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Plastic from Plants: Synthesis and evaluation of new polymers from sustainable bio-based sources

Thesis submitted to the University of Nottingham for the degree of Master of Research in Chemistry

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Table of Contents

Abstract

Conventional plastics impose a significant burden on the natural environment due to their non-biodegradability and reliance on fossil resources. Therefore, the use of renewable energy sources for synthesising polymers is gaining increasing attention. This thesis details the synthesis of six novel monomers derived from the renewable biological source α-pinene. Multiple synthetic routes were systematically explored during the ring-opening step to generate key intermediates, enabling the synthesis of diol monomers bearing diverse functional groups.

Chapter 2 outlines the derivatization of α-pinene to access terpenoid-based monomers, resulting in compounds including diols, diallyl esters, and bifunctional monomers containing both acrylate and hydroxyl groups.

Chapter 3 begins with an evaluation of catalysts for subsequent polycondensation reactions, establishing $Ti(OBu)_4$ as the most suitable catalyst for diol monomers derived from α-pinene. Subsequently, various polymerization strategies were applied to the synthesized monomers. Polycondensation of different diol monomers afforded a series of novel polyesters, while step-growth polymerization yielded polyurethane prepolymers. Radical polymerization of the diacrylate monomer was attempted to form cross-linked polyacrylates; however, as the reaction did not proceed to the gel point, only linear polyacrylate was obtained.

Acknowledgements

I wish to express my immense gratitude to Professor Robert Stockman for the privilege of joining his research group. His invaluable guidance and patience gave me the confidence to overcome challenges. My sincere thanks also go to all members of the Stockman Group and the C13 lab for their camaraderie and support. I am equally indebted to my family and friends, and to my little dog Tutu, whose unwavering encouragement made my year abroad a joyful and memorable experience.

List of Abbreviations

(ACS Plus Extra Listed Below):

AA	Adipic acid
ADA	Aliphatic dicarboxylic acid
AIBN	Azobisisobutyronitrile
APO	α-Pinene oxide
ATR	Attenuated total reflection
ATRP	Atom transfer radical polymerization
BDO	1,4-Butanediol
BioPE	Bio-polyethylene
CA	Camphoric anhydride
CHO	Cyclohexene oxide
Đ, Mw/Mn	Dispersity
DBSA	*p*-Dodecylbenzenesulfonic acid
DMC	Dimethylcarbonate
DRI	Differential refractive index detector
EBiB	Ethyl 2-bromoisobutyrate
FDCA	2,5-Furandicarboxylic acid
GPC	Gel permeation chromatography
LDC	Limonene dicarbonate
LDO	Limonene dioxide
LO	Limonene epoxide
LPG	Liquefied petroleum gas
Mn	Number average molecular weight
Mw	Weight average molecular weight
MWD	Molecular weight distribution

PAPC	Poly(α-pinene carbonate)
PBS	Polybutylene succinate
PC	Polycarbonate
PE	Polyethylene
PET	Polyethylene terephthalate
PHB	Polyhydroxybutyrate
PLA	Polylactic acid
PLC	Limonene carbonate
PMDETA	N,N,N′,N′,N″-Pentamethyldiethylenetriamine
PMMA	Polymethyl methacrylate
POM	Polyoxometalate
PP	Polypropylene
PS	Polystyrene
PTA	Phosphotungstic acid
PVC	Polyvinyl Chloride
ROCOP	Ring-opening copolymerization
SA	Succinic acid
SSP	Solid-state polymerization
St	Styrene
T3P	Propylphosphonic anhydride
T_e	Decomposition temperature
Tg	Glass transition temperature
T_m	Melting temperature

List of Figures

List of Schemes

Plastics from Plants: Synthesis and evaluation of new polymers from sustainable bio-based sources

1.0 Chapter 1: Introduction

1.1 Plastic

Plastics are primarily composed of organic polymers, with conventional plastics mostly made from thermoplastic resins such as polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polypropylene (PP).[1] They are widely used in modern life due to their advantages of being lightweight, durable, and sturdy. However, the rapid expansion of global plastic production, with a cumulative output reaching 8.3 billion tons between 1950 and 2015,[2] has occurred alongside persistently inadequate management of plastic waste. As a result, significant quantities of plastic are discarded in landfills or released into natural ecosystems, presenting a pressing environmental challenge worldwide.[3]

1.2 Polymers

A polymer is a substance composed of molecules, formed of repeating units through a polymerization reaction to create macromolecules. The word 'polymer' was introduced by the Swedish chemist J. J. Berzelius.[4] The fundamental requirement for polymerization is that each monomer molecule must be capable of chemically bonding with two (or more) other monomer

molecules, meaning the monomer must possess two or more functional groups.[5] The structure, molecular weight, distribution, and terminal groups of polymers can all be precisely controlled through catalytic methods.

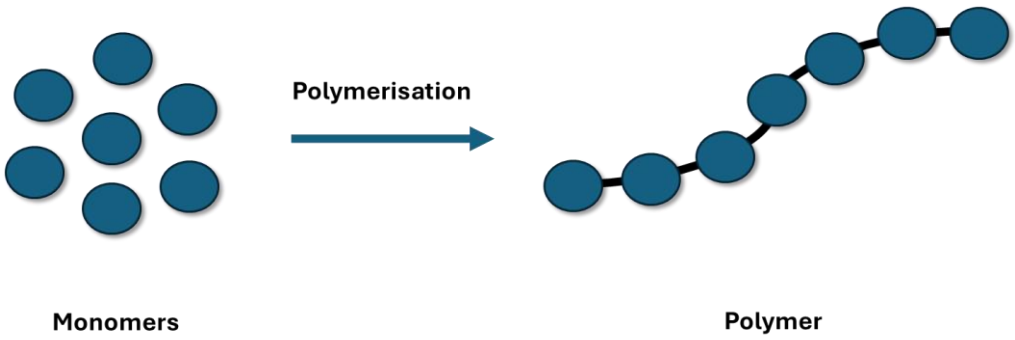


Figure 1: Simplified version of the polymer synthesis process.

Polymers are fundamentally classified into two categories based on their source: petroleum-based synthetic polymers and bio-based polymers. Petroleum-based synthetic polymers are primarily derived from non-renewable resources such as petroleum, natural gas, or coal. These materials are generally non-biodegradable and can persist in the environment for extended periods. In contrast, bio-based polymers originate from renewable resources. These materials are usually biodegradable (such as polylactic acid, PLA) and to a lesser extent non-biodegradable (such as bio-polyethylene, BioPE).[6]

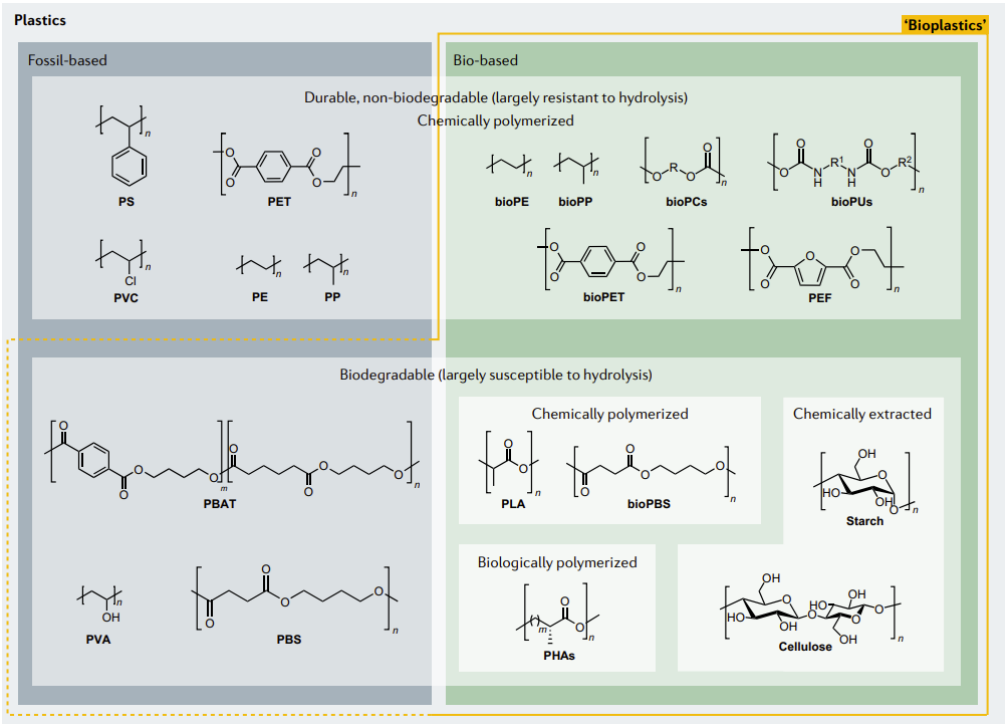


Figure 2: Structures of different Fossil-based and Bio-based polymers.[7] *Reproduced with permission from Springer Nature.*

Nevertheless, they are considered more environmentally sustainable due to their reduced reliance on finite fossil resources and their significantly lower carbon footprint compared to petroleum-based alternatives. Industrially relevant natural bio-based polymers are largely obtained from plant sources (including cellulose, hemicellulose, starch, and pectin) or animal sources (such as chitin and chitosan). A smaller proportion are chemically synthesized either from bacterial fermentation products or from bio-derived monomers. Certain bio-based polymers, notably polyhydroxybutyrate (PHB) and polylactic acid (PLA),[6] are extensively employed in the manufacture of biocompatible devices for surgical applications, drug delivery systems, cardiovascular implants, and dental materials. These biopolymers represent competitive alternatives to

conventional hydrocarbon-based polymers such as polyethylene (PE) and polystyrene (PS). In particular, PLA fulfils all the criteria of an ideal biomaterial. In contrast, PE faces limitations due to concerns regarding potential carcinogenicity, which may arise from contamination with residual styrene monomers.

Based on backbone structure, polymers can be categorized as linear, cyclic, branched, or network polymers. Variations in backbone architecture lead to distinct material properties. For instance, linear polyethylene exhibits a melting point approximately 20 degrees higher than that of its branched counterpart.[5] Network polymers demonstrate even more pronounced differences: they do not melt upon heating nor dissolve in solvents, although they may undergo significant swelling in certain solvents.[4,5]

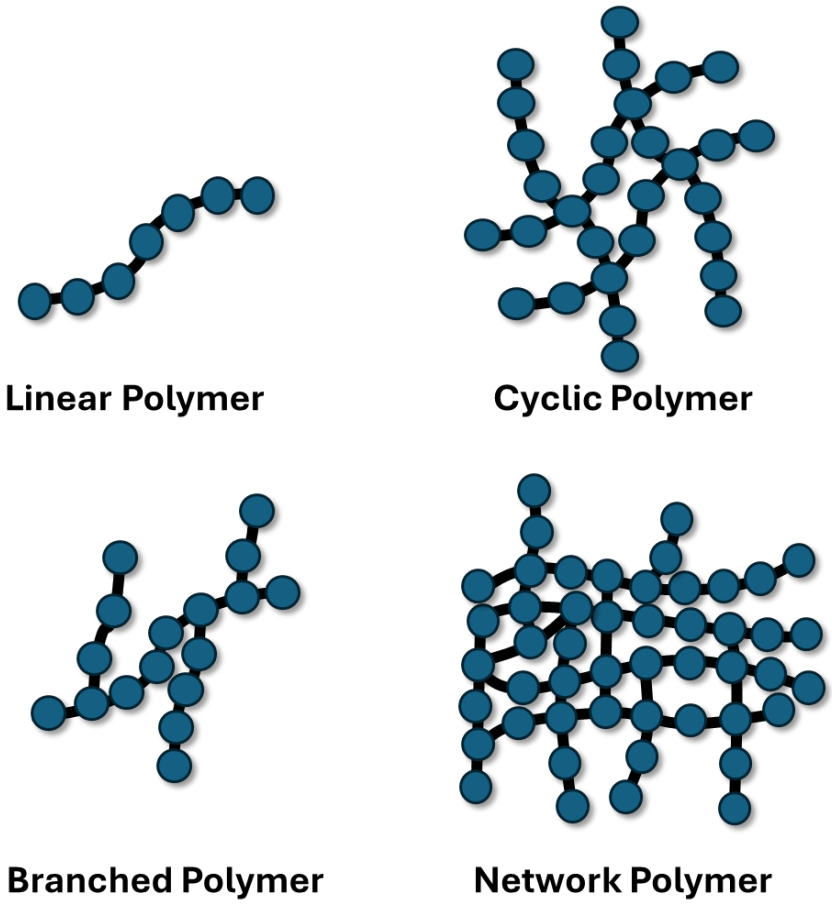
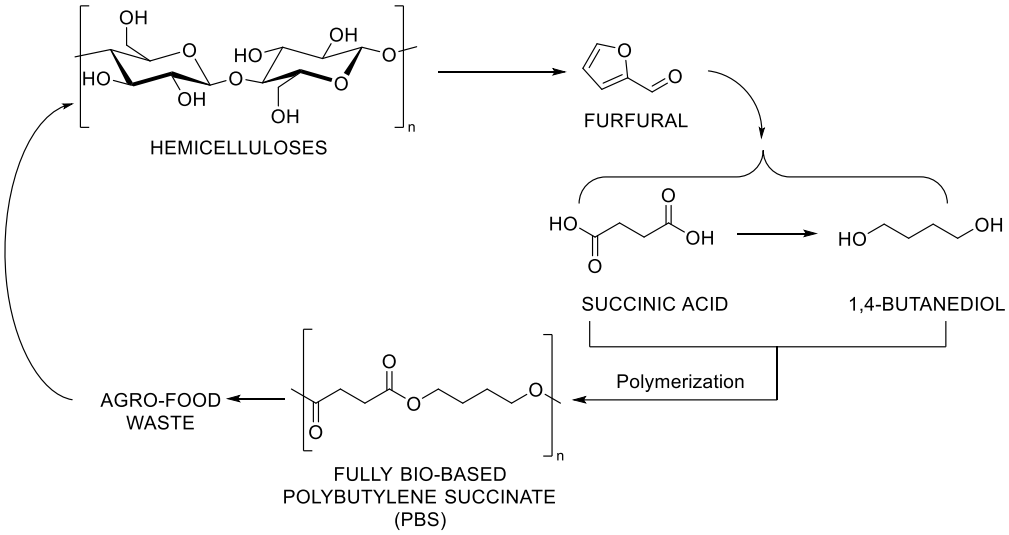


Figure 3: Four different types of polymer: Linear, Branched, Cyclic and Network.

Polybutylene succinate (PBS), produced from bio-based succinic acid (SA),[8] is a biodegradable and sustainably sourced polyester. Bio-based SA is made from a variety of renewable biomass wastes, including bagasse, corn fibre hydrolysate, cotton stalks and others. Instead of using unsustainable fossil resources such as oil or liquefied petroleum gas (LPG) in the conventional production of SA, bio-based SA made from renewable raw materials is more cost-effective and environmentally friendly.[6,8]

Polybutylene succinate (PBS) is produced by the polycondensation of bio-based succinic acid (SA) with 1,4-butanediol (BDO). BDO can be produced

from bio-based succinic acid (SA), wherein the SA is derived from biomass fermentation.[9] The resulting PBS retains the characteristic copolymer properties, solid-state behavior, biodegradability, chemical stability, thermal performance, and biocompatibility typical of aliphatic polyesters. Moreover, it exhibits a relatively short decomposition time in soil after disposal, facilitating recycling.[8] These attributes make bio-based PBS a highly promising alternative to conventional plastics in applications such as packaging, biomedical devices, and agricultural mulch.



Scheme 1: Synthesis and life cycle of bio-renewable Polybutylene Succinate (PBS) from hemicelluloses derived from Agro-food waste.

1.3 Polymerization

Since the most basic requirement for polymerization is that each molecule of the monomer must be able to be chemically linked to two (more) other monomer molecules, a large number of chemical reactions and related monomer types can be used to achieve polymerization. [5]

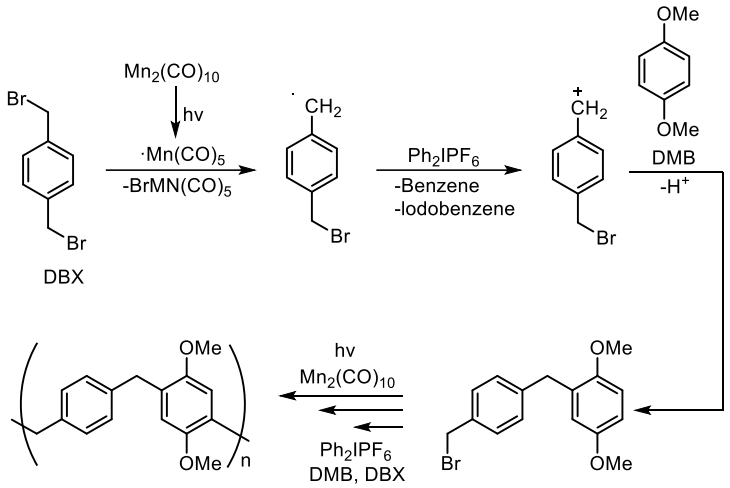
Two primary mechanisms are recognized in modern polymer synthesis: step-growth polymerization and chain-growth polymerization.[10] Step-growth polymerization is characterized by the progressive reaction between any two mutually reactive molecular species, leading to the gradual formation of polymer chains. In contrast, chain-growth polymerization occurs exclusively through the addition of monomers to the active end groups of a growing polymer chain.[5]

Formation of	**Step Polymerization**	**Chain Polymerization**
Dimer	$A + A \rightarrow A\text{-}A$	$B + A \rightarrow B\text{-}A$
		$B\text{-}A + A \rightarrow B\text{-}A\text{-}A$
Trimer	$A\text{-}A + A \rightarrow A\text{-}A\text{-}A$	$B\text{-}A\text{-}A + A \rightarrow B\text{-}A\text{-}A\text{-}A$
Tetramer	$A\text{-}A\text{-}A + A \rightarrow A\text{-}A\text{-}A\text{-}A$	$B\text{-}A\text{-}A\text{-}A + A \rightarrow B\text{-}A\text{-}A\text{-}A\text{-}A$
	$A\text{-}A + A\text{-}A \rightarrow A\text{-}A\text{-}A\text{-}A$	
Pentamer	$A\text{-}A\text{-}A\text{-}A + A \rightarrow A\text{-}A\text{-}A\text{-}A\text{-}A$	$B\text{-}A\text{-}A\text{-}A\text{-}A + A \rightarrow B\text{-}A\text{-}A\text{-}A\text{-}A\text{-}A$
	$A\text{-}A + A\text{-}A\text{-}A \rightarrow A\text{-}A\text{-}A\text{-}A\text{-}A$	

Figure 4: Step Polymerisation vs Chain Polymerisation in the synthesis of polymers.

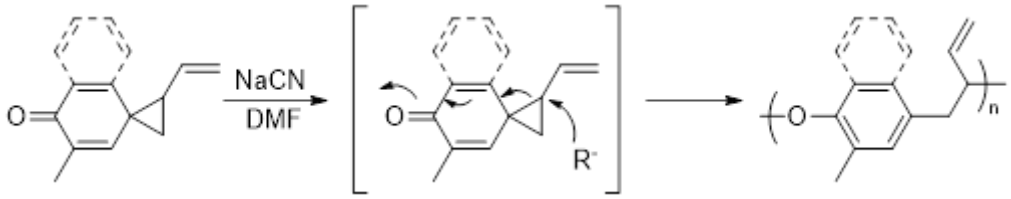
Step-growth polymerization reactions are in most cases a logical extension of simple organic chemical chain formation reactions. For instance, in Huseyin *et al.*'s study in 2021, described a visible-light-driven stepwise polymerisation approach that ingeniously combined the photochemical halogen extraction/oxidation process with electrophilic aromatic substitution, thereby establishing a novel stepwise polymerisation methodology. The process was initiated by the photogeneration of radicals. Upon visible-light irradiation, dimanganese decacarbonyl underwent homolytic cleavage to yield

pentacarbonyl manganese radicals. These species subsequently abstracted bromine atoms from α,α'-dibromo-p-xylene, generating benzyl radicals that were then oxidized to the corresponding benzyl carbocations. These carbocations, acting as electrophiles, underwent Friedel-Crafts alkylation with electron-rich aromatic comonomers to form a carbon-carbon bond. This step represents the essential chain-growth event, which iteratively repeats between bifunctional monomers to achieve molecular weight increase.[11]



Scheme 2: Dimanganese decacarbonyl step growth polymerisation.

The polymerization of *p*-quinonedimethane and its analogues proceeds via a chain-growth mechanism. This process utilizes derivatives in which one or more methylene carbon atoms in the parent *p*-quinonedimethane structure are formally replaced by heteroatoms or functional groups, yielding electron-deficient quinoid monomers. These compounds serve as key substrates that polymerize to form polymers with a main-chain structure consisting of alternating aromatic and linker units.[12]



Scheme 3: General chain-growth polymerisation to access polymeric products.

The reaction is typically initiated by an external radical source such as azobisisobutyronitrile (AIBN). Chain propagation then occurs through successive monomer addition to the active chain end. Each incorporation event is accompanied by aromatization-driven ring-opening—particularly evident in strained or cyclic analogues—which provides a strong thermodynamic driving force. Throughout the process, the active site is regenerated at the propagating chain end, enabling controlled molecular weight growth and narrow molecular weight distribution, both hallmarks of chain-growth polymerization.[12]

For polymers, their molecular weight determines their mechanical properties. Polymers used in different applications often require different mechanical properties, for example, polymers used in structural applications must have a molecular weight greater than 10,000, whereas for films low molecular weight polymers or oligomers are often sufficient. Mechanical strength does not increase indefinitely with increasing molecular weight, but rather, rises rapidly with increasing molecular weight (from A to B) until a critical point is reached (from B to C). By controlling molecular weight and molecular weight

distribution (MWD), it is often possible to achieve and enhance certain specific physical properties of polymer products.[10]

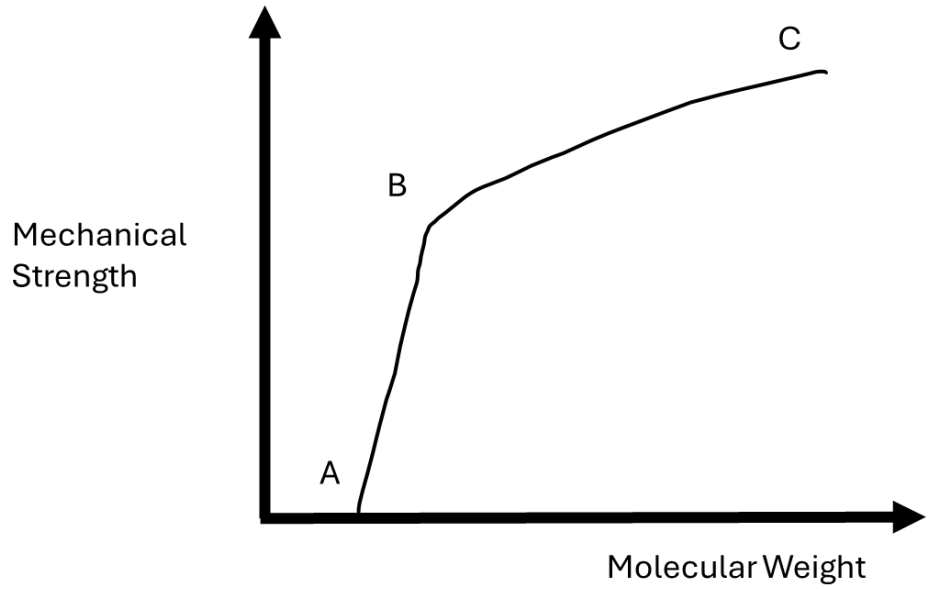


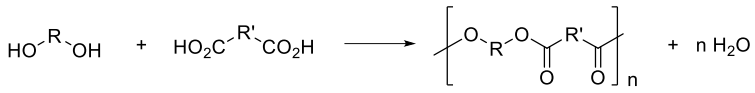
Figure 5: Plot showing correlation between Mechanical Strength vs Molecular Weight of polymers.

1.4 Polycondensation

In step-growth polymerization, the elimination of small molecules through the reaction process is known as a polycondensation.[5] Polyesters, polyamides and polyethers can be synthesised by polycondensation. The traditional polycondensation is usually carried out in the molten state above 200 degrees Celsius to drive off the condensate, because the reaction is usually accompanied by an equilibrium between the esterification and hydrolysis

reaction, but new and more energy-efficient ways to improve this are being explored.[13]

Polyester is an important polymer material synthesised by polycondensation of dibasic acids and diols, and is widely used in fibres, bottles and films.[5] In recent years, significant progress has been made in aqueous emulsion polymerization, an environmentally friendly synthetic strategy.



Scheme 4: General polymerisation of diols and diacids to access polyesters.

A notable example is the polycondensation of carboxylic acids and alcohols conducted directly in aqueous media under mild conditions using *p*-dodecylbenzenesulfonic acid (DBSA) as a catalyst.[13] This method utilizes water as the reaction medium. DBSA serves simultaneously as a surfactant and a catalyst, promoting the formation of micelles at moderate temperatures, specifically up to 100 °C. These micelles provide a hydrophobic microenvironment that accommodates water-insoluble monomers, such as long-chain dicarboxylic acids and diols, and facilitates the growth of polyester chains, resulting in the production of stable polymer particles.[13] This approach not only avoids the use of organic solvents and reduces energy consumption, but also yields products with a narrow molecular weight distribution.

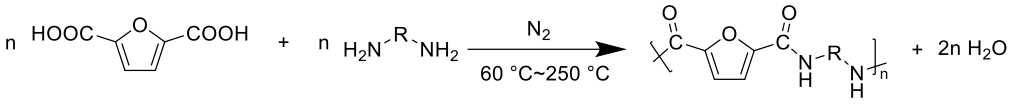
In step-growth polymerization, the selection of a suitable solvent presents a significant challenge, as the polymers produced are often semi-crystalline and exhibit limited solubility. Furthermore, isolating the final polymer from the reaction medium can be difficult. Consequently, many step-growth polymerization systems designed for laboratory or industrial use are performed in the absence of solvent, relying instead on the direct mixing of liquid monomers.[4,14]

For instance, high-molecular-weight polyamides can be synthesized by reacting ester derivatives of 2,5-furandicarboxylic acid with diamines under carefully controlled diamine stoichiometry and temperature conditions.

A significant challenge in conventional melt polycondensation arises from the fact that the melting temperature (T_m) of salts formed between 2,5-furandicarboxylic acid (FDCA) and diamines is 33 °C higher than their decomposition temperature (T_e).[14] Moreover, FDCA itself exhibits a lower decomposition temperature compared to other diacids such as adipic acid (AA). These factors impose serious constraints on processing. Additionally, decarboxylation may occur at elevated temperatures, converting the diacid into a monoacid and thereby hindering the formation of high-molecular-weight polymers.[14]

High-molecular-weight furan-based polyamides have been successfully prepared via solvent-free melt polycondensation of diamines with ester

derivatives of 2,5-furandicarboxylic acid—specifically, those derived from C_2 to C_{12} aliphatic diols or polyols. Key to this process was the use of a diamine excess of at least 1 mol% relative to the diester, coupled with polycondensation conducted between 60 °C and 250 °C under an inert atmosphere.[14] The molecular weight of the resulting polymer was further increased through solid-state polymerization (SSP).



Scheme 5: Solvent-free melt polycondensation of diamines with 2,4-furandicarboxylic acid derivatives.

Aliphatic polyesters have gained significant attention as biodegradable materials. Among these, polyesters synthesized via polycondensation of α,ω-alkanediols and aliphatic dicarboxylic acids (ADAs) or their derivatives are of particular interest. They exhibit a higher rate of hydrolytic degradation compared to polyesters derived from longer-chain ADAs. Moreover, succinic acid—a monomer obtainable from renewable resources—differs from most longer-chain ADAs, which are typically petroleum-based.[15] In conventional polysuccinate preparation, the native polycondensation based on α,ω-alkanediols and succinic acid needs to be carried out at temperatures of up to 250 degrees celsius.[16]

1.5 Free radical polymerization

Organic molecules containing unpaired electrons are known as free radicals or

radicals. Free radicals can undergo four types of reactions: transfer or abstraction, elimination, addition, and combination or coupling.[17] Free radical polymerization is the most widely used and versatile type of polymerization for unsaturated monomers containing C=C bonds.

As with other types of chain polymerization, the reaction is divided into three basic stages: initiation, propagation and termination, and the resulting polymer chain consists mainly of a tandem sequence of the heads and tails of repeating units.

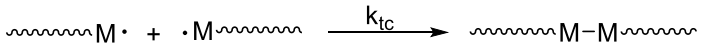
The initiation stage involves the formation of free radical active centres, firstly by generating free radicals using an initiator and secondly by adding one of these radicals to the monomer molecule.

Propagation is the process whereby the active centre in the monomer is added in rapid succession to grow the polymer chain, with each addition of a monomer typically taking about a millisecond, so that thousands of additions can be made in a matter of seconds. If a head-to-head addition reaction occurs, a tail-to-tail addition reaction follows rapidly to produce a more stable active centre which will continue to diffuse mainly through the head-to-tail addition reaction.

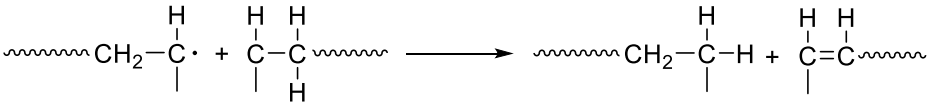
The common termination mechanisms in free-radical polymerization include combination and disproportionation, wherein combination refers to the coupling of two propagating radicals to form a single stable polymer chain,

while disproportionation involves hydrogen atom transfer from one radical to another, yielding one saturated and one unsaturated polymer chain. These two pathways compete during polymerization and their relative prevalence significantly influences the resulting polymer architecture and molecular weight distribution. Notably, combination increases the degree of polymerization, whereas disproportionation terminates chains without such an increase, directly affecting the polymer's final properties.[17]

1. Combination (coupling):



2. Disproportionation:



Scheme 6: Two different termination mechanisms in free radical polymerisation: Combination (coupling) and Disproportionation.

In 2002, Traian Sarbu, Tomislav Pintauer, Blayne McKenzie, and Krzysztof Matyjaszewski from Carnegie Mellon University introduced a two-phase aqueous–organic system for atom transfer radical polymerization (ATRP).[18] As a prominent controlled/living radical polymerization technique, ATRP enables the synthesis of polymers with predetermined molecular weights and narrow molecular weight distributions.[19] Nevertheless, the broader application of ATRP has been limited by a practical constraint: the difficulty in removing

residual transition metal catalysts, which are typically copper complexes, after polymerization. These catalyst residues often impair the properties of the final polymer product. The authors presented a simple and efficient catalyst removal strategy that retains excellent control over the polymerization process. They used styrene (St) as the monomer, ethyl 2-bromoisobutyrate (EBiB) as the initiator, $CuBr/CuBr_2$ as the catalyst system, and N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDETA) as the ligand.[18] ATRP is usually carried out neat, but can also be performed in a solvent. When the resulting polymer is insoluble in its monomer, such as polyacrylonitrile, the use of a solvent is required.

A two-phase system consisting of toluene as the organic phase and water as the aqueous phase was selected for this polymerization. The reaction was conducted in a Schlenk flask following standard ATRP procedures, including deoxygenation and heating. After polymerization, the system separated naturally into two layers. Although the polymerization control in the toluene/water two-phase system is slightly lower than in a homogeneous system, this method offers a notable advantage by greatly reducing copper residues in the polymer through a simple post-polymerization treatment. When polymerization is complete, both Cu(I) complexes, which act as activators and are mainly distributed in the organic phase, and Cu(II) complexes, which act as deactivators and strongly prefer the aqueous phase, are present. By exposing the system to air and stirring for 30 minutes, Cu(I) is

oxidised to Cu(II), causing the majority of the copper species to migrate into the aqueous phase.[18]

1.Initiation

$$\text{R-Br} + \text{Cu(I)Br/PMDETA} \rightarrow \text{R}^{\bullet} + \text{Cu(II)Br}_2\text{/PMDETA}$$

2.Propagation

$$\text{R} + n\ \text{CH}_2 = \text{CHPh} \rightarrow \text{P}_n$$

3.Activation-Deactivation Equilibrium

$$\text{P}_n^{\bullet} + \text{Cu(II)Br}_2\text{/PMDETA} \rightleftharpoons \text{P}_n\text{-Br} + \text{Cu(I)Br/PMDETA}$$

4.Post-polymerization Catalyst Removal

$$2\ \text{Cu(I)Br/PMDETA} + 1/2\text{O}_2 + 2\text{H} \rightarrow 2\ \text{Cu(II)Br}_2\text{/PMDETA} + \text{H}_2\text{O}$$

Scheme 7: Atom transfer radical polymerization (ATRP) system developed by Sarbu and coworkers.[20]

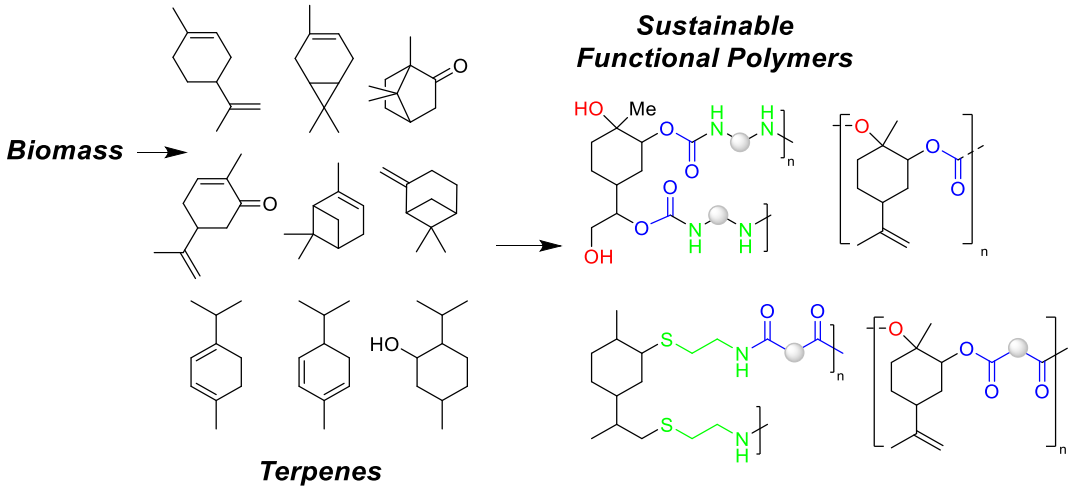
This approach provides a simple and efficient way to remove catalyst residues, specifically copper complexes, supporting the industrial application of ATRP technology.

1.6 Terpenoids

Future generations are now faced with the urgent question of how to develop sustainable societies, given that the reserves of fossil fuels for energy production and plastics manufacturing are finite, and that they may be virtually depleted within the next century. At the same time, most plastics from non-renewable sources are causing serious pollution of land and sea as they are not biodegradable. This has led to a growing interest in the development of green plastics from renewable natural resources, with natural polymers from natural

resources receiving much of the attention.[21] Terpenes present a compelling case as superior biorenewable feedstocks compared to petroleum-based alternatives. Their hydrocarbon nature, featuring lightly oxygenated C_{10} frameworks with alkene functionalities, ensures seamless compatibility with established petrochemical purification and derivatization technologies. This facilitates their direct integration into existing supply chains. Crucially, large-volume monoterpenes like α-pinene, β-pinene, and 3-carene are available as low-cost waste by-products from the forestry and paper industries, exemplified by crude sulfate turpentine (CST) produced at ~330,000 tonnes annually for approximately $220 per tonne.[22] This positions them as economically viable and sustainable raw materials. Beyond their accessibility, these compounds serve as versatile chiral building blocks, already widely utilized in synthesizing high-value flavors, fragrances, and pharmaceuticals. Promising advances in synthetic biology further suggest the potential for scalable microbial production from lignocellulosic waste, enhancing future supply flexibility. Therefore, terpenes offer a unique combination of technical compatibility, economic feasibility, and inherent chirality, making them attractive for sustainable chemical synthesis and justifying the development of green catalytic processes, such as the solvent-free H_2O_2 epoxidation reported, to fully unlock their potential. Terpenoids are an important natural resource found in nature and are often introduced into the design of polymer molecules due to their polychiral centres and good bioactivity, which can bring unique stereo

configurations, good bioactivity and biocompatibility to polymers. They are primarily derived from turpentine, with an annual global production of approximately 350,000 tonnes.[23,24] Terpenes and terpenoids, a very important class of natural compounds, are the main constituents of tree resin (a natural exudate); rosin is a solid form derived from resin. Of these, a mixture of terpenes make up the turpentine, the volatile portion of the resin, and most of the terpenes have a basic cycloaliphatic structure. Rosin is the non-volatile solid residue obtained after the distillation of the volatile terpene fraction from fresh resin.[18]



Scheme 8: Use of Biomass feedstocks to generate terpene building blocks towards the synthesis of sustainable functional polymers.

1.7 Polymers from Terpene

Terpene-based polymers can be classified as terpene-based chain-growth polymers, step-growth polymers and polymers with terminal, intermediate and side-hanging terpene units. Since now, many cyclic and linear terpene

monomers have been used for the synthesis of different polymers, such as alpha-pinene, beta-pinene, limonene, hydrocotylene, menthol and others. [25]

For the synthesis of polymers derived from terpenes, the main focus is currently on the copolymerisation of terpenes with fuel-derived monomers either directly or by chemically converting the terpenes into different monomers before continuing the polymerisation process. Polymers derived from terpene monomers can be classified into three main types: those with terpene-based main chains, those bearing terpene groups as side-chain pendants, and those containing terpenes as terminal groups.

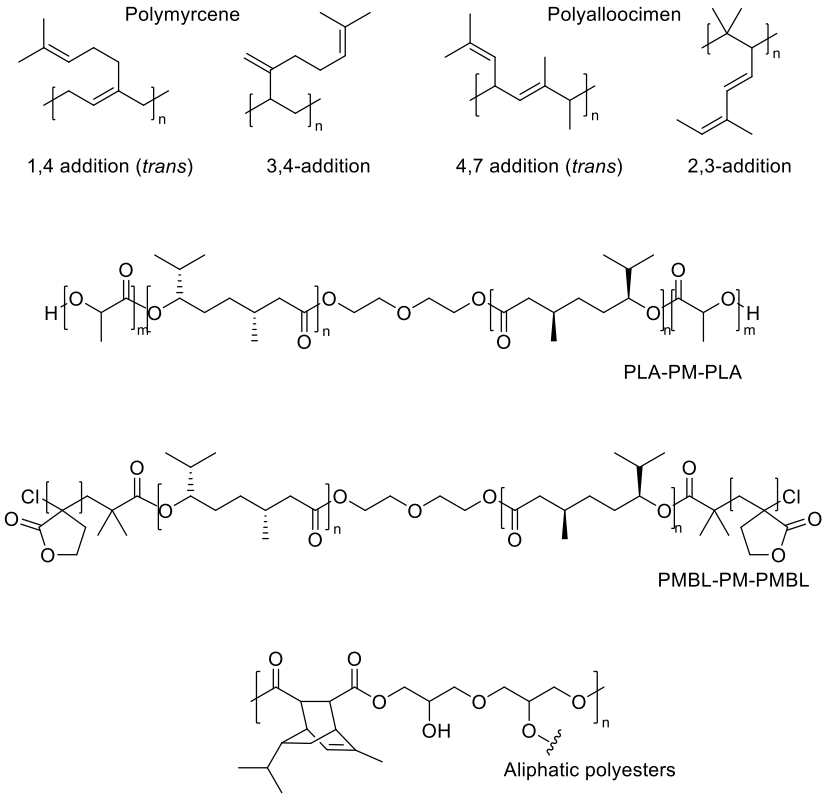


Figure 6: Structures of various polymers derived from terpene monomers.

Among these, polymers whose main chains consist of terpene units are formed

through the direct polymerization of terpene monomers via their reactive sites, such as C=C double bonds or other functional groups. This category includes polyterpenes synthesized from monomers such as β-pinene, myrcene, ocimene, and limonene.[25]

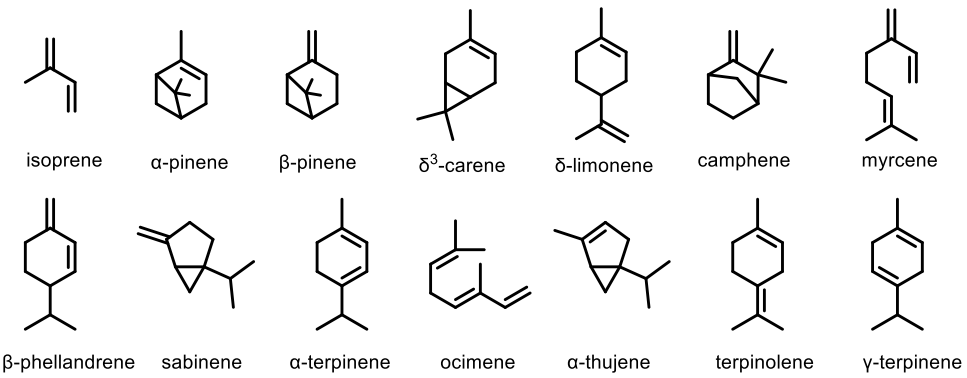
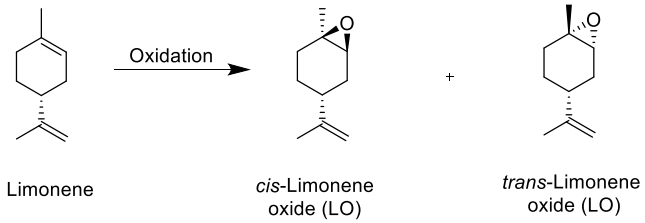


Figure 7: Terpene and terpenoid derived monomer building blocks for use in functionalised polymer synthesis.

Of these, limonene can be obtained not only by isomerization of pinene, but is also naturally synthesized by over 300 plant species.[26] In the conversion of citrus waste to ethanol, it serves as an integral by-product, contributing approximately 8 kg per ton of processed fresh waste (20% dry matter)[27] to the overall product stream and process economics. It is a chiral molecule that has been widely used in the flavor and fragrance industry. Limonene contains a trisubstituted alkene within the ring and a disubstituted alkene at the terminal position. The trisubstituted alkene is more electron-rich and thus more reactive toward electrophilic agents. In contrast, the exocyclic disubstituted alkene, while less electron-rich, is significantly less sterically hindered, making it the preferred site for reactions with bulky reagents or radical polymerization. The

rigid bicyclic structure of limonene, along with its two double bonds (one within the ternary ring and the other at a terminal position), offers versatile opportunities for polymerization and enables a broader selection of polymer monomers. This has led to a growing focus on limonene-based polymerization in recent research.[28–32] Limonene epoxide (LO) is obtained through the epoxidation of limonene,[33] and limonene carbonate (PLC) is prepared via ring-opening copolymerization (ROCOP) of LO with carbon dioxide.[34] LO exists as both *cis* and *trans* stereoisomers, and its structural resemblance to cyclohexene oxide (CHO), a common monomer,[35] makes it a promising renewable alternative monomer for producing aliphatic polycarbonates.



Scheme 9: Cis and trans isomers of limonene epoxide (LO) obtained from oxidation of limonene.

Polyesters can also be synthesized by polycondensation of limonene-derived diols or hydroxy acid monomers.[36] For example, the use of limonene-based diols with succinic acid in a Lewis acid-catalyzed condensation reaction affords polyesters with relatively high molecular weights (up to 30 kDa) and low glass transition temperatures ranging from –7 to 23 °C. These polyesters can be depolymerized under alkaline conditions to regenerate the original limonene diol monomer.[36]

The reaction of limonene dioxide (LDO) with carbon dioxide to form limonene dicarbonate (LDC), as well as the use of thiol-ene click chemistry to produce a limonene diamine followed by its conversion to a dicarbamate using dimethyl carbonate (DMC), have also been investigated.[37]

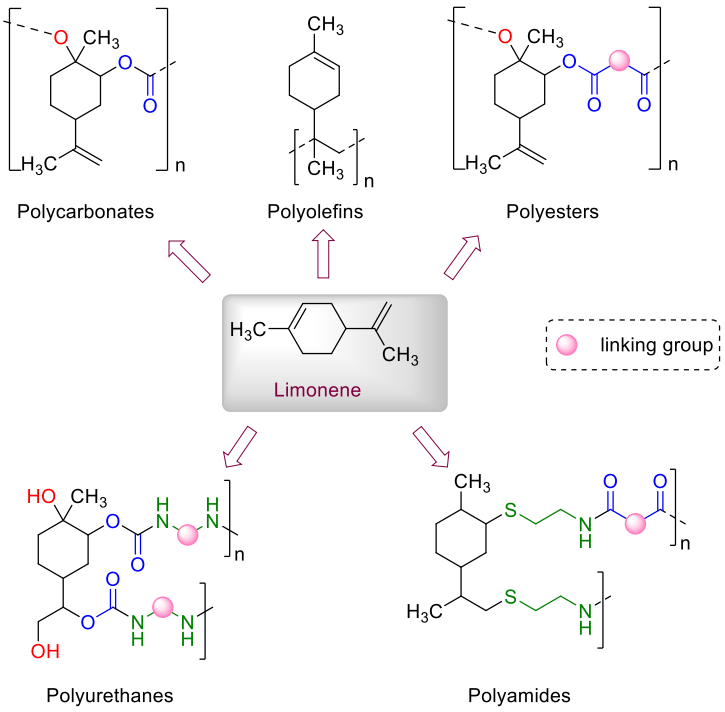


Figure 8: Limonene derived functionalised polymer synthesis.

1.8 Pinene

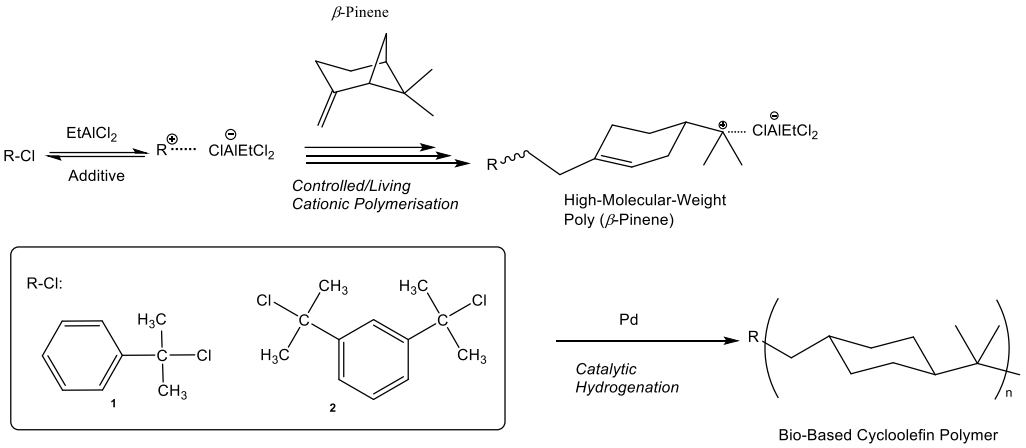
Monoterpenes are hydrocarbon compounds, some of which may contain oxygen, formed by the head-to-tail linkage of two isoprene units. Pinene, a class of bicyclic monoterpenes, is the most abundant and readily isolated terpene, usually obtained by steam distillation of the resinous sap of pine or coniferous trees.[21] It exists in two isomeric forms: α-pinene and β-pinene. In α-pinene, the carbon–carbon double bond is situated within the six-membered

ring. Despite its inherent high reactivity, this double bond exhibits relative inertness due to significant steric hindrance. As a result, the preparation of α-pinene-based polymers typically requires either highly reactive catalyst systems or the use of activated α-pinene monomers.[24] The vast majority of pinene polymerisations use beta-pinene because its structure contains highly reactive extracyclic methylene double bonds, which are more conducive to obtaining homopolymers and copolymers from cationic polymerisation reactions.[21]

One disadvantage of the polymers obtained from pinene as a source, however, is the low molecular weight of their polymers, which limits their mechanical properties.[38] To achieve considerably higher molecular weights, the cationic polymerization of β-pinene followed by hydrogenation can be employed.[39]

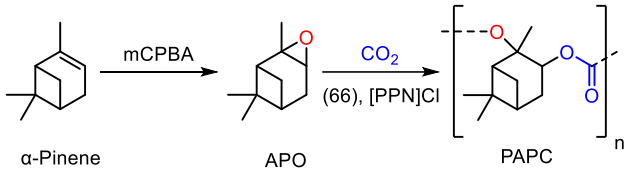
In the study by Satoh *et al.*, a high-molecular-weight poly(β-pinene) (Mw > 100,000)[39] was synthesized via living cationic polymerization employing an initiating system of a protic acid, a Lewis acid, and a Lewis base. The incremental addition of monomer was utilized to suppress chain transfer reactions, enabling precise control over molecular weight. The resulting hydrogenated polymer exhibits a combination of exceptional properties, including high optical transparency (92%), low density (0.93 g/cm³), a high glass transition temperature (130 °C), and low hygroscopicity.[39] These characteristics are comparable to those of conventional petroleum-based optical plastics like

polymethyl methacrylate (PMMA) and polycarbonate (PC), demonstrating the material's significant potential for developing sustainable high-performance optical materials.



Scheme 10: β-Pinene polymerisation process yielding Poly-β-Pinene and subsequent catalytic hydrogenation to Bio-Based Cycloolefin Polymers.

Among these, α-pinene can be epoxidized to yield α-pinene oxide (APO), which subsequently serves as a monomer in ring-opening copolymerization (ROCOP) with CO_2 to produce poly(α-pinene carbonate) (PAPC). Furthermore, APO can be copolymerized via ring-opening with other terpene-based derivatives, such as camphoric anhydride (CA), to form fully bio-based polyesters. These polyesters leverage the inherent structural rigidity imparted by the APO units, thereby exhibiting enhanced glass transition temperatures (Tg).[23]

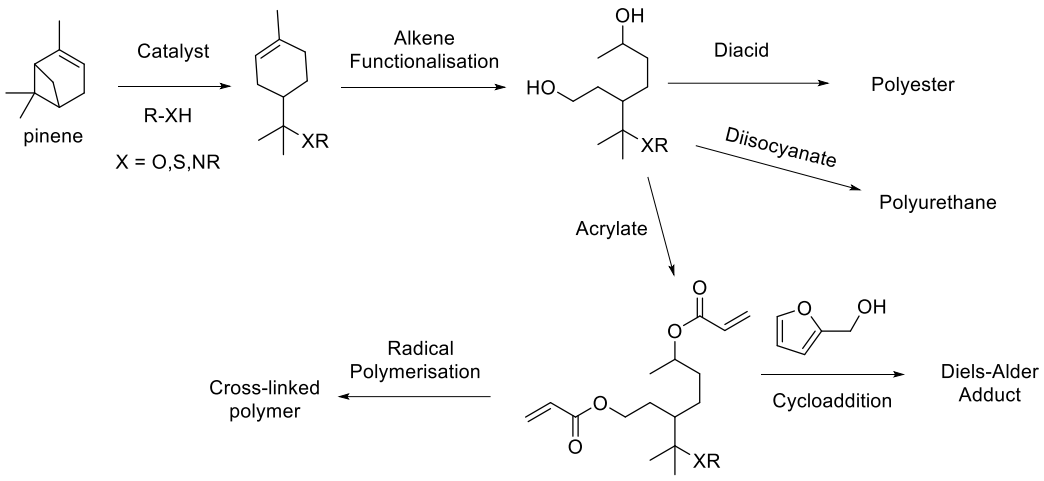


Scheme 11: Application of oxidation chemistry to α-Pinene to access functional polymers.

2.0 Chapter 2: Results and Discussion

As established in the introduction, terpene-derived monomers represent a promising platform for sustainable, bio-based polymers. This section details the synthesis of novel monomers and polymers originating from α-pinene. Structural diversification was achieved through a series of transformations, including acid-catalyzed ring-opening, dihydroxylation, oxidative cleavage, and reduction reactions.

To achieve the synthesis of a series of novel renewable polymers based on alpha-pinene, it was first necessary to prepare a set of new monomers. Initial efforts focused on acid-catalyzed reactions of alpha-pinene with different alcohols (R–OH) to produce key ring-opened intermediates with systematically varied side-chain length, flexibility, and terminal functional groups. These intermediates were subsequently converted into diol monomers by transforming the non-polymerisable C=C double bond into two highly reactive hydroxyl groups (–OH), thereby establishing a foundation for further polycondensation reactions. Additionally, derivatisation of the resulting diol monomer was carried out via esterification with acrylic acid to obtain new polymerisable macromolecular monomers.



Scheme 12: Overall scheme summarising the approach to novel functionalised polymers.

As established in the introduction, terpene-derived monomer building blocks represent a significant opportunity for developing more sustainable bio-based polymers. This results and discussion section details the synthesis of novel monomers and polymers from this class of compounds. Specifically, the polymers described herein are derived from α-pinene and functionalized through a sequence of acid-catalyzed ring-opening, dihydroxylation, oxidative cleavage, and reduction reactions.

2.1 Acid Catalyzed Ring-Opening Coupling of Pinene

In this section, two catalytic systems were tested for a ring-opening addition of a nucleophile to pinene: the first employed ferric chloride ($FeCl_3$) as the catalyst with dichloromethane as the solvent; the second utilized PTA as the catalyst with 2-methyl-tetrahydrofuran (2-MeTHF) as the solvent.

In a 2007 study, Pierre Lemechko proposed that Lewis acids such as stannic

triflate could catalyze the intermolecular addition of primary alcohols to non-activated alkenes under mild conditions. The investigation utilized natural terpene derivatives as starting materials in common alcoholic solvents; however, when pinene was reacted with ethanol, the yield remained low at only 15%.[40]

In contrast, Yadav's 2009 work employed ferric chloride as a catalyst for similar terpenoid substrates and achieved significantly higher yields, ranging from 70% to 92%.[41]

Cunningham *et al.* (2020) demonstrated that tungsten-based polyoxometalate (POM) catalysts, particularly those of the Venturello type, exhibit high efficiency in catalyzing the epoxidation of olefins using hydrogen peroxide as an oxidant.[42] These systems maximize oxygen atom transfer efficiency while significantly suppressing nonproductive peroxide decomposition. The catalytic system is especially suitable for terpene substrates, showing good tolerance toward various functional groups such as alcohols and esters, and has been successfully applied to the epoxidation of fourteen biorenewable terpenes[42], including limonene and α-pinene. In the case of α-pinene epoxidation, the authors adopted a strategy reported by Sato and coworkers[43] by incorporating sodium sulfate as an additive to optimize the reaction performance.

Given the structural and mechanistic similarities between the Venturello catalyst and phosphotungstic acid (PTA), a widely available polyoxometalate

(POM) catalyst, we were inspired to explore PTA as a potential catalyst for the epoxidation of terpenes. Subsequently, in the present study, we further investigated the use of PTA as a Brønsted acid catalyst to promote the carbocation-induced rearrangement of α-pinene. The solvent 2-methyltetrahydrofuran (2-MeTHF) was selected for its ability to dissolve both the nonpolar terpene substrate and the polar PTA catalyst, thereby facilitating the reaction.

The essence of proton acid catalysis is the transfer of a proton, specifically a hydrogen ion (H^+), from an acidic catalyst such as a carboxyl group (-COOH) to a basic atom on the reactant molecule. The catalyst functions as the proton donor. This mechanism differs fundamentally from Lewis acid catalysis, which operates through electron pair acceptance rather than direct proton transfer.[44–46]

In the derivatization of α-pinene to synthesize key intermediates, a series of alcohols—ethanol, propanol, octanol, benzyl alcohol, furfuryl alcohol, and allyl alcohol—were investigated, along with thiophenol.

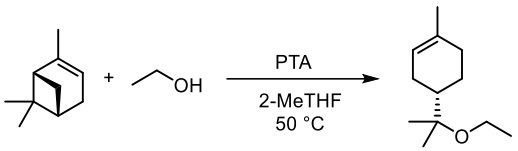
The progression from ethanol and propanol to octanol establishes a continuous variation in alkyl chain length from short to long. This systematic approach enables a subsequent detailed investigation into the influence of side-chain length on polymer properties, such as glass transition temperature, crystallinity, mechanical performance, hydrophobicity, and compatibility.

The incorporation of allyl alcohol provides additional functional versatility. The terminal double bond in the resulting allyl ether side chain can participate in free-radical polymerization alongside the main-chain acrylate groups. This enables the formation of a denser and more robust cross-linked network, potentially enhancing the polymer's hardness, thermal stability, and chemical resistance.

Furthermore, experiments involving benzyl alcohol, thiophenol, aniline, and furfuryl alcohol aimed to introduce distinct chemical functional groups, including rigid benzene rings, thioether linkages, aromatic amino groups, and biorenewable furan rings, respectively. These modifications are intended to impart advanced functionalities to the resulting polymers, expanding their potential applications.

2.1.1 4-(2-Ethoxypropan-2-yl)-1-methylcyclohex-1-ene (1)

For the synthesis of key intermediates from alpha-pinene, phosphotungstic acid hydrate (PTA) was selected as the catalyst in 2-methyltetrahydrofuran (2-MeTHF). In the initial attempt, ethanol was employed to participate in a nucleophilic addition with the pinene cation generated via PTA-catalyzed ring-opening. This step introduced an alkoxyl group, which subsequently underwent rearrangement and deprotonation to yield the target product **1**.



1 51%

*Scheme 13: Phosphotungstic acid (PTA) reaction of (-)-α-Pinene with ethanol to generate ethyl ether **1** (51% yield).*

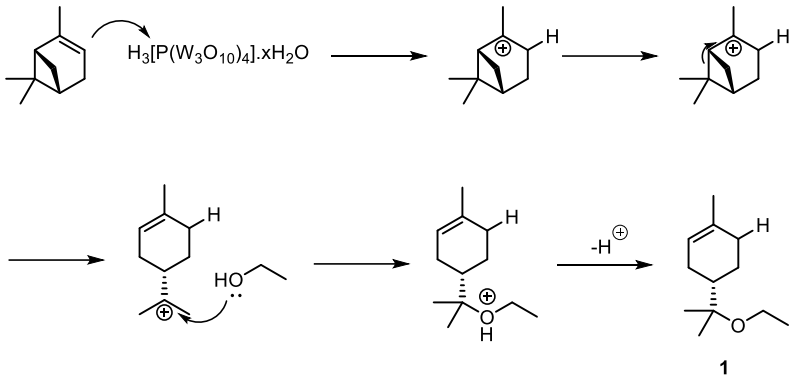
Phosphotungstic acid hydrate, a strong Bronsted acid, can dissociate protons (H^+) in polar solvents. In the reaction, the proton preferentially attacks the double bond on the tensile four-membered ring of the α-pinene molecule (lower site resistance) to give a protonated carbocation intermediate.

Subsequently, since the carbocation generated in the previous step is very unstable due to its location adjacent to the four-membered ring, it undergoes an immediate rearrangement to stabilise itself. At the same time, neighbouring carbon-carbon bonds migrate, leading to ring opening of the four-membered ring and the generation of a more stable, resonance-isolated pinacene-based cation.[40] This is a classical Wagner-Meerwein rearrangement reaction,[47] and this step ultimately produces a more stable tertiary carbocation.

Immediately afterwards, ethanol acts as a nucleophilic reagent with a lone pair of electrons on its oxygen atom attacking the centre of the carbocation with the lower site resistance generated in the previous step, thus forming a new C-O bond.

Finally, the oxygen atom after addition carries a positive charge on it, forming an oxonium ion. This ion is unstable and subsequently loses a proton

(deprotonation) to produce the final neutral ether product and regenerate the PTA catalyst, thus completing the catalytic cycle.



*Scheme 14: Mechanism of the acid catalysed reaction converting (-)-α-Pinene into ethyl ether **1.***

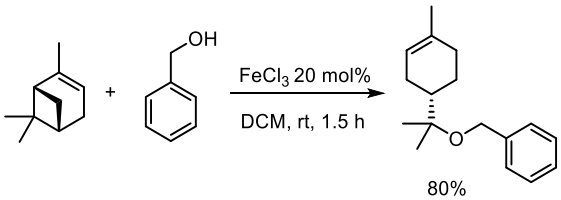
The reaction was conducted using phosphotungstic acid (PTA) as the catalyst, enabling the efficient and selective synthesis of the key intermediate, 4-(2-ethoxypropan-2-yl)-1-methylcyclohex-1-ene, from the bio-based feedstock α-pinene via an acid-catalyzed electrophilic addition accompanied by a Wagner–Meerwein rearrangement. As this is a reversible acid-catalyzed electrophilic addition, the product ether can undergo acid-induced cleavage under the reaction conditions, reforming the olefin and alcohol. To shift the equilibrium toward product formation and enhance the conversion of α-pinene, a significant excess of ethanol was employed. Consequently, upon reaction completion, the crude mixture contained a substantial amount of unreacted ethanol. Additionally, α-pinene is prone to side reactions under acidic conditions, such as isomerization and oligomerization, leading to the formation of byproducts that contribute to the complexity of the crude mixture.

Furthermore, incomplete removal of PTA—which may persist in the form of submicron-sized colloidal particles—poses a risk of continued catalytic activity during subsequent thermal processing steps, such as solvent removal or distillation.

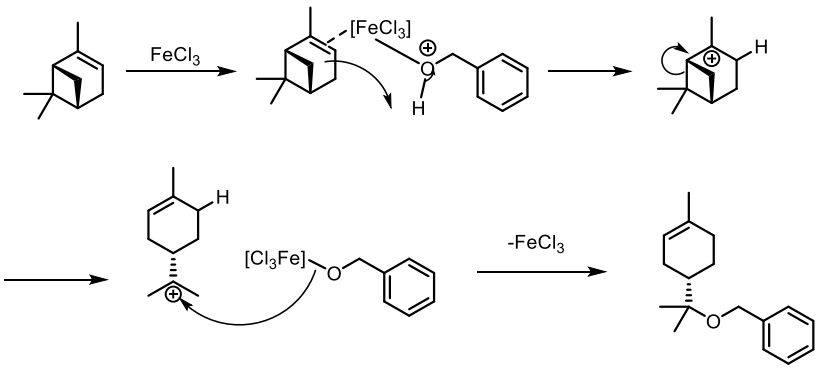
Therefore, careful purification of the crude product is essential. Upon completion of the reaction, the mixture was subjected to vacuum filtration using a glass sand-core funnel containing a layer of silica gel powder, followed by rinsing with a small amount of a weakly polar solvent, such as petroleum ether. The strong acidic character of PTA promotes robust electrostatic interactions and hydrogen bonding with the silanol groups on the silica gel surface, resulting in effective adsorption of the catalyst. This procedure yielded a clear filtrate, free from residual solid catalyst, suitable for subsequent purification steps. Finally, compound was obtained by column chromatography in 51% yield as a yellow oil.

2.1.2 4-(2-Propoxypropan-2-yl)-1-methyl-cyclohex-1-ene (2)

In 2009, Yadav *et al.* reported an $FeCl_3$-catalysed system for the functionalisation of monoterpenes. [41]

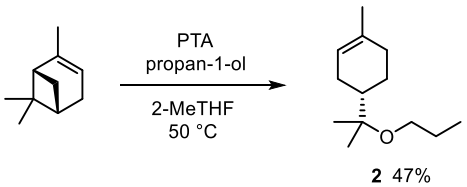


Scheme 15: Iron(III) chloride catalysed reaction of (-)-α-Pinene with benzyl alcohol to generate benzyl ether product, reported by Yadav et al. [41]



Scheme 16: Postulated reaction mechanism for Iron(III) chloride catalysed reaction to generate benzyl ether product.

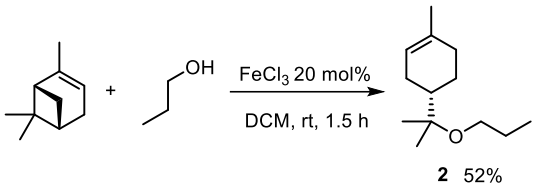
Mechanistically, the reaction is proposed to proceed via initial Lewis acid-base interaction between $FeCl_3$ and the electron-rich double bond of α-pinene. This activation polarizes the alkene, facilitating its protonation to form a carbocation intermediate. This carbocation subsequently undergoes a Wagner-Meerwein-type 1,2-alkyl shift, leading to the rearrangement of the pinane skeleton to a more stable bornyl cation. The nucleophilic oxygen of the alcohol then attacks this carbocation, resulting in the formation of the corresponding bornyl alkyl ether. Dichloromethane was chosen as the solvent for its ability to dissolve both the non-polar terpene and the ionic catalyst species, while providing a non-coordinating environment that does not interfere with the Lewis acid activity of $FeCl_3$.



*Scheme 17: Phosphotungstic acid (PTA) reaction of α-Pinene with 1-propanol to generate propyl ether **2** (47% yield).*

In order to determine the effect of side-chain length on polymer properties,

the next target was the propyl side-chain. Inspired by the work of Yadav and coworkers,[41] the reaction of α-pinene with 1-propanol to obtain propyl ether **2** was investigated using both the established PTA conditions and using ferric chloride ($FeCl_3$) as a Lewis acid catalyst in dichloromethane as the solvent. The change from ethanol to propanol expands the reaction to create a continuous gradient of variables. For example, for monomers that are eventually converted to diols and then further synthesised into polyesters or polyacrylates, the propyl side chain may enable the glass transition temperature of the polymer to be further lowered, and the material to become softer and more resilient (relative to ethyl).



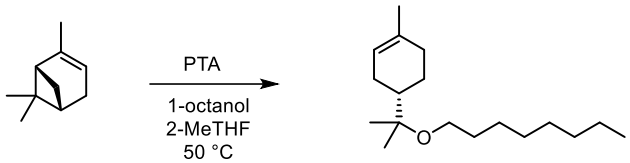
Scheme 18: Iron(III) chloride catalysed reaction of α-Pinene with 1-propanol to generate propyl ether 2 (52% yield).

Although both ferric chloride ($FeCl_3$) and phosphotungstic acid (PTA) function as competent catalysts for the reaction between α-pinene and 1-propanol, their fundamental classification as a Lewis acid and a Brønsted acid, respectively, results in divergent mechanistic pathways and consequent experimental outcomes. The reaction catalyzed by $FeCl_3$ proceeds through a classical Lewis acid-mediated process,[41] wherein $FeCl_3$ coordinates to the electron-rich double bond of α-pinene. This activation facilitates protonation and the formation of a carbocation intermediate that undergoes

rearrangement, leading to a relatively simple product distribution with fewer impurities. This system achieved a 52% yield within a short reaction time of 1.5 hours, and the crude product was readily separable and purifiable. A significant limitation, however, is the generation of metal-containing wastewater, which presents disposal challenges and conflicts with the principles of green chemistry. In contrast, catalysis using PTA, a strong Brønsted acid, offers advantages in terms of environmental compatibility and potential catalyst recyclability. Nevertheless, the acidic conditions promote undesirable side reactions such as polymerization, isomerization, and esterification, resulting in a complex mixture of products that complicates purification. The products were characterised by 'H NMR, lR and mass spectrometry.

2.1.3 4-(2-(Octyloxy)propan-2-yl)-1-methylcyclohex-1-ene (3)

The effectiveness of alcohols as nucleophiles in typical acid-catalyzed reactions, such as addition, ring-opening, and etherification, is influenced by their structure. An increase in the carbon chain length elevates steric hindrance around the hydroxyl group, which can reduce the alcohol's efficacy in attacking carbocation intermediates. Additionally, differences in polarity and miscibility present another structural influence: short-chain alcohols (e.g., 1-propanol) are highly polar and water-miscible, while long-chain alcohols (e.g., 1-octanol) are more compatible with hydrophobic solvents like 2-methyltetrahydrofuran (2-MeTHF). These factors collectively affect the local reactant concentration and the overall reaction efficiency.



3 65%

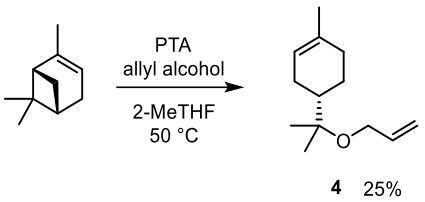
*Scheme 19: Phosphotungstic acid (PTA) reaction of α-Pinene with 1-octanol to generate octyl ether **3** (65% yield).*

The reaction was conducted in 2-methyltetrahydrofuran (2-MeTHF) using PTA as a catalyst and stirred at 50 °C for 48 hours. Upon completion, the mixture was filtered through a Büchner funnel lined with filter paper and containing silica gel powder. The filtrate was concentrated under reduced pressure, after which distillation was performed to remove the bulk of unreacted α-pinene and 1-octanol. This preliminary distillation step was necessary due to the high 1-octanol content, which made direct purification by column chromatography impractical. The distilled material was subsequently purified by column chromatography, affording the target product **3** in 65% yield.

2.1.4 4-(2-(Allyloxy)propan-2-yl)-1-methylcyclohex-1-ene (4)

Following the successful reactions of α-pinene with ethanol, propanol, and octanol, which consistently afforded the target ether products, the more reactive allyl alcohol was examined. Under the acidic reaction conditions, the carbocation derived from α-pinene primarily serves as an electrophile, undergoing intermolecular nucleophilic substitution with the hydroxyl group of allyl alcohol. This pathway leads to C–O bond formation and, after deprotonation, yields the desired product. Competing side reactions, however, such as isomerization to other monoterpenes or polymerization of the reactive

intermediates, remain possible. Furthermore, within the PTA-catalyzed system, the highly susceptible C=C double bond of allyl alcohol itself may also be protonated, generating an allylic cation and thus introducing significant intramolecular competition into the reaction network.



*Scheme 20: Phosphotungstic acid (PTA) reaction of α-Pinene with allyl alcohol to generate allyl ether **4** (25% yield).*

Upon purification and characterization of the reaction product, the target compound **4** was successfully obtained, albeit in a low yield of 25%. This value is significantly lower than the approximately 50% yield achieved in the reactions of α-pinene with straight-chain primary alcohols. The diminished yield may be attributed to the following factors:

1. Competitive side reactions of α-pinene, including isomerization and polymerization, which consume the starting material and generate undesired by-products;
2. The susceptibility of allyl alcohol to undergo side reactions under acidic conditions at elevated temperatures, leading to the consumption of this nucleophilic reagent;
3. The potential reversibility of the etherification reaction and post-reaction processing losses, wherein the formed ether bond may be

partially hydrolyzed under acidic conditions.

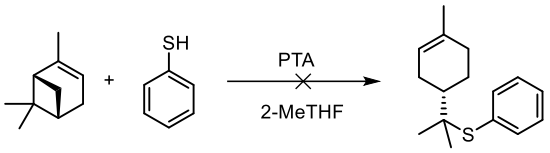
4. The occurrence of E1 elimination under the acidic and thermal reaction conditions. Both α-pinene and the intermediate carbocation derived from allyl alcohol may undergo E1 elimination, leading to the formation of alkene by-products. This side pathway not only consumes the starting materials but also diverts the reaction from the desired etherification route, thereby further reducing the yield of the target allyl ether.

2.1.5 Monomer from Thiophenol

Following the exploration of four distinct intermediates derived from α-pinene, further attempts were made to incorporate other chemical functional groups, thiophenol, benzyl alcohol, aniline, and furfuryl alcohol. This approach aimed to move beyond the structural limitations imposed by simple alkyl chains.

In the experiments with benzenethiol, a phosphotungstic acid (PTA) catalytic system was employed. The sulfur atom in benzenethiol serves as an effective ligand, capable of forming stable coordination bonds with various metal ions. This characteristic suggests potential applications in developing polymers for heavy metal ion adsorption or antimicrobial materials. Furthermore, the polarity of the resulting thioether group is distinct from that of an ether bond. Successful incorporation of this functional group could lead to modified material properties, such as adjusted compatibility and performance, in

subsequent polymer studies.



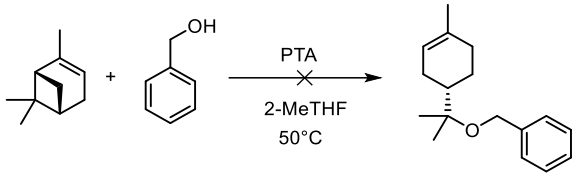
Scheme 21: Phosphotungstic acid (PTA) reaction of α-Pinene with thiophenol to generate thiophenyl ether product.

However, experimental attempts to react thiophenol with α-pinene under these conditions proved unsuccessful. A plausible explanation involves the strong coordination between the sulfur atom of thiophenol, which acts as a soft Lewis base, and the tungsten center of the phosphotungstic acid catalyst, a soft Lewis acid. This interaction likely forms a stable complex that deactivates the catalytic active sites. As a result, the protonation of α-pinene is inhibited, and competing pathways, such as oxidative coupling of thiophenol, may become predominant.

2.1.6 Monomer from Benzyl Alcohol

In a 2010 study by Yadav *et al.*, ferric chloride was employed as a Lewis acid catalyst for the direct hydroalkylation of α-pinene with benzyl alcohol.[41] The reaction proceeded at room temperature and reached completion within 1.5 hours, affording the product in 80% yield. Mechanistically, the process involves metal-catalyzed activation of the alkene, followed by double-bond migration via ring opening of the quaternary cyclobutane structure. Yadav's method exhibited notable regioselectivity, with the Lewis acid selectively activating the terminal alkene and nucleophilic attack following Markovnikov's rule,

successfully converting monoterpenes into terpene-alcohol derivatives.

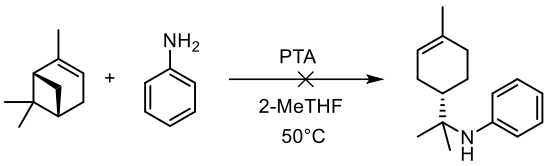


Scheme 22: Phosphotungstic acid (PTA) reaction of α-Pinene with benzyl alcohol to generate benzyl ether compound.

However, the attempt to employ PTA as a catalyst proved unsuccessful. Analysis indicates the following probable causes for this outcome. First, PTA functions as a strong Brønsted acid, which typically promotes a vigorous and less selective catalytic pathway. In contrast, ferric chloride, a Lewis acid, operates via a more controlled and precise coordination-based mechanism. Second, the catalytic action of PTA involves the direct protonation of the double bond in α-pinene, generating a highly reactive, non-coordinated carbocation intermediate. Under the reaction conditions, this transient species likely participated preferentially in unproductive side reactions such as isomerization or oligomerization. This outcome was exacerbated by the significant steric hindrance presented by the benzyl alcohol nucleophile, whose hydroxyl group is attached to a bulky benzene ring, slowing its attack on the carbocation centre. Finally, the strongly acidic environment provided by PTA, combined with elevated temperature, may have induced intermolecular dehydration of benzyl alcohol itself, consuming the starting material through formation of dibenzyl ether.

2.1.7 Monomer from Aniline

Following the experiments with phenylthiol and benzyl alcohol, the study was extended to *p*-aniline. If intermediates containing aromatic amine groups can be successfully synthesized and further converted into diols, they may serve as precursors for conductive polymers in subsequent explorations. Such polymers could potentially be applied in antistatic coatings or organic electronic devices.



Scheme 23: Phosphotungstic acid (PTA) reaction of α-Pinene with aniline to generate aniline product.

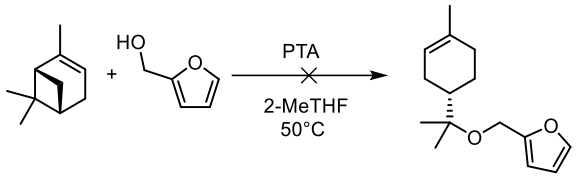
Additionally, the use of aniline with α-pinene under the PTA catalytic system was intended to probe the upper pH limit tolerable in the reaction environment, given that aniline acts as a weak Brønsted base. However, the reaction did not proceed under the tested conditions. A plausible explanation is that aniline underwent neutralization with the acidic PTA catalyst, forming aniline salts that led to catalyst deactivation.

2.1.8 Monomer from furfuryl alcohol

To explore the feasibility of incorporating a bio-based furan ring into the intermediate, reactions between α-pinene and furfuryl alcohol were attempted using both PTA and ferric chloride catalysts. Neither approach yielded the desired product.

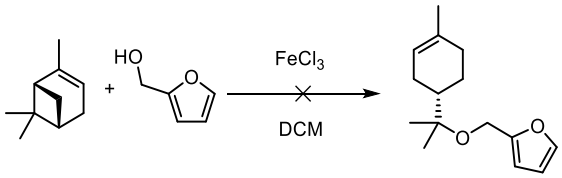
Under PTA catalysis, the reaction mixture rapidly darkened and thickened,

eventually forming an insoluble, infusible black solid. This outcome is attributed to the acid sensitivity of the furan ring in furfuryl alcohol. Protons from PTA protonate the furan ring, generating a highly reactive carbocation that initiates rapid cationic polymerization with other furfuryl alcohol molecules.



Scheme 24: Phosphotungstic acid (PTA) reaction of α-Pinene with furfuryl alcohol to generate ether product.

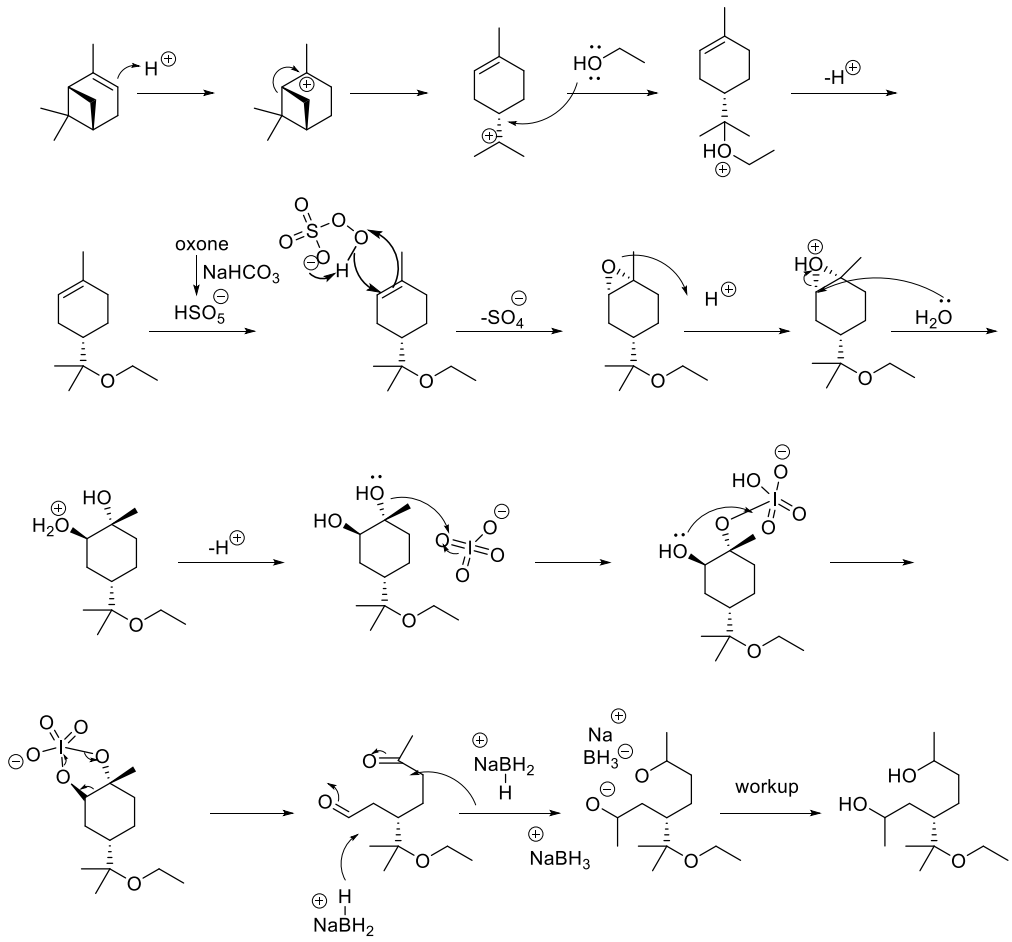
In the $FeCl_3$ system, a reddish-brown viscous paste was obtained. Here, Fe^{3+} ions act as strong Lewis acids, coordinating with the oxygen atoms of either the furan ring or the hydroxyl group of furfuryl alcohol. This coordination activates the molecule toward intermolecular reactions, leading to furan ring-opening and complex polymer formation. Although ferric chloride successfully activates the double bond in α-pinene in Yadav's reported case, its presence was preempted by furfuryl alcohol in this system. The oxygen atoms in furfuryl alcohol act as stronger Lewis bases than the vinyl double bond in α-pinene, diverting the catalyst from the intended pathway.



Scheme 25: Iron(III) chloride catalysed reaction of α-Pinene with furfuryl alcohol to generate ether product.

2.2 Oxidative Cleavage and Dihydroxylation

Following the acquisition of the intermediate derived from α-pinene, the subsequent steps are designed to produce a diol monomer suitable for polymerization. This transformation is achieved through an oxidative cleavage sequence. First, the alkene moiety present in the intermediate is oxidized to form a diol. This diol then undergoes C–C bond scission between the hydroxylated carbons, leading to ring opening of the cyclohexene system. Simultaneously, the cleaved carbon atoms are oxidized to carbonyl functionalities. This two-step strategy, which combines dihydroxylation and oxidative cleavage, effectively rearranges the cyclic skeleton into an open-chain fragment equipped with two highly reactive carbonyl groups. These groups provide handles for further functionalization, yielding key intermediates that can be elaborated into diol monomers for use as polymerization precursors.

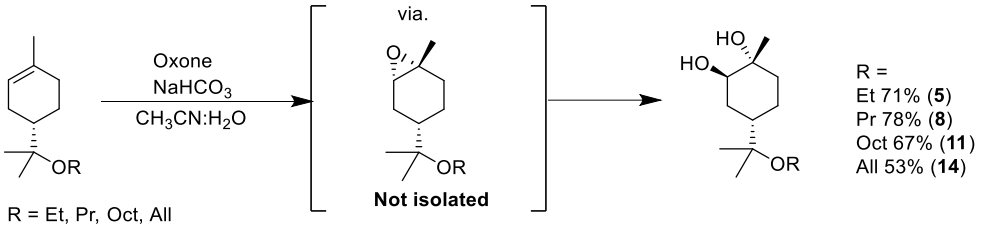


Scheme 26: Overall reaction summary for generation of bio-based diol monomers.

2.2.1 Dihydroxylation by Using Oxone/$NaHCO_3$

The dihydroxylation of α-pinene derivatives is efficiently catalyzed by Oxone under mild conditions. In a mixed acetonitrile/water solvent system at ambient temperature, the alkene moiety is directly converted to the corresponding vicinal diol. This transformation proceeds via an oxone epoxidation and subsequent hydrolysis mechanism, avoiding the isolation of an intermediate epoxide. $NaHCO_3$ is employed to buffer the reaction system at a weakly basic pH by neutralizing the acidic by-product, $KHSO_4$, generated from Oxone. For α-pinene alcohol derivatives, the reaction proceeds cleanly to afford the diol

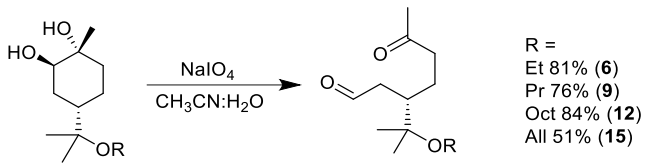
product in high yield, typically around 70%.[48] The postulated directing effect from tertiary ether group is believed to direct the epoxidation to one face of the alkene, giving high selectivity for the *cis* isomer of the epoxide product, prior to hydrolysis to give the anti-diol product.[49]



Scheme 27: Oxone-mediated dihydroxylation to yield diol monomers.

2.2.2 Oxidative cleavage of diols into ketone-aldehyde

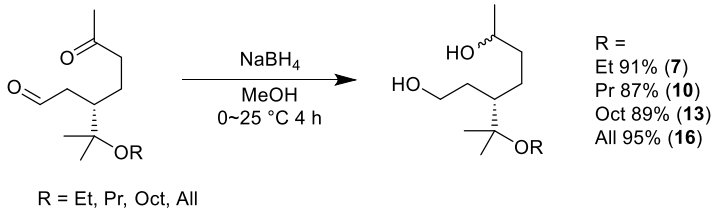
Subsequently, the diol was subjected to oxidative cleavage using sodium periodate ($NaIO_4$), yielding the corresponding aldehyde and ketone functional groups. Mechanistically, the periodate ion (IO_4^-) first coordinates with the 1,2-diol unit, forming a cyclic periodate ester intermediate. This five-membered ring intermediate facilitates a concerted rearrangement, leading to the cleavage of the carbon-carbon bond linking the two hydroxyl-bearing carbons. In this process, periodate is reduced to iodate (IO_3^-), while the two carbon atoms are simultaneously oxidized to carbonyl groups—specifically a ketone and an aldehyde—thus generating the final keto-aldehyde product. The ratio 4:3 acetonitrile:water yielded over 80% of the desired products.



Scheme 28: Sodium periodate-mediated oxidative cleavage of diols to yield keto-aldehyde monomers.

2.3 Aldehyde-ketone to diols

Sodium borohydride is a mild and highly selective nucleophilic reducing agent that reduces carbonyl compounds through hydride ion transfer. Aldehydes, by virtue of their lower steric hindrance and higher electrophilicity, are reduced preferentially over ketones. When applied to α-pinene-derived intermediates in methanol over four hours, this reduction afforded the corresponding diol monomers in all cases, with isolated yields exceeding 87%.



Scheme 29: Sodium borohydride reduction of keto-aldehyde monomers to yield diol products.

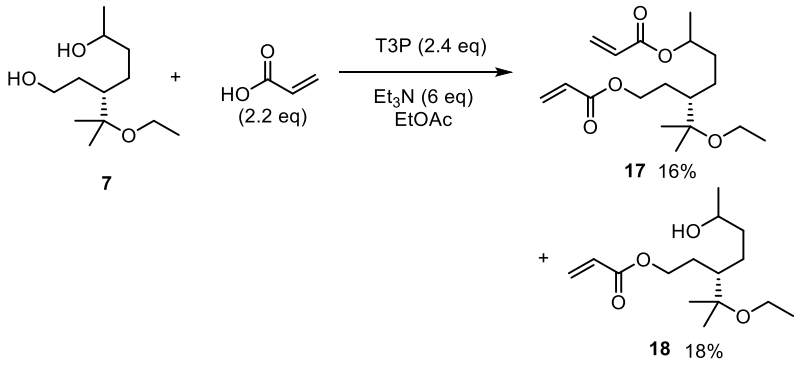
These four α-pinene-derived diol monomers serve as versatile precursors for developing new monomeric structures and polymerization strategies, providing a foundation for accessing a wide range of polymer materials.

2.4 Derivatives of diol monomers

Following the synthesis of four distinct α-pinene-derived diol monomers, these compounds were functionalized into more reactive acrylate derivatives via

esterification. This transformation yielded the desired diacrylate alongside a monoacrylate species.

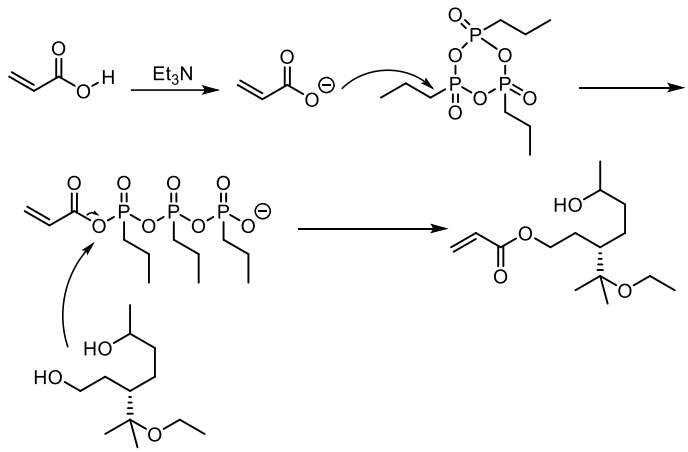
The diacrylate monomers are pivotal for subsequent radical polymerization, as the terminal acrylic double bonds at both ends enable chain-growth reactions under photo- or thermo-initiation. This strategy incorporates the chiral, biobased backbone of α-pinene into the polymer main chain, a feature anticipated to impart specific functionalities such as optical activity or hydrophobicity. Conversely, the monoacrylate derivatives, bearing both a polymerizable double bond and a hydroxyl group, offer potential for synthesizing graft copolymers or serving as functional chain-transfer agents, thereby expanding the scope of accessible polymeric architectures.



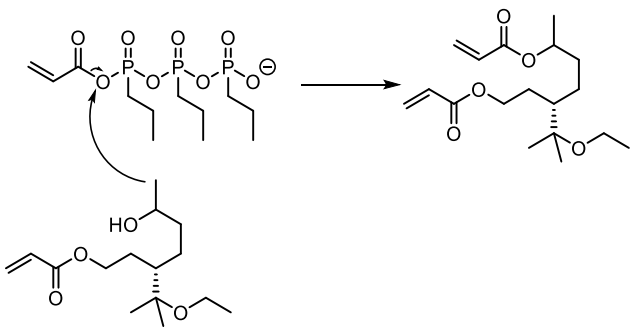
*Scheme 30: Propylphosphonic anhydride (T3P) esterification of diol monomer **7** to yield di- and mono-acrylate products (**17** and **18**).*

The esterification reaction is catalyzed by propylphosphonic anhydride (T3P) in the presence of triethylamine (Et_3N), proceeding through a conventional acid-catalyzed mechanism that is enhanced by the efficiency of T3P as a condensing agent. Initially, T3P activates the carboxylic acid group of acrylic acid via

nucleophilic addition–elimination at one of its anhydride bonds, generating a reactive mixed anhydride intermediate along with a phosphoric acid derivative. Subsequently, a hydroxyl group of the diol monomer acts as a nucleophile and, assisted by Et_3N, attacks the carbonyl carbon of the activated mixed anhydride. This leads to C–O bond formation and release of a T3P-derived byproduct, affording the monoacrylate intermediate. Repetition of this process at the remaining hydroxyl group ultimately yields the diacrylate product.



Scheme 31: Propylphosphonic anhydride (T3P) mechanism for esterification of diol monomer to yield the monoacrylate product.



Scheme 32: Propylphosphonic anhydride (T3P) mechanism for further esterification of monacrylate monomer to yield the diacrylate product.

3.0 Chapter 3: Polymer Synthesis

With a range of diol-derived monomers obtained from alpha-pinene already available, the subsequent study focused on the polymerization of these novel bio-based monomers. The objective was to explore polymerization reactions using the monomers synthesised in Chapter 2, by screening and optimising various reaction conditions to access different classes of polymers. Free radical polymerization was attempted for the acrylate-functionalised monomers. Polycondensation via esterification between dibasic acids and diols was also conducted. Additionally, transesterification polycondensation employing the diol monomers was investigated to synthesize a novel polyester incorporating long-chain ether groups in the side chains.

3.1 Polycondensation using diol monomers

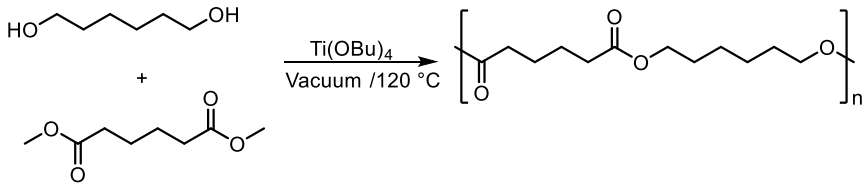
This experiment primarily employs a polycondensation reaction to catalyse the ester exchange polycondensation of side-chain-bearing diol monomers derived from renewable energy sources (alpha-pinene) with dimethyl adipate, in an attempt to synthesise polyester. The objective is to investigate whether bio-based polymeric materials with novel structures and properties can be obtained.

3.1.1 Attempts to match the catalyst with different structural monomers

Prior to the polycondensation of the novel diol monomer, two model reactions were conducted using hydroxyl-bearing starting compounds under literature-based conditions. The first involved the condensation of 1,6-hexanediol with

dimethyl adipate at 120 °C catalyzed by $Al(OTf)_3$, which proceeded successfully. In the second attempt, cyclohexane-1,4-diol was reacted with dimethyl adipate under identical conditions using $Al(OTf)_3$ as the catalyst; however, no polymerization was observed. Subsequently, $Ti(OBu)_4$ was employed as an alternative catalyst, which afforded the target polymer effectively.

According to the method established by Takao *et al.* (2009), the first experiment made use of a metal triflate catalytic system with $Al(OTf)_3$ as the catalyst. A stepwise temperature and vacuum protocol was applied: ester exchange was initially conducted at 100 °C to form oligomers, followed by polycondensation at 120 °C under a reduced pressure of 20 mbar. Finally, the pressure was further lowered to 1 mbar to facilitate the removal of methanol byproducts.[50]



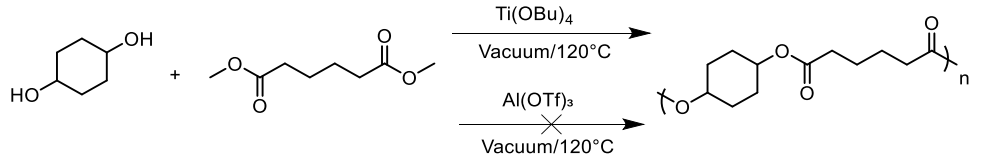
Scheme 33: Titanium(IV) butoxide-mediated polycondensation reaction of diols with dimethyl adipate to yield polymer products.

^{1}H NMR analysis confirmed the successful synthesis of the target polyadipate. The polymer had a molecular weight of 15,140 g/mol as determined by gel permeation chromatography (GPC).

However, when cyclohexane-1,4-diol was used instead, the reaction failed to proceed under $Al(OTf)_3$ catalysis. This outcome is likely attributable to the steric

hindrance associated with the secondary alcohol groups of cyclohexane-1,4-diol, which impedes the direct nucleophilic attack on the activated carbonyl. Consequently, $Ti(O^iPr)_4$ was employed as an alternative catalyst.

$Ti(O^iPr)_4$ is a well-established and highly effective catalyst for polyester synthesis, as exemplified in the production of poly(ethylene terephthalate) and poly(butylene terephthalate). Its mechanism involves an initial reaction with the hydroxyl group of the diol to form a titanium alkoxide intermediate. The Ti–O bond in this species is highly reactive, enabling efficient nucleophilic attack on the carbonyl carbon of dimethyl adipate and thereby facilitating the transesterification step. This pathway effectively bypasses the steric limitations associated with the direct reaction of the hindered secondary alcohol.



Scheme 34: Titanium(IV) butoxide and aluminium triflate reactions of 1,4-cyclohexanediol with dimethyl adipate to yield polymer products.

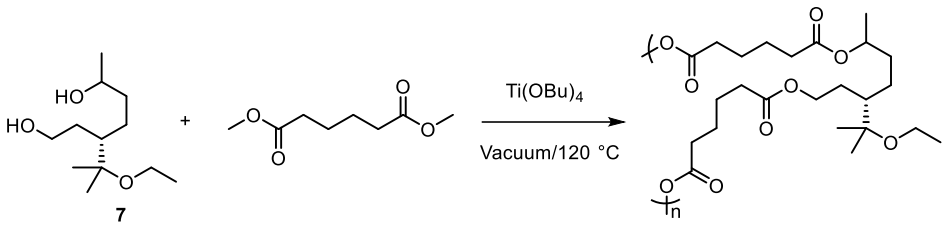
These comparative experiments underscore the necessity of prioritizing catalysts such as $Ti(OBu)_4$, or others functioning via similar mechanisms, for the synthesis of polyesters derived from α-pinene-based diol monomers. Furthermore, polymerization conditions employing stepwise heating and high vacuum are recommended.

3.1.2 Polycondensation of new diols monomers

Subsequent attempts were carried out to perform condensation reactions

using 3-(2-ethoxypropan-2-yl)heptane-1,6-diol and 1-(2-(octyloxy)propan-2-yl)heptane-1,6-diol. In both monomers, the secondary hydroxyl groups are sterically hindered, which is expected to result in a slower polymerization rate compared to conventional monomers such as 1,6-hexanediol.

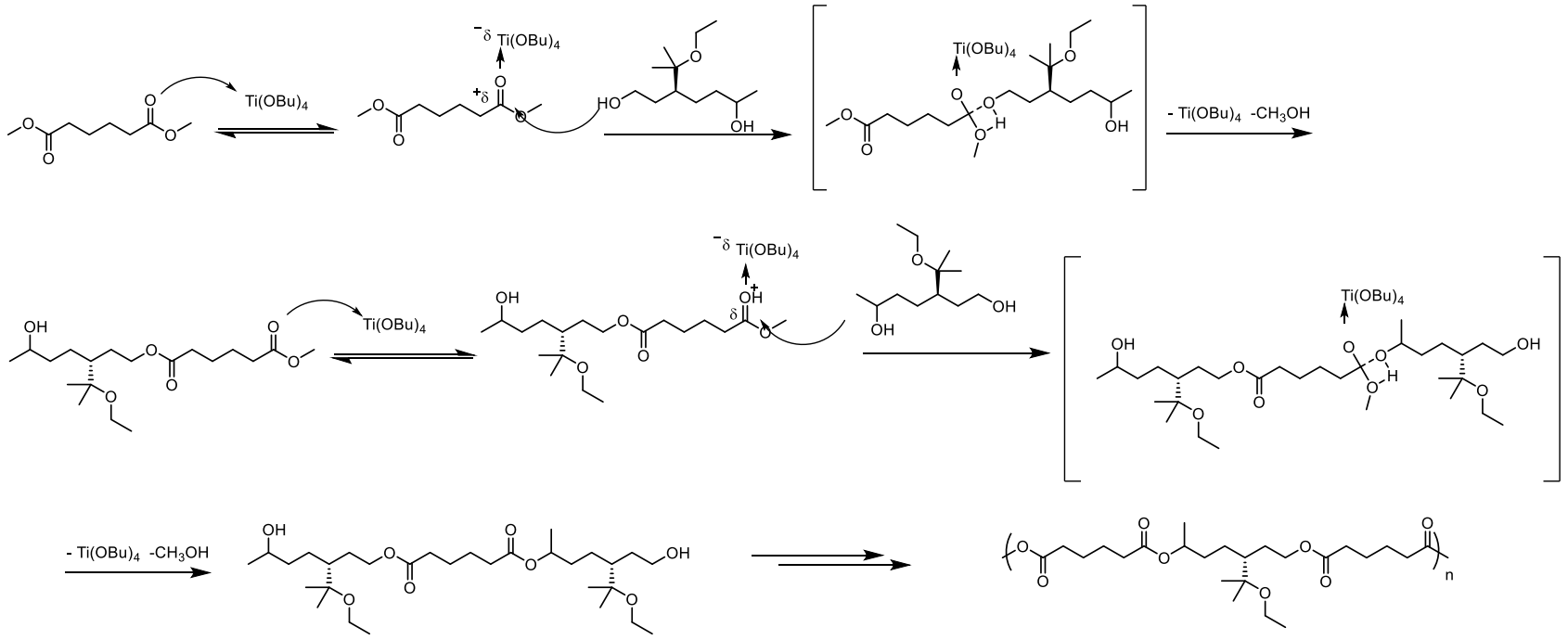
First, we tested whether this catalytic system was suitable for 3-(2-ethoxypropan-2-yl)heptane-1,6-diol.



*Scheme 35: Titanium(IV) butoxide reaction of 3-(2-ethoxypropan-2-yl)heptane-1,6-diol **7** with dimethyl adipate to yield polymer products.*

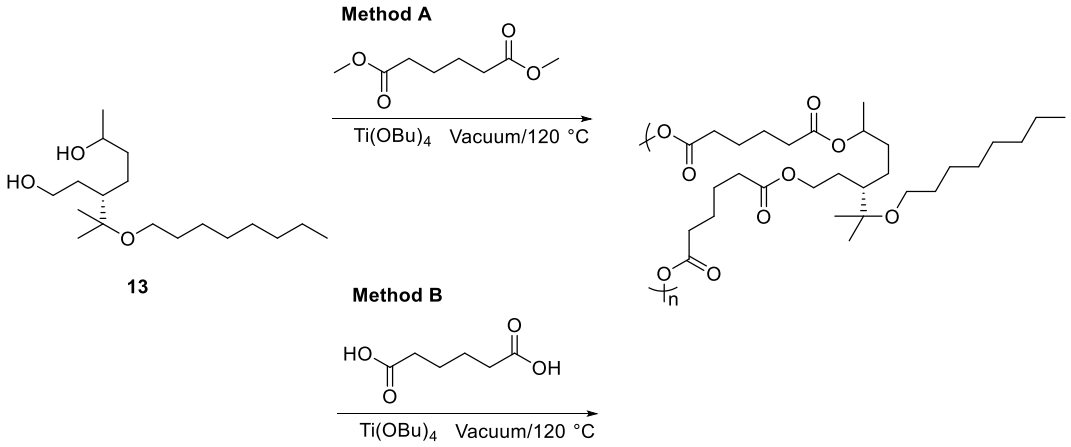
The diol monomer was first combined with dimethyl adipate in a 1:1 molar ratio, along with a small quantity of $Ti(OBu)_4$ catalyst. The mixture was heated to 100 °C under stirring while the pressure was gradually reduced to 20 mbar. The temperature was then raised to 120 °C under high vacuum (1 mbar). After the reaction was complete and heating was discontinued (21 hours), stirring under vacuum was continued for an additional 8 hours to allow removal of methanol byproduct. During this period, condensed methanol was visibly collected at the joint between the two-necked flask and the three-way adapter. ^{1}H NMR analysis confirmed the synthesis of the polyadipate. The diagnostic changes included a significant reduction in the signal intensity corresponding to the hydroxymethylene protons (–CH_2–OH) of the diol monomer, observed in

the range of δ 3.3–3.6 ppm. Concurrently, a new characteristic signal emerged in the region of δ 4.0–4.2 ppm, which is attributed to the methylene protons adjacent to the newly formed ester linkages (–O–CH_2–). This distinct shift—from the hydroxymethylene protons of the starting material to the ether-linked methylene protons of the polymer backbone—provides direct spectroscopic evidence for the consumption of hydroxyl groups via esterification and confirms the formation of the target polyadipate structure.



*Scheme 36: Postulated mechanism of titanium(IV) butoxide reaction of diol **7** with dimethyl adipate.*

Then, we attempted the condensation of 1-(2-(octyloxy)propan-2-yl)heptane-1,6-diol with both adipic acid dimethyl ester and adipic acid, to compare the efficiency and challenges of two distinct polymerisation mechanisms when synthesising the same target polymer.



*Scheme 37: Method A and method B for titanium(IV) butoxide reaction of diol **13** with adipates.*

In Experiment A, dimethyl adipate was subjected to polycondensation via ester exchange with diol monomers. As the primary by-product, methanol has a low boiling point (64.7 °C) and was effectively removed by applying high vacuum. The molecular weight of the resulting polyadipate was determined to be 6944 g/mol by GPC. GPC separates polymers based on the size-exclusion principle, whereby larger molecules are eluted first, followed by smaller ones. By constructing a calibration curve of elution volume versus the logarithm of molecular weight using narrow-dispersity standards of known molecular weights, the elution profile of the polymer under analysis—such as the

polyadipate synthesized in this study—can be converted into a molecular weight distribution. This allows the determination of key molecular weight parameters, including the number-average molecular weight (M_n), thereby enabling accurate measurement of the polymer's molecular weight.

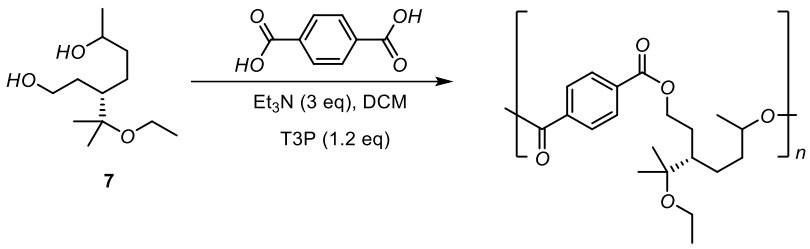
In Experiment B, direct polycondensation between adipic acid and diol monomers was attempted. In this process, Ti^{4+} acted as a Lewis acid catalyst by coordinating with the carbonyl oxygen of the carboxyl group, thereby activating it for nucleophilic attack by the hydroxyl group of the diol. However, the reaction produced water, which has a relatively high boiling point (100 °C). Despite the reaction temperature of 120 °C, the high viscosity of the oligomeric medium impeded water diffusion and removal. This residual water severely limited further increase in molecular weight (obtained the polyadipate with a molecular weight of 1888 g/mol). Although the ideal polymer obtained in Experiment A was not achieved, ^{1}H NMR analysis confirmed the occurrence of direct polycondensation. Despite its challenges, this route presents advantages in economic and environmental sustainability.

Table 1: Reaction conditions for experiment A and B and the resulting M_n obtained.

Entry	Method	Temperature (°C)	M_n (g/mol)
1	A	120	6944
2	B	120	1888

3.1.3 Coupling agent-mediated stepwise polymerization

A stepwise polycondensation was subsequently attempted between a novel diol monomer and terephthalic acid, using the coupling agent T3P. In the presence of triethylamine as a base, the carboxylic acid group of terephthalic acid is deprotonated to form a carboxylate anion. This anion then acts as a nucleophile, attacking the phosphorus center of T3P to generate an acylphosphonium intermediate. The hydroxyl group of the diol monomer subsequently attacks this activated intermediate, forming a tetrahedral transition state that collapses to yield the ester bond. In this mechanism, an activated dicarboxylic acid monomer reacts with a diol to form a hydroxyl-terminated dimer. This dimer can, in turn, be activated by the T3P/Et_3N system and react with another activated acid monomer or dimer, thereby enabling a cyclical process for stepwise chain elongation.



*Scheme 38: Propylphosphonic anhydride (T3P) reaction of diol **7** with terephthalic acid to yield polymeric product.*

Initial combination of terephthalic acid, the diol, and dichloromethane in the flask resulted in incomplete dissolution of the solids. The subsequent dropwise addition of triethylamine promoted the gradual dissolution of the remaining solid material. The reaction mixture was then stirred as a solution of T3P was

added dropwise.

For the initial workup, water was used to quench the reaction, leading to the formation of three distinct layers: an upper aqueous phase, a middle emulsified layer, and a lower dichloromethane organic phase. Concentration of the isolated dichloromethane phase under reduced pressure failed to yield the target product. It was hypothesized that the polar character of the polyester product, together with the surfactant-like properties of the water-soluble phosphate byproducts generated from T3P, resulted in a highly stable emulsion that entrapped the polymer.

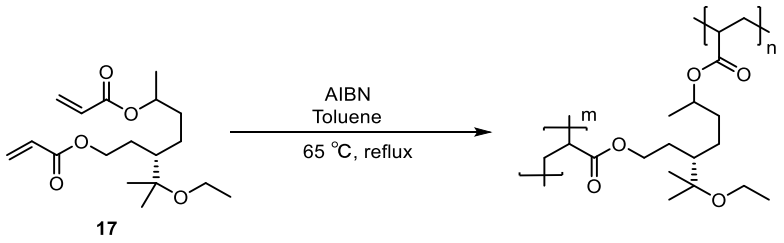
To test this hypothesis, a modified workup procedure was employed in a subsequent experiment. The reaction mixture was sequentially treated with water and methanol, then filtered directly. This alternative procedure successfully yielded the desired polymer as a white solid.

To confirm the progression of the reaction, the product was analyzed by IR and ^{1}H NMR spectroscopy. The IR spectrum revealed considerable broadening and weakening of the characteristic carboxyl and hydroxyl peaks. This evidence was corroborated by GPC, which measured a molecular weight of 2513 g/mol for the resulting white solid, thereby verifying the successful polymerization.

3.1.4 Free radical polymerization of the new diacrylate monomer

Following derivatisation, the diol derived from alpha-pinene was converted into a diacrylate monomer. As each molecule of this monomer contains two

polymerisable acrylic double bonds, it can form connections at multiple points during polymerisation, leading to a three-dimensional crosslinked network. Consequently, its polymerisation was attempted via a free-radical process.



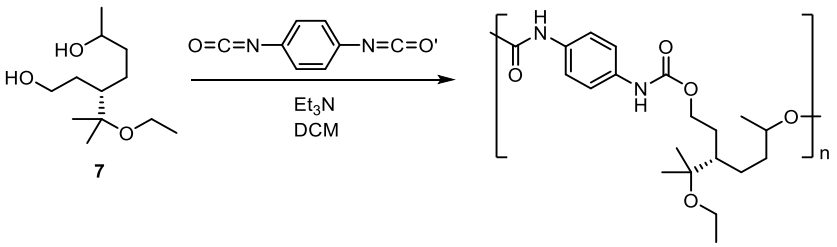
*Scheme 39: AIBN free radical polymerisation of diacrylate monomer **17** to yield polymeric product.*

The monomer and AIBN were dissolved in toluene in a round-bottom flask. The solution was frozen using a dry ice/acetone bath, and the flask was equipped with a three-way connector to establish a nitrogen flow. The system was subjected to three evacuation-nitrogen refill cycles to ensure an oxygen-free atmosphere. Subsequently, the reaction mixture was heated at 65 °C on a hot plate. After completion, the mixture was cooled to room temperature, and the polymer was precipitated by direct addition into methanol followed by refrigeration. The precipitate was isolated by filtration. ^{1}H NMR and IR spectra confirmed the complete consumption of the acrylic C=C double bonds. Gel permeation chromatography (GPC) analysis indicated a molecular weight of 7662 g/mol.

3.1.5 Polyurethane formed by polymerization of diol monomers

Following the investigation of various polymeric systems, polyurethane

synthesis was attempted using diol monomers derived from alpha-pinene. This reaction is a characteristic step-growth polymerization driven by the nucleophilic addition of isocyanate groups to alcohol hydroxyl groups. Since both monomers are difunctional, containing either two hydroxyl or two isocyanate groups, the reaction proceeds sequentially from both ends of the growing chain. The initial reaction between a diisocyanate and a diol yields a dimer terminated with isocyanate groups. This dimer can then react with another diol molecule or with a second dimer, enabling the molecular chain to grow in a stepwise manner and ultimately form a linear polymer.



*Scheme 40: Diisocyanate reaction with diol **7** to generate polyurethane product.*

Based on the 1:2 feed ratio of diol to diisocyanate, the reaction was designed to produce an NCO-terminated prepolymer through the coupling of one diol molecule with two isocyanate molecules, rather than a high-molecular-weight polymer. Analysis of the resulting white solid confirmed the near-complete consumption of the diol hydroxyl groups. However, as the reaction was performed under non-anhydrous and non-oxygen-free conditions, and the measured molecular weight of 918.5 g/mol significantly exceeded the theoretical value for the target prepolymer, it is proposed that water molecules

reacted with the terminal –NCO groups of the initially formed prepolymers. This side reaction likely resulted in the formation of urea linkages, connecting individual prepolymer units and leading to the observed increase in molecular weight.

4.0 Conclusions and Further Work

In this project, we explored the derivation of monomers bearing polymerizable groups from the renewable biomass feedstock α-pinene, and further attempted the synthesis of various functional polymers. The process began with acid-catalyzed ring-opening reactions, followed by sequential dihydroxylation and oxidative cleavage steps to afford diol monomers. Derivatization studies were subsequently performed on one of the resulting diols. Polymerization trials were then conducted using these novel bio-based monomers, including ester exchange polymerization, direct polycondensation, and radical polymerization.

In Chapter 2, we examined the use of α-pinene as a starting material for the preparation of 4 distinct monomer precursors and 6 monomers functionalized with polymerizable groups. This effort resulted in the successful synthesis of four diol monomers and one diacrylate monomer. We adapted the catalytic system reported by Cunningham *et al.*, which employs a tungsten-based polyoxometalate catalyst for terpenoid substrates. When ethanol, propanol, or octanol were used as reagents, the diol yield reached approximately 26%. In

contrast, the use of allyl alcohol led to a markedly lower diol yield of about 6.4%.

Chapter 3 first aimed to identify the most suitable catalyst for the polycondensation of the novel diols. Polymerization attempts were then carried out using two α-pinene-derived diol monomers with different side-chain lengths, via both ester exchange and direct polycondensation methods. Additionally, radical polymerization was performed using the diacrylate monomer. In all cases, polymeric products were successfully obtained.

Future work could involve exploring the benzyl ether methodology reported by Yadav, with the goal of synthesizing diol monomers containing benzene rings. This approach will facilitate the development of novel polymers with tailored performance characteristics.

When conducting polyester synthesis using these new diol monomers, the polycondensation duration should be systematically varied to assess the potential for achieving higher molecular weights. Parallel polymerization trials with the allyl-functional diols are also recommended. If linear polymers are successfully obtained, these could function as prepolymers for subsequent crosslinking reactions initiated via their side-chain double bonds.

Additionally, polymerization of diol monomers toward polyurethane formation requires further optimization of reaction conditions and workup procedures. Potential strategies include the use of polar aprotic solvents such as DMF to

enhance reactivity, as well as ensuring that all reactions are conducted under strictly anhydrous and oxygen-free conditions.

Experimental

Materials. All solvents and reagents were purchased from commercial suppliers and used directly without further purification. All water was deionised before use, and experiments were carried out under an inert atmosphere of nitrogen. Cooling to 0 °C was affected using an ice-water bath. Cooling to -78 °C using dry ice and acetone. The term petroleum ether refers to the fraction with boiling point between 40 and 60 °C. All solutions are saturated unless stated otherwise. Brine refers to a saturated solution of sodium chloride.

Reaction monitoring. TLCs were performed on either silica gel on aluminium or on aluminium oxide on PET foil. They were visualised using a potassium permanganate stain, phosphomolybdic acid, or vanillin dip. Flash column chromatography was performed using Fluorochem silica gel 60, 40–63 μm, unless otherwise noted.

NMR. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, DMSO-d_6 at ambient temperature using Bruker DPX400 (400 MHz), AV400 (400 MHz), AV3400HD (400 MHz), AV3400 (400 MHz). Data are expressed as chemical shifts in parts per million (ppm). ^{1}H NMR chemical shifts (δ) were reported in ppm relative to the ^{1}H signals in the solvent – $CDCl_3$: δ 7.26 ppm, DMSO-d_6: δ 2.50 ppm. ^{13}C NMR was recorded on a 75 MHz spectrometer and chemical shifts (δ) were reported in ppm relative to the ^{13}C signals in the solvent – $CDCl_3$: 77.16 ppm,

DMSO-d_6: δ 39.51 ppm. Couplings (J) are given in Hertz (Hz), and abbreviations for NMR multiplet analysis were used as follows: s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, sep = septet, br = broad, app = apparent, m = multiplet. Where appropriate, assignments were aided using COSY, HMQC and HMBC spectra.

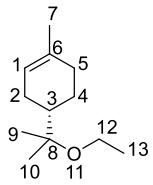
Infra-Red. Infra-red spectra were recorded using a Bruker Tensor 27 FT-IR spectrophotometer using either an ATR attachment or a solution cell using $CHCl_3$ as the solvent and their peaks are quoted as υ_{max} in cm^{-1}. High-resolution mass spectra were obtained using a Bruker MicroTOF mass spectrometer operating in electrospray ionisation (ESI) mode.

Gel Permeation Chromatography. Gel permeation chromatography (GPC), an Agilent 1260 Infinity Series HPLC (Agilent Technologies, USA), at room temperature using two Agilent PLgel 5 µm mixed-C columns (300 x 7.5 mm) in series with a PL-gel 10 µm Guard Column (50 x 7.5 mm) fitted with a differential refractive index detector (DRI) was used. THF (HPLC grade, Fisher Scientific) was used as the eluent at room temperature with two Agilent PL-gel mixed-E columns in series at a flow rate of 1 mL min−1. Poly(methyl methacrylate) standards were used as a calibration curve with ASTRA software (Wyatt Technology, USA). This was used to determine the Mn, Mw and molecular weight distribution and dispersity (Đ, Mw/Mn).

Compound Experimental Data

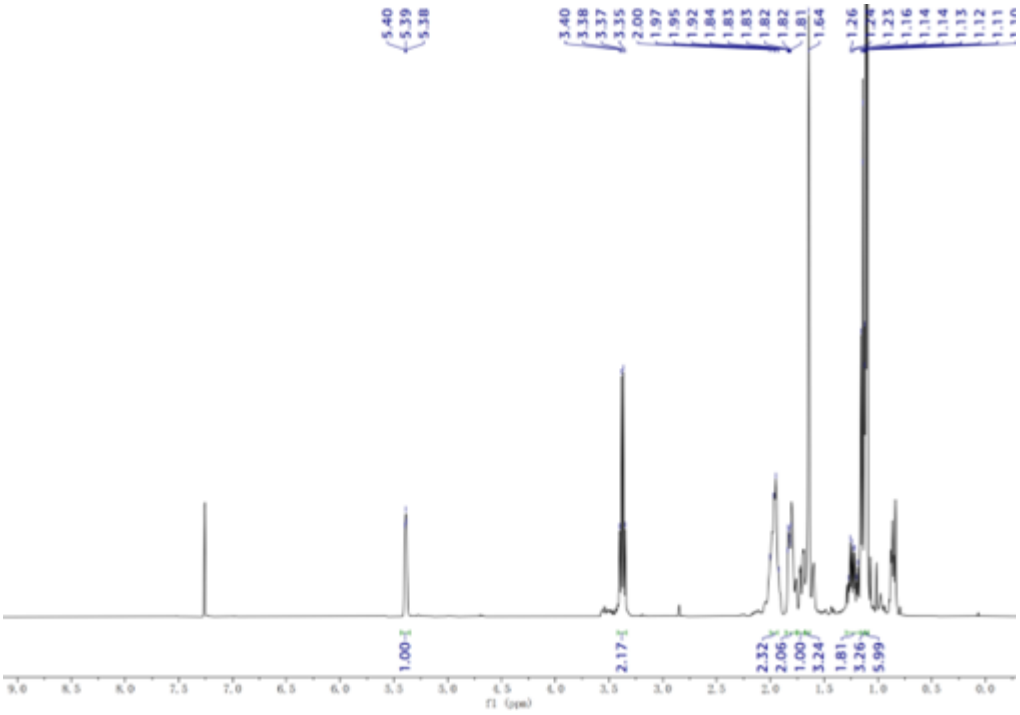
Monomers synthesis

4-(2-ethoxypropan-2-yl)-1-methylcyclohex-1-ene (1)



(-)-(α)-Pinene (6.81 g, 50 mmol) and ethanol (23 g, 500 mmol) were dissolved in 2-MeTHF (50 mL). PTA (2.16 g, 0.75 mmol) was added portion-wise. The reaction was heated to 50 °C and stirred under reflux for 48 hours. After 48 hours, the reaction mixture was allowed to cool to room temperature and filtered with silica gel under reduced pressure. The solvent was removed under reduced pressure. The mixture was purified by silica gel chromatography (0-10% ethyl acetate in petroleum ether) to give alkene **1** as a yellow oil (3.31 g, 18.1 mmol, 51% yield).

IR ν_{max} cm^{-1} 3314 (olefin), 2955, 2923, 2854, 1464 (olefin), 1378, 1248, 1226, 1160, 1119, 1056; **δ_H** (400 MHz, $CDCl_3$) 5.39 (1H, m, 1-H), 3.37 (2H, q, *J* 7.0 , 12-H_2), 1.96 (2H, m, 2-Ha, 5-Ha), 1.83 (2H, m, 2-Hb, 5-Hb), 1.71 (1H, m, 3-H), 1.64 (3H, s,7-H_3), 1.23 (2H, m, 4-H_2), 1.14 (3H, t, *J* 7.0, 13-H_3), 1.11 (6H, s, 9-H_3, 10-H_3); **δ_C** (100 MHz, $CDCl_3$) 134.1 (C-6), 121.1 (C-1), 76.6 (C-8), 56.0 (C-12), 41.8 (C-3), 31.3 (C-5), 27.0 (C-2), 24.2 (C-9), 23.5 (C-10), 23.2 (C-4), 22.8 (C-7), 16.4 (C-13); **HRMS** (ESI positive): Calculated for $C_{12}H_{23}O$ $[M+H]^+$ 183.1743, obtained 183.1737.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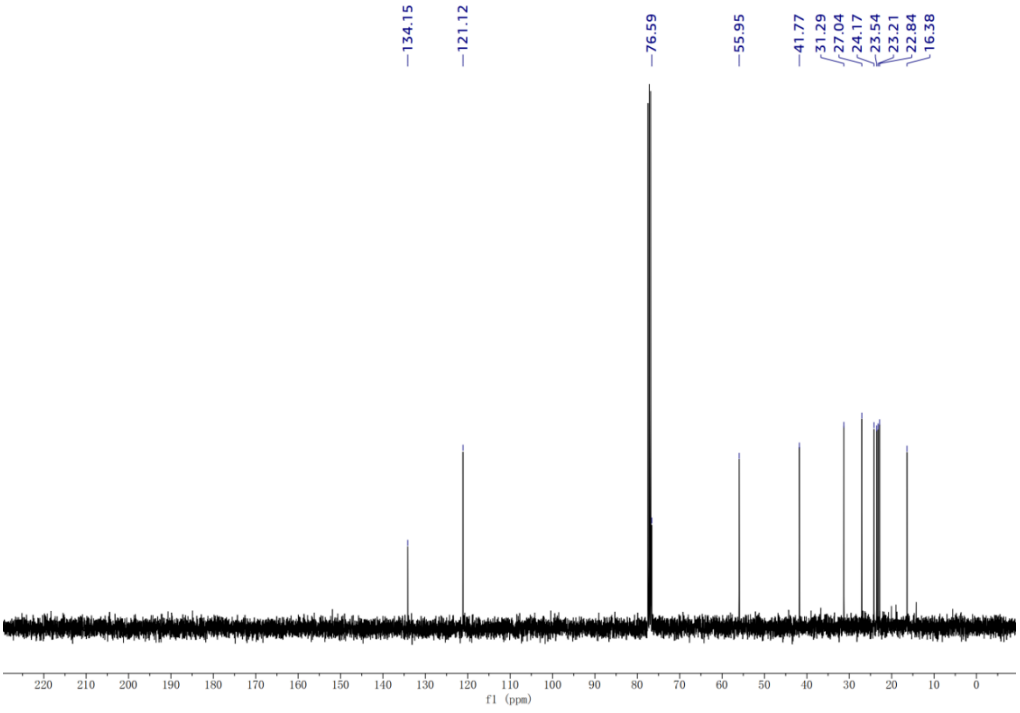
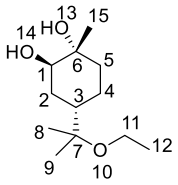
5.39
5.38
3.40
3.38
3.37
3.35
2.00
1.97
1.95
1.92
1.84
1.83
1.82
1.81
1.64
1.26
1.16
1.14
1.13
1.12
1.00
2.17
2.32
2.06
1.00
3.24
1.81
3.26
5.99
f1 (ppm)

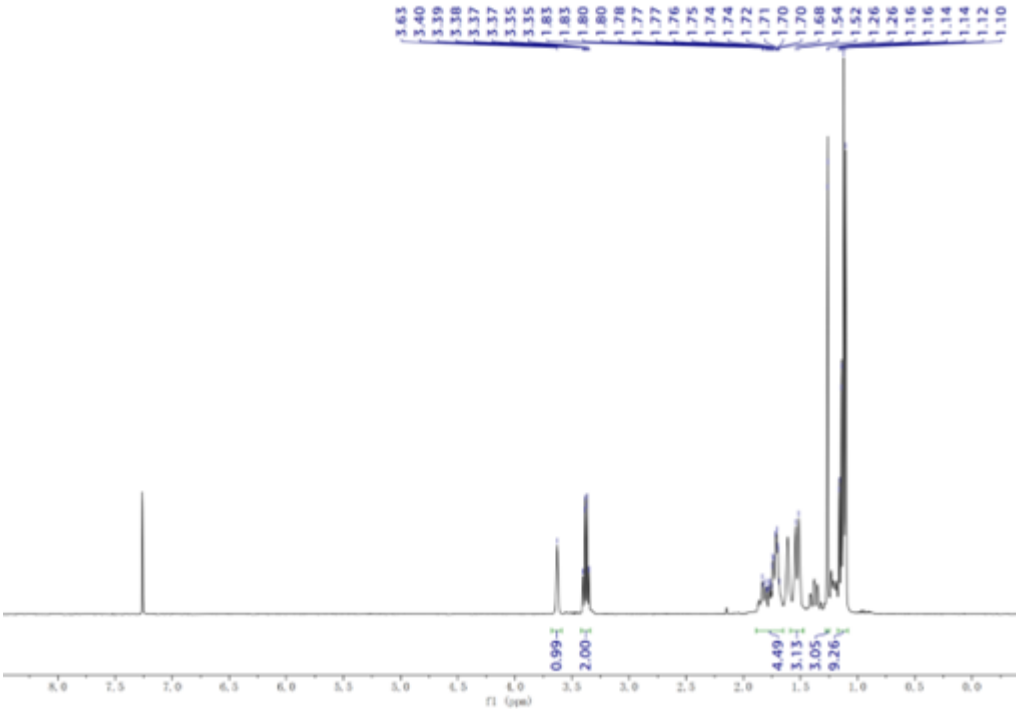

134.15
121.12
76.59
55.95
41.77
31.29
27.04
24.17
23.54
23.21
22.84
16.38
f1 (ppm)

5-(2-ethoxypropan-2-yl)-1-methylcyclohexane-1,2-diol (5)



Alkene **1** (6.49 g, 35.7 mmol) was dissolved in CH_3CN (250 mL) and H_2O (190 mL). A mixture of OXONE (32.8 g, 106.9 mmol) and $NaHCO_3$ (7.49 g, 89.1 mmol) was added portion-wise, and the reaction was stirred for 72 hours at room temperature. The reaction mixture was filtered and extracted with diethyl ether (3 × 150 mL). The organic layers were combined and dried over magnesium sulfate, filtered, and the solvent removed under reduced pressure to give ethoxy-isopropyl diol **5** as a pale-yellow gel (5.47 g, 25.3 mmol, 71% yield).

IR ν_{max} cm^{-1} 3404 (hydroxyl), 2972, 2931, 2876, 1709, 1444, 1387, 1367, 1325, 1313, 1286, 1247, 1175, 1127 (hydroxyl), 1107, 1054 (hydroxyl), 1034, 1000; **δ_H** (400 MHz, $CDCl_3$) 3.63 (1H, s, 1-H), 3.38 (2H, m, 11-H_2), 1.65 (7H, m, 2-H_2, 3-H, 4-H_2, 5-H_2), 1.26 (3H, s, 15-H_3), 1.14 (9H, s, 8-H_3, 9-H_3, 12-H_3); **δ_C** (100 MHz, $CDCl_3$) 76.3 (C-7), 74.4 (C-1), 71.2 (C-6), 56.0 (C-11), 38.0 (C-3), 33.9 (C-5), 30.2 (C-2), 27.7 (C-15), 23.3 (C-8), 23.0 (C-9), 22.2 (C-4), 16.4 (C-12); **HRMS** (ESI positive): Calculated for $C_{12}H_{25}O_3$ $[M+H]^+$ 217.1798, obtained 217.1795.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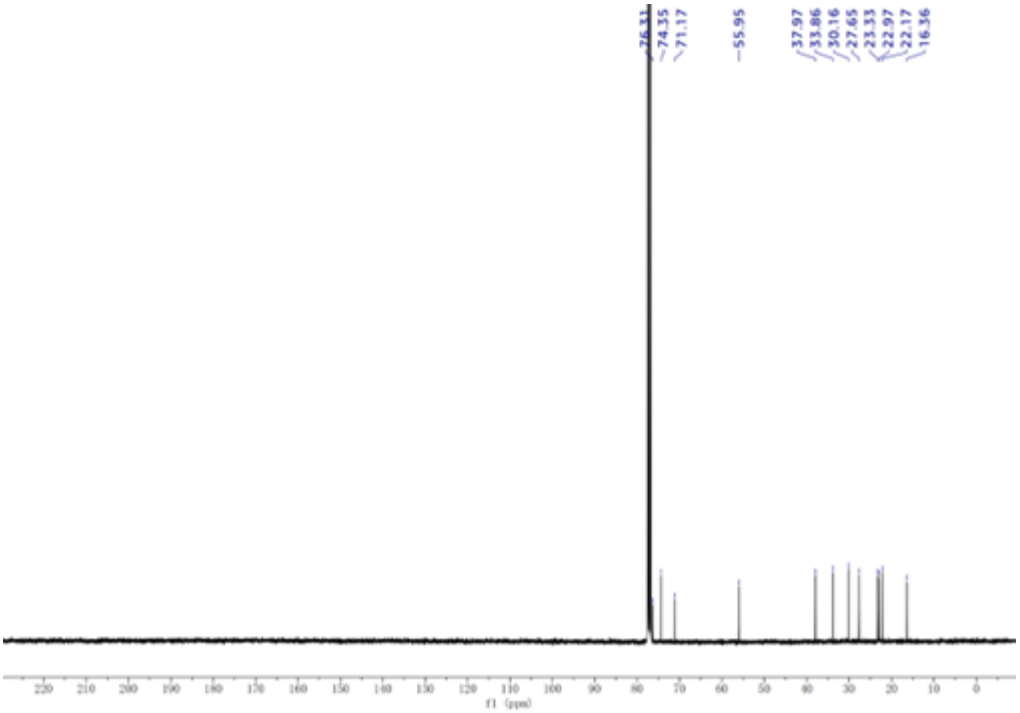
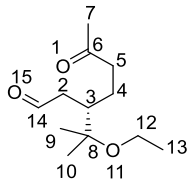
3.40
3.39
3.38
3.37
3.37
3.35
3.35
1.83
1.83
1.80
1.80
1.78
1.77
1.77
1.76
1.75
1.74
1.74
1.72
1.71
1.70
1.70
1.68
1.54
1.52
1.26
1.26
1.16
1.16
1.14
1.14
1.12
1.10
0.99
2.00
4.49
3.13
3.05
9.26
f1 (ppm)

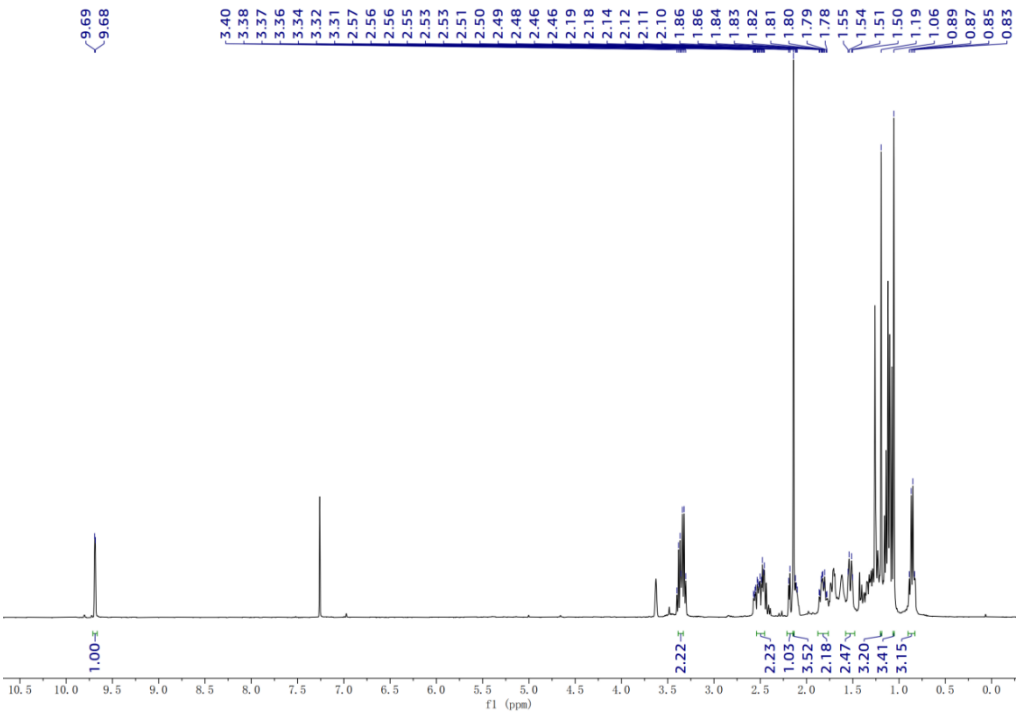

76.31
74.35
71.17
55.95
37.97
33.86
30.16
27.65
23.33
22.97
22.17
16.36
f1 (ppm)

3-(2-ethoxypropan-2-yl)-6-oxoheptanal (6)



Ethoxy-isopropyl diol **5** (1.40 g, 6.51 mmol) was dissolved in CH_3CN (50 mL) and H_2O (38 mL). $NaIO_4$ (2.08 g, 9.77 mmol) was added portion-wise, and the reaction was stirred for 48 hours at room temperature. The reaction mixture was filtered and extracted with diethyl ether (3 × 100 mL). The organic layers were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure to give keto-aldehyde **6** as a pale-yellow liquid (1.12 g, 5.27 mmol, 81% yield).

IR ν_{max} cm^{-1} 3469, 3437, 3402, 2973, 2931, 2895 (formyl), 2875 (formyl), 2727 (formyl), 2119, 1711 (carbonyl), 1484, 1459, 1442, 1412, 1389, 1364, 1308, 1237, 1169, 1145, 1116, 1065, 1037; **δ_H** (400 MHz, $CDCl_3$) 9.69 (1H, d, *J* 2.9, 14-H), 3.36 (2H, m, 12-H_2), 2.49 (2H, m, 2-Ha, 5-Ha), 2.14 (1H, m, 3-H), 2.14 (3H, s, 7-H_3), 1.83 (2H, m, 2-Hb, 5-Hb), 1.53 (2H, m, 4-H_2), 1.19 (3H, s, 9-H_3), 1.06 (3H, s, 10-H_3), 0.86 (3H, t, *J* 7.3, 13-H_3); **δ_C** (100 MHz, $CDCl_3$) 208.8 (C-6) 202.2 (C-14), 74.3 (C-8), 56.3 (C-12), 44.9 (C-5), 42.9 (C-2), 42.4 (C-3), 30.2 (C-7), 24.7 (C-9), 23.9 (C-10), 20.7 (C-4), 15.9 (C-13); **HRMS** (ESI positive): Calculated for $C_{12}H_{22}NaO_3$ $[M+Na]^+$ 237.1461, obtained 237.1457.


9.69
9.68
3.40
3.38
3.37
3.36
3.34
3.32
3.31
2.57
2.56
2.56
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2.53
2.53
2.51
2.50
2.49
2.48
2.46
2.46
2.19
2.18
2.14
2.12
2.11
2.10
1.86
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1.84
1.83
1.82
1.81
1.80
1.79
1.78
1.55
1.54
1.51
1.50
1.19
1.06
0.89
0.87
0.85
0.83
1.00
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2.23
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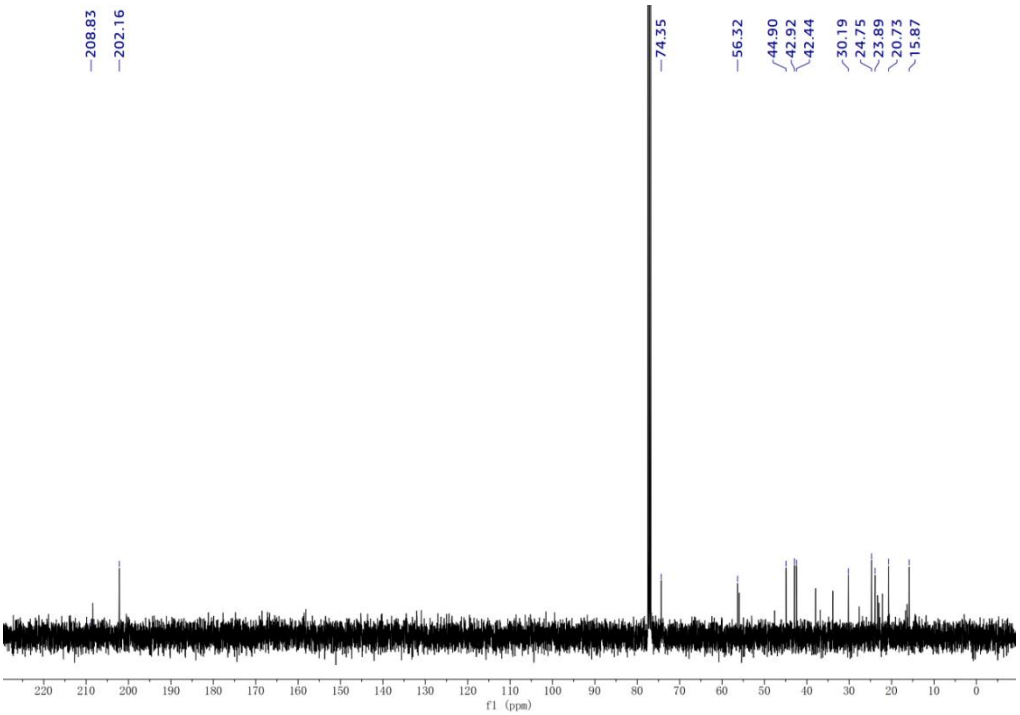
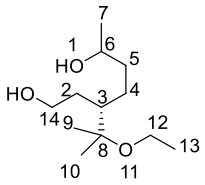
2.47
3.20
3.41
3.15
f1 (ppm)

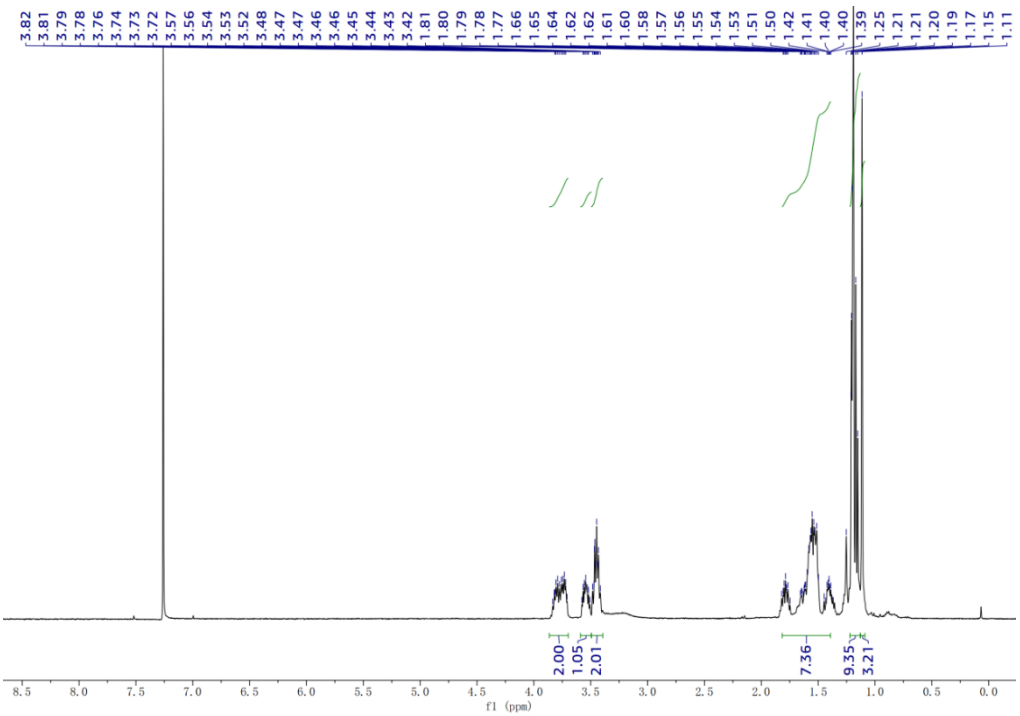

208.83
202.16
74.35
56.32
44.90
42.92
42.44
30.19
24.75
23.89
20.73
15.87
f1 (ppm)

3-(2-ethoxypropan-2-yl)heptane-1,6-diol (7)



Keto-aldehyde **6** (1.12 g, 5.27 mmol) was dissolved in methanol (25 mL) and cooled to 0 °C. $NaBH_4$ (0.43 g, 11.5 mmol) was added portion-wise. The mixture was allowed to warm to room temperature and stirred for 4 hours. The reaction was quenched by addition of water (30 mL) and stirred for 1 hour. The reaction mixture was filtered and extracted with ethyl acetate (3 × 50 mL). The organic layers were combined and washed with brine (25 mL). The solvent was removed under reduced pressure to give diol **7** as a transparent gel (1.04 g, 4.79 mmol, 91% yield).

IR ν_{max} cm^{-1} 3360 (hydroxyl), 2971, 2931, 2873, 2725, 1702, 1686, 1638, 1560, 1459, 1440, 1406, 1391, 1367, 1337, 1237, 1179, 1148 (hydroxyl), 1115 (hydroxyl), 1063 (hydroxyl), 1025; **δ_H** (400 MHz, $CDCl_3$) 3.77 (2H, m, 15-H_2), 3.54 (1H, m, 6-H), 3.45 (2H, m, 12-H_2), 1.57 (7H, m, 2-H_2, 3-H, 4-H_2, 5-H_2), 1.19 (9H, m, 9-H_3, 10-H_3, 14-H_3), 1.11 (3H, s, 7-H_3); **δ_C** (100 MHz, $CDCl_3$) 78.0 (C-8), 78.0 (C-8), 68.8 (C-6), 67.9 (C-6), 62.4 (C-14), 62.4 (C-14), 56.6 (C-12), 56.6 (C-12), 46.8 (C-3), 46.3 (C-3), 38.5 (C-5), 38.3 (C-5), 33.5 (C-2), 33.3 (C-2), 27.7 (C-7), 27.4 (C-7), 23.8 (C-9), 23.5 (C-10), 21.1 (C-4), 21.1 (C-4), 15.9 (C-13); **HRMS** (ESI positive): Calculated for $C_{12}H_{26}NaO_3$ $[M+Na]^+$ 241.1774, obtained 241.1775.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3.72
3.57
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1.54
1.53
1.51
1.50
1.42
1.41
1.40
1.40
1.39
1.25
1.21
1.21
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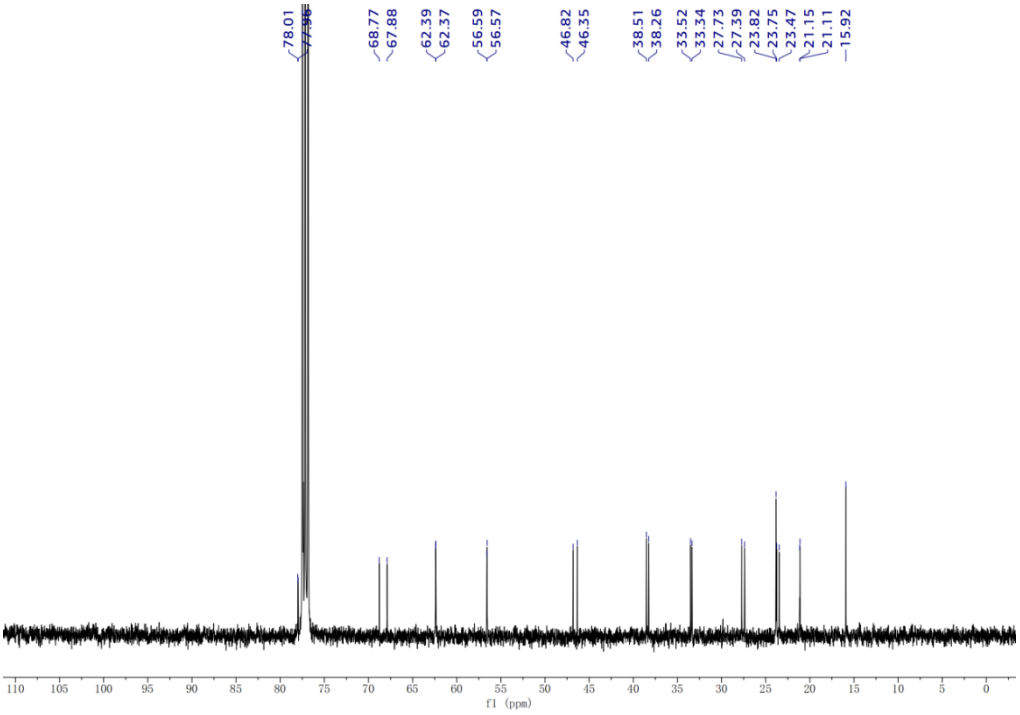
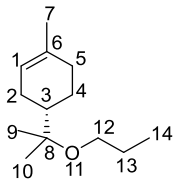
3.21
f1 (ppm)


78.01
68.77
67.88
62.39
62.37
56.59
56.57
46.82
46.35
38.51
38.26
33.52
33.34
27.73
27.39
23.82
23.75
23.47
21.15
21.11
15.92
f1 (ppm)

1-methyl-4-(2-propoxypropan-2-yl)cyclohex-1-ene (2)

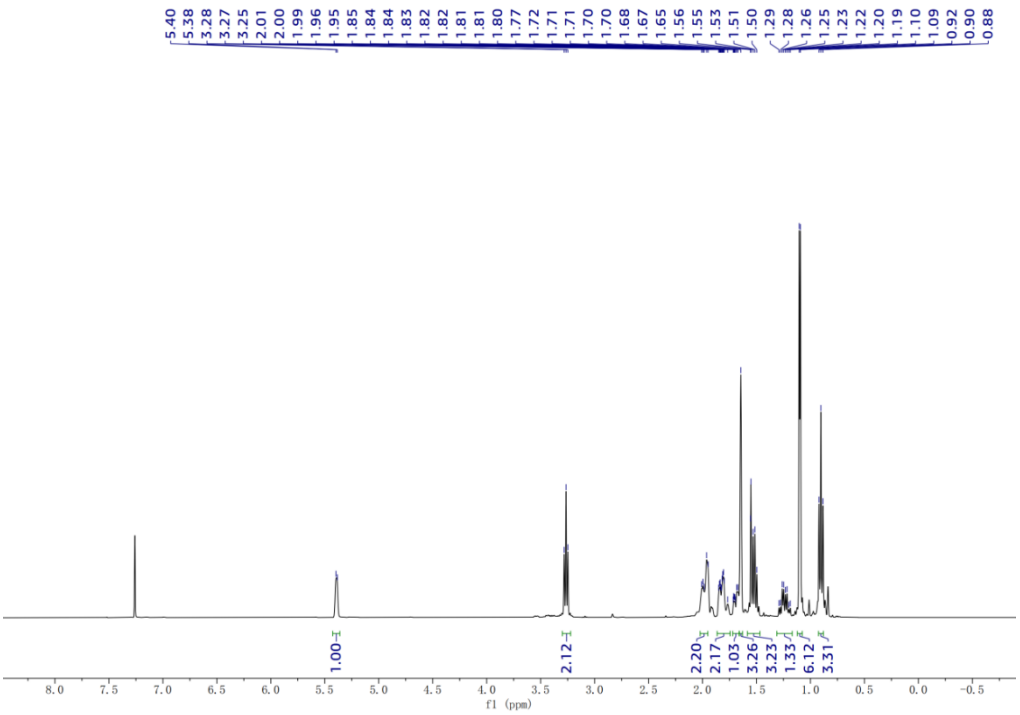


Method 1: (-)-(α)-pinene (5.0 g, 36.7 mmol) and 1-propanol (11.0 g, 367 mmol) were dissolved in 2-MeTHF (50 mL). PTA (1.58 g, 0.55 mmol) was added portion-wise. The reaction was heated to 50 °C and stirred under reflux for 48 hours. After 48 hours, the reaction mixture was allowed to cool to room temperature and filtered with silica gel under reduced pressure. The organic layer was washed with water (3 × 100 mL) to remove a large proportion of 1-propanol. The organic layers were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. Purification by silica gel chromatography (0-10% ethyl acetate in petroleum ether) gave alkene **2** as a transparent oil (3.38 g, 17.2 mmol, 47% yield).

Method 2: (-)-(α)-pinene (5.0 g, 36.7 mmol) and 1-propanol (11.0 g, 367 mmol) were dissolved in dichloromethane (36.5 mL). Anhydrous $FeCl_3$ (1.50 g, 9.24 mmol) was added portion-wise at 0 °C. The reaction mixture was stirred at room temperature for 1.3 hours. After complete conversion as indicated by TLC, the reaction mixture was quenched with water (2 x 200 mL) and extracted with dichloromethane (3 x 100 mL). The organic layer was washed with water (3 × 100 mL) to remove a large proportion of 1-propanol. The organic layers were dried over anhydrous sodium sulfate and the solvent was removed under

reduced pressure. Purification by silica gel chromatography (0-10% ethyl acetate in petroleum ether) gave alkene **2** as a transparent oil (3.74 g, 19.08 mmol, 52% yield).

IR ν_{max} cm^{-1} 3314 (olefin), 2955, 2923, 2854, 1464 (olefin), 1378, 1248, 1226, 1160, 1119, 1056; **δ_H** (400 MHz, $CDCl_3$) 5.39 (1H, d, *J* 5.1, 1-H), 3.27 (2H, t, *J* 6.7, 12-H_2), 1.99 (2H, m, 2-Ha, 5-Ha), 1.82 (2H, m, 2-Hb, 5-Hb), 1.69 (1H, m, 3-H), 1.65 (3H, s, 7-H_3), 1.52 (3H, dd, *J* 14.6 and 7.5, 13-H_2, 4-Ha), 1.24 (1H, qd, *J* 12.1 and 5.7, 4-Hb), 1.10 (6H, d, *J* 4.3, 9-H_3, 10-H_3), 0.90 (3H, t, *J* 7.3, 14-H_3); **δ_C** (100 MHz, $CDCl_3$) 134.2 (C-6), 121.2 (C-1), 76.3 (C-8), 62.5 (C-12), 42.1 (C-3), 31.3 (C-5), 27.0 (C-2), 24.1 (C-9), 24.0 (C-10), 23.5 (C-13), 23.1 (C-4), 22.8 (C-7), 11.0 (C-14).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3.27
3.25
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1.99
1.96
1.95
1.85
1.84
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1.83
1.82
1.82
1.81
1.81
1.80
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1.72
1.71
1.71
1.70
1.70
1.68
1.67
1.65
1.56
1.55
1.53
1.51
1.50
1.29
1.28
1.26
1.25
1.23
1.22
1.20
1.19
1.10
1.09
0.92
0.90
0.88
1.00
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2.20
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1.03
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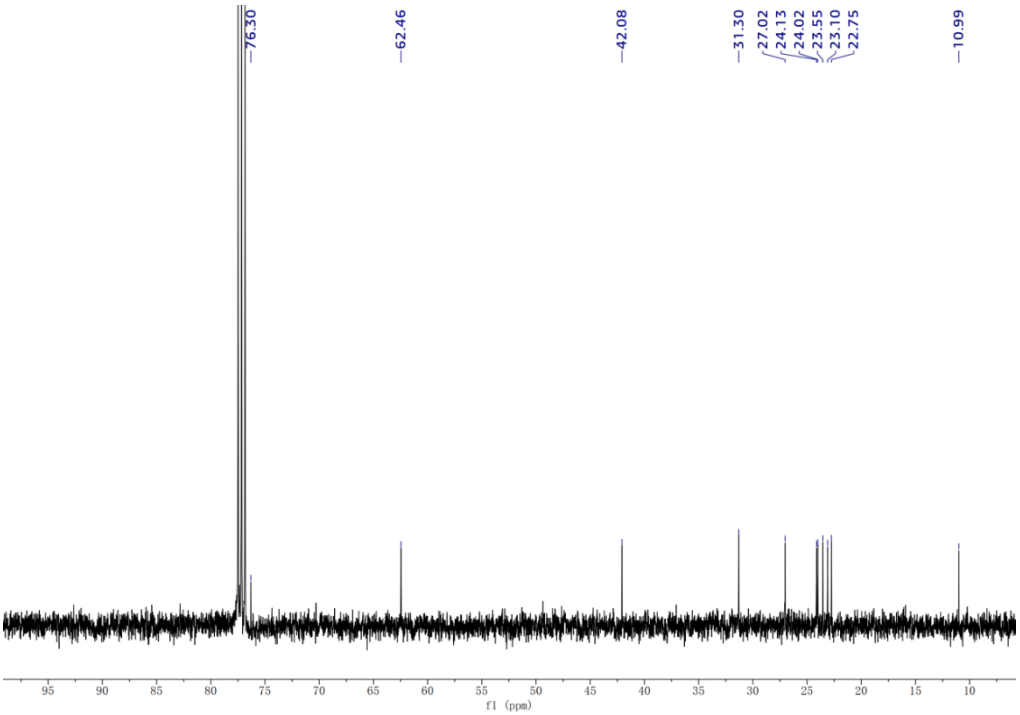
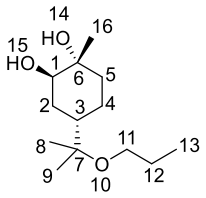
3.23
1.33
6.12
3.31
f1 (ppm)


76.30
62.46
42.08
31.30
27.02
24.13
24.02
23.55
23.10
22.75
10.99
f1 (ppm)

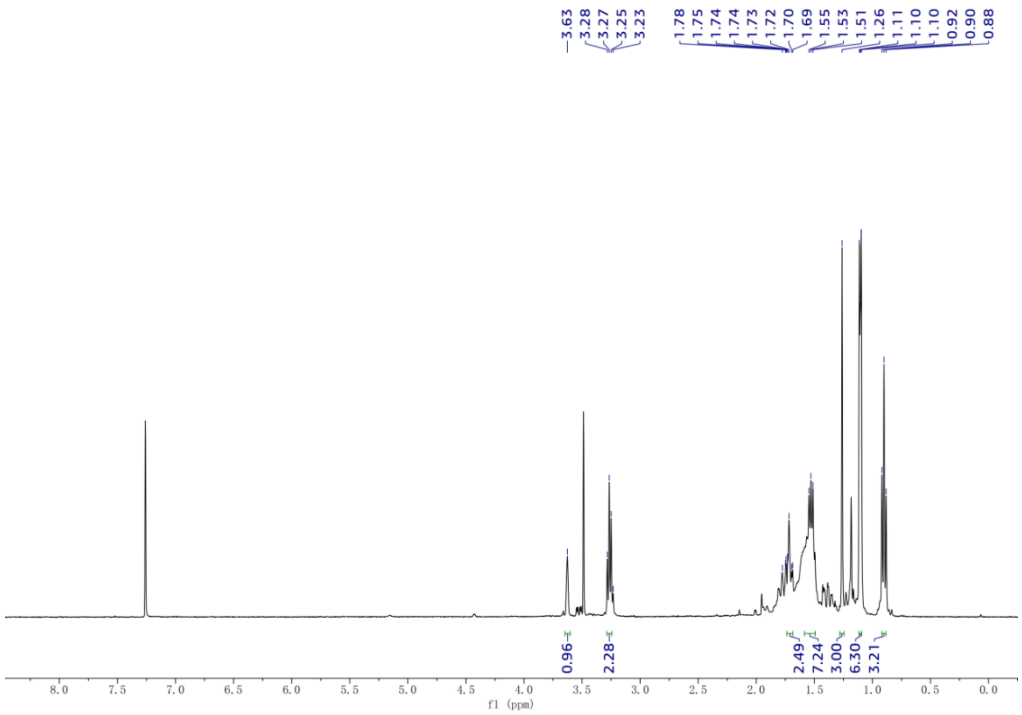
1-methyl-4-(2-propoxypropan-2-yl)cyclohexane-1,2-diol (8)

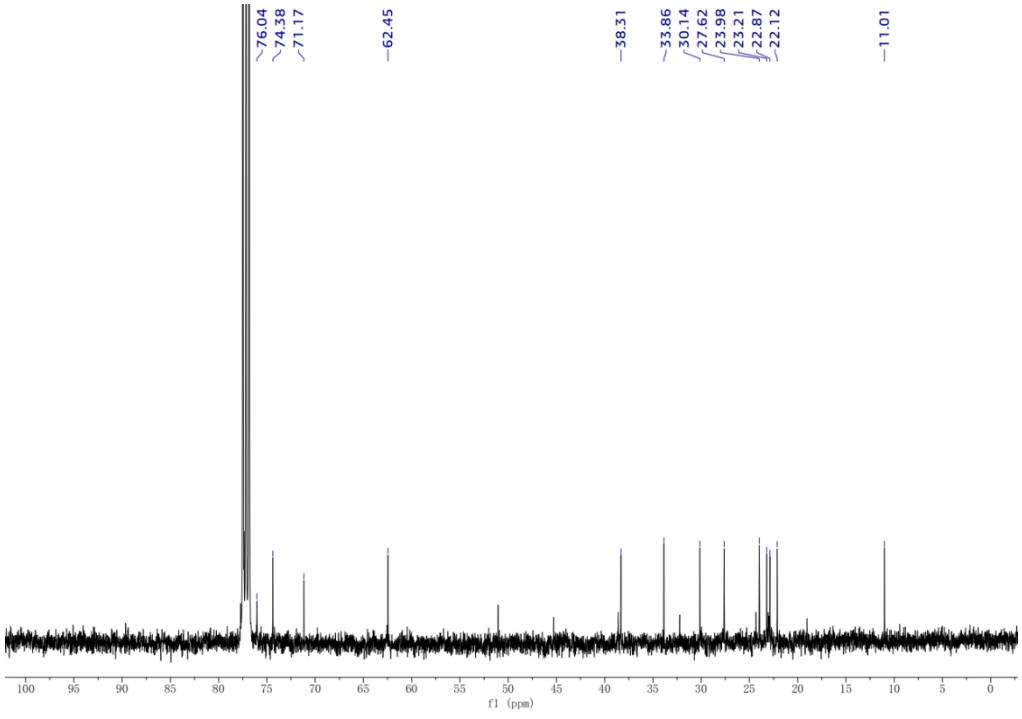


Alkene **2** (3.0 g, 15.2 mmol) was dissolved in CH_3CN (80 mL) and H_2O (60 mL). A mixture of OXONE (13.9 g, 45.8 mmol) and $NaHCO_3$ (3.21. g, 38.2 mmol) was added portion-wise and the reaction was stirred for 72 hours at room temperature. The reaction mixture was filtered and extracted with diethyl ether (3 × 150 mL). The organic layers were combined and dried over magnesium sulfate, filtered, and the solvent removed under reduced pressure to give ethoxy-isopropyl diol **8** as a white gel (2.74 g, 11.9 mmol, 78% yield).

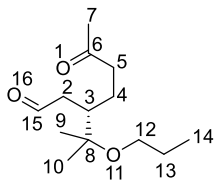
IR ν_{max} cm^{-1} 3382 (hydroxyl), 2960, 2936, 2874, 1738, 1727, 1657, 1544, 1460, 1379, 1364, 1217, 1202, 1175, 1128 (hydroxyl), 1072 (hydroxyl), 1055 (hydroxyl), 1034; **δ_H** (400 MHz, $CDCl_3$) 3.63 (1H, s, 1-H), 3.27 (2H, t, *J* 6.7, 11-H_2), 1.70 (2H, m, 4-Ha, 5-Ha), 1.53 (7H, m, 4-Hb, 5-Hb, 2-H_2, 3-H, 12-H_2), 1.26 (3H, s, 16-H_3), 1.10 (6H, s, 8-H_3, 9-H_3), 0.91 (3H, d, *J* 7.4, 13-H_3); **δ_C** (100 MHz, $CDCl_3$) 76.0 (C-7), 74.4 (C-1), 71.2 (C-6), 62.5 (C-11), 38.3 (C-3), 33.9 (C-5), 30.1 (C-2), 27.6 (C-16), 24.0 (C-8), 23.2 (C-9), 22.9 (C-12), 22.1 (C-4), 11.0 (C-13).

HRMS (ESI positive): Calculated for $C_{13}H_{26}NaO_3$ $[M+Na]^+$ 253.1780, obtained 253.1782.


3.63
3.28
3.27
3.25
3.23
1.78
1.75
1.74
1.74
1.73
1.72
1.70
1.69
1.55
1.53
1.51
1.26
1.11
1.10
1.10
0.92
0.90
0.88
0.96
2.28
2.49
7.24
3.00
6.30
3.21
f1 (ppm)

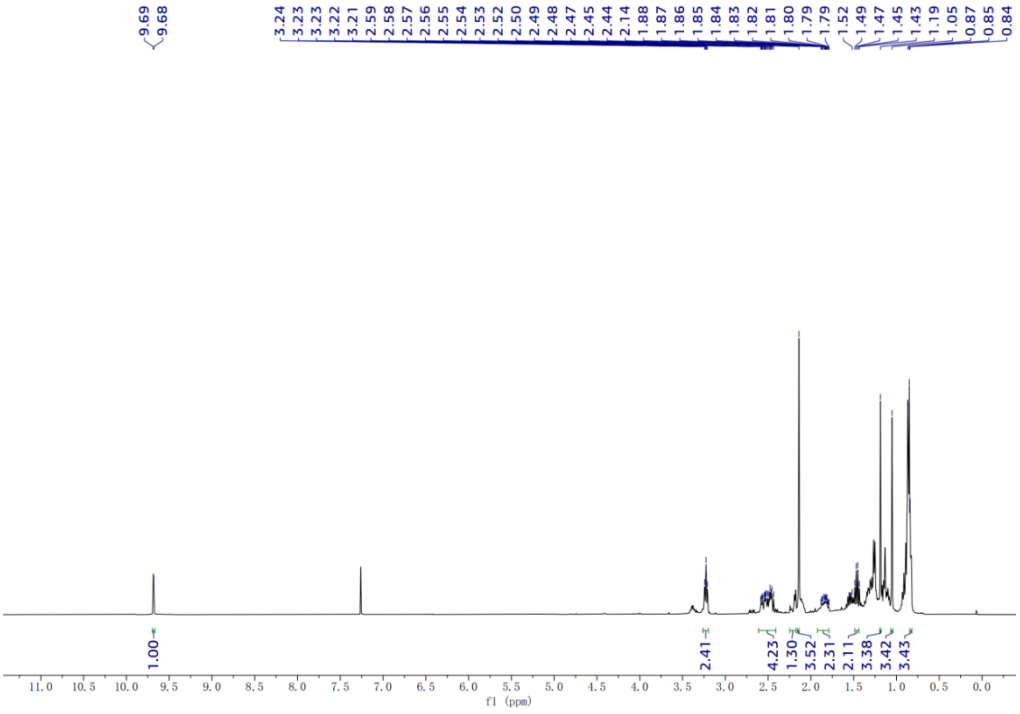

76.04
74.38
71.17
62.45
38.31
33.86
30.14
27.62
23.98
23.21
22.87
22.12
11.01
f1 (ppm)

6-oxo-3-(2-propoxypropan-2-yl)heptanal (9)



Diol **8** (1.30 g, 5.64 mmol) was dissolved in CH_3CN (56 mL) and H_2O (40 mL). $NaIO_4$ (1.8 g, 8.46 mmol) was added portion-wise, and the reaction was stirred for 48 hours at room temperature. The reaction mixture was filtered and extracted with diethyl ether (3 × 100 mL). The organic layers were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure to give keto-aldehyde **9** as transparent liquid (0.97 g, 4.28 mmol, 76% yield).

IR ν_{max} cm^{-1} 2960, 2923, 2874 (formyl), 2853 (formyl), 2727 (formyl), 1715 (carbonyl), 1546, 1460, 1414, 1365, 1279, 1236, 1166, 1143, 1111, 1075, 1006; **δ_H** (400 MHz, $CDCl_3$) 9.68 (1H, d, *J* 2.8, 15-H), 3.22 (2H, m, 12-H_2), 2.51 (4H, m, 2-H_2, 5-H_2), 2.20 (1H, m, 3-H), 2.14 (3H, s, 7-H_3), 1.84 (2H, m, 4-H_2), 1.47 (2H, m, 13-H_2), 1.19 (3H, s, 9-H_3), 1.05 (3H, s, 10-H_3), 0.84 (3H, t, *J* 7.0, 14-H_3); **δ_C** (100 MHz, $CDCl_3$) 208.7 (C-6), 202.3 (C-15), 76.7 (C-8), 62.7 (C-12), 44.9 (C-5), 43.1 (C-2), 42.4 (C-3), 30.2 (C-7), 24.7 (C-9), 23.9 (C-10), 23.6 (C-13), 22.8 (C-4), 10.9 (C-14); **HRMS** (ESI positive): Calculated for $C_{13}H_{24}NaO_3$ $[M+Na]^+$ 251.1618, obtained 251.1625.


9.69
9.68
3.24
3.23
3.23
3.22
3.21
2.59
2.58
2.57
2.56
2.55
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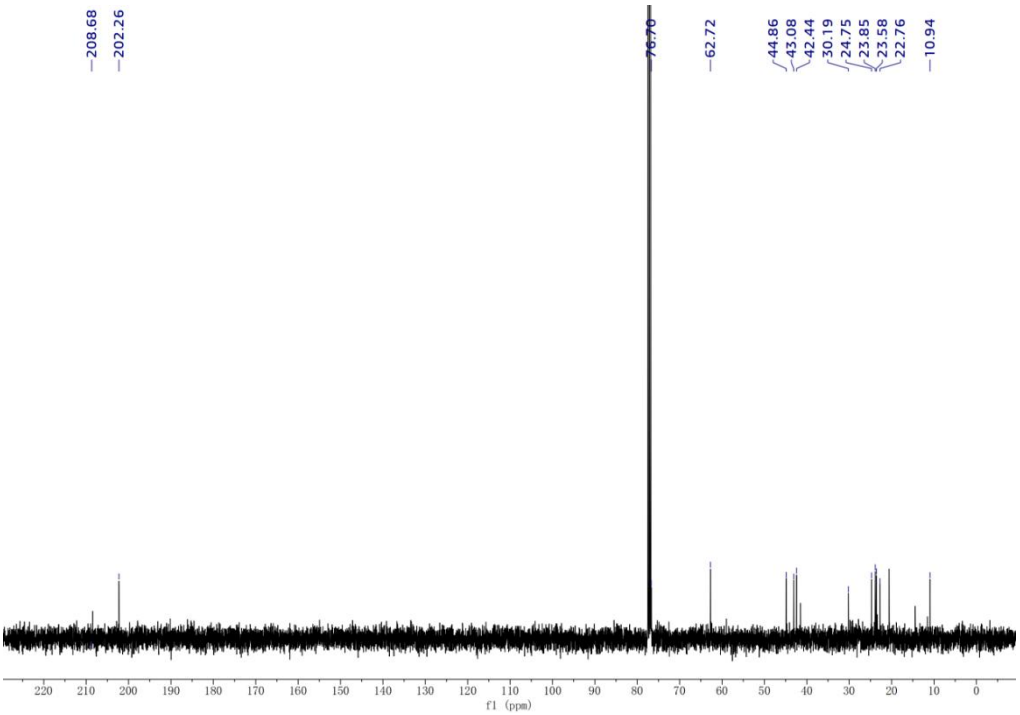
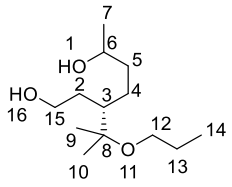
2.53
2.52
2.50
2.49
2.48
2.47
2.45
2.44
2.14
1.88
1.87
1.86
1.85
1.84
1.83
1.82
1.81
1.80
1.79
1.79
1.52
1.49
1.47
1.45
1.43
1.19
1.05
0.87
0.85
0.84
1.00
2.41
4.23
1.30
3.52
2.31
2.11
3.38
3.42
3.43
f1 (ppm)

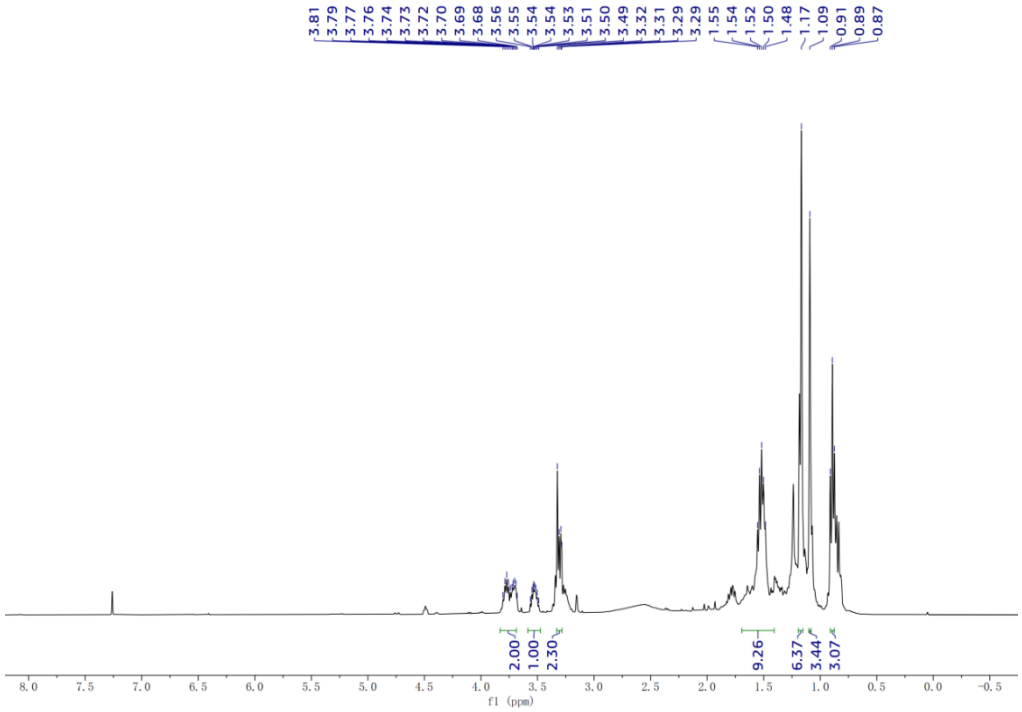

208.68
202.26
76.70
62.72
44.86
43.08
42.44
30.19
24.75
23.85
23.58
22.76
10.94
f1 (ppm)

3-(2-propoxypropan-2-yl)heptane-1,6-diol (10)



Keto-aldehyde **9** (0.51 g, 2.19 mmol) was dissolved in methanol (15 mL) and cooled to 0 °C. $NaBH_4$ (0.06 g,1.73 mmol) was added portion-wise. The mixture was allowed to warm to room temperature and stirred for 4 hours. The reaction was quenched by addition of water (15 mL) and stirred for 1 hour. The reaction mixture was filtered and extracted with ethyl acetate (3 × 50 mL). The organic layers were combined and washed with brine (25 mL). The solvent was removed under reduced pressure to give diol **10** as a transparent gel (0.44 g, 1.90 mmol, 87% yield).

IR ν_{max} cm^{-1} 3408 (hydroxyl), 2972, 2929, 2873, 1721, 1637, 1619, 1459, 1407, 1382, 1366, 1295, 1274, 1192, 1153 (hydroxyl), 1115, 1062 (hydroxyl), 983, 962; **δ_H** (400 MHz, $CDCl_3$) 3.74 (2H, m, 15-H_2), 3.53 (1H, m, 6-H), 3.30 (2H, m, 12-H_2), 1.52 (9H, m, 2-H_2, 3-H, 4-H_2, 5-H_2, 13-H_2), 1.17 (6H, s, 9-H_3, 10-H_3), 1.09 (3H, s, 7-H_3), 0.89 (3H, t, *J* 7.4, 14-H_3); **δ_C** (100 MHz, $CDCl_3$) 77.8 (C-8), 77.8 (C-8), 68.6 (C-6), 67.8 (C-6), 63.0 (C-12), 63.0 (C-12), 62.3 (C-15), 62.2 (C-15), 46.6 (C-3), 46.2 (C-3), 38.4 (C-5), 38.2 (C-5), 33.4 (C-2), 33.3 (C-2), 27.6 (C-7), 27.3 (C-7), 23.7 (C-9), 23.6 (C-10), 23.6 (C-13), 23.3 (C-13), 21.1 (C-4), 10.9 (C-14), 10.8 (C-14). **HRMS** (ESI positive): Calculated for $C_{13}H_{28}NaO_3$ $[M+Na]^+$ 255.1931, obtained 255.1925.


3.81
3.79
3.77
3.76
3.74
3.73
3.72
3.70
3.69
3.68
3.56
3.55
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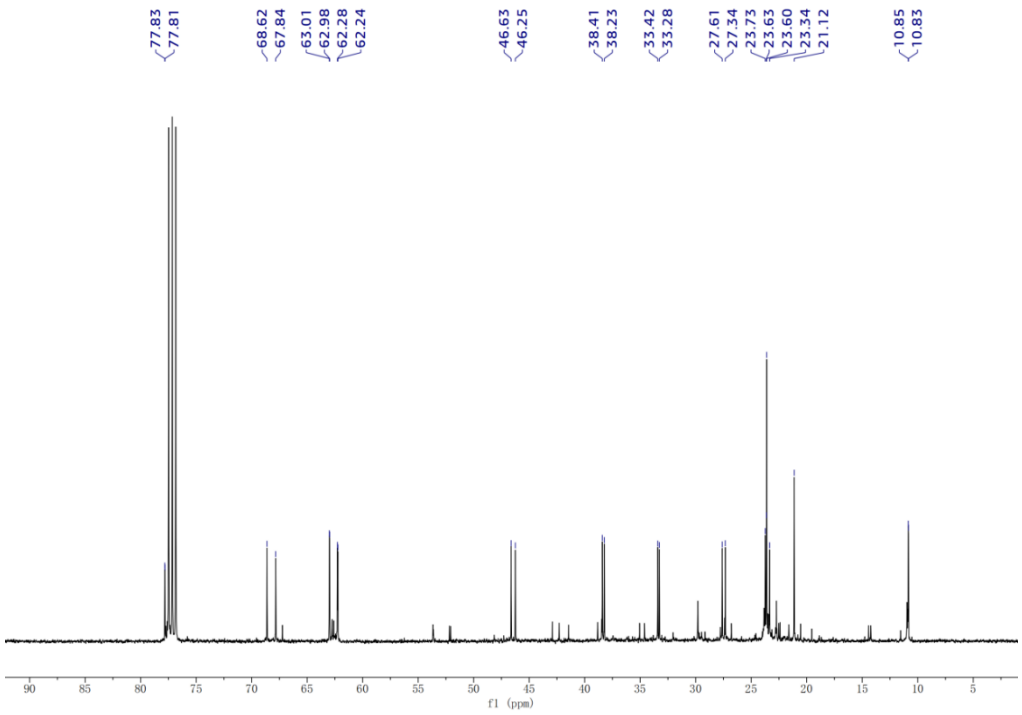
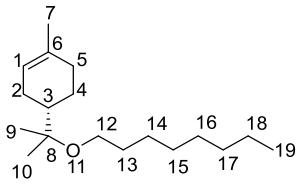
3.53
3.51
3.50
3.49
3.32
3.31
3.29
3.29
1.55
1.54
1.52
1.50
1.48
1.17
1.09
0.91
0.89
0.87
2.00
1.00
2.30
9.26
6.37
3.44
3.07
f1 (ppm)


77.83
77.81
68.62
67.84
63.01
62.98
62.28
62.24
46.63
46.25
38.41
38.23
33.42
33.28
27.61
27.34
23.73
23.63
23.60
23.34
21.12
10.85
10.83
f1 (ppm)

4-(2-(Octyloxy)propan-2-yl)-1-methylcyclohex-1-ene (3)

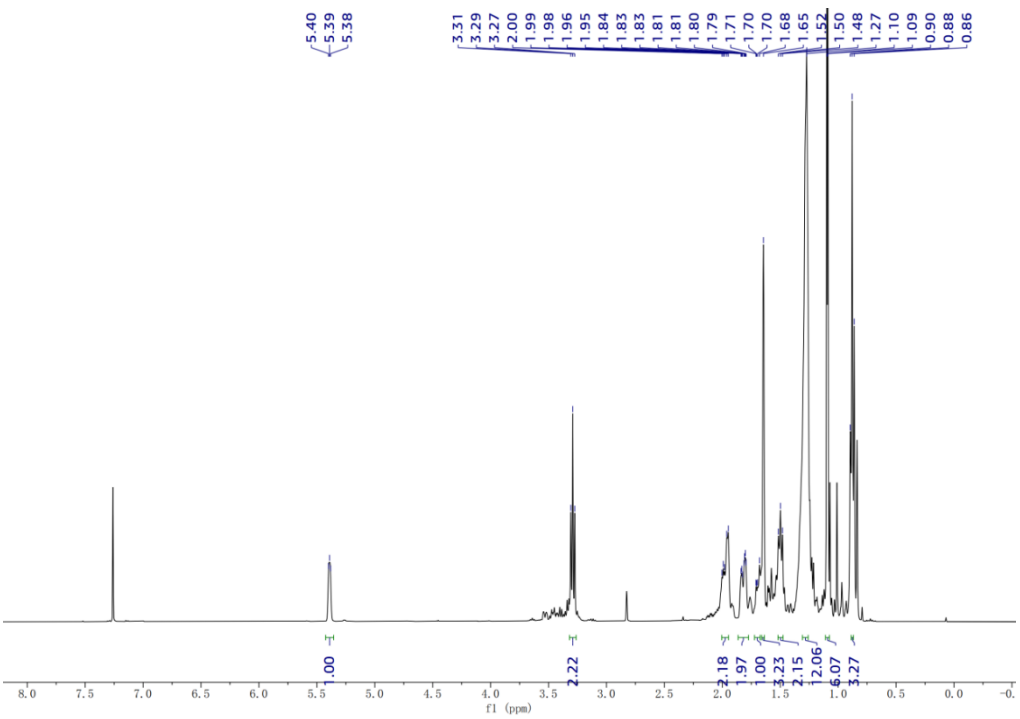


Method 1: (-)-(α)-Pinene (5.0 g, 36.7 mmol) and 1-octanol (23.9 g, 183 mmol) were dissolved in 2-MeTHF (50 mL). PTA (1.58 g, 0.55 mmol) was added portion-wise. The reaction was heated to 50 °C and stirred under reflux for 48 hours. After 48 hours, the reaction mixture was allowed to cool to room temperature and filtered with silica gel under reduced pressure. The aqueous layer was concentrated under reduced pressure to remove the solvent and then subjected to fractional distillation under reduced pressure to remove (-)-(α)-pinene and 1-octanol. Purification by silica gel chromatography (0-10% ethyl acetate in petroleum ether) gave alkene **3** as a pale-yellow oil (6.34 g, 23.8 mmol, 65% yield).

Method 2: (-)-(α)-Pinene (5.0 g, 36.7 mmol) and 1-propanol (11.0 g, 367 mmol) were dissolved in dichloromethane (36.5 mL). Anhydrous $FeCl_3$ (1.26 g, 7.76 mmol) was added portion-wise at 0 °C. The reaction mixture was stirred at room temperature for 1.3 hours. After complete conversion as indicated by TLC, the reaction mixture was quenched with water (2 x 200 mL) and extracted with dichloromethane (3 x 100 mL). The organic layer was washed with water (3 × 100 mL) to remove a large proportion of 1-propanol. The organic layers were dried over anhydrous sodium sulfate and the solvent was removed under

reduced pressure. Purification by silica gel chromatography (0-10% ethyl acetate in petroleum ether) gave alkene **3** as a yellow oil (4.98 g, 18.7 mmol, 51% yield).

IR ν_{max} cm^{-1} 3333 (olefin), 2953, 2923, 2854, 1718, 1677, 1458 (olefin), 1377, 1363, 1301, 1247, 1224, 1157, 1076; **δ_H** (400 MHz, $CDCl_3$) 5.39 (1H, m, 1-H), 3.29 (2H, t, *J* 6.7, 12-H_2), 1.98 (2H, m, 2-Ha, 5-Ha), 1.82 (2H, m, 2-Hb, 5-Hb), 1.70 (1H, m, 3-H), 1.65 (3H, s, 7-H), 1.50 (2H, t, *J* 7.2, 4-H), 1.27 (12H, s, 13-H_2, 14-H_2, 15-H_2, 16-H_2, 17-H_2, 18-H_2), 1.09 (6H, s, 9-H_3, 10-H_3), 0.88 (3H, s, 19-H_3); **δ_C** (100 MHz, $CDCl_3$) 134.1 (C-6), 121.2 (C-1), 76.3 (C-8), 60.8 (C-12), 42.0 (C-3), 32.0 (C-17), 31.3 (C-5), 30.9 (C-13), 29.7 (C-15), 29.5 (C-16), 27.0 (C-14), 26.5 (C-2), 24.1 (C-9), 23.5 (C-10), 23.1 (C-4), 22.8 (C-7), 22.8 (C-18), 14.3 (C-19). **HRMS** (ESI negative): Calculated for $C_{18}H_{34}O$ $[M-H]^-$ 265.2531, obtained 265.1469.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5.38
3.31
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3.27
2.00
1.99
1.98
1.96
1.95
1.84
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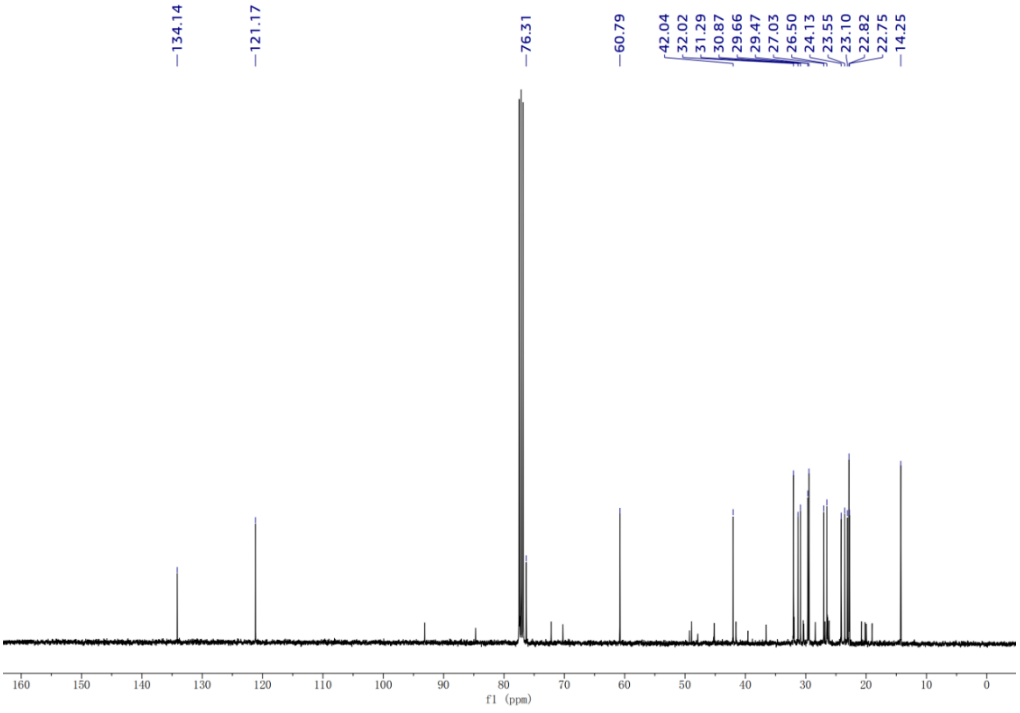
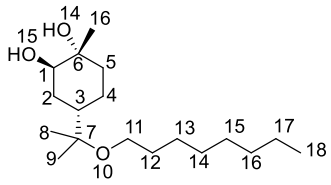
1.83
1.81
1.81
1.80
1.79
1.71
1.70
1.70
1.68
1.65
1.52
1.50
1.48
1.27
1.10
1.09
0.90
0.88
0.86
1.00
2.22
2.18
1.97
1.00
3.23
2.15
12.06
6.07
3.27
f1 (ppm)

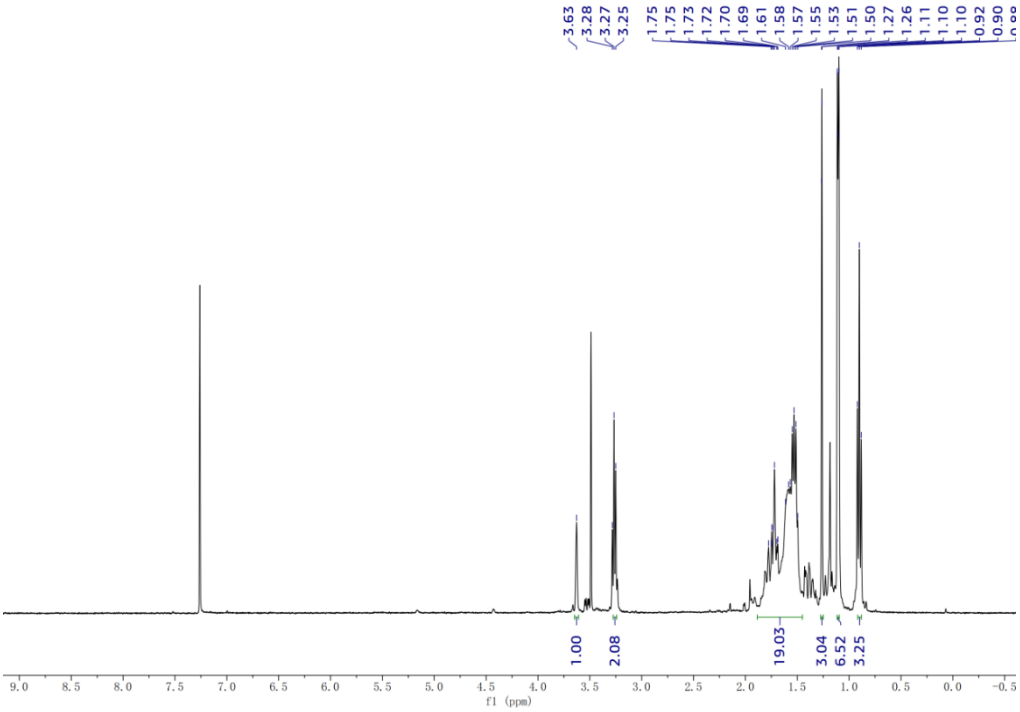

134.14
121.17
76.31
60.79
42.04
32.02
31.29
30.87
29.66
29.47
27.03
26.50
24.13
23.55
23.10
22.82
22.75
14.25
f1 (ppm)

1-methyl-4-(2-(octyloxy)propan-2-yl)cyclohexane-1,2-diol (11)



Alkene **3** (3.96 g, 14.8 mmol) was dissolved in CH_3CN (104 mL) and H_2O (80 mL). A mixture of OXONE (13.7 g, 44.5 mmol) and $NaHCO_3$ (3.12 g, 37.1 mmol) was added portion-wise, and the reaction was stirred for 72 hours at room temperature. The reaction mixture was filtered and extracted with diethyl ether (3 × 200 mL). The organic layers were combined and dried over magnesium sulfate, filtered, and the solvent removed under reduced pressure to give octyloxy-isopropyl diol **11** as a pale-yellow gel (3.01 g, 10.0 mmol, 67% yield).

IR ν_{max} cm^{-1} 3542 (hydroxyl), 3164 (hydroxyl), 3001, 2943, 2293, 2253, 1633, 1443, 1417, 1375, 1181, 1154 (hydroxyl), 1040 (hydroxyl), 918, 749; **δ_H** (400 MHz, $CDCl_3$) 3.63 (1H, s, 1-H), 3.26 (2H, d, *J* 6.7, 11-H_2), 1.62 (19H, m, 2-H_2, 3-H, 4-H_2, 5-H_2, 12-H_2, 13-H_2, 17-H_2, 18-H_2, 19-H_2,20-H_2), 1.26 (3H, s, 16-H_3), 1.10 (6H, s, 8-H_3, 9-H_3), 0.89 (3H, t, *J* 7.4, 21-H_3); **δ_C** (100 MHz, $CDCl_3$) 76.1 (C-7), 74.4 (C-1), 71.2 (C-6), 62.5 (C-11), 38.3 (C-3), 33.9 (C-5), 32.2 (C-2), 30.1 (C-19), 27.6 (C-16), 24.3 (C-8), 24.0 (C-9), 23.9 (C-18), 23.2 (C-17), 23.1 (C-13), 23.0 (C-12), 22.8 (C-4), 22.1 (C-20), 11.0 (C-21). **HRMS** (ESI positive): Calculated for $C_{18}H_{36}NaO_3$ $[M+Na]^+$ 323.2562, obtained 323.2555.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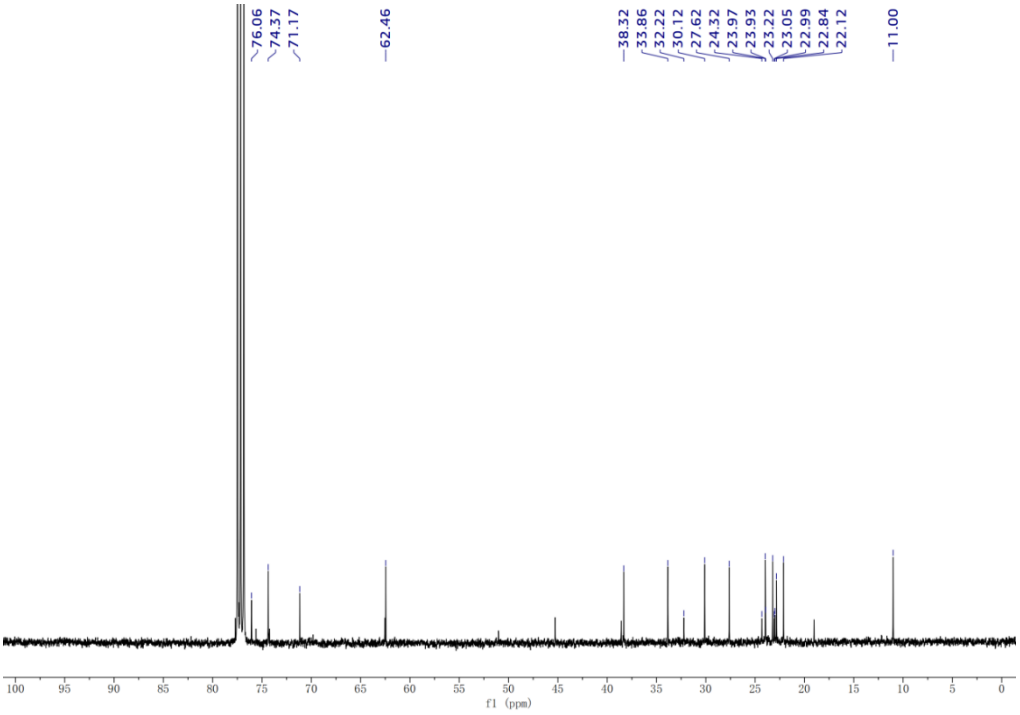
3.28
3.27
3.25
1.75
1.75
1.73
1.72
1.70
1.69
1.61
1.58
1.57
1.55
1.53
1.51
1.50
1.27
1.26
1.11
1.10
1.10
0.92
0.90
1.00
2.08
19.03
3.04
6.52
3.25
f1 (ppm)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30.12
27.62
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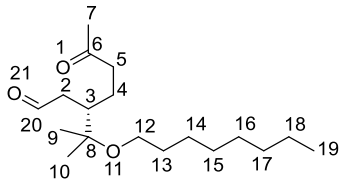
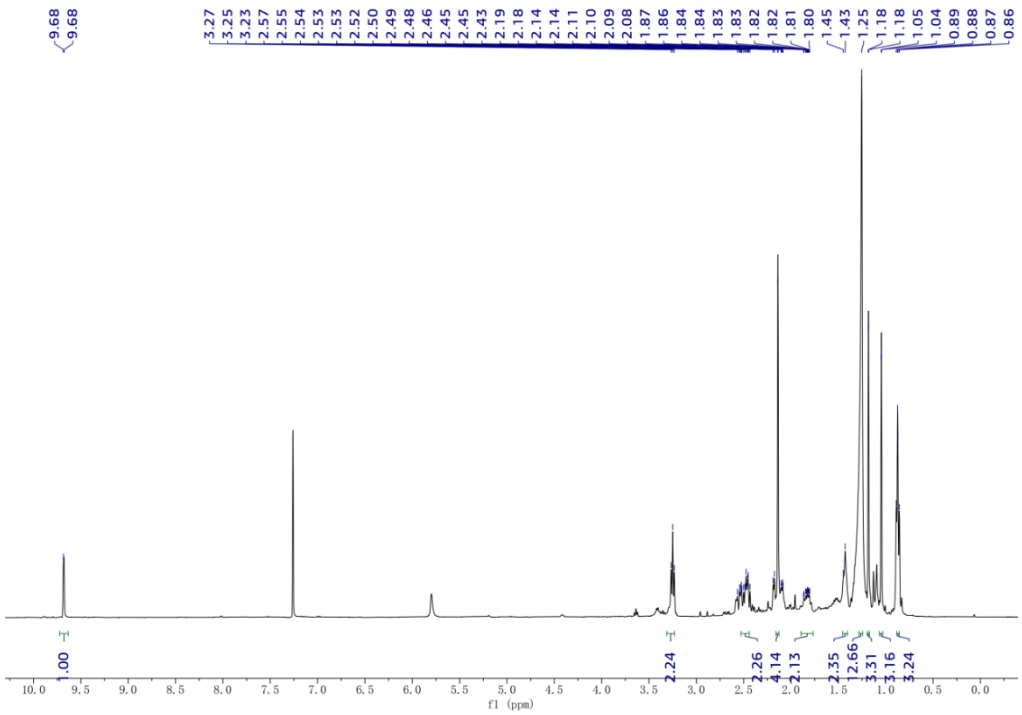
23.97
23.93
23.22
23.05
22.99
22.84
22.12
11.00
f1 (ppm)

3-(2-(octyloxy)propan-2-yl)-6-oxoheptanal (12)



Octyloxy-isopropyl diol **11** (3.01 g, 10.0 mmol) was dissolved in CH_3CN (100 mL) and H_2O (76 mL). $NaIO_4$ (3.20g, 15.0 mmol) was added portion-wise and the reaction was stirred for 48 hours at room temperature. The reaction mixture was filtered and extracted with diethyl ether (3 × 150 mL). The organic layers were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure to give keto-aldehyde **12** as yellow liquid (3.75 g, 12.6 mmol, 84% yield).

IR ν_{max} cm^{-1} 3447, 3394, 3084, 2954, 2925, 2855 (formyl), 2731 (formyl), 2076, 1715 (carbonyl), 1665, 1544, 1459, 1420, 1365, 1238, 1166, 1142, 1076, 1003; **δ_H** (400 MHz, $CDCl_3$) 9.68 (1H, d, *J* 2.6, 20-H), 3.25 (2H, t, *J* 6.8, 12-H_2), 2.48 (2H, m, 2-Ha, 5-Ha), 2.14 (1H, m, 3-H), 2.14 (3H, s, 7-H_3), 1.83 (2H, m, 2-Hb, 5-Hb), 1.44 (2H, d, *J* 8.0, 4-H_2), 1.25 (12H, s, 13-H_2, 14-H_2, 15-H_2, 16-H_2, 17-H_2, 18-H_2), 1.18 (3H, s,9-H_3), 1.05 (10H, s, 10-H_3), 0.87 (3H, t, *J* 7.0, 19-H_3). **δ_C** (100 MHz, $CDCl_3$) 208.5 (C-6), 202.3 (C-20), 76.7 (C-9), 61.1 (C-12), 44.9 (C-5), 43.0 (C-2), 42.4 (C-3), 32.0 (C-17), 30.4 (C-13), 30.2 (C-7), 29.6 (C-16), 29.4 (C-15), 26.4 (C-14), 24.8 (C-9), 23.8 (C-10), 22.8 (C-18), 20.7 (C-4), 14.2 (C-19). **HRMS** (ESI positive): Calculated for $C_{18}H_{34}NaO_3$ $[M+Na]^+$ 321.2400, obtained 321.2386.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9.68
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2.50
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1.82
1.81
1.80
1.45
1.43
1.25
1.18
1.18
1.05
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0.88
0.87
0.86
1.00
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2.26
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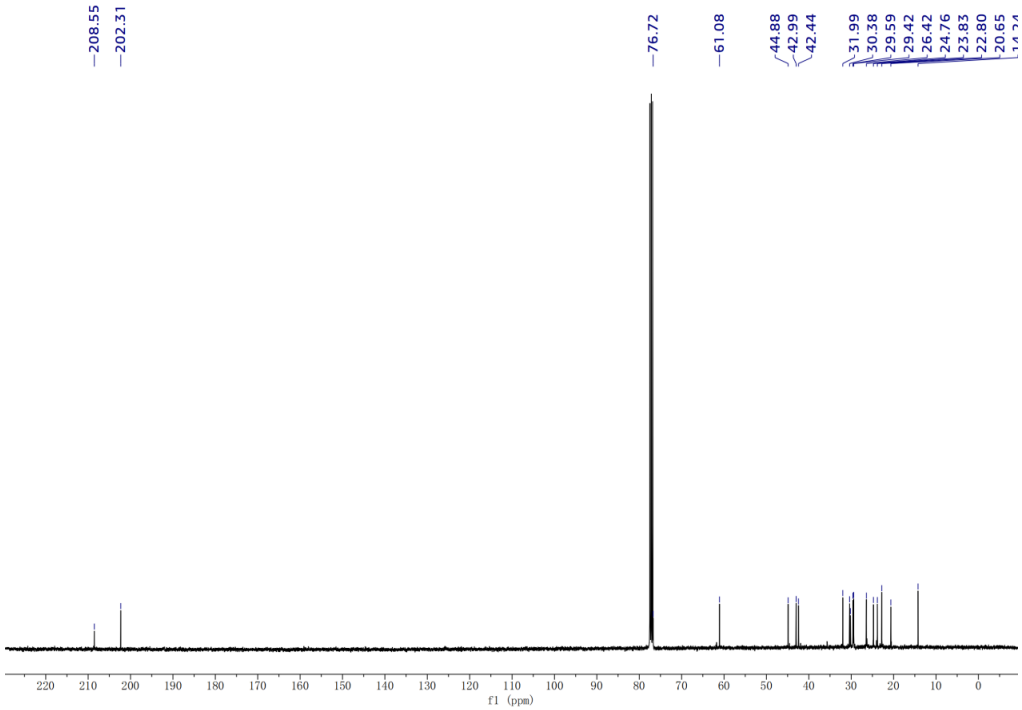
2.13
2.35
12.66
3.31
3.16
3.24
f1 (ppm)


208.55
202.31
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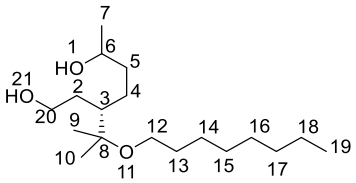
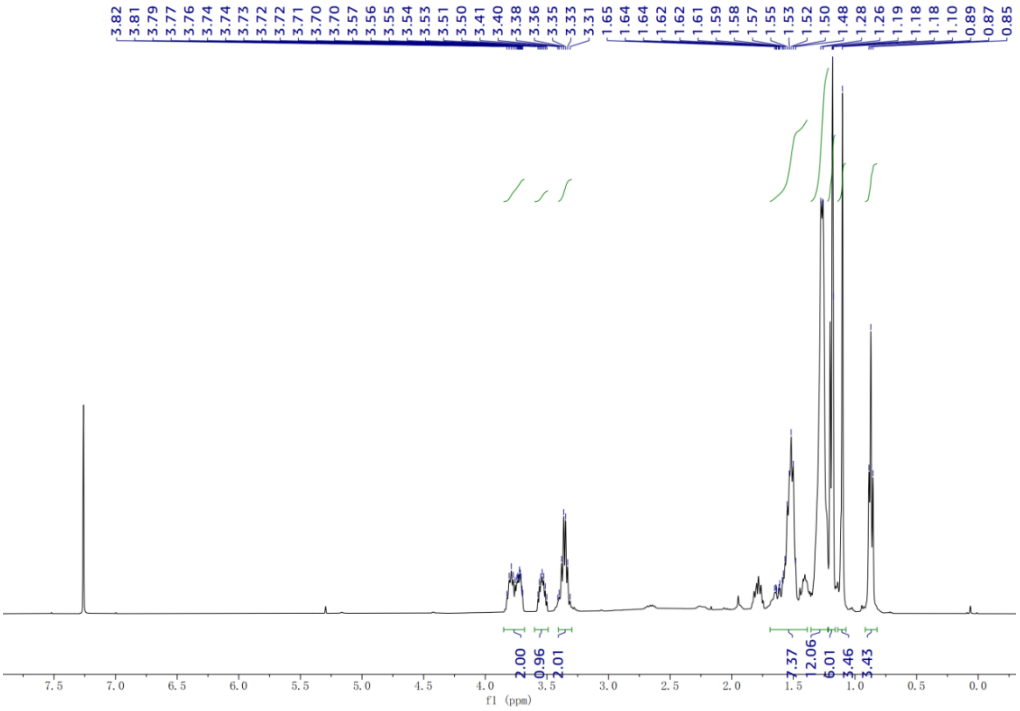
61.08
44.88
42.99
42.44
31.99
30.38
29.59
29.42
26.42
24.76
23.83
22.80
20.65
f1 (ppm)

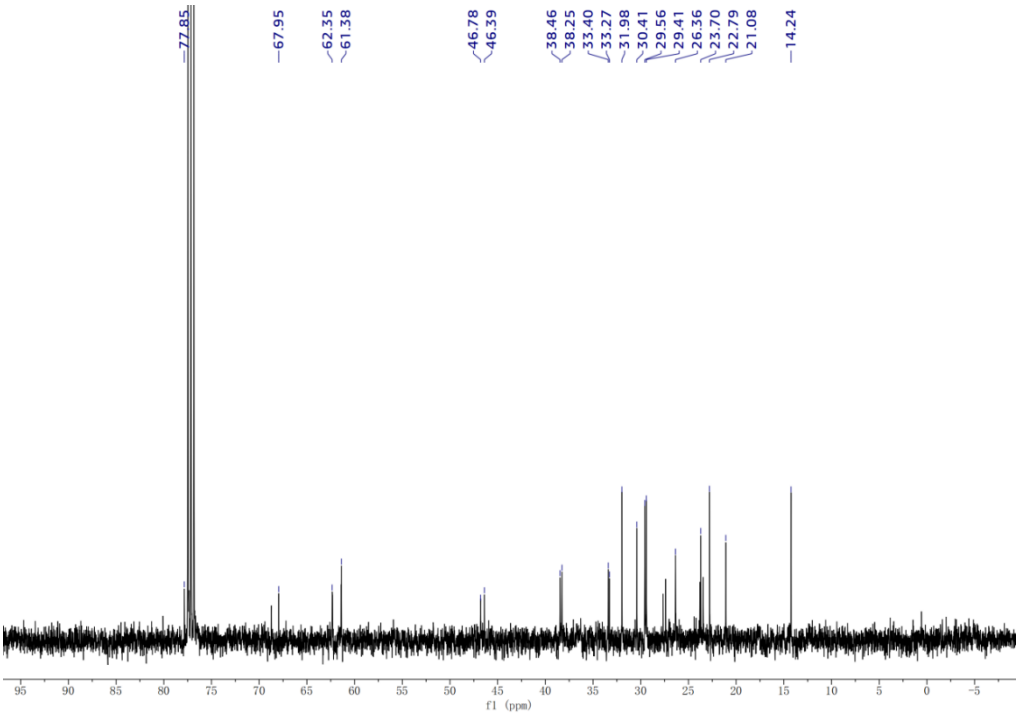
1-(2-(octyloxy)propan-2-yl)heptane-1,6-diol (13)



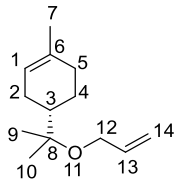
Keto-aldehyde **12** (1.6 g, 5.36 mmol) was dissolved in methanol (30 mL) and cooled to 0 °C. $NaBH_4$ (0.44 g, 11.7 mmol) was added portion-wise. The mixture was allowed to warm to room temperature and stirred for 4 hours. The reaction was quenched by addition of water (30 mL) and stirred for 1 hour. The reaction mixture was filtered and extracted with ethyl acetate (3 × 50 mL). The organic layers were combined and washed with brine (25 mL). The solvent was removed under reduced pressure to give diol **13** as a perfam gel (1.44 g, 4.77 mmol, 89% yield).

IR ν_{max} cm^{-1} 3344 (hydroxyl), 2955, 2924, 2855, 1656, 1566, 1459, 1364, 1306, 1242, 1175, 1148 (hydroxyl), 1126 (hydroxyl), 1054 (hydroxyl); **δ_H** (400 MHz, $CDCl_3$) 3.74 (2H, m, 20-H_2), 3.54 (1H, tt, *J* 10.1 and 4.9, 6-H), 3.36 (2H, t, *J* 8.2, 12-H_2), 1.53 (7H, m, 2-H_2, 3-H, 4-H_2, 5-H_2), 1.27 (12H, m, 13-H_2, 14-H_2, 15-H_2, 16-H_2, 17-H_2, 18-H_2), 1.18 (6H, s, 9-H_3, 10-H_3), 1.10 (3H, s, 7-H_3), 0.87 (3H, t, *J* 6.5, 19-H_3); **δ_C** (100 MHz, $CDCl_3$) 77.8 (C-8), 67.9 (C-6), 62.3 (C-12), 61.4 (C-20), 46.8 (C-3), 46.4 (C-3), 38.5 (C-5), 38.3 (C-5), 33.4 (C-2), 33.3 (C-2), 32.0 (C-17), 30.4 (C-13), 29.6 (C-14, C-16), 29.4 (C-15), 26.4 (C-9), 23.7 (C-10), 22.8 (C-18), 21.1 (C-4), 14.2 (C-19). **HRMS** (ESI positive): Calculated for $C_{18}H_{38}NaO_3$ $[M+Na]^+$ 325.2713, obtained 325.2726.


3.82
3.81
3.79
3.77
3.76
3.74
3.74
3.73
3.72
3.72
3.71
3.70
3.70
3.57
3.56
3.55
3.54
3.53
3.51
3.50
3.41
3.40
3.38
3.36
3.35
3.33
3.31
1.65
1.64
1.64
1.62
1.62
1.61
1.59
1.58
1.57
1.55
1.53
1.52
1.50
1.48
1.28
1.26
1.19
1.18
1.18
1.10
0.89
0.87
0.85
2.00
0.96
2.01
7.37
12.06
6.01
3.46
3.43
f1 (ppm)


77.85
67.95
62.35
61.38
46.78
46.39
38.46
38.25
33.40
33.27
31.98
30.41
29.56
29.41
26.36
23.70
22.79
21.08
14.24
f1 (ppm)

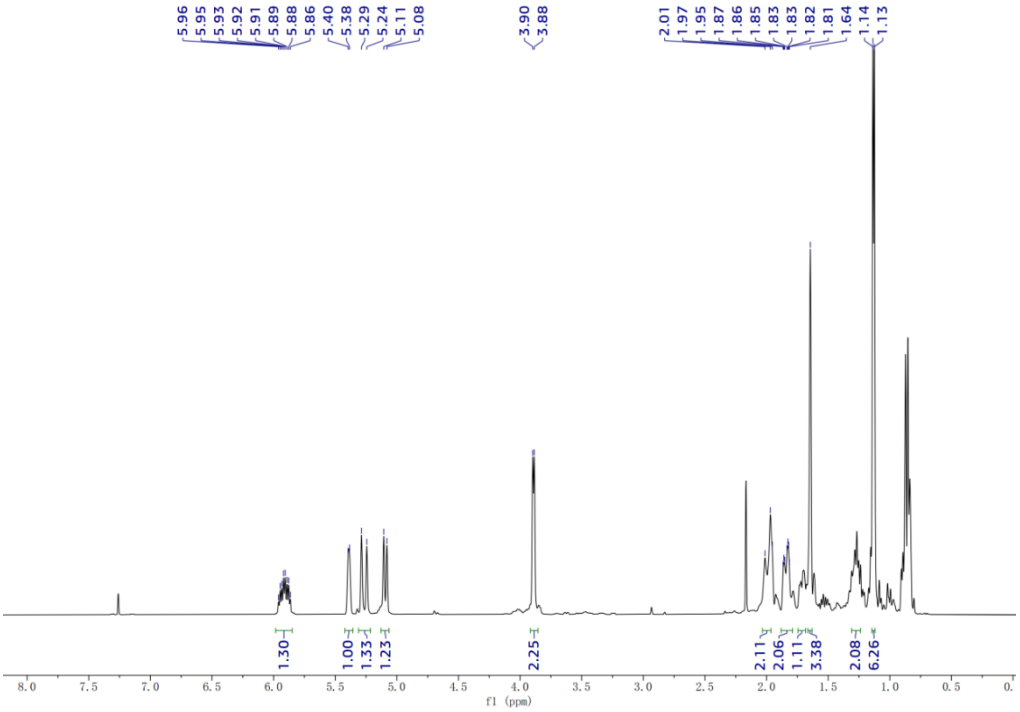
4-(2-(allyloxy)propan-2-yl)-1-methylcyclohex-1-ene (4)



(-)-(α)-Pinene (5.0 g, 36.7 mmol) and allyl alcohol (10.6 g, 183.4 mmol) were dissolved in 2-MeTHF (50 mL). PTA (1.58 g,0.55 mmol) was added portion-wise. The reaction was heated to 50 °C and stirred at reflux for 48 hours. After 48 hours, the reaction mixture was allowed to cool to room temperature and filtered with silica gel under reduced pressure. The organic layer was washed with water (3 × 100 mL) to remove a large proportion of allyl alcohol. Then the organic layers were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. Purification by silica gel chromatography (0-10% ethyl acetate in petroleum ether) gave alkene **4** as a pale-yellow oil (1.8 g, 9.27 mmol, 25% yield).

IR ν_{max} cm^{-1} 3079 (olefin), 3010 (olefin), 2965, 2924, 2891, 2872, 2723, 1646 (olefin), 1439, 1422, 1403, 1381, 1363, 1299, 1246, 1223, 1158, 1138, 1118, 1064, 1025; **δ_H** (400 MHz, $CDCl_3$) 5.91 (1H, ddt, *J* 16.5, 10.6, and 5.3, 13-H), 5.39 (1H, d, *J* 4.8, 14-Ha), 5.27 (1H, d, *J* 17.0, 1-H), 5.09 (1H, d, *J* 10.4, 14-Hb), 3.89 (2H, d, *J* 5.3, 12-H_2), 1.99 (2H, m, 2-Ha, 5-Ha), 1.84 (2H, m, 2-Hb, 5-H), 1.71 (1H, m, 3-H), 1.64 (3H, s, 7-H_3), 1.28 (2H, dt, *J* 13.2 and 6.3, 4-H_2), 1.13 (6H, s, 9-H_3, 10-H_3); **δ_C** (100 MHz, $CDCl_3$) 136.5 (C-13), 134.1 (C-6), 121.0 (C-1), 115.4 (C-14), 77 (C-8, overlapped), 62.3 (C-12), 42.2 (C-3), 31.3 (C-5), 27.0 (C-2), 24.2 (C-9),

23.5 (C-10), 23.1 (C-4), 22.7 (C-7); **HRMS** (ESI positive): Calculated for $C_{12}H_{23}O_3$ $[M+H]^+$ 195.1748, obtained 195.1730.


5.96
5.95
5.93
5.92
5.91
5.89
5.88
5.86
5.40
5.38
5.29
5.24
5.11
5.08
3.90
3.88
2.01
1.97
1.95
1.87
1.86
1.85
1.83
1.83
1.82
1.81
1.64
1.14
1.13
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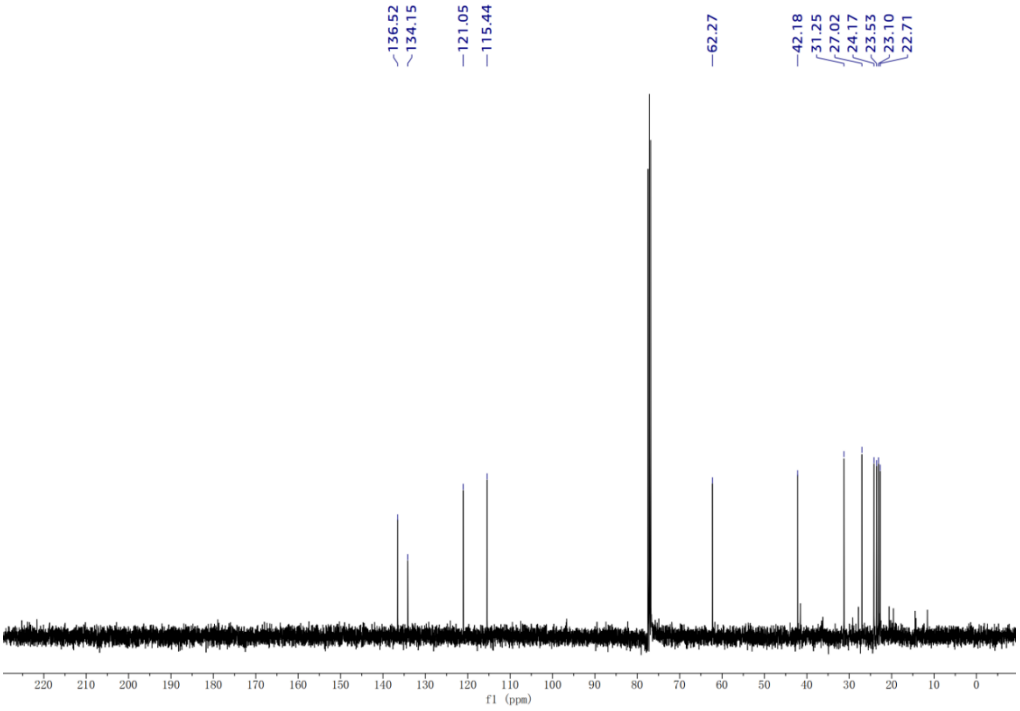
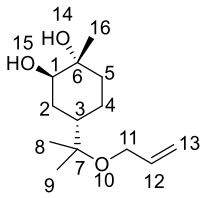
2.06
1.11
3.38
2.08
6.26
f1 (ppm)

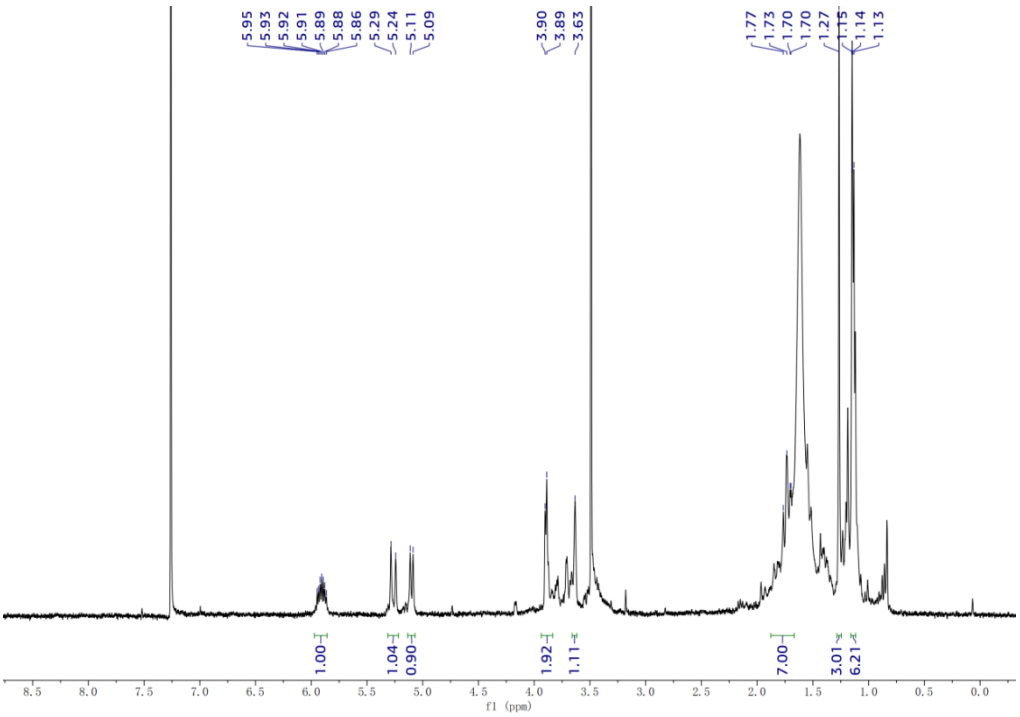

136.52
134.15
121.05
115.44
62.27
42.18
31.25
27.02
24.17
23.53
23.10
22.71
f1 (ppm)

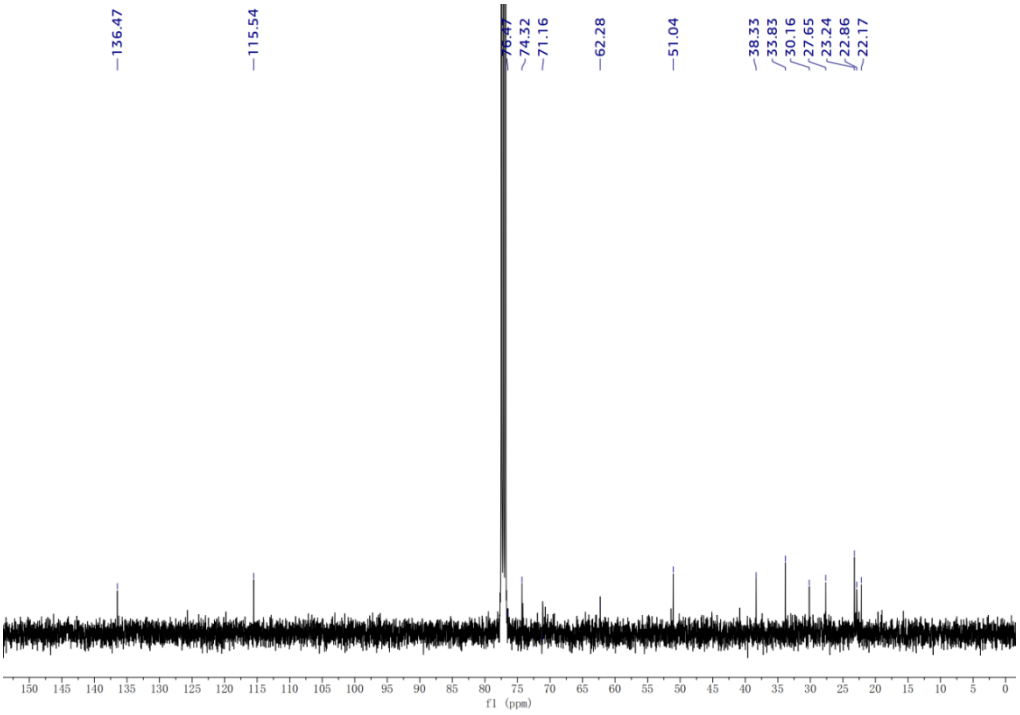
1-(2-(allyloxy)propan-2-yl)-1-methylcyclohexane-1,2-diol (14)



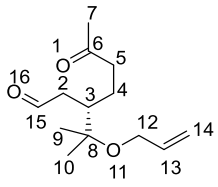
Alkene **4** (1.30 g, 6.69 mmol) was dissolved in CH_3CN (40 mL) and H_2O (30 mL). A mixture of OXONE (6.69 g, 20.0 mmol) and $NaHCO_3$ (1.4 g, 16.7 mmol) was added portion-wise and the reaction was stirred for 72 hours at room temperature. The reaction mixture was filtered and extracted with diethyl ether (3 × 100 mL). The organic layers were combined and dried over magnesium sulfate, filtered, and the solvent removed under reduced pressure to give allyl ether diol **14** as a pale-yellow gel (0.81 g, 3.54 mmol, 53% yield).

IR ν_{max} cm^{-1} 3404 (hydroxyl), 2972, 2931, 2876, 1709, 1444, 1387, 1367, 1325, 1313, 1286, 1247, 1175, 1127 (hydroxyl), 1107, 1054 (hydroxyl), 1034, 1000; **δ_H** (400 MHz, $CDCl_3$) 3.63 (1H, s, 1-H), 3.38 (2H, m, 11-H_2), 1.65 (7H, m, 2-H_2, 3-H, 4-H_2, 5-H_2), 1.26 (3H, s, 15-H_3), 1.14 (9H, s, 8-H_3, 9-H_3, 12-H_3); **δ_C** (100 MHz, $CDCl_3$) 76.3 (C-7), 74.4 (C-1), 71.2 (C-6), 56.0 (C-11), 38.0 (C-3), 33.9 (C-5), 30.2 (C-2), 27.7 (C-15), 23.3 (C-8), 23.0 (C-9), 22.2 (C-4), 16.4 (C-12); **HRMS** (ESI positive): Calculated for $C_{13}H_{24}NaO_3$ $[M+Na]^+$ 251.1623, obtained 251.1617.


5.95
5.93
5.92
5.91
5.89
5.88
5.86
5.29
5.24
5.11
5.09
3.90
3.89
3.63
1.77
1.73
1.70
1.70
1.27
1.15
1.14
1.13
1.00
1.04
0.90
1.92
1.11
7.00
3.01
6.21
f1 (ppm)

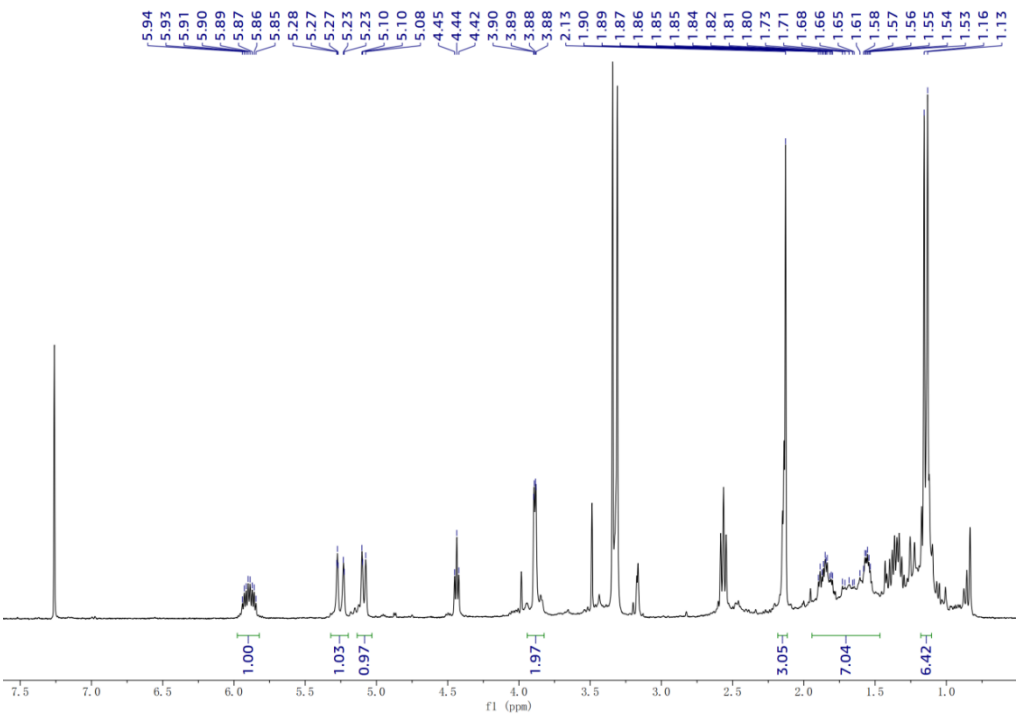

136.47
115.54
76.47
74.32
71.16
62.28
51.04
38.33
33.83
30.16
27.65
23.24
22.86
22.17
f1 (ppm)

3-(2-(allyloxy)propan-2-yl)-6-oxoheptanal (15)



Allyl ether diol **14** (0.7 g, 3.06 mmol) was dissolved in CH_3CN (30 mL) and H_2O (23 mL). $NaIO_4$ (0.981 g, 4.59 mmol) was added portion-wise, and the reaction was stirred for 48 hours at room temperature. The reaction mixture was filtered and extracted with diethyl ether (3 × 100 mL). The organic layers were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure to give keto-aldehyde **15** as yellow liquid (0.35 g, 1.54 mmol, 51% yield).

IR ν_{max} cm^{-1} 3400 (olefin), 3080 (olefin), 2970, 2935, 2876 (formyl), 2833 (formyl), 2723 (formyl), 2116, 1714 (carbonyl), 1646, 1544, 1453, 1422, 1382, 1366, 1233, 1164, 1123, 1095, 1058, 1000; **δ_H** (400 MHz, $CDCl_3$) 5.89 (1H, ddt, *J* 16.4, 10.4, and 5.2, 13-H), 5.26 (1H, m, 14-Hb), 5.09 (1H, m, 14-Ha), 3.89 (2H, m, 12-H_2), 2.13 (3H, s,7-H_3), 1.72 (7H, m, 2-H_2, 3-H, 4-H_2, 5-H_2), 1.14 (6H, s, 9-H_3, 10-H_3); **δ_C** (100 MHz, $CDCl_3$) 209.4 (C-6), 201.9 (C-15), 136.3 (C-13), 115.4 (C-14), 78.1 (C-8), 62.4 (C-12), 42.8 (C-2, C-5), 42.2 (C-3), 30.2 (C-7), 25.0 (C-9), 23.0 (C-10), 22.5 (C-4). **HRMS** (ESI positive): Calculated for $C_{13}H_{22}NaO_3$ $[M+Na]^+$ 249.1467, obtained 249.1454.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5.91
5.90
5.89
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5.86
5.85
5.28
5.27
5.27
5.23
5.23
5.10
5.10
5.08
4.45
4.44
4.42
3.90
3.89
3.88
3.88
2.13
1.90
1.89
1.87
1.86
1.85
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1.81
1.80
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1.65
1.61
1.58
1.57
1.56
1.55
1.54
1.53
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1.03
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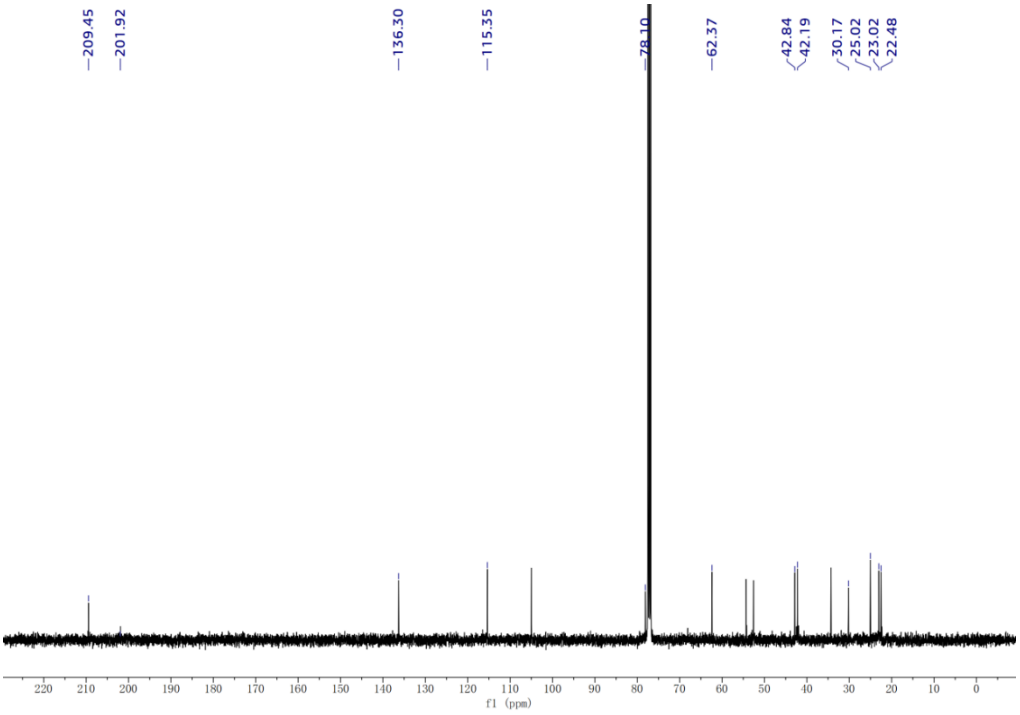
3.05
7.04
6.42
f1 (ppm)


209.45
201.92
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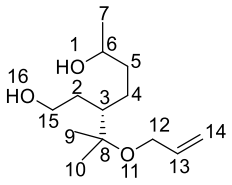
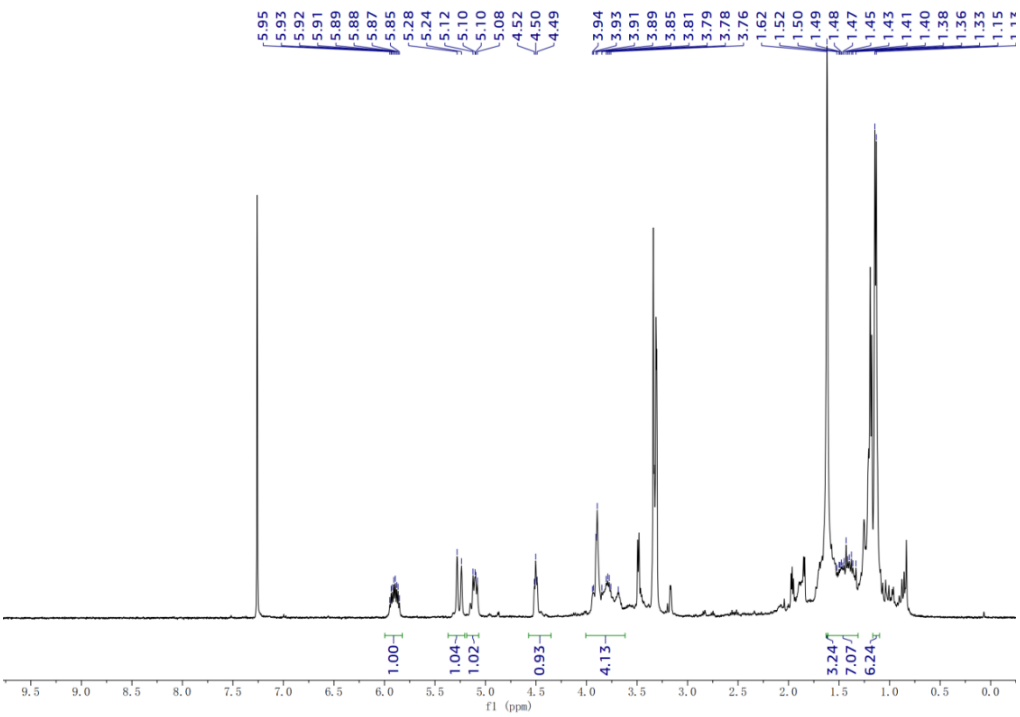
115.35
78.10
62.37
42.84
42.19
30.17
25.02
23.02
22.48
f1 (ppm)

3-(2-(allyloxy)propan-2-yl)heptane-1,6-diol (16)



Keto-aldehyde **15** (300 mg, 1.32 mmol) was dissolved in methanol (10 mL) and cooled at 0 °C. $NaBH_4$ (90 mg, 2.64 mmol) was added portion-wise. The mixture was allowed to warm to room temperature and stirred for 4 hours. The reaction quenched by addition of water (10 mL) and stirred for 1 hour. The reaction mixture was filtered and extracted with ethyl acetate (3 × 25 mL). The organic layers were combined and washed with brine. The solvent was removed under reduced pressure to give diols **16** as a perfam gel (0.29 g, 1.25 mmol, 95% yield). **IR ν_{max}** cm^{-1} 3855 (hydroxyl), 3382 (hydroxyl), 3079, 2965, 2934, 2873, 2833, 2725, 1647, 1572, 1509, 1458 (olefin), 1422, 1405, 1382, 1368, 1331, 1234, 1181, 1122 (olefin), 1053 (olefin), 1034; **δ_H** (400 MHz, $CDCl_3$) 5.90 (1H, m, 13-H), 5.26 (1H, d, *J* 17.1, 14-Ha), 5.10 (1H, dd, *J* 10.2 and 7.1, 14-Hb), 4.50 (1H, t, *J* 5.5, 6-H), 3.81 (4H, m, 12-H_2, 15-H_2), 1.62 (3H, s, 7-H_3), 1.45 (7H, m, 2-H_2, 3-H, 4-H_2, 5-H_2), 1.14 (6H, s, 9-H_3, 10-H_3); **δ_C** (100 MHz, $CDCl_3$) 136.1 (C-13), 115.9 (C-14), 115.5 (C-14), 78.4 (C-8), 78.3 (C-8), 68.7 (C-6), 67.5 (C-6), 62.5 (C-15), 62.4 (C-12), 42.5 (C-3), 42.2 (C-3), 38.9 (C-5), 38.6 (C-5), 35.0 (C-2), 34.5 (C-2), 27.4 (C-7), 26.9 (C-7), 23.6 (C-9), 23.0 (C-10), 22.6 (C-4); **HRMS** (ESI positive): Calculated for $C_{13}H_{26}NaO_3$ $[M+Na]^+$ 253.1774, obtained 253.1760.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1.47
1.45
1.43
1.41
1.40
1.38
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1.02
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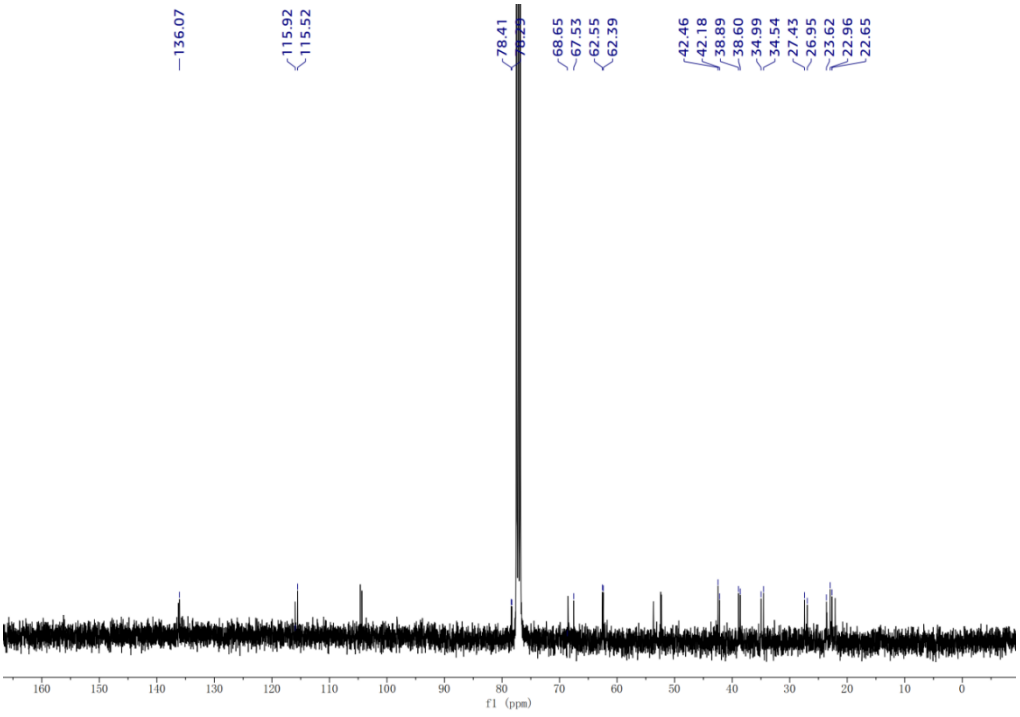
3.24
7.07
6.24
f1 (ppm)


136.07
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78.29
68.65
67.53
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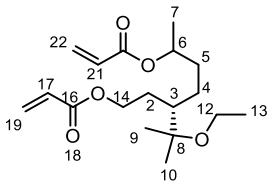
42.46
42.18
38.89
38.60
34.99
34.54
27.43
26.95
23.62
22.96
22.65
f1 (ppm)

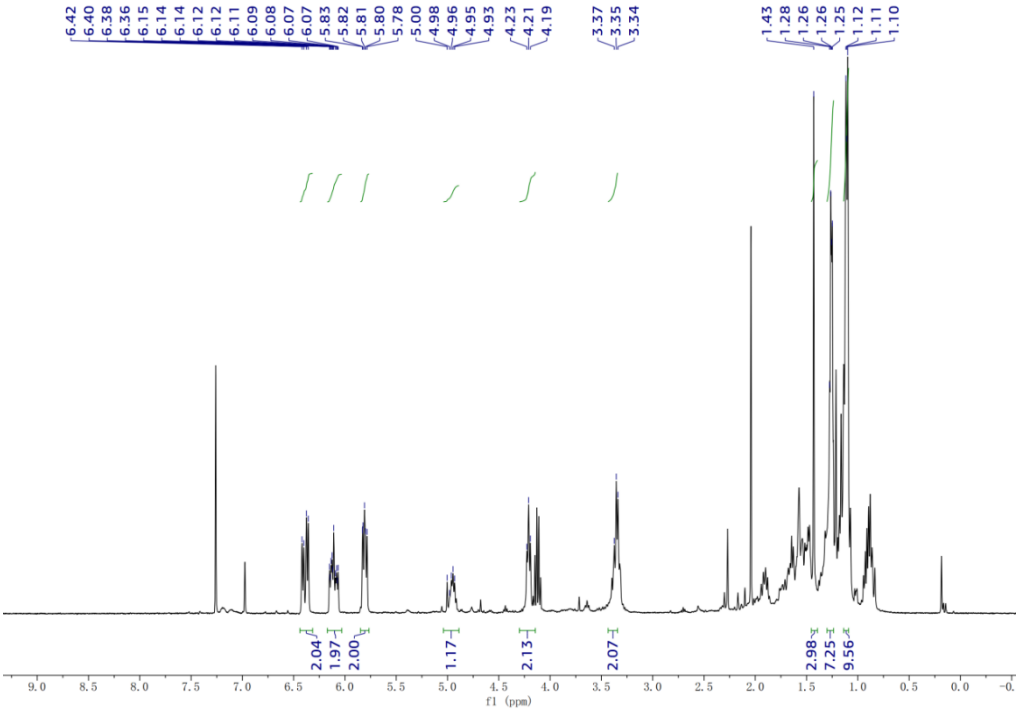
3-(2-ethoxypropan-2-yl)heptane-1,6-diyl diacrylate (17)



Diol **16** (0.5 g, 2.29 mmol) and acrylic acid (0.36 g, 5.03 mmol) were dissolved in 2-MeTHF (20 mL). Triethylamine (1.39 g, 13.7 mmol) was added dropwise. Propylphosphonic anhydride (1.74 g, 5.49 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 72 hours. The reaction was quenched by addition of water (20 mL) and stirred for 5 hours. The aqueous layer was extracted with diethyl ether (3 × 50 mL). The organic layers were combined and washed with hydrochloric acid (1 M, 10 mL), then water (10 mL), then saturated aqueous $NaHCO_3$ (10 mL) then water (10 mL). The aqueous layer was washed with brine, separated and the solvent was removed under reduced pressure. Purification using column chromatography (0-10% ethyl acetate in petroleum ether) gave diacrylate **17** as a perfam oil (0.12 g, 0.36 mmol, 16% yield)

IR ν_{max} cm^{-1} 2973, 2930, 2873, 1720 (carbonyl), 1637, 1619, 1459 (olefin), 1406, 1382, 1365, 1295, 1272, 1192, 1156, 1118, 1065, 984, 964, 916, 847, 810; **δ_H** (400 MHz, $CDCl_3$) 6.39 (2H, dd, J 17.4 and 7.1, 19-Hb, 22-Ha), 6.11 (2H, ddd, J 17.1, 10.5, and 6.0, 21-H, 17-H), 5.85 – 5.77 (2H, m, 19-Ha, 22-Hb), 5.04 – 4.89 (1H, m, 6-H), 4.21 (2H, t, J 6.9, 14-H2), 3.36 (2H, d, J 8.0, 12-H2), 1.43 (3H, s, 7-

H3), 1.26 (7H, m, 2-H2, 3-H, 4-H2, 5-H2), 1.11 (9H, s, 9-H3, 10-H3, 13-H3); **δ_C** (100 MHz, $CDCl_3$) 166.4 (C-16), 166.0 (C-20), 130.6 (C-22), 130.4 (C-19, 129.2 (C-21), 128.8 (C-17), 77.3 (C-8), 77.2 (C-8), 71.7 (C-6), 71.4 (C-6), 64.8 (C-14), 64.7 (C-14), 56.1 (C-12), 43.7 (C-3), 43.5 (C-3), 35.5 (C-5), 35.4 (C-5), 30.5 (C-9), 30.0 (C-10), 30.0 (C-10), 26.8 (C-2), 26.7 (C-2), 22.6 (C-7), 22.6 (C-7), 20.2 (C-4), 20.1 (C-4), 16.2 (C-13). **CHN** Found: C, 61.87; H, 8.65; Na, 6.58; O, 22.89. **HRMS** (ESI positive): Calculated for $C_{18}H_{30}NaO_5$ $[M+Na]^+$ 349.1991, obtained 349.1992.


6.42
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2.13
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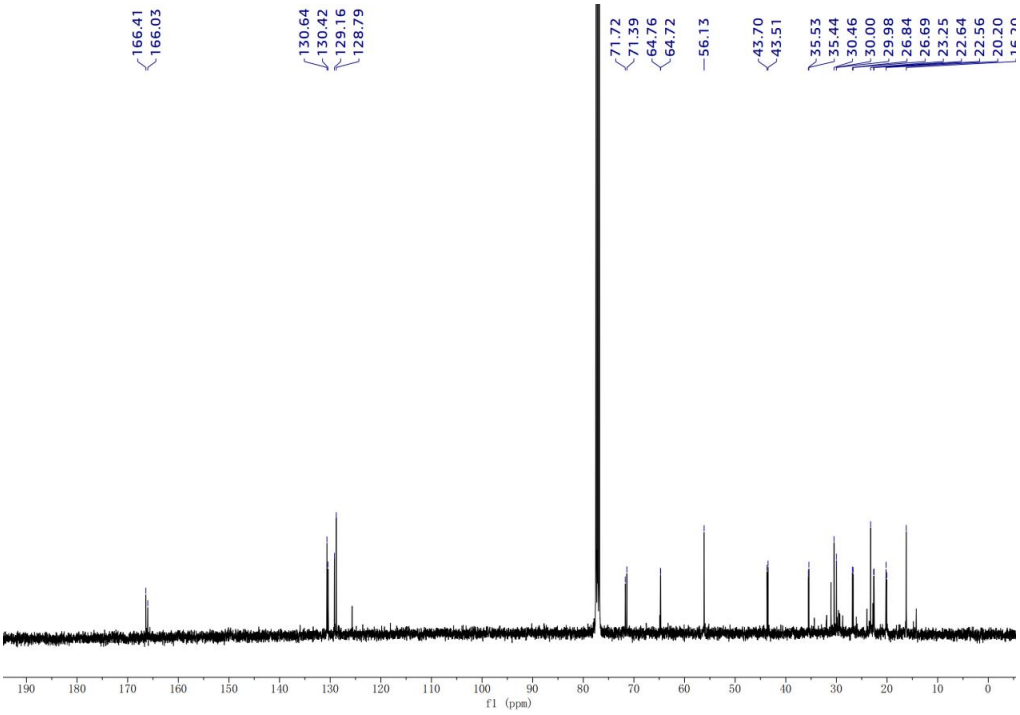
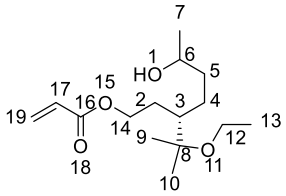
2.98
7.25
9.56
f1 (ppm)


166.41
166.03
130.64
130.42
129.16
128.79
71.72
71.39
64.76
64.72
56.13
43.70
43.51
35.53
35.44
30.46
30.00
29.98
26.84
26.69
23.25
22.64
22.56
20.20
f1 (ppm)

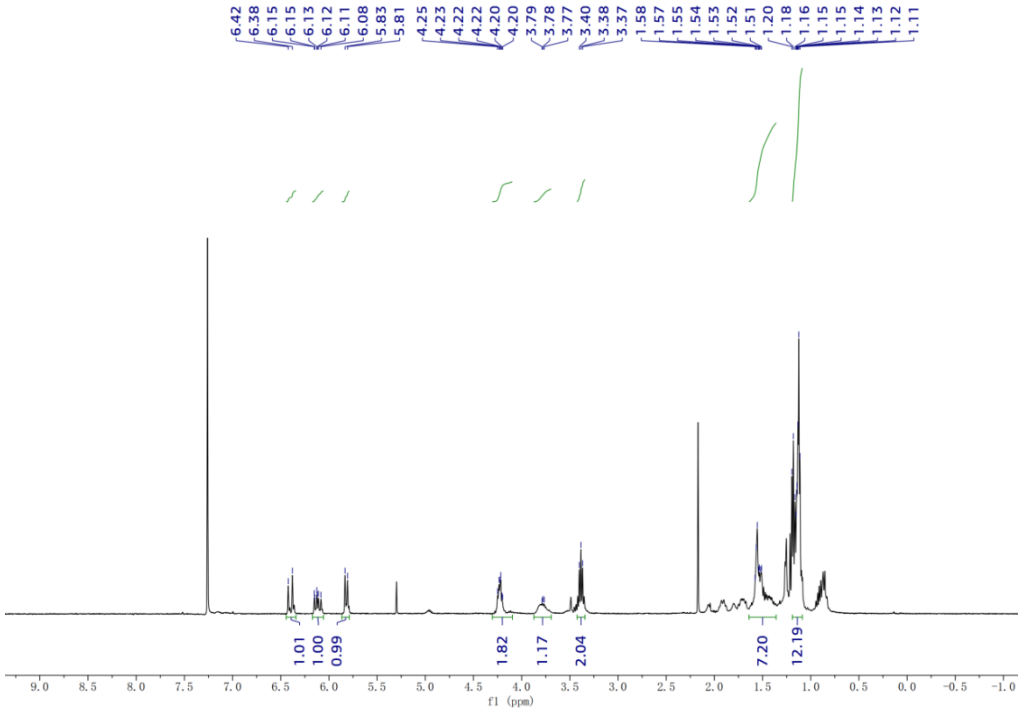
3-(2-ethoxypropan-2-yl)-6-hydroxyheptyl acrylate (18)

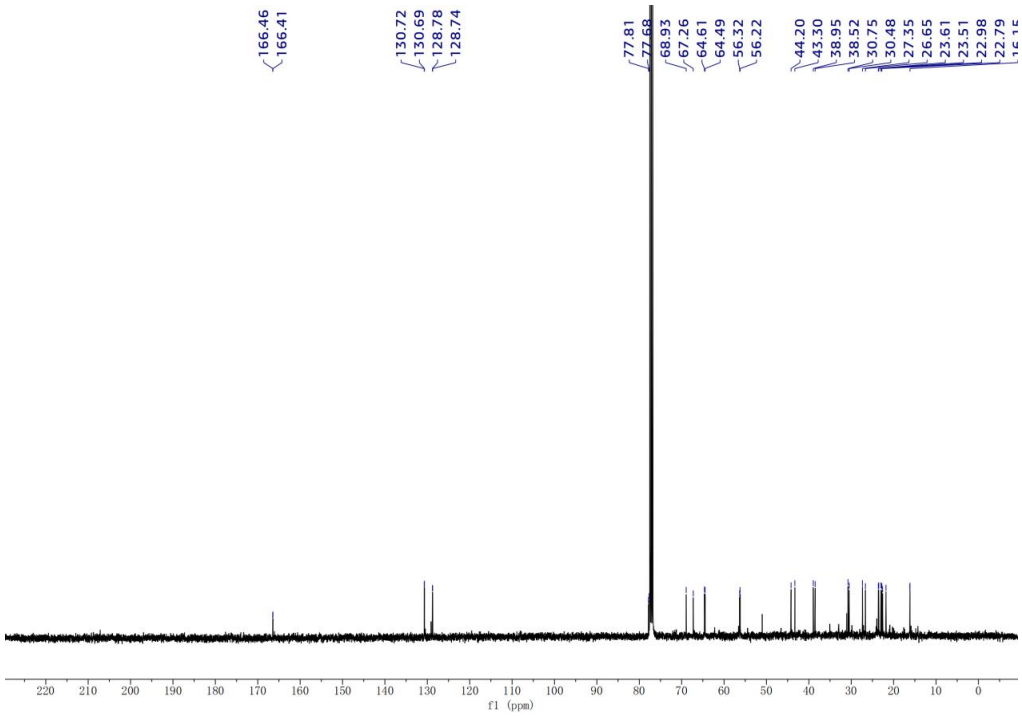


Diol **16** (0.5 g, 2.29 mmol) and acrylic acid (0.17 g, 2.40 mmol) were dissolved in 2-MeTHF (20 mL). Triethylamine (0.695 g, 6.87 mmol) was added dropwise. Propylphosphonic anhydride (10.9 g, 2.75 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 72 hours. The reaction was quenched by addition of water (20 mL) and stirred for 5 hours. The aqueous layer was extracted with diethyl ether (3 × 50 mL). The organic layers were combined and washed with hydrochloric acid (1 M, 10 mL), then water (10 mL), then saturated aqueous $NaHCO_3$ and the solvent was removed under reduced pressure. Purification using column chromatography (20-45% ethyl acetate in petroleum ether) gave acrylate **18** as a perfam oil (0.11 g, 0.40 mmol, 18% yield).

IR ν_{max} cm^{-1} 3408 (hydroxyl), 2972, 2929, 2873, 1721 (carbonyl), 1637, 1619, 1459 (olefin), 1407, 1382, 1366, 1295, 1274, 1192, 1153, 1115, 1062; **δ_H** (400 MHz, $CDCl_3$) 6.40 (1H, d, J 17.3, 17-H), 6.17 – 6.06 (1H, m, 19-Hb), 5.82 (1H, d, J 10.4, 19-Ha), 4.22 (2H, q, J 7.0 12-H2), 3.78 (1H, m, 6-H), 3.38 (2H, m, 14-H2), 1.54 (7H, m, 2-H2, 3-H, 4-H2, 5-H2), 1.14 (12H, s, 7-H3, 9-H3, 10-H3, 13-H3); **δ_C** (100 MHz, $CDCl_3$) 166.5 (C-16), 166.4 (C-16), 130.7 (C-19), 130.7 (C-19), 128.8 (C-17), 128.7 (C-17), 77.8 (C-8), 77.7 (C-8), 68.9 (C-6), 67.3 (C-6), 64.6 (C-14),

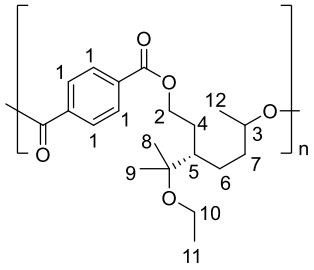
64.5 (C-14), 56.3 (C-12), 56.2 (C-12), 44.2 (C-3), 43.3 (C-3), 38.9 (C-5), 38.5 (C-5), 30.8 (C-9), 30.5 (C-9), 27.4 (C-10), 26.7 (C-10), 23.6 (C-7), 23.5 (C-7), 23.0 (C-2), 22.8 (C-2), 22.6 (C-4), 21.8 (C-4), 16.2 (C-13), 16.1 (C-13); **HRMS** (ESI positive): Calculated for $C_{15}H_{28}NaO_4$ $[M+Na]^+$ 295.1880, obtained 295.1886.


6.42
6.38
6.15
6.15
6.13
6.12
6.11
6.08
5.83
5.81
4.25
4.23
4.22
4.22
4.20
4.20
3.79
3.78
3.77
3.40
3.38
3.37
1.58
1.57
1.55
1.54
1.53
1.52
1.51
1.20
1.18
1.16
1.15
1.15
1.14
1.13
1.12
1.11
1.01
1.00
0.99
1.82
1.17
2.04
7.20
12.19
f1 (ppm)


166.46
166.41
130.72
130.69
128.78
128.74
77.81
77.68
68.93
67.26
64.61
64.49
56.32
56.22
44.20
43.30
38.95
38.52
30.75
30.48
27.35
26.65
23.61
23.51
22.98
22.79
f1 (ppm)

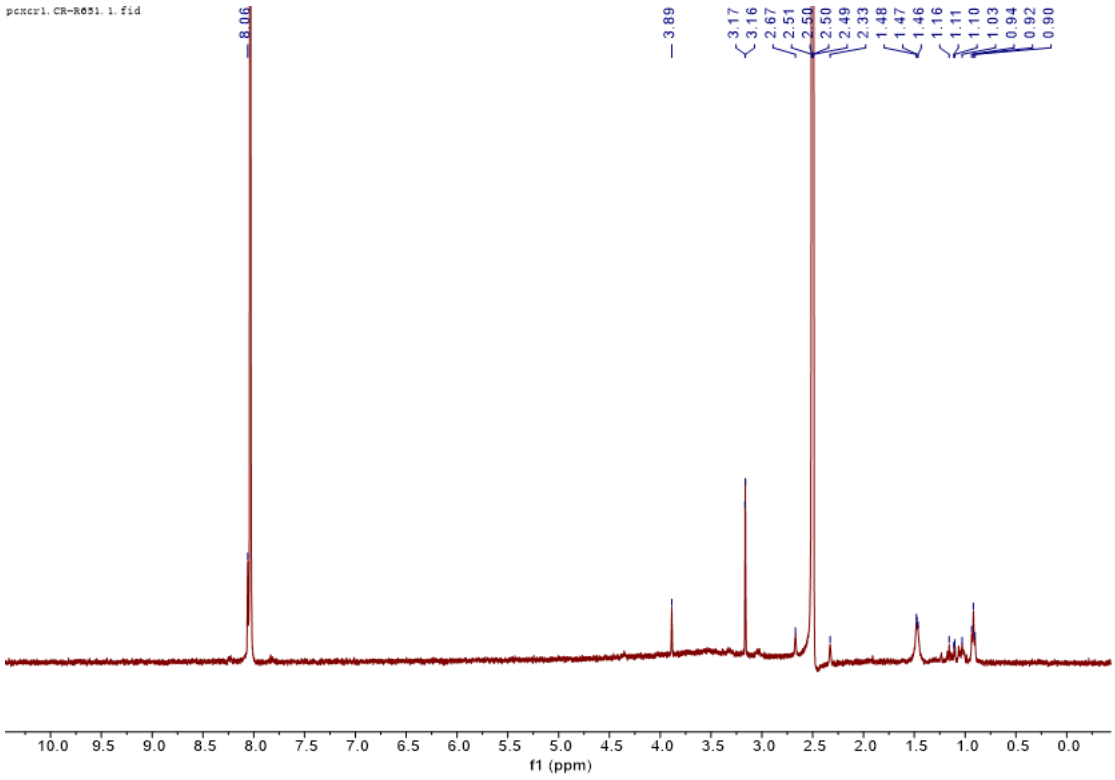
Polymer synthesis

poly(3-(2-ethoxypropan-2-yl)hexane-1,6-diyl terephthalate) (19)



Diol **16** (0.5 g, 2.29 mmol) and terephthalic acid (0.42 g, 2.29 mmol) were dissolved in dichloromethane (20 mL). Triethylamine (1.75 g, 5.49 mmol) was added dropwise. Propylphosphonic anhydride (1.39 g, 13.74 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 48 hours. The reaction was quenched by addition of water (20 mL) and stirred for 5 hours. The aqueous layer was extracted with ethyl acetate (3 × 50 mL). The organic layers were combined and washed with hydrochloric acid (1 M, 10 mL), water (10 mL), saturated aqueous $NaHCO_3$ (10 mL), and water (10 mL). The organic phase was washed with brine, separated and the solvent was removed under reduced pressure to give the poly(3-(2-ethoxypropan-2-yl)hexane-1,6-diyl terephthalate) **19** as a white solid.

IR ν_{max} cm^{-1} 3064 (alkyl), 2969 (alkyl), 2872 (alkane), 1717 (carbonyl), 1273 (ester), 1249 (alkane), 1152 (aryl), 1065 (ether), 781 (aryl), 766 (aryl); **δ_H** (400 MHz, $CDCl_3$) 8.18 – 8.02 (m, H-1), 4.48 – 4.36 (m, H-2), 3.88 – 3.68 (m, H-3), 3.48 – 3.27 (m, H-10), 1.83 – 1.71 (m, H-4), 1.69 – 1.58 (m, H-5), 1.57 – 1.48 (m, H-6), 1.49 – 1.37 (m, H-7), 1.26 (d, *J* 7.2, H-12), 1.19 (s, H-8,9), 1.18 – 1.08 (m, H-11).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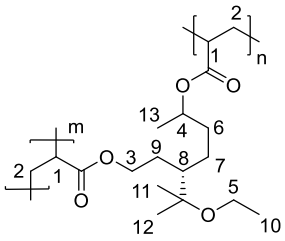
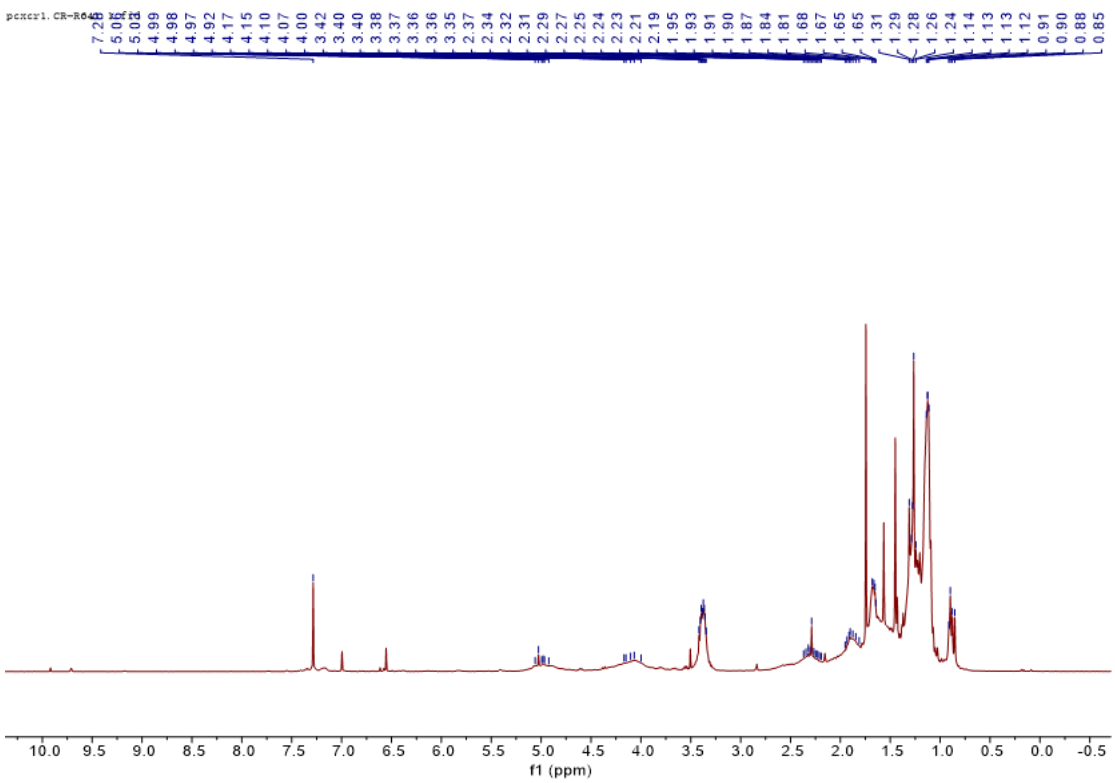
3.89
3.17
3.16
2.67
2.51
2.50
2.50
2.49
2.33
1.48
1.47
1.46
1.16
1.11
1.10
1.03
0.94
0.92
0.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

poly(3-methyl-8-ethylnonane-1,9-diyl acrylate) (20)



Diacrylate **17** (0.2 g, 0.613 mmol) was gradually dissolved in toluene (2.5 mL). AIBN (32 mg, 0.02 mmol) was dissolved in toluene (2.5 mL) and added to the reaction mixture. The reaction mixture was degassed using five freeze-pump-thaw cycles and then filled with argon and sealed. The reaction mixture was allowed to warm to room temperature and stirred for 24 hours at 65 °C. After 24 hours, the reaction mixture was added to methanol and cooled to -18 °C for 72 hours. Then resulting precipitate was filtered to give poly(3-methyl-8-ethylnonane-1,9-diyl acrylate) **20** as a white powder.

IR ν_{max} cm^{-1} 2970 (alkyl), 2926 (alkyl), 2870 (alkyl), 1728 (carbonyl), 1447 (alkyl), 1243 (alkane), 1162 (ether), 1116 (ether), 1020 (ether), 732 (alkane); **δ_H** (400 MHz, $CDCl_3$) 5.08 – 4.81 (m, H-4), 4.18 – 3.91 (m, H-3), 3.47 – 3.21 (m, H-5), 2.41 – 2.17 (m, H-1), 1.95 – 1.81(m, H-2,6,7,8), 1.70 – 1.63 (m, H-9), 1.34 – 1.22 (m, H-13), 1.16 – 1.06 (m, H-11,12), 0.96 – 0.78 (m, H-10).


7.28
5.06
5.03
4.99
4.98
4.97
4.92
4.17
4.15
4.10
4.07
4.00
3.42
3.40
3.40
3.38
3.37
3.36
3.36
3.35
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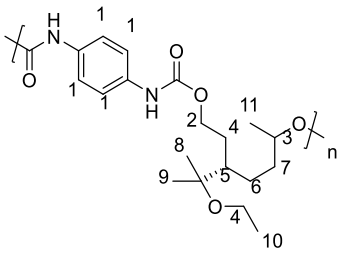
2.27
2.25
2.24
2.23
2.21
2.19
1.95
1.93
1.91
1.90
1.87
1.84
1.81
1.68
1.67
1.65
1.65
1.31
1.29
1.28
1.26
1.24
1.14
1.13
1.13
1.12
0.91
0.90
0.88
0.85
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

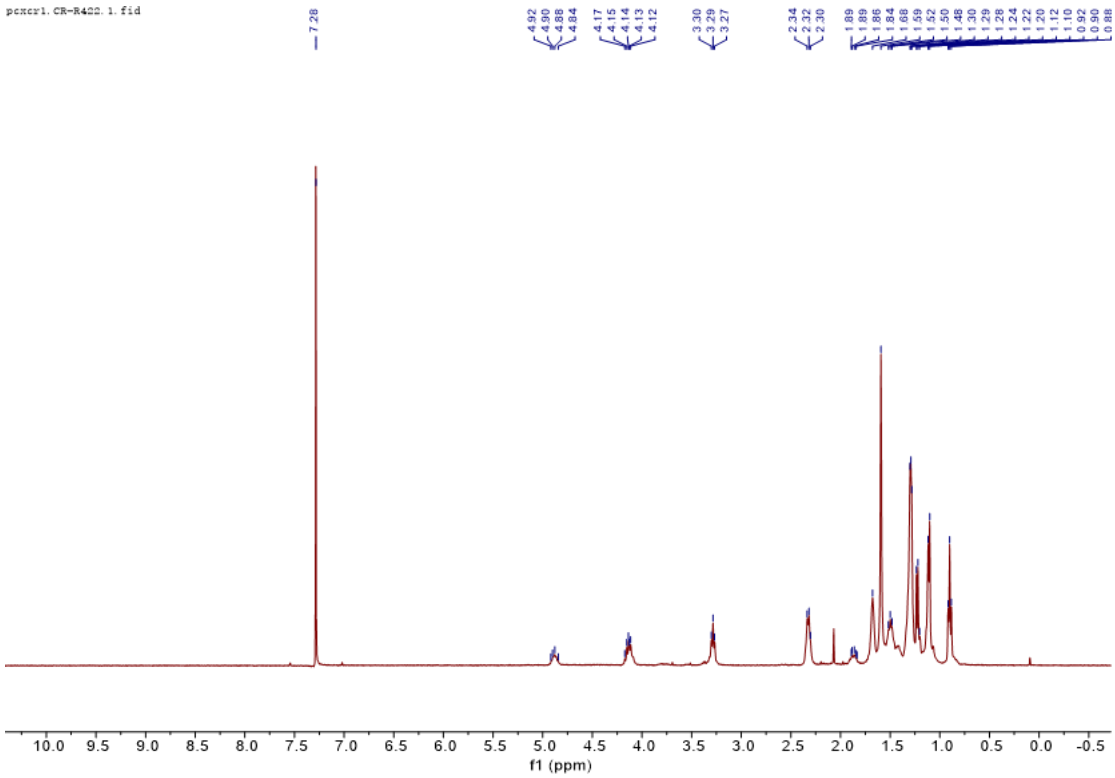
poly(3-(2-ethoxypropan-2-yl)heptane-1,6-diyl 1,4-phenylene dicarbamate)

(21)



Diol **7** (0.5 g, 2.29 mmol) was dissolved in dichloromethane (10 mL), then 1,4-phenylene diisocyanate (0.733 g, 4.58 mmol) was dissolved in dichloromethane (10 mL) and added to the reaction mixture. Triethylamine (0.05 g, 0.49 mmol) was added dropwise. The reaction was stirred at room temperature for 24 hours. After 24 hours, the reaction mixture was added to methanol and cooled to -18 °C for 48 hours. Then precipitate filtered to give poly(3-(2-ethoxypropan-2-yl)heptane-1,6-diyl 1,4-phenylene dicarbamate) **21** as a white powder.

IR ν_{max} cm^{-1} 3061 (alkyl), 2874 (alkane), 1682 (carbonyl), 1278 (ester), 1248 (alkane), 1167 (aryl), 1053 (ether), 780 (amide), 719 (aryl), 764 (aryl); **δ_H** (400 MHz, $CDCl_3$) 8.06 (s, H-1), 3.89 (s, H-2), 2.67 (s, H-3), 2.33 (s, H-4), 1.51 – 1.43 (m, H-4,5,6,7), 1.16 (s, H-8), 1.11 (d, *J* 4.4, H-11), 1.03 (s, H-9), 0.92 (t, *J* 6.9, H-10).


pcxcr1.CR-R422.1.fid
7.28
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4.84
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3.29
3.27
2.34
2.32
2.30
1.89
1.89
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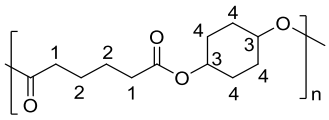
1.52
1.50
1.48
1.30
1.29
1.28
1.24
1.22
1.20
1.12
1.10
0.92
0.90
0.88
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

Poly(1,4-cyclohexanediyl adipate) (22)

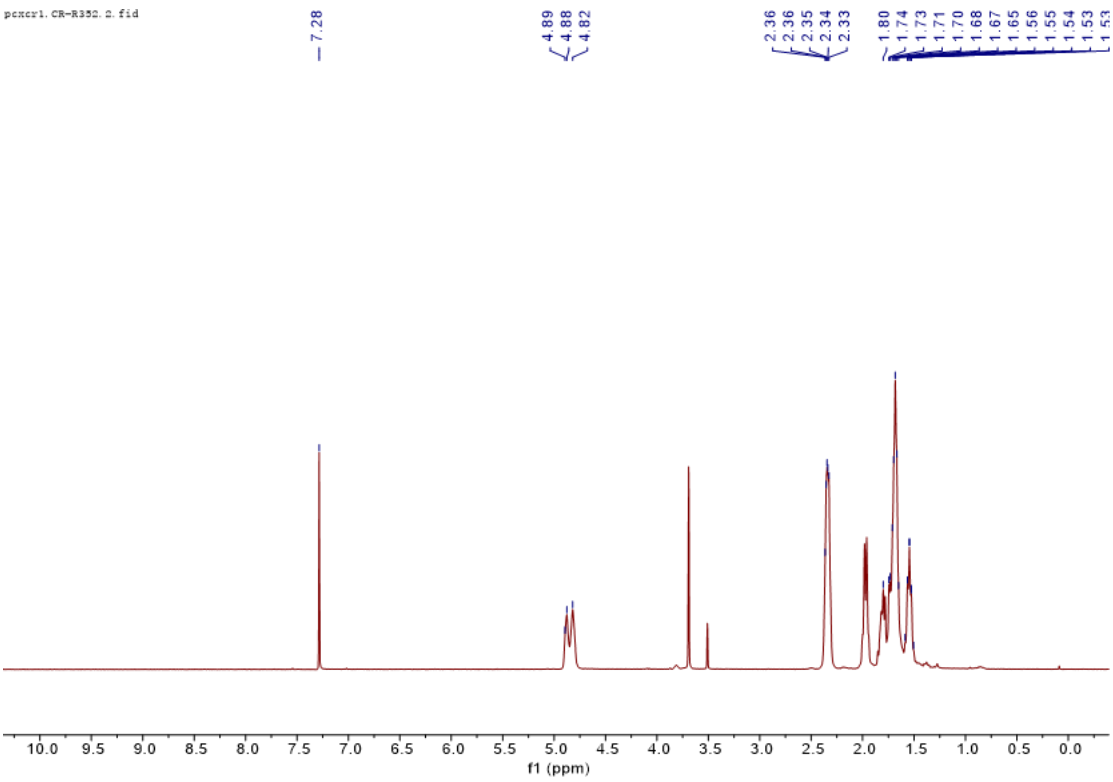


Method 1: Adipic acid (3.65 g, 25 mmol), cyclohexane-1,4-diol (2.90 g, 25 mmol), titanium butoxide (85 mg, 0.25 mmol) were weighed into a two-necked glass vessel equipped with a stirrer. The reaction was placed on a hot plate preheated to 100 °C with stirring, vacuum was gradually applied over a period of 1 hour and a vacuum of 20 mbar was then maintained for 21 hours at 120 °C. After 21 hours, stirring was continued for 8 hours under a vacuum of approximately 1 mbar. The reaction product was dissolved in CH_2Cl_2 and precipitated into methanol. This mixture was filtered to give poly(1,4-cyclohexanediyl adipate) **22** as a white powder.

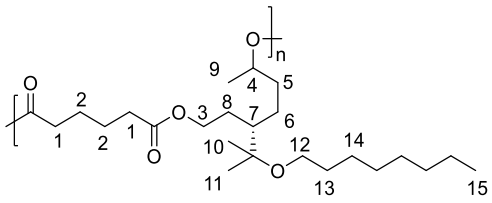
Method 2: Dimethyl adipate (4.35 g, 25 mmol), cyclohexane-1,4-diol (2.90 g, 25 mmol), titanium butoxide (85 mg, 0.25 mmol) were weighed into a two-necked glass vessel equipped with a stirrer. The reaction was placed on a hot plate preheated to 100 °C with stirring, vacuum was gradually applied over a period of 1 hour and a vacuum of 20 mbar was then maintained for 21 hours at 120 °C. After 21 hours, stirring was continued for 8 hours under a vacuum of approximately 1 mbar. The reaction product was dissolved in CH_2Cl_2 and precipitated into methanol. This mixture was filtered to give poly(1,4-cyclohexanediyl adipate) **22** as a white powder.

δ_H (400 MHz, $CDCl_3$) 4.89 – 4.82 (m, H-3), 2.46 – 2.20 (m, H-1), 1.85 – 1.63 (m,

H-4), 1.61 – 1.44 (m, H-2).



3-(2-(octyloxy)propan-2-yl)heptane-1,6-diol and adipic acid (23)

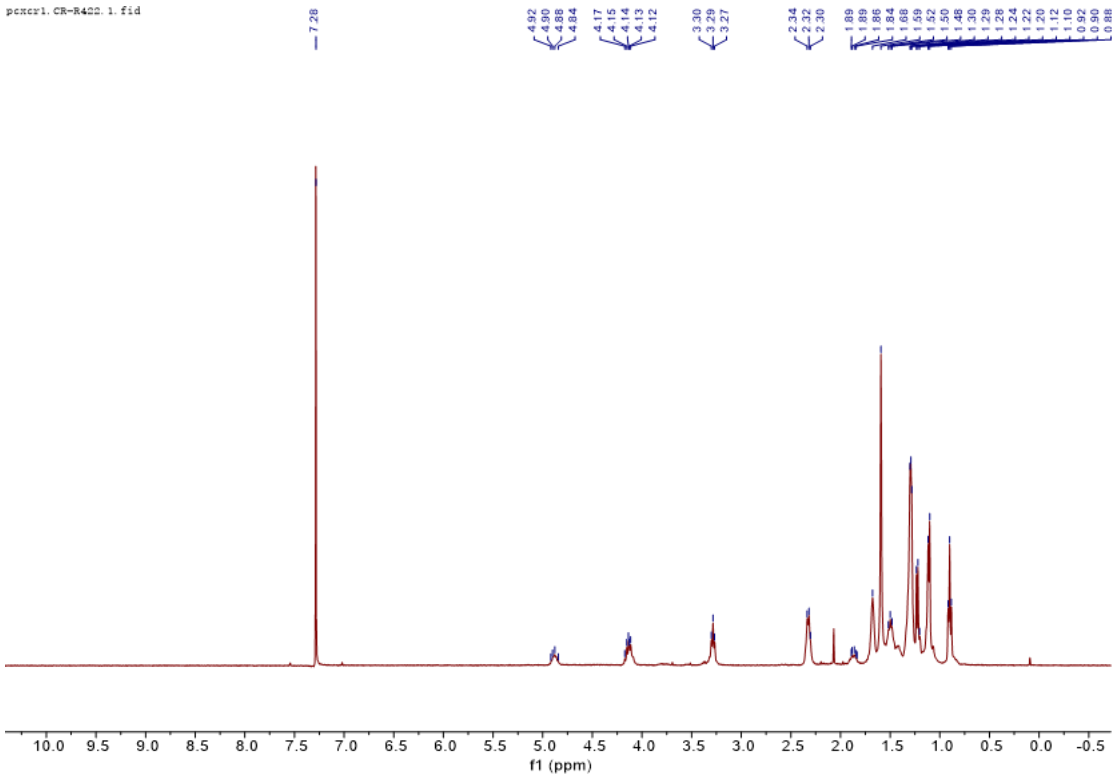


Method 1: Diol **13** (1.0 g, 4.50 mmol), dimethyl adipate (0.70 g, 4.50 mmol) and titanium butoxide (15 mg, 0.04 mmol) were weighed into a two-necked glass vessel equipped with a stirrer. The reaction was placed on a hot plate preheated to 100 °C with stirring, vacuum was gradually applied to 20 mbar for 1 hour, a vacuum of 1 mbar was then maintained for 21 hours with the temperature heat to 120 °C. After 21 hours, stirring was continued for 8 hours under a vacuum of approximately 1 mbar. The reaction product was dissolved in CH_2Cl_2 and precipitated into methanol. The reaction mixture was frozen for 72 hours. This mixture was then filtered to give poly(ester-ether) based on 3-(2-(octyloxy)propan-2-yl)heptane-1,6-diol and adipic acid **23** as a brown oil.

Method 2: Diol **13** (1.0 g, 4.50 mmol), adipic acid (0.48 g, 3.30 mmol) and titanium butoxide (33 mg, 0.1 mmol) were weighed into a two-necked glass vessel equipped with a stirrer. The reaction was placed on a hot plate preheated to 100 °C with stirring, vacuum was gradually applied to 20 mbar for 1 hour, a vacuum of 1 mbar was then maintained for 21 hours with the temperature heat to 120 °C. After 21 hours, stirring was continued for 8 hours under a vacuum of approximately 1 mbar. The reaction product was dissolved

in CH_2Cl_2 and precipitated into methanol. The reaction mixture was frozen for 72 hours. This mixture was then filtered to give poly(ester-ether) based on 3-(2-(octyloxy)propan-2-yl)heptane-1,6-diol and adipic acid **23** as a brown oil.

IR ν_{max} cm^{-1} 2929 (alkyl), 2871 (alkyl), 2857 (alkyl), 1721 (carbonyl), 1460 (alkyl), 1258 (ether), 1221 (alkane), 1074 (ether), 904 (ester), 727 (alkane); **δ_H** (400 MHz, $CDCl_3$) 4.95 – 4.69 (m, H-12), 4.14 (dd, *J* 14.9, 8.1, H-3), 3.29 (t, *J* 6.7, H-4), 2.41 – 2.19 (m, H-1), 1.94 – 1.79 (m, H-5), 1.68 (s, H-10), 1.59 (s, H-11), 1.50 (t, *J* 7.5, H-13), 1.35 – 1.26 (m, H-14), 1.23 – 1.20 (m, H-2), 1.11 (d, *J* 6.3, H-9), 0.90 (t, *J* 6.5, H-15).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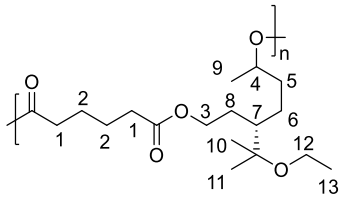
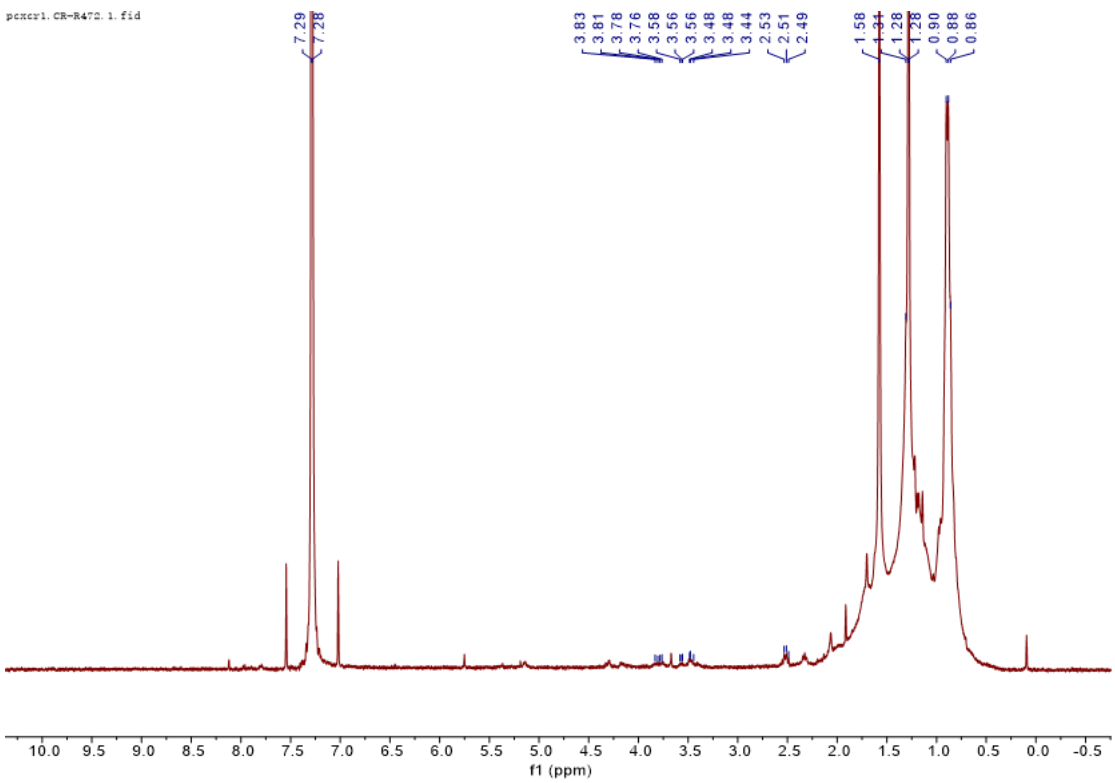
1.52
1.50
1.48
1.30
1.29
1.28
1.24
1.22
1.20
1.12
1.10
0.92
0.90
0.88
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

3-(2-(ethyloxy)propan-2-yl)heptane-1,6-diol and adipic acid (24)



Diol **7** (0.2 g, 0.66 mmol), dimethyl adipate (0.11 g, 0.66 mmol) and titanium butoxide (22 mg, 0.06 mmol) were weighed into a two-necked glass vessel equipped with a stirrer. The reaction was placed on a hot plate preheated to 100 °C with stirring, vacuum was gradually applied to 20 mbar for 1 hour, a vacuum of 1 mbar was then maintained for 21 hours with the temperature heat to 120 °C. After 21 hours, stirring was continued for 8 hours under a vacuum of approximately 1 mbar. The reaction product was dissolved in CH_2Cl_2 and precipitated into methanol. The reaction mixture was frozen for 72 hours. This mixture was filtered to give poly(ester-ether) based on 3-(2-(ethyloxy)propan-2-yl)heptane-1,6-diol and adipic acid **24** as a purple oil.

δ_H (400 MHz, $CDCl_3$) 3.87 – 3.71 (m, H-3), 3.60 – 3.52 (m, H-4), 3.52 – 3.42 (m, H-12), 2.65 – 2.38 (m, H-1), 1.58 (s, H-9,10,11), 1.40 – 1.17 (m, H-2,5,6,7,8), 1.03 – 0.78 (m, H-13).


pcncr1.CR-R472.1.fid
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7.28
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3.81
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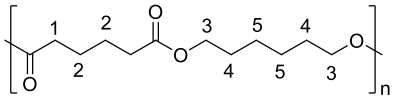
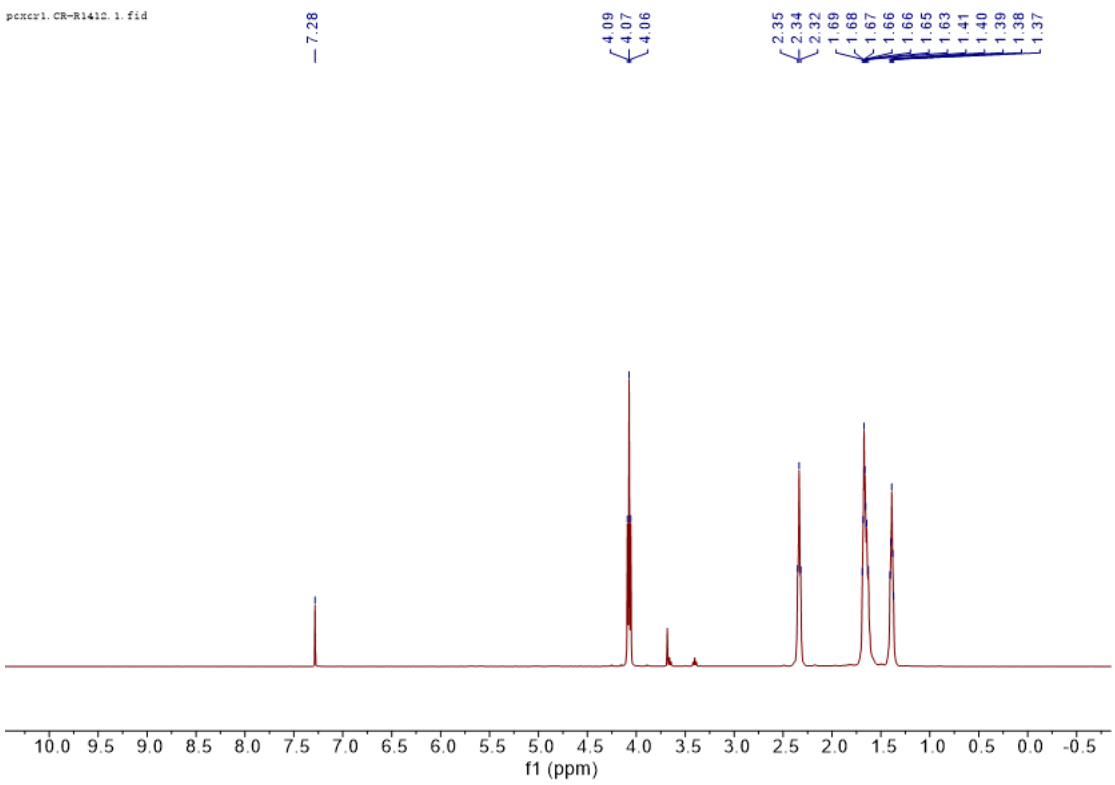
3.48
3.44
2.53
2.51
2.49
1.58
1.34
1.28
1.28
0.90
0.88
0.86
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

6-methoxyhexyl 6-oxoheptanoate (25)



1,6-hexanediol (2.95 g, 25 mmol), dimethyl adipate (4.35 g, 25 mmol) and aluminium trichloromethanesulfonate (0.118 g, 0.25 mmol) were weighed into a two-necked glass vessel equipped with a stirrer. The reaction was placed on a hot plate preheated to 100 °C with stirring, vacuum was gradually applied to 20 mbar for 1 hour, a vacuum of 1 mbar was then maintained for 21 hours with the temperature heat to 120 °C. After 21 hours, stirring was continued for 8 hours under a vacuum of approximately 1 mbar. The reaction product was dissolved in CH_2Cl_2 and precipitated into methanol. The reaction mixture was frozen for 72 hours. This mixture was filtered to give 6-methoxyhexyl 6-oxoheptanoate **25** as a white powder.

δ_H (400 MHz, $CDCl_3$) 4.07 (t, *J* 6.7, H-3), 2.48 – 2.22 (m, H-1), 1.80 – 1.56 (m, H-2, 4), 1.48 – 1.26 (m, H-5).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1.66
1.66
1.65
1.63
1.41
1.40
1.39
1.38
1.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

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