct peaks were observed for the asymmetric triol **4(b)** with an intensity ratio of 2:1:2:1. This further establishes our assignment of the symmetric and asymmetric triols **4(a)** and **4(b)**.

When **4(a)** and **4(b)** were analyzed on a TLC plate with hexane and ethyl acetate (1:1) as the eluent, the $R_f$ of **4(a)** and **4(b)** were 0.45 and 0.55 respectively. The symmetric isomer beeing more polar than the asymmetric one could be as a result of intra-molecular hydrogen bonding. Triol **4(b)** has two adjacent side chains with terminal hydroxyl groups, which could potentially increase the formation of intra-molecular hydrogen bonding between the two hydroxyl groups, resulting in a little lower polarity of the molecule.

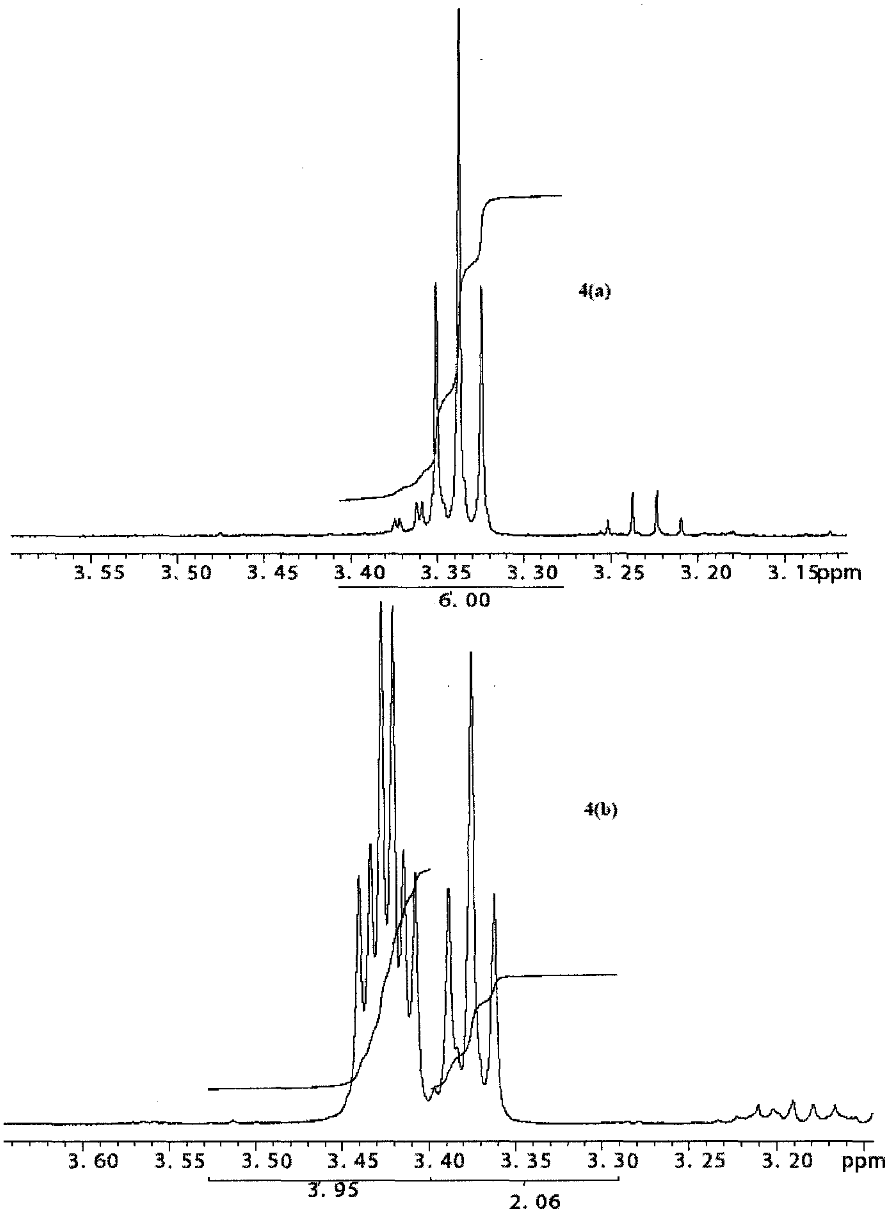


**Figure 5-3:** $^1$H-NMR Splitting Patterns of Methylene Protons ($CH_2OH$) on Aromatic Triols 4(a) and 4(b) in $C_6D_6$

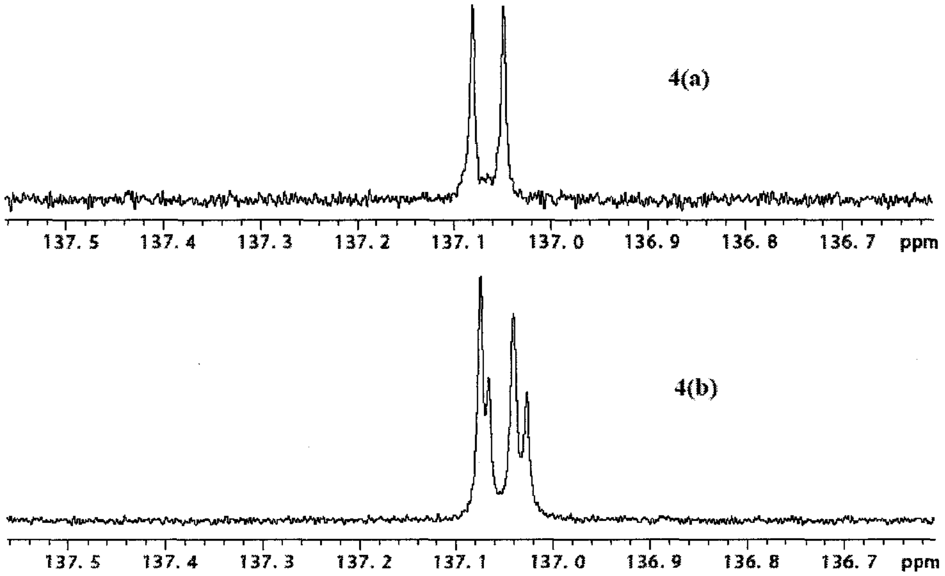


**Figure 5-4:** $^{13}$C-NMR Splitting Patterns of Aromatic Carbons on Aromatic Triols 4(a) and 4(b) in $C_6D_6$

In the IR spectra of the fatty alkynes, the carbon- carbon triple bond stretch which usually occurs at 2150 $cm^{-1}$ was not observed. Infrared absorption spectra result from changes of the molecular dipole caused by bond vibration (stretching, bending, scissoring, etc) in a molecule. The greater the changes in dipole, the more intense the peaks become. However, the disubstituted fatty alkynes possess two long saturated carbon chains on either side of the centrally located triple bond, so that the triple bond stretch changes very little of the molecular dipole, making detection of the triple bond stretch difficult by infra-red spectroscopy.

DMSO was used in the dehydrobromination step to accelerate the reaction rate. This method was developed by Silbert (Silbert, 1984), who found that a 3-5 mol ratio of DMSO to dibromostearic acid (DBSA) at a reaction temperature of 100 °C favorably converted the dibromide to stearolic acid within 2 hours. In our study, a higher ratio was used considering that the starting oleic acid or erucic acid was 90 % pure, and the impurities could be some polyunsaturated fatty acids, which could lead to poly-brominated substrates.

In conclusion, we have reported a general strategy for the synthesis and purification of symmetric and asymmetric aromatic triols and triacids along with the analytical techniques useful for isomer-specific analysis. This general synthetic scheme should also prove useful for the synthesis of hexa-substituted benzene derivatives from other fatty alkynes.

## 5.4. References

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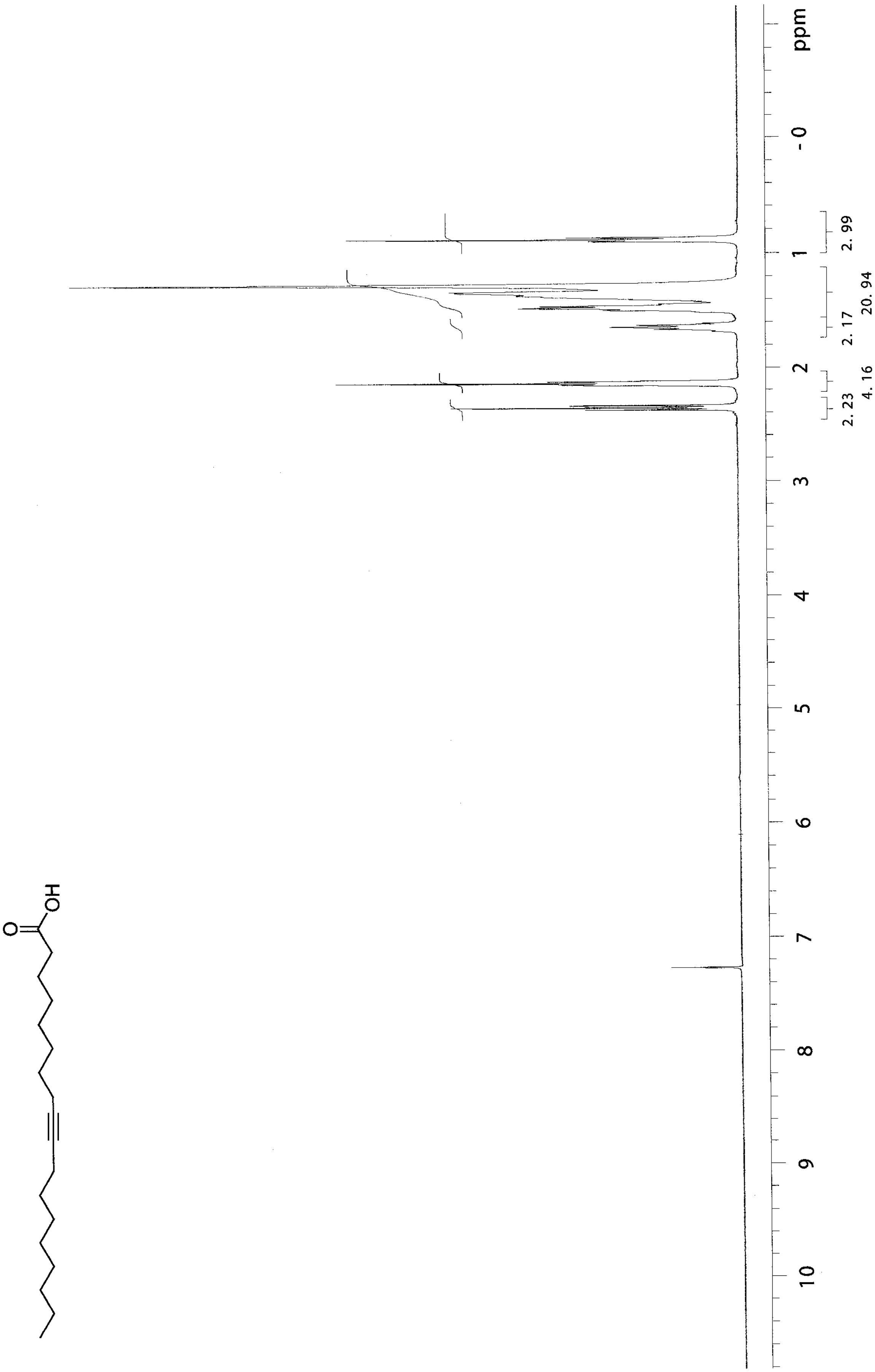
## 5.5. Appendix: Chapter 5 NMR Spectra



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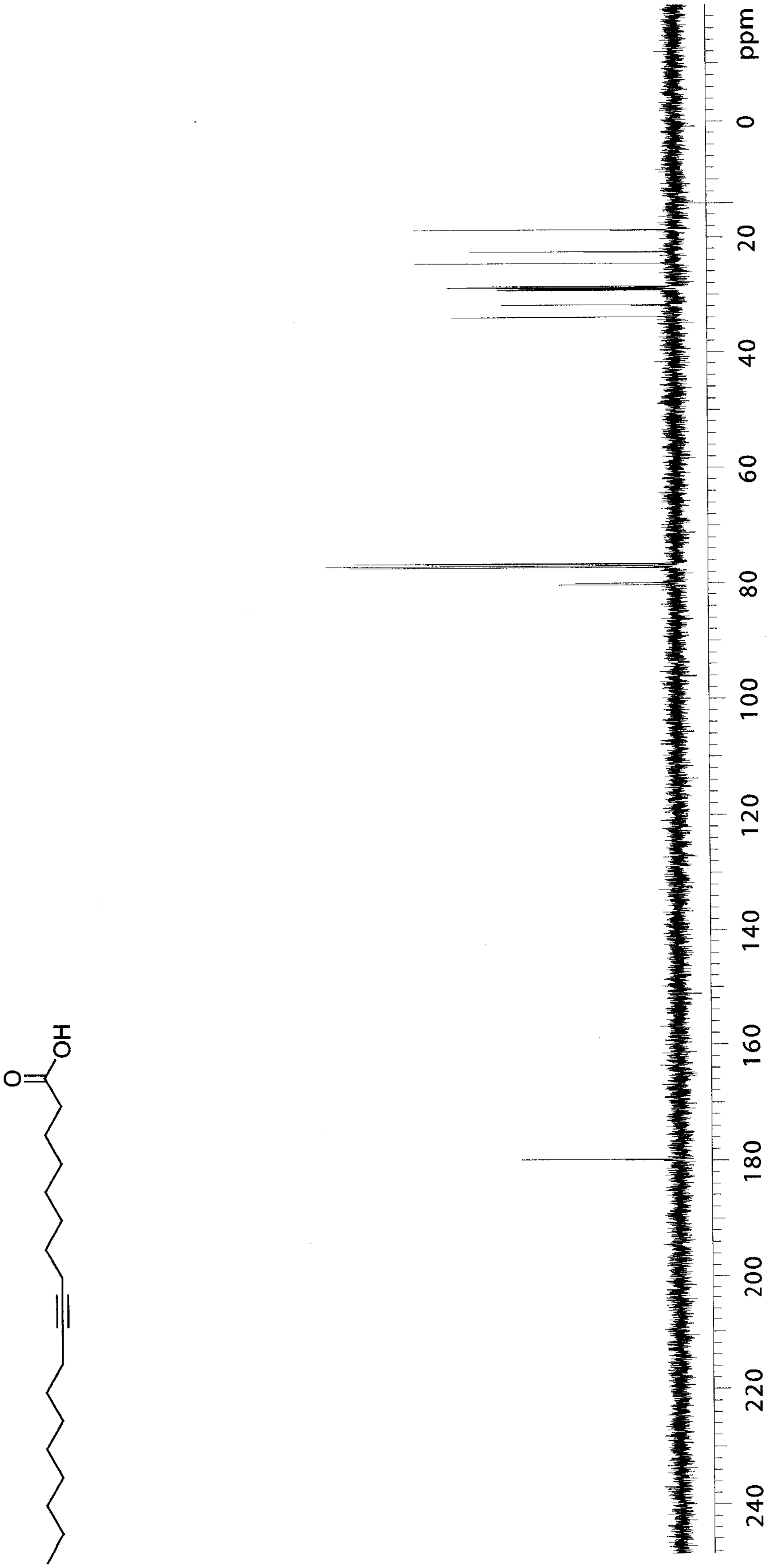
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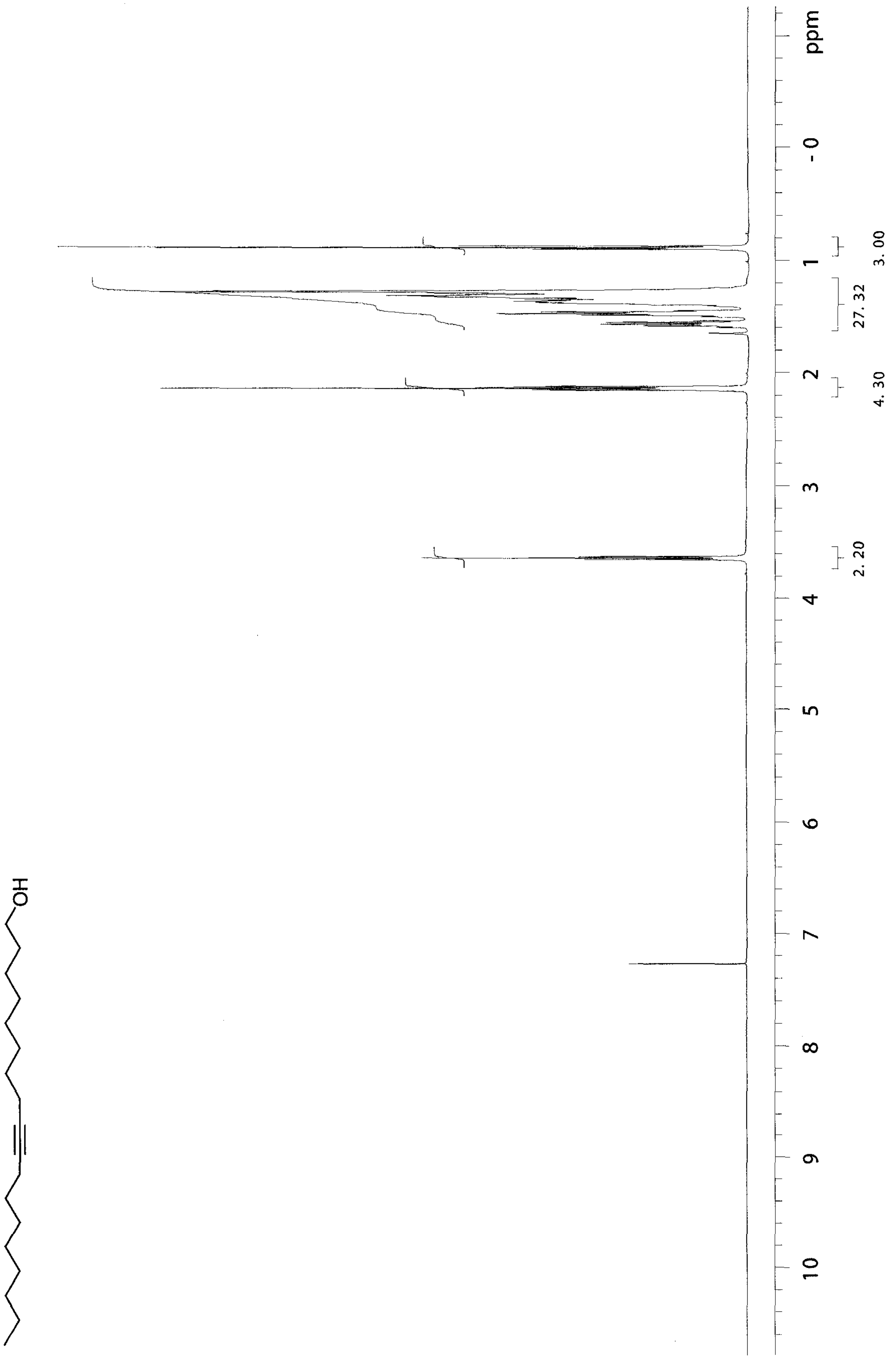
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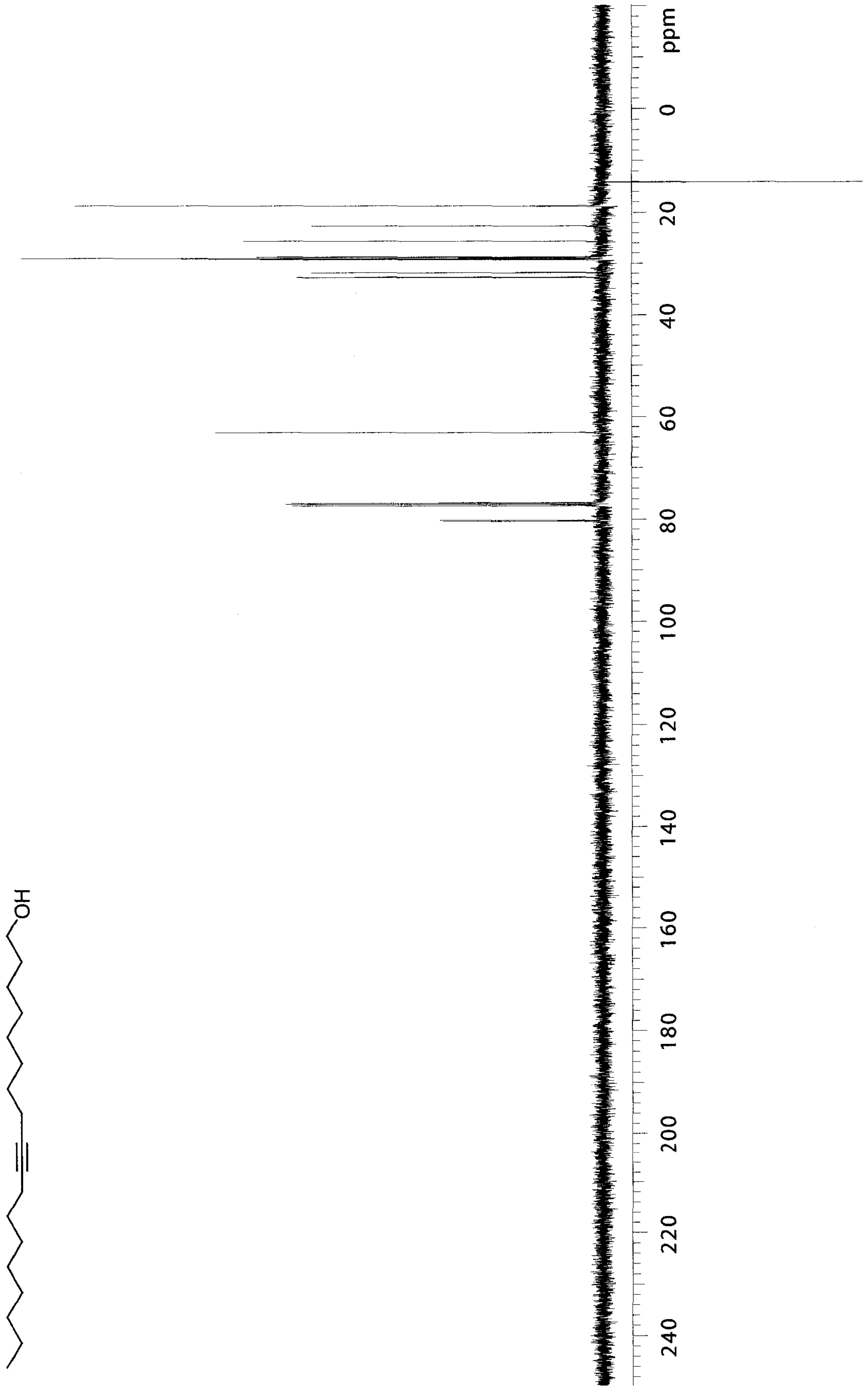
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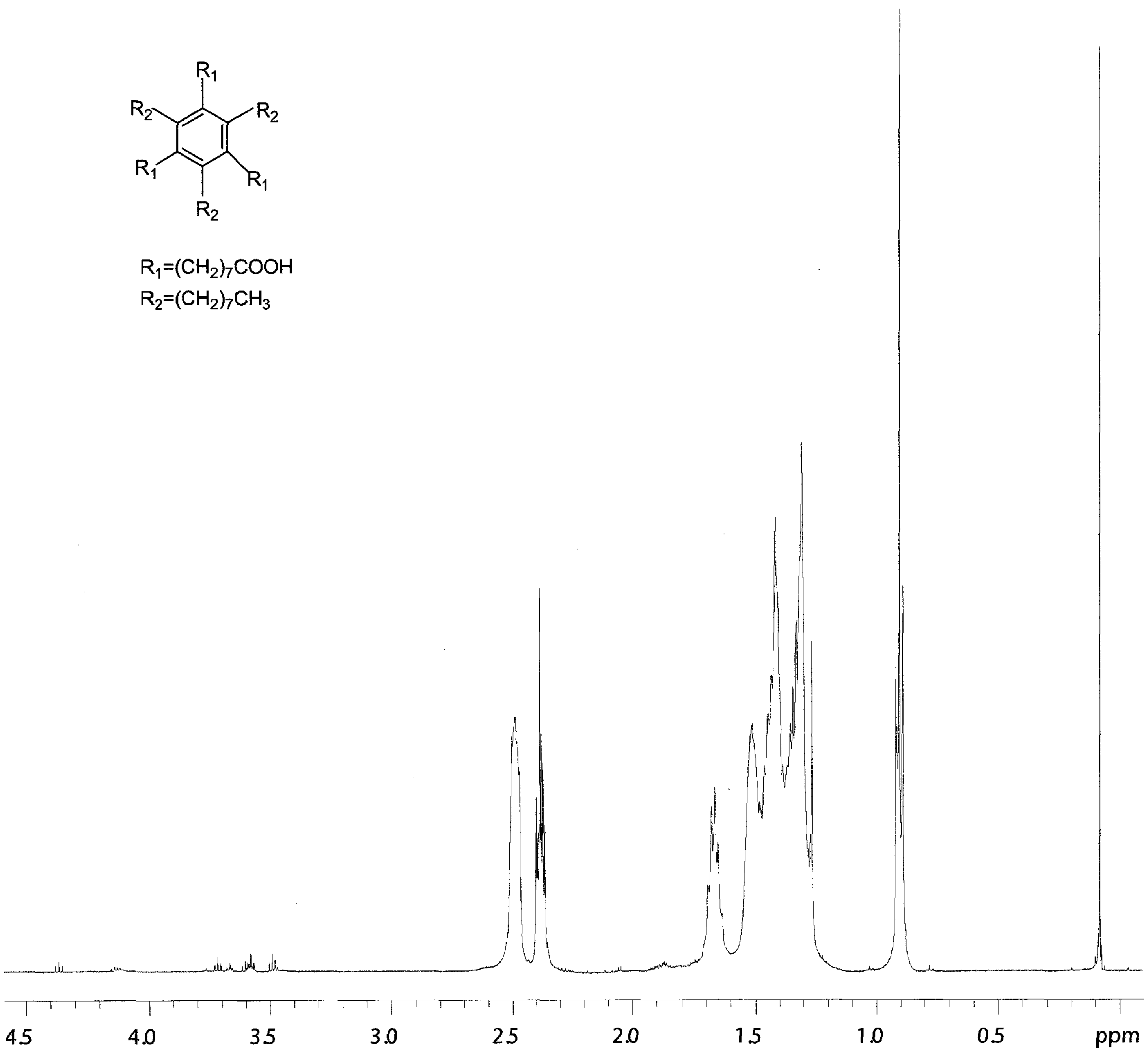
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R2
R1
R1
R2
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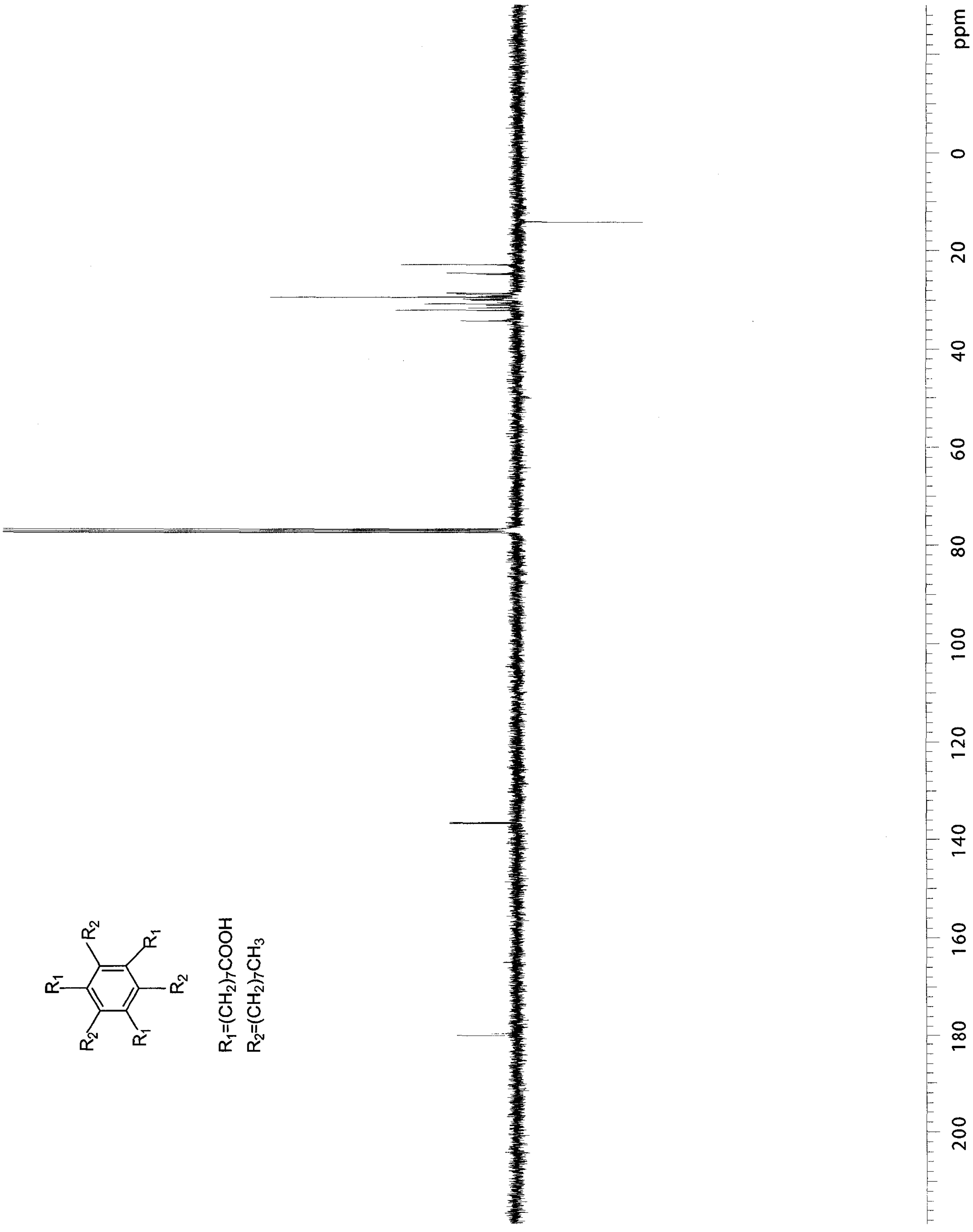
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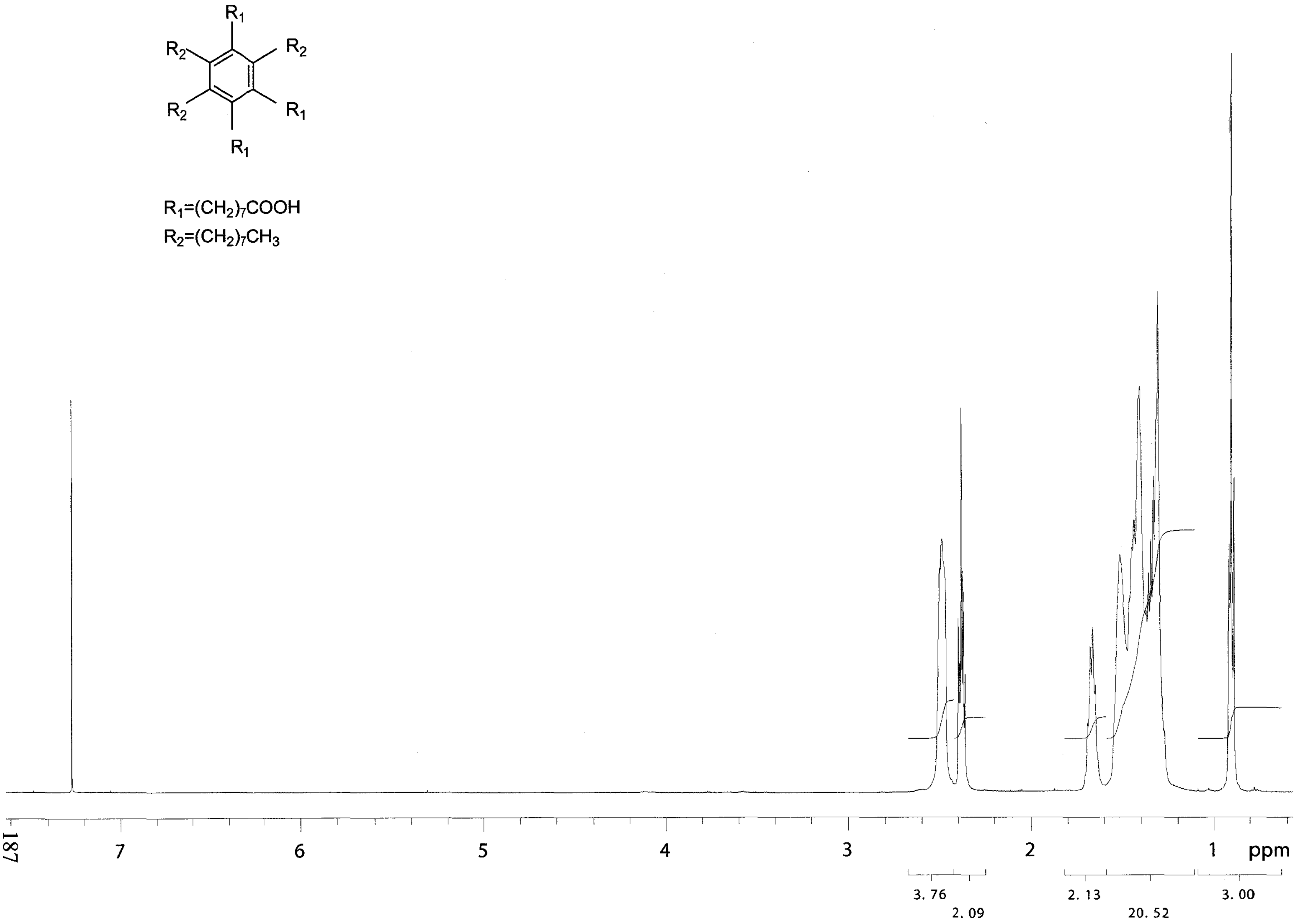

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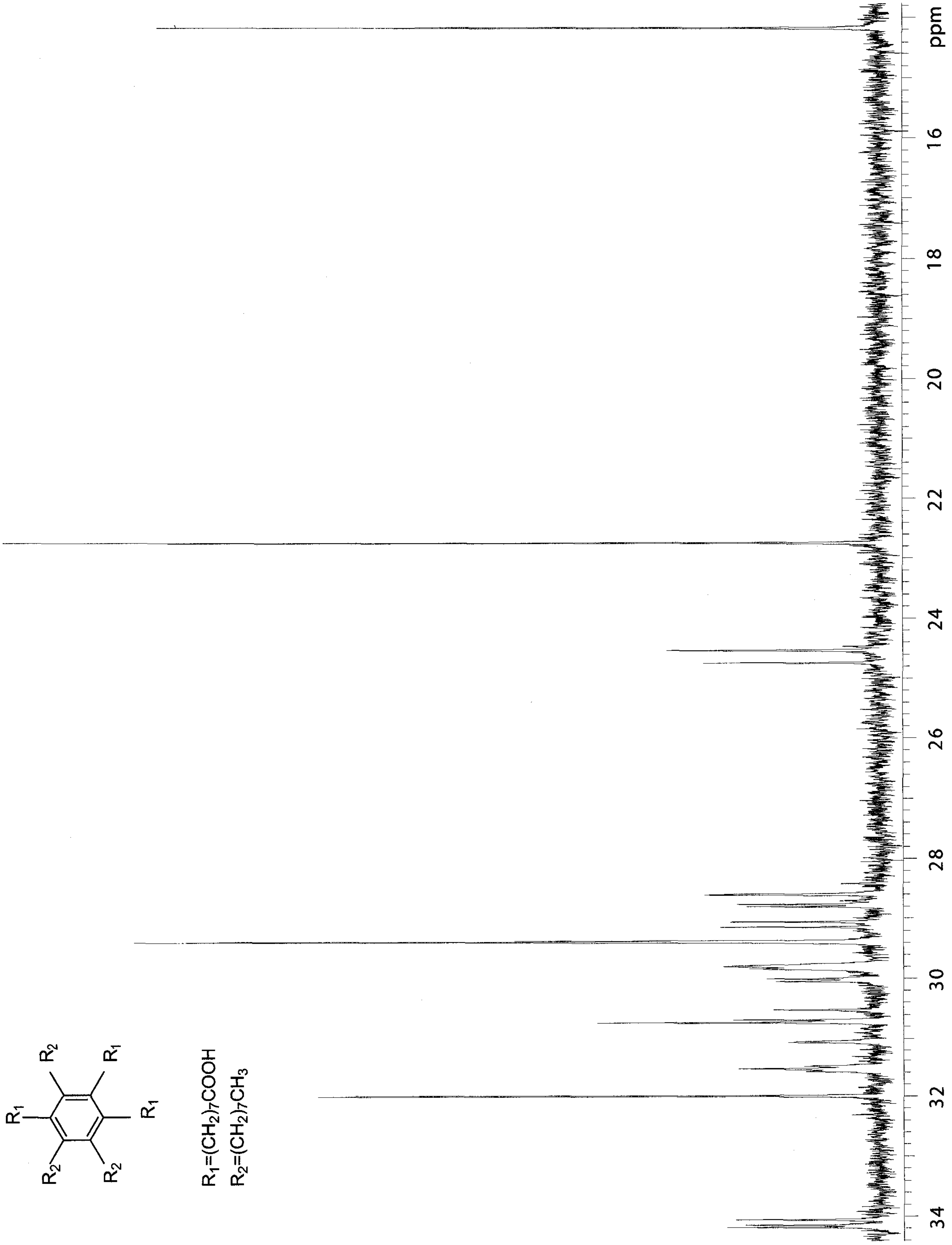

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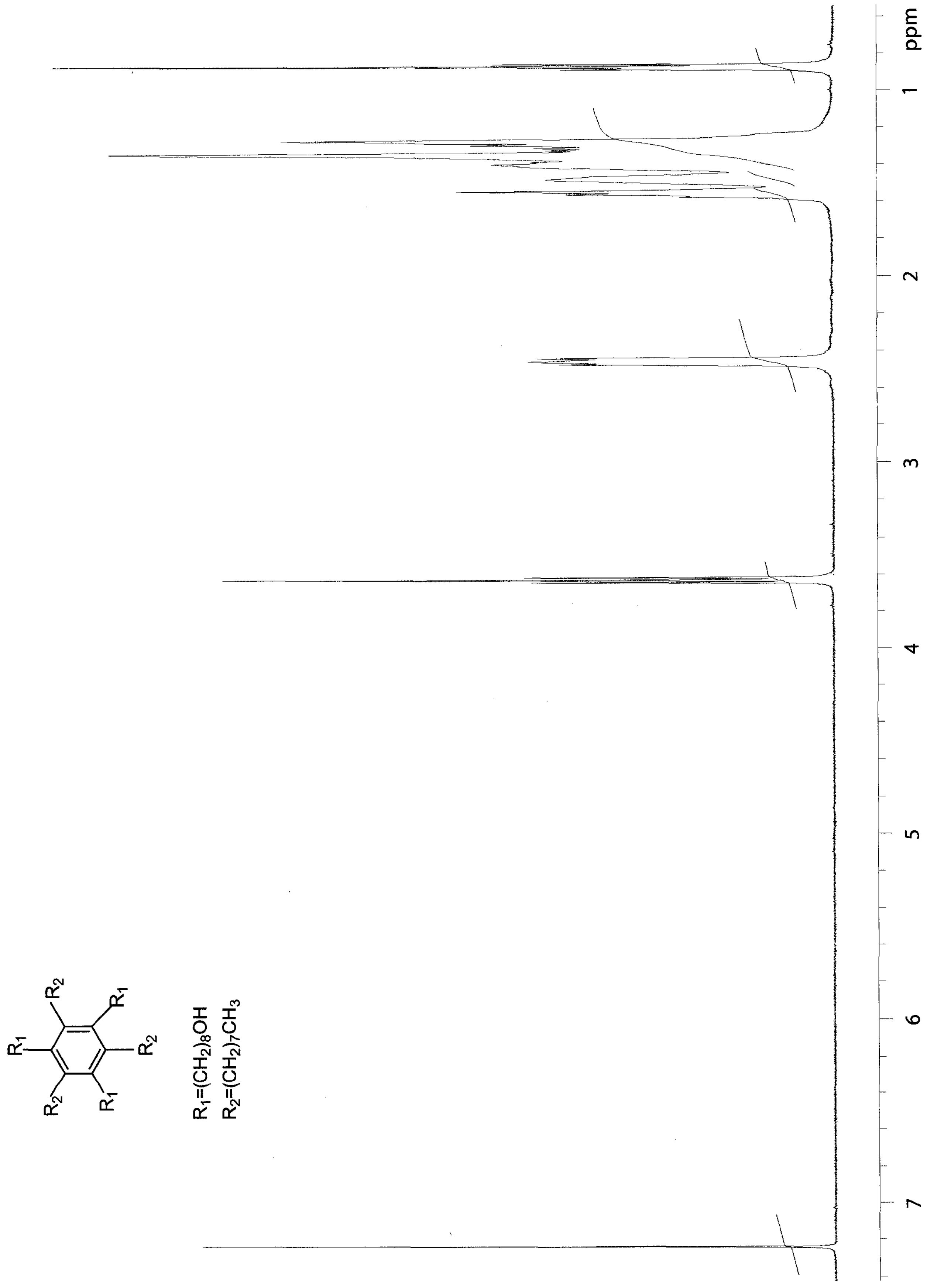
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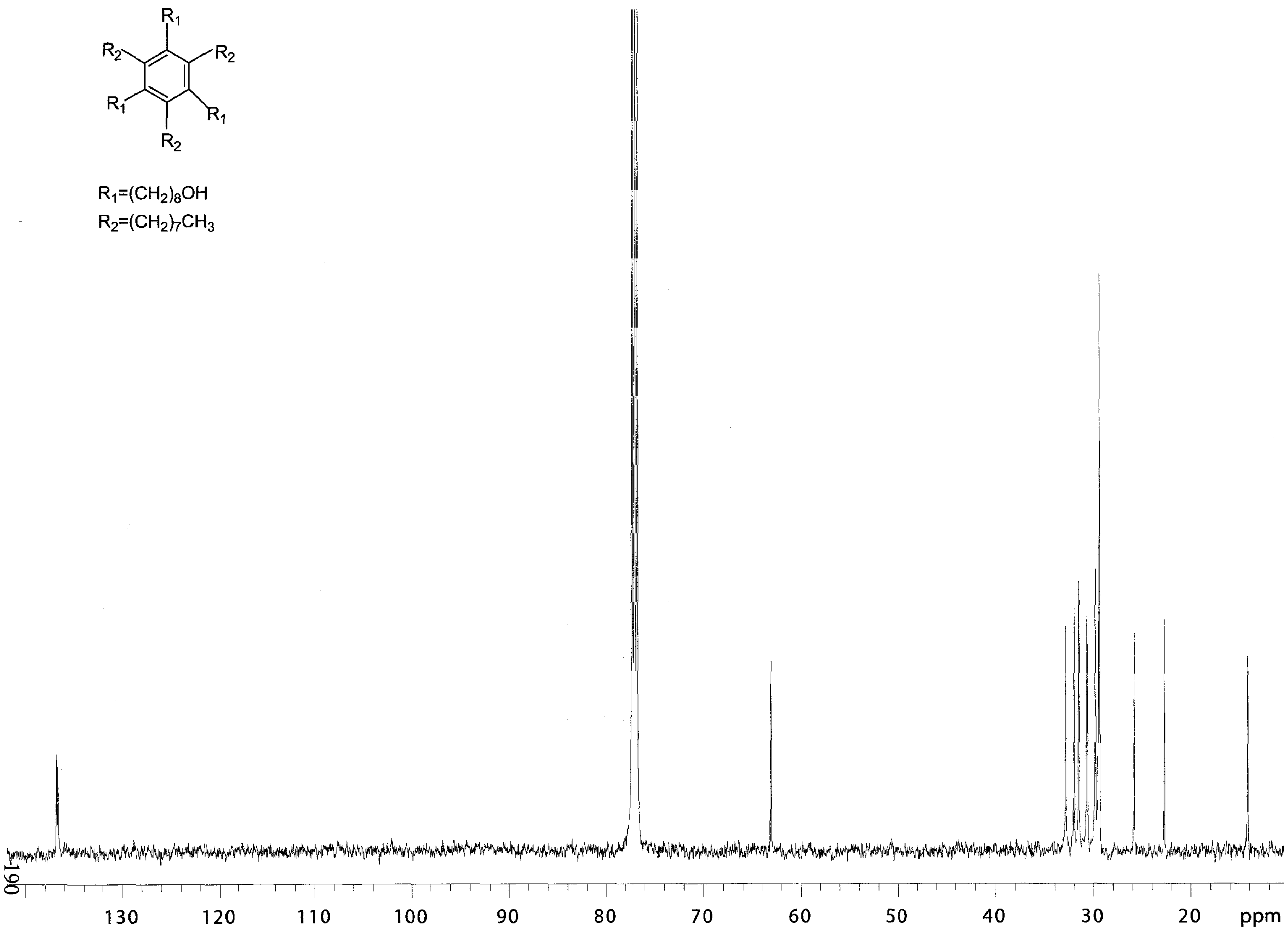
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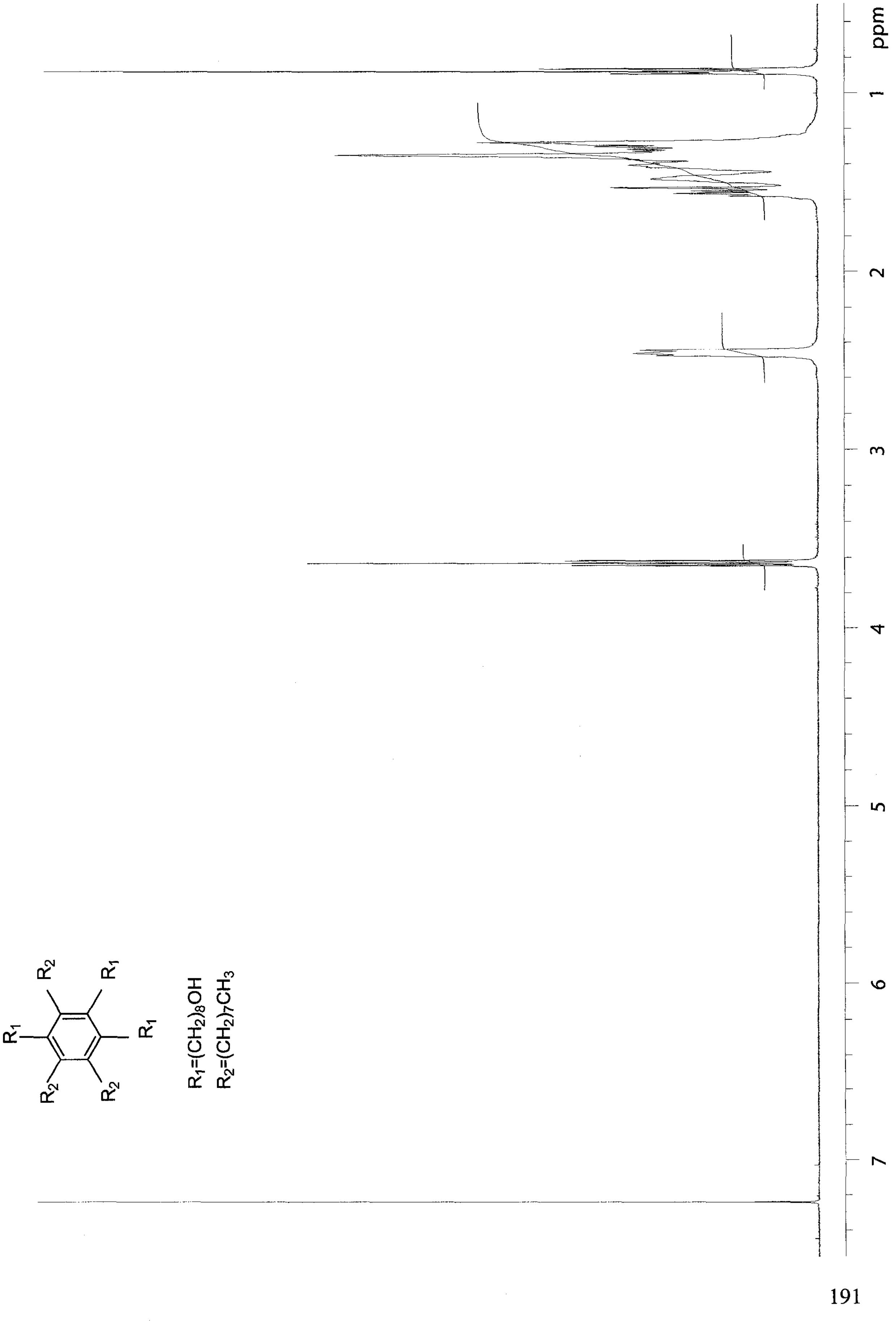
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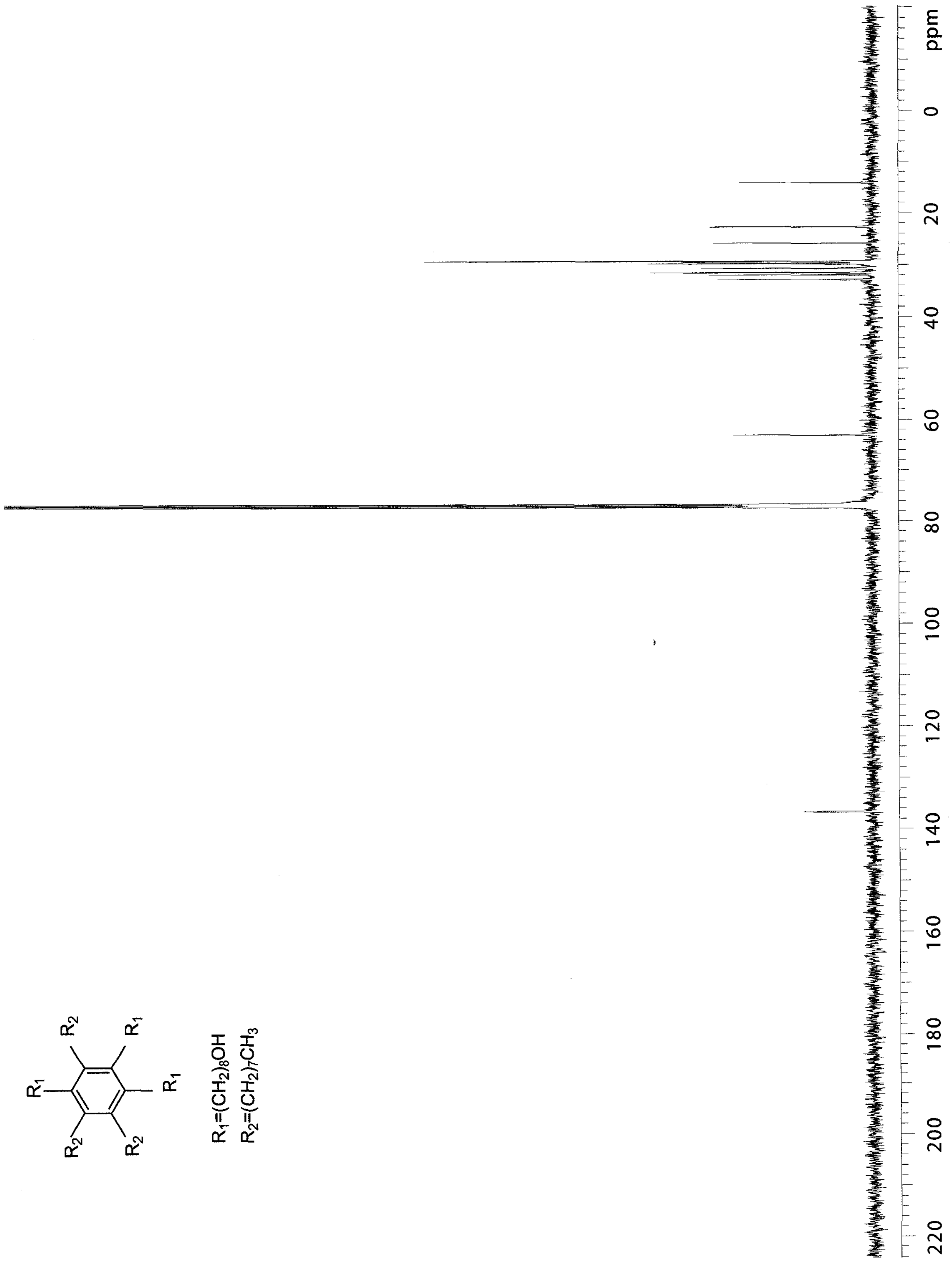
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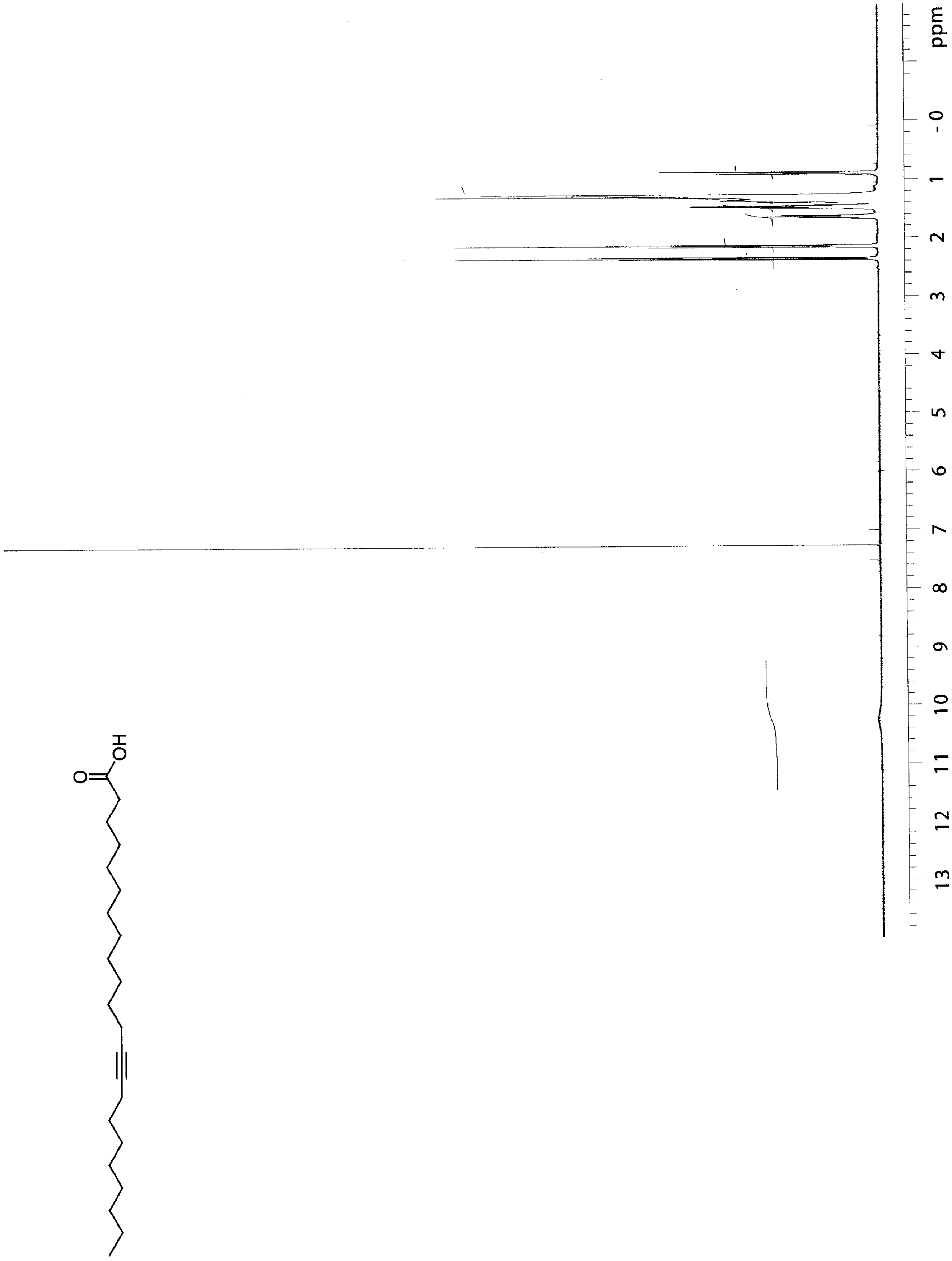
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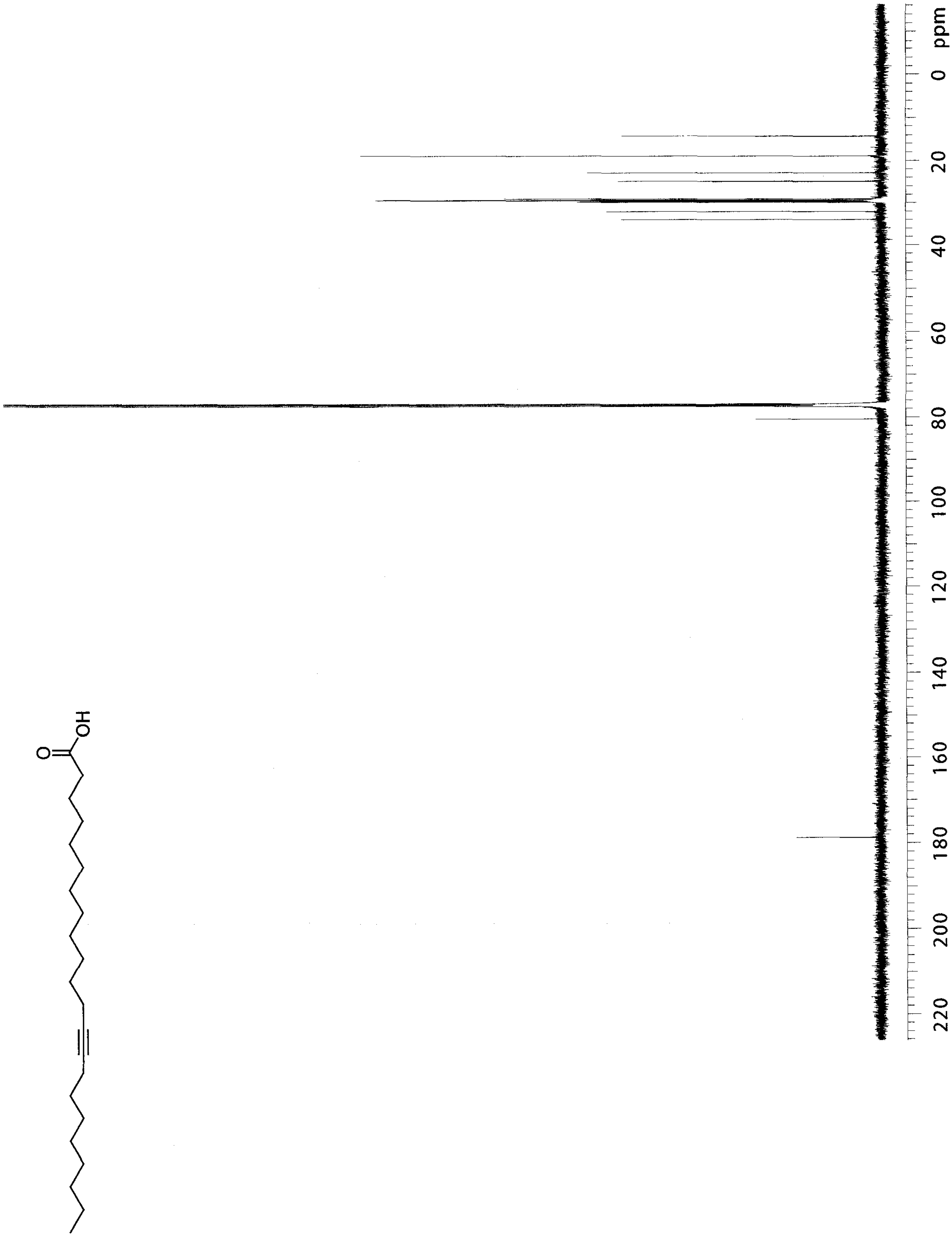
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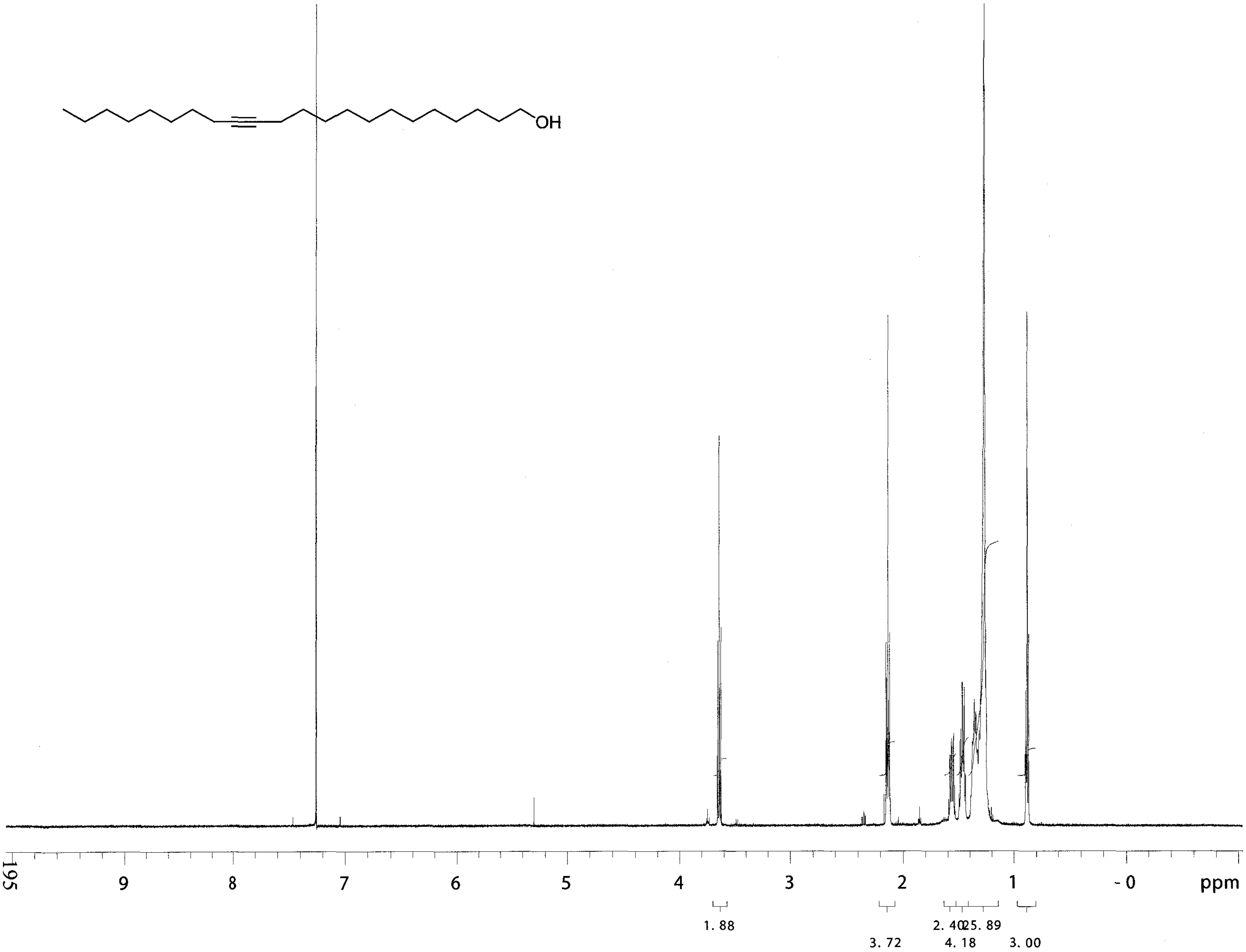
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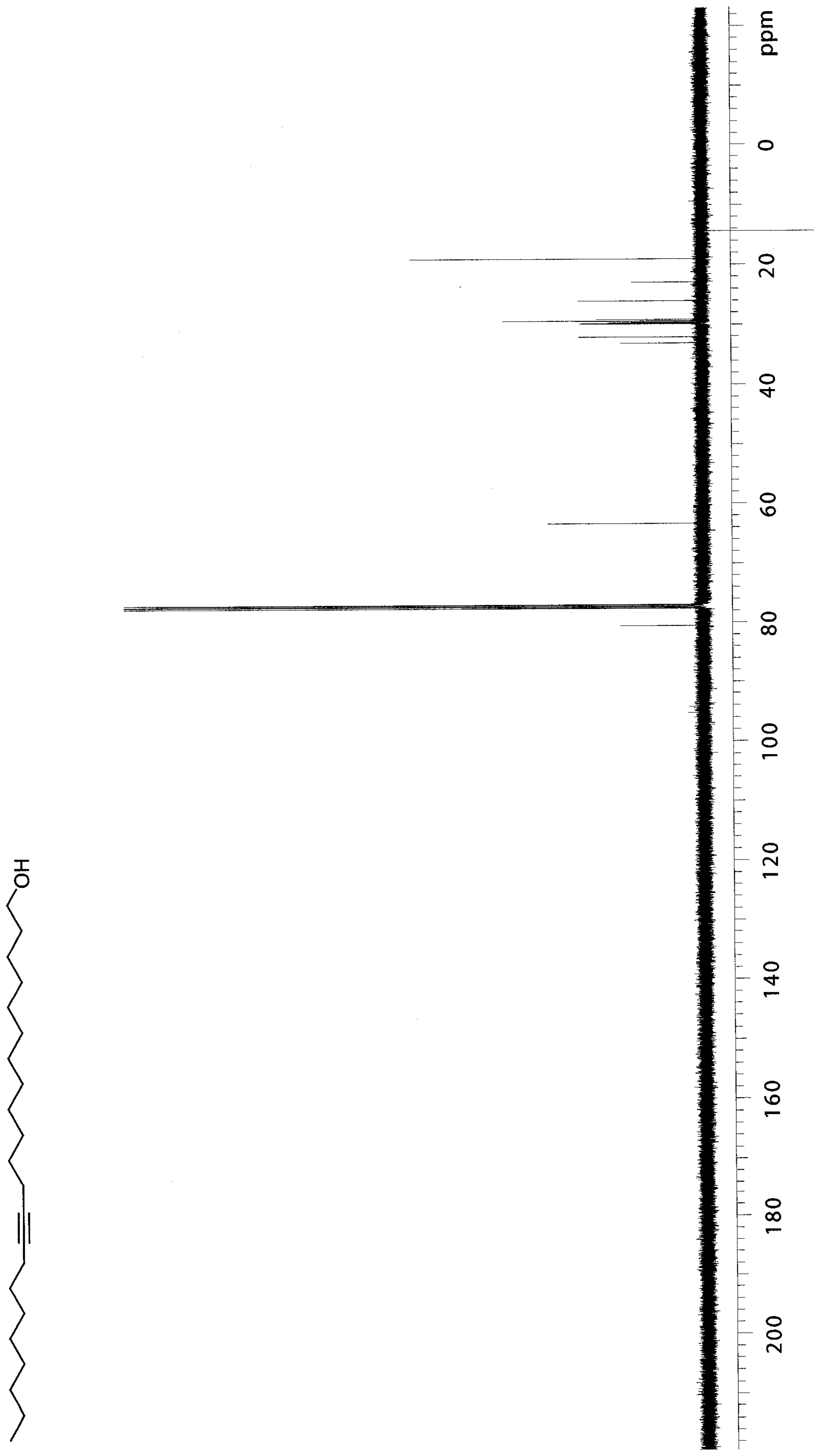
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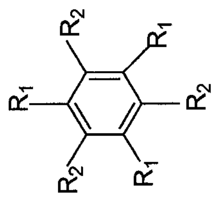

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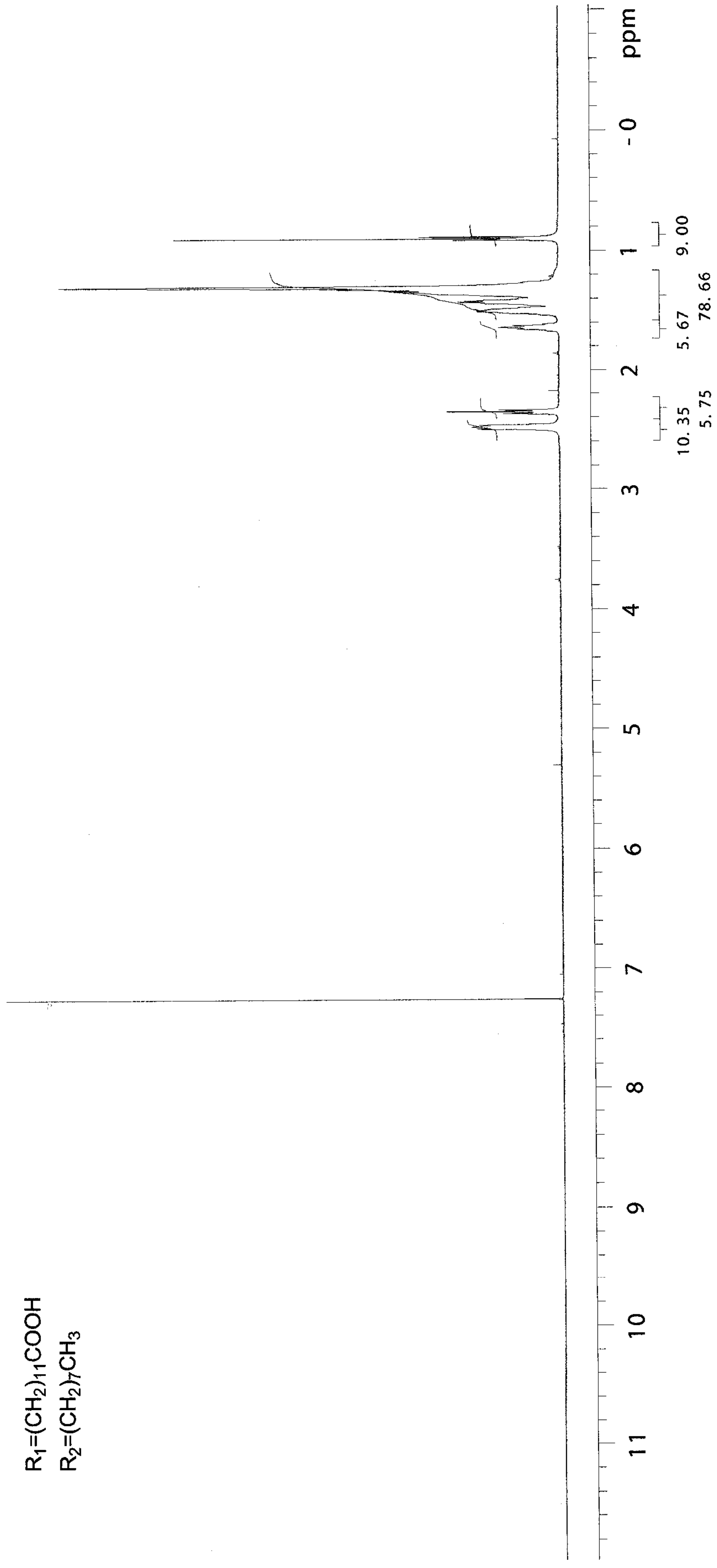

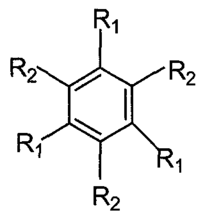

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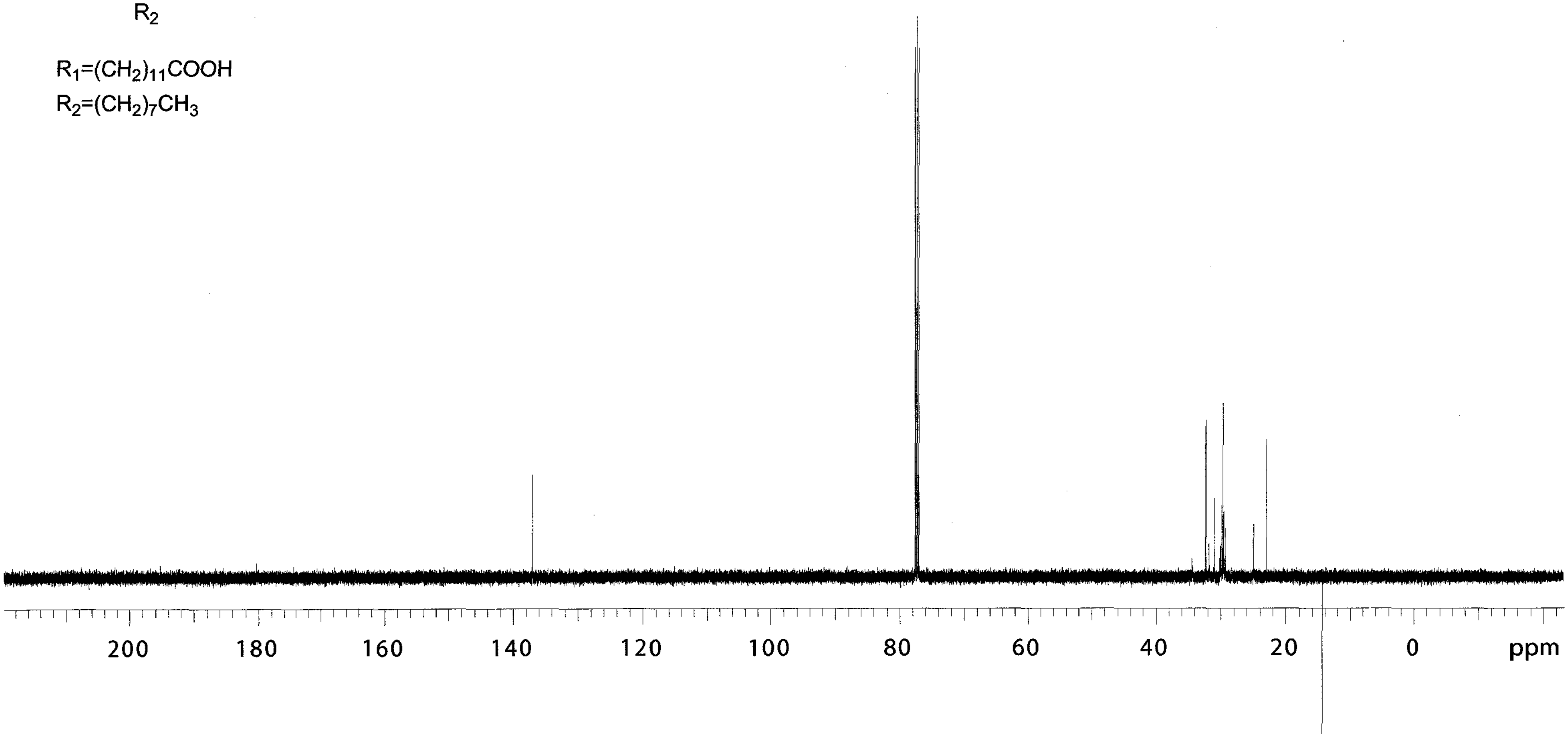

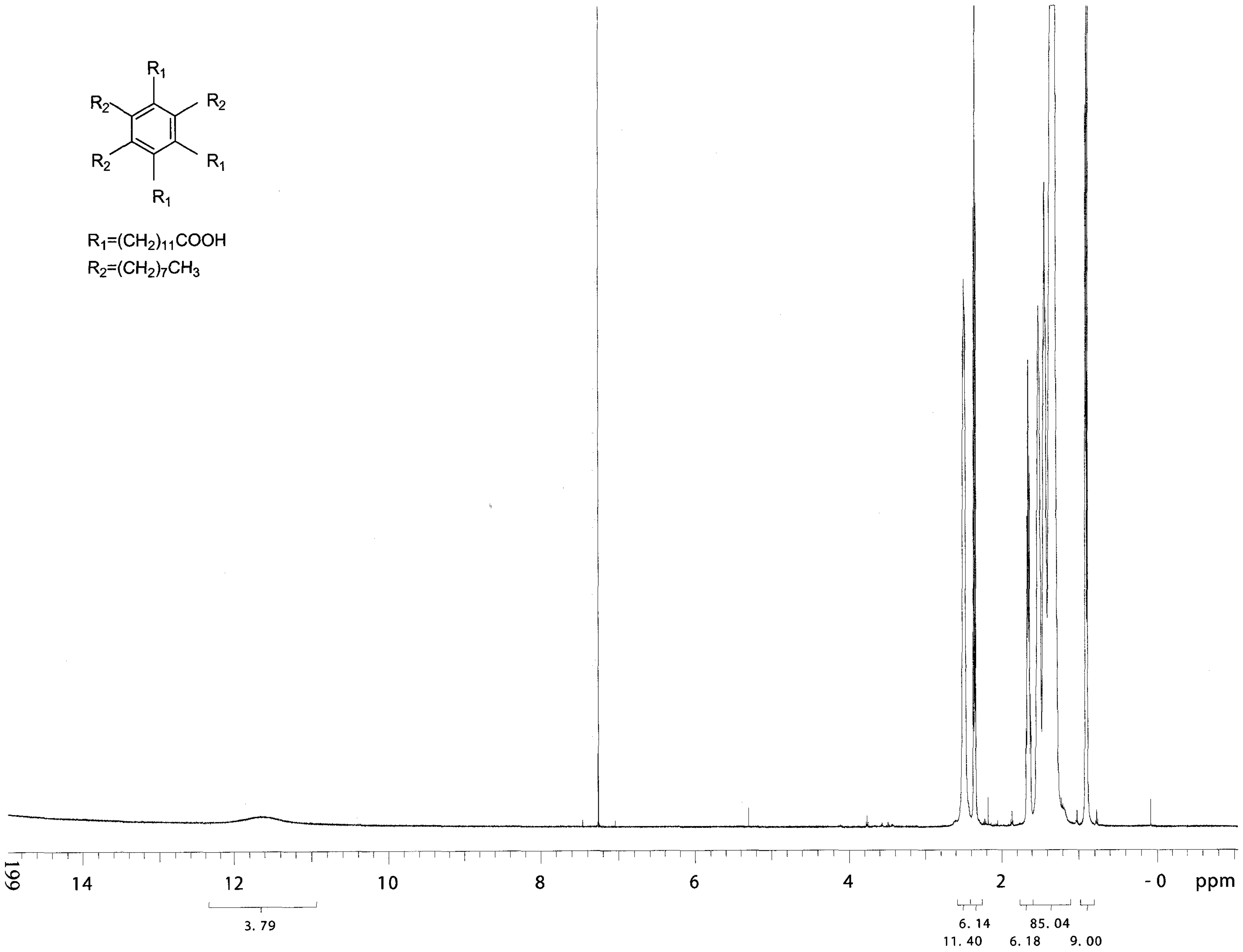

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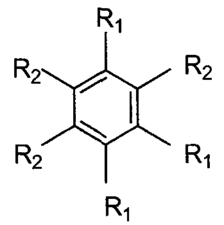

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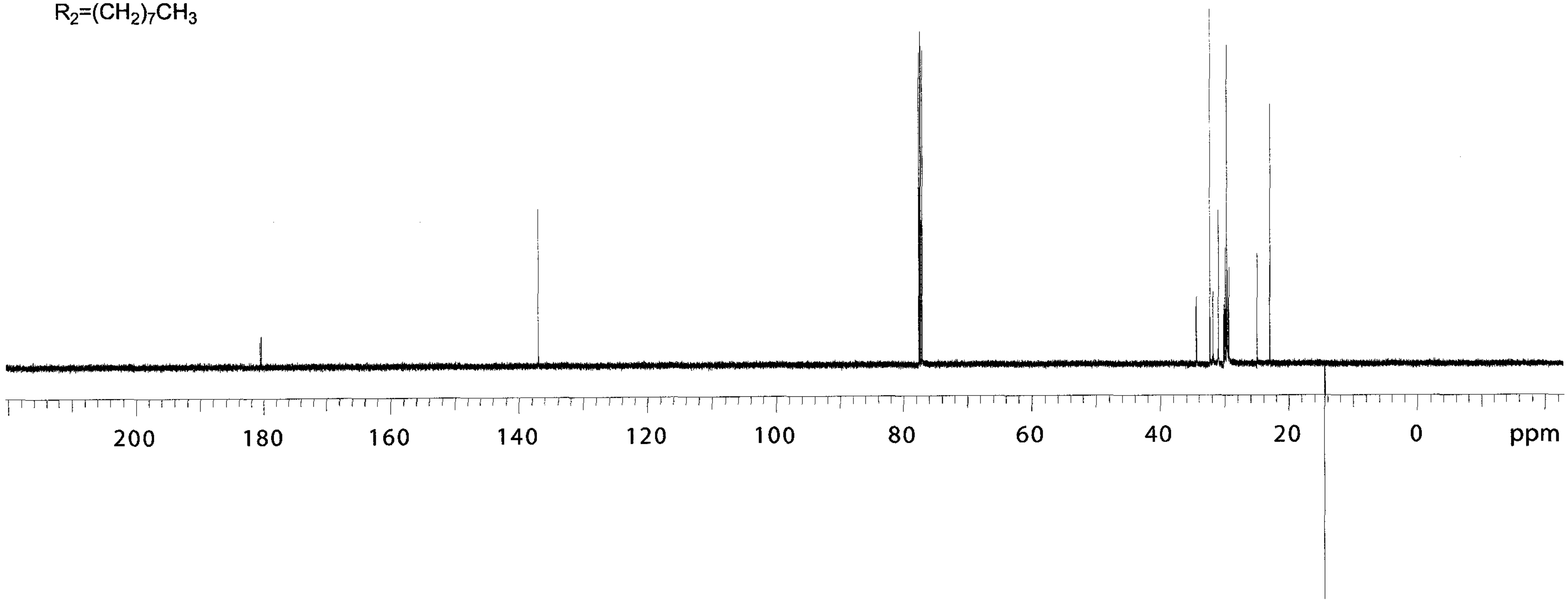
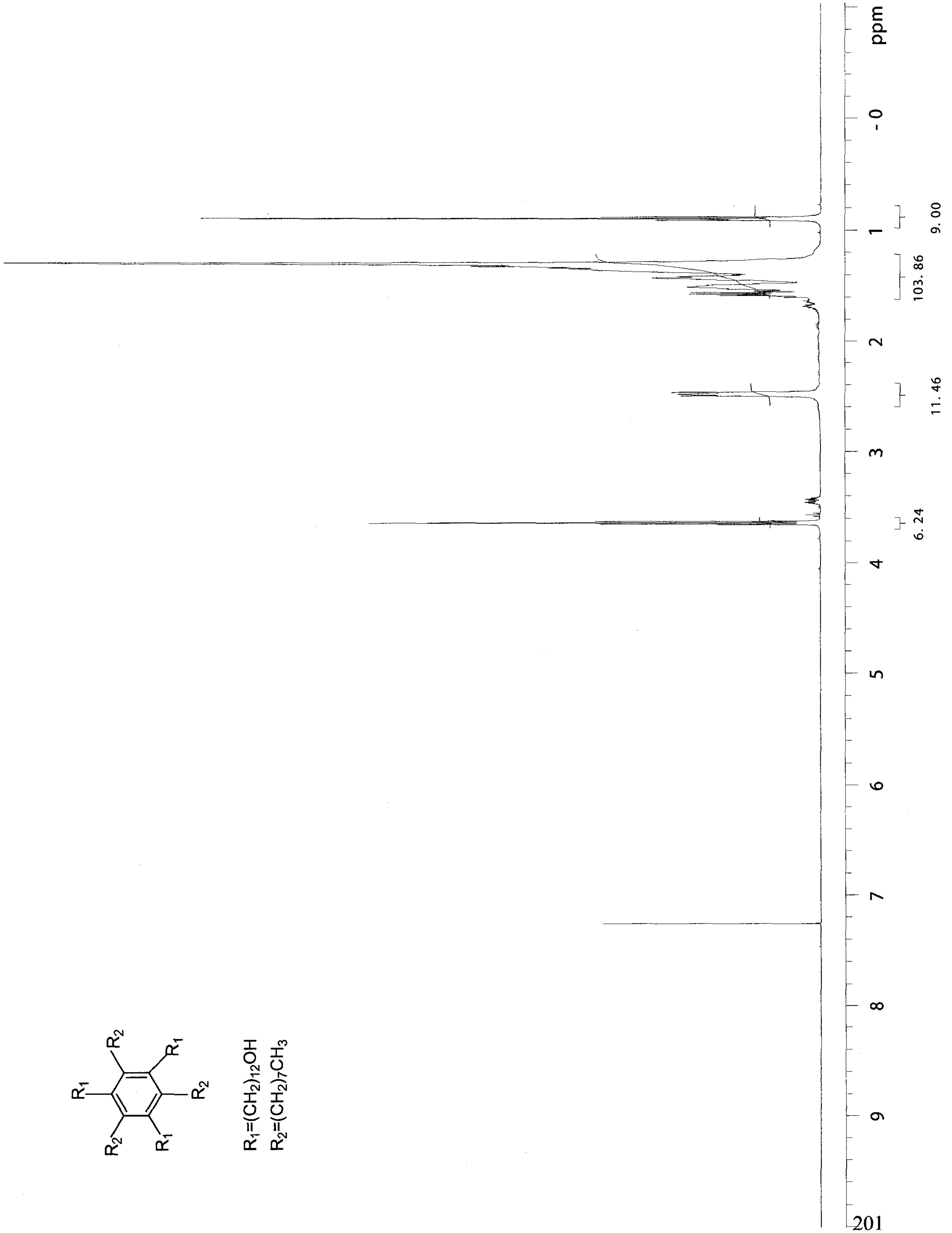
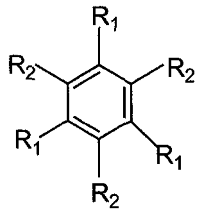
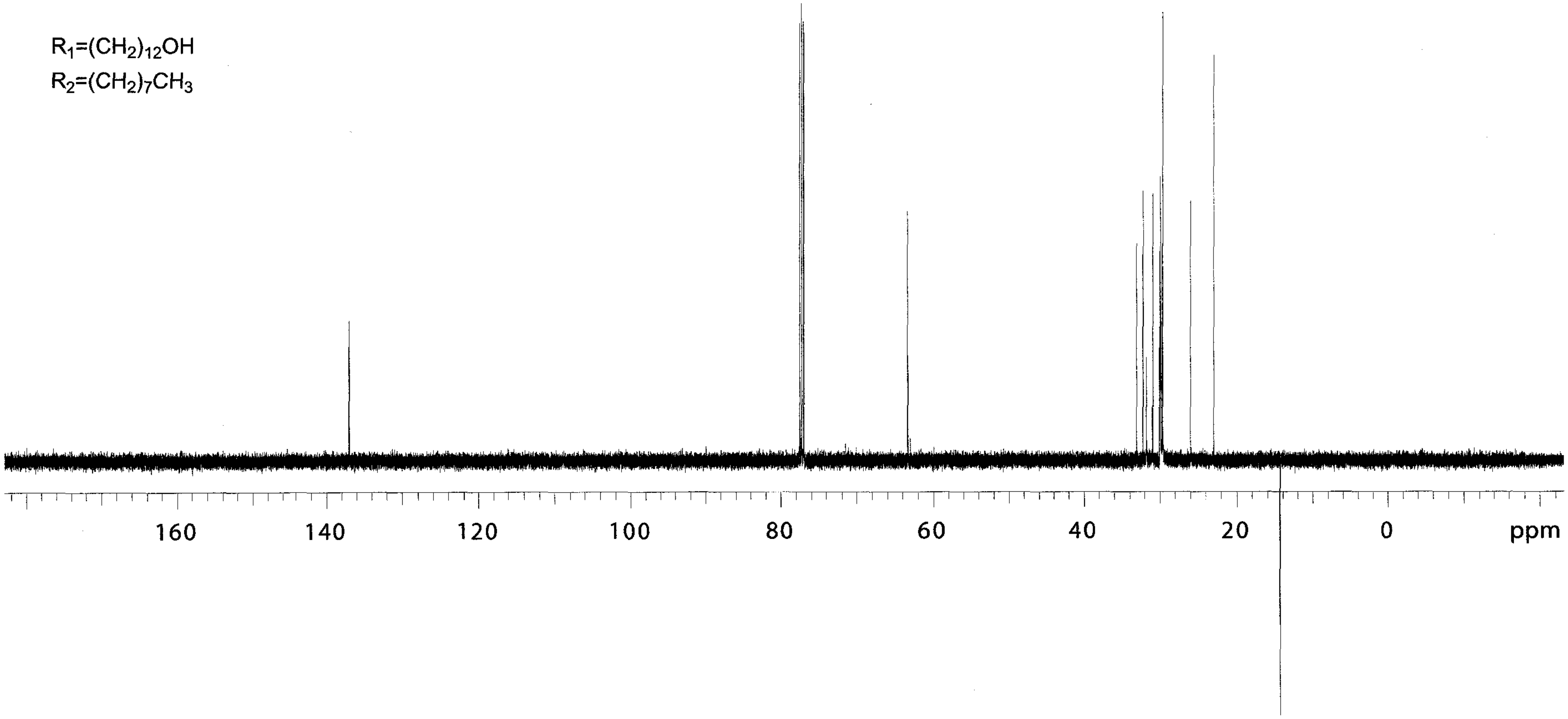


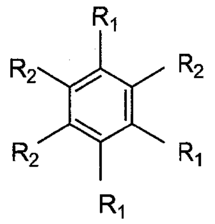


$R_1=(CH_2)_{12}OH$
$R_2=(CH_2)_7CH_3$



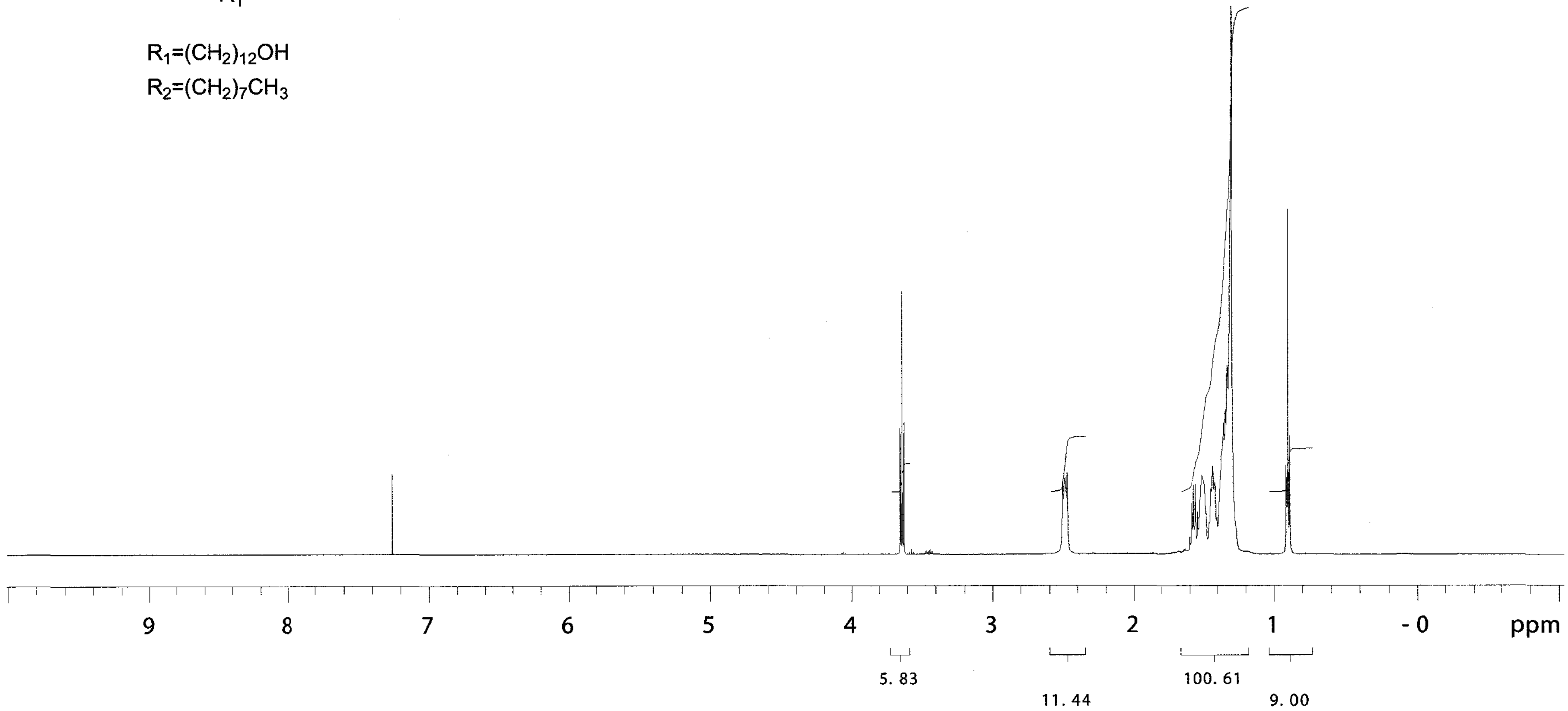
$R_1$=$(CH_2)_{12}OH$
$R_2$=$(CH_2)_7CH_3$

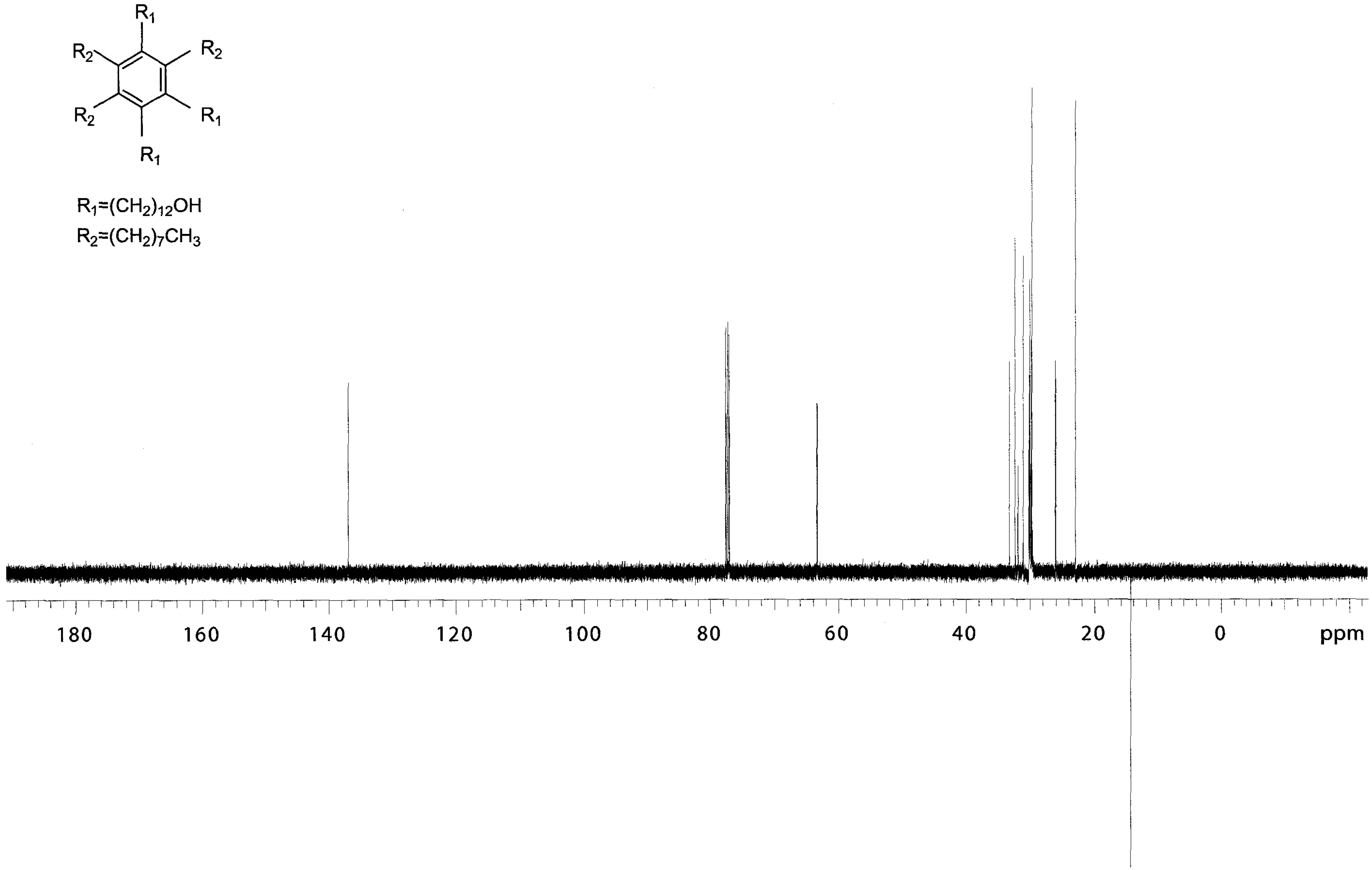




$R_1=(CH_2)_{12}OH$

$R_2=(CH_2)_7CH_3$




R1
R2
R2
R2
R1
R1
R1=(CH2)12OH
R2=(CH2)7CH3
180
160
140
120
100
80
60
40
20
0
ppm

# 6 Conclusion

This research project was focused on chemically modifying vegetable oil and its derivatives into aliphatic or aromatic triols and triacids, which will act as potential monomers for the production of polymeric materials such as polyurethanes, polyesters, polyamides etc. Analytical methods have also been developed in order to identify or separate the products obtained.

Aliphatic polyols with terminal hydroxyl functionalities have been produced from canola oil, as shown in Chapter 2. Ozonolysis has been utilized to cleave the double bonds on the unsaturated TAGs and this has been followed by a catalytic hydrogenation step to reduce the ozonides into alcohols. Flash chromatography with gradient flow elution has been used to separate out the products from the polyol reaction mixture. After identifying the structures by IR, $^1$H NMR, $^{13}$C NMR and Mass Spectrometry, it has been found that the components were saturated TAGs, mono-ols, diols and triols. Thereby hypotheses 1, 2, and 3 have been addressed and whilst not conclusively proven, have been shown to be applicable.

In the first case where first generation polyols are produced (Generation I), as described in Chapter 2, ozonolysis has been carried out in water and hydrogenation has been carried out in THF. For production of the second generation of polyols (Generation II), as discussed in Chapter 4, ethyl acetate has been used as the only solvent for all reactions. An aldehyde product has been formed after zinc treatment of the ozonide. The aldehyde ester has then been reduced to the corresponding alcohol ester by catalytic hydrogenation under comparatively mild conditions. Following these modifications, the hydroxyl number has been highly improved while the acidity number decreased.

An HPLC-ELSD method as stated in hypothesis 4 has been developed for separating and quantifying the polyol products; This is shown in Chapter 3. Linear calibration curves have been obtained for the mono-ol, diol and triol components with correlations ($r^2$) above 0.98. According to the standard curves and their HPLC-ELSD chromatograms, the content of mono-ol, diol and triol have been obtained.

Utilizing pure oleic acid and erucic acid as the precursors, hexasubstituted benzene derivatives such as aromatic triols and triacids have been synthesized, as shown in Chapter 5. Bromination of the alkene functionality in the fatty acids (oleic acid or erucic acid) followed by dehydrobromination have produced the corresponding alkynoic acids (stearolic acid or behenolic acid). Cyclotrimerization of these alkynoic acids using palladium-on-carbon (Pd/C) and chlorotrimethylsilane (TMSCl) yielded a mixture of two isomers: the symmetric and asymmetric forms. The asymmetric isomer, which is the main product, has been separated from its symmetric isomer by flash chromatography and a gradient flow elution. Hence hypothesis 5 has been demonstrated to be plausible.

Since aromatic tracids and triols have been successfully synthesized from oleic acid, which is the main fatty acid component of canola oil, the same procedures have been tried on pure canola oil. Canola oil has been first saponified with sodium hydroxide in methanol. After acidification, the mixture of fatty acids (including oleic, linoleic, linolenic, palmitic and stearic acid) underwent a bromination step, followed by dehydrobromination. The product was then poured into 2 N hydrochloride acid containing ice chips, a solid was precipitated. The solid has been collected, dried and analyzed by $^{1}H$-NMR, $^{13}C$-NMR and GC-FID. The product has been identified to be pure stearolic acid, the alkynoic acid derived from oleic acid. It is assumed that the same aromatic triacids and triols could be synthesized from canola oil as from pure oleic acid, which supports hypothesis 6.

In this study, methods have been developed to synthesize some value-added materials from vegetable oil (a renewable resource). These bio-based products are potentially useful monomers for the production of polymeric materials, which traditionally are mainly synthesized from petro-chemicals. Since petroleum resources are limited and declining, this study has shown the practicality and significance of this research.

Based on the techniques developed and results obtained in the lab, the future research has been planned as follows:

1. Production of polyols from canola oil via ozonolysis and hydrogenation will be scaled up in a pilot plant;
2. Hydrogention will be attempted in order to reduce the alkynoic acids into corresponding alkynols, which is a precursor to produce aromatic triol;
3. Other catalyst (instead of Pd-C/TMSCl) will be tried on cyclotrimerization of alkynoic acid to produce a more regioselective product, i.e. asymmetric isomer only;
4. Fatty acids extracted from waste steams of the refining process of canola and flax oils (soapstock and deodorizer distillate) will be utilized as the starting material to synthesize aromatic triacids and triols.