Monomers and Polymers via Catalytic Oxyfunctionalization of Renewable Resources

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Meinen Eltern

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Abstract

In recent decades, the development of sustainable chemical processes as well as the synthesis of monomers and polymers from renewable resources has become of great interest in polymer chemistry, mainly due to the depletion of crude oil and a generally increasing environmental awareness. Within this context, renewable raw materials, such as fatty acids and terpenes, have been proven to be remarkable platform chemicals to address the aforementioned goals. The structural diversity of fatty acids and terpenes allows, in some cases their direct polymerization, demonstrating a major advantage regarding sustainable production processes. However, most of these renewable building blocks require further chemical modification to obtain monomers, which are needed to access the thereof derived polymers. Among all possible functionalization processes, double bond transformations have become of particular interest in organic chemistry. The development of highly selective catalytic oxidation reactions applying transition metals accompanied by environmentally-friendly oxidants, such as molecular oxygen or hydrogen peroxide are of particular importance.

The aim of this thesis was to develop and investigate novel catalytic oxidation processes of renewable resources in order to synthesize monomers and the thereof derived polymers. For this purpose, various unsaturated fatty acids were employed in a co-catalyst-free Wacker oxidation process, which provide access to keto-fatty acids. The follow-up chemistry of these up to know hardly described materials is quite promising, due to the versatile possibilities to obtain platform chemicals, dimer fatty acids and AB-monomers thereof, which enable the synthesis of the resulted polyesters and polyamides.

Terpenes are part of another class of renewable materials, which is of great interest in this context. Limonene in particular, was already successfully investigated in the synthesis of regioselective acetoxylated products.[1] The follow-up chemistry of the obtained product, selectively acetoxylated at the terminal double bond, allowed access to an aldehyde derivative. This substrate was further used as starting material in multi-component reactions (e.g. Passerini reaction or Ugi reaction). Thus, in the presence of various

isocyanides and acrylic acid several acrylate monomers were obtained, and successful polymerized into the corresponding polyacrylates.

Zusammenfassung

Die Weiterentwicklung chemischer Prozesse im Hinblick auf die Berücksichtigung nachhaltiger Aspekte, insbesondere die Synthese von Monomeren und Polymeren aus nachwachsenden Rohstoffen, haben in der Polymerchemie in den vergangenen Jahrzehnten stark an Bedeutung gewonnen. Die Hauptgründe für diesen Wandel liegen sowohl in der Verknappung fossiler Rohstoffe, als auch in einem stetig wachsenden Umweltbewusstsein der Bevölkerung sowie von Industrieunternehmen. In diesem Prozess, welcher die Nutzung nachwachsender Rohstoffe in den Vordergrund stellt, haben sich Fettsäuren und Terpene als besonders geeignet herausgestellt. Auf Grund der Strukturvielfalt der genannten Substanzklassen können ausgewählte Derivate zur direkten Synthese von Polymeren verwendet werden. Dies trägt im besonderen Maße zur Erhöhung der Nachhaltigkeit im Produktionsprozess bei. Die meisten Fettsäure- und Terpenderivate müssen jedoch, um geeignete Monomere für die Polymersynthese zu erhalten, vorab chemisch modifiziert werden. Die Funktionalisierung von Fettsäuren und Terpenen ist auf unterschiedliche Weise möglich, jedoch haben sich Modifizierungen der Doppelbindung als besonders vielseitig erwiesen und dadurch großes Forschungsinteresse in der organischen Chemie hervorgerufen. Die Entwicklung von hochselektiven übergangsmetallkatalysierten Oxidationsreaktionen, unter Verwendung von molekularem Sauerstoff oder Wasserstoffperoxid als umweltfreundliche Oxidantien, hat hierbei eine besondere Bedeutung erlangt.

Das Ziel dieser Dissertation ist die Entwicklung und Untersuchung von neuen Ansätzen zur katalytischen Oxidation nachwachsender Rohstoffe, welche zur Synthese von Monomeren und davon abgeleiteten Polymeren herangezogen werden. Hierzu wurden zunächst verschiedene ungesättigte Fettsäurederivate in einem cokatalysatorfreien Wackeroxidationsprozess untersucht, welche den Zugang zu keto-Fettsäurederivaten ermöglichten. Diese bisher recht unerforschte Substanzklasse bietet vielseitige Möglichkeiten zur chemischen Modifizierung, wodurch die Synthese von Basischemikalien, Dimerfettsäuren sowie AB-Monomeren ermöglicht wird. Einige der vorhergenannten Substanzen konnten als Monomere zur Synthese von entsprechenden Polyestern und Polyamiden herangezogen werden.

Terpene sind in diesem Zusammenhang eine weitere Klasse nachwachsender Rohstoffe, welche interessante Bausteine zur katalytischen Funktionalisierung darstellen. Insbesondere Limonen wurde bereits erfolgreich zur Synthese regioselektiver acetoxylierter Derivate verwendet. Das Produkt, welches durch selektive Acetoxylierung der terminalen Doppelbindung aus Limonen erhalten werden kann, ermöglicht die Synthese eines Aldehyd-Derivates. Mittels Multikomponentenreaktionen (z.B. Passerini-Reaktion, Ugi-Reaktion) kann dieser Aldehyd, in Gegenwart von Isocyaniden und Acrylsäure, in Acrylat-Monomere umgesetzt werden, welche zur Synthese der entsprechenden Polyacrylate herangezogen wurden.

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1 Introduction

The beginning of the industrial revolution in the 19th century, constitutes one of the most important turning points in human being's history. The introduction of steam power, gained from coal, enabled the transition of manufacturing processes from handmade production methods to machine and chemical production, and thus led to the rise of many different fabrication technologies.[2] Now, at the beginning of the 21th century, the success of this ongoing process has driven science and technology extremely forward, and enabled a world population of almost 7.4 billion people.[3] However, the enormous increase in population already led to some serious problems as for instance evidenced in shortages of energy and food supply.[4] The massive consumption of fossil resources led to a heavy dependence on coal, gas and fossil oil for the production of diverse daily life commodities (e.g. electricity, fuels and textiles). Moreover, the fast growing population and enhanced living standards lead to drastic increase of environmental pollution. Thus, these problems urgently require solutions. The exploration of fossil oil as well as the subsequent transportation all over the world constitutes an elementary conflict due to the continuous increase of global energy consumption and depletion of crude oil.[5] Additionally, the constant rise in demand for crude oil resulted in significant price increases in the last decades and will lead to supply bottlenecks in the near furture.[6] Due to these aspects, a reasonable and sustainable use of fossil resources should be a major goal of the (academic) society in order to keep them available for the next generations. The term for "sustainable development", which was introduced by the "Brundtland commission", has defined sustainability as a "development that meets the needs of the present without compromising the ability of future generations to meet their own needs".[7] Furthermore, the UN World Summit on Sustainable Development, held in Johannesburg in 2002, declared the sustainable use of biomass as key factor to keep fossil resources available and to counter the increasing production of greenhouse gases like CO_2.[8] In this context, it is highly important to mention that the utilization of biomass for industrial applications should not compete with the food production sector.[9] The development of novel processes and technologies in the agricultural and forestry sectors have shown that biomass can be produced in sufficient quantities. For instance, lignin, which is obtained as by-product in processes of the pulp and paper industry, is mainly used to generate energy, but can also

be further chemically modified to produce renewable polymeric materials for various applications.[10,11] Another example is limonene, a terpene derivative, which can be obtained as waste product from citrus peel oil (90%).[12] Remarkably, with an annual production of 88 × 10^6 tons per year, citrus is the most abundant crop.[13]

However, the tremendous development in science and technology using fossil oil led to novel manufacturing processes, which allowed access to a wide variety of materials. Especially, synthetic polymeric materials have changed our daily life in many fields, due to their various application possibilities.[14] At the beginning of the 20th century, the invention of Bakelit® has opened a new chapter for unprecedented synthetic resins, which revolutionized the industrial production of phones, radios or electric transformers.[15] The novel material was able to substitute the commonly used shellac, a secrete resin produced by the female lac bug.[16] It was the starting point for many other synthetic polymers (e.g. poly(styrene) (PS), poly(ethylene) (PE), nylon, poly(vinylchloride) (PVC)), which have become extremely important materials for the production of our daily life commodities (e.g. automotive, packaging, electronic devices, medicine). The worldwide production of 322 million tons of plastics in 2015 clearly demonstrate this fact.[17] However, the synthesis of all these functional polymeric materials, resulted in an increased fossil oil consumption that goes along with a drastic increase of environmental pollution. Especially, the distribution of plastic and the thereof derived micro plastic in the landscape as well as in the seas, destroys habitats of many living beings. Due to these aspects, the efficient recycling of plastic waste and replacing fossil oil by renewable resources, will be still one of mankind’s greatest challenges to create a sustainable future.

1.1 Green Chemistry

Green Chemistry describes the design of chemical products and processes regarding the hazardous impact on environment by the used substances.[18] Moreover, the concept of Green Chemistry addresses various global issues such as energy production, food production, water supply or climate change, and how those are effected by toxic substances. Thus, the major goal of green chemistry is the introduction of sustainability into human mind, in order to develop a reasonable use with available resources and the thereof derived products. Moreover, the term sustainability also comprises ecologic and social aspects, such as maintenance of growth, stability of the economy or human rights.

The "**12 principles of Green Chemistry**" that were introduced by Anastas and co-workers can be considered as a general guideline for the design of sustainable chemical processes.[19]

- **Prevention**
  It is better to prevent waste than to treat or clean up waste after it has been created.

- **Atom Economy**
  Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

- **Less Hazardous Chemical Syntheses**
  Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

- **Designing Safer Chemicals**
  Chemical products should be designed to affect their desired function while minimizing their toxicity.

- **Safer Solvents and Auxiliaries**
  The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary whenever possible and innocuous when used.

- **Design for Energy Efficiency**
  Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

- **Use of Renewable Feedstocks**
  A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

- **Reduce Derivatives**
  Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

- **Catalysis**
  Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

- **Design for Degradation**
  Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

- **Real-time analysis for Pollution Prevention**

  Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

- **Inherently Safer Chemistry for Accident Prevention**
  Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

The concept of Green Chemistry mainly highlights the design of chemical products and processes to reduce or eliminate hazardous substances in order to minimize their impact on living beings as well as on the environment. The general goal of designing chemical reactions is to maximize the efficiency, thus under optimized reaction conditions the desired product is formed in excellent yield and purity without any by-product. Especially, if reactions are performed on industrial scale, ecologic aspects often compete with economic aspects, which is in contrast to the principles of Green Chemistry. Moreover, the first rule of Green Chemistry, stating that it is always better to prevent waste than to clean-up waste afterwards, has to be a key aim for chemical synthesis processes on industrial scale. Therefore, the concept of the E-factor (environmental impact factor), introduced by R. A. Sheldon in 1996, is often used. The E-factor is defined by the ratio of the mass of total waste per mass of product.[20] It is an efficient and easy to apply tool to evaluate the environmental impact of chemical reactions (Table 1).

Table 1: E-factors of selected chemical production processes.

Product	**Production [tons/year]**	**E-factor [kg waste/kg product]**
Oil refining	$10^6 – 10^8$	< 0.1
Bulk chemicals	$10^4 – 10^6$	< 1 – 5
Fine chemicals	$10^2 – 10^4$	5 – 50
Pharmaceutical products	$10 – 10^3$	25 – 100

1.2 The utilization of renewable resources

Despite the development of novel processes and technologies as well as the discovery of new oil reserves, fossil resources will be depleted sooner or later. However, currently crude oil is still the most utilized resource of the German chemical industry, and thus of great importance for the synthesis of monomers and polymers (Figure 1).[21] The illustration clearly demonstrate the massive dependence on fossil resources, using 17.3 million tons of fossil oil, gas and coal every year, which represents 87% of the total consumption of raw materials (19.9 million tons) in Germany. On the contrary, only 13% (2.6 million tons) are derived from biogeneric resources. Hereby, the term biogeneric resources comprises all renewable resources of agricultural and forestry origin, which are not used for the production of food.

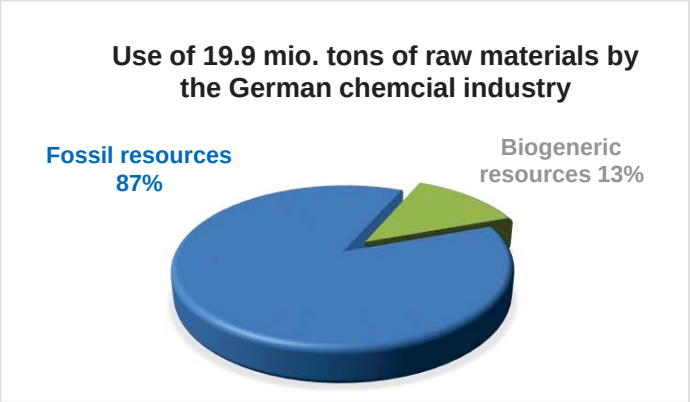
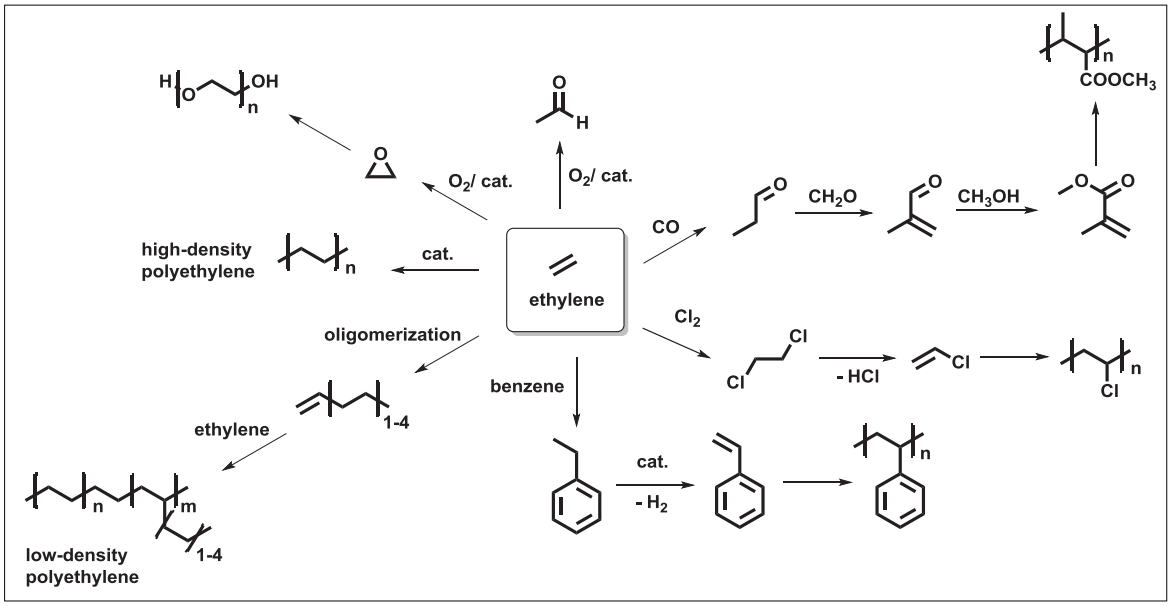


Figure 1: Use of raw materials by the German chemical industry.[21]

The synthesis of diverse bulk chemicals is usually accomplished by cracking processes of crude oil. In the presence of catalysts at high temperature, complex organic molecules are broken down into smaller hydrocarbons such as ethylene, acetylene, 1,4 butadiene or aromatics. The obtained platform chemicals can be further chemically modified resulting in various monomer building blocks for the synthesis of polymeric materials. For instance, the follow-up chemistry of ethylene towards various monomers and the thereof derived polymers is depicted in Scheme 1.[22]



Scheme 1: Synthesis pathways of monomers and polymers derived from ethylene.[22]

The obtained polymers such as PE or PVC are industrially produced of several million tons per year. The major goal of science and technology is to overcome the massive dependence on fossil oil by the development of sustainable processes, best by using monomers and polymers from renewable resources. Therefore, renewable raw materials, such as cellulose, starch, plant oils, sugars and terpenes exhibit potential candidates, due to their abundance and remarkable variety. Interestingly, most of the aforementioned renewable raw materials have already been used for centuries in order to synthesize clothes, fuels or dyes.[23] Moreover, in contrast to fossil resources, renewable feedstocks can be obtained every year (e.g. fats and oils from oilseed crops) or at least within few years (e.g. cellulose, lignin from trees). The European industry used more than nine million tons of renewable materials (without wood) in 2011, demonstrating their remarkable potential as sustainable alternatives. Hereby, various industries processed 2.65 million tons of renewable materials, whereas the European chemical industry is making use of 6.4 million tons: divided into starch (35%), fats and oils (31%), natural cellulose fibers (16%), sugar (14%), and others (4%) (Figure 2).[24]

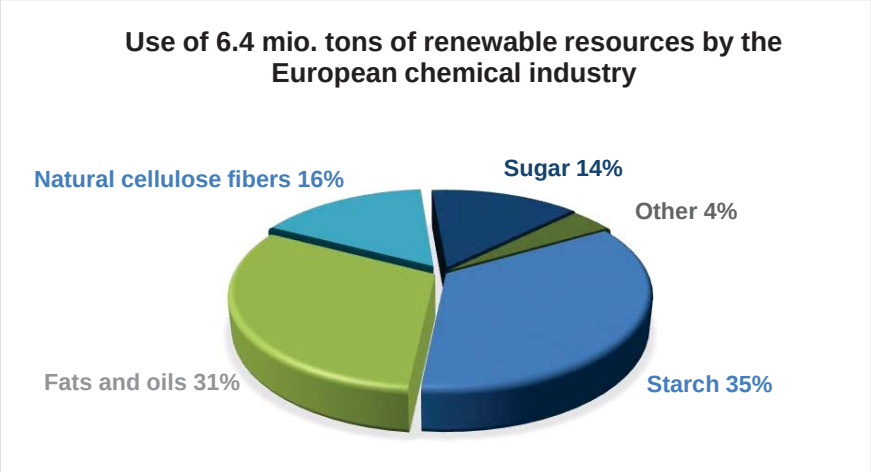


Figure 2: Utilization of renewable raw materials by the European chemical industry (2011).[24]

Remarkably, the German chemical industry processed 2.6 million tons of renewable raw materials in 2013, which exhibit 40% of the total consumption of renewable resources used by the European chemical industry (Figure 3). Hereby, fats and oils clearly dominate with 1.22 million tons (46%).[21] However, the import of currently 90% of fossil oil and gas from foreign countries demonstrates the precarious situation in Germany.[25] Thus, the major challenge will be to overcome the leading position of crude oil, which is based on the well-established plants and processes for the production of countless chemicals.

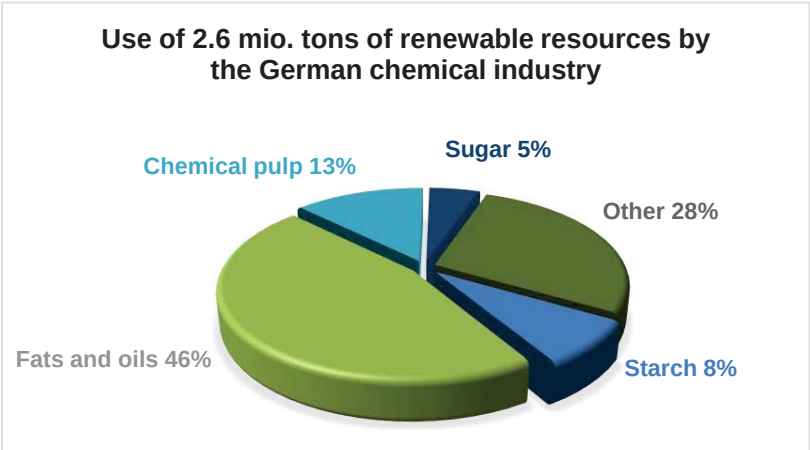
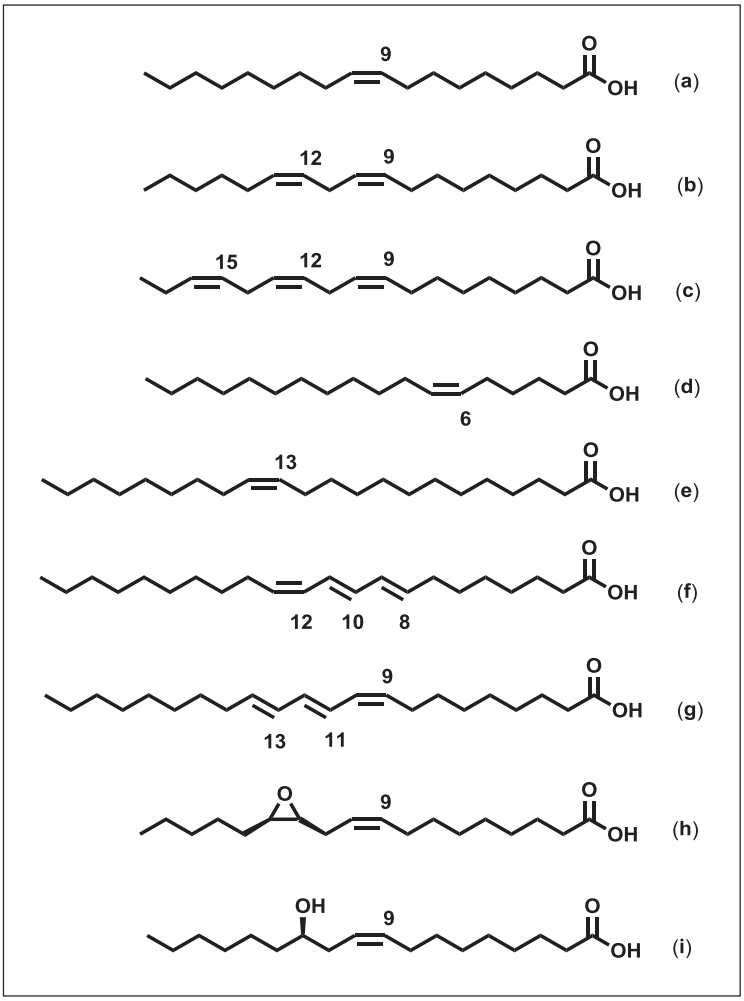


Figure 3: Utilization of renewable raw materials by the German chemical industry (2013).[21]

1.2.1 Plant oils

The global production of plant oils significantly increased from 90 million tons (2000) to almost 186 million tons (2016).[26] The rising tendency demonstrates that plant oils are highly desirable, both as renewable materials for the Chemical industry as well as for food and feed. Fatty acids, which can be obtained from triglycerides, are constituted by their structure diversity of saturated and unsaturated aliphatic chains as well as their varying in chain lengths. In contrast to other renewables, such as cellulose or sugars, fatty acids are structurally closer to fossil oil products, and thus of great interest.



Scheme 2: Fatty acids compounds with different functional groups: (a) oleic acid, (b) linoleic acid, (c) linolenic acid, (d) petroselinic acid, (e) erucic acid, (f) calendic acid, (g) *α*-eleostearic acid, (h) vernolic acid, (i) ricinoleic acid.[27]

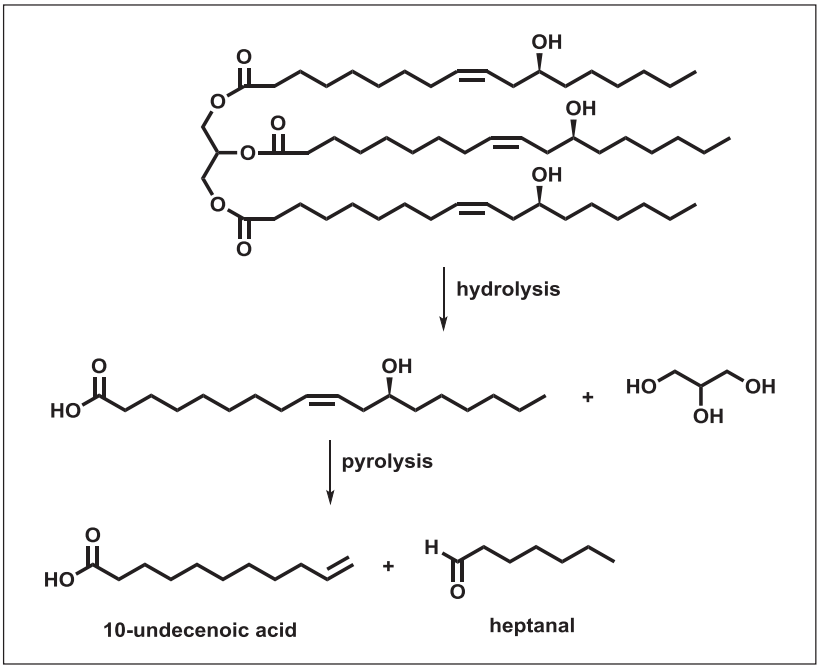
Vegetable fats and oils are mainly composed of palmitic acid (16:0), stearic acid (18:0), oleic acid (18:1), linoleic acid (18:2) and linolenic acid (18:3). However, the amount of the aforementioned fatty acids considerably varies with the corresponding crop, which significantly influences their physical properties (Table 2).[28] Moreover, this class of renewables include derivatives with versatile functional groups, such as multiple double bonds, epoxy- or hydroxy-groups, which allow their utilization without further chemical modification (Scheme 2).[27]

Table 2: Fatty acid composition of plant fats and oils.[28]

Fat or oil	**Fatty acid composition [%]**				
	16:0	**18:0**	**18:1**	**18:2**	**18:3**
Corn	10.9	2.0	25.4	59.6	1.2
Cotton seed	21.6	2.6	18.6	54.4	0.7
Linseed	5.5	3.5	19.1	15.3	56.6
Olive	13.7	2.5	71.1	10.0	0.6
Palm	44.4	4.1	39.3	10.0	0.4
Soybean	11.0	4.0	23.4	53.2	7.8
Sunflower	6.1	3.9	42.6	46.4	1.0
High oleic	6.4	3.1	82.6	2.3	3.7

Generally, fatty acids are industrially produced through hydrolysis of triglycerides. Hereby, glycerol is formed as by-product, which exhibits an interesting building block for further chemical modification processes.[29] Another approach is based on the acid-catalyzed transesterification with methanol resulting in fatty acid methyl esters (FAMEs), which are important substances for the production of Biodiesel as green alternative to fossil fuels.[30] Moreover, the synthesis of lubricants and waxes can be accomplished *via* esterification of fatty acids with alcohols.[31]

Castor oil, a non-edible oil with a high content of ricinoleic acid (up to 90%) exhibits one of the most interesting renewable resources for the oleochemical industry, due to the hydroxyl functional groups, which are of great importance for the synthesis of polyurethanes (PU).[32] Interestingly, castor oil was already cultivated by the ancient Egyptians more than 6000 years ago. Nowadays, castor oil is available on commercial scale and its production is accomplished by presses and/or extraction processes of the seeds, which can be usually harvested from September till November in temperate zones of China, India or Brazil.[33,34] Hydrolysis of castor oil leads to ricinoleic acid as main product as well as glycerol and low amounts of stearic acid and palmitic acid as by-products. Moreover, subsequent pyrolysis of ricinoleic acid at high temperature enables the selective formation of 10-undecenoic acid and heptanal as by-product (Scheme 3). Remarkably, 10-undecenoic acid containing a terminal double, exhibits a valuable renewable building block, which allows a variety of chemical modification processes. For instance, Arkema (French company) developed a synthesis route for polyamide-11 (Rilsan®) based on 10-undecenoic acid.[35]



Scheme 3: Hydrolysis of castor oil and pyrolysis of ricinoleic acid to 10-undecenoic acid.

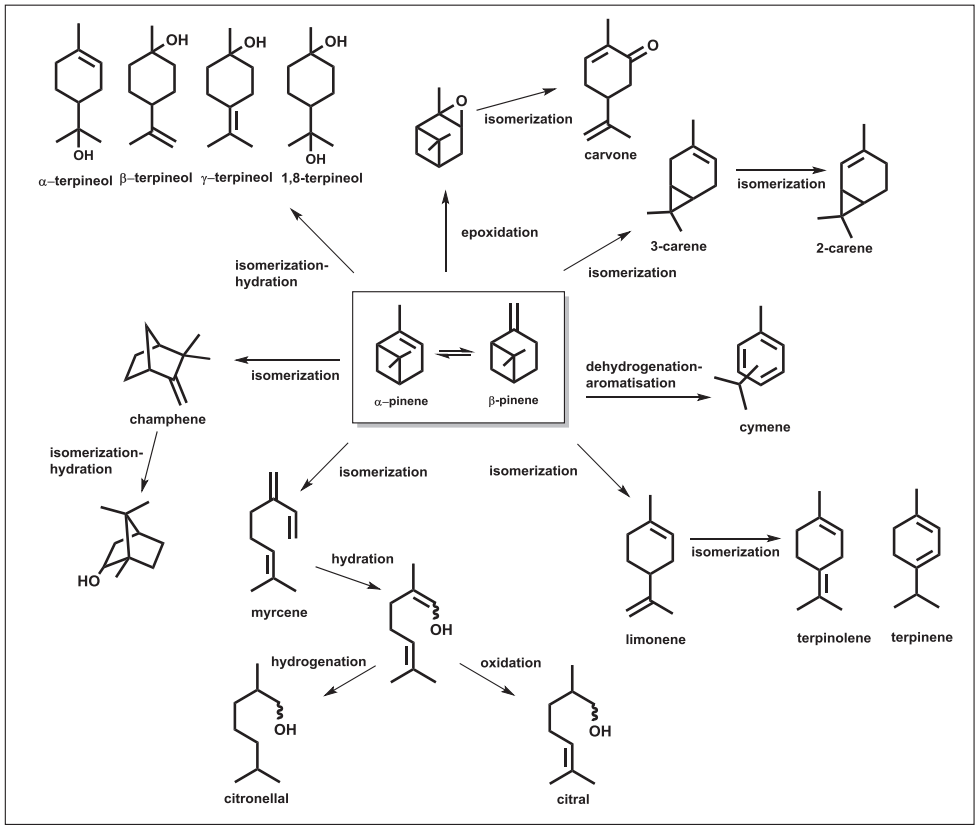
1.2.2 Terpenes

Among the renewable raw materials, terpenes demonstrate a valuable biomass resource, which are accessible from various essentials oils and resins. Additionally, terpenes are found as secondary metabolites synthesized by plants, fungi, insects and microorganisms. Isoprene (2-methyl-1,3 butadiene) constitute the core unit of terpenes and is biosynthetically connected “head-to-tail” resulting in linear and cyclic structures. Terpenes are classified by the repeating unit of isoprene (n): divided in monoterpene (n = 2), sesquiterpene (n = 3), diterpene (n = 4), sesterterpene (n = 5) and so on.[36,37] Thus, these renewables constitute one of the largest class of naturally-occurring compounds with a remarkable structural diversity, containing aliphatic, cycloaliphatic and aromatic backbones.[36,38]

Table 3: Essential oils and the thereof derived main terpenes and terpenoids.[37]

Essential oil	**Botanical name**	**Main constituents**
Turpentine	*Pinus* spp.	Terpenes (pinenes, champhene)
Coriander	*Coriandrum sativum*	Linalool (65 %/ 80%)
Otto of rose	*Rosa* spp.	Geraniol, citronellol (> 70 %)
Geranium	*Pelargonium* spp.	Geraniol, citronellol
Lemon	*Cirtus limon*	Limonene (90 %)
Lemon grass	*Cymbopogen* spp.	Citral, citronellal (75/ 85 %)
Citron scented	*Eucalyptus citridora*	Citronellal (70 %)
Spearmint	*Mentha spicata and Mentha cardiac*	Carvone (55/ 70 %)
Peppermint	*Mentha piperita*	Menthol (45 %)
Continental lavender	*Lavandula officinalis*	Linallol, linalyl acetate (much), ethyl penthyl ketone
Cinnamon bark	*Cinnamomum verum* Presl.	Cinnamic aldehyde (60/ 75 %)
Cassia	*Cinnamomum cassia*	Cinnamic aldehyde (80 %)
Cinnamon leaf Presl.	*Cinnamomum verum*	Eugenol (up to 80 %)

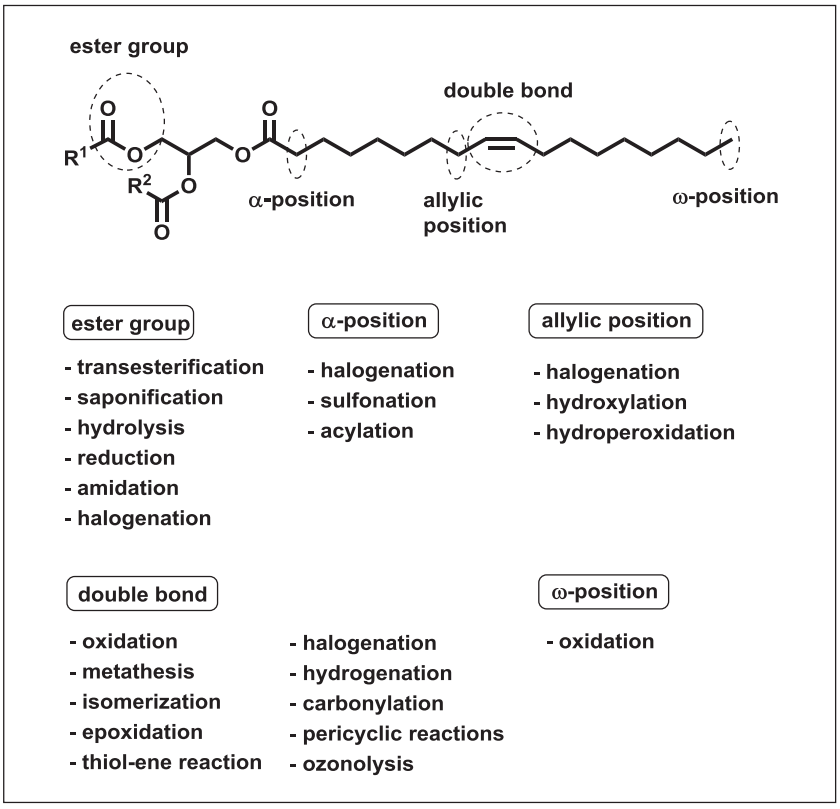
Furthermore, terpenes bearing functional groups, such as hydroxy-, aldehyde- or ketone-groups, are classified as terpenoids, which are also well known as traditional herbal remedies. Some of the most commonly used terpenes and terpenoids derived from essential oils are listed in Table 3.[38] Moreover, various terpene derivatives often have an intense odor, which serves as protecting mechanism against diverse enemies. On the other hand, the odor can also have an attracting effect, which is important for the reproduction of various insects and plants. Due to these aspects, terpenes exhibit an essential renewable resource for the production of diverse products, such as flavors, fragrances, nutrients, pheromones or as pharmacological substrates in treatment of different diseases.[39-41] One of the most important terpene resources are turpentine resins available from coniferous trees and terebinth. The world production of turpentine is estimated to be 35×10^4 tons per year,[36] which allow access to the unsaturated monoterpenes *α*-pinene (45 – 97%) or *β*-pinene (0.5 – 28%). The follow-up chemistry (e.g. rearrangements, oxidation) of these monoterpenes is illustrated in Scheme 4. Another derivative of great interest is limonene, which can be obtained as waste product from citrus peel oil (90%). The annual world production of citrus (88×10^6 tons) demonstrates its remarkable potential.[38]



Scheme 4: Derivatization products of pinene.

2 Theoretical background

The development of sustainable processes as well as the synthesis of monomers and polymers from renewable resources is an important and currently intensively investigated research topic.[42-47] Fatty acid derivatives bear different functional groups, such as ester groups, double bonds, as well as catalytically addressable positions, such as the *α*-position, the allylic position or the *ω*-position. This allows for diverse functionalization possibilities (Scheme 5). Among all the available modification positions, double bond transformations are of particular interest in organic chemistry. One possible modification exhibit oxidation processes, which will be discussed in more detail in the following chapters.



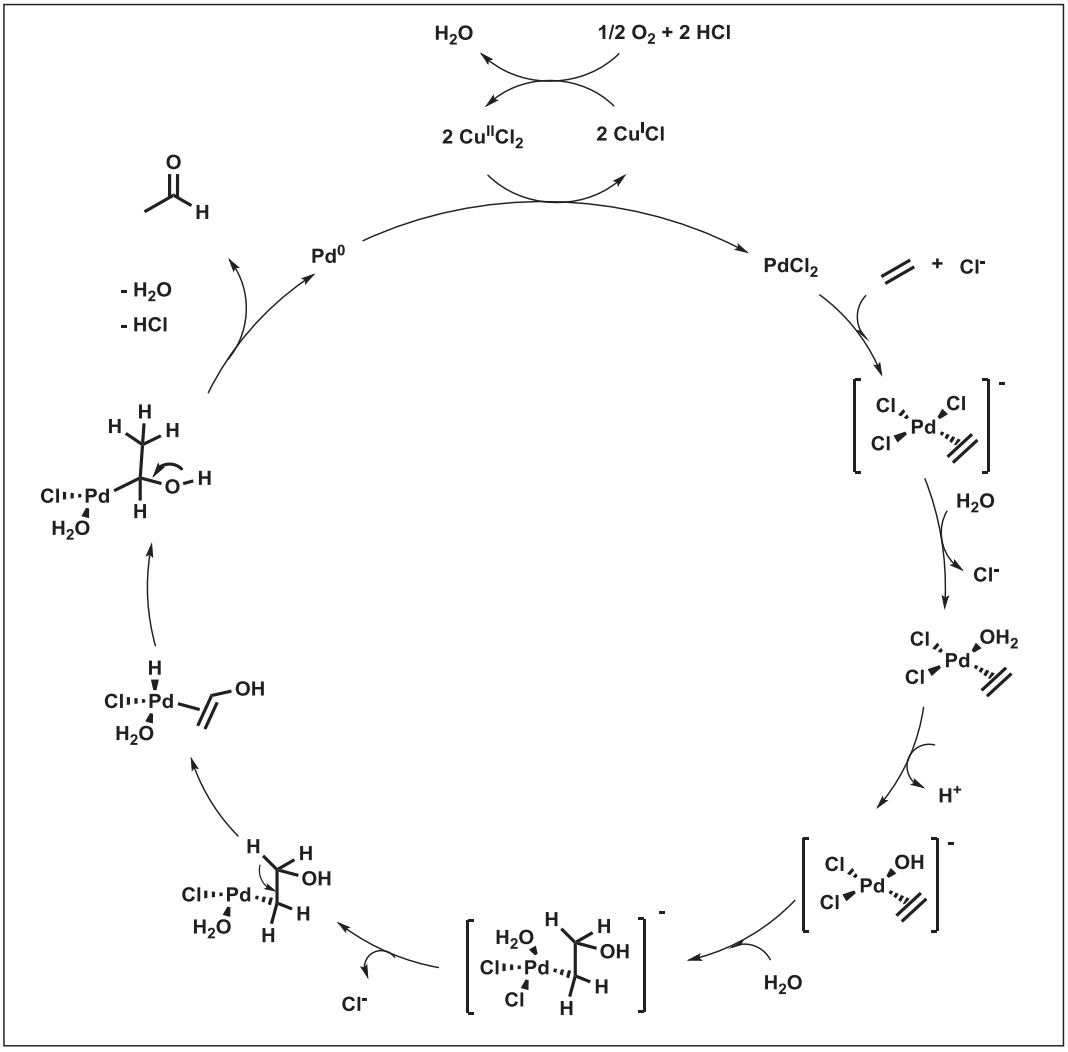
Scheme 5: Possible modification processes of fatty acid derivatives.

2.1 Catalytic oxidation processes

Oxidation reactions play an essential role in nature and thus in many parts of human daily life. With respect to chemistry, it is a key reaction for valuable transformations in organic synthesis. Hence, the development of highly selective catalytic synthesis routes applying transition metals accompanied by environmentally-friendly oxidants, such as molecular oxygen or hydrogen peroxide, constituted one of the major goals in the field of organic synthesis. Unfortunately, the use of these oxidants in catalytic processes to directly oxidize organic substances is often kinetically hindered. One approach to solve this problem, can be accomplished by a coupled catalytic system, e.g. using electron-transfer mediators (ETM).[38,48]

2.1.1 Wacker oxidation process

The Wacker process or Hoechst-Wacker process has become one of the most important and well-known chemical industry processes after the Second World War, and was developed in 1956 at Wacker chemistry.[49,50] The dependence on acetylene, before and during the Second World War, represented a critical era in the chemical industry, due to the high production cost and the limited number of thereof obtained products. The major goal was to develop a synthesis route using a much cheaper and less energy intensive raw material. Thus, a new procedure was developed for the catalytic oxidation of ethylene in order to obtain acetaldehyde. This was achieved by a palladium(II) chloride/copper(II) chloride catalyst system in the presence of molecular oxygen and a specific amount of water. The major advantage of using ethylene as starting material is shown in the product diversity: besides acetaldehyde, vinyl chloride or vinyl acetate can also be obtained by this catalytic oxidation procedure.[51,52] The reaction mechanism of the process was studied over some decades and first results about the initially stoichiometric reaction were reported by Phillips.[53,54] However, further investigations were required for the elucidation of the general mechanism, which was reported for the first time by Smidt *et. al.* (Scheme 6).[38,55]

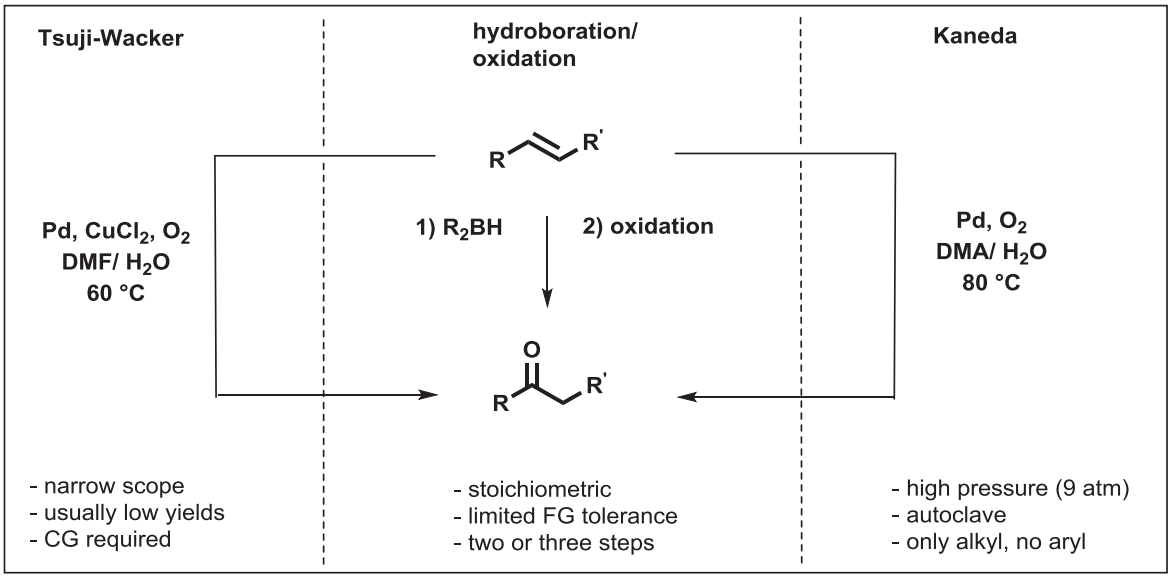


Scheme 6: General mechanism of the Wacker oxidation process proposed by Smidt and co-workers.[55]

The key step of the Wacker oxidation process is the redox couple of a palladium-copper system that promotes the conversion of ethylene with molecular oxygen to acetaldehyde. Furthermore, all catalytic species are regenerated in this process and only ethylene and oxygen are consumed. The employed copper(II) chloride reacts with molecular oxygen and enabled the reoxidation of the palladium(0) species, which is formed in the last reaction step. Additionally, this step constitutes a crucial role in the entire catalytic process in order to prevent the formation of palladium black. Subsequently, the formed copper(I) chloride is reoxidized by molecular oxygen in water to copper(II) chloride which closes the catalytic cycle.[38,49]

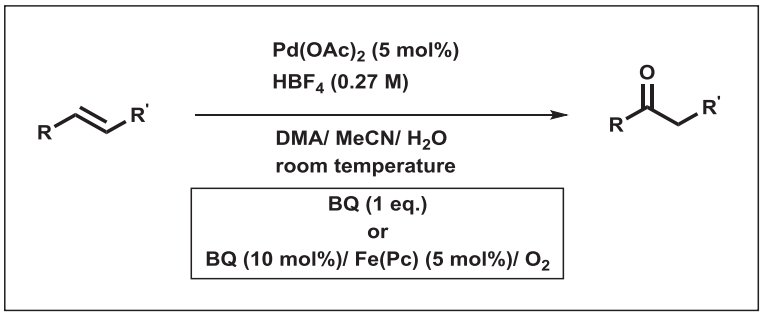
2.1.2 Wacker-type oxidation processes

Since the development of the Wacker oxidation process in 1956 many scientific groups investigated this oxidation procedure, continuously studying the different mechanistic steps and applying new routes to various classes of substances.[56,57] A well-established synthetic route for the transformation of terminal olefins into the corresponding methyl ketone is known as the Tsuji - Wacker reaction (Scheme 7).[58] In this catalytic process a redox couple of a palladium-copper system is used in the presence of water, oxygen and additional dimethylformamide (DMF) as co-solvent. However, a major drawback of this procedure is the limited scope of substrates and usually low yields. Applying this catalytic process to internal olefins is not possible, since they are highly unreactive in this procedure and only provide very low yields. Because of this, coordinating groups (CG) are required to promote the oxidation. There are also numerous synthetic procedures for the functionalization of internal alkenes, for example the cabonyl olefination[59] or olefin metathesis.[60] Nevertheless, an efficient catalytic system to synthesize ketones from internal olefins is still a challenging goal of organic synthesis. The commonly used method by a hydroboration/oxidation approach is often employed in target-oriented synthesis (Scheme 7).[61] However, this procedure also includes some drawbacks for instance the low-functional group (FG) compatibility of highly reactive borane reagents. Additionally, stoichiometric amounts and multiple steps are necessary for this process. In recent years, Kaneda and co-workers introduced a new synthesis route using an oxygen-coupled, copper free Wacker oxidation to functionalize internal olefins.[57] In comparison to the aforementioned synthesis routes one great advantage of this procedure is the increased substrate scope. Furthermore, they found out that a combination of a palladium(II) chloride system and dimethylacetamide (DMA) enables a direct oxygen-coupled Wacker-type oxidation of terminal olefins into the corresponding methyl ketones (Scheme 7).[62] Additionally, DMA was shown to be a reliable and highly efficient solvent promoting the reoxidation of the palladium(0) species. From a practical point of view, there is a limitation with regard to possible applications of this method. For instance, it is usually used only on laboratory-scale, and due to the high used oxygen pressure (up to 9 atm) a special equipment (e.g. an autoclave) is required (Scheme 7).[63]



Scheme 7: Oxidation procedures to synthesize ketones from alkenes, abbreviations: coordinating group (CG), functional group (FG).[64]

In the beginning of 2013, Grubbs and co-workers reported about a straightforward catalytic procedure that addresses some of the previous problems. The major advantage of this palladium catalyzed oxidation process is its highly improved functional-group tolerance (alcohol, acid, aldehyde, ester, phenol, amide, alkyl, aryl, cyclic). Furthermore, within this process at ambient conditions only simple reagents are required, such as palladium(II) acetate, *p*-benzoquinone (*p*-BQ) as oxidant, a solvent mixture of DMA/acetonitrile (MeCN)/water, and a diluted acid (Scheme 8).[64]

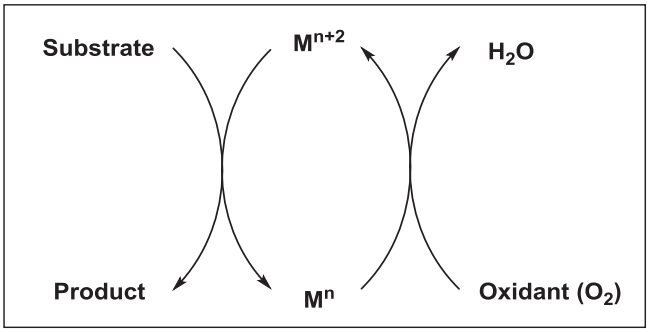


Scheme 8: Wacker-type oxidation procedure by Grubbs and co-workers.[64]

2.1.3 Oxidation by tandem catalytic systems

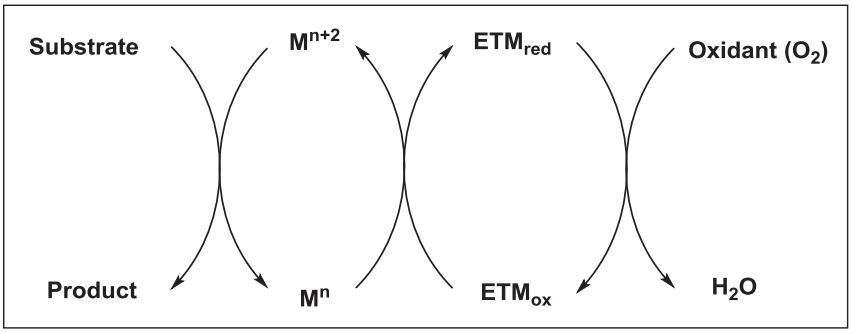
The development of highly efficient oxidation processes constitutes an important goal in organic synthesis. This aim is often accomplished by the use of transition metals, which are substrate-selective.[65] Furthermore, with regard to economic and ecological aspects there is a strong interest in oxidation technologies, which are going along with sustainable and environmentally-friendly reaction procedures. Accordingly, the use of environmentally-friendly and readily available oxidants, such as molecular oxygen and hydrogen peroxide are highly interesting in order to fulfill these requirements.[66] Additionally, major advantages of these oxidants are represented on the one hand by their high efficiency per weight of oxidant and on the other hand especially in case of molecular oxygen its readily availability from air.[67] In comparison to molecular oxygen, hydrogen peroxide has the advantage to be a liquid, thus it is miscible with water and preferably used for industrial applications.[68] However, hydrogen peroxide has one essential drawback, namely its high reactivity towards metals and causes radical-induced decompositions. A major challenge for the direct oxidation of organic substances is constituted by the nature of molecular oxygen, which has a triplet ground state. Thus, the direct oxidation of organic substances is energetically disfavored.[69] Due to this fact, usually a high energy barrier for the electron transfer has to be overcome in an oxidation process. However, nature is giving some very interesting examples of highly efficient mechanisms and controlled aerobic oxidation procedures, which proceed under very mild conditions.[70,71] These biological processes are often complicated, due to several enzyme complexes and their corresponding redox cofactors. An interesting natural oxidation process is represented by the redox couple $NAD^+/NADH+H^+$ in the presence of a dehydrogenase enzyme that is able to be a substrate-selective catalyst. Furthermore, cyctochrome C, which is an essential small protein that consist of an iron porphyrin[72] can uptake electrons to form cytochrome C oxidase followed by reduction of molecular oxygen into water.[73] Using these conditions for a catalytic oxidation process requires a transition metal (M^{n+2}/M^n) that is able to be a substrate-selective catalyst. Whereby the applied substrate is oxidized into the desired product and the reduced catalyst species is then reoxidized by a stiochiometric oxidant, e.g. molecular oxygen or hydrogen peroxide (Scheme 9).[48] Thus, this catalytic process involves elementary steps that go along with

the principles of green chemistry, especially with regard to the efficient and environmentally benign conditions.[38]



Scheme 9: Catalytic oxidation process using a substrate-selective redox catalyst.[48]

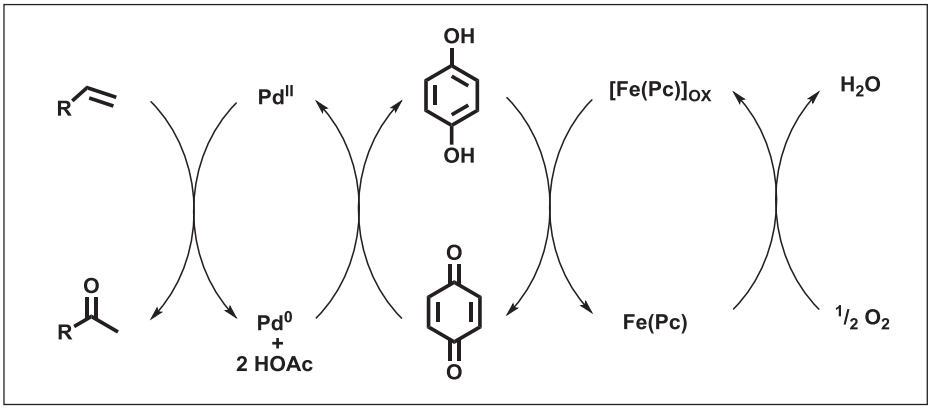
Beyond, there are various catalytic procedures using molecular oxygen or hydrogen peroxide for a direct reoxizidation of the corresponding transition metal.[74-79] These catalytic systems promote efficient oxidations, but in some cases they are limited by the rate of electron transfer between the metal and the oxidant since the transfer-process is much slower than the decomposition of the reduced metal. For instance, in case of the palladium-catalyzed aerobic oxidation, two processes are competing with each other. On the one hand the precipitation of palladium black from the soluble species (Pd-H, Pd^0) and on the other hand the reoxidation by oxygen.[74] In order to overcome this problem two strategies can be employed either the palladium(0) species can be stabilized by an oxidant resistant ligand or an oxidation system that introduces a further ETM similar to the approach nature applies.[80] The ETM takes a key role in the catalytic system, by transferring the electron from M^n to the oxidant by a low-energy pathway. Simultaneously, it prevents the system from the aforementioned kinetic hindrance (Scheme 10).[38,48]



Scheme 10: Mechanism of the catalytic oxidation process using an ETM.[48]

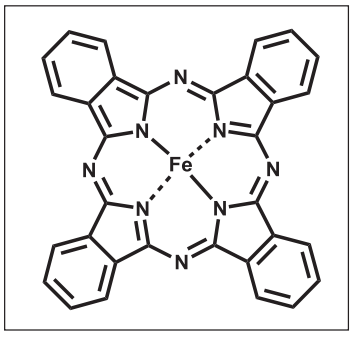
2.1.4 Palladium-catalyzed aerobic oxidation

Since some decades, many research groups are focused on palladium-catalyzed oxidation processes and also improved procedures applying aerobic conditions.[81] As mentioned before, the reoxidation of palladium by molecular oxygen is still a great challenge. However, in some cases a direct reoxidation of palladium by oxygen without any ETM can be observed. For example, such a direct reoxidation was reported for the oxidantion of alcohols to ketones, alkenes to carbonyl compounds, or intramolecular heterocyclizations of alkenes.[74,82-84] Thereby, an interesting example was reported by Sheldon and co-workers using a water-soluble phenanthrolinepalladium(II) complex to oxidize several alcohols.[79] Also, the industrially used Wacker oxidation is a well-known example for an ETM process. In this case, a redox couple system of palladium and copper is used to transform ethylene into the corresponding aldehyde in the presence of molecular oxygen. Here, the presence of chloride ions is of crucial importance since they are stabilizing the different catalytic relevant intermediates. However, a major drawback of a high concentration of chloride ions is the decreasing reaction rate and formation of chlorinated by-products, which makes the reaction non selective.[85,86] Therefore, a chloride-free Wacker oxidation was developed in order to overcome these disadvantages. Such an efficient and chloride-free system to oxidize alkenes is illustrated in Scheme 11. Here, palladium acetate is used in combination with *p*-BQ and a complex including a macrocyclic ligand (**ML^m**) that represents the ETM.[38,87]

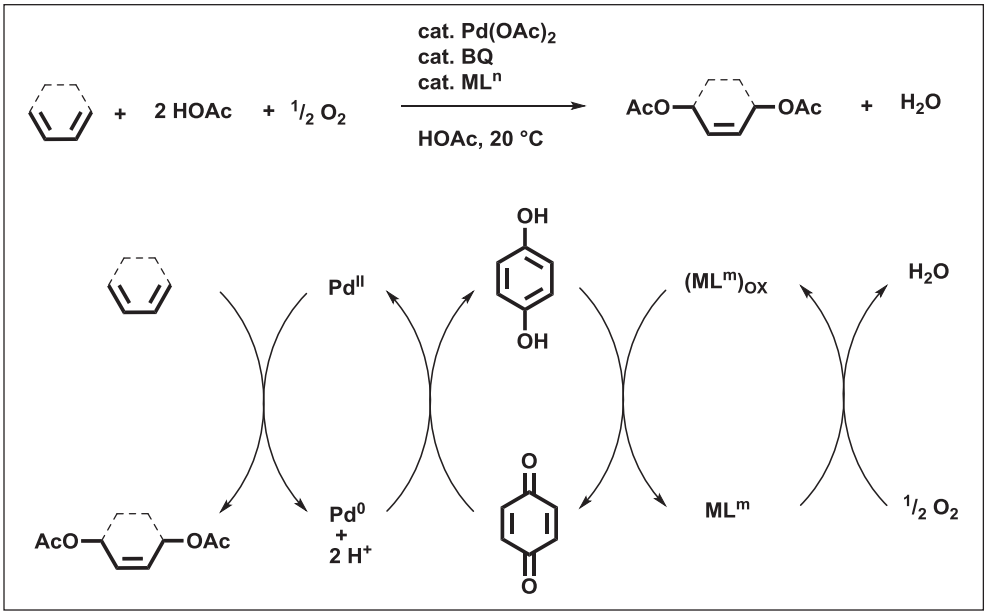


Scheme 11: Mechansim of the chloride-free Wacker oxidation of alkenes.[87]

Furthermore, it was found that iron(II) phthalocyanine (Fe(Pc)) (Scheme 12) highly accelerate the oxidation of alkenes into the corresponding ketones. Additionally, the use of a strong acid in this catalytic process is required to keep the palladium in solution. The same procedure was also applied to an aerobic 1,4-oxidation of 1,3-dienes using hydroquinone (HQ) and Fe(Pc) as ETMs (Figure 10).[38,88,89]



Scheme 12: Structure of iron(II) phatholcyanine (Fe(Pc)).

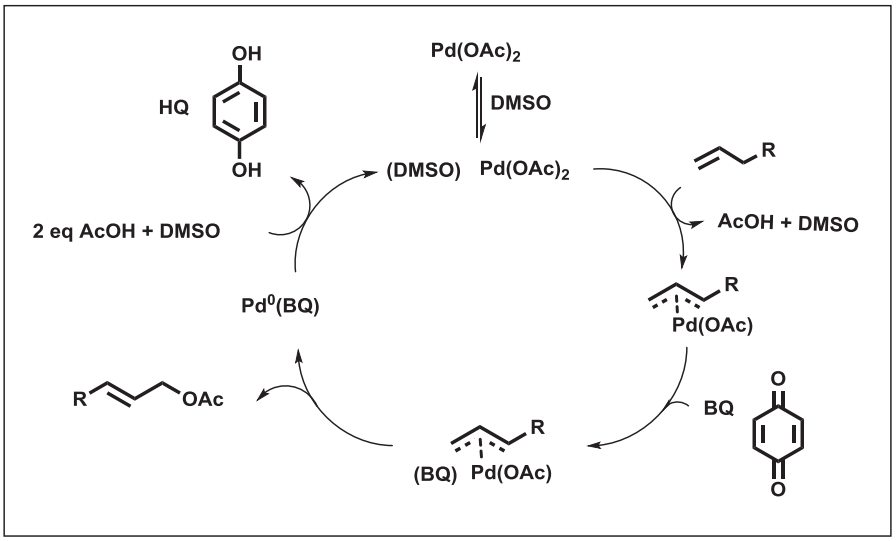


Scheme 13: Mechanism of the aerobic 1,4-diacetoxylation of 1,3-dienes.[89]

Palladium(II) acetate was used as substrate-selective redox catalyst in the presence of acetic acid as solvent in order to form a 1,4-diacetoxy-2-alkene.[90] A well-known class of oxidant is represented by quinone, which is often employed as an electron carrier in palladium-catalyzed oxidations.[91] However, the formed hydroquinone cannot be directly reoxidized by molecular oxygen. Thus, a stoichiometric amount is usually required in such a "catalytic" procedure. In order to overcome this problem an ETM that forms a complex with a macrocyclic ligand, e.g. Fe(Pc) can be used.[92] Additionally, utilization of these ETMs, the amount of oxidant can be dramatically decreased. Thus only a catalytic amount of quinone is necessary to obtain an efficient oxidation process. Furthermore, the couple quinone/metal macrocycle system was also successfully applied for the allylic oxidation of olefins.[88] For this purpose, cyclohexene was used as model substrate to obtain the corresponding allylic acetate in high yields.[38]

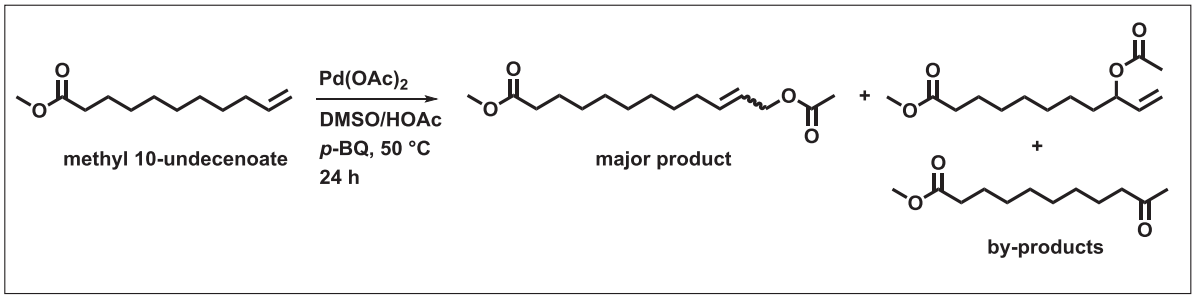
2.1.5 Palladium-catalyzed oxidation using dimethyl sulfoxide

An interesting palladium-catalyzed approach for the allylic oxidation of *α*-olefins was reported by White and co-workers.[93] Within this process a redox couple of palladium(II) acetate/ *p*-BQ in acetic acid is supported by DMSO in order to promote efficient C-H oxidation. This remarkable catalytic system allows the direct C-H oxidation of monosubstituted olefins to linear (*E*)-allylic acetates in high yields, regio- and stereoselectivity (Scheme 14). Additionally, the procedure is compatible with a wide range of functional groups (e.g. amides, carbamates, esters, and ethers). The oxidation process using the palladium(II) acetate/ *p*-BQ/ HOAc system is extensively studied by many research groups since some decades. The impact of sulfoxide addition (e.g. DMSO) to highly promote the formation of linear (*E*)-allylic acetates is a key feature of this reaction.[94] The catalytic system involving DMSO was successfully applied to 1-decene, which was used as model substance. The corresponding allylic actetate was obtained as main product, whereas the formation of undesired Wacker-type products, such as vinyl acetate or methyl ketone was highly suppressed.[95] However, a major drawback of this procedure is the use of stoichiometric amounts of *p*-BQ compared to the aforementioned aerobic oxidation procedures. Since *p*-BQ is a toxic reagent it is highly desirable to reduce the required amount to a minimum.[38]



Scheme 14: Mechanism of the palladium-catalyzed C-H activation using DMSO.[94]

The palladium-catalyzed system with DMSO/HOAc, was also investigated for the catalytic acteoxylation of methyl 10-undecenoate.[96] For this purpose, the process was optimized with regard to the twelve principles of Green Chemistry, resulting in 89% conversion (GC-MS) after 24 h. The linear (*E*)-allylic acetoxylated product was formed as major product in 73%. Moreover, the corresponding vinyl acteate as well as the methyl ketone were obtained as by-products in 6% and 21%, respectively (Scheme 15).

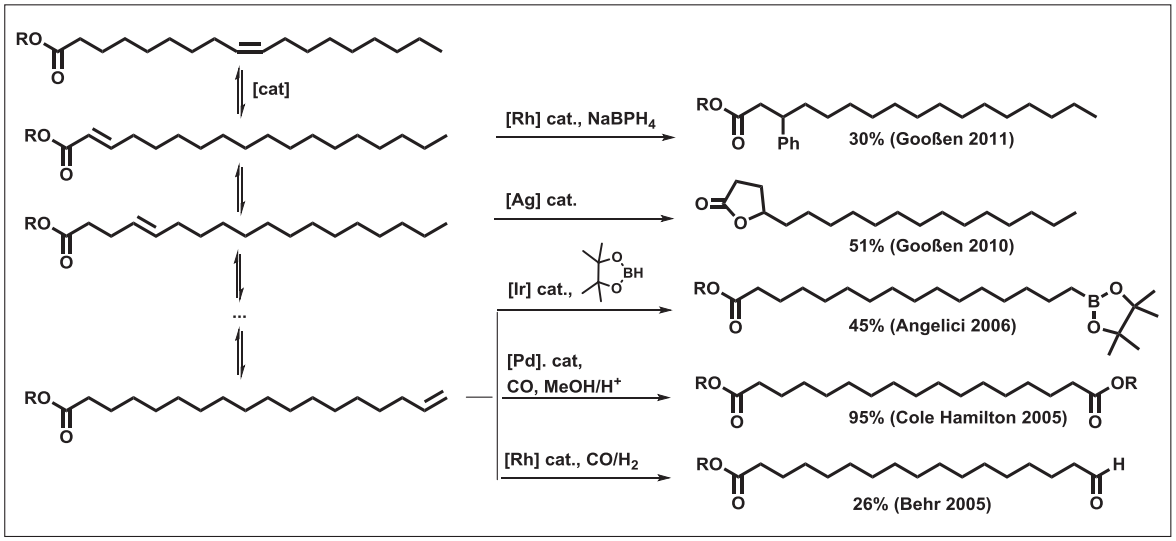


Scheme 15: Catalytic acetoxylation of methyl 10-undecenoate.

(Note that parts of this chapter were taken from the previously authored master thesis (M. von Czapiewski, *Catalytic Oxidation of Terpenes*, 2013, Karlsruher Institut für Technologie (KIT)).

2.2 Catalytic isomerization processes

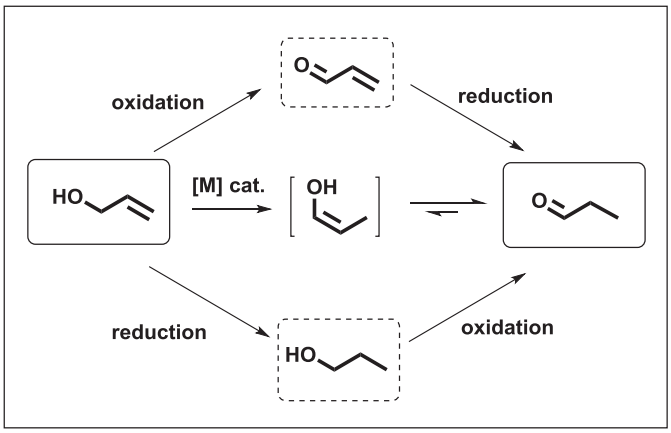
The synthesis of various polymeric materials is accomplished by step-growth polymerization processes, which comprises polyaddition and polycondensation reactions. Furthermore, monomers with at least two functional groups, such as hydroxy-, amine-, carboxylic acid- or ester-groups, are usually required to undergo polycondensation processes. However, most of the naturally occurring unsaturated fatty acids consist of one carboxylic-acid group and one double bond, mainly situated in the middle of the chain, which do not allow their direct polymerization. In order to overcome this problem many research groups have started to investigate catalytic isomerization processes. Therefore, catalysts based on transition metals, such as rhodium, iridium or palladium, are usually utilized, enabling the isomerization of the internal double along the fatty acid chain.[97-99] The resulting terminal double bond, obtained in equilibrium with all other isomers, can in some cases selectively chemically modified, which allow access to precursor for the monomer synthesis, and thus for polycondensation processes (Scheme 16).[100] For instance, Jiménez-Rodriguez *et al.* described a highly efficient alkoxycarbonylation protocol of methyl oleate, induced by a palladium-catalyzed isomerization process. Remarkably, the new ester group is always introduced at the end of the chain, resulting in 95% yield of the corresponding C19-diester.[98]



Scheme 16: Catalytic isomerization functionalization processes of fatty acids.[100]

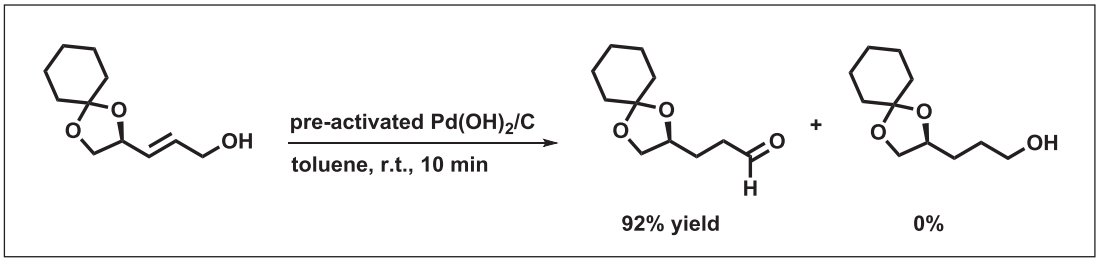
Mecking *et al.* used the process for the synthesis of long-chain diester and diols, which served as AA-monomers for the preparation of long-chain polyesters.[101] In 2005, Behr and co-workers reported on a rhodium-catalyzed *ω*-selective hydroformylation of fatty acids and its esters. However, the low yield of 26%, which was obtained by the process, requires further steps of optimization, but has proven as a principle of concept.[97] Furthermore, Angelici *et al.* described an iridium-catalyzed process for the selective *ω*-hydroboration.[99] In contrast, Gooßen *et al.* published a protocol for the selective formation of *γ*-lactones, which was accomplished by silver-catalyzed double bond isomerization to the 4-position.[102] Moreover, the same group described the rhodium-catalyzed synthesis of *β*-acrylates and *β*-amino acids using mono-unsaturated FAMEs. Thus, moderate yields were achieved by the aforementioned synthesis strategies (Scheme 16).[103] More recently, Riepl and co-workers reported the iridium-catalyzed isomerization trialkylsilylation of methyl oleate.[100] For this purpose, the authors used $[Ir(O\text{-}Me)(cod)]_2$, which enables the synthesis of terminal vinylsilanes *via* a dehydrogenation silylation process.

Another interesting application of catalytic isomerization processes exhibits allylic alcohol transformations to saturated carbonyl compounds. The mentioned transformation usually requires a two-step sequence of oxidation/reduction or reduction/oxidation (Scheme 17).[104] Additionally, those two-step procedures often use stoichiometric amounts of oxidizing/reducing agents and usually require several steps for purification as well as for product isolation, which is a significant drawback with regard to sustainability.



Scheme 17: Possible transformation processes of allylic alcohols to saturated carbonyl compounds.[104]

The catalytic isomerization of allylic alcohols demonstrates an efficient alternative to overcome the aforementioned problems. Yadav *et al.* described an efficient isomerization process of primary allylic alcohols. The utilization of a hydrogen pre-activated palladium catalyst enables the selective synthesis of aldehydes under mild reactions conditions (Scheme 18).

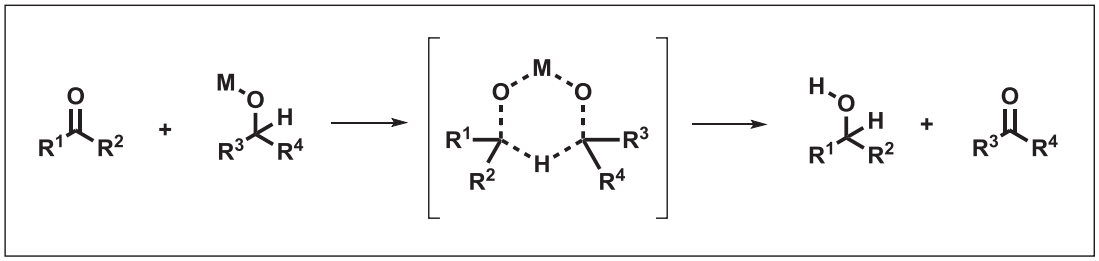


Scheme 18: Selective aldehyde formation *via* catalytic isomerization of primary allylic alcohols.

However, metal-catalyzed isomerization processes are also restricted and become more difficult with an increasing amount of substituents on the allylic alcohol double bond. Moreover, the established mechanism propose various species depending on the applied reaction conditions. For instance, alkyl and η^3-allyl intermediates in neutral and acid medium or alkoxide intermediates in basic environment.[105,106] Further mechanistic studies, expecting steric and electronic factors as crucial parameters in the formation of such intermediates, which again has a significant impact on the resulting selectivity.[107,108] Most of the established metal-catalyzed isomerization processes are carried out in organic solvents.[109,110] However, with an increasing environmental awareness, several research groups have started to investigate synthesis protocols, which include water as the appropriate (co-)solvent.[111,112] The development of water-soluble metal catalysts contain ligands, which are based on tertiary phosphine or ammonium substrates, provide manifold application possibilities. Remarkably, the presence of water often leads to higher yields, improved reactivity, and milder reactions conditions than in dry organic solvents.[104] Moreover, efficient catalyst recycling as well as product isolation can be accomplished by water/organic biphasic systems.

2.3 Transfer hydrogenation processes

Hydrogenation processes are one of the most fundamental transformations in organic synthesis, constituted by manifold applications in laboratory scale as well as on industrial scale.[113-115] In general, hydrogenation processes can be divided in two types, direct hydrogenation with pressure of hydrogen gas, and transfer hydrogenation (TH). The TH reaction describes the addition of hydrogen, which is obtained from a non-hydrogen source, to a molecule. This reaction-type has become a powerful tool to achieve various hydrogenated products, and exhibits a remarkable alternative to direct hydrogenation, due to several advantages. For instance, TH processes do not require high pressure of hydrogen gas nor expensive experimental equipment, most of the hydrogen donors are inexpensive and easy to handle, the major side-product can be recycled and the involved catalysts usually are readily accessible and not sensitive.[116-119] First investigations of TH reactions have been made by Knoevenagel in 1903,[120] when he discovered that palladium black enables the disproportionation of dimethyl 1,4-dihydroterephthalate to dimethyl terephthalate and *cis*-hexahydroterephthalate.[121] TH reactions were classified by Braude and Linstead in 1952 [122] (a) hydrogen migration, taking place within one molecule, (b) hydrogen disproportionation, transfer between identical donor and acceptor units, and (c) transfer hydrogenation-dehydrogenation, occurring between unlike donor and acceptor units. All of the aforementioned reactions can be accomplished by homogenous catalysis, heterogeneous catalysis, photochemical- as well as biochemical-processes. Moreover, TH reactions are divided according to the catalyst type in Meerwein-Pondorf-Verley (MPV) reductions, late transition metal-catalyzed reactions, organocatalytic, enzyme-catalyzed, thermal, base-catalyzed, and uncatalytic processes.[116] In 1925, Meerwein and Verley reported independently the first TH reaction of carbonyl compounds that is known as MPV reduction. The process describes the reduction of a ketone compound into the corresponding alcohol, which is promoted by an aluminium alkoxide as catalyst and a secondary alcohol as hydrogen donor (Scheme 19). The mechanism of the homogenous MPV reduction proposed a direct TH process, in which the carbonyl compound and the secondary alcohol are coordinated to the metal catalyst leading to a cyclic six-membered transition state.[123] The reversibility of the catalytic cycle was investigated more in detail by Oppenauer in 1937.[124]

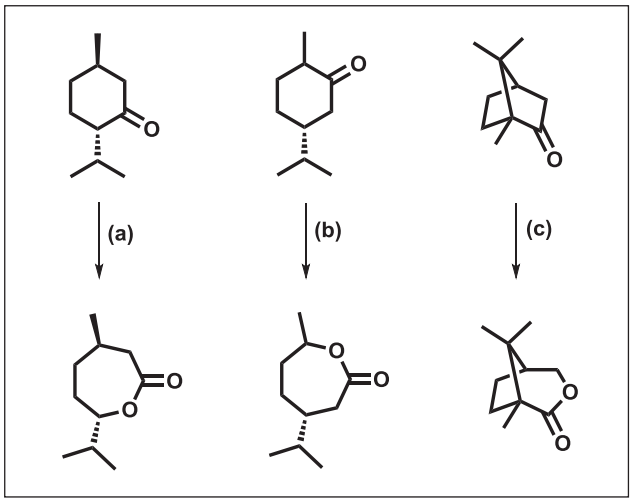


Scheme 19: Hydrogen transfer in the:Meerwein-Pondorf-Verley (MPV) reduction.

The discovery of the MPV reduction constitute a turning point in hydrogenation reactions. Inspired by the MPV reduction, many research groups have focused on this topic and developed several TH protocols, which include besides aluminium other metal catalysts, such as zirconium, cerium, lanthanum, samarium or ytterbium. Furthermore, heterogeneous Lewis acid or basic catalysts became of great interest, including supported aluminum alkoxides, hydrotalcites, zeolites or grafted lanthanide alkoxides.[125,126] Especially, hydrotalcites, zeolites and mesoporous materials containing aluminium, lanthanum or hafnium demonstrate remarkable catalytic activity for MPV reduction. Thus, some of the aforementioned catalysts have been used for industrial purposes, for instance in the synthesis of flavor agents. In the 1960s, the development of late transition metal-catalysts led to a new class of highly efficient TH catalysts, such as iridium hydride complexes. Henbst *et al.* investigated those catalysts for TH of cyclohexanones and *α,β*-unsaturated ketones to obtain the corresponding alcohols.[127] In recent years, with an increasing environmental awareness, sustainability has become a major focus in the design of catalysts as well as for the design of synthetic processes. Due to these aspects, more environmentally-friendly TH protocols have been developed, which utilizes abundant glycerol as green alternative to isopropanol.[128,129] Crotti *et al.* reported on a chemoselective TH process using organoiridium complexes, which efficiently catalyze the hydrogen transfer reaction from glycerol to actephenone, resulting dihydroxyacetone and phenylethanol.[130] Tavor *et al.* described a ruthenium-catalyzed transfer hydrogenation-dehydrogenation of benzaldhyde using glycerol as green solvent as well as hydrogen donor.[131] Another interesting application was published by Cadierno *et al.*, who investigated the ruthenium-catalyzed reduction of allylic alcohols with glycerol as hydrogen donor.[132]

2.4 Baeyer-Villiger Oxidation

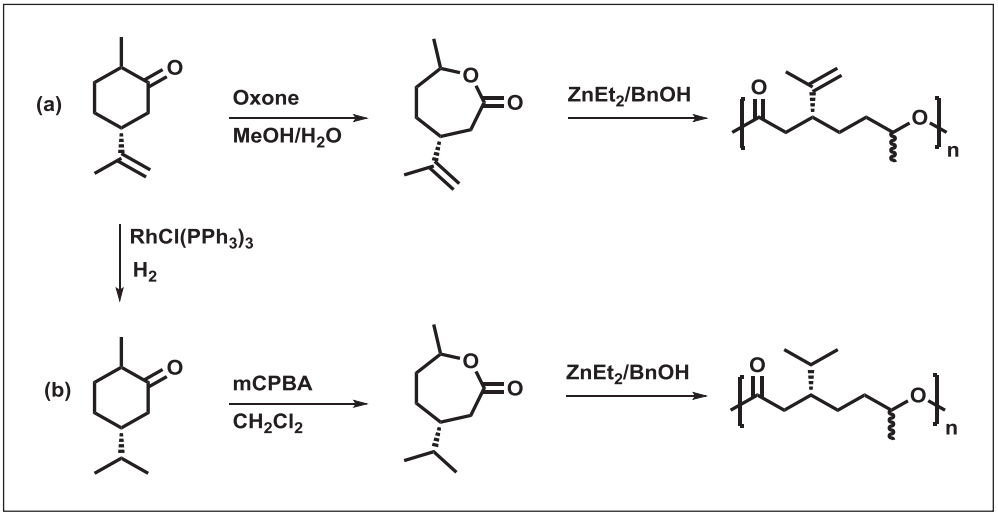
The discovery of the oxidation process, which allow the transformation of ketones into esters and cyclic ketones into lactons, have been made by Baeyer and Villiger in 1899.[133] During their investigations using cyclic ketones derived from terpenes, such as menthone, carvomenthone and camphor, they observed the formation of lactons instead of the expected ring cleavage (Scheme 20).[134] For this purpose, Baeyer and Villiger employed the oxidant, potassium monosulfate ($KHSO_5$), which was discovered by Caro one year before.[135] The oxidation reactions were performed at room temperature for 24 h, resulted in 40 - 50% yield of the lactone as well as 15 – 20% of the starting material were recovered.



Scheme 20: Baeyer-Villiger-oxidation of cyclic ketones into lactons using terpenes: (a) menthone, (b) carvomenthone and (c) camphor.

Furthermore, Baeyer and Villiger investigated the reaction more in detail and applied various oxidizing agents.[136] Thereby, they observed that peracids also enable the oxidation of cyclic ketones into lactones, and thus led to the process known as Baeyer-Villiger oxidation. However, it took almost 50 years until the mechanism was elucidated by Criegee.[137] Now, more than 100 years later, the Baeyer-Villiger oxidation is still of great interest, which resulted in countless publications due to the wide scope of this oxidation process. Interestingly, several protocols have been developed, which are based on

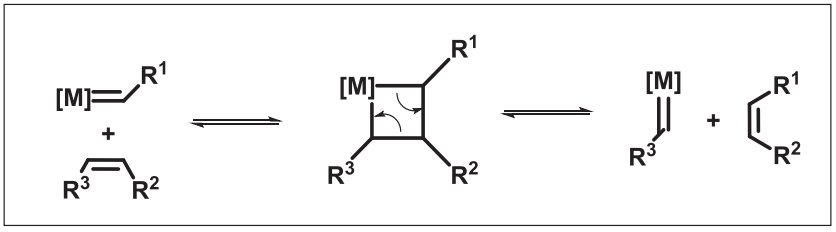
hydrogen peroxide as oxidizing agent. Hölderich *et al.* described the heterogeneous-catalyzed Baeyer-Villiger oxidation of cyclopentanone with hydrogen peroxide, yielding γ-valerolactone in good selectivity.[138] Remarkably, the formation of water as by-product results in a more environmentally-friendly synthesis benign. Andreae *et al.* reported on a catalytic approach for the Baeyer-Villiger oxidation of cyclohexanone with hydrogen peroxide. The authors performed the oxidation reaction in the presence of hexafluoro-2-propanol (HFIP) as solvent and Brønsted acids, leading to *ε*-caprolactone in quantitative yield.[139] The aforementioned oxidation protocols clearly demonstrate the efficient synthesis of versatile cyclic monomers, which allow to undergo ring opening polymerization (ROP). Hillmyer *et al.* studied dihydrocarvone and carvomenthone in the Baeyer-Villiger oxidation with *m*-chloroperbenzoic acid (*m*-CPBA) and Oxone® as oxidizing agents. Thus, the corresponding lactones were obtained in up to 86% conversion as well as additional 10% epoxide as side-product, if dihydrocarvone was used. The lactones were employed for ring opening polymerization, resulting in aliphatic polymers with a molecular weight of up to 53 kDa and low glass transition temperatures (T_g) of -27 °C (Scheme 21).



Scheme 21: Baeyer-Villiger oxidation and subsequent ring opening polymerization of terpenes: (a) dihydrocarvone and (b) carvomenthone.

2.5 Metathesis in polymer chemistry

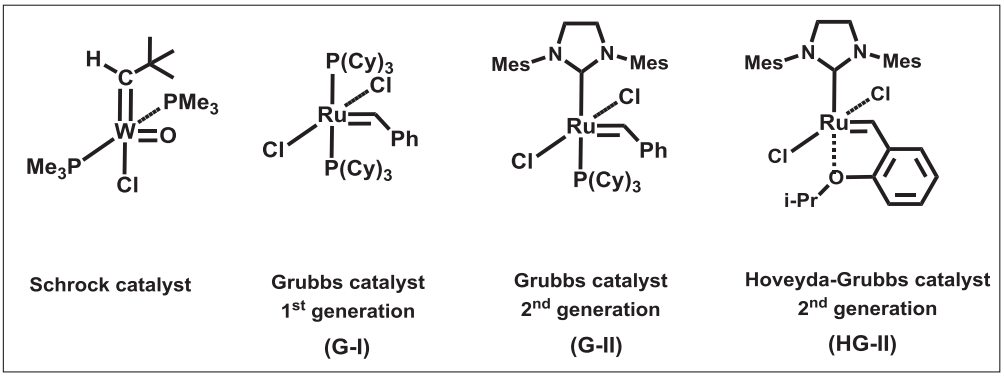
The discovery of olefin metathesis, the elucidation of the reaction mechanism as well as the development of various highly efficient catalysts was recognized with the Noble Prize in Chemistry in 2005, awarded to Grubbs, Schrock and Chauvin.[140-142] Olefin metathesis has become very important processes for organic synthesis, which target the formation of carbon-carbon bonds. The remarkable efficiency of metathesis reactions led to practical applications on industrial scale including the syntheses of monomers and polymers. First observations in this field were made by researchers at DuPont in 1955, while investigating the polymerization of norbonene with titanium-based catalysts. Expecting a product, which can also be obtained by Ziegler-Natta processes, they instead obtained an unsaturated polymer.[143] The term metathesis is derived from the Greek words meta = change and thesis = position, and describes the metal-catalyzed exchange process of alkylidene species between olefin substrates. The mechanism of the olefin metathesis reaction was elucidated and published by Hérrison and Chavin in 1971.[144] They described the metathesis reaction as a [2+2]-cycloaddition of an olefin and a metal alkylidene species, yielding a metallacyclobutane intermediate. The process is based on an equilibrium reaction, where either the initial metal alkylidene or a new metal alkylidene is formed by cycloreversion, which subsequently reacts with another olefin in a [2+2]-cycloaddition (Scheme 22).[145]



Scheme 22: Reaction mechanism of the olefin metathesis reaction.[145]

After elucidation of the olefin metathesis reaction mechanism, Schrock *et al.* developed several highly efficient metathesis catalysts based on tungsten, molybdenum or niobium, which are known as Schrock-catalysts (Scheme 23).[146,147] However, the low tolerance

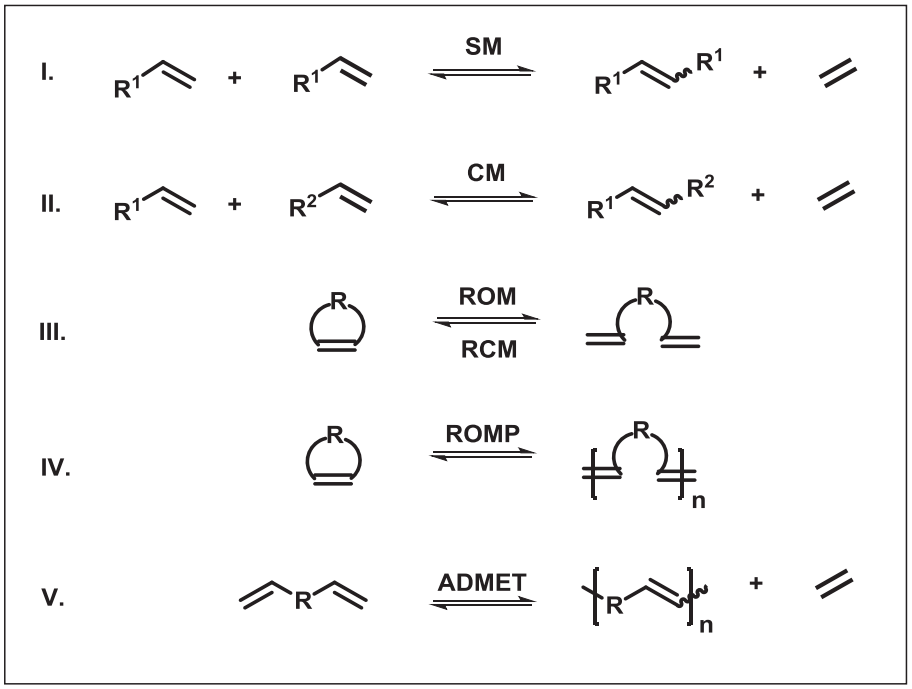
towards functional groups as well as against moisture and air constitutes a major drawback for diverse applications, especially on industrial scale.[148] The breakthrough in olefin metathesis was achieved in 1993 with the development of the Grubbs catalyst of the first generation (G-I) (Scheme 23).[149] In contrast to the Schrock-catalysts, the developed ruthenium-based catalysts by Grubbs *et al.* led to active metathesis catalysts, which are characterized by high tolerance towards functional groups as well as improved air and moisture stability. Additionally, these advantages enabled the commercialization of these metathesis catalysts. For instance, the obtained catalyst G-I was successfully investigated in ring-closing metathesis (RCM).



Scheme 23: Metathesis catalysts: Schrock-catalyst based on tungsten and Grubbs-catalysts based on ruthenium.[96]

However, the catalytic activity was relatively low compared with Schrock-type catalysts. Grubbs *et al.* assumed the dissociation of a phosphine ligand as key step for the activation process, which is why they started to investigate *N*-heterocyclic carbenes as ligands. However, kinetic studies using the Grubbs catalyst of the second generation (G-II) showed a lower ligand dissociation, compared with the G-I, but an improved binding of olefin substrates, which was not expected (Scheme 23).[150] Further investigations also revealed an improved thermal stability of the G-II. These fundamental developments in the design of catalysts led to the implementation of olefin metathesis for several applications on laboratory scale as well as on industrial scale. In 1998, Hoveyda *et al.* studied the metathesis reaction of 2-propoxy styrene using the G-I catalyst. They observed that during the reaction a new catalyst species is formed from the employed catalyst G-I and the

monomer. Interestingly, further investigations on the novel catalyst showed an improved stability against moisture and air, leading to the successful establishment of the Hoveyda-Grubbs of the second generation (HG-II) (Scheme 23). Due to the aforementioned aspects, the Grubbs-type catalysts have become a versatile tool in solving diverse synthetic problems. The possible applications of olefin metathesis are manifold, however the most common processes for the synthesis of monomers are self-metathesis (SM), cross-metathesis (CM), ring-closing metathesis (RCM) or ring-opening metathesis (ROM). Furthermore, ring-opening metathesis polymerization (ROMP) as well as acyclic diene metathesis (ADMET) are well-established techniques for the synthesis of polymeric materials (Scheme 24)



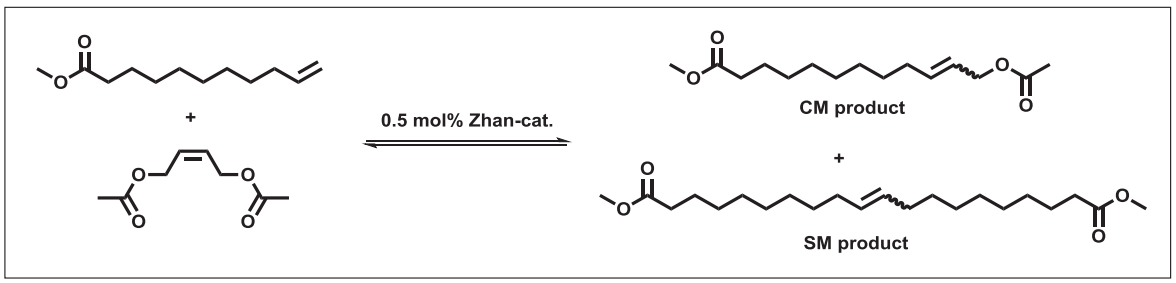
Scheme 24: Metathesis reactions for the synthesis of monomers and polymers: (I) self-metathesis (SM), (II) cross-metathesis, (III) ring-opening/ring-closing metathesis (ROM/RCM), (IV) ring-opening metathesis polymerization (ROMP), (V) acyclic diene metathesis (ADMET).

Moreover, Grubbs and co-workers investigated metathesis reactions in more detail and developed a concept, which serves as prediction tool for the expected selectivity in cross-metathesis processes.[151] The concept describes the ability of olefins to undergo self-

metathesis (homo-dimerization) relative to other olefins. Therefore, the authors distinguished between four categories, wherein the activity of olefins to undergo self-metathesis decreases from type I to type IV.

- Olefins of type I: rapid homodimerization and secondary metathesis of the homomdimers (e.g. terminal olefins, allylic alcohols)
- Olefins of type II: slow homodimerization, unreactive homodimers (e.g. acrylates, vinyl ketones)
- Olefins of type III: no homodimerization (e.g. allylic tertiary alcohols)
- Olefins of type IV: no cross-metathesis, no catalyst deactivation (e.g. vinyl nitro olefins)

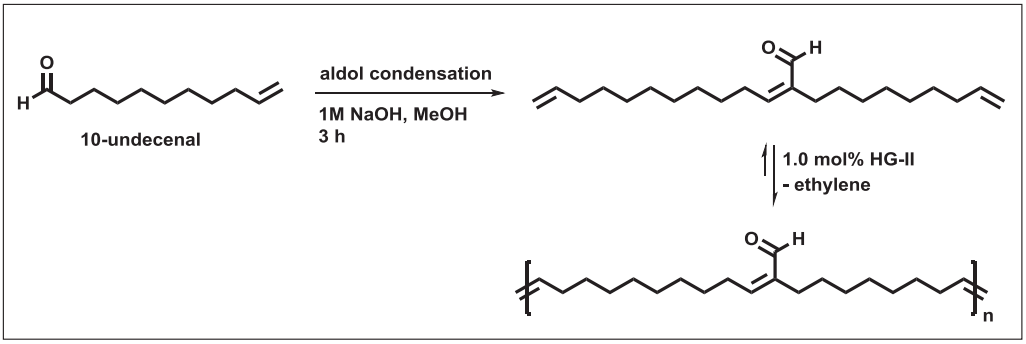
For instance, the reaction of two olefins of the same type leads to a non-selective CM processes, which exhibits a statistical product distribution. In contrast, if two olefins are used that significantly differ in their homo-dimerization rates, results in a selective CM process.[151] For example, the cross-metathesis reaction of methyl 10-undecenoate and *cis*-1,4-diacetoxy-2-butene under neat conditions was investigated (Scheme 25).[96] Therefore, 0.5 mol% of a ruthenium-based catalyst (Zhan-catalyst) was used, which enabled 96% conversion of methyl 10-undecenoate after 3 h at 50 °C. Moreover, the CM product was selectively formed, whereas the possible SM product of a C20 diester was not observed, clearly demonstrating the remarkable efficiency of the catalytic system, in both product formation and selectivity.



Scheme 25: Cross-metathesis (CM) of methyl 10-undecenoate and *cis*-1,4-diacetoxy-2-butene.

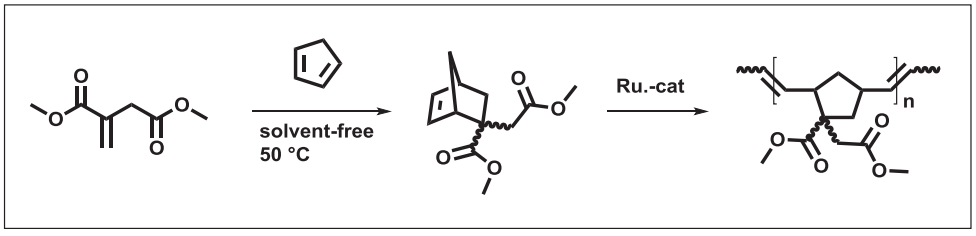
However, the aforementioned reaction represents only one example of the countless possible monomer syntheses, which can be accomplished by metathesis reactions.[152-155]

The introduction of olefin metathesis to polymer science constitutes another important application, due to the increasing demand of polymers as advanced functional materials. Especially, ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) reactions became interesting techniques for the synthesis of polymers. For instance, the synthesis of poly-*α,β*-unsaturated aldehydes *via* ADMET polymerization was described using an *α,ω*-diene monomer derived from castor oil (Scheme 26).[156] For this purpose, 10-undecenal was applied in an aldol condensation reaction leading to the *α,ω*-diene in 98% yield. The subsequent polymerization of the monomer using the ADMET technique, resulted in polymers with molecular weights (M_n) of up to 11 kDa.



Scheme 26: ADMET polymerization of *α,ω*-diene derived from castor oil.

The synthesis of polynorbornenes, using an itaconic acid-derived norbornene monomer, exhibit an interesting example of the ROMP technique as an efficient tool in polymer synthesis. Thus, by varying the monomer to initiator ratio, polymers with molecular weights (M_n) of up to 88 kDa were obtained (Scheme 27).[157]



Scheme 27: Synthesis of polynorbornene *via* ROMP using an itaconic acid-derived norbornene monomer.

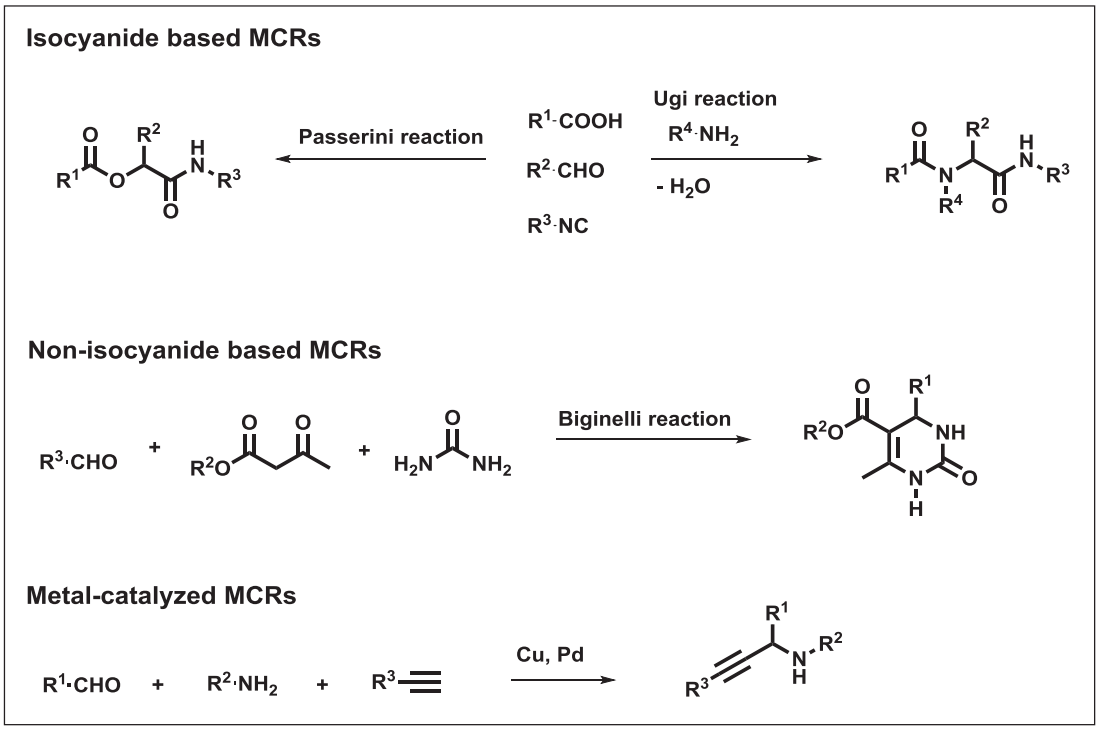
2.6 Multi-component reactions in polymer chemistry

In a multicomponent reaction (MCR), three or more substances react in a highly atom-efficient manner, whereby most of the starting materials become part of the final product. Furthermore, MCRs are characterized by high yields, their simplicity in reaction control as well as in the reduction of work-up steps, if compared to a sequential reaction course. MCRs have been known in organic chemistry since the discovery of the Strecker synthesis in 1850 (Scheme 28).[158,159] This three-component reaction of an aldehyde, ammonia and hydrogen cyanide enabled the synthesis of *α*-amino acids.

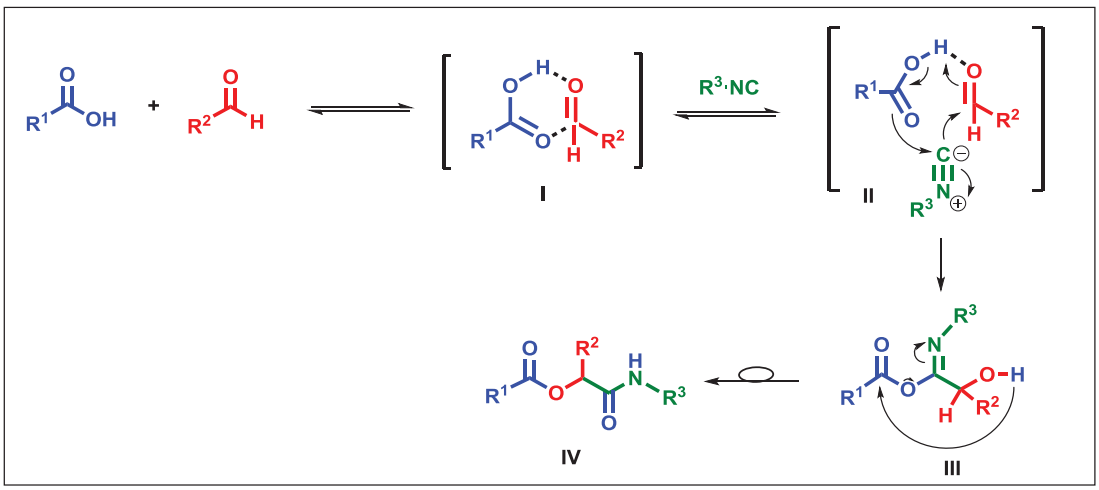
Scheme 28: Strecker reaction for the synthesis of *α*-amino acids.

The remarkable efficiency of MCRs became of great interest in organic chemistry and led to the development of several synthesis protocols. For instance, the Hantzsch reaction,[160] the Mannich reaction,[161] the Gewald reaction,[162] the van-Leusen reaction,[163] or the Biginelli reaction.[164] However, the turning point of MCRs is marked in the 1990s with an increasing demand of combinatorial reactions for drug synthesis.[165] Especially, isocyanide based MCRs, such as the Passerini three-component reaction (P-3CR),[166] and the Ugi four-component reaction (Ugi-4CR)[167] as well as the non-isocyanide based MCRs, such as the Biginelli reaction[164] have proven as key reactions for drug synthesis concepts, since metal residues can be avoided in contrast to palladium- or copper-catalyzed MCRs approaches (Scheme 29).[168-171] The P-3CR, which was discovered in 1921 by M. Passerini,[166] utilizes a carboxylic acid, an aldehyde/ketone and an isocyanide resulting in *α*-acyloxycarboxamides (IV) (Scheme 29). The postulated mechanism of the P-3CR starts with the formation of an adduct of the carboxylic acid and the aldehyde (**I**). In this process, the aldehyde compound is activated, which enables the isocyanide to undergo the *α*-addition, forming a cyclic transition state (II). Subsequently, the resulting intermediate undergoes a rearrangement process (III),[172] whereby the product (IV) is formed (Scheme 30). In contrast, the Ugi-4CR includes an additional primary amine compound. During the

latter reaction water is released, which leads to *α*-aminoacylamides as products (Scheme 29).

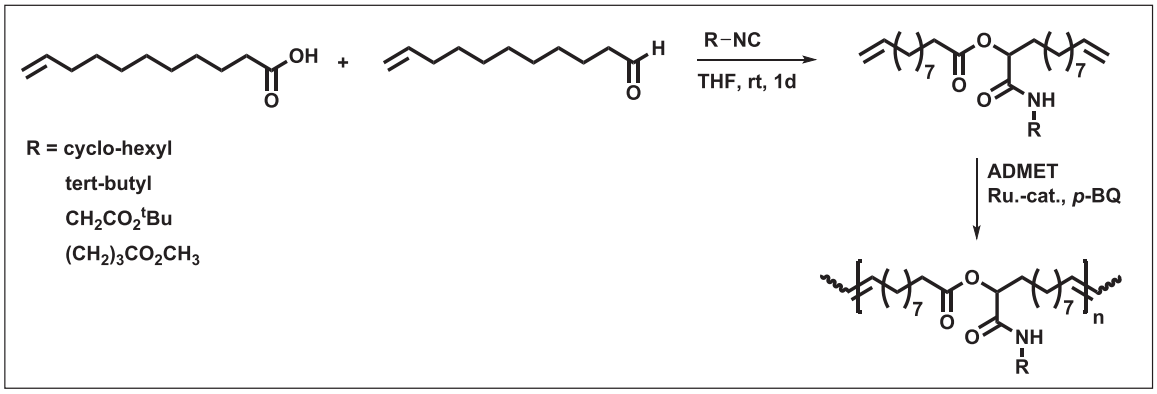


Scheme 29: Isocyanide based MCRs (top), non-isocyanide based MCRs (middle) and metal-catalyzed MCRs (bottom).



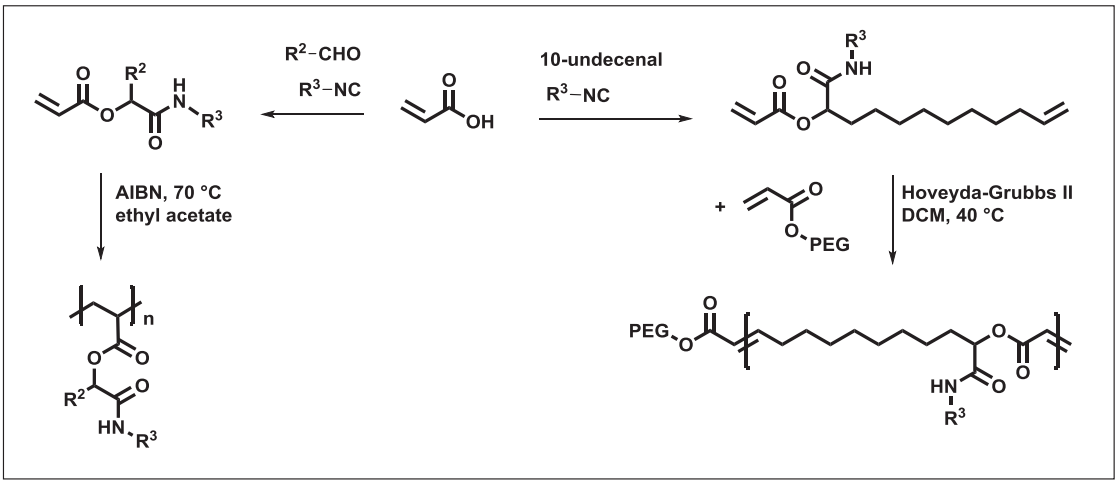
Scheme 30: Reaction mechanism of the Passerini reaction (P-3CR).

Moreover, the rising environmental awareness in the last centuries led to rethinking the design of chemical reactions by the implantation of the 12 principles of Green Chemistry. Herein, MCRs clearly show several advantages to fulfill these criteria. The introduction of MCRs to polymer science in 2011, using renewable raw materials, constitute a milestone for the synthesis of advanced functional polymeric materials.[173] Therefore, methyl 10-undecenoate, the thereof derived aldehyde, 10-undecenal, and various isocyanides were investigated in the P-3CR (Scheme 31). The reactions were carried out under mild conditions leading to *α,ω*-diene monomers in 59-83% yield, which were subsequently polymerized *via* acyclic diene metathesis (ADMET). The obtained polymers reached molecular weights (M_n) of up to 22 kDa. Moreover, saponification of the *tert*-butyl ester in the polymer side-chain allowed postsynthetic modification through a grafting-onto process using the P-3CR. An alternative approach in this study, is based on step-growth polymerization. For this purpose, AA-monomers (dicarboxylic acids, dialdehydes) were synthesized *via* self-metathesis, and subsequently applied for the polyaddition with various isocyanides. Thus, polymers with molecular weights (M_n) of up to 56 kDa were obtained.



Scheme 31: Products derived from ricinoleic acid for the monomer synthesis *via* P-3CR and subsequent ADMET polymerization.

Recently, the synthesis of acrylate monomers via P-3CR was described, using acrylic acid in the presence of various aldehydes and isocyanides (Scheme 32). Subsequent free-radical polymerization enabled the synthesis of polyacrylates with high molecular weights of up to 99 kDa. Furthermore, the glass transition temperature (T_g) of the obtained polymers could be tuned by varying the aldehyde compound, thus T_g values in a range of 30 – 123 °C were achieved. Additionally, highly polar polyacrylates showed a thermoresponsive behavior (upper critical solution temperature, UCST) in methanol or ethanol as solvent.[174]



Scheme 32: The synthesis of diverse acrylate monomers via P-3CR, and the thereof derived polyacrylates.[174,175]

Another synthesis approach using acrylic acid, allowed the synthesis of unsymmetric *α,ω*-diene monomers. Therefore, 10-undecenal, derived from ricinoleic acid (Scheme 2), and various isocyanides were employed to the P-3CR (Scheme 32). The major advantage of acrylate monomers bearing an acrylate and a terminal olefin is constituted by the high cross-metathesis selectivity, thus head-to-tail monomer addition in ADMET polymerization is favored.[176,177] Moreover, the use of a monofunctional PEG-acrylate as chain-transfer agent enabled the synthesis of amphiphillic block copolymers as well as the control over the molecular weight during the ADMET polymerization.[175]

3 Motivation of this work

As already described in the beginning of this thesis, the global situation urgently requires solutions to address the drastically increasing of environmental pollution, which is among other caused by the growing population. The production of polymeric materials for diverse daily life commodities, consumes several million tons of crude oil every year, and is thus one essential reason for the depletion of this resource. A major goal of our (academic) society is the development of alternative processes using renewable resources, which are able to fulfill the needs of the growing population on the one hand, and minimize the impact on the environment on the other.

The aim of this thesis is to investigate novel catalytic oxidation approaches for the synthesis of monomers and polymers utilizing fatty acids and terpenes. Herein, the development of efficient and selective oxidation protocols, which go along with the twelve principles of Green Chemistry, are of particular interest. The synthesis of keto-fatty ester methyl esters, derived from methyl oleate and methyl erucate, using a co-catalyst-free Wacker oxidation process exhibits such an efficient oxidation protocol.[178] The reaction conditions of this remarkable process should be further improved with regard to sustainability and subsequently transferred to other fatty acid derivatives, such as triglycerides and poly-unsaturated fatty acids. The resulting keto-fatty acid derivatives lead to a variety of further possible modifications, which allow access to various promising renewable materials. For instance, the synthesis of platform chemicals, such as fatty alcohols and short esters, can be accomplished by Baeyer-Villiger Oxidation and subsequent transesterification of keto-fatty acids. Furthermore, poly-ketones derived from triglycerides can be used for the synthesis of polyols *via* transfer hydrogenation processes. The resulting products are valuable starting materials for the synthesis of polyurethanes.

Another opportunity of this research is the regioselective catalytic acetoxylation of limonene, enabling the selective acetoxylation of its terminal double bond. The obtained product can be transferred into an aldhehyde derivative through saponification and subsequent catalytic isomerization of the corresponding allylic alcohol. Furthermore, it can be used as starting material in multicomponent reactions (e.g. Passerini reaction) in order to synthesize various monomers and novel polymeric materials.

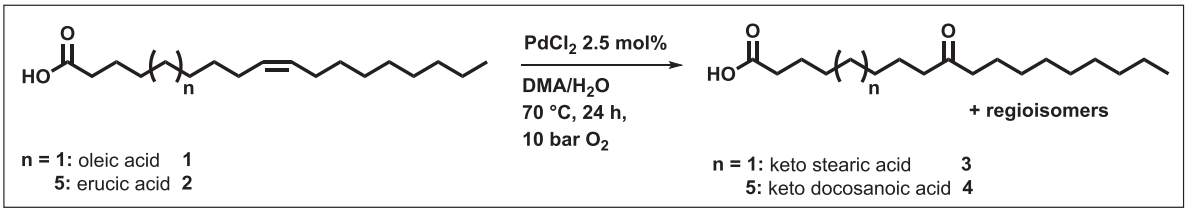
4 Results and Discussion

4.1 Wacker Oxidation of fatty acid derivatives

The catalytic oxyfunctionalization of renewable resources, especially using indigenous fatty acid derivatives (e.g. oleic acid, erucic acid) allow access to various interesting platform chemicals, which can be further utilized as monomers for the synthesis of polymeric materials. In this context, the Wacker oxidation process as an efficient catalytic system was exploited to synthesize keto-fatty acids derived from mono- and poly-unsaturated fatty acid derivatives. The Wacker oxidation process developed at Wacker Chemie is based on a palladium(II) chloride/copper(II) chloride system that enables the oxidation of olefins in an efficient manner. Herein, the catalytic active species is re-oxidized by a copper co-catalyst to avoid the formation of palladium black. In order to introduce a more environmentally-friendly catalytic process, we were focused on a co-catalyst-free Wacker oxidation protocol. The utilization of dimethylacetamide (DMA) as an active solvent enables the re-oxidation of palladium(0) species in the presence of high oxygen pressure. Moreover, the employed solvent mixture (DMA/water) retains the catalyst, which allows a straightforward product isolation by simple extraction with *n*-heptane or diethyl ether as well as the recycling of the catalyst-solvent system.

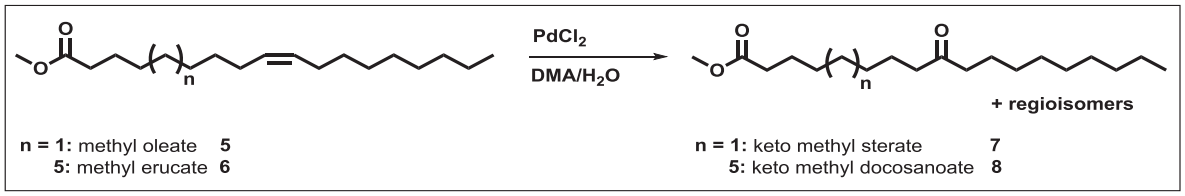
4.1.1 Mono-unsaturated fatty acids

We started our investigations using mono-unsaturated fatty acids (oleic acid **1**, erucic acid **2**) in order to synthesize the corresponding keto stearic acid **3** and keto docosanoic acid **4** (Scheme 33). For this purpose, the modified Wacker oxidation protocol for the synthesis of keto-fatty acid methyl esters (keto-FAMEs) was applied.[178] However, the reactions conditions of the aforementioned procedure led to low conversions (< 10%, determined by ^{1}H NMR analysis), even if a more concentrated solution as well as an increased amount of catalyst was used. The significant decrease in catalytic activity can be explained by coordination of the carboxylic acid group to the palladium catalyst, which forms a complex and thus inhibits the oxidation process of the double bond.



Scheme 33: Wacker Oxidation of mono-unsaturated fatty acids.

Due to these observations, further experiments were carried out with the corresponding fatty acid methyl esters (FAME) which have been studied for the synthesis of polyamides by our group before.[178] However, in order to develop a more sustainable and environmentally-friendly oxidation process, the influence of various parameters, such as catalyst loading, the amount of solvent as well as the oxygen source and pressure were investigated. The screening was performed with methyl oleate **5** as model substance and the obtained optimized reaction conditions were subsequently transferred to the oxyfunctionalization of methyl erucate **6** (Scheme 34).



Scheme 34: Wacker Oxidation of mono-unsaturated FAMEs.

In a first attempt, the reactions conditions of the aforementioned Wacker oxidation protocol were applied to synthesize keto-FAME **7**. Thus, full conversion was obtained after 24 h at 70 °C using 5.0 mol% of the catalyst and 10 bar pure oxygen (Table 4, entry 1). The same results could be achieved, if half of the amount of palladium(II) chloride (2.5 mol%) as well as half of the amount of solvents were used (Table 4, entry 2, 3). Subsequently, **7** was obtained as white solid in 89% yield after flash column chromatography (Figure 4). Further investigations were carried out with synthetic air as oxygen source, since its production is less expensive and exhibits a decreased risk with regard to a possible application on industrial scale compared to pure oxygen.

In a first approach, 5.0 mol% of catalyst and 10 bar of synthetic air led to a slightly decreased conversion of 90% (Table 4, entry 4). Due to this observation, the pressure was increased to 30 bar which resulted in full conversion of **5** (Table 4, entry 4). This was also achieved if 2.5 mol% of catalyst and half of the amount of solvent was used (Table 4, entry 6, 7). However, if the catalyst loading was reduced to 1.0 mol%, only 72% conversion was observed (Table 4, entry 8). With the optimized conditions in hand, methyl erucate **6** was successfully modified into keto-FAME **8**, and subsequently obtained as white solid in 86% yield (Table 4, entry 9).

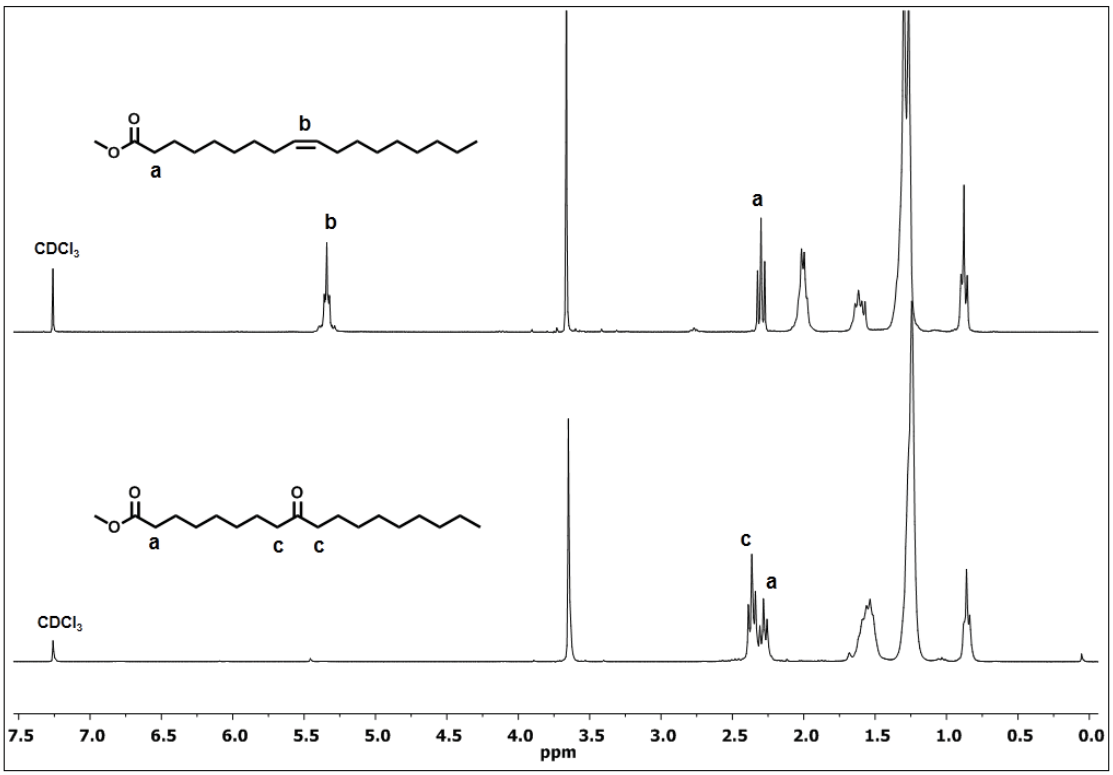


Figure 4: ^{1}H NMR of methyl oleate **5** (top) and the thereof derived keto-FAME **7** (bottom).

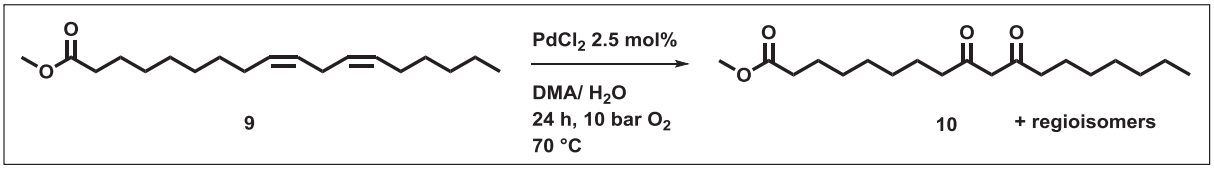
Table 4: Screening of reaction conditions for the Wacker Oxidation of methyl oleate **1**.

Entry	DMA [mL]	H_2O [mL]	Cat. [mol%]	p [bar]	Conversion [d] [%]
1	5.50	0.50	5.00	10	> 99 [a]
2	5.50	0.50	2.50	10	> 99 [a]
3	2.75	0.25	2.50	10	> 99 [a]
4	5.50	0.50	5.00	10	90 [b]
5	5.50	0.50	5.00	30	> 99 [b]
6	5.50	0.50	2.50	30	> 99 [b]
7	2.75	0.25	2.50	30	> 99 [b]
8	2.75	0.25	1.00	30	72 [b]
9	2.75	0.25	2.50	10	> 99 [a, c]

Conditions: 1.0 mmol **5**, 70 °C, 24 h. a) pure oxygen; b) synthetic air; c) 1.00 mmol **6**; d) Conversion was determined by ^{1}H NMR analysis.

4.1.2 Poly-unsaturated fatty acids

In this section, the Wacker oxidation of poly-unsaturated fatty acid methyl esters was studied. We started our investigations using methyl linoleate **9**, which can be obtained from safflower oil (≥ 80%) as well as sunflower oil (≥ 70%). The catalytic oxyfunctionalization of **9** was performed with the optimized reaction conditions developed for the oxidation of mono-unsaturated FAMEs with pure oxygen (Scheme 35).



Scheme 35: Wacker Oxidation of methyl lineoleate (expected products).

The crude reaction mixture was analyzed by ^{1}H NMR analysis, which revealed full conversion of the double bond after 24 h (Figure 5).

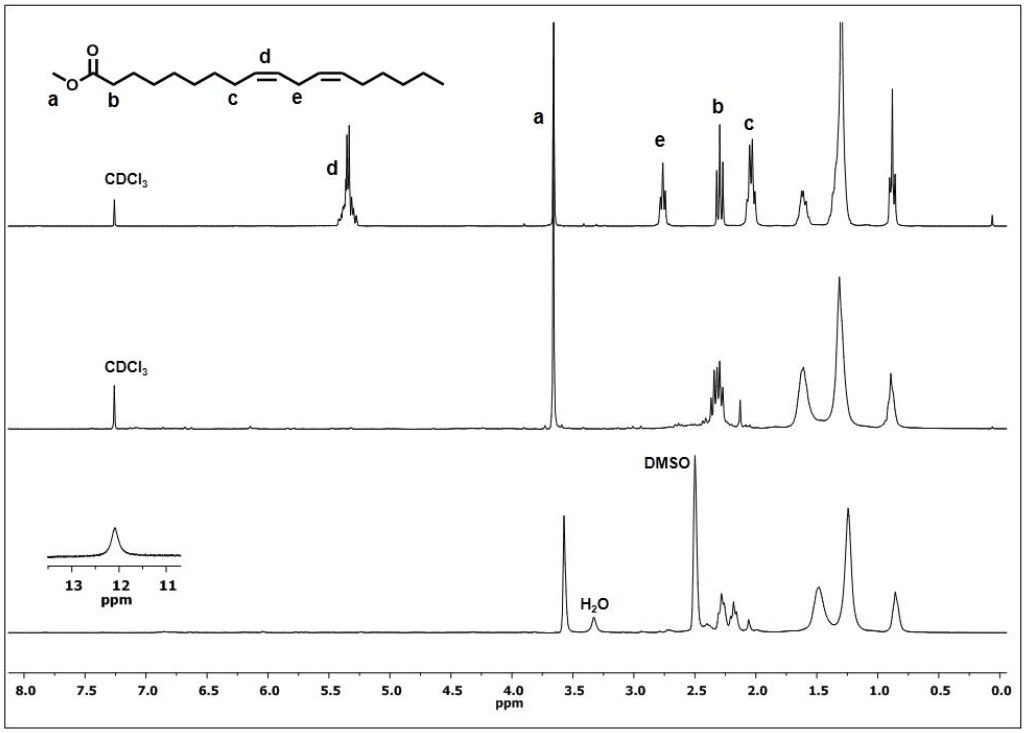


Figure 5: ^{1}H NMR of methyl linoleate (top), crude mixture after Wacker oxidation ($CDCl_3$, middle) and crude mixture after Wacker oxidation (DMSO, bottom).

However, the determined integrals were not in agreement with the expected amount of protons of the desired product **10**. Moreover, if the ^{1}H NMR experiment was carried out with *d*-DMSO as solvent, a signal at 12 ppm was observed indicating the formation of acid derivatives (Figure 5). Additionally, FTIR and ^{13}C NMR measurement of the crude reaction mixture confirmed the formation of acid derivatives and the expected ketone signal at 210 ppm was not observed. Furthermore, gas chromatography (GC) and gas chromatography–mass spectrometry (GC-MS) measurements of the crude mixture showed several product peaks, which could be identified as shorter chain carboxylic acids and carboxylic acid methyl esters (Figure 6). The obtained results indicate that an oxidative cleavage occurred during the Wacker oxidation process.[179] Due to these observations, milder reactions conditions were investigated. However, if the reaction was performed at 50 °C identical results were obtained.

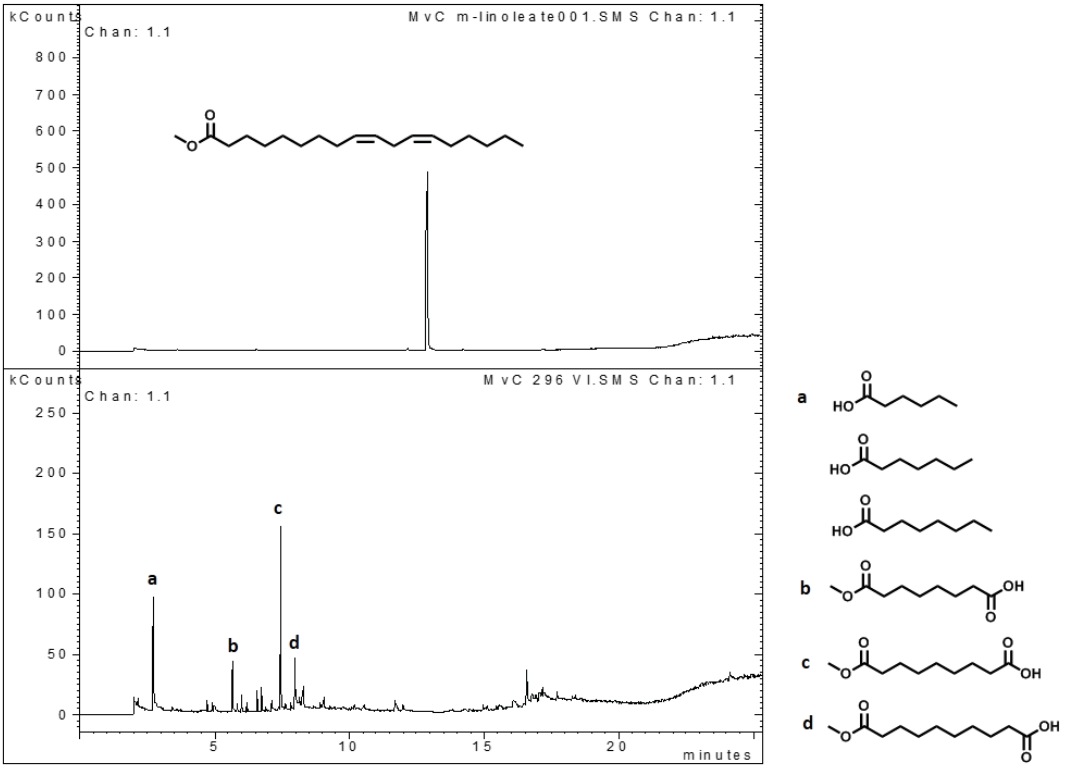
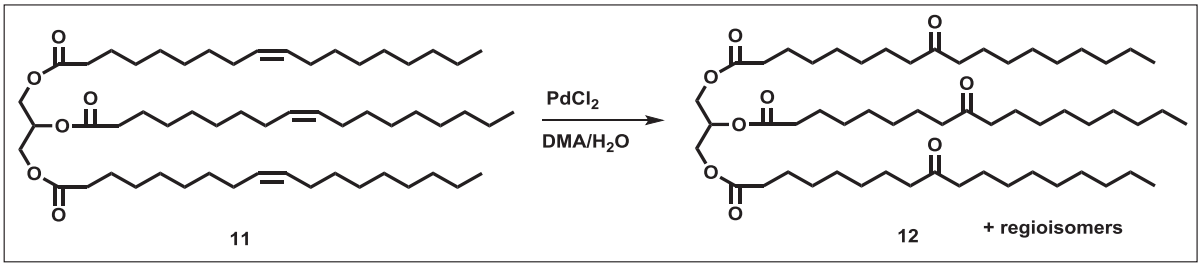


Figure 6: GC-MS chromatograms of methyl linoleate (top) and product distribution after Wacker oxidation (bottom).

4.1.3 Triglycerides

The goal of further investigations was the synthesis of poly-ketones derived from triglycerides. For this purpose, commercially available olive oil with a high content of mono-unsaturated fatty acids was employed as model substance for the Wacker oxidation process.



Scheme 36: Wacker Oxidation of triglycerides (e.g. high oleic sunflower oil).

First experimental studies were carried out with the optimized conditions obtained from the keto-FAME synthesis, except that 10 mol% of catalyst were employed due to the increased amount of double bonds. After 24 h, the crude mixture was analyzed by ^{1}H NMR measurement, which revealed 80% conversion of the double bonds (Table 5, entry 1). The same result was achieved with a more concentrated reaction mixture, if half of the amount of solvent was used (Table 5, entry 2). In order to reach full conversion, longer reaction times of 48 h were necessary (Table 5, entry 3). In further studies, the influence of temperature was investigated. Therefore, an increased temperature of 100 °C was applied which led to 93% conversion after 24 h and full conversion after 48 h (Table 5, entry 4, 5). Moreover, if the oxidation was performed with a decreased catalyst loading of 5.0 mol% still resulted in full conversion (Table 5, entry 6). The optimized reactions conditions were applied for the synthesis of poly-ketones derived from high oleic sunflower oil **11** (HOSO), which consists of > 80% mono-unsaturated fatty acids (Scheme 36). ^{1}H NMR analysis of poly-ketone **12** revealed a content of 2.3 ketone units/molecule, which could be increased to 2.6 ketone units/molecule after recrystallization (Figure 7). Thus, the resulting poly-ketone **12** was obtained as white solid in 79% yield.

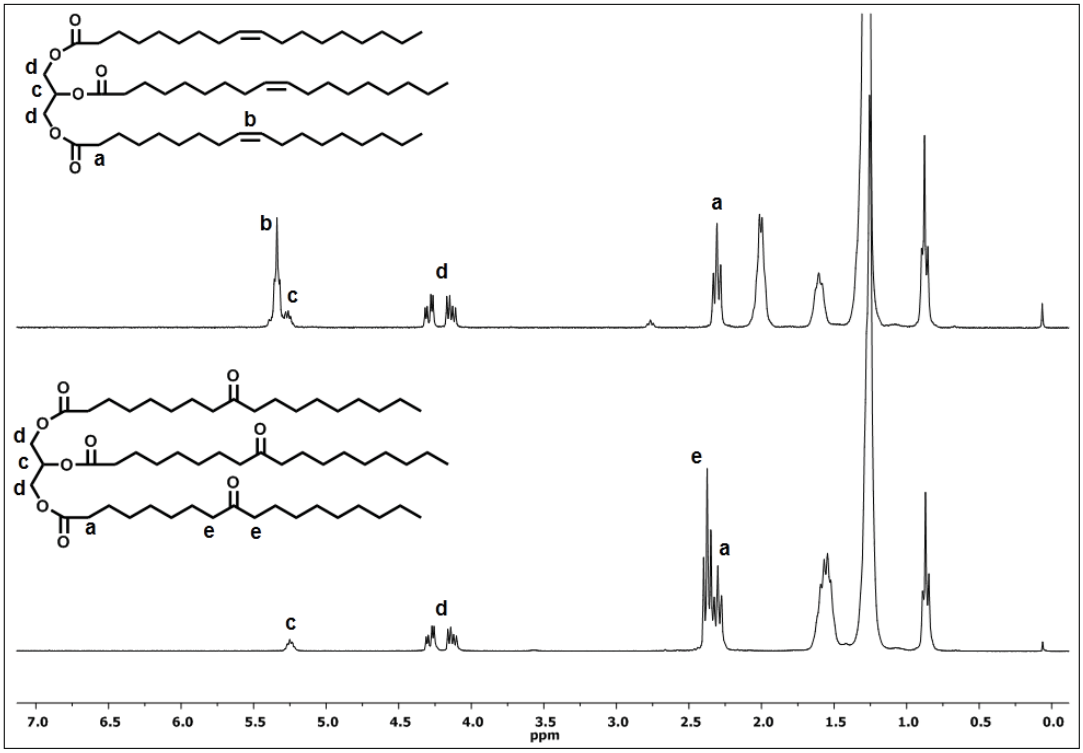


Figure 7: ^{1}H NMR of **11** (top) and thereof derived poly-keto triglyceride **12** (2.6 ketone units/molecule) after recrystallization (bottom).

Table 5: Screening of reaction conditions for the Wacker Oxidation of triglycerides with pure oxygen.

Entry	DMA [mL]	H_2O [mL]	T [°C]	t [h]	Conversion [b] [%]
1	5.50	0.50	70	24	80
2	2.75	0.25	70	24	78
3	2.75	0.25	70	48	> 99
4	2.75	0.25	100	24	93
5	2.75	0.25	100	48	> 99
6	2.75	0.25	100	24	> 99 [a]

Conditions: 1.0 mmol **11**, 10 mol% $PdCl_2$, 10 bar oxygen pressure. a) 5.0 mol% $PdCl_2$; b) Conversion was determined by ^{1}H NMR analysis.

Further steps of optimization were carried out with synthetic air as oxygen source. We started our investigations using the aforementioned reaction conditions, with an increased amount of solvent (6.0 mL) and a reaction temperature of 70 °C. For this purpose, 30 bar of synthetic air were applied, which resulted in a moderate conversion of 51% (Table 6, entry 1). Further reactions were performed at 100 °C, since an increased temperature has proven to accelerate the catalytic oxidation. Hereby, almost full conversion of **11** could be achieved (Table 6, entry 2). Reducing the amount of solvent to 3.0 mL led to a decreased conversion of 89% (Table 6, entry 3), and resulted in an even lower conversion of 80% if a catalyst loading of 5.0 mol% was used (Table 6, entry 4). Due to these observations, further experiments were carried out with an increased pressure of synthetic air. Therefore, 40 bar of synthetic air were applied in the oxidation process which led to almost full conversion after 24 h (Table 6, entry 5). Remarkably, the same result could be accomplished, if a reduced amount of 2.5 mol% of the catalyst was used (Table 6, entry 6). However, reducing the catalyst loading to 1.0 mol% resulted in a decreased conversion of 83% (Table 6, entry 7).

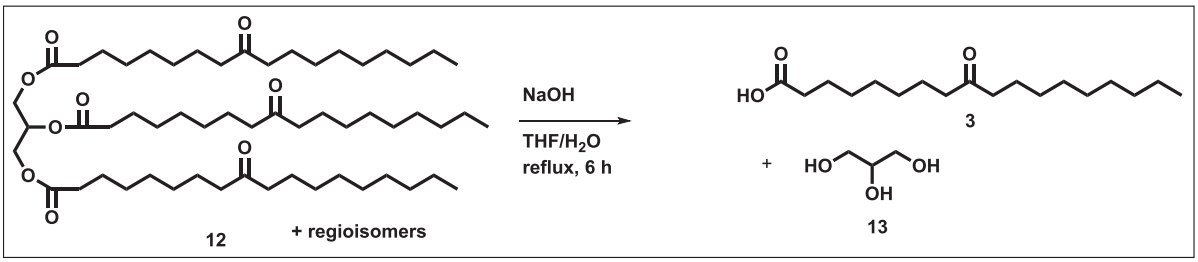
Table 6: Screening of the Wacker Oxidation of triglycerides using synthetic air.

Entry	DMA [mL]	H_2O [mL]	Cat. [mol%]	p [bar]	Conversion [b] [%]
1	5.5	0.5	10	30	51 [a]
2	5.5	0.5	10	30	96
3	2.75	0.25	10	30	89
4	2.75	0.25	5.0	30	80
5	2.75	0.25	5.0	40	97
6	2.75	0.25	2.5	40	96
7	2.75	0.25	1.0	40	83

Conditions: 1.0 mmol **11**, 100 °C, 24 h; a) 70 °C; b) Conversion was determined by ^{1}H NMR analysis.

At the beginning of this study, the catalytic oxyfunctionalization of free fatty acids was investigated, however their direct oxidation was only accomplished with very low conversion (< 10%). An alternative synthesis approach towards keto fatty acids was established by saponification of poly-ketone **12** (Scheme 37*).* For this purpose, **12** was

dissolved in a THF/water mixture with sodium hydroxide as base. After six hours under reflux conditions and a subsequent washing process, the desired keto fatty acid **3** was obtained as white solid (Figure 8). Due to 2.6 ketone units/molecule **12** (determined by ^{1}H NMR analysis) the product represented a mixture of **3** (87%) and other saturated fatty acids (13%).



Scheme 37: Synthesis of keto fatty acid **3** by saponification of **12**.

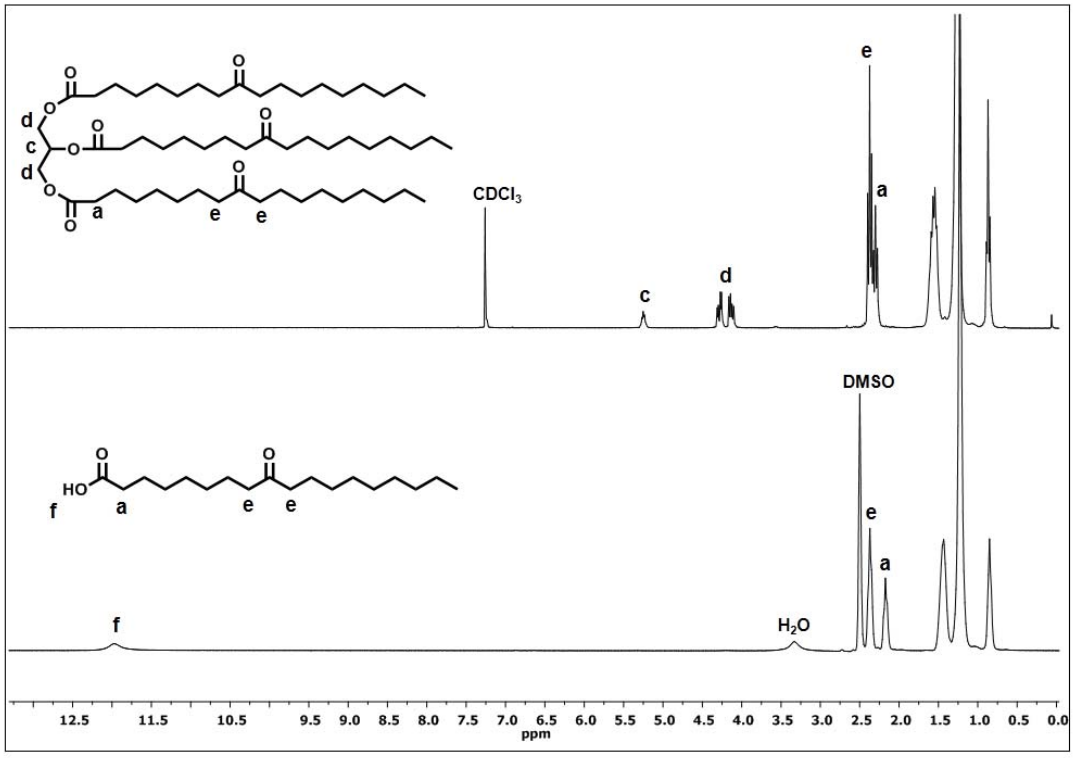
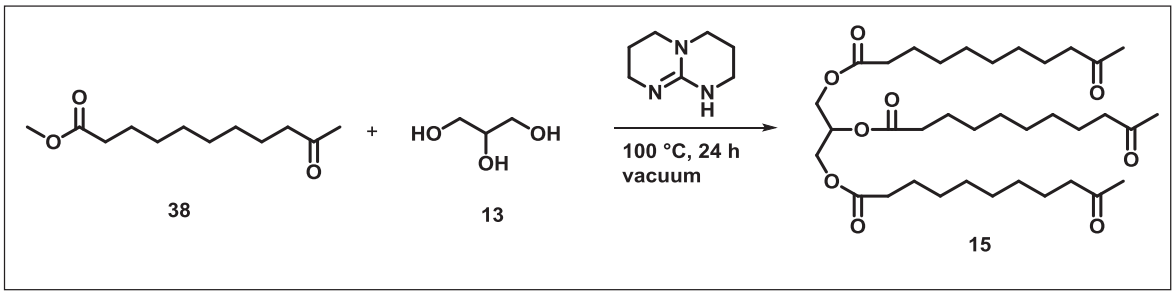


Figure 8: ^{1}H NMR of **12** (top) and thereof derived keto fatty acid **3** (bottom).

4.1.4 Homogenous poly-keto triglycerides

The naturally occurring triglycerides are always composed of saturated and unsaturated fatty acids, even if specifically cultivated triglycerides such as HOSO **11** with an increased amount of mono-unsaturated fatty acids (> 80%) are employed. Thus, the obtained poly-keto triglycerides always constituted a mixture of oxyfunctionalized and unmodified fatty acids. The goal of further investigations was thus the synthesis of more defined poly-keto triyglcerides (Scheme 38). Therefore, keto-FAMEs derived from methyl oleate **7**, methyl erucate **8** and methyl 10-undecenoate **37** were used in a transesterification process with glycerol and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as catalyst. The reactions were carried out under vacuum for 24 h at 100 °C. Subsequently, the crude reaction mixtures were purified by flash column chromatography, due to the formation of di- and tri-substituted products. This can be explained by a lower reactivity of the secondary alcohol compared to the primary alcohol groups of glycerol. Moreover, the functionalization of both primary alcohol groups, resulted in an increased sterically hindrance at the secondary position. Poly-keto trigylcerides **14** - **16** were obtained as white solids in moderate yields of 67%, 60% and 76%, respectively (Table 7, entry 1-3).



Scheme 38: Synthesis of homogenous poly-keto triglyceride **15** derived from keto-FAME **38**.

Table 7: Synthesis of homogenous poly-keto triglycerides

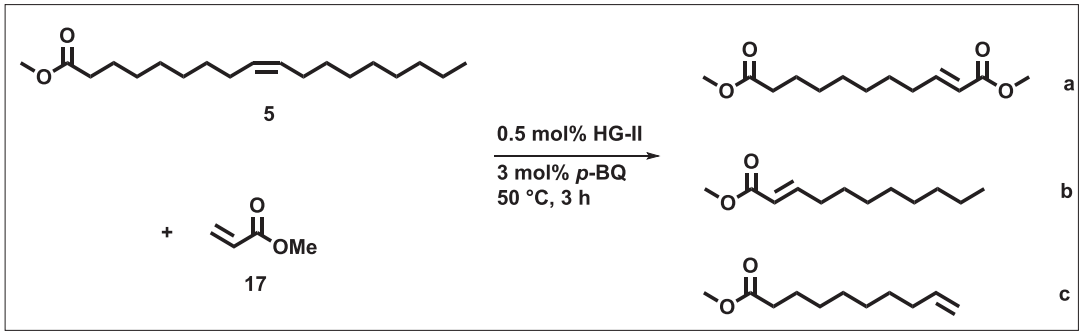
Entry	Keto-FAME	Poly-ketone	Yield [%]
1	**7** (C18)	**14**	67
2	**8** (C22)	**15**	60
3	**38** (C11)	**16**	76

Conditions: 4.00 g (43.3. mmol, 1.00 eq.), 136.0 mmol (3.15 eq.) keto-FAME, 100 °C, 24 h, vacuum.

4.1.5 Investigation of isomerization side-reaction

The applied modified Wacker Oxidation process has proven to be an efficient oxidation tool for the synthesis of keto fatty acid derivatives. However, the remarkable efficiency is based on a palladium catalyst, which is well-known to initiate isomerization of double bonds. This process followed by oxidation would lead to the formation of various keto fatty acid regioisomers. In order to investigate the possible side-reaction, two synthesis strategies were studied in detail.

First approach: The Wacker oxidation of **5** was studied under argon atmosphere at 70 °C and 100 °C, but otherwise identical reaction conditions. ^{1}H NMR analysis of the crude mixtures revealed that no oxidation of the double bond occurred during the reaction. Subsequently, the products from the reaction at 70 °C (**5a**), and the reaction at 100 °C (**5b**) were isolated by flash column chromatography in order to remove the catalyst-solvent mixture. The obtained substances **5a, b** were further used in a cross-metathesis reaction with an excess of 5.0 eq. of methyl methacrylate **17** and 0.5 mol% Hoveyda-Grubbs II (HG-II) as catalyst. Moreover, 3.0 mol% *p*-benzoquinone (*p*-BQ) were used to avoid isomerization by the ruthenium catalyst. Additionally, a cross-metathesis reaction with **5** was performed, which has not been employed to the Wacker oxidation process before, and used as reference to compare the product selectivity (Scheme 39).



Scheme 39: Cross-metathesis of **5** with methyl methacrylate **17**.

The reactions were carried out for three hours at 50 °C and were subsequently analyzed by GC-MS (Figure 9). Thereby, an identical product selectivity was obtained for all three reactions (Scheme 39, Figure 9), which confirmed that double bond isomerization did not occur during the Wacker oxidation process, at least in the absence of oxygen.

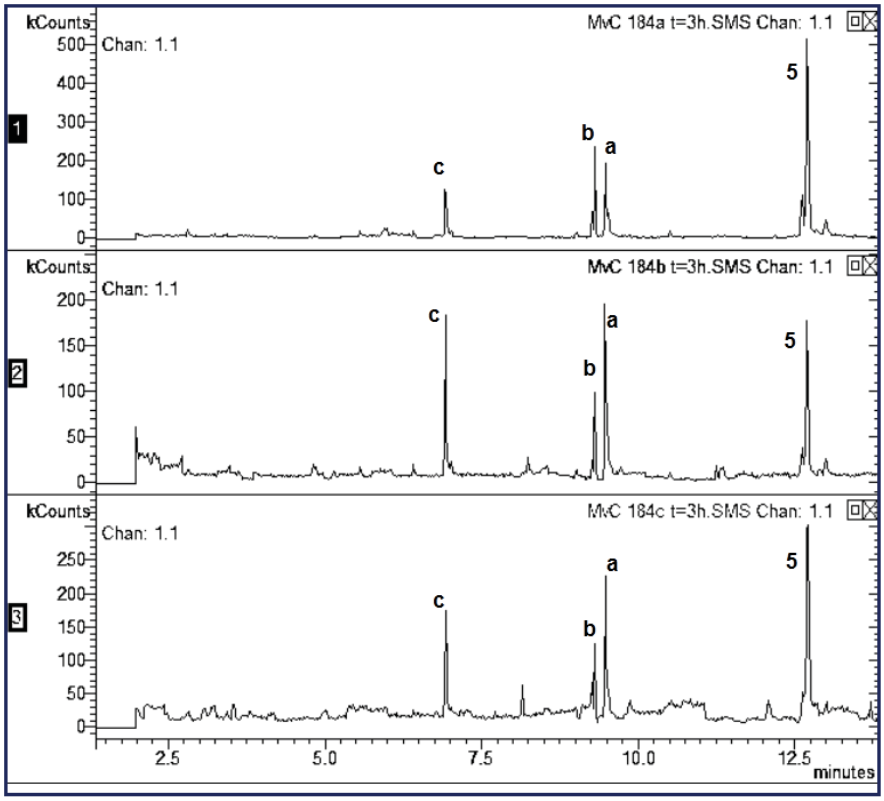
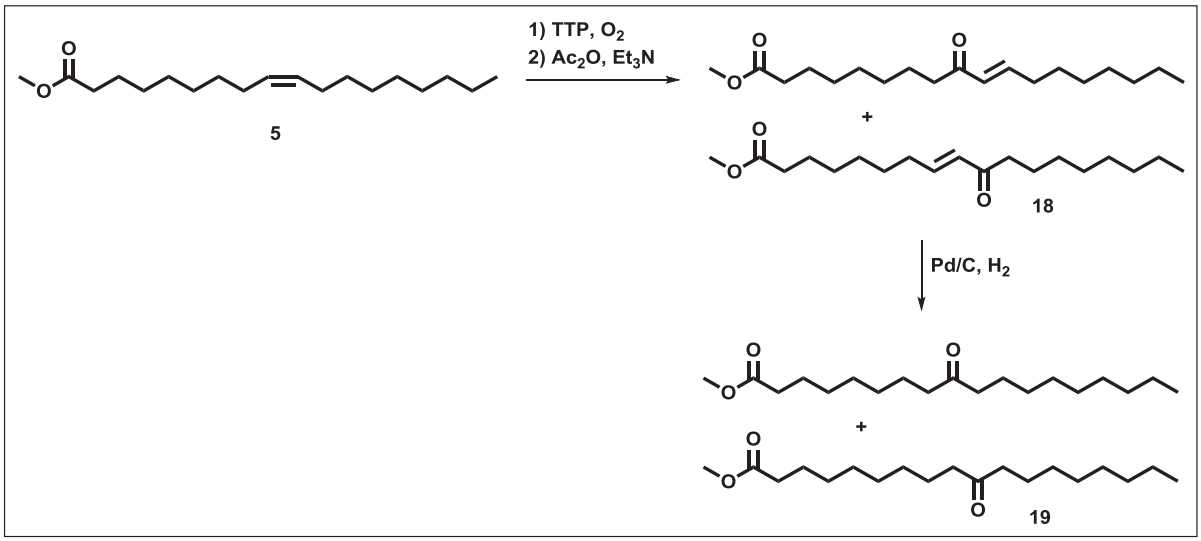


Figure 9: Product selectivity of the cross-metathesis reaction of reference **5** (top), **5a** (middle), and **5b** (bottom) with methyl methacrylate **17**.

Second approach: A two-step synthesis protocol of a photoperoxidation – hydrogenation process enabled the selective oxidation of **5**, which led to two keto-FAME regioisomers that are also expected to be formed by the Wacker oxidation process (Scheme 8). For this purpose, methyl oleate **5** was dissolved in dichloromethane with tetraphenylporphyrin (TPP) as photosensitizer, while a gentle stream of oxygen was bubbled through the solution. In the presence of visible light, TTP enabled the generation of singulett oxygen that subsequently underwent a Schenk Ene reaction with **5**, resulting in an allylic hydroperoxide intermediate. The addition of acetic anhydride (Ac_2O) and triethylamine (Et_3N) led to the desired enone derivative **18**, obtained as mixture of two regioisomers, which was obtained as yellowish liquid in 70% yield after column chromatography. The subsequent hydrogenation of **18** using palladium on charcoal enabled the formation of the corresponding keto-FAME **19** in quantitative yield (Scheme 40).



Scheme 40: Synthesis of keto-FAME **19** via photoperoxidation/hydrogenation process.

The synthesized keto-FAME **19** was used as reference for MS-MS measurements to compare the fragmentation process with keto-FAME **7**, which was obtained by the Wacker oxidation process. First, the ESI-MS spectra of both keto-FAMEs were recorded, whereby the main peak (313.2 g/mol) represents the mass of the $[M+H^+]$ ion (Figure 10, Figure 11). In addition, the mass of the $[M+Na^+]$ adduct at 335.2 g/mol was found in the spectrum of keto-FAME **19** (Figure 10).

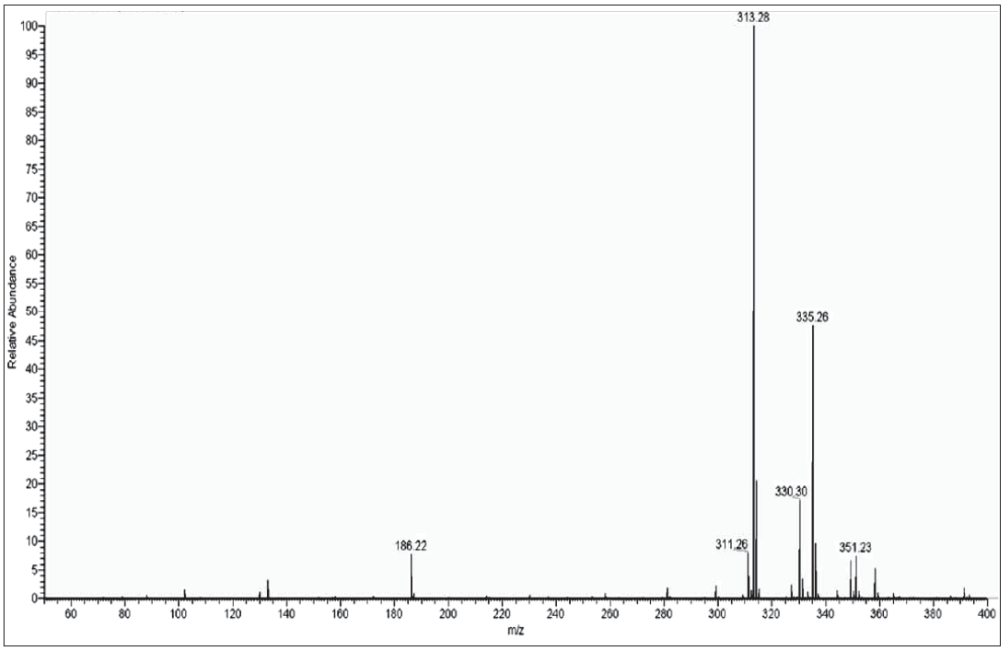


Figure 10: ESI-MS spectrum of keto-FAME **19**.

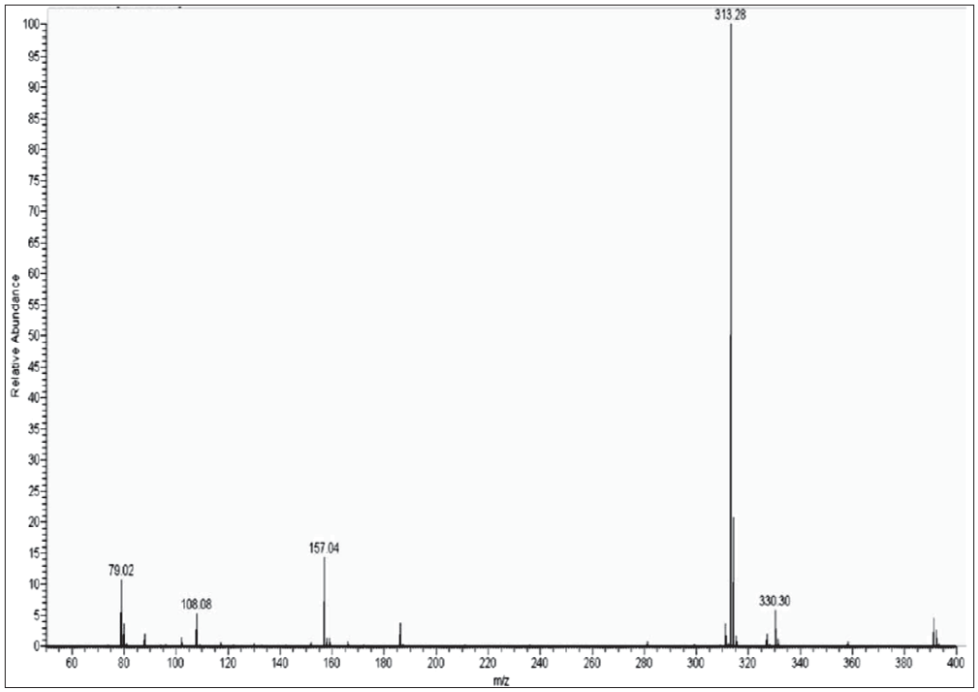


Figure 11: ESI-MS spectrum of keto-FAME **7**.

In a second step, the mass of the [M+H$^+$] ion was isolated using an orbitrap (ion trap mass analyzer) and subsequently fragmented, whereby identical fragmentation pattern were obtained (Figure 12, Figure 13). The results confirmed that double bond isomerization did not occur during the Wacker oxidation process, and thus are in good agreement with the observations of the first approach.

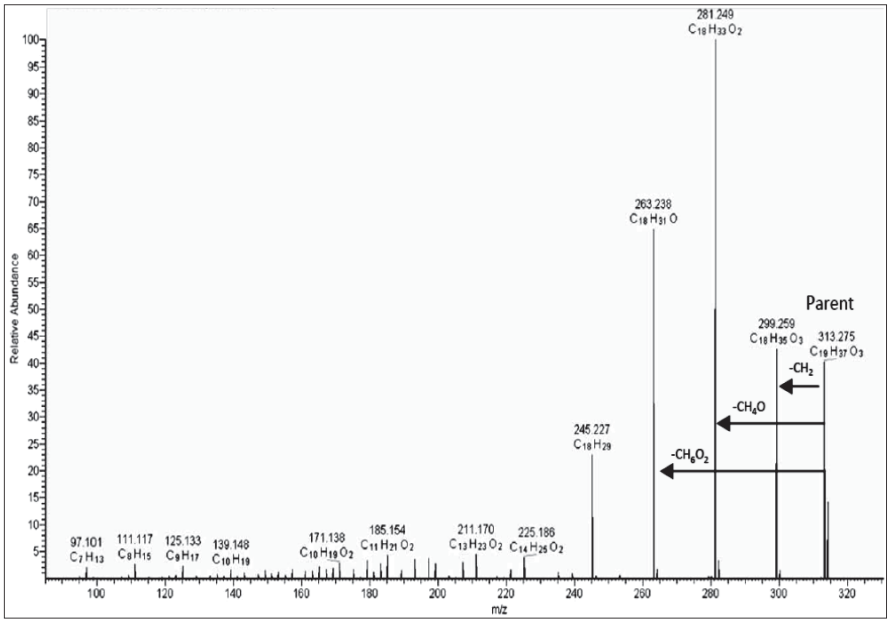


Figure 12: ESI-MS/MS spectrum of the single charged species at 313.28 m/z of keto-FAME **19**.

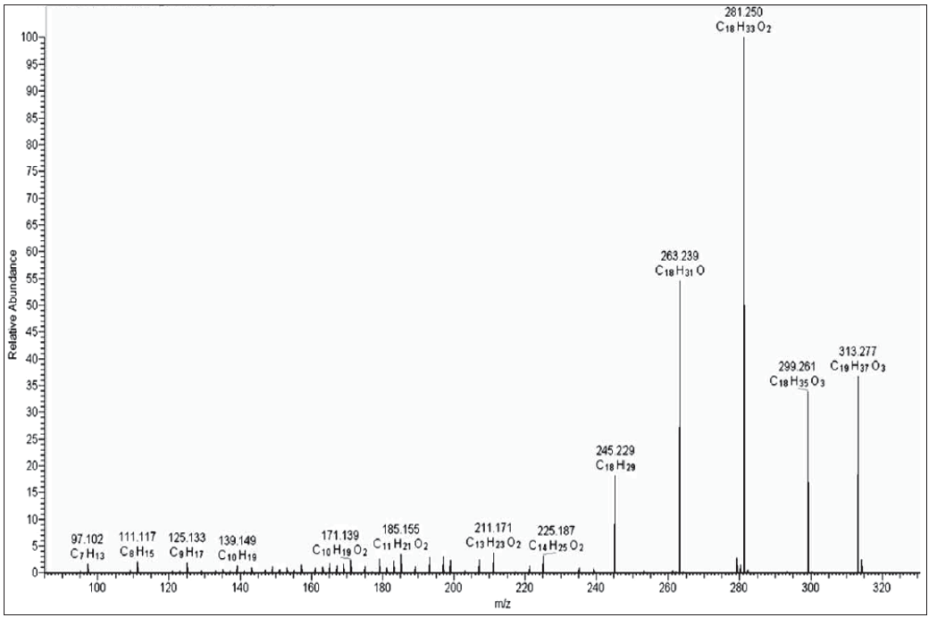
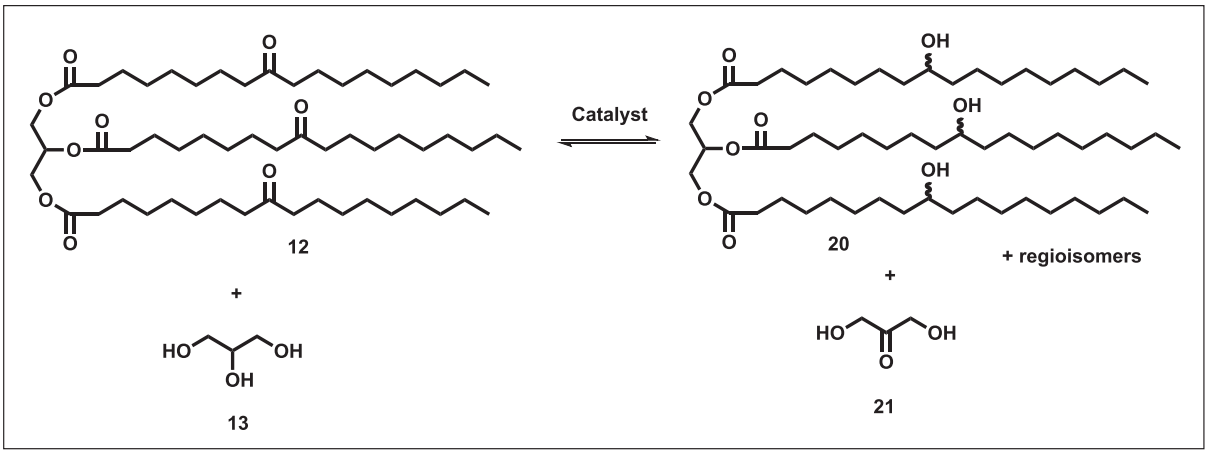


Figure 13: ESI-MS/MS spectrum of the single charged species at 313.28 m/z of keto-FAME **7**.

4.2 Follow-up chemistry of keto-FAMEs

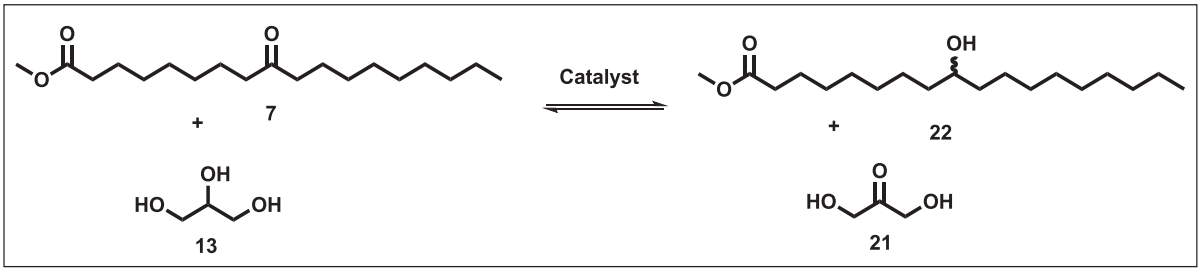
4.2.1 Transfer hydrogenation using keto-FAMEs

In this section, keto fatty acid derivatives were investigated in catalytic transfer hydrogenation processes, which allow access to the corresponding hydroxy derivatives. The major goal of this study was to develop a sustainable synthesis protocol using poly-ketone **12** and glycerol **13** as hydrogen donor. Thus, poly-hydroxy triglycerides **20** can be obtained, which are important starting materials for the synthesis of polyurethanes. Moreover, dihydroxyacetone **21**, which is formed as by-product, exhibits an interesting monomer for the synthesis of renewable based polyester (Scheme 41).



Scheme 41: Synthesis of poly-hydroxy triglycerides **20**.

We started our investigations with a test system based on keto-FAME **7**, whereby the optimized reaction conditions will be transferred at a later point to poly-ketone **12** (Scheme 42).



Scheme 42: Transferhydrogenation process of keto-FAME **7** using glycerol **13**.

For this purpose, ruthenium-based catalysts **23** and **24** were used, which are established catalysts in transfer hydrogenation processes (Figure 14). The reactions were carried out in the presence of sodium hydroxide (NaOH) and/or potassium hydroxide (KOH) as base in a temperature range between 70 °C and 100 °C (Table 8, entry 1-4). However, the formation of the corresponding hydroxy-FAME **22** could not be accomplished by the applied conditions. The utilization of ultrasound irradiation led to an improved miscibility of the starting materials with the applied catalyst, but the desired product could not be obtained (Table 8, entry 5, 6). The same result was achieved, if DMA was used as co-solvent (Table 8, entry 7, 8).

Table 8: Screening of the transferhydrogenation process of **7** with glycerol **13.**

Entry	Glycerol [g]	Cat.	NaOH [mol%]	KOH [mol%]	T [°C]	t [h]	Yield [%]
1[a)]	1.8	**23**	-	15	70	24	-
2	1.8	**23**	2.0	2.0	70	3	-
3	1.8	**24**	2.0	2.0	70	3	-
4	4.0	**23**	-	10	100	24	-
5[b)]	4.0	**23**	-	5.0	80	6	-
6[b)]	4.0	**24**	-	-	80	6	-
7[c)]	1.6	**23**	-	-	70	24	-
8[c)]	1.6	**24**	-	-	70	24	-

Conditions: 1.0 mmol **7**, 5.0 mol% catalyst; a) 10 mol% catalyst; b) ultrasound irradiation; c) 0.2 mL DMA.

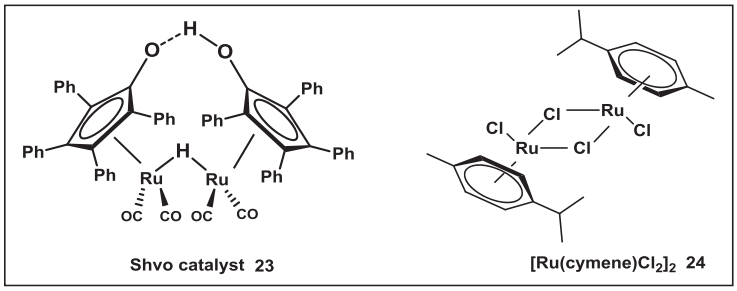
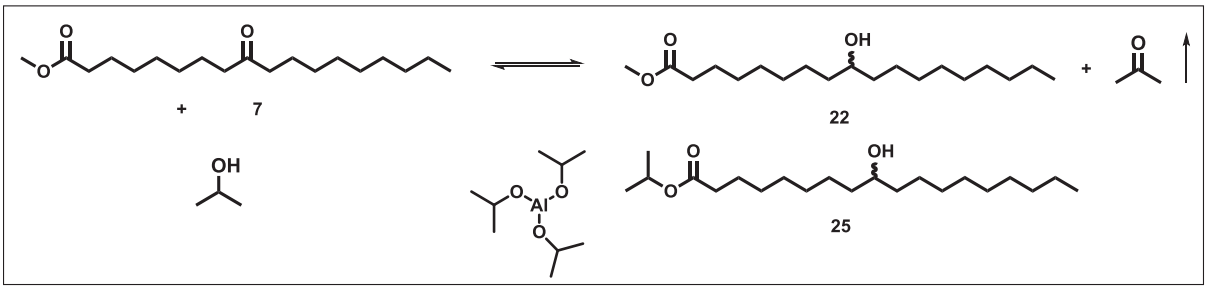


Figure 14: Ruthenium catalysts for transfer hydrogenation processes.

Due to these observations, the Meerwein-Ponndorf-Verley-reduction (MPV-reduction) was investigated as an alternative to the ruthenium-catalyzed transfer hydrogenation process. Therefore, **7** was used in the presence of aluminium isopropoxide and 2-propanol as hydrogen donor (Scheme 43). Acetone, which is formed during the process, can be removed by distillation, thus allowing a shift of the equilibrium to the product side. The MPV-reduction enabled the synthesis of hydroxy-FAME **22** in moderate yields of 50 – 57% (Table 9, entry 1-3). However, transesterification of **7** was observed as side reaction, yielding a product mixture of methyl- and propyl-ester (**22, 25**). Thus, the reaction protocol could not be used for the synthesis of poly-hydroxy triglycerides.



Scheme 43: MPV-reduction of keto-FAME **7**.

Table 9: MPV-reduction of keto-FAME **7**.

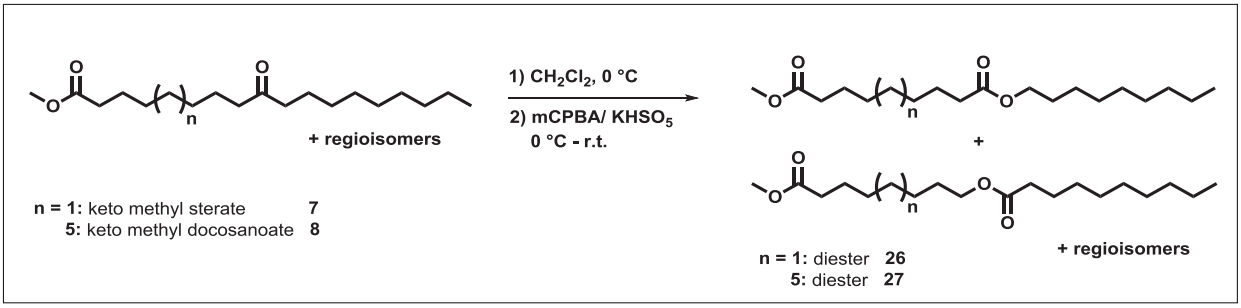
Entry	2-propanol [mL]	T [°C]	Yield [%]
1	10	65	50
2	10	75	55
3	5.0	75	57

Conditions: 1.0 mmol **7**, 10 mol% aluminium isopropoxide, 24 h.

4.2.2 Synthesis of platform chemicals

In this section, the Baeyer-Villiger-oxidation of keto-FAMEs was studied in order to synthesize diester derivatives, which allow access to various renewable platform chemicals (e.g. hydroxy-ester, fatty alcohols).

In a first approach, **7** was used as model substance in the presence overstoichiometric amounts of *m*-chloroperbenzoicacid (*m*-CPBA) or potassium peroxymonosulfate ($KHSO_5$) as oxidation agent (OA) and dichloromethane as solvent (Scheme 44).



Scheme 44: Baeyer-Villiger-oxidation of keto-FAMEs.

We started our investigations with *m*-CPBA as oxidation agent for the synthesis of diester **26** derived from keto-FAME **7** (Scheme 44). Thin layer chromatography (TLC) indicated the formation of a new product after 24 hours at room temperature. ^{1}H NMR analysis of the crude reaction mixture confirmed 36% conversion of **7** (Table 10, entry 1). The insertion of oxygen during the oxidation process occurs from both sides, and thus the product was obtained as mixture of regioisomers (Scheme 44). Due to the low conversion, the reaction was carried out for six more days at room temperature, resulting in a conversion of 96% (Table 10, entry 1; Figure 15). Furthermore, keto-FAME **8** was employed to the oxidation process using the aforementioned reaction conditions, which led to 95% conversion after seven days (Table 10, entry 2; Figure 15). If the reaction was performed with $KHSO_5$ as oxidation agent no conversion was achieved (Table 10, entry 3). Moreover, an enzymatic approach was investigated in order to introduce a more environmentally-friendly oxidation process. Therefore, hydrogen peroxide (H_2O_2) and octanoic acid were used, which form in the presence of novozyme P435 *in situ* the

peracidic acid. The reactions were carried out in concentrations of 0.1, 0.5 and 1.0 mol/L (Table 10, entry 4 – 6). However, TLC and ^{1}H NMR analysis of the crude mixture revealed that only the starting material was present after 24 hours at 40 °C.

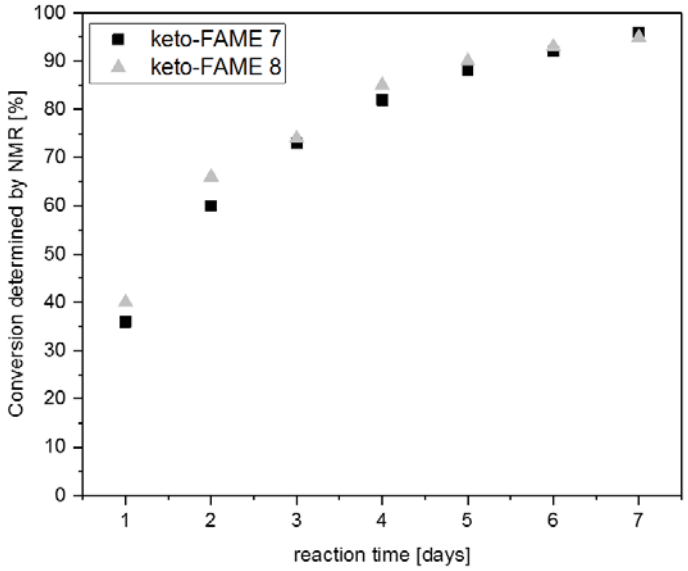


Figure 15: Baeyer-Villiger-oxidation of keto-FAMEs **7** and **8** using *m*-CPBA.

Table 10: Baeyer-Villiger-oxidation of keto-FAMEs.

Entry	Keto-FAME	OA [a]	c [mol/L]	Conversion [c]		
				1 d	**3 d**	**7 d**
1	**7**	*m*-CPBA	0.33	36	73	96
2	**8**	*m*-CPBA	0.33	40	74	95
3	**7**	$KHSO_5$	0.33	-		
4 [b]	**7**	H_2O_2	0.10	-		
5 [b]	**7**	H_2O_2	0.50	-		
6 [b]	**7**	H_2O_2	1.00	-		

Conditions: 1.0 mmol keto-FAME, 1.5 eq. OA, 3.0 mL CH_2Cl_2, r.t.; a) OA – oxidation agent; b) 1.0 eq. octanoic acid, 20 wt% novozyme P435, 1.0 mL toluene, 1.8 eq. H_2O_2, 40 °C, 24 h; c) Conversion was determined by 1H NMR analysis.

Due to the aforementioned results, the Baeyer-Villiger-oxidation with *m*-CPBA as oxidation agent was further investigated and optimized with respect to sustainability. For this purpose, the amount of solvent (CH_2Cl_2) was successively reduced from 3.0 mL to 0.5 mL, which resulted in a significant increase of conversion (Table 11, entry 1 – 3). Using 0.5 mL CH_2Cl_2 led to a conversion of 70%, which almost corresponds to a doubling of the conversion within the same reaction time (Table 11, entry 3). Furthermore, the amount of the needed stoichiometric oxidation agent was reduced to 1.1 eq. However, the reactions using 1.1.eq *m*-CPBA in the presence of 1.0 mL and 0.5 mL of CH_2Cl_2, resulted in a decreased conversion of 53% and 56%, respectively (Table 11, entry 4, 5). The most promising reactions conditions with 0.5 mL CH_2Cl_2 and 1.5 eq. *m*-CPBA were employed for the diester synthesis. Thus, the diester mixture **26** was obtained as white solid in 70% yield after 72 h (Table 11, entry 6; Figure 16). The same reactions conditions were applied for the synthesis of **27** using keto-FAME **8** as starting material, which resulted in yield of 80% (Table 11, entry 7).

Table 11: Screening of the Baeyer-Villiger-oxidation using **7.**

Entry	CH_2Cl_2 [mL]	*m*-CPBA [eq.]	Conversion [%] [c]	Yield [%]
1	2.0	1.5	53	n.i.
2	1.0	1.5	66	n.i.
3	0.5	1.5	70	n.i.
4	1.0	1.1	53	n.i.
5	0.5	1.1	56	n.i.
6 [a]	0.5	1.5	92	70
7 [b]	0.5	1.5	95	80

Conditions: 1.0 mmol **7**, 24 h, r.t.; a) 1.0 mmol keto-FAME **7**, 72 h; b) 1.0 mmol keto-FAME **8**, 72 h; c) Conversion was determined by ^{1}H NMR analysis; n.i. – not isolated.

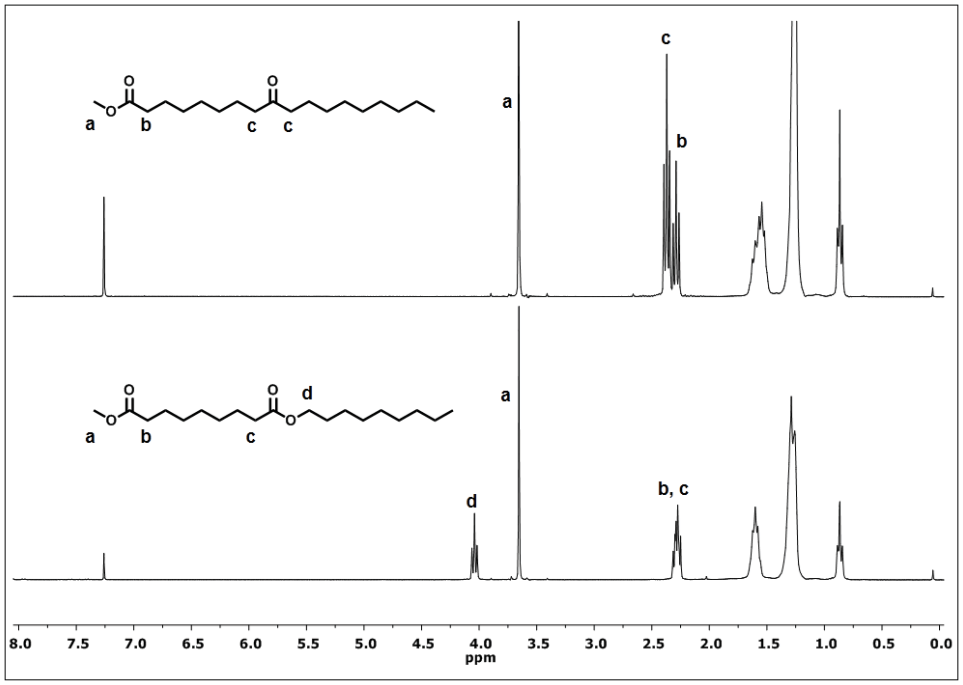
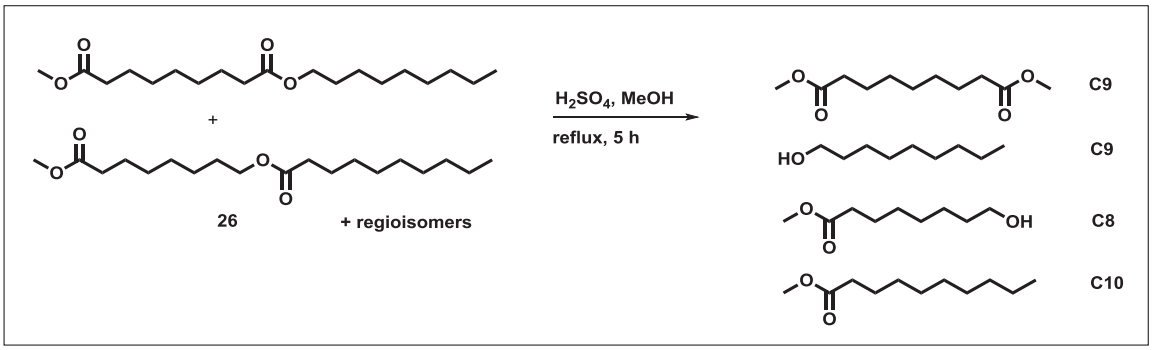


Figure 16: ^{1}H NMR of keto-FAME **7** (top) and derived diester **26** (bottom).

The obtained diesters were further investigated for the synthesis of various platform chemicals. Therefore, **26** was used in an acid-catalyzed transesterification process with methanol, whereby full conversion was obtained after five hours under reflux conditions. This concept allows access to shorter diester, ester, hydroxy-ester as well as fatty alcohols (Scheme 45). The obtained product mixture was analyzed by GC-MS measurement, but was not further purified by column chromatography, since the obtained products are well known and readily available (Figure 17).



Scheme 45: Transesterification of diester **26** with methanol.

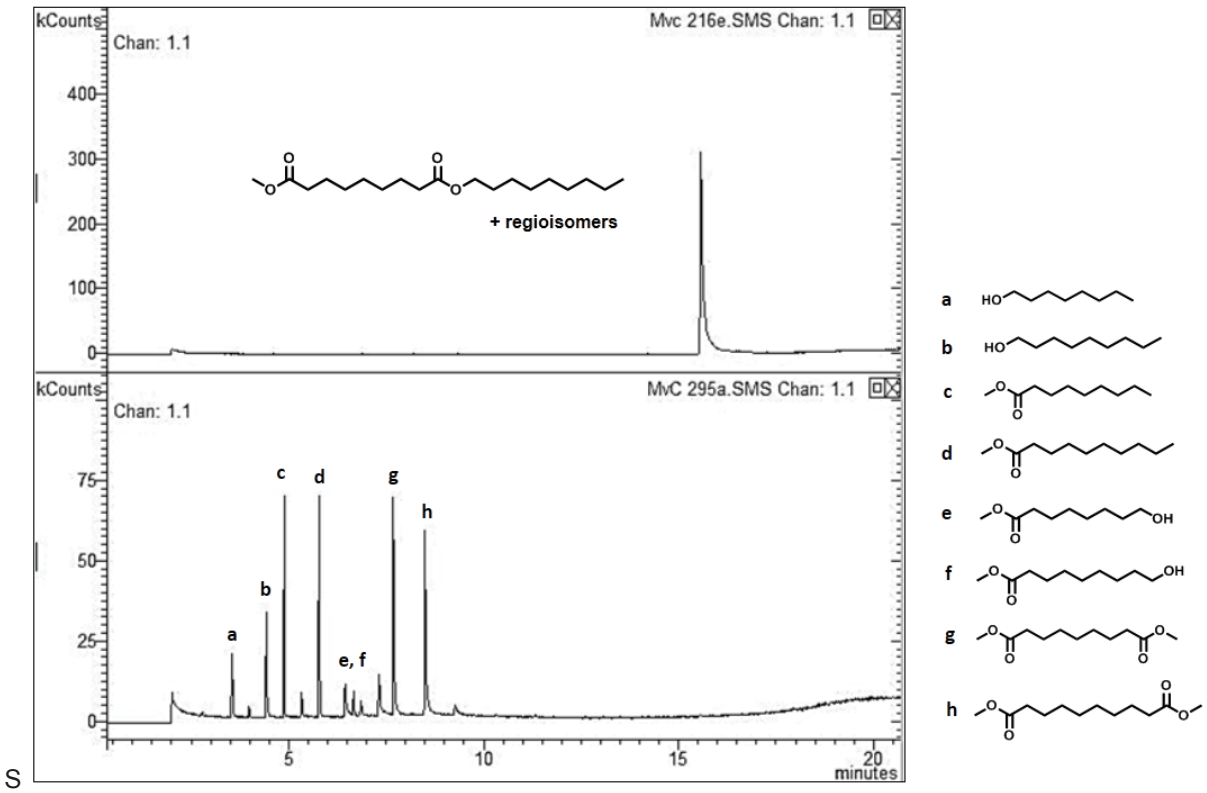


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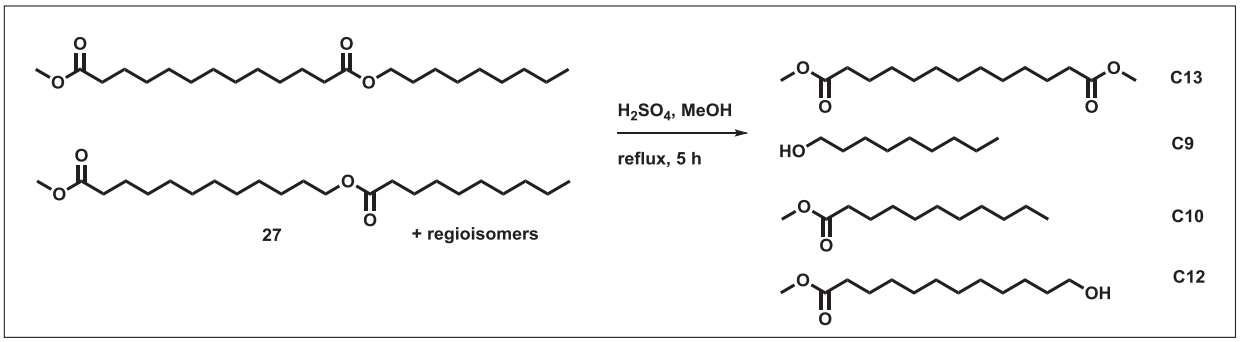
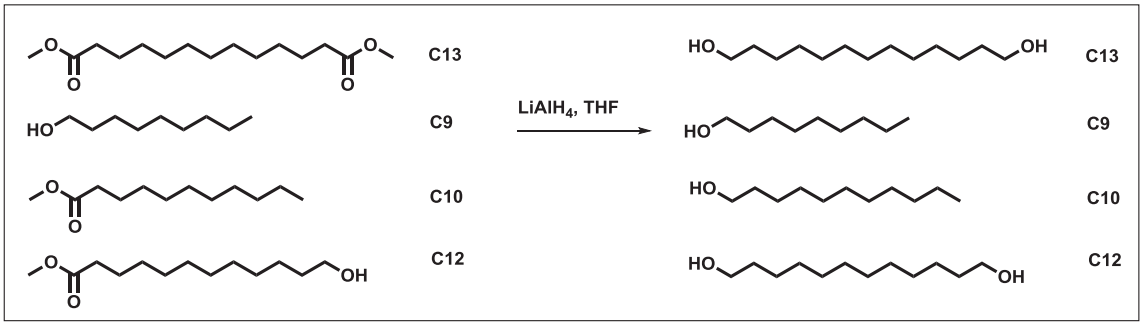
Figure 17: GC-MS chromatogram of diester **26** (top) and derived products after transesterification with methanol (bottom).

Moreover, the acid-catalyzed transesterification was carried out with diester **27** ot obtain products bearing a longer aliphatic chain (Scheme 46). The product mixture was analyzed by GC-MS, and subsequently used without further purification (Figure 18). The obtained product mixture of diester, ester, hydroxy-ester and fatty alcohols was studied in a reduction process in order to synthesize the corresponding mono- and dialcohol derivatives (Scheme 47). For this purpose, lithium aluminiumhydride was used as reducing agent. The resulting product mixture was analyzed by GC-MS, whereby the expected products could be identified (Figure 18). Further purification of the mono- and dialcohol mixture was not carried out, since these products are well known and readily available.



Scheme 46: Transesterification of diester **27** with methanol.



Scheme 47: Reduction of alcohol-ester mixture into mono- and dialcohols.

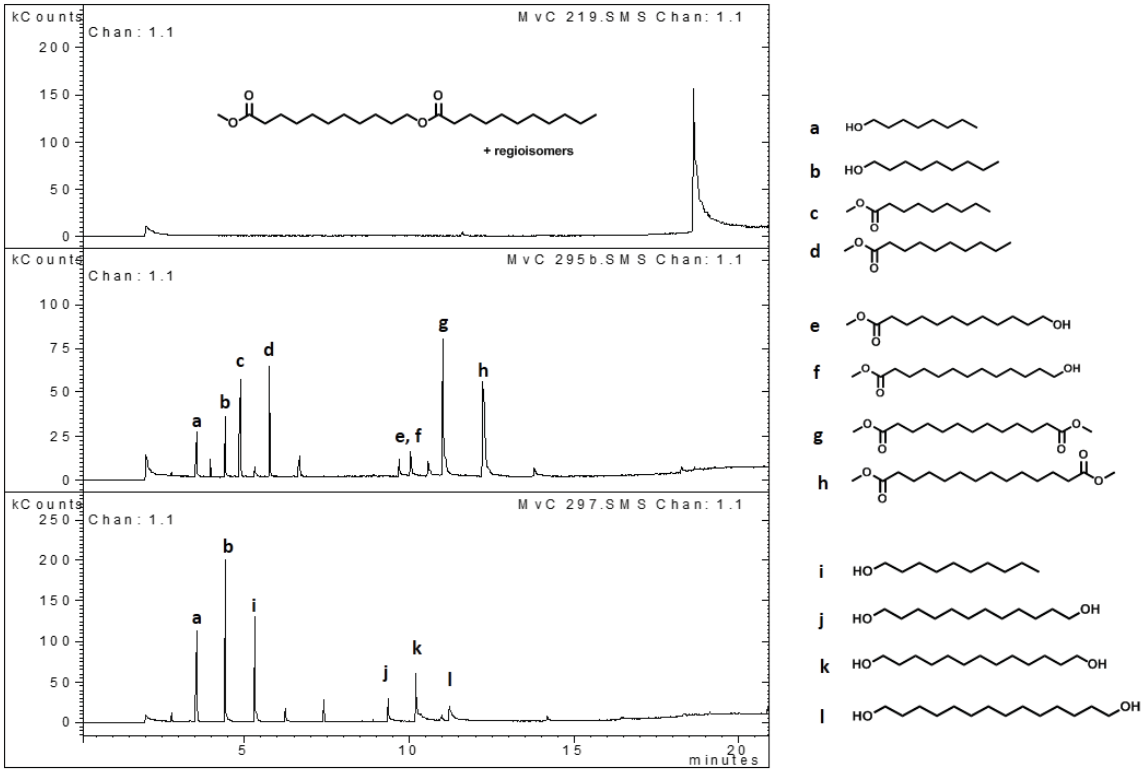


Figure 18: GC-MS chromatogram of diester **27** (top), after transesterification with methanol (middle) and after reduction (bottom).

4.2.3 Synthesis strategy of AB_2 – monomers

In this section, a novel synthesis strategy towards AB_2 monomers *via* self-metathesis-Wacker Oxidation reductive amination is described.

Self-metathesis (SM)

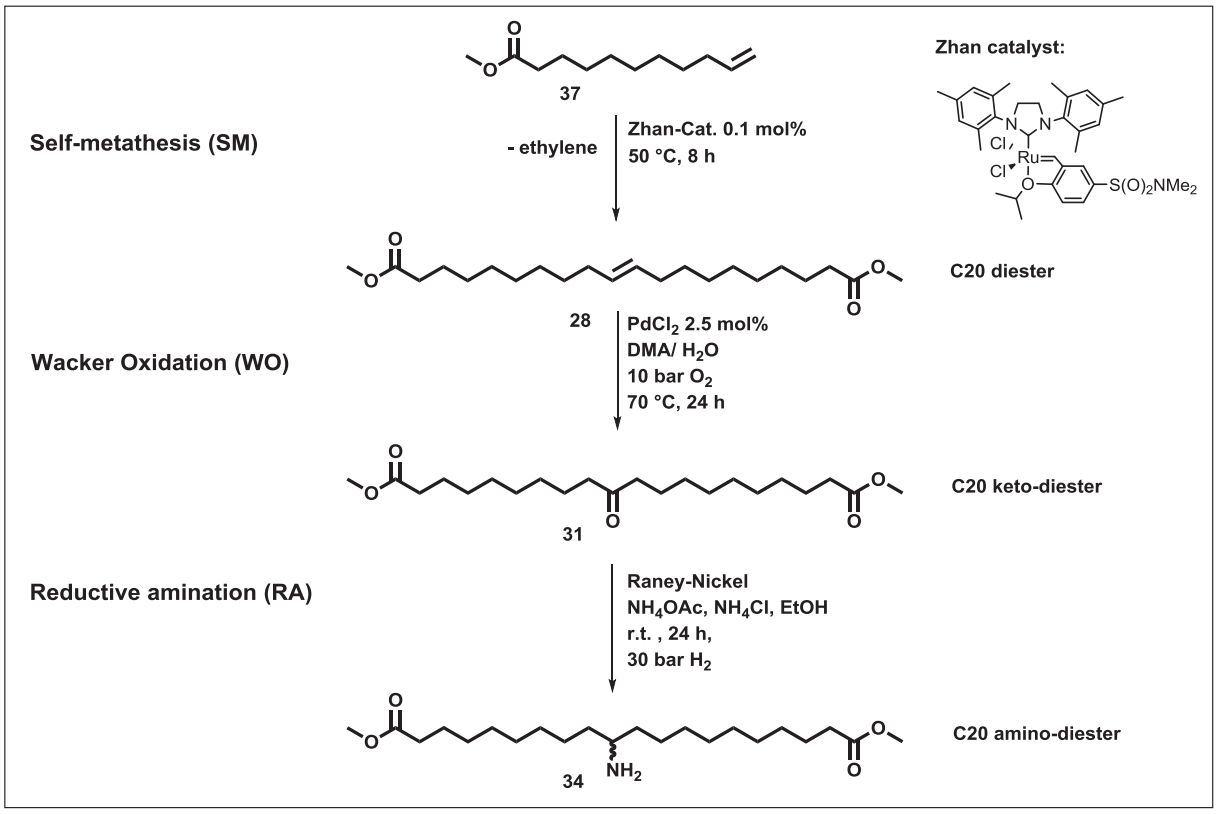
At first, the synthesis of diester *via* self-metathesis of FAMEs was investigated (Scheme 48). Therefore, **5**, **6** and **37** were used, which enabled the formation of three diesters due to different chain lengths and different position of the double bond. The self-metathesis was carried out in bulk at 50 °C using 0.1 mol% of Zhan-catalyst (Scheme 48). If, FAME **37** was employed to the reaction, a C20 diester **28** was obtained as white solid in 61% after column chromatography (Scheme 48, Table 12, entry 1). Moreover, methyl oleate **5** and methyl erucate **6** were used for the synthesis of C18 and C26 diester, which were obtained as white solids in 37% (**29**) and 26% (**30**) yield after column chromatography, respectively (Table 12, entry 2, 3). The significant decrease in yield can be explained by the formation of high boiling olefins as side products, which react with the desired product in an equilibrium reaction and cannot be easily removed. In contrast to that, the self-metathesis reaction of **37** led to ethylene as volatile side product, which can be removed by applying an argon stream, which results in an increased yield.

Wacker Oxidation (WO)

The catalytic oxyfunctionalization of the obtained diesters were investigated in further experiments. For this purpose, the optimized reaction conditions for the synthesis of keto-FAMEs were applied. Thus, keto-diesters were obtained as white solids in moderate yields of 70% (**31**), 69% (**32**) and 62% (**33**), respectively (Scheme 48, Table 12, entry 1-3). The aforementioned results could be improved by using an increased amount of catalyst as well as longer reactions times.

Reductive amination (RA)

Finally, the obtained keto-diesters were employed to a reductive amination process in order to synthesize the corresponding amino-diester (Scheme 48). The reactions were performed with Raney-Nickel as catalyst in the presence of ammonium acetate/ammonium chloride as ammonia source and 30 bar of hydrogen pressure. Thus, after 24 h at room temperature or 70 °C, the desired amino-diester were obtained as white solids in good yields of 92% (**34**), 85% (**35**) and 70% (**36**), respectively (Scheme 48; Table 12, entry 1-3).



Scheme 48: Synthesis strategy of AB_2 monomers derived from FAMEs via self-metathesis – Wacker oxidation – reductive amination (example using methyl 10-undecenoate **37**).

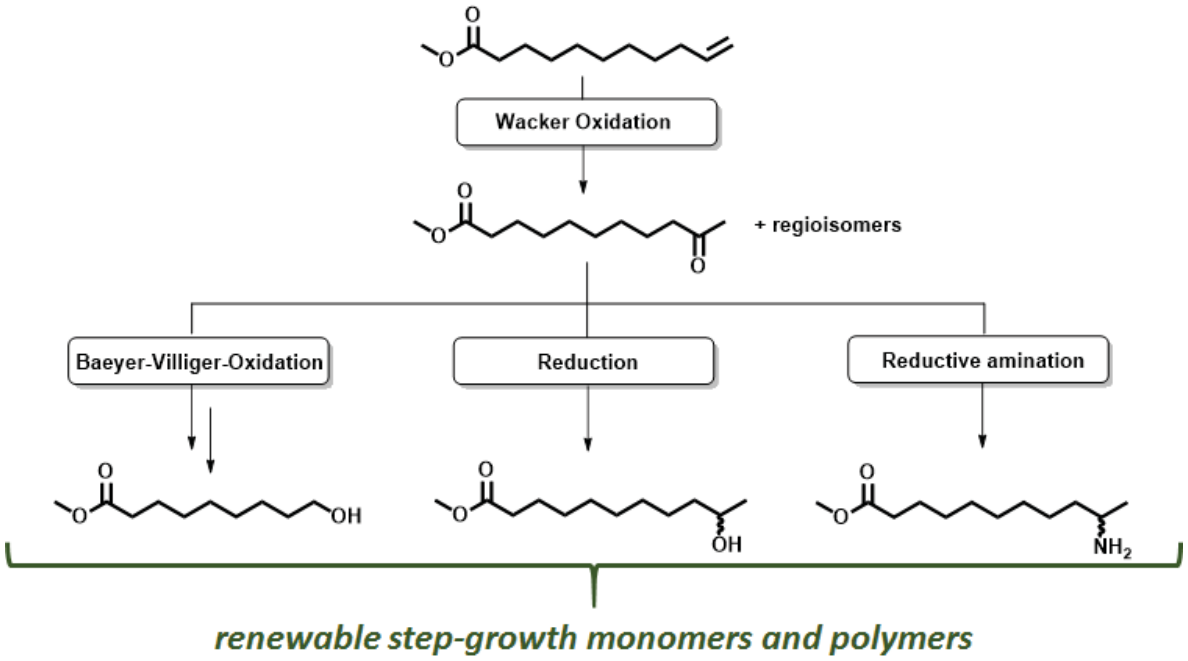
Table 12: Synthesis of AB_2 monomers using FAMEs.

Entry	FAME	Diester [%] [a)]	Keto-diester [%] [b)]	Amino-diester [%] [c)]
1	C11 (**37**)	61 (**28**)	70 (**31**)	92 (**34**)
2	C18 (**5**)	37 (**29**)	69 (**32**)	85 (**35**)
3	C22 (**6**)	26 (**30**)	62 (**33**)	70 (**36**) [d)]

Conditions: a) 10.0 g FAME, 0.3 mol% *p*-BQ, 0.10 mol% Zhan-catalyst, 50 °C, 8 hours; b) 4.00 mmol diester **28**-**30**, 2.50 mol% $PdCl_2$, 24.0 mL DMA/H_2O (v:v 9:1), 70 °C, 10 bar oxygen, 24 h; c) 2.00 mmol keto-diester **31**-**33**, 20.0 wt% Raney-Nickel, 4.00 eq. ammonium acetate, 1.00 eq. ammonium chloride, 30 bar hydrogen, 70 °C, 24 h; d) 70 °C; isolated yields after column chromatography.

4.2.4 Catalytic oxyfunctionalization of Methyl 10 – undecenoate for the synthesis of step-growth polymers

(This section was previously published by M. v. Czapiewski *et al*. in *Macromol. Chem. Phys.* **2017**, 218, 1700153. Copyright © 2017, with permission from John Wiley and Sons.)



Abstract

An efficient synthesis strategy for the preparation of two renewable polyesters and one renewable polyamide *via* catalytic oxyfunctionalization of methyl 10-undecenoate, a castor oil derived platform chemical, is described. The keto-fatty acid methyl ester (keto-FAME) was synthesized applying a co-catalyst-free Wacker Oxidation process using a high pressure reactor system. For this purpose, catalytic amounts of palladium chloride were used in the presence of a dimethylacetamide/water mixture and molecular oxygen as sole re-oxidant. The thus derived AB-monomers (hydroxy-esters, amine-ester) were synthesized from the obtained keto-FAME through Baeyer-Villiger-Oxidation and subsequent transesterification, reduction or reductive amination, respectively. The resulting AB step-growth monomers were then studied in homopolymerizations using TBD, DBU and titanium(IV) isopropoxide as transesterification catalyst, yielding polymers

with molecular weights (M_n) up to 15 kDa. The polyesters and the polyamide were carefully characterized by FTIR, SEC, ^{1}H–NMR spectroscopy and DSC analysis.

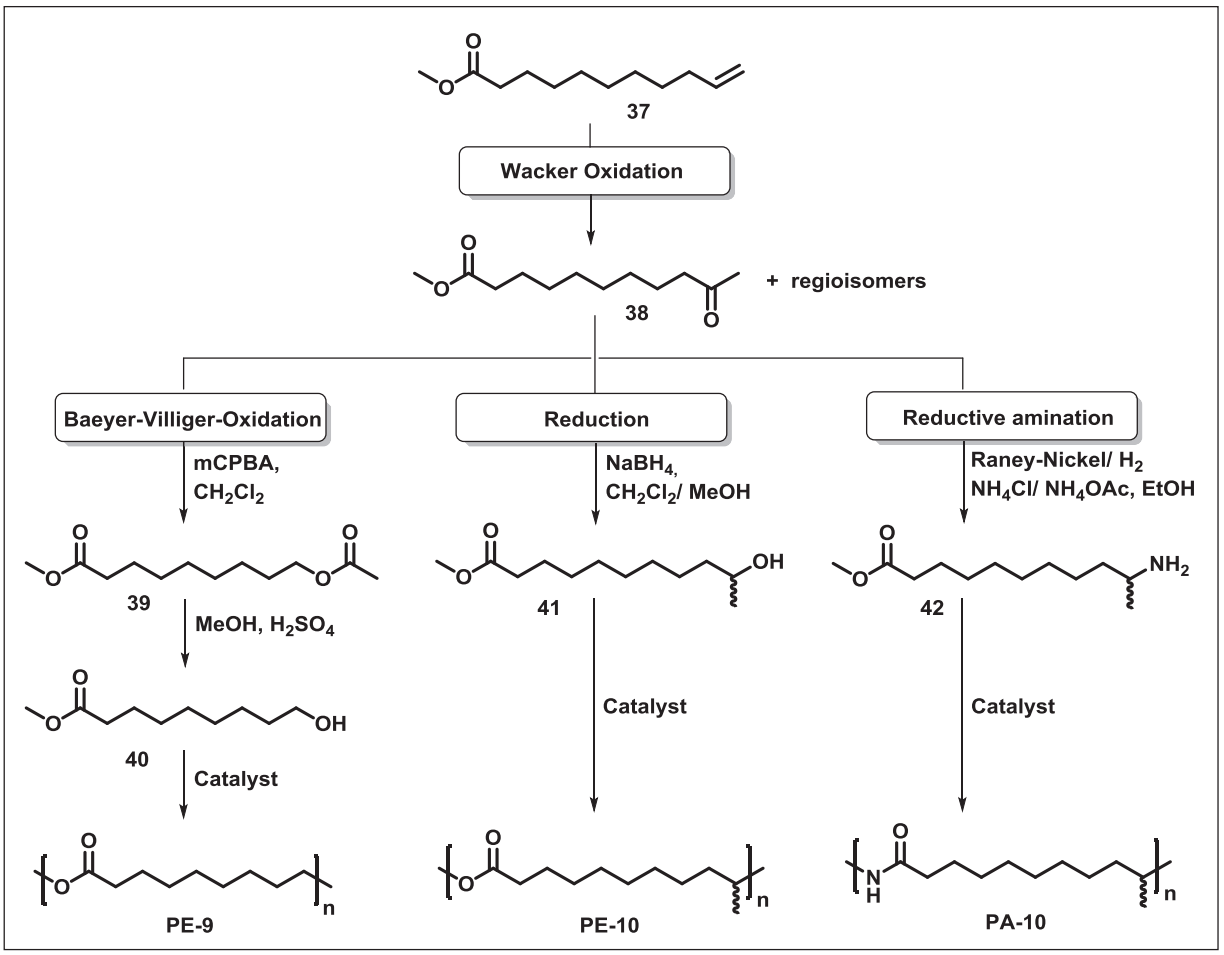
Introduction

The development of sustainable processes as well as the synthesis of monomers and polymers from renewable feedstocks is an important and currently intensively investigated research topic, mainly due to the depletion of crude oil and a generally increasing environmental awareness.[180-184] Among the various renewable resources, fats and oils gained widespread interest over the last decades, since these materials are easily accessible in large scale. Moreover, triglycerides, composed of fatty acids with various functional groups (i.e. double bonds, ester, hydroxyl or epoxy groups), are interesting raw materials for the synthesis of polymeric materials. Especially mono- and polyunsaturated fatty acids can readily be functionalized *via* epoxidation, hydroformylation, thiol-ene or metathesis reactions and subsequently further polymerized.[185-191] Castor oil, a non-edible oil with high content of ricinoleic acid (> 90%), offers many application possibilities due to its unsaturated structure bearing hydroxyl groups. Typical examples are the synthesis of polyurethanes, plasticizers and lubricants.[32] The thereof derived 10-undecenoic acid, which can be obtained selectively by pyrolysis of castor oil, is an important raw material for pharmaceuticals, cosmetics or parfume.[192,193] Moreover, the corresponding methyl-ester, methyl 10-undecenoate, was investigated as starting material for polymer synthesis after modification of the terminal double bond by self-/cross-metathesis, thiol-ene reaction or aminocarbonylation for the formation of AA- and AB-monomers.[194-196] In recent years, the aforementioned procedures have become of great interest in macromolecular chemistry for the synthesis of both monomers and the thereof derived polymers.[197-199] Advantageously, these reactions show a remarkable efficiency that goes along with high atom economy as well as high functional group tolerance. They represent good examples to highlight the importance of catalytic approaches for more sustainable and environmentally-friendly syntheses. The discovery of the Wacker oxidation process in 1959 at Wacker Chemie constitutes one of the most important catalytic oxidation routes of olefins at industrial scale. A tandem catalytic system of palladium(II) chloride and copper(II) chloride provides access to acetaldehyde from ethylene under aerobic conditions in an efficient manner.[49,50] The potential of the catalytic process was recognized

by many research groups and further investigated, thus leading to the development of versatile protocols over the last decades.[58] Very recently, Grubbs *et al.* reported a methodology for an efficient ketonization of internal alkenes. The oxidation was carried out at room temperature under atmospheric pressure using a palladium acetate/*p*-benzoquinone or an iron co-catalyst system.[56] An example for a Wacker oxidation procedure including fatty acid methyl esters (FAMEs) (i.e. methyl 10-undecenoate and methyl oleate) has already been described by Lam *et al*.[200] For this purpose, a palladium chloride/*p*-benzoquinone catalytic system was used in the presence of a THF/water mixture and ultrasound irradiation. However, a substitution of the copper co-catalyst by an excess of toxic *p*-benzoquinone only benefit the product selectivity, since chlorinated products can be avoided, but exhibit a drawback with regard to the principles of green chemistry.[201] Recently, Kaneda and colleagues reported about an efficient co-catalyst free Wacker oxidation process using molecular oxygen as sole re-oxidant.[202] Interestingly, the employed dimethylacetamide acts as active solvent, allowing a recycling of the catalyst-solvent system as well as the product isolation by simple extraction. Inspired by the aforementioned catalytic oxidation procedure, our group successfully synthesized ketone FAMEs from renewable methyl oleate and methyl erucate, which were subsequently modified into amino-esters for the synthesis of polyamides.[178] With such an efficient oxidation tool in hands, we have started our investigations by the synthesis of the ketone derived from methyl 10-undecenoate, which acts as platform chemical for the synthesis of renewable monomers and thereof derived polymers. For this purpose, the ketone FAME was modified *via* Baeyer-Villiger oxidation/transesterification, reduction and reductive amination to yield AB step-growth monomers (hydroxy-esters, amino-ester) readily employed for homopolymerizations.

Results and Discussion

The aim of this investigation is the catalytic oxyfunctionalization of renewable methyl 10-undecenoate **37** in order to synthesize the corresponding methyl-ketone derivative **38**, which is used as precursor for the synthesis of AB step-growth monomers and the thereof derived polymers (Scheme 49).



Scheme 49: Reaction pathways to renewable polymers derived from methyl 10-unedecenoate.

Monomer synthesis

The co-catalyst-free Wacker oxidation process, an established convenient protocol for the synthesis of oxo-FAMEs derived from methyl oleate and methyl erucate,[178] was applied to **37**. The use of 5.0 mol% palladium chloride in a dimethylacetamide/water solvent mixture with 10 bars of oxygen pressure led to full conversion of **37** after 24 hours at 70 °C (Table 13, entry 1). ^{1}H-NMR analysis of the crude reaction mixture revealed that the desired product **38** was formed in 86% selectivity; 14% of regioisomers were also produced due to double bond isomerization during the catalytic process. The oxidation on C-11 leading to an aldehyde was not observed. With regard to a more environmentally-friendly oxidation process, the amount of catalyst, amount of solvent as well as the influence of temperature were investigated to yield a maximum conversion and product selectivity. The first optimization step was carried out by using half of the amount of solvents (Table 13, entry 2). No significant difference, both in conversion and product selectivity, was observed. A reduced catalyst loading of 2.5 mol% led to the same observation (Table 13, entry 3). When the reaction was performed at 50 °C, full conversion was still achieved, but a slightly decreased selectivity from 85% to 78% was observed (Table 13, entry 5). Conducting the catalytic oxidation of **37** at room temperature led to 56% conversion, whereby the selectivity dropped to 69% of **38** (Table 13, entry 5). A decrease of the catalyst loading to 2.0 mol% still led to full conversion and a selectivity of 82% of the methyl ketone for a reaction performed at 70 °C (Table 13, entry 6). However, further reducing the amount of palladium chloride to 1.0 mol% decreased the conversion as well as the selectivity (Table 13, entry 7). The best results of the catalytic oxyfunctionalization of **37** in terms of sustainability/efficiency were thus achieved with 2.5 mol% of catalyst at 70 °C, leading to **38** as colorless liquid in 74% yield after column chromatography (Table 13, entry 3).

Table 13: Results of the catalytic oxyfunctionalization of methyl 10-undecenoate **37**.

Entry	$PdCl_2$ [mol%]	T [°C]	Conversion [%] [a]	Selectivity [%] [a]	
				38 [%]	regioisomers [%]
1	5.0	70	> 99	86 [b]	14
2	5.0	70	> 99	83	17
3	2.5	70	> 99	85 [c]	15
4	2.5	50	> 99	78	22
5	2.5	r.t.	56	69	31
6	2.0	70	> 99	82	18
7	1.0	70	74	76	24

Conditions: 2.0 g (10.0 mmol) **37**, 30.0 mL dimethylacetamide/water (9:1 v/v), 10 bar oxygen pressure, 24 hours, pressure reactor; a) Conversion and selectivity were determined by ^{1}H-NMR analysis; b) 60.0 mL dimethylacetamide/water (9:1 v/v); c) 74% yield of **38** after column chromatography.

With the desired methyl ketone **38** in hands, we performed another classic oxidation procedure, the Baeyer-Villiger oxidation, in order to synthesize the corresponding diester **39**. For this purpose, **38** was dissolved in dichloromethane and cooled to 0 °C. Subsequently, 1.5 eq. of 3-chloroperbenzoic acid (*m*-CPBA) were added and the reaction was stirred at room temperature. As the conversion only reached 26% after 24 hours (Table 14, entry 1), the reaction was stirred for six additional days, resulting in 83% conversion (Table 14, entry 1). Interestingly, ^{1}H-NMR analysis revealed a selective formation of diester **39**, whereby the oxygen is introduced into the chain and not into side of the methyl group.[133] Thus, only one regioisomer was obtained in 77% yield after column chromatography (Table 14, entry 1). However, a long reaction time of 7 days was necessary to achieve high conversion under the applied mild reaction conditions. In further investigations, we noticed that an increased temperature of 50 °C led to 96% conversion after only 24 hours, while an identical selectivity was observed. Thus, **39** was obtained as colorless liquid in 92% yield after column chromatography (Table 14, entry 2).

Table 14: Results of peroxidation of **38** using *m*-CPBA.

Entry	t [d]	T [°C]	Conversion [%] [a)]	Yield **39** [%] [b)]
1	1	0 – r.t.	26	n.i.
	2	r.t.	45	n.i.
	5	r.t.	70	n.i.
	7	r.t.	83	77
2	1	0 – 50	96	92

Conditions: 428 mg (2.00 mmol) **38**, 673 mg (3.00 mmol, 1.50 eq.) *m*-CPBA, 3.0 mL dicholoromethane. a) Conversion was determined by ^{1}H-NMR analysis; b) isolated yield of **39** after column chromatography; n.i. = not isolated).

The formation of AB-monomers was part of further investigations. First, we were interested in the synthesis of hydroxy-ester **40**, enabling the formation of the linear polyester-9 (**PE-9**). A simple acid-catalyzed transesterification protocol using diester **39** in the presence of an excess of methanol under reflux conditions allowed the formation of **40** as colorless liquid in quantitative yield (Table 15, entry 1). In order to synthesize another AB-monomer for polyester synthesis, the reduction of methyl ketone **38** was performed, yielding the hydroxy-ester **41**. The reaction was accomplished by reacting **38** in a dichloromethane/methanol mixture with sodium borohydride as reducing agent, leading to the desired product **41** after 16 hours at room temperature as colorless liquid in quantitative yield (Table 15, entry 2). Finally, a promising synthesis route to convert methyl ketone **38** into the corresponding amino-ester consists in reductive amination using activated Raney-Nickel (Table 15, entry 3). For this purpose, **38** was dissolved in ethanol in the presence of ammonium acetate/ammonium chloride as ammonia source. Subsequently, 20 wt% of the activated catalyst were added and the reaction mixture was stirred for 24 hours at room temperature and 30 bar of hydrogen pressure. ^{1}H-NMR analysis of the crude reaction mixture revealed full conversion of **38**. Thus, after simple extraction and washing workup, the desired product **42** was obtained in 95% yield (Table 15, entry 3).

Table 15: Results of AB-monomer synthesis **40** – **42** from methyl ketone **38**.

Entry	AB-monomer	Conversion [%] [d)]	Yield [%] [e)]
1	hydroxy-ester **40**	> 99	> 99 **a)**
2	hydroxy-ester **41**	> 99	> 99 **b)**
3	amino-ester **42**	> 99	95 **c)**

Conditions: a) 730 mg (3.00 mmol) **39**, 5.0 mL methanol, sulfuric acid, reflux, 5 hours; b) 2.00 g (9.34 mmol, 1.00 eq.) **38**, 20 mL dichloromethane/methanol (9:1 v/v), 0.50 eq. sodium borohydride, r.t., 16 hours; c) 3.20 g (15.0 mmol, 1.00 eq.), 4.00 eq. ammonium acteate, 1.00 eq. ammonium chloride, 20.0 wt% Raney-Nickel, 30 bar hydrogen, r.t., 24 hours; d) Conversion was determined by ^{1}H-NMR analysis; e) isolated yield.

Polymer synthesis

Having the AB-monomers **40**-**42**, derived from renewable methyl 10-undecenoate **37**, in hands the final step of this study was to polymerize the obtained hydroxy- and amino-esters in order to investigate the properties of the corresponding polyesters and the polyamide. First, the synthesis of the linear polyester **PE-9** was performed using hydroxy-ester **40** and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as transesterification catalyst. In a first attempt, **40** and 5.0 mol% TBD were heated to 120 °C. Subsequently, vacuum was applied and the reaction was stirred for 24 hours at 120 °C. After this reaction, polyester **PE-9a** was obtained as a white solid in 72% yield with a molecular weight of 8.2 kDa (Table 16, entry **PE-9a**). Using 1.0 mol% titanium(IV) isopropoxide as catalyst in the same polymerization procedure resulted in an increased molecular weight of 14.9 kDa as well as an increased yield of 90% (Table 16, entry **PE-9c**, Figure 19). The hydroxy-ester **40** was synthesized by a two-step reaction procedure involving the diester **39** as intermediate. We also tested the direct polymerization of **39** using TBD first in the presence of an excess of methanol in order to synthesize the hydroxy-ester **40** *in situ*. After five hours under reflux conditions, vacuum was applied to evaporate the solvent and to start the polymerization (Table 16, entry **PE-9b**). Thus, **PE-9b** was obtained in 86% yield, however the molecular weight of 5.1 kDa was lower compared to the aforementioned polymerizations, indicating that the two step procedure is more efficient. Afterwards, the polymerization of hydroxy-ester **41** was investigated employing 1.0 mol%

of the titanium catalyst to yield the branched **PE-10a** in 76% yield and a molecular weight of 8.2 kDa (Table 16, entry **PE-10a**). Since low concentrations of titanium(IV) isopropoxide has proven to be efficient for transesterification processes,[203] 0.5 mol% of the catalyst were employed for the polymerization of **41**, resulting in a slightly increased molecular weight of 8.7 kDa (Table 16, entry **PE-10b**). The lower molecular weight of **PE-10b**, compared to **PE-9c**, is a result of the steric hindrance due to the methyl group branching within the monomer and polymer.

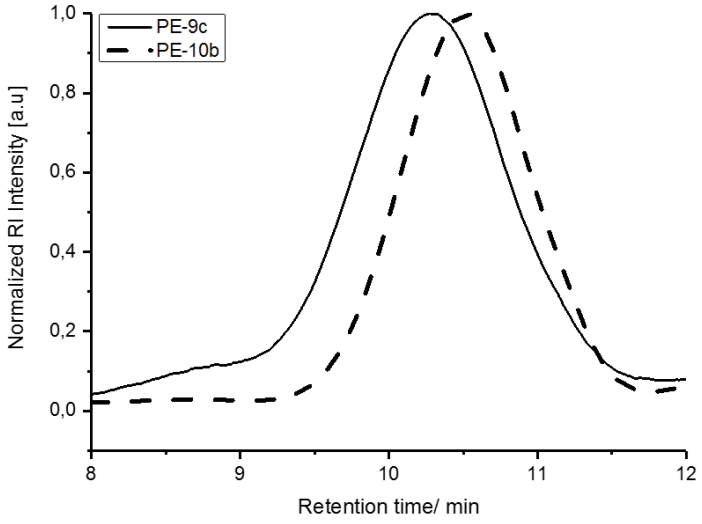


Figure 19: SEC curves of linear **PE-9c** and branched **PE-10b** polyester (measured on the THF-SEC system).

The thermal properties of the polyesters were investigated by DSC. **PE-9a**, prepared with a molecular weight of 8.2 kDa exhibited a melting point of 65 °C (Table 16, entry **PE-9a**). A slight increase in the melting point to 72 °C was observed when the molecular weight was increased to 14.9 kDa (Table 16, entry **PE-9c** and Figure 20). The methyl group in the side chain of polyester **PE-10** influences the thermal properties significantly, resulting in a highly viscous amorphous liquid with a glass transition temperature (T_g) of -57 °C (Figure 20, **PE-10a**).

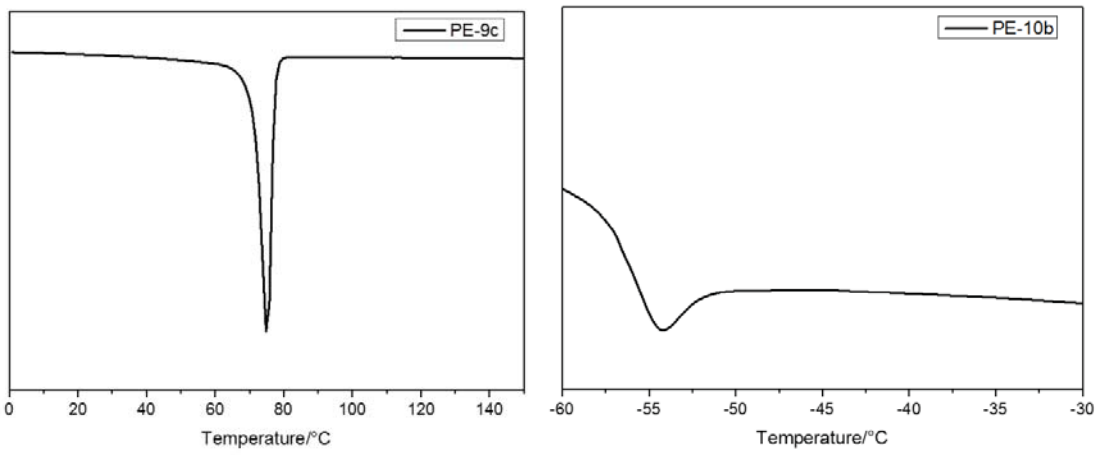


Figure 20: DSC curves of polyesters **PE-9c** and **PE-10a** derived from methyl 10-undecenoate.

In the last part of this study, the polymerization of amino-ester **42** was investigated using 10.0 mol% TBD and 120 °C as initial temperature (**42** shows a melting point of 97 °C). After one hour reaction time and the formation of oligomers, vacuum was applied to remove the formed methanol and the temperature was subsequently increased by 20°C each hour. During the polymerization, white crystals were observed on the neck of the round bottom flask due to monomer sublimation. SEC analysis of the crude mixture revealed that monomer is still present (Table 16, entry **PA-10a**). Subsequently, the crude reaction mixture was precipitated from hexafluoroispropanol (HFIP) into diethylether. The precipitated branched polyamide **PA-10a** was obtained as a black solid in 55% yield with a molecular weight of only 1.4 kDa (Table 16, entry PA1a). Similar results were achieved employing 5.0 mol% TBD, yielding **PA-10b** with a molecular weight of only 1.2 kDA (Table 16, entry PA1b). As **42** started to sublimate under the aforementioned reactions conditions, the polymerization was investigated using a temperature program without vacuum at the beginning. For this purpose, **42** and 5.0 mol% TBD were heated in a range of 120 °C to 200 °C (20°C/h); afterwards, vacuum was applied for an additional five hours at 200 °C (Table 16, entry PA1c). Thus, the formation of white crystals, which indicates remaining monomer during the polymerization, could almost completely be avoided. However, a distinct peak was observed in the SEC chromatogram of the crude reaction mixture at a retention time of ~6 minutes. This peak might be correlated to the formation of macrocycles, but MS investigations indicated that a linear dimer was formed in high

amounts. After precipitation the peak disappeared in the SEC chromatogram and the branched polyamide **PA-10c** was obtained in 78% yield with a molecular weight of 6.0 kDa (Table 16, entry **PA-10c** and Figure 21). The utilization of DBU as catalyst and applying the aforementioned polymerization procedure resulted in a similar molecular weight of 5.7 kDa (Table 16, entry **PA-10d**).

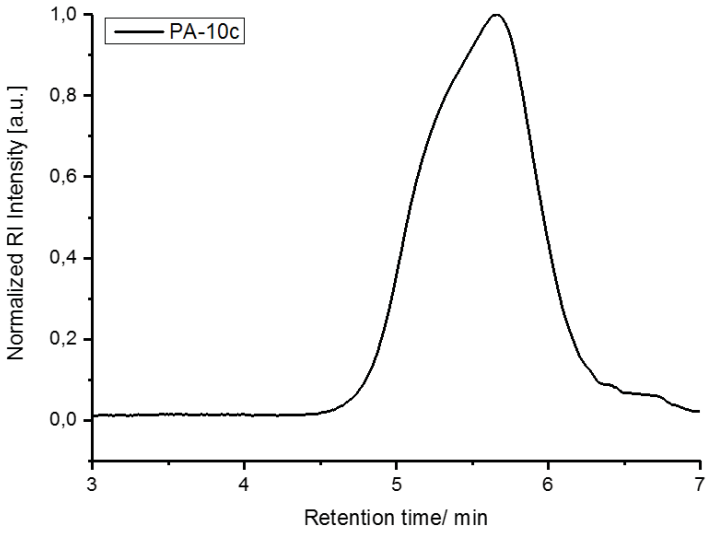


Figure 21: SEC curve of Polyamide **PA-10c** (measured on HFIP-SEC system).

The polyamide bears a methyl group in the side chain, similar to **PE-10** that influences the thermal properties and reactivity significantly compared to linear polyamides. Thus, it was difficult to reach higher molecular weights. **PA-10c** showed a T_g of -21 °C and a melting point of 148 °C. Moreover, a cold crystallization was observed during the DSC measurement at 108 °C (Figure 22). The effect occurs if sterically hindered polymer chains become flexible during heating. Thus, subsequent reorientation of the polymer chains enable the formation of hydrogen bonding resulting in crystallization. This indicates that the polymer needs time and elevated temperature for proper crystallization. A decreased cooling rate from 10 to 5 °C/min led to similar results (Table 16, entry **PA-10c** and Figure 22).

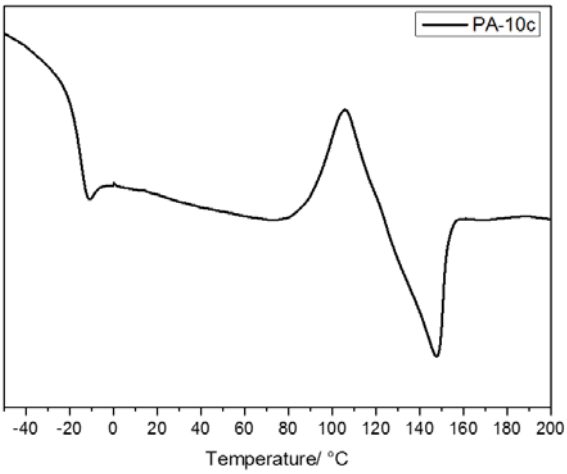


Figure 22: DSC curve of polyamide **PA-10c** derived from methyl 10-undecenoate.

Table 16: Results of homopolymerization using AB-type monomers **40** – **42**.

Entry	Cat.	Cat. [mol%]	M_n [kDa]	M_w/M_n	T_g [°C]	T_m [°C]	Yield [%]
PE-9a	TBD	5.0	8.2	2.2	-	65	72
PE-9b	TBD	5.0	5.1	2.0	-	-	86 [a)]
PE-9c	$Ti(O^iPr)_4$	1.0	14.9	2.0	-	72	90
PE-10a	$Ti(O^iPr)_4$	1.0	8.2	2.3	-57	-	76
PE-10b	$Ti(O^iPr)_4$	0.5	8.7	2.1	-55	-	82
PA-10a	TBD	10.0	1.4	2.2	-	-	55 [b)]
PA-10b	TBD	5.0	1.2	2.2	-	-	59 [c)]
PA-10c	TBD	5.0	6.0	2.1	-21	148	78 [c)]
PA-10d	DBU	5.0	5.7	2.3	-	-	n.i.

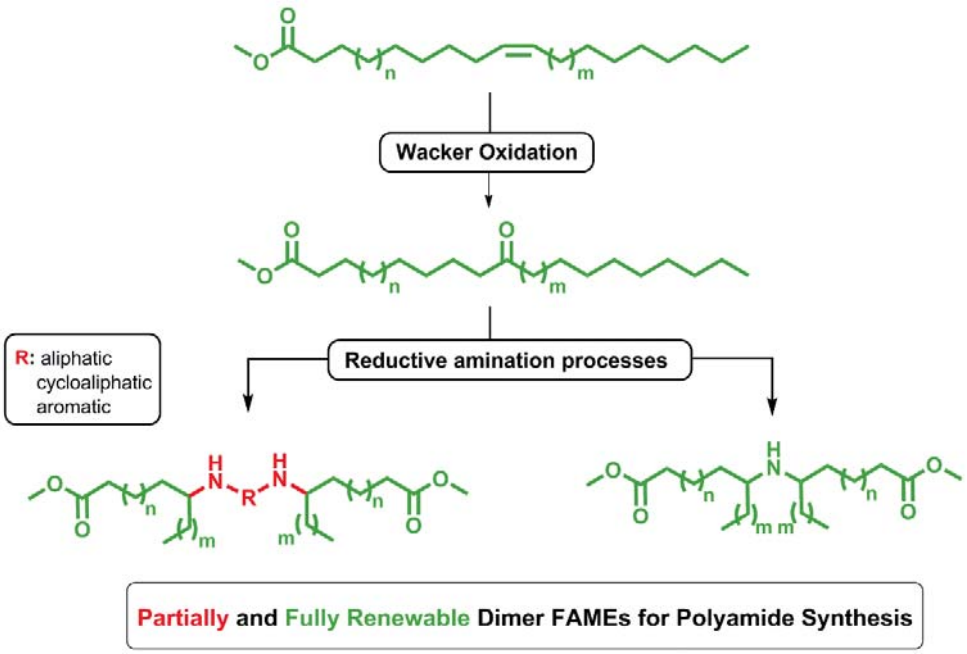
Conditions: polyester synthesis: 1.00 mmol **40** or **41**, 1.0 mL THF, 120 °C, vacuum, 24 hours; a) 1.00 mmol **39**, 3.0 mL methanol, reflux, 4 hours – afterwards additional 20 hours vacuum at 120 °C; polyamide synthesis: 2.00 mmol **42**; b) 120 - 180 °C (20 °C/h), vacuum (from 140 °C), 24 h; c) 120 - 200 °C (20°C/h), additional five hours vacuum at 200 °C; n.i. = not isolated.

Conclusion

In this study, an efficient synthesis strategy to prepare two polyesters and one polyamide from renewable methyl 10-undecenoate *via* catalytic oxyfunctionalization was established. The co-catalyst free Wacker oxidation constitutes a straightforward and high yielding oxidation process, allowing a product isolation by simple extraction and recycling of the catalyst-solvent mixture. Thus, full conversion was achieved and the desired methyl ketone was obtained in good yield after column chromatography. The subsequent derivatization *via* Baeyer-Villiger-Oxidation/transesterification, reduction or reductive amination enabled the formation of hydroxy- and amino-ester monomers in high yields. These AB-monomers were further studied in homopolymerizations using TBD, DBU and titanium(IV) isopropoxide as transesterification catalysts. The thermal properties of these polymers were studied and could be correlated to their structure.

4.2.5 Synthesis of dimer fatty acid methyl esters by catalytic oxidation and reductive amination: an efficient route to polyamides

(This section was previously published by M. v. Czapiewski *et al*. in *Eur. J. Lipid Sci. Technol.* **2017**, 1700350. Copyright © 2017, with permission from John Wiley and Sons.)



A novel and versatile route towards dimer fatty acid methyl esters (dimer FAMEs) *via* catalytic oxidation and reductive amination is described. The oxyfunctionalization of mono-unsaturated FAMEs bearing different chain lengths (C11, C18, C22) was accomplished by a co-catalyst-free Wacker Oxidation process in a high pressure reactor. The applied catalytic system of palladium(II) chloride in a dimethylacetamide/water mixture enabled the formation of keto-FAMEs in the presence of molecular oxygen as sole re-oxidant. In a first attempt, partially renewable dimer FAMEs were synthesized by reductive amination of keto-FAME (C18) in the presence of various aliphatic and aromatic diamines and sodium triacetoxyborohydride as selective reducing agent. In another approach, the keto-FAMEs directly underwent reductive amination using Raney-Nickel in order to obtain the corresponding amino-FAMEs. Subsequently, the keto- and amino-FAMEs were used for the synthesis of fully renewable dimer FAMEs *via* reductive amination with sodium triacetoxyborohydride as reducing agent. In order to demonstrate

a possible application for these new dimer FAMEs, three out of the thirteen synthesized dimer FAMEs were selected and studied in a polycondensation with renewable 1,10-diaminodecane using TBD as catalyst. The polyamides were obtained in molecular weights (M_n) of up to 33 kDa and were carefully characterized by ^{1}H-NMR spectroscopy, FTIR, SEC and DSC analysis.

Introduction

Recently, the utilization of high value products derived from renewable resources as alternatives to petrochemical products has become a major focus in polymer chemistry, mainly due to the depletion of crude oil and an increasing environmental awareness.[204] Among the available renewable raw materials, plant oils considerably contribute to a sustainable development, since monomers, fine chemicals and polymers can be obtained from these resources.[182] In this context, the advantages of unsaturated fatty acids for the synthesis of dimer fatty acids (DFA) and the thereof derived polymers are discussed. Dimer fatty acids are usually obtained by an intermolecular reaction of two or more unsaturated fatty acids and are industrially produced mainly by a clay-catalyzed high temperature process since the 1950s.[205] During this process, isomerization, leading to conjugated double bonds, followed by Diels-Alder reactions, leads to a mixture of monomer, dimer, trimer fatty acids bearing linear, cyclic and aromatic structures.[206] Depending on the application, this mixture has to be purified extensively. The obtained products are high boiling, viscous liquids that are relatively non-toxic and not flammable. Due to their long aliphatic chains, providing flexibility and hydrophobicity, DFAs are highly attractive renewable building blocks for the production of polymers and more especially thermoplastic polyamides *via* polycondensation. DFA derived polyamides exhibit a range of possible applications and are mostly used as hot-melt adhesives or as reactive components for the formulation of epoxy resins.[207-210] The resulting polyamides generally show a lower crystallinity as well as lower melting temperatures. Furthermore, DFA based polyamides were investigated for the synthesis of bio-composites using pure cellulose short fibers, showing an enhancement of the Young's modulus, the yield stress as well as the flow stress compared to the employed unmodified polyamide.[211] Besides diverse

applications for polyamides, DFA can be reduced into the corresponding diols, which are interesting starting materials for polyester and polyether synthesis. Additionally, DFA derived polyurethanes were reported to show improved hydrolytic and oxidative stability.[212] Finally, DFA are also used for the production of lubricating oils and corrosion inhibitors.[213] The aforementioned application possibilities of DFA highly depend on the thermal properties, which correlate with the structure of the used mixture. Only few strategies for the synthesis of defined DFA have been reported in the literature so far. Behr and co-workers studied the influence of metal salts (i.e. tin(II)chloride) for the synthesis of DFA. However, the applied protocol resulted in an increased formation of trimer fatty acid derivatives.[214] Another approach towards defined DFA has been described by Nützel and Haslinger in 1995. The established protocol including a McMurry coupling allowed access to DFA, but column chromatography purification after each reaction of the four-step synthesis constitute a drawback.[215] Very recently, our group reported an efficient one-pot procedure using thiol-ene chemistry for the synthesis of a DFA. Therefore, methyl-oleate and ethane-1,2-dithiol were reacted under UV-light resulting in the formation of a C_{36}-dimer fatty acid (obtained as a mixture of regioisomers) in high yield and purity. The thus obtained DFA could be directly co-polymerized with hexamethylendiamine and dimethyl adipate without further purification. The obtained copolyamides showed a decreased water uptake compared to commercial Nylon-6,6 when DFA is incorporated.[216]

Generally, not only the use of renewable resources, but also the development of sustainable processes that go along with the “12 principles of green chemistry” are of great importance.[217] Thus, the development of catalytic approaches constitute a major goal for both monomer and polymer synthesis. One of the most important catalytic oxidation processes of olefins was developed at Wacker Chemie in 1959. The oxidation process provides access to acetaldehyde from ethylene using a tandem catalytic system of palladium(II) chloride/copper(II) chloride under aerobic conditions.[49,50] Kaneda *et al.* described an efficient protocol for a co-catalyst-free Wacker oxidation process using molecular oxygen as sole re-oxidant.[202] The aforementioned protocol was employed by our group for the synthesis of ketone fatty acid methyl ester (keto-FAMEs), which enabled the formation of amino-ester and the thereof derived polyamides.[178] Following this work,

we investigated the reductive amination of the keto-FAME (C18) derived from methyl oleate with various commercially available diamines in order to synthesize partially renewable DFAs. Furthermore, the catalytic oxidation process and further reductive amination were applied to methyl 10-undecenoate (C11), methyl oleate (C18) and methyl erucate (C22) in order to build a library of keto- and amino-FAMEs bearing different chain lengths. Through combination of the aforementioned derivatives, six fully renewable DFAs were obtained *via* reductive amination. Finally, three out of the thirteen synthesized DFAs were selected and polymerized with 1,10-diaminodecane yielding polyamides.

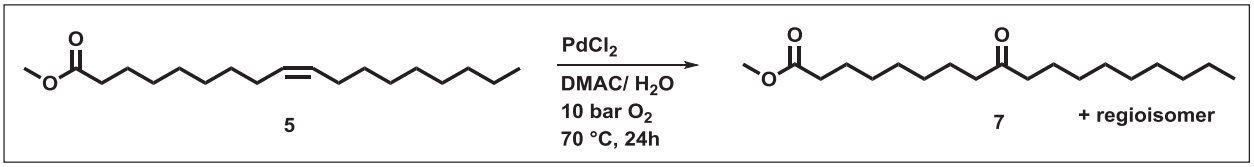
Results and discussion

The aim of this investigation was the catalytic oxyfunctionalization of mono-unsaturated fatty acid methyl esters (FAMEs) towards keto-FAMEs, which were used as precursor for the synthesis of dimer fatty acids (DFA) *via* a reductive amination processes. Thus, different partially and fully renewable DFAs were obtained that allow access to renewable polyamides.

Monomer synthesis

In a first approach, methyl oleate **5** was used in the co-catalyst-free Wacker oxidation process in order to synthesize the corresponding methyl-ketone **7** (Scheme 50). For this purpose, the catalytic mixture of palladium(II) chloride - dimethylacetamide/water in the presence of 10 bar oxygen pressure enabled full conversion after 24 hours at 70 °C. The desired keto-FAME **7** was obtained as white solid in 89% yield after an extraction and washing process (Table 17, entry 1). The double bond oxidation using **5** resulted in mainly two regioisomers, which could be confirmed by MS/MS experiments. In further investigations, methyl erucate **6**, bearing a longer aliphatic chain (C22), was successfully modified into keto-FAME **8**. The aforementioned reaction conditions led to full conversion and **6** was isolated as white solid in 86% yield (Table 17, entry 2). Another interesting starting material is methyl 10-undecenoate **37** due to the short aliphatic chain (C11) including a terminal double bond. The catalytic oxyfunctionalization of **37** resulted in full conversion after 24 hours at 70 °C. However, NMR analysis of the crude reaction mixture revealed that methyl-ketone **38** was formed in 85% and additionally 15% of regioisomers

were present due to double bond isomerization. The purification by subsequent column chromatography led to the pure desired product **38** as colorless liquid in 74% yield (Table 17, entry 3).[218]



Scheme 50: Wacker Oxidation of mono-unsaturated FAMEs (i.e. methyl oleate **5**).

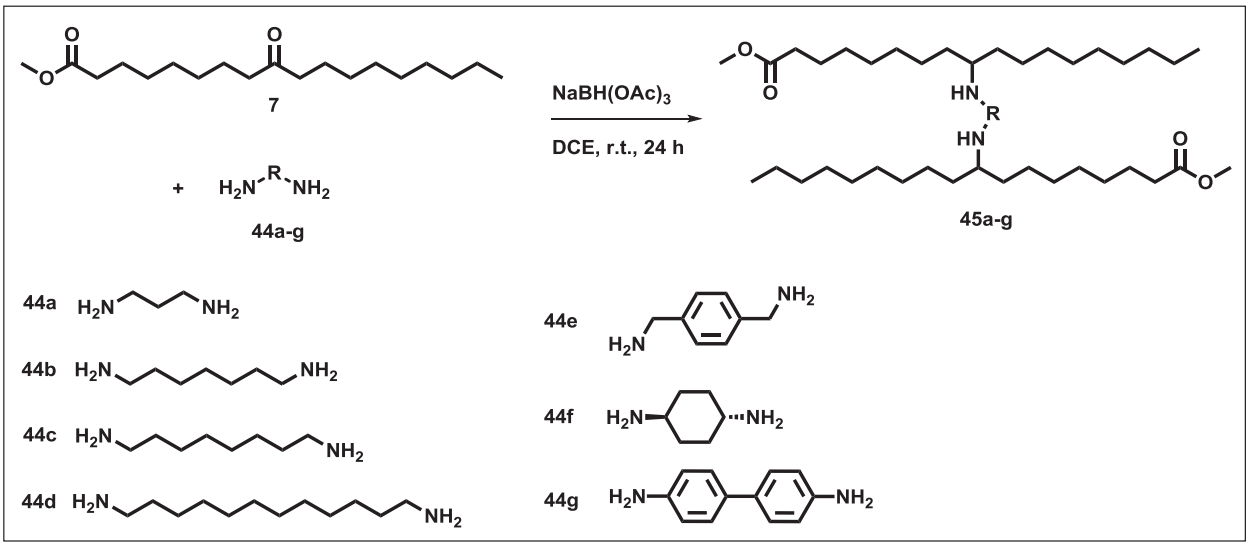
Table 17: Synthesis of keto-FAMEs via catalytic oxidation.

Entry	FAME	Keto-FAME	Conversion [%] [a)]	Yield [%] [b)]
1	**5** (C18)	**7** (C18)	> 99	89
2	**6** (C22)	**8** (C22)	> 99	86
3	**37** (C11)	**38** (C11)	> 99	74

Conditions: 10.0 mmol FAME **5, 7, 37**, 30.0 mL DMA/water (v:v 9:1), 2.50 mol% $PdCl_2$, 70 °C, 10 bar oxygen, 24 h. a) conversion was determined by ^{1}H-NMR analysis; b) isolated yield.

The goal of further investigations was the synthesis of partially renewable DFAs using keto-FAME and various commercially available diamines (Scheme 51). For this purpose, four aliphatic diamines with chain lengths between 3 to 12 carbon atoms (**44a-d**) were employed in a reductive amination process using sodium triacetoxyborohydride as selective and mild reducing agent. The reaction was performed in 1,2-dichloroethane at room temperature using a small excess of **7** (ratio: 2.05 eq. ketone/1.00 eq. diamine) to avoid mono-functionalization and thus to reach a high conversion of **7** and high yield of the desired DFA. After 24 hours reaction time, the crude mixture was purified by column chromatography and the corresponding DFAs were obtained as yellowish solids in 68 - 93% yield (Table 18, entry 1, 2, 5, 6). The employed toxic 1,2-dichloroethane constitutes a drawback regarding the aim to develop an environmentally-friendly synthetic approach. Therefore, dichloromethane and tetrahydrofuran (THF) were used as alternative solvents

in order to synthesize **45b**. However, the lower solubility of the starting materials even if the amount of solvent was increased, led to the production of **45b** in decreased yields of 68% and 15%, respectively (Table 18, entry 3, 4). Less toxic solvents are thus unfortunately no alternative in this synthetic process. Further investigations using cycloaliphatic and aromatic diamines were carried out with the same procedure in 1,2-dichloroethane as the most appropriate solvent. The synthesis of DFA **45e** employing *p*-xylenediamine resulted in a low yield of 30% (Table 18, entry 7). If sterically demanding diamines, such as *trans*-1,4-diaminocyclohexane and benzidine were used, the yields of **45f** and **45g** dropped to 6% and 5%, respectively (Table 18, entry 8, 9).



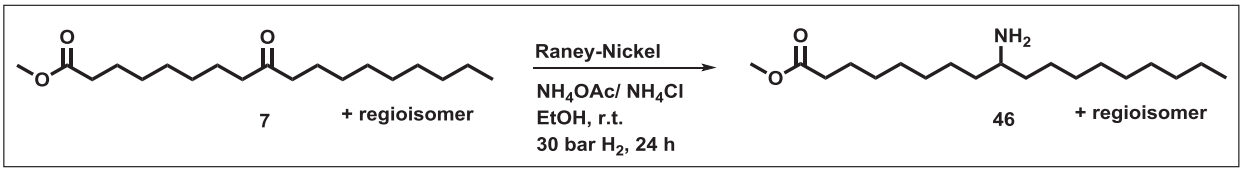
Scheme 51: Synthesis of dimer FAMEs using keto-FAME **7** and different diamines.

Table 18: Synthesis of dimer FAMEs using keto-FAME **7** and different diamines.

Entry	Diamine	Dimer FAME	Yield [%]
1	**44a**	**45a**	80
2	**44b**	**45b**	76
3	**44b**	**45b**	68 [a)]
4	**44b**	**45b**	15 [b)]
5	**44c**	**45c**	93
6	**44d**	**45d**	84
7	**44e**	**45e**	30
8	**44f**	**45f**	6.0
9	**44g**	**45g**	5.0

Conditions: 6.30 mmol **7**, 3.00 mmol diamine **44a-g**, 6.0 mL dichlorethane, 1.5 eq/keto-FAME sodium triacetoxyborohydride, r.t., 24 h; a) 10.0 mL dichloromethane; b) 10.0 mL tetrahydrofuran (THF).

Inspired by the aforementioned procedure, which resulted in seven partially renewable DFAs, we developed a synthesis strategy towards fully renewable DFAs. For this purpose, the obtained keto-FAMEs (**7**, **8**, **38**) were employed in a reductive amination process in order to synthesize the corresponding amino-FAMEs (**42**, **46**, **47**).[178] The reactions were carried out in ethanol at room temperature using an activated Raney-Nickel catalyst in the presence of ammonium acetate/ammonium chloride as ammonia source and 30 bar hydrogen pressure. Thus, after 24 hours full conversion was achieved for all three keto-FAMEs. The subsequent purification of amino-FAMEs (**42**, **46**, **47**) was accomplished by a washing process, which led to quantitative yields for **46** and **47** as brownish oils. Amino-FAME **42** was obtained as white solid in a slightly decreased yield of 95% (Table 19, entry 1-3).



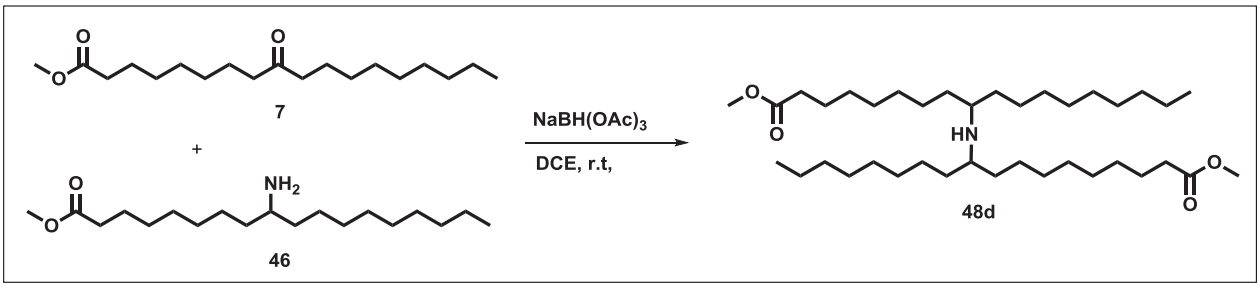
Scheme 52: Reductive amination of keto-FAMEs (i.e. keto-FAME **7** derived from methyl oleate).

Table 19: Synthesis of amino-FAMEs via reductive amination of keto-FAMEs.

Entry	Keto-FAME	Amino-FAME	Conversion [%] [a)]	Yield [%]
1	**7** (C18)	**46** (C18)	> 99	> 99
2	**8** (C22)	**47** (C22)	> 99	> 99
3	**38** (C11)	**42** (C11)	> 99	95

Conditions: 15.0 mmol (1.00 eq) keto-FAME **7**, **8** or **38**, 4.00 eq ammonium acetate, 1.00 eq ammonium chloride, 25 mL ethanol, 20 wt% Raney-Nickel, 30 bar hydrogen, r.t., 24 h; a) Conversion was determined by ^{1}H-NMR analysis.

Finally, the aforementioned reductive amination process was applied for the reaction of the different keto- and amino-FAMEs in order to synthesize fully renewable DFAs (Scheme 53). Through variation of the keto- and amino-FAMEs bearing different chain lengths, six DFAs were obtained as viscous oils, except of DFA **48a** that appeared as white solid, in 69 – 93% yield after column chromatography (Table 20, entry 1, 2, 4-7). The syntheses were carried out using the ketone compound in 1.05 fold-excess in order to reach a maximum conversion. With an increasing chain length, the steric hindrance also increased and thus reactions times of 1 – 7 days were required to achieve the aforementioned yields. Moreover, the combination of starting materials has a significant impact on the conversion, due to possible differences in polarity. For instance, if keto-FAME **38** (C11) and amino-FAME **47** (C22) were employed in the reductive amination process, DFA **48c** (C33) was obtained in 69% yield (Table 20, entry 4), whereas the synthesis of the analogous DFA (C33) with another combination of keto- and amino-FAME (**2b** and **3c**) resulted in 21% yield (Table 20, entry 3).



Scheme 53: Synthesis of renewable dimer FAMEs (i.e. dimer FAME **48d** (C36) derived from keto-FAME (C18) **7** and amino-FAME (C18) **46**, Table 20, entry 5).

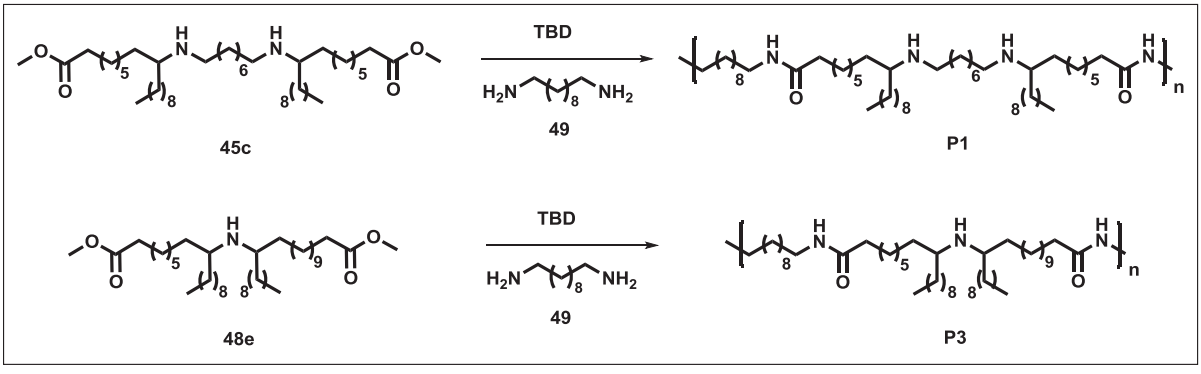
Table 20: Synthesis of renewable dimer FAMEs from keto- and amino-FAMEs.

Entry	Keto-FAME	Amino-FAME	Dimer FAME	Yield [%]
1	**38** (C11)	**42** (C11)	**48a** (C22)	93
2	**38** (C11)	**46** (C18)	**48b** (C29)	82
3	**8** (C22)	**42** (C11)	**48c** (C33)	21
4	**38** (C11)	**47** (C22)	**48c** (C33)	69
5	**7** (C18)	**46** (C18)	**48d** (C36)	70 [a)]
6	**8** (C22)	**46** (C18)	**48e** (C40)	73 [a)]
7	**8** (C22)	**47** (C22)	**48f** (C44)	76 [a)]

Conditions: 10.0 mmol keto-FAME **7**, **8** or **38**, 9.50 mmol amino-FAME **42**, **46** or **47**, 20 mL dichlorethane, 1.5 eq/ketone-FAME sodium triacetoxyborohydride, r.t., 24 h; a) after seven days.

Polymer synthesis

The final step of this study was to polymerize the obtained DFAs with a renewable diamine in order to investigate the properties of the corresponding polyamides. For this purpose, three out of the thirteen synthesized DFAs were exemplarily selected and studied in the polycondensation with 1,10-diaminodecane **49**, a renewable diamine derived from sebacic acid,[219,220] using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as catalyst**.** In a first attempt, the polymerization of partially renewable DFA **45c** was performed using 5.0 mol% TBD and 100 °C as initial temperature (Scheme 54). Subsequently, the temperature was increased 20 °C/hour until 180 °C was reached. During this period of time, the product mixture turned into a brown viscous oil. Afterwards, vacuum was applied for two more hours in order to remove the formed methanol and shift the reaction equilibrium, thus to increase the degree of polymerization. After precipitation in diethyl ether at room temperature, polyamide **P1** was obtained as brown solid in 85% yield with a molecular weight (M_n) of 24.4 kDa (Table 21, entry 1; Figure 23). Further investigations were carried using DFAs **48b** and **48e**, which allowed access to fully renewable polyamides. Applying the aforementioned polymerization procedure resulted in 92% yield of **P2** and 88% yield of **P3** (Scheme 54). The obtained polyamides reached molecular weights of 26.5 kDa and 33.5 kDa, respectively (Table 21, entry P2-3, Figure 23).



Scheme 54: Synthesis of partially renewable polyamide **P1** (top) and fully renewable polyamide **P3** (bottom).

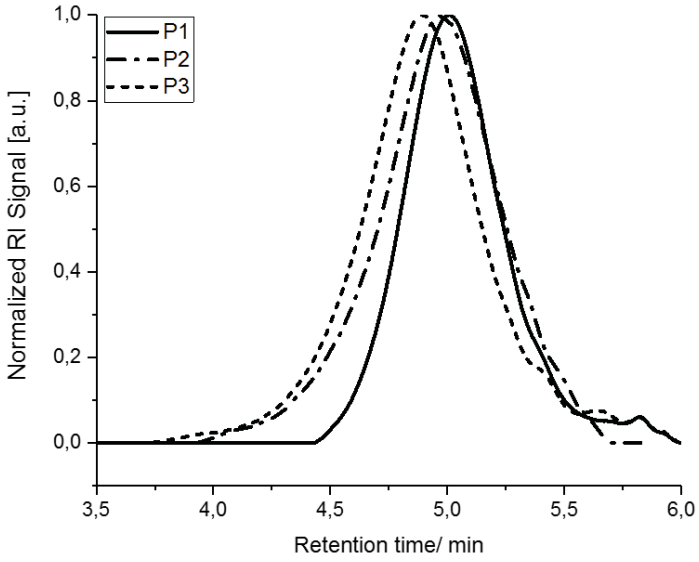


Figure 23: SEC traces of polyamides **P1-3** derived from dimer FAMEs.

The thermal properties of the polyamides were studied by DSC analysis. Polyamide **P1** derived from partially renewable DFA **5c** with a molecular weight of 24.4 kDa exhibited a glass transition temperature (T_g) of 9 °C and a melting point (T_m) of 161 °C (Table 21, entry P1). In comparison, **P2** and **P3** based on fully renewable DFAs showed a lower T_g of -4 °C and -16 °C as well as a lower T_m of 106 °C and 70 °C, respectively (Table 21, entry P2-3). Generally, the presence of longer "dangling" aliphatic chains in the polymer structure lowers the glass transition temperature, which is in good agreement with the obtained results of **P2** and **P3**.[221] Moreover, the crystallization as well as the melting temperature are significantly influenced by steric hindrance. **P1** showed the highest T_m of 161 °C of all three polyamides, although **P2** bears shorter aliphatic main and side chains. These results could be explained by the amount of possible of hydrogen bonding. The synthesized partially renewable polyamides includes four H-bonding donors and acceptors per repeating unit, whereas the fully renewable polyamides consist of one donor less per repeating unit. Additionally, the secondary amine group of **P2** and **P3** is more sterically hindered than in **P1**, thus possible formation of hydrogen bonding will be suppressed, which results in a lower T_m, as typically reported for polyamides.[155,199,222]

Table 21: Results of the polyamide synthesis using dimer FAMEs.

Entry	Dimer FAME	M_n [kDa]	Đ	T_g [°C]	T_m [°C]	Yield [%]
P1	**45c**	24.4	1.65	9.0	161	85
P2	**48b**	26.5	1.96	-4.0	106	92
P3	**48e**	33.5	1.86	-16	70	88

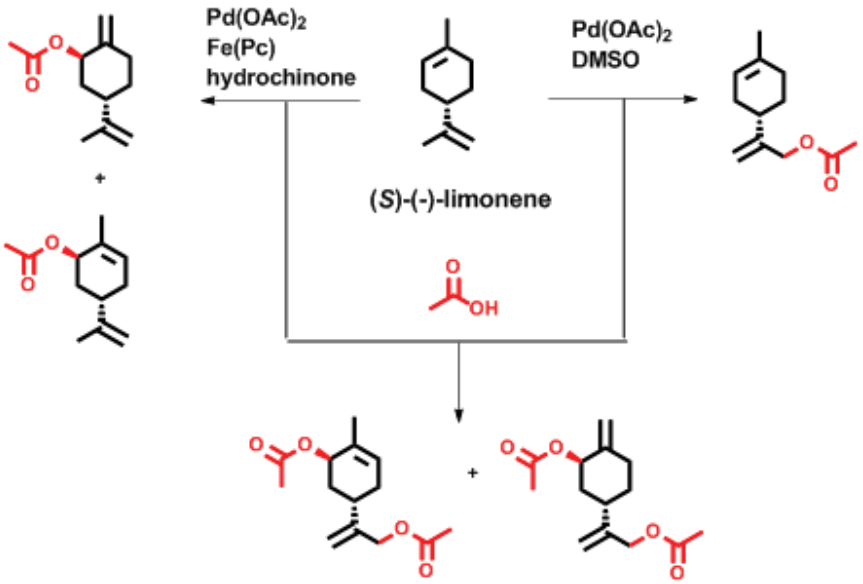
Conditions: 0.50 mmol dimer FAME **45c**, **48b** or **48e**, 0.50 mmol 1,10-diaminodecane **49**, 1.00 mL *o*-xylene, 5.0 mol% TBD, 100 – 180°C (20°C/h), additional two hours vacuum at 180 °C.

Conclusion

In this study, an efficient synthesis strategy to prepare partially and fully renewable dimer fatty acid methyl esters (DFA) from mono-unsaturated fatty acids *via* catalytic oxyfunctionalization and reductive amination was established. The applied co-catalyst free Wacker oxidation constitutes a straightforward and high yielding oxidation process, allowing a product isolation by simple extraction and recycling of the catalyst-solvent mixture. Thus, full conversion was achieved for three different fatty acid derivatives resulting in the corresponding methyl ketones in good yields. The keto-FAMEs were employed in a reductive amination process using various aliphatic and aromatic diamines, allowing access to seven partially renewable DFAs in good yields. Moreover, the synthesis of amino-esters from keto-FAMEs enabled the formation of six defined and fully renewable DFAs in good yields *via* reductive amination. Three out of thirteen the synthesized DFAs were selected and studied in the synthesis of polyamides with 1,10-diaminodecane using TBD as catalyst in order to exemplarily demonstrate application possibilities of the obtained DFAs in polymeric materials.

4.2.6 Regioselective acetoxylation of limonene

(This section was previously published by M. v. Czapiewski *et al*. in *Cat. Sci. Tech.* **2014**, *4*, 2318-2325.



Abstract

Two efficient strategies for a direct catalytic and regioselective acetoxylation of terpenes are described. Acetoxylated limonene derivatives were synthesized *via* palladium-catalyzed C-H activation utilizing *para*-benzoquinone (*p*-BQ) as reoxdidation agent and acetic acid as solvent and reactant. Addition of dimethyl sulfoxide (DMSO) to the catalytic system led to highly selective functionalization of the exocyclic double bond of limonene. This catalytic acetoxylation of limonene was further optimized with regard to a more sustainable and environmentally-friendly procedure. On the other hand, the use of an aerobic tandem catalytic system using iron(II) phthalocyanine (Fe(Pc)) as co-catalyst, which acts as electron transfer mediator (ETM), enabled a highly selective acetoxylation of the endocyclic double bond of limonene with high conversions. Moreover, diacetoxylated products were prepared by a reaction sequence applying the aforementioned catalytic systems.

Introduction

The development of sustainable processes using renewable feedstocks is an important and urgent challenge, not only due to the depletion of fossil resources.[182] With an increasing demand of fossil-derived raw materials the price of crude oil will increase dramatically, thus promoting the search for suitable alternatives.[204] Renewable raw materials (e.g. starch, fats and oils, cellulose, and others), represent a valuable alternative to fossil resources. Already today, nine million tons of renewable raw material derived products are used within the European industry per year, demonstrating their remarkable potential.[24] Among the available renewable materials, terpenes constitute a valuable and cheap biomass resource, which are available in large scales from various essential oils or as by-product from diverse industrial processes.[12,13,37] Terpenes are secondary metabolites synthesized by plants, fungi and microorganisms. Furthermore, terpenes are of great interest for humans, due to their versatile application possibilities, e.g. as flavors, fragrances, nutrients, pheromones or as pharmacological substrates.[39-41] The remarkable structural diversity of terpenes, containing cycloaliphatic, aromatic or diene moieties offers versatile functionalization possibilities.[36] Thus, in order to synthesize diverse value added terpene compounds, the development of efficient and catalytic derivatization processes are of great interest. Especially, a selective oxidation of terpenes is highly desirable from an economic and ecologic point of view, since these terpene derivatives are used in a wide range of applications. Wilson and Shaw reported the synthesis of oxygenated limonene derivates using a selenium dioxide/hydrogen peroxide system. The resulting products bear hydroxy- and epoxy functional groups, which are obtained by oxidation at the corresponding allylic position or double bond.[223] Da Silva *et. al.* reported an oxyfunctionalization protocol for the autoxidation of limonene using acetic acid or acetonitrile as solvent and a cobalt(II) chloride catalyst. Within this catalytic procedure, the respective internal epoxidized limonene, carvone and carveolis were obtained in moderate yields after four hours at 60 °C.[224] Another interesting approach for the oxyfunctionalization of limonene is realized by a tandem catalytic system using palladium(II) chloride/copper(II) chloride in the presence of lithium chloride and acetic acid. Gusevskaya and Gonsalves described an efficient catalytic process that enabled the preparation of *trans*-carveyl acetate with high conversion of 87% after four hours at 80 °C.

However, small amounts of different oxidized and isomerized products were formed as well.[225] Firdoussi *et. al.* reported the synthesis of regioselectively acetoxylated limonene derivates under mild reaction conditions and long reaction times of 48 hours. By using a tandem catalytic system consisting of palladium(II) chloride/copper(II) chloride and sodium acetate in acetic acid as solvent, high conversion of 90% were obtained. However, due to allylic acetoxylation at the endocyclic double bond, three different products were formed. The same group also described a catalytic system making use of palladium(II) acetate as catalyst and stoichiometric amounts of *p*-benzoquinone as reoxidation agent.[226] Under mild reaction conditions of 20 °C, two internally acetoxylated products were formed in good conversion of 80%. Unfortunately, long reaction times (72 h) were required to obtain the corresponding products.[227] White and colleagues reported the synthesis of acetoxylated *α*-olefins by a highly selective allylic C-H oxidation process. The remarkable selectivity of this catalytic procedure is accomplished by a sulfoxide-promoted oxidation using palladium(II) acetate as catalyst and *p*-benzoquinone. Depending on the employed sulfoxide agent, linear or branched acetoxylated products were obtained. The aforementioned catalytic systems usually require stoichiometric amounts of a oxidizing agent (e.g. *p*-benzoquinone) to facilitate the regeneration of palladium(II) species and to avoid the precipitation of the catalyst. Interestingly, Piera and Bäckvall recently published an oxidation protocol for the aerobic 1,4-diacetoxylation of 1,3 dienes by a tandem catalytic system that involved an electron transfer mediator (ETM), which allowed for an efficient oxidation reaction. One major advantage of such an aerobic tandem procedure is the use of catalytic amounts of the oxidizing agent, e.g. *p*-benzoquinone, which is regenerated during the catalytic process by an iron(II) phthalocyanine co-catalyst (ETM).[228,229] Thus, it would be highly interesting to make use of such an oxidation protocol to achieve an efficient and selective functionalization of terpene substrates. Therefore, in order to allow an efficient and regioselective functionalization of limonene, we report two oxidation methods: the palladium-catalyzed C-H activation process using dimethyl sulfoxide and an aerobic tandem catalytic system using an ETM. Moreover, the two catalytic procedures were used in a sequential reaction procedure to synthesize diacetoxylated limonene derivatives. The thus prepared limonene derivatives are valuable precursors for step-growth polymerizations. Additionally, these limonene derivatives are

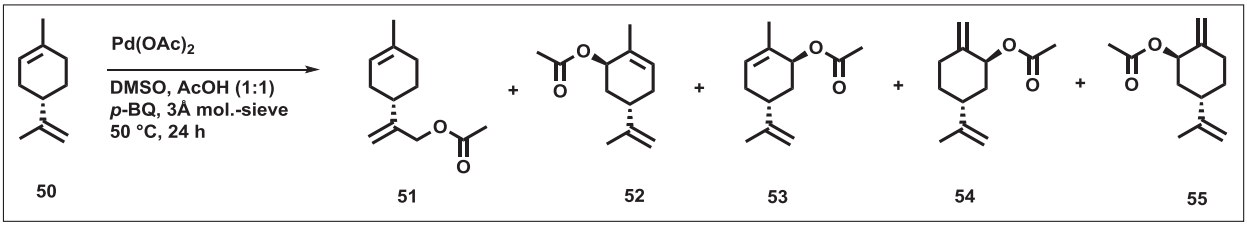
valuable precursors for organic synthesis, i.e. for transition metal catalyzed allylic substitution reactions.

Results and discussion

The aim of this investigation was the catalytic functionalization of terpenes in order to synthesize regioselectively acetoxylated compounds that also have the potential to be used for the synthesis of renewable platform chemicals, especially for step-growth polymerization procedures. In this context,(*S*)-(-)-limonene (**50**), which can be obtained from renewable feedstock, was explored towards its reactivity in two different catalytic oxidations procedures.

Acetoxylation at the exocyclic double bond of (*S*)-(-)-limonene 50

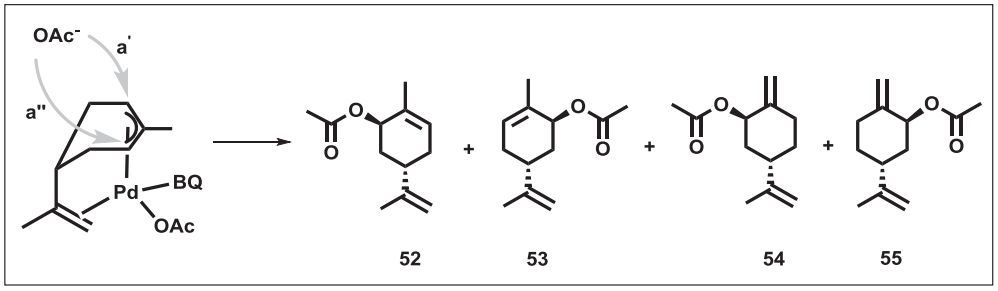
At first, a palladium-catalyzed C-H activation process using DMSO in the presence of *p*-benzoquinone (*p*-BQ) as oxidation agent in acetic acid as solvent was investigated. The reaction was optimized with regard to an acetoxylation of the exocyclic double bond of limonene (Scheme 55).



Scheme 55: Palladium-catalyzed acetoxylation of (*S*)-(-)-limonene.

The first catalytic system, which was introduced by White and co-workers and highly promotes the allylic oxidation of *α*-olefins,[94] was transferred to (*S*)-(-)-limonene. The procedure uses palladium(II) acetate/*p*-BQ and a solvent mixture of DMSO and acetic acid. One major advantage of this catalytic oxidation system is the formation of linear (*E*)-allylic acetates, which can be obtained in good yields and with high regio- and stereoselectivity. A similar procedure has been successfully applied to unsaturated fatty acid methyl esters (FAMEs) in order to obtain the corresponding linear allylic acetates.[96] Transferring the procedure of White *et. al.*, who used 10 mol% of palladium catalyst, to (*S*)-(-)-limonene resulted mainly in an acetoxylation of the exocyclic double bond, which

afforded the corresponding functionalized product **51**. As by-products, enantiomers **52** and **53** as well as enantiomers **54** and **55** were formed due to an acetoxylation of the endocyclic double bond (Scheme 55). In this process, a new stereocenter is created by two possible attacks of the acetate (a', a'', Scheme 56), respectively. Since NMR cannot distinguish between **52** and **53** as well as **54** and **55**, it is fair to assume and in accordance with the acetoxylation mechanism that the enantiomer pairs (**52**/**53** or **54**/**55**, respectively) are formed in a 1:1 ratio. The attack of the nucleophile only occurred as depicted in Scheme 56, explaining why only one of the two possible configurations of the new stereocenters was observed by NMR analysis.



Scheme 56: Explanation of the observed stereoselectivity in the palladium-catalyzed acetoxylation process.[227]

These results are also in agreement with the results reported by El Firdoussi *et al.*, who employed (*R)*-(+)-limonene as substrate for palladium-catalyzed oxidation using *p*-BQ and sodium acetate. In this case, the internal acetoxylation occurred, which led to a new stereocenter. Generally, the specific formation of these enantiomers can be explained by coordination of the palladium catalyst, which coordinates to the limonene substrate *via* π-allyl and olefin bonding. The given stereo-configuration of the limonene substrate enabled the formation of a palladium complex, wherein the acetate can only attack from the backside (Scheme 56).[227] To optimize the catalytic oxidation of **50**, the amounts of palladium(II) acetate, *p*-BQ, DMSO, and acetic acid were varied to yield a maximum conversion and product selectivity. In order to minimize the catalyst loading, while still obtaining high yields of **51**, a first reaction screening was performed (Table 22).

Table 22: Results of the catalytic acetoxylation process of **50** using different amounts of palladium catalyst.

Entry	Catalyst[mol%]	Conversion [%][a)]	Selectivity [%][a)]		
			51 [%]	**52**/**53** [%]	**54**/**55** [%]
1	10	63	89	6	5
2	8	66	86	9	5
3	6	63	87	8	5
4	4	65	89	8	3
5	2	28	86	11	3

Conditions: 200 mg (1.47 mmol) **50**, 1.0 mL acetic acid, 1.0 mL DMSO, 2.0 eq. *p*-BQ, 250 mg 3 Å molecular sieve, 50 °C, 24 h. a) Conversion and selectivity were determined by GC-MS using tetradecane as internal standard.

The catalyst loading was varied between 2 and 10 mol%. No significant difference, both in conversion and in product selectivity, was observed if the acetoxylation was performed with 10 to 4mol% (Table 22). However, if the amount of catalyst was further reduced to 2 mol%, the conversion significantly decreased. Based on these results, further studies were carried out using 4 mol% of palladium(II) acetate. Since the employed oxidant (*p*-BQ) is a toxic reagent and usually used in excess, the next step was to try to reduce the required amount of *p*-BQ (Table 23).

Table 23: Results of the catalytic acetoxylation of **50** using different amounts of *para*-benzoquinone and 4mol% $Pd(OAc)_2$.

Entry	*p*-BQ [eq]	Conversion [%][a)]	Selectivity [%][a)]		
			51 [%]	**52**/**53** [%]	**54**/**55** [%]
1	2.0	64	89	6	5
2	1.5	63	83	9	8
3	1.0	60	85	10	5
4	0.5	44	86	11	3
5	0	12	50	25	25

Conditions: 200 mg (1.47 mmol) **50**, 1.0 mL acetic acid, 1.0 mL DMSO, 250 mg 3 Å molecular sieve, 4.0 mol% $Pd(OAc)_2$, 50 °C, 24 h. a) Conversion and selectivity were determined by GC-MS using tetradecane as internal standard.

Reducing the amount of oxidant (from two to one equivalents) has only a marginal effect on the observed conversion and selectivity. With regard to a more environmentally-friendly acetoxylation process, this optimization constitutes a remarkable improvement and clearly shows that an excess of the oxidant is not necessary. However, if the amount of oxidant was further decreased, the conversion significantly dropped. Subsequent optimization studies were performed in order to investigate the influence of the amount of solvent. According to the above mentioned reaction screenings, 4 mol% of the palladium catalyst and one equivalent of the oxidant were used (Table 24).

Table 24: Results of the catalytic acetoxylation of **50** using different amounts of DMSO and acetic acid.

Entry	AcOH [mL]	DMSO [mL]	Conversion [%][a)]	Selectivity [%][a)]		
				51 [%]	**52**/**53** [%]	**54**/**55** [%]
1	0.5	0.5	53	87	8	5
2	1.0	1.0	60	85	10	5
3	1.5	1.5	72	88	8	4
4	2.0	2.0	73	89	8	3
5	1.0	1.5	51	90	6	4
6	1.5	1.0	80	75	15	10

Conditions: 200 mg (1.47 mmol) **50**, 1.0 eq. *p*-BQ, 250 mg 3 Å molecular sieve, 4.0 mol% $Pd(OAc)_2$, 50 °C, 24 h. a) Conversion and selectivity were determined by GC-MS using tetradecane as internal standard.

Generally, increasing the total amount of solvent (AcOH + DMSO) from 1.0 mL to 3.0 mL has a positive effect on the obtained conversion, without negatively influencing the good product selectivity (Table 24). The dilution might favor a stabilization of the active palladium species. However, if one of the solvents was used in excess, either the conversion or the product selectivity considerably decreased, suggesting that an intermediate as depicted in Scheme 56 plays indeed a key-role in this transformation. If an increased amount of DMSO was used, lower conversions were observed (Table 24, entry 5). Contrary, if an excess of acetic acid was used, the conversion was slightly improved, but the product selectivity decreased (Table 24, entry 6). As a further parameter, the reaction temperature and its impact on the conversion and product selectivity of the catalytic acetoxylation was investigated (Table 25).

Table 25: Results of the catalytic acetoxylation of **50** at different temperatures.

Entry	T [°C]	Conversion [%][a)]	Selectivity [%][a)]		
			51 [%]	**52**/**53** [%]	**54**/**55** [%]
1	50	72	88	8	4
2	60	72	85	11	4
3	70	73	81	13	6

Conditions: 200 mg (1.47 mmol) **50**, 1.5 mL acetic acid, 1.5 mL DMSO, 1.0 eq. *p*-BQ, 250 mg 3 Å molecular sieve, 4.0 mol% $Pd(OAc)_2$, 24 h. a) Conversion and selectivity were determined by GC-MS using tetradecane as internal standard.

The obtained results revealed that increasing the temperature had no significant effect on the conversion, whereas the product selectivity slightly decreased. Therefore, performing the catalytic acetoxylation at 50 °C provided the most promising results. Applying the optimized reaction conditions to (*R*)-(+)-limonene yielded similar conversions as well as the same product selectivitiy. The remarkable selectivity, which can be achieved in the catalytic acetoxylation using DMSO as solvent, represents a highly efficient and promising procedure. Moreover, to the best of our knowledge, these results demonstrate the first direct catalytic acetoxylation (one-step) of the exocyclic double bond of limonene. Further investigations were performed with some other polar aprotic solvents in order to study their effect in the catalytic acetoxylation process (Table 26).

Table 26: Results of the catalytic acetoxylation of **50** using different solvents.

Entry	Solvent [x]	Conversion [%] [c]	Selectivity [%] [c]		
			51 [%]	**52**/**53** [%]	**54**/**55** [%]
1	DMA	84	11	51	38
2	DMF	81	16	37	47
3	MeCN	30	47	32	21
4	THT [a]	78	6	50	44
5	$PhCF_3$ [b]	96	5	52	41

Conditions: 200 mg (1.47 mmol) **50**, 1.5 mL acetic acid, 1.5 mL x-solvent, 1.0 eq. *p*-BQ, 250 mg 3 Å molecular sieve, 4.0 mol% $Pd(OAc)_2$,50 °C, 24 h. a) 136 mg (1.00mmol) **50**, 2.0 ml acetic acid, 2.0 eq. *p*-BQ, 5.0 mol% THT, 5.0 mol% $Pd(OAc)_2$, 50 °C, 24 h. b) 136 mg (1.00mmol) **50**, 2.0 ml acetic acid, 2.0 eq. *p*-BQ, 5.0 mol% $PhCF_3$, 5.0 mol% $Pd(OAc)_2$, 50 °C, 24 h c) Conversion and selectivity were determined by GC-MS correlated using tetradecane as internal standard.

Interestingly, depending on the used polar and aprotic solvent, considerably different results were obtained. In reactions using DMA or DMF as solvent, the catalytic acetoxylation of **50** is highly promoted. However, mainly the functionalization at the endocyclic double bond was observed, and almost exclusively product **52** and **54** (+ enantiomers) are formed. This is a very interesting result and demonstrates that the product selectivity and thus regioselectivity of this process can be inverted by simple choice of solvent. If acetonitrile was used, only a low conversion and product selectivity was observed. In a further test reaction, tetrahydrothiophene (THT) was used as additive, since Stambuli *et. al.* described THT as highly reactive and selective ligand in acetoxylation reactions to obtain (*E*)-linear allylic acetates.[230] Applying this catalytic process to **50**, primarily the endocyclic double bond of **50** was functionalized, thus the enantiomers **52** and **53** as well as **54** and **55** were formed as major products (Table 26, entry 4). However, THT is toxic and thus replacing it with another additive, such as *α,α,α*-trifluorotoluene ($PhCF_3$), was also investigated. Using $PhCF_3$ instead of THT under same reaction conditions, an almost quantitatively conversion was achieved. In this case, the functionalization also highly occurred at the endocyclic double bond. All in all, the best results were obtained if the acetoxylation of **50** was performed with a catalyst loading of

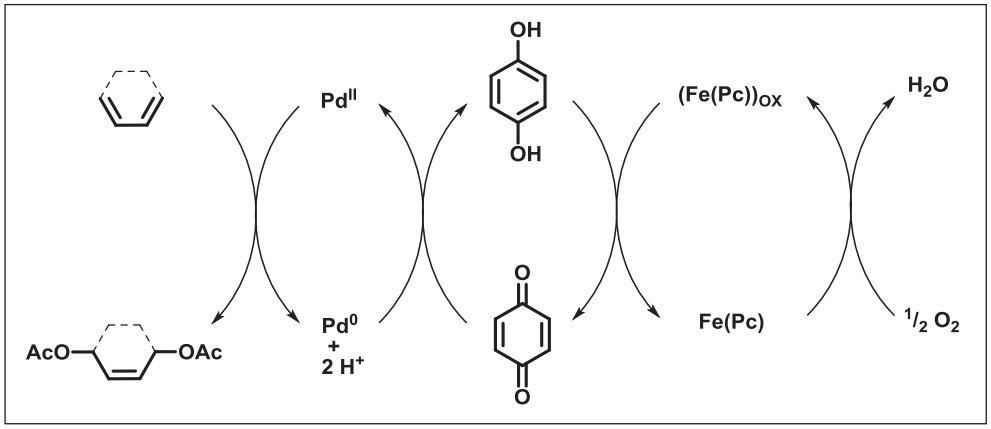
4mol%, stoichiometric amounts of *p*-BQ, DMSO/acetic acid as solvent in a 1:1 ratio at a temperature of 50 °C. As shown in Table 27, increasing the reaction time from 24 to 48 hours leads to almost full conversion with this optimized system without compromising its selectivity.

Table 27: Results of the Pd-catalyzed acetoxylation of **50** using DMSO.

Entry	t [h]	Conversion [%][a)]	Selectivity [%][a)]		
			51 [%]	**52**/**53** [%]	**54**/**55** [%]
1	2	7	72	28	0
2	4	13	77	23	-
3	6	23	70	22	8
5	24	73	85	10	5
6	48	91	86	10	4

Conditions: 200 mg (1.47 mmol) **50**, 1.5 mL acetic acid, 1.5 mL DMSO, 1.0 eq. *p*-BQ, 250 mg 3 Å molecular sieve, 4.0 mol% $Pd(OAc)_2$, 50 °C. a) Conversion and selectivity were determined by GC-MS using tetradecane as internal standard.

To further reduce the environmental impact of this acetoxylation procedure, we investigated acetoxylations of **50** using an aerobic tandem catalytic system. The major advantage of this catalytic procedure is the use of an ETM that is able to reoxidize the employed oxidant (e.g. *p*-BQ). For this purpose, a coupled system of palladium(II) acetate, hydroquinone (HQ) as oxidant precursor, and iron(II) phthalocyanine (Fe(Pc), ETM) were used in the presence of acetic acid and sodium acetate. In this case, oxygen (air) is the primary oxidant. First reactions were carried out using conditions reported by Bäckvall and co-workers for the catalytic diacetoxylation of dienes (Scheme 57).[231,232]



Scheme 57: Mechanism of the aerobic 1,4-diacetoxylation of 1,3-dienes using oxygen as primary oxidant.

The obtained results of the aerobic process using **50** revealed that very good conversions as well as a high selectivity can be achieved. Since the applied catalyst highly promotes C-H activation at the endocyclic double bond, it enabled the formation of the enantiomers **52** and **53** as well as **54** and **55** as major products. However, the acetoxylation also occurred at the exocyclic double bond, and thus **51** was obtained as by-product. Furthermore, with this catalytic system high conversions can be obtained in shorter reaction times, if compared to the aforementioned catalytic system involving DMSO (Table 28).

Table 28: Results of the Pd-catalyzed acetoxylation of **50** using an aerobic tandem catalytic system.

Entry	t [h]	Conversion[%][a)]	Selectivity [%][a)]		
			51 [%]	**52**/**53** [%]	**54**/**55** [%]
1	2	39	-	39	61
2	4	69	8	36	56
3	6	78	9	37	54
4	24	98	10	33	57

Conditions: 200 mg (1.47mmol) **50**, 3.0 mL acetic acid,0.5 eq. sodium acetate, 20 mol% HQ, 5.0 mol% Fe(Pc), 5.0 mol% $Pd(OAc)_{2'}$, 60 °C, 24 h. a) Conversion and selectivity were determined by GC-MS using tetradecane as internal standard.

Additionally, the required amount of oxidant in the catalytic aerobic process was tremendously reduced. Thus, a catalytic amount of oxidant instead of stoichiometric amount is sufficient to perform the acetoxylation in a very efficient manner. Compared to the reaction conditions described above, the aerobic oxidation process represents a notable improvement in the development of a sustainable and environmentally-benign catalytic acetoxylation procedure. Further studies were carried out to investigate the effect of sodium acetate and DMSO as an additive (Table 29).

Table 29: Results of the Pd-catalyzed acetoxylation of **50** using a modified aerobic tandem catalytic system.

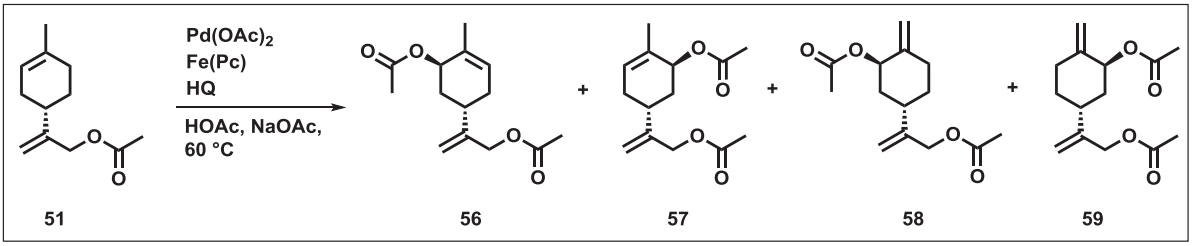
Entry	Conversion [%] [a)]	Selectivity [%][a)]		
		51 [%]	**52**/**53** [%]	**54**/**55** [%]
1	97 [b)]	11	32	57
2	89 [c)]	9	36	55

Conditions: 200 mg (1.47mmol) **50**, 3.0 mL acetic acid,0.5 eq. sodium acetate, 20 mol% HQ, 5.0 mol% Fe(Pc), 5.0 mol% $Pd(OAc)_2$,60 °C, 24 h. a) Conversion and selectivity were determined by GC-MS using tetradecane as internal standard, b) without sodium acetate, c) 20 mol% DMSO.

The obtained results show that the absence of sodium acetate has no significant effect on conversion or selectivity. If DMSO was added, a slightly lower conversion and improved selectivity was observed, whereas the expected (see results above) selective formation of **51** was not achieved. Moreover, if an equivalent amount of DMSO was used, only a very low conversion was obtained after 24 hours. Thus, DMSO might prevent the reoxidation of the oxidant by the used ETM.

With respect to the established catalytic acetoxylation processes, it would be very interesting to apply both acetoxylation procedures sequentially in order to efficiently functionalize the exo- and endocyclic double bond of **50** to obtain the respective diacetoxylated products. Therefore, the mono-acetoxylated products of **50** were used in further investigations. First the mixture of enantiomers (**52**, **53**, **54** and **55**) obtained by the aerobic tandem catalytic system was used for the acetoxylation process using DMSO and stoichiometric amounts of *p*-BQ. After 48 hours of reaction, no conversion was observed.

Therefore, as a second approach, the reverse strategy was tested (Scheme 58). Herein, the product mixture obtained from the DMSO/*p*-BQ system was used in the aerobic tandem catalytic acetoxylation procedure. Indeed, the diacetoxylated products **56** and **57** as well as **58** and **59** were formed as respective enantiomers, although only a moderate conversion of 45 % was obtained after a reaction time of 5 days. The presented sequential catalytic acetoxylation process resulted in a product selectivity of **56** and **57** (72%) as well as **58** and **59** (28%).



Scheme 58: Diacetoxylation of **51** using the aerobic tandem catalytic system.

The presented sequential diacetoxylation process is interesting although the reaction conditions still need to be optimized. However, this is the first catalytic two step procedure to obtain the diacetoxylated products directly from limonene; usually, longer reaction sequences are reported.[233] *Inter alia*, with such a diacetoxylation protocol, precursors for polycondensation reactions can be obtained. Simple saponification leads to the corresponding diol compounds. Moreover, these products as well as the mono-acetoxylated limonene are valuable precursors for transition metal catalyzed allylic substitution reactions.[234,235]

Conclusion

The successful synthesis of regioselectively acetoxylated limonene derivatives *via* two efficient catalytic systems is described. The redox couple system of palladium(II) acetate/*p*-BQ using DMSO and acetic acid as solvents enabled the acetoxylation of limonene at the exocyclic double bond. The catalyst loading, amount of oxidant, amount of solvent and temperature was systematically optimized with regard to a maximum conversion and product selectivity. Using the optimized reaction conditions, good conversions as well as remarkable selectivity were obtained. Additionally, some other polar and aprotic solvents were investigated, which showed a different selectivity to the aforementioned catalytic system using DMSO. On the other hand by utilizing an aerobic tandem catalytic system of palladium(II) acetate/hydroquinone/iron(II) phthalocyanine in acetic as solvent, very good conversions and selectivities were obtained. Herein, the substrate-selective catalyst highly promoted the acetoxylation of limonene at the endocyclic double bond. Furthermore, contrary to the redox coupled system, the use of an ETM allowed for use of only catalytic amounts oxidant (HQ). Thus, this catalytic system revealed to be highly efficient and more environmentally benign due to the reduction the amount of toxic *p*-BQ, which is further supported by a reduction of the E-factor by 1.4 (meaning 1.4 kg less waste are produced per kg of product). Finally, both catalytic procedures were combined in a sequential acetoxylation that facilitated the synthesis of diacetoxylated products and provide access to various limonene derivatives.

4.2.7 Polyacrylates from limonene by catalytic acetoxylation and multi-component reaction

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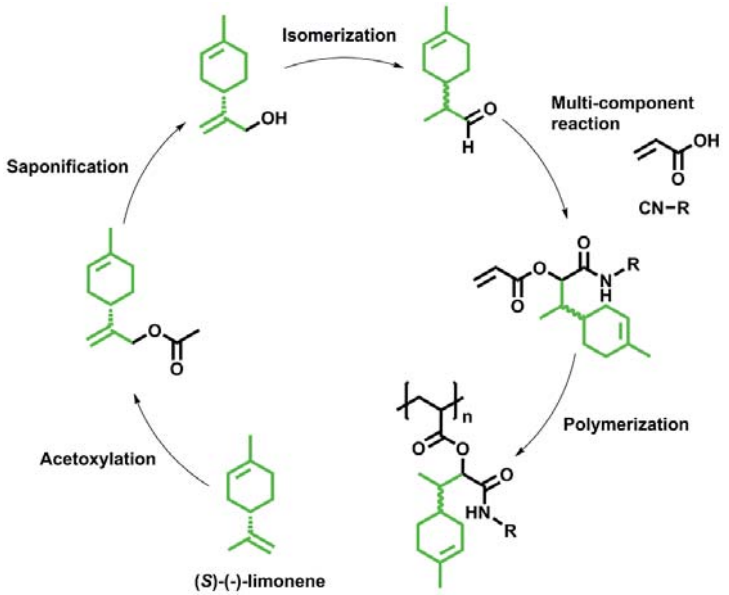


Abstract

A new strategy to obtain polyacrylates from limonene *via* regioselective catalytic acetoxylation, catalytic isomerization and subsequent Passerini three-component reaction (P-3CR) is described. The acetoxylated limonene derivative, selectively functionalized at the exocyclic double bond, was synthesized by a palladium-catalyzed C-H activation process in the presence of *para*-benzoquinone (*p*-BQ) as reoxidation agent and acetic acid in dimethyl sulfoxide. The obtained product was further saponified and subsequently isomerized under mild conditions into the corresponding aldehyde using a hydrogen-activated palladium catalyst. The resulting aldehyde, acrylic acid and various isocyanides were then used in the Passerini three-component reaction (P-3CR) in order to obtain several acrylate monomers in a straightforward and atom economic process. In subsequent free radical polymerizations using AIBN as thermal initiator, polyacrylates with molecular weights (M_n) up to 30 kDa were obtained and carefully characterized by SEC, NMR and DSC analysis.

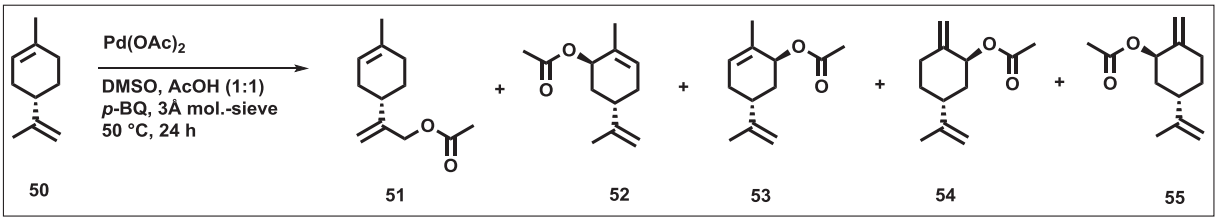
Introduction

The challenge to find sustainable solutions in terms of environmental concerns as well as raw material availability has become a major focus in polymer chemistry in recent years.[204] The tremendous potential of cellulose, lignin, sugars as well as fats and oils in this regard is already demonstrated by the use of more than nine million tons per year of these renewable raw materials by the European industry.[24] Among the available renewable materials, also terpenes constitute a valuable and cheap biomass resource, which can be obtained in large amounts from various essential oils or as by-product from diverse industrial processes.[12,13,37] Terpenes are also widely synthesized in nature as secondary metabolites by plants, fungi and microorganisms and offer versatile functionalization possibilities, due to their remarkable structural diversity. As a result, terpenes exhibit diverse properties and thus finds manyfold applications, *e.g.* for flavors, fragrances, nutrients, pheromones or as pharmacological substrates in treatments of different diseases.[39-41] Limonene, a naturally occuring dipentene (present as L-(-)-limonene in noble fir or as D-(+)-limonene in the peels of citrus fruits), is one of the many terpenes considered as valuable renewable feedstock.[22] Interestingly, the annual world production of citrus fruits has been estimated to be 88 × 10^6 tons per year, whereby D-(+)-limonene can be obtained as a waste product in considerable amounts (> 90%) from orange peel oil.[13] Chemically of interest, limonene incorporates an exocyclic- and an endocyclic double-bond in its structure. The most straightforward approach to polymerize natural terpenes is their direct cationic polymerization by living or conventional mechanism, as it was already investigated by Robert and Day in 1950.[205] The homo-polymerization of D-(+)-limonene into poly(D-(+)-limonene) was also conducted in 1965 by Marvel and coworkers using a Ziegla-Natta catalyst.[236] However, applying the aforementioned protocols, only low molecular weights of 1200 g × mol^{-1} were obtained. The free radical copolymerization of limonene with *N*-vinyl pyrrolidone[237] as well as methyl methacrylate[238] or styrene[239] was reported by Sharma and Srivastava. Moreover, Shiono and coworkers have described a protocol for the copolymerization of limonene with ethylene using a titanium catalyst. However, low molecular weights were achieved if compared to ethylene homo-polymerization or copolymerization of ethylene with isobutylene.[240] Nakatani *et al.* studied a different approach to incorporate limonene. For this purpose, poly(1-butene)

was modified *via* a free-radical graft polymerization process in order to introduce functional groups along the polymer backbone.[241] Due to their unsaturated cyclic structures, ring-opening metathesis polymerization (ROMP) constitutes a key polymerization methodology of terpenes. Mathers *et al*. published a ROMP protocol for the preparation of functional hyperbranched polymers from dicyclopentadiene with limonene as well as limonene oxide using an appropriate Grubb's catalyst.[242] Additionally, in former studies the same group clearly demonstrated that limonene is acting as a green solvent as well as a chain-transfer agent in ROMP. Another very interesting modification of limonene is accomplished by free-radical thiol-ene chemistry.[243] Recently, Meier *et al.* described the efficient synthesis of limonene-based polyesters, polyamides as well as non-isocyanate polyurethanes (NIPU's) *via* solvent and initiator-free thiol-ene addition.[244,245] Johansson *et al.* have taken advantage of this concept using limonene in the presence of polythiols to synthesize thermoset coatings under thermal and photoinitiated conditions.[246] Moreover, in order to broaden the use of terpenes, the development of catalytic and selective oxidation processes is of great interest and allows access to potential new precursors for polymer chemistry. Howdle *et al.* recently reported the synthesis and further radical polymerization of new renewable-based arcylates from monoterpenes. The acrylate monomers were first synthesized *via* a non-sustainable two step procedure, starting with a hydroboration/oxidation or reduction process, by employing (meth)acryloyl chloride afterwards. Further investigations were carried out on a one-pot greener catalytic approach, using a palladium-catalyzed oxidation process to couple *β*-pinene with methacrylic acid, yielding *β*-pinene derived methacrylates with up to 82% yield.[247] Inspired by a different catalytic approach, we have started our investigations on the synthesis of polyacrylates using limonene as a renewable raw starting material. For this purpose, we focused on a regioselective catalytic acetoxylation process that allows access to a precursor for the synthesis of an aldehyde derivative, which was then employed in the Passerini three-component reaction. Thus, by simple variation of the isocyanide component in this multi-component reaction, different acrylate monomers were obtained and subsequently studied in a free-radical polymerization process to lead to polymers with different thermal properties.

Results and discussion

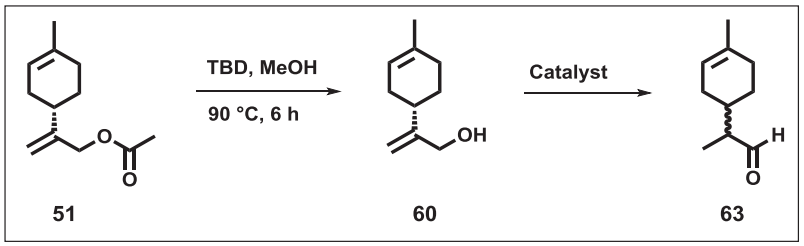
The aim of this study was to synthesize polyacrylates using renewable limonene **50**. We started our investigations based on a palladium-catalyzed C-H oxidation protocol, which is known to efficiently introduce an acetoxy moiety to methyl 10-undecenoate, a product obtained by pyrolysis of castor oil.[96] In 2004, White and co-workers first reported about this catalytic oxidation procedure, which allows a highly selective allylic C-H oxidation of *α*-olefins. The remarkable selectivity of the catalytic process is accomplished by a sulfoxide-promoted oxidation using palladium(II) acetate in the presence of *p*-benzoquinone (*p*-BQ) as reoxidation agent.[248] Inspired by the aforementioned catalytic oxidation procedure and some steps of optimization regarding a more sustainable reaction control (e.g. amount of catalyst, amount of solvent, temperature), we successfully synthesized the (*E*)-allylic acetate of limonene **51** in a moderate yield of 52 % under mild conditions (Scheme 59). Moreover, to the best of our knowledge, these results demonstrated the first direct catalytic acetoxylation (one-step) of the exocyclic double bond of limonene.[1] However, the functionalization of the endocyclic double bond of limonene could not be avoided, thus two by-products were obtained (~14 %), both as enantiomeric mixture (**52**/**53** and **54**/**55**).



Scheme 59: Palladium-catalyzed acetoxylation of (*S*)-(-)-limonene **50** using DMSO and acetic acid.

With the desired acetoxylated limonene derivative in hand, we continued our investigations by performing the saponification of **51** using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as catalyst in the presence of an excess of methanol. Thus, the corresponding allylic alcohol **60** was obtained in quantitative yield (Scheme 60). Additionally, the formation of allylic alcohol (**61**, **62**) derived from **52**-**55** was observed in

an amount of ~10 %: These byproducts could not be completely separated from the reaction mixture, but they also did not negatively influence the following reactions.



Scheme 60: Synthesis pathway to aldehyde 6 derived from (*S*)-(-)-limonene **51**.

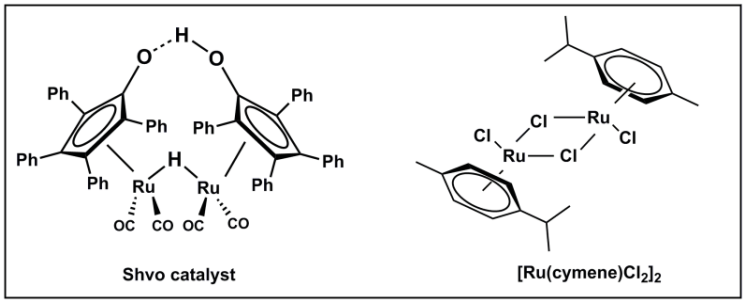
The next challenging step was to find suitable conditions for a mild isomerization of **60** into the aldehyde **63**. A promising synthesis approach to convert allylic alcohols (*via* vinylic alcohols and subsequent keto-enol tautomerism) into carbonyl compounds consists in catalytic isomerization processes using transitions metals (e.g. palladium, ruthenium). Yadav *et al*. reported an efficient catalytic isomerization of terminal allylic alcohols into aldehydes using hydrogen pre-activated palladium hydroxide on carbon.[249] In a first attempt, we applied their optimized conditions using 7.0 mol% palladium hydroxide on carbon suspended in toluene and activation with hydrogen for 30 minutes at room temperature in order to isomerize **60**. The reaction was performed for 16 hours at room temperature, and a subsequent GC-MS measurement confirmed the formation of **63** in high conversion (> 80%) (Table 30, entry 2). However, another peak with low intensity was observed and identified as the starting material **50**, which indicates the decomposition of an intermediate of terminal allylic alcohol **60** during the catalytic isomerization. After the work-up process, applying a standard washing procedure followed by column chromatography purification, the desired aldehyde was obtained in only 12 % yield (Table 30, entry 1). Therefore, the purification was optimized (reaction mixtures were evaporated to dryness and directly subjected to column chromatography) finally leading to 72 % yield (Table 30, entry 2) of the pure product. Additionally, NMR analysis revealed that the endocyclic double bond remained in the target molecule, which offers the possibility of further modification (e.g. thiol-ene chemistry, epoxidation). Moreover, ruthenium based catalysts were investigated for the isomerization of allylic alcohol **60**. For

this purpose, the *Shvo* catalyst (Scheme 61) was used in tetrahydrofuran (THF) as solvent. However, after seven hours reaction time at 75 °C, GC-MS measurements confirmed no conversion (Table 30, entry 3). Another attempt was carried out using $[Ru(cymene)Cl_2]_2$ (Scheme 3) and catalytic amounts of potassium carbonate as base leading to 12 % yield (Table 30, entry 4). By increasing the amount of solvent from 2.0 mL to 5.0 mL a slightly higher yield of 28 % was achieved using this catalyst (Table 30, entry 5). Unfortunately, if an increased amount of catalyst of 2.5 mol% was used, the yield dropped to 21% (Table 30, entry 6). Thus, Table 30 entry 2 provided the most suitable conditions for the synthesis of the required aldehyde **63**.

Table 30: Results of the catalytic isomerization of allylic alcohol **60** derived from limonene.

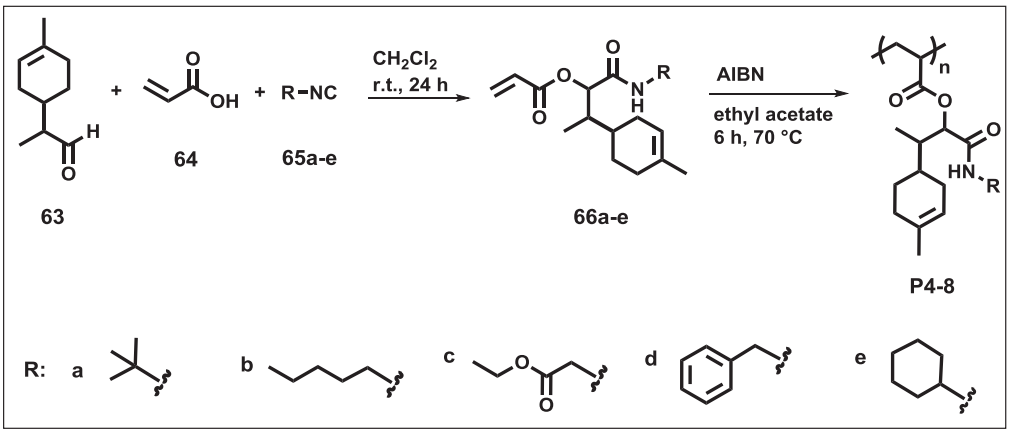
Entry	Catalyst	Amount of cat. [mol%]	Yield [%]
1	$Pd(OH)_2/C$	7.0	12 [a)]
2	$Pd(OH)_2/C$	7.0	72 [b)]
3	Shvo[c)]	0.2	-
4	$[Ru(cymene)Cl_2]_2$	1.0	12 [b, d)]
5	$[Ru(cymene)Cl_2]_2$	1.0	28 [b, e)]
6	$[Ru(cymene)Cl_2]_2$	2.5	21 [b, e)]

Conditions: 1.0 mmol **5**, 6.0 mL toluene, a) washing procedure + column chromatography, b) column chromatography, c) 1.0 mmol **5**, 2.0 mL THF d) 1.0 mmol **5**, 3.0 mol% K_2CO_3, 2.0 mL THF e) 1.0 mmol **5**, 3.0 mol% K_2CO_3, 5.0 mL THF.



Scheme 61: Ruthenium catalysts for catalytic isomerization of allylic alcohol **5**.

In 1921, Mario Passerini first reported the highly efficient synthesis of *α*-acyloxycarboxamides using a multi-component procedure, including an oxo-compound (aldehyde or ketone), an acid and an isocyanide.[166] The approach takes advantage of a simple one-pot reaction, mild conditions, and offers the possibility to introduce different functional groups into the synthesized molecule by varying the aforementioned starting materials. Moreover, the high atom economy of 100% shows a remarkable advantage regarding the sustainability of this approach. Thus, the Passerini reaction seems to be a promising tool to synthesize various acrylate monomers.[174,250] Here, by using acrylic acid **64** and the aldehyde **63** derived from limonene, only the isocyanide **65** can be varied to obtain different monomers and achieve different polymer structures and properties (Scheme 62). However, the remarkable diversity of isocyanides **65a-e** bearing unpolar aliphatic or aromatic moieties enables the formation of polymers with tunable properties by simple varying of the isocyanide component.



Scheme 62: Synthesis of acrylate monomers (**66a-e**) derived from limonene and its free-radical polymerization.

We started our investigations applying a convenient protocol, whereby acrylic acid and the isocyanide are used in a little excess of 1.1 equivalents (compared to **63**), and stirred for 24 hours at room temperature in dichloromethane as a suitable solvent. The subsequent work-up was accomplished by simple evaporation of the solvent followed by column chromatography purification. Thus, different acrylate monomers were obtained as colorless viscous liquid or white solid in good yields of 67-72 % (**66a-e**, Table 31,

entry a-e). Furthermore, using a higher excess of 1.5 equivalents of acrylic acid and the corresponding isocyanide resulted in an increased yield of 78 % **66d** (Table 31, entry 4). The obtained acrylates were then polymerized by free-radical polymerization using 2,2′-azobis(2-methylpropionitril) (AIBN) as thermal initiator. For this purpose, the monomers **66a-e** and AIBN were dissolved in ethyl acetate, degassed with argon for 10 minutes, and subsequently stirred for six hours at 70°C. The reaction was stopped by cooling and the crude mixture was added dropwise into cold ether in order to precipitate the formed polymers **P4-8**. After filtration and drying, polyacrylates were obtained as white solids in good to excellent yield and reached molecular weights in a range between 12.8 kDa (**P7**, Table 31, entry 4) to 29.8 kDa (**P6**, Table 31, entry 3) (Figure 24). The difference in molecular weights can most likely be explained by steric hindrance, for instance comparing the result of **P5** (26.1 kDa) bearing a flexible pentyl-moiety with **P7** (12.8 kDa) bearing a bulky benzyl-moiety. Furthermore, DSC analysis was performed in order to investigate the thermal properties. All synthesized polymers showed a glass transition temperature (T_g), but no melting point (Table 31, Figure 25). The lowest T_g was observed for **P6** (86 °C). In contrast, polyacrylates **P4** and **P5** showed much higher T_g of 134 °C and 143 °C, respectively. This can be explained by the bulky and inflexible structure of a *tert*-butyl or cyclohexyl moiety. However, polyacrylate **P7** bearing a benzyl substituent showed a lower T_g of 117 °C compared to **P4** and **P8**, despite the bulky structure. This is most likely due to the lower molecular weight of 12.8 kDA. In summary, T_g values of polyacrylates (here 86 - 143 °C) can be easily tuned by varying the isocyanide component.

Table 31: Results of the synthesis of acrylate monomers **66a-e** and derived polymers **P4-8**.

Entry	Isocyanide [x] [a]	Yield **66**x [%]	M_n [kDa] [c]	Đ [M_w/ M_n]	T_g [°C]	Yield [%]	
1	*tert*-butyl (**a**)	72	23.7	1.81	134	**P4**	95
2	pentyl (**b**)	70	26.1	2.30	105	**P5**	92
3	ethylacetate (**c**)	70	29.8	1.95	86	**P6**	75
4	Benzyl (**d**)	67 [b]	12.8	2.32	117	**P7**	74
5	Cyclohexyl (**e**)	69	25.8	2.95	143	**P8**	83

Conditions: a) 4.0 mmol **63**, 4.4 mmol acrylic acid **64**, 4.4 mmol isocyanide **65a-e**, 4.0 mL dichloromethane, r.t., 24 hours, b) 1.0 eq **6**, 1.5 eq. acrylic acid, 1.5 eq. isocyanide, 78 % yield, c) 250 mg **65a-e**, 1.0 mol% AIBN, 1.0 mL ethyl acetate.

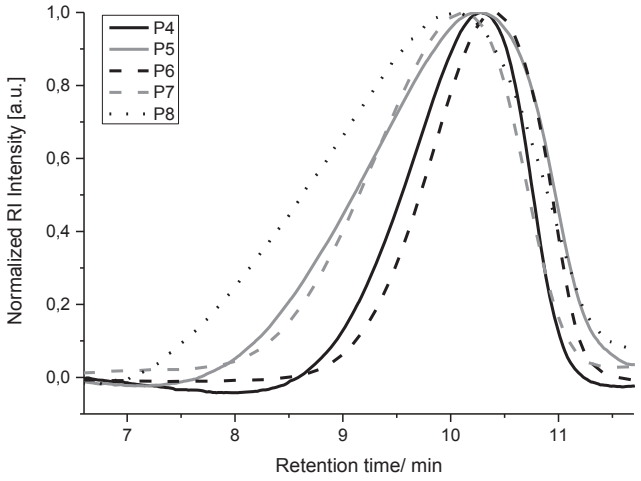


Figure 24: SEC curves of polyacrylates (**P4-8)** derived from limonene **50**.

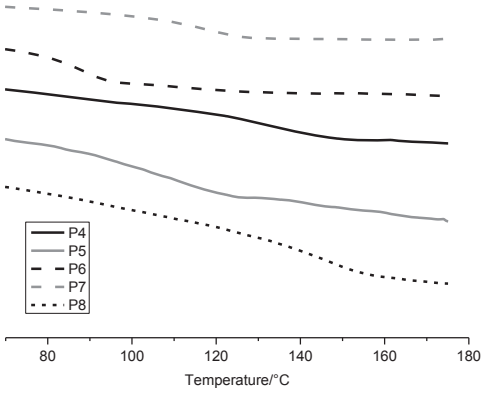


Figure 25: DSC curves of polyacrylates (**P4**-**8**) derived from limonene (second heating cycle).

Conclusion

In this study, a new approach to (partially) renewable polyacrylates based on limonene was established only using sustainable catalytic or multi-component reactions. A sulfoxide-promoted oxidation procedure using palladium(II) acetate and *para*-benzoquinone as reoxidation agent allowed the regioselective acetoxylation of limonene. After saponification and subsequent catalytic isomerization of the allylic alcohol, the key aldehyde was obtained. With the aldehyde in hand, Passerini three-component (P-3CR) reactions were performed using acrylic acid and various isocyanides to synthesize partially renewable acrylate monomers. These monomers were further studied in a free-radical polymerization process using AIBN as thermal initiator and the obtained polymers were carefully characterized by NMR, SEC, and DSC analyses. Polyacrylates with molecular weights (M_n) up to 30 kDa were synthesized, showing a glass transition temperature in a range between 86 °C and 143 °C. In summary, an alliance of catalytic oxidation processes and the Passerini three-component reaction demonstrates a fruitful synthesis strategy to obtain (partially) renewable acrylate monomers from limonene and the thereof derived polyacrylates with tunable properties. Moreover, the established synthesis route can be transferred to other terpene derivatives such as β-pinene, camphene or myrcene, which also bear a terminal bond. This would allow the use of the thereof derived aldehydes in multi-component reactions (e.g. Passerini-reaction or Ugi-reaction) in order to synthesize versatile acrylate monomers.

5 Conclusion and Outlook

Within this thesis, two efficient catalytic oxidation processes of renewable raw materials were investigated in order to synthesize various monomers and the thereof derived polymers. The first approach enabled the synthesis of several keto-fatty acids by a co-catalyst-free Wacker oxidation process using a high-pressure reactor system. In contrast, the second approach uses a C-H functionalization strategy, which allows the regioselective acetoxylation of limonene.

The first part of this thesis is related to the co-catalyst-free Wacker oxidation process, which was introduced by Meier *et al.* for the synthesis of keto-fatty acids, derived from methyl oleate and methyl erucate.

The aforementioned synthesis protocol was applied to oleic acid and erucic acid, as mono-unsaturated fatty acid derivatives, in order to broaden the substrate scope (4.1.1). However, the synthesis of the corresponding keto-fatty acids was accomplished in low conversion (< 10%). Due to these observations, further investigations were carried out with fatty acid methyl esters (FAMEs). Thus, after some steps of optimization, the keto-fatty acids derived from methyl oleate and methyl erucate were obtained in good yields. The optimized reaction conditions, obtained for the aforementioned oxidation of mono-unsaturated fatty acids, were applied for the oxidation of methyl linoleate, as poly-unsaturated fatty acid derivative (chapter 4.1.2). Hereby, full conversion of the double bond was achieved. However, instead of the expected ketonization, the formation of short carboxylic acids as well as carboxylic ester was observed, due to oxidative cleavage. Furthermore, high oleic sunflower oil, as triglyceride derivative with high content of mono-unsaturated fatty acids, was investigated in the catalytic oxidation process. After some steps of optimization, the corresponding poly-ketone (2.6 ketone units/molecule) was achieved in good yield (chapter 4.1.3). Moreover, the synthesis of three homogenous poly-ketone derivatives *via* transesterification of keto-fatty acids, derived from methyl oleate, methyl erucate and methyl 10-undecenoate, with glycerol was accomplished in moderate yields (chapter 4.1.4). In conclusion, the aforementioned examples clearly demonstrate that various keto-fatty acid derivatives (mainly from mono-unsaturated fatty acids) can be efficiently synthesized by the modified Wacker oxidation process. Moreover, the

straightforward product isolation by simple extraction as well as the recycling of the catalyst-solvent mixture clearly demonstrate the advantages of this catalytic oxidation process.

The possible isomerization of the double bond, induced by the palladium catalyst, was investigated in chapter 4.1.5. In the first approach, the Wacker oxidation of methyl oleate was carried out under argon atmosphere, and subsequently applied in a cross-metathesis reaction with methyl methacrylate. The resulting product distribution was identical with a reference sample, which has not been employed to the Wacker oxidation before. This was a first proof that double bond isomerization did not occur during the Wacker oxidation, at least in the absence of oxygen. In the second approach, a two-step synthesis protocol of photoperoxidation – hydrogenation enabled the synthesis of two keto-FAMEs that are also expected to be formed by the Wacker oxidation. Subsequent MS-MS measurements of the products, obtained by the two-step process and Wacker oxidation, led to an identical fragmentation pattern. This was a second evidence that two keto-fatty acid derivatives are formed by the Wacker oxidation process, and demonstrate a remarkable advantage in product selectivity.

The follow-up chemistry of keto-FAMEs was investigated in chapter 4.2.

The introduction of keto methyl stearate to transition metal catalyzed transfer hydrogenation processes using glycerol as green hydrogen donor, was part of investigations shown in chapter 4.2.1. However, the synthesis of the corresponding hydroxy-FAME could not be accomplished by the applied reaction conditions, and thus did not allow us to use this concept for the synthesis of polyols derived from poly-ketones. In contrast, the Meerwein-Pondorf-Verley reduction enabled the formation of the hydroxy-FAME in moderate yield. However, transesterification as side reaction led to a product mixture of methyl- and isopropyl-esters, thus this concept also could not be used for the synthesis of polyols from poly-ketones.

The synthesis of platform chemicals derived from keto-FAMEs was investigated in chapter 4.2.2. Therefore, keto methyl sterate and keto methyl docosanoate were employed to a Baeyer-Villiger oxidation process with mCPBA as oxidation agent. Thus, after some optimization, the corresponding diesters were obtained in good yields. The acid-catalyzed transesterification process with methanol allowed access to shorter diester, ester, hydroxy-ester as well as fatty alcohols. Moreover, depending on the applied keto-FAME, the aforementioned products can be obtained with different chain lengths. Furthermore, the product mixture was studied in a reduction process, whereby mono- and dialcocols were obtained. In conclusion, this synthesis concept demonstrate an efficient route to valuable platform chemicals, which are of great interest for the chemical industry.

A synthesis strategy towards AB_2-monomers is shown in chapter 4.2.3. The alliance of self-metathesis, Wacker oxidation and reductive amination enabled the synthesis of various unsaturated diesters, keto-diesters as well as amino-diesters. The aforementioned products were synthesized from methyl 10-undecenoate, methyl oleate and methyl erucate, and obtained in moderate to good yields. These products can be further used as monomers for the synthesis of various polymeric materials. For instance, the direct polymerization of the amino-diester into polyamides, or the keto-diester for synthesis of polyester with keto groups in the polymer backbone.

The synthesis strategy to prepare two polyesters and one polyamide from methyl 10-undecenoate *via* catalytic oxyfunctionalization is shown in chapter 4.2.4. Hereby, the co-catalyst-free Wacker oxidation allowed full conversion of the starting material. Isomerization of the double bond during the process led to a mixture of keto-FAMEs, thus after column chromatography the desired methyl ketone was obtained in good yield. However, the purification step can be avoided, if the amount of 15% of keto-FAME regioisomers do not significantly influence the product properties in further synthesis. The methyl-ketone was successfully transferred into hydroxy-esters as well as amino-esters *via* Baeyer-Villiger-Oxidation/transesterification, reduction or reductive amination. The AB-monomers, were obtained in excellent yields and further studied in homopolymerization. In conclusion, this synthesis concept demonstrates a highly efficient and high yielding strategy to obtain AB-monomers. The process can be further employed

to other fatty acid derivatives, which would allow the synthesis of various valuable AB-monomers and the thereof derived polymers.

The synthesis strategy to prepare partially and fully renewable dimer fatty acids from mono-unsaturated fatty acids *via* catalytic oxidation and reductive amination is shown in chapter 4.2.5. Hereby, the synthesis of seven different partially renewable DFAs was accomplished by reductive amination of keto methyl sterate with different aliphatic and aromatic diamines. Furthermore, six fully renewable DFAs were synthesized from keto- and amino-fatty acids, derived from methyl 10-undecenoate, methyl oleate and methyl erucate. Three out of the thirteen DFAs were selected and studied in the synthesis polyamides with 1,10 diaminodecane. In conclusion, this synthesis concept demonstrates two efficient strategies to obtain various DFAs, which are valuable products for the synthesis of polyamides.

The second catalytic oxidation process in this thesis describes the regioselective acetoxylation of limonene (chapter 4.2.6). Therefore, a redox couple system of palladium(II) acetate/*p*-BQ using DMSO and acetic acid as solvents enabled the selective acetoxylation of limonene at the double bond. Moreover, if a tandem catalytic system of palladium(II) acetate/hydroquinone/iron(II) phthalocyanine in acetic as solvent was employed, the selective acetoxylation of limonene at the internal double bond was obserevd. Finally, both catalytic procedures were combined in a sequential acetoxylation that facilitated the synthesis of diacetoxylated products and provide access to various limonene derivatives. In conclusion, these remarkable synthesis strategies address selectively double bonds in different chemical environment, which led to valuable products for further application. Due to this facts, these processes are quite promising for the functionalization of other terpene derivatives as well as for fatty acid derivatives.

The synthesis strategy of partially renewable polyacrylates based on limonene was accomplished by catalytic oxidation processes and multicomponent reaction (chapter 4.2.7). The limonene derivative, acetoxylated in allylic position to the terminal double bond, was successfully transferred into an aldehyde derivative through saponification and catalytic isomerization. The aldehyde was subsequently applied in the Passerini three-component reaction (P-3CR). Thus, in the presence of acrylic acid and various

isocyanides, five different acrylate monomers were obtained, which enabled the synthesis of partially renewable polyacrylates *via* free-radical polymerization. Accordingly, this synthesis concept demonstrates an efficient synthesis route towards acrylate monomers and the thereof derived polymers. In general, aldehydes are of particular interest in organic synthesis as well as in polymer synthesis. Moreover, the renewable aldehyde can be used for the synthesis of Ugi-products, which allow access to other valuable polymeric materials.

6 Experimental part

6.1 Materials

α,α,α-trifluorotouluene (> 99%, Sigma Aldrich), 1,2-dichloroethane (> 99%, Fisher Chemical), 1,3-diaminopropane (99%, Sigma Aldrich), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (98%, Sigma Aldrich), 1,7-diaminoheptane (98%, Sigma Aldrich), 1,8-diaminooctane (98%, Sigma Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (> 99%, Sigma Aldrich), 1,10-diaminodecane (> 97%, TCI), 1,12-diaminododecane (98%, Sigma Aldrich), 2,2′-azobis(2-methylpropionitrile) (98 %, Sigma Aldrich), 3-chloroperbenzoic acid (> 99%, 77 wt%, Sigma Aldrich), 10-undecenoic acid (98%, Sigma Aldrich), acetic acid (> 96%, Roth), acetic anhydride (> 98%, Sigma Aldrich), (acetonitrile (99.8%, Sigma Aldrich), aluminium isopropoxide (> 98%, Sigma Aldrich), (ammonium acetate (> 98%, Sigma Aldrich), ammonium chloride (> 99.5%, Sigma Aldrich), benzidine (98%, Sigma Aldrich), benzyl isocyanide (98%, Sigma Aldrich), chloroform (> 99%, Fisher Chemical), chloroform-d ($CDCl_3$, 99.8 atom % D, Armar Chemicals), cyclohexyl isocyanide (98%, Sigma Aldrich), dichloromethane (> 99%, Fisher Chemical), dimethyl sulfoxide (DMSO, > 99,5%, Roth), erucic acid (> 90%, technical grade, Sigma Aldrich), ethanol (> 99%, Fisher Chemical), ethyl acetate (> 99.5%, Fisher Chemical), ethyl isocyanoacetate (95%, Sigma Aldrich), hexafluoroisopropanol (HFIP, 99.9%, ChemPur), hydrogen (> 99.999, Air Liquide), hydroquinone (99%, Sigma Aldrich), iron(II) phthalocyanine (dye content ~ 90%, Sigma Aldrich), lithium aluminium hydride (95%, Sigma Aldrich), methanol (> 99%, VWR Chemicals), methanol-d4 (CD_3OD, 99.8 atom % D, Sigma Aldrich), molecular sieve (3A, Sigma Aldrich), *n*-heptane (> 99%, Fisher Chemical), *n*-hexane (95%, Fisher Chemical), *N,N*-dimethylacetamide (99%, abcr), *N,N*-dimethylformamide (99.8%, Sigma Aldrich), *n*-pentylisocyanide (97%, Sigma Aldrich), *n*-tetradecane (> 99%, Sigma Aldrich), oleic acid (98%, Sigma Aldrich), oxygen (99.5 %, technical grade, Air Liquide), *o*-xylene (> 98%, Sigma Aldrich), palladium(II) acetate (98%, Sigma Aldrich), palladium(II) chloride (99.5%, abcr), palladium hydroxide on carbon (20 wt.% loading on dry weight, Sigma Aldrich), *p*-benzoquinone (> 98%, Sigma Aldrich), potassium carbonate (99.7%, Sigma Aldrich), potassium permanganate (> 99%, Sigma Aldrich), *p*-xylenediamine (99%, Sigma Aldrich), Raney®-Nickel alloy (Sigma Aldrich), silica gel 60 (0.040 - 0.063, Sigma Aldrich), (*S*)-(-)-

limonene (96%, Sigma Aldrich), sodium acetate (anhydrous, Sigma Aldrich), sodium borohydride (98%, Sigma Aldrich), sodium hydrogen carbonate (> 95%, Sigma Aldrich), sodium hydroxide (98%, Sigma Aldrich), sodium sulfate (> 99% anhydrous, Acros Organics), sodium triacetoxyborohydride (98%, Sigma Aldrich), sulfuric acid (> 95%, Sigma Aldrich), *tert*-butyl isocyanide (98%, Sigma Aldrich), tetrahydrofuran (> 99.5%, Roth), tetrahydrothiophene (99%, Sigma Aldrich), tetraphenylporphyrin (> 99%, Sigma Aldrich), TLC silica gel F254 (Merck), titanium(IV) isopropoxide (> 97%, Sigma Aldrich), toluene. (99.8%, Sigma Aldrich), *trans*-1,4-diaminocyclohexane (98%, Sigma Aldrich), triethylamine (99.9%, Acros Organics). Fatty acid methyl esters (FAMEs) were synthesized by acidic esterification of corresponding fatty acid with methanol.

6.2 Characterization methods

TLC: Thin layer chromatography was performed on silica gel TLC-cards. Permanganate reagent (solution of potassium permanganate (3.00 g), potassium carbonate (20.0 g), sodium hydroxide (5.0 mL, 5.0 mol%) and water (300 mL) was used for staining.

Column chromatography was carried out using silica gel 60 (0.040 - 0.063) and all solvents used as mobile phase were technical grade, unless otherwise indicated.

NMR: ^{1}H and ^{13}C NMR spectra were recorded on Bruker Advance DPX spectrometers (Billerica, MA) with a 5-mm dual proton/carbon probe (300, 400, 500 MHz ^{1}H/ 75.5 or 126MHz ^{13}C) and on Bruker Advance III with a 5-mm z-gradient cryogenically cooled probe head (CPTCI, 600 MHz ^{1}H/ 75.5 MHz). ^{1}H-NMR spectra were reported in ppm relative to TMS or to the solvent signal $CDCl_3$ at 7.26 ppm, and ^{13}C-NMR spectra were reported in ppm relative to the central signal of the triplet for $CDCl_3$ at 77.00 ppm. Data for ^{1}H-NMR were reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), coupling constant (Hz), integration, and assignment. Furthermore, heteronuclear multiple quantum coherence (HMQC), heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond correlation (HMBC) methods were carried out in order to determine the structures.

GC: Gas chromatography (GC) analysis of the synthesized malonates was performed on a Bruker 430 GC instrument equipped with a capillary column FactorFour™ VF-5 ms (30.0 m × 0.25 mm × 0.25 µm), using flame ionization detection. The oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C min^{-1} to 220 °C, hold for 4 min, ramp at 15 °C min^{-1} to 300 °C, hold for 2 min, ramp at 15 °C min^{-1} to 325 °C, hold for 3 min. Measurements were performed in split–split mode using hydrogen as the carrier gas (flow rate 30 mL min^{-1}).

GC-MS: GC-MS analyses were conducted using a Varian 431-GC instrument with a capillary column Factor Four TM VF-5ms (30 m × 0.25 mm × 0.25 µm) and a Varian 210-MS detector. Scans were performed from 40 to 650 m/z at rate of 1.0 scans × s^{-1}. The oven temperature program applied during the analysis was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C × min^{-1} to 200 °C, hold for 2 min , ramp at 15 °C× min^{-1} to 300 °C, hold for 5 min. The injector transfer line temperature was set to 250 °C. Measurements were performed in the split-split mode (split ratio 50:1) using helium as carrier gas (flow rate 1.0 ml × min^{-1}).

MS: Electron spray ionization mass spectra (ESI-MS) were recorded on a Micromass Q-TOF instrument and high resolution mass spectra (HMRS) with electron impact ionization (EI) were recorded on a GC-TOF. Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT 95 instrument. The protonated molecule ion is expressed by the term: $[(M + H^+)]$.

IR: Infrared spectra (IR) were recorded on a Bruker Alpha-p instrument in a frequency range from 3997.21 to 373.942 cm^{-1} applying ATR-technology.

SEC: Polyesters were characterized on a SEC System LC-20A (Shimadzu) equipped with a SIL-20A autosampler, RID-10A refractive index detector in THF (flow rate 1 mL/min) at 50 °C. The analysis was performed on the following column system: main-column PSS SDV analytical (5 µm, 300 mm × 8.0 mm, 10000 Å) with a PSS SDV analytical precolumn (5 µm, 50 mm × 8.0 mm). Polyamides were characterized on a Tosoh EcoSEC HLC-8320 GPC system with HFIP containing 0.1 wt% potassium trifluoroacetate as solvent. The solvent flow was 0.40 mL min^{-1} at 30 °C. The analysis was performed on a 3-column

system: PSS PFG Micro precolumn (3.0 × 0.46 cm, 10 000 Å), PSS PFG Micro (25.0 × 0.46 cm, 1000 Å) and PSS PFG Micro (25.0 × 0.46 cm, 100 Å). Both systems were calibrated with linear poly(methyl methacrylate) standards (Polymer Standard Service, Mp 1100–981 000 Da).

DSC: Thermal properties of the prepared polymers were studied *via* differential scanning calorimetry (DSC) with a Mettler Toledo DSC stare system operating under nitrogen atmosphere using about 10 mg of the respective polymer for the analysis. The glass transition (T_g) and melting temperature (T_m) were recorded on the second heating scan by using the following method: starting from 0 to 220 °C (heating rate of 10°C ×min^{-1}), cooling from 220 to -75 °C (cooling rate of 10 °C × min^{-1}), and heating from -75 to 220 °C (heating rate of 10 °C ×min^{-1}).

SEC/ESI-MS: spectra were recorded on a LXQ mass spectrometer (Thermo Fisher Scientific, San Jose, CA) equipped with an atmospheric pressure ionization source operating in the nebulizer-assisted electrospray mode. The instrument was calibrated in the m/z range 195 - 1822 using a standard containing caffeine, Met-Arg-Phe-Ala acetate (MRFA), and a mixture of flourinated phosphazenes (Ultramark 1621) (all from Aldrich). A constant spray voltage of 4.5 kV, a dimensionless sweep gas flow rate of 2, and a dimensionless sheath gas flow rate of 12 were applied. The capillary voltage, the tube lens offset voltage, and the capillary temperature was set to 60 V, 110 V, and 275 °C, respectively. The LXQ was coupled to a Series 1200 HPLC-system (Agilent, Santa Clara, CA) consisting of a solvent degasser (G1322A), a binary pump (G1321A), and a high-performance autosampler (G1367B), followed by a thermostated column compartement (G1316A). Separation was performed on two mixed bed sized exclusion chromatography columns (Polymer Laboratories, Mesopore 2504.6 mm, particle diameter 3 μm) with precolumn (Mesopore 50-4.6 mm) operating at 30 °C. THF at a flow rate of 0.30 mL x min^{-1} was used as eluent. The mass spectrometer was coupled to the column in parallel to an RI-detector (G1362A with SS420x A/D) in a set-up described previously, 0.27 mL×min^{-1} of the eluent was directed through the RI detector, and 30 µL × min^{-1} was infused into the electrospray source after post column addition of a 100 µM solution of sodium iodide in methanol at 20 µL × min^{-1}by micro flow HPLC syringe pump (Teledyne ISCO, Model

100DM). 20µL of sample solution with a concentration of ~ 3 mg ×mL^{-1} was injected onto the HPLC system.

MS-MS (ESI-MS): spectra were recorded on a LTQ orbitrap XL spectrometer (Thermo Fisher Scientific, San Jose, CA) equipped with an atmospheric pressure ionization source operating in the nebulizer-assisted electrospray mode.

Reactions under high hydrogen and oxygen pressure were performed with a High-Pressure Laboratory Reactor (highpreactorTM) BR-100 of the company Berghof equipped with grease-free valves and connections.

Optimization: Screening reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK).

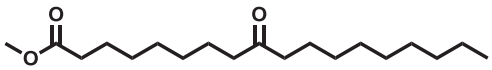
6.3 Experimental procedures

6.3.1 Wacker oxidation of fatty acid derivatives

Chapter 4.1.1 Mono-unsaturated fatty acids

10.0 mmol (1.00 eq.) fatty acid methyl ester (**5**, **6**) were dissolved in 30 mL of *N,N*-dimethylacetamide - deionized water (9:1 v/v). Subsequently, 45.0 mg (0.25 mmol, 2.5 mol%) palladium(II) chloride were added and the reaction mixture was stirred in a high pressure reactor system for 24 hours at 70 °C and 10 bar of oxygen pressure. The crude reaction mixture was extracted with *n*-heptane (3 x 10 mL) and the combined organic phases were washed with water and brine, dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified by flash column chromatography (*n*-hexane/ ethyl acetate gradient 95:5 to 4:1).

Methyl 9(10)-oxosterate **7** (mixture of regioisomers)



White solid, T_m = 41 °C, 89% yield.

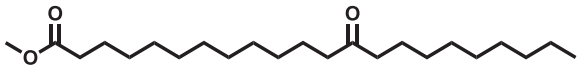
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.65 (s, 3H, *CH*$_3$OCO), 2.37 (t, *J* = 7.4 Hz, 4H, *CH*$_2$CO*CH*$_2$), 2.29 (t, *J* = 7.5 Hz, 2H, CH_3OCO*CH*$_2$), 1.69 – 1.45 (m, 6H, 3 CH_2), 1.36 – 1.14 (m, 18H, 9 CH_2), 0.87 (t, *J* = 6.7 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 211.7, 174.4, 51.5, 42.9, 34.1, 31.9, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 25.0, 24.0, 22.7, 14.2.

HRMS (FAB) of [$C_{19}H_{36}O_3H^+$]: calculated: 313.2737, found: 313.2735.

IR (ATR platinum diamond): 2916.2, 2846.7, 1737.6, 1704.9, 1462.2, 1434.8, 1412.5, 1376.9, 1325.4, 1302.7, 1286.0, 1246.5, 1213.9, 1173.4, 1128.1, 1109.4, 1027.2, 966.5, 882.9, 771.4, 750.1, 719.6., 680.6.

Methyl 13(14)-oxodocosanoate **8** (mixture of regioisomers)



White solid, T_m = 56 °C, 86% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.66 (s, 3H, *CH*$_3$OCO), 2.38 (t, *J* = 7.4 Hz, 4H, *CH*$_2$CO*CH*$_2$), 2.30 (t, *J* = 7.5 Hz, 2H, CH_3OCO*CH*$_2$), 1.69 – 1.46 (m, 6H, 3 CH_2), 1.36 – 1.16 (m, 26H, 13 CH_2), 0.87 (t, *J* = 6.7 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 211.8, 174.4, 51.2, 43.0, 34.2, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 25.1, 24.0, 22.8, 14.2.

HRMS (FAB) of [$C_{23}H_{44}O_3H^+$]: calculated: 369.3363, found: 369.3364.

IR (ATR platinum diamond): 2914.1, 2846.5, 1739.0, 1709.4, 1461.9, 1434.9, 1412.6, 1376.9, 1308.7, 1257.6, 1227.6, 1198.9, 1174.0, 1115.8, 1053.5, 1038.6, 964.8, 883.0, 756.6, 729.2, 719.2, 680.1, 432.9, 398.8, 380.4.

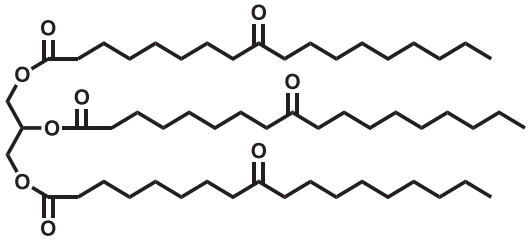
Chapter 4.1.2 Poly-unsaturated fatty acids

2.00 mmol (1.00 eq.) methyl linoleate **9** were dissolved in 6.0 mL of *N,N*-dimethylacetamide - deionized water (9:1 v/v). Subsequently, 17.7 mg (0.25 mmol, 5.0 mol%) palladium(II) chloride were added and the reaction mixture was stirred in a high pressure reactor system for 24 hours at 70 °C and 10 bar of oxygen pressure. The crude reaction mixture was extracted with *n*-heptane or diethyl ether (3 x 10 mL) and the combined organic phases were washed with water and brine, dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was analyzed by GC, GC-MS, ASAP-MS, IR and NMR.

Chapter 4.1.3 Triglycerides

1.0 mmol (1.00 eq.) triglyceride **11** was dissolved in 3.0 mL of *N,N*-dimethylacetamide - deionized water (9:1 v/v). Subsequently, 13.5 mg (0.075 mmol, 2.5 mol%/double bond) palladium(II) chloride were added and the reaction mixture was stirred in a high pressure reactor system for 24 hours at 100 °C and 10 bar of oxygen pressure. The crude reaction mixture was extracted with *n*-heptane (3 x 10 mL) and the combined organic phases were washed with water and brine, dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified by flash column chromatography (*n*-hexane/ ethyl acetate gradient 95:5 to 4:1).

Polyketone **12** (2.6 keto-units/molecule) derived from high oleic sunflower oil



White solid, T_m = 56 °C, 79% yield (after recrystallization).

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 5.25 (tt, *J* = 9.6, 4.5 Hz 1H, *CH*OCO), 4.28 (dd, *J* = 11.9, 4.3 Hz, 2H, CH_2OCO), 4.13 (dd, *J* = 11.9, 5.9 Hz, 2H, CH_2OCO), 2.37 (t, *J* = 7.4 Hz, 10H, CH_2(CO)CH_2), 2.30 (t, *J* = 7.5 Hz, 6H, 3 CH_2COO), 1.67 – 1.45 (m, 18H, 9 $CH_{2,\ backbone}$), 1.35 – 1.18 (m, 54H, 27 $CH_{2,\ backbone}$), 0.87 (t, *J* = 6.6 Hz, 9H, 3 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 211.7, 211.6, 211.6, 173.3, 173.3, 172.9, 172.9, 69.0, 62.2, 59.1, 42.9, 42.8, 42.8, 34.2, 34.2, 34.1, 34.1, 32.0, 31.9, 29.8, 29.8, 29.7, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 29.1, 29.1, 29.0, 29.0, 25.0, 24.9, 24.9, 24.8, 24.0, 23.9, 23.8, 22.8, 22.7, 14.2.

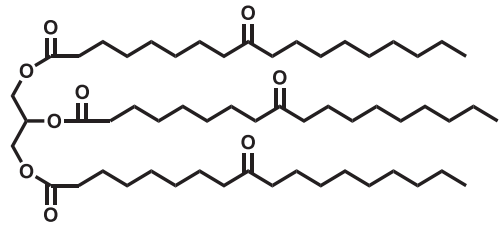
HRMS (FAB) of [$C_{57}H_{104}O_9H^+$]: calculated: 933.7753, found: 933.7755.

IR (ATR platinum diamond): 2914.1, 2848.3, 1735.3, 1704.3, 1469.8, 1412.7, 1378.9, 1284.1, 1247.4, 1214.3, 1177.1, 1109.7, 1060.2, 1026.8, 967.7, 717.4, 680.2.

Chapter 4.1.4 Homogenous keto-triglycerides.

4.00 g (43.3 mmol, 1.00 eq.) glycerol **13** and 136 mmol (3.15 eq.) ketone FAME (**7**, **8**, **37**) were placed in a round bottom flask. Subsequently, 2.16 mmol (5.00 mol%) TBD were added and the reaction was stirred under vacuum for 24 hours at 100 °C. The crude reaction mixture was purified by column chromatography (*n*-hexane/ ethyl acetate gradient 9:1 to 6:4).

Polyketone **14** derived from glycerol and keto-FAME **7**



White solid, T_m = 58 °C, 67% yield.

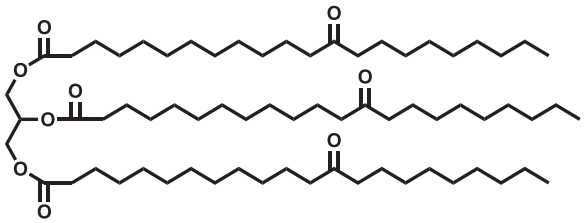
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 5.25 (tt, *J* = 9.0, 4.3 Hz 1H, *CH*OCO), 4.28 (dd, *J* = 11.9, 4.3 Hz, 2H, CH_2OCO), 4.13 (dd, *J* = 11.9, 5.9 Hz, 2H, CH_2OCO), 2.37 (t, *J* = 7.4 Hz, 12H, 3 CH_2(CO)CH_2), 2.30 (t, *J* = 7.5 Hz, 6H, 3 CH_2COO), 1.67 – 1.45 (m, 18H, 9 $CH_{2,\ backbone}$), 1.36 – 1.17 (m, 54H, 27 $CH_{2,\ backbone}$), 0.87 (t, *J* = 6.6 Hz, 9H, 3 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 211.6, 173.3, 172.9, 69.0, 62.2, 42.9, 34.2, 34.1, 32.0, 31.9, 29.8, 29.8, 29.7, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 29.1, 29.1, 29.0, 29.0, 25.0, 24.9, 24.9, 24.8, 24.0, 23.9, 23.8, 22.8, 22.7, 14.2.

HRMS (FAB) of [$C_{57}H_{104}O_9H^+$]: calculated: 933.7753, found: 933.7755.

IR (ATR platinum diamond): 2914.4, 2848.1, 1734.9, 1704.3, 1469.5, 1412.1, 1378.9, 1284.1, 1246.2, 1214.3, 1177.1, 1109.7, 1060.2, 1026.5, 967.7, 717.4, 680.1.

Polyketone **15** derived from glycerol and keto-FAME **8**



White solid, T_m = 73 °C, 60% yield.

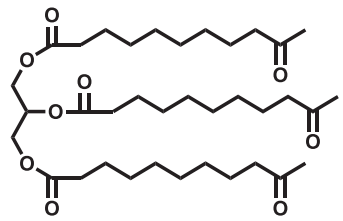
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 5.24 (tt, *J* = 9.0, 4.8 Hz 1H, *CH*OCO), 4.28 (dd, *J* = 11.9, 4.3 Hz, 2H, *CH*$_2$OCO), 4.13 (dd, *J* = 11.9, 5.9 Hz, 2H, *CH*$_2$OCO), 2.37 (t, *J* = 7.4 Hz, 12H, 3 *CH*$_2$(CO)*CH*$_2$), 2.30 (t, *J* = 7.5 Hz, 6H, 3 *CH*$_2$COO), 1.67 – 1.45 (m, 18H, 9 $CH_{2,\ backbone}$), 1.35 – 1.18 (m, 78H, 39 $CH_{2,\ backbone}$), 0.87 (t, *J* = 6.7 Hz, 9H, 3 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 211.6, 173.2, 172.8, 68.8, 62.0, 42.8, 34.2, 34.0, 31.8, 31.8, 29.5, 29.5, 29.4, 29.4, 29.2, 29.1, 29.0, 24.8, 24.8, 23.8, 22.6, 22.6, 14.1.

HRMS (FAB) of [$C_{69}H_{128}O_9H^+$]: calculated: 1101.9631, found: 1101.9633.

IR (ATR platinum diamond): 2914.3, 2848.5, 1736.2, 1706.3, 1470.1, 1414.3, 1380.3, 1277.4, 1258.1, 1230.7, 1199.1, 1178.3, 1115.0, 1088.4, 1038.1, 966.3, 981.7, 719.3, 681.9, 443.1.

Polyketone **16** derived from glycerol and keto-FAME **37**



White solid, T_m = 45 °C, 76% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 5.24 (tt, *J* = 7.5, 4.2 Hz 1H, *CH*OCO), 4.27 (dd, *J* = 11.9, 4.3 Hz, 2H, CH_2OCO), 4.12 (dd, *J* = 11.9, 5.9 Hz, 2H, CH_2OCO), 2.35 (t, *J* = 5.4 Hz, 6H, 3 CH_2(CO)CH_3), 2.24 (t, *J* = 5.7 Hz, 6H, CH_2COO), 2.06 (s, 9H, 3 CH_3), 1.60 – 1.43 (m, 12H, 6 $CH_{2,\ backbone}$), 1.29 – 1.16 (m, 24H, 12 $CH_{2,\ backbone}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 209.2, 209.1, 173.2, 172.8, 68.9, 62.1, 43.7, 34.1, 34.0, 29.8, 29.2, 29.2, 29.1, 29.0, 29.0, 28.9, 24.8, 24.8, 23.7.

HRMS (FAB) of [$C_{36}H_{62}O_9H^+$]: calculated: 639.4467, found: 639.4467.

IR (ATR platinum diamond): 2910.5, 2849.0, 1729.0, 1706.1, 1470.2, 1411.4, 1360.5, 1334.2, 1278.4, 1258.0, 1210.5, 1178.4, 1157.5, 1109.3, 1059.0, 1014.0, 944.6, 897.2, 775.5, 714.9, 594.9, 497.2, 454.8.

Chapter 4.1.5 Investigation of isomerization side-reaction

First approach:

(I) Wacker Oxidation under inert atmosphere

0.30 g (1.00 mmol, 1.00 eq.) methyl oleate **5** were dissolved in 3.0 mL of *N,N*-dimethylacetamide - deionized water (9:1 v/v). Subsequently, 4.5 mg (2.5 mol%) palladium(II) chloride were added and the reaction mixture was stirred in a round bottom flask for 24 hours at 70 °C and 100 °C under argon atmosphere. Afterwards, the crude product was flashed through a short filter column using a 20 mL syringe equipped with cotton wool/ silica gel and ethyl acetate as eluent. The obtained product was analyzed by GC-MS analysis and then purified by column chromatography (*n*-hexane/ ethyl acetate 9:1).

(II) Cross-metathesis with methyl methacrylate (MMA)

100 mg (0.34 mmol, 1.00 eq.) methyl oleate (**5**, **5a**, **5b**), 153 µL (145 mg, 1.69 mmol, 5.00 eq.) methyl methacrylate **17** and 1.1 mg (3.0 mol%) *p*-benzoquinone were introduced into

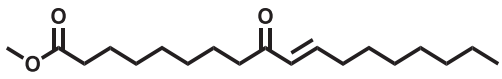
a 10 mL round bottom flask, and heated to 50 °C. Afterwards, 1.1 mg (0.5 mol%) Hoveyda-Grubbs 2nd Generation catalyst was added and the reaction was stirred for 3 hours taking a sample for GC-MS analysis each hour.

Second approach:

Synthesis of Methyl 9(10)-oxosterate **19** *via* photoperoxidation (**I**) followed by hydrogenation (II) as reference for MS-MS measurements.

(**I**) In a 450-mL standard immersion-well photochemical reactor with a 400 W high pressure sodium vapor lamp, 50.0 g (169 mmol, 1.00 eq.) methyl oleate **5**, 30.0 mg (0.05 mmol) tetraphenylporphyrin (TPP), and 300 mL dichloromethane were placed. Cold water was circulated through the lamp jacket, while a gentle stream of oxygen was bubbled through the stirred reaction mixture. After 7 hours of irradiation, 52.6 mL (557 mmol, 3.03 eq.) acetic anhydride and 37.8 mL (270 mmol, 1.6 eq.) triethylamine were added and stirred for 30 min at room temperature. Afterwards, the solvent was evaporated under reduced pressure. The crude mixture was diluted in 300 mL ethyl acetate and washed successively with water, saturated $NaHCO_3$, HCl (10% v/v), and brine. After drying over sodium sulfate and concentrating under reduced pressure, the product was purified by column chromatography (*n*-hexane/ ethyl acetate 9:1).[251]

Methyl (E)-9-oxooctadec-10-enoate **18** (two regioisomers)



Yellowish liquid, 70% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 6.78 (dt, *J* = 15.8, 6.9 Hz, 1H, *CH*CH_2), 6.05 (d, *J* = 15.9 Hz, 1H, (CO)CH), 3.63 (s, 3H, *CH*$_3$OCO) 2.48 (t, *J* = 7.4 Hz, 2H, *CH*$_2$(CO)CH), 2.27 (t, *J* = 7.5 Hz, 2H, $CH_3O(CO)$*CH*$_2$), 2.17 (dt, *J* = 7.5, 6.6 Hz, 2H, CH-*CH*$_2$-CH_2), 1.66 – 1.17 (m, 20H, 10 $CH_{2,\ backbone}$), 0.84 (t, *J* = 6.7 Hz, 3H, CH_3).

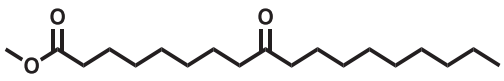
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 200.9, 200.8, 174.2, 174.1, 147.3, 146.9, 132.9, 130.3, 130.3, 51.4, 51.4, 40.1, 39.9, 34.0, 33.9, 32.4, 32.3, 31.8, 31.7, 29.4, 29.3, 29.1, 29.0, 29.0, 28.9, 28.8, 28.7, 28.1, 27.8, 24.8, 24.7, 24.3, 24.2, 24.0, 22.6, 22.6, 14.0, 14.0.

HRMS (FAB) of [$C_{19}H_{34}O_3H^+$]: calculated: 311.2581, found: 311.2579.

IR (ATR platinum diamond): 2924.3, 2853.5, 1737.2, 1696.1, 1671.4, 1627.6, 1457.8, 1434.9, 1362.5, 1247.3, 1194.5, 1169.0, 977.9, 878.5, 722.9.

(II) 30.0 g (96.7 mmol, 1.00 eq.) **18** were dissolved in 100 mL ethyl acetate. Subsequently, 3.0 g (10.0 wt%) palladium on charcoal were added and the reaction mixture was stirred for 24 hours at 60 °C and 20 bar of hydrogen pressure. Afterwards, the catalyst was filtered off and the crude product was purified by flash column chromatography (*n*-hexane/ ethyl acetate gradient 9:1 to 7:3).

Methyl 9(10)-oxosterate **19** (mixture of regioisomers)



White solid, T_m = 41 °C, quant. yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.65 (s, 3H, *CH*$_3$OCO), 2.37 (t, *J* = 7.4 Hz, 4H, *CH*$_2$CO*CH*$_2$), 2.29 (t, *J* = 7.5 Hz, 2H, CH_3OCO*CH*$_2$), 1.69 – 1.45 (m, 6H, 3 CH_2), 1.36 – 1.14 (m, 18H, 9 CH_2), 0.87 (t, *J* = 6.7 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 211.7, 174.3, 51.5, 42.9, 34.1, 31.9, 29.5, 29.4, 29.3, 29.3, 29.2, 29.2, 29.1, 29.1, 29.0, 24.9, 23.9, 22.7, 14.2.

HRMS (FAB) of [$C_{19}H_{36}O_3H^+$]: calculated: 313.2737, found: 313.2735.

IR (ATR platinum diamond): 2916.2, 2846.7, 1737.6, 1704.9, 1462.2, 1434.8, 1412.5, 1376.9, 1325.4, 1302.7, 1286.0, 1246.5, 1213.9, 1173.4, 11.3, 1109.4, 1027.2, 966.5, 882.9, 771.4, 750.1, 719.6., 680.6.

6.3.2 Follow-up chemistry of ketone-FAMEs

Chapter 4.2.1 Transfer hydrogenation using keto-FAMEs

(I) Transfer hydrogenation using glycerol **13**

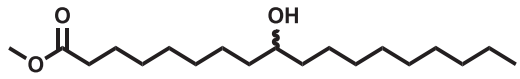
312 mg (1.00 mmol, 1.00 eq.) **7**, 4.00 g (43.4 mmol, 43.0 eq.) **13** and 2.0 – 15 mol% sodium hydroxide and/or potassium hydroxide as co-catalyst were placed in a round bottom flask, and heated to 80 °C. Afterwards, 5.0 mol% ruthenium-catalyst (**23**, **24**) were added and the reaction was stirred for 3 - 24 hours at 80 °C. The crude reaction mixture was analyzed by TLC and GC-MS measurement.

(II) Transfer hydrogenation using isopropanol

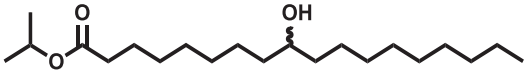
312 mg (1.00 mmol, 1.00 eq.) **7** were dissolved in 10 mL isopropanol. Afterwards, 10 mol% aluminium isopropoxide were added and the reaction mixture was stirred for 16 hours at 65 °C in an open system to allow the formed acetone to evaporate from the solution. The crude reaction mixture was extracted with ethyl acetate (3 x 10 mL) and the combined organic phases were washed with water and brine, dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified by flash column chromatography (*n*-hexane/ ethyl acetate gradient 95:5 to 4:1).

Mixture of hydroxy-FAMEs: methyl-ester **22** and propyl-ester **25**

Methyl 9-hydroxyoctadecanoate (+ regioisomer) **22**



Isopropyl 9-hydroxyoctadecanoate (+ regioisomer) **25**



White solid, 57% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 5.09 (dq, *J* = 18.0, 6.0 Hz, 1H, CH_3-*CH*-CH_3), 3.65 (s, 3H, *CH*$_3$OCO), 2.27 (t, *J* = 7.5 Hz, 2H, $CH_3O(CO)CH_2$), 1.67 – 1.15 (m, 30H, 15 CH_2), 0.87 (t, *J* = 6.7 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.4, 173.5, 72.1, 67.4, 51.6, 37.6, 37.6, 37.5, 34.82, 34.2, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 25.8, 25.7, 25.7, 25.1, 25.0, 22.8, 22.0, 14.2.

FAB-MS of [$C_{19}H_{38}O_3H^+$] methyl-ester: calculated: 315.3, found: 315.4.

FAB-MS of [$C_{21}H_{42}O_3H^+$] propyl-ester: calculated: 343.3, found: 343.4.

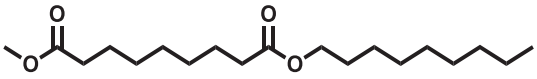
IR (ATR platinum diamond): 3318.2, 2919.1, 2848.3, 1733.1, 1466.1, 1435.7, 1376.0, 1291.6, 1254.4, 1214.3, 1173.2, 1108.0, 1028.1, 950.7, 891.8, 822.2, 721.8, 592.8, 418.4.

Chapter 4.2.2 Synthesis of platform chemicals

(I) Baeyer-Villiger-Oxidation of ketone-FAMEs

1.00 mmol (1.00 eq.) **7** was dissolved in 3.0 mL dichloromethane and then cooled in an ice bath to 0 °C. Subsequently, 1.50 mmol (1.50 eq., 77.0 wt%) 3-chloroperbenzoic acid were added and the reaction mixture was stirred for 3 days at room temperature. The crude reaction mixture was washed with water and brine, the water phase was extracted with ethyl acetate (3 × 10 mL) and the combined organic phases were dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified by flash column chromatography (*n*-hexane/ ethyl acetate gradient 95:5 to 4:1).

1-methyl 9-nonyl nonanedioate (+ regioisomers) **7** derived from ketone-FAME **26**



White solid, 70% yield.

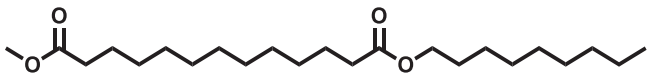
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 4.04 (t, *J* = 6.7 Hz, 2H, $CH_2O(CO)CH_2$), 3.66 (s, 3H, CH_3OCO), 2.31 (t, *J* = 7.5 Hz, 2H, $CH_2O(CO)CH_2$), 2.28 (t, *J* = 7.5 Hz, 2H, $CH_3O(CO)CH_2$), 1.67 – 1.53 (m, 6H, 3 CH_2 backbone), 1.38 – 1.20 (m, 18H, 9 CH_2 backbone), 0.87 (t, *J* = 6.4 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.3, 174.1, 64.5, 64.4, 51.5, 34.5, 34.2, 31.9, 31.9, 29.6, 29.5, 29.3, 29.3, 29.2, 29.2, 29.0, 29.0, 28.7, 26.0, 26.0, 25.9, 25.1, 25.1, 25.0, 22.8, 14.2.

HRMS (FAB) of [$C_{19}H_{36}O_4H^+$]: calculated: 329.2686, found: 329.2688.

IR (ATR platinum diamond): 2924.3, 2853.9, 1734.9, 1458.5, 1434.9, 1357.6, 1244.1, 1165.7, 1102.1, 723.1, 388.9.

1-methyl 13-nonyl tridecanedioate (+ regioisomers) **8** derived from ketone-FAME **27**



White solid, 80% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 4.04 (t, *J* = 6.7 Hz, 2H, $CH_2O(CO)CH_2$), 3.66 (s, 3H, CH_3OCO), 2.31 (t, *J* = 7.5, 2H, $CH_2O(CO)CH_2$), 2.28 (t, *J* = 7.5 Hz, 2H, $CH_3O(CO)CH_2$), 1.67 – 1.53 (m, 6H, 3 CH_2 backbone), 1.38 – 1.20 (m, 26H, 13 CH_2 backbone), 0.87 (t, *J* = 6.4 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.2, 173.9, 64.7, 64.3, 63.9, 51.7, 51.5, 51.2, 34.3, 34.0, 31.8, 31.8, 29.5, 29.4, 29.4, 29.2, 29.1, 28.9, 28.6, 25.9, 25.0, 24.9, 22.6, 14.0.

HRMS (FAB) of [$C_{23}H_{44}O_4H^+$]: calculated: 385.3312, found: 385.3313.

IR (ATR platinum diamond): 2922.5, 2852.8, 1735.6, 1693.5, 1434.7, 1461.5, 1253.9, 1162.7, 1107.9, 1026.1, 875.2, 762.6, 724.0, 475.6.

(II) Transesterification of diester derived from Baeyer-Villiger-Oxidation

1.00 mmol (1.00 eq.) diester (**26**, **27**) was dissolved in 20 mL methanol. Subsequently, five drops of concentrated sulfuric acid were added, and the reaction mixture was stirred for five hours under reflux. After cooling to room temperature, the crude mixture was diluted with 20 mL dichloromethane and washed successively with water and brine. After drying over sodium sulfate and concentrating under reduced pressure, the product mixture was analyzed by GC-MS.

(III) Reduction of fatty acid hydroxy-ester mixture into alcohol derivatives

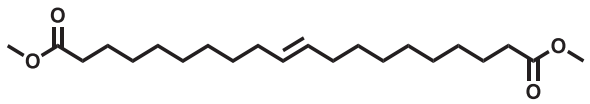
5.0 mL dry THF and 1.00 mL (1M, 1.00 mmol, 1.00 eq.) lithium aluminium hydride in THF were placed in a two necked round bottom flask equipped with a septum and reflux condenser. Subsequently, 300 mg of hydroxy-ester mixture dissolved in 3.0 mL dry THF were added dropwise at room temperature. After 30 min the temperature was increased to 70 °C and the reaction mixture was stirred for four hours under reflux. After cooling to room temperature, 5.0 mL water were added dropwise to quench the catalyst. The crude mixture was diluted with 10 mL dichloromethane and washed successively with water and brine. Few drops of concentrated sulfuric acid were used to dissolve the precipitated aluminum hydroxide. After drying over sodium sulfate and concentrating under reduced pressure, the product mixture was analyzed by GC-MS.

Chapter 4.2.3 Synthesis strategy of AB_2 – monomers

(I) Self-metathesis of mono-unsaturated FAMEs

10.0 g FAME (**5**, **6**, **37**) and 0.3 mol% *p*-benzoquinone were placed in a 50 mL round bottom flask und heated to 50 °C. Afterwards, 0.1 mol% Zhan-catalyst were added and the reaction mixture was stirred for eight hours, while a gentle stream of argon was bubbled through the solution. Afterwards, the crude product was purified by flash column chromatography (*n*-hexane/ ethyl acetate gradient 1:0 to 5:1).

Dimethyl (E)-icos-10-enedioate **28** derived from FAME **37**



White solid, 61% yield.

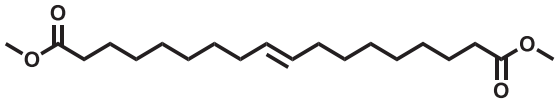
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 5.40 – 5.33 (m, 2H, CH=CH), 3.66 (s, 6H, 2 CH_3OCO), 2.30 (t, *J* = 7.5 Hz, 4H, 2 $CH_3O(CO)CH_2$), 2.00 – 1.90 (m, 4H, 2 $CH_{2\ backbone}$), 1.68 – 1.54 (m, 4H, 2 $CH_{2\ backbone}$), 1.38 – 1.20 (m, 20H, 10 $CH_{2\ backbone}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.3, 130.3, 51.3, 50.7, 34.1, 32.5, 29.6, 29.3, 29.2, 29.1, 29.0, 27.3, 26.9, 24.9.

HRMS (FAB) of [$C_{22}H_{40}O_4H^+$]: calculated: 369.2999, found: 369.3001.

IR (ATR platinum diamond): 2911.2, 2848.0, 1734.6, 1470.6, 1434.9, 1421.0, 1382.9, 1336.3, 1309.6, 1282.1, 1246.2, 1206.7, 1168.0, 1065.5, 1029.6, 1007.8, 995.1, 962.0, 883.4, 847.0, 746.0, 715.7, 587.2, 527.0, 494.7, 454.5.

Dimethyl (E)-octadec-9-enedioate **29** derived from FAME **5**



White solid, 37% yield.

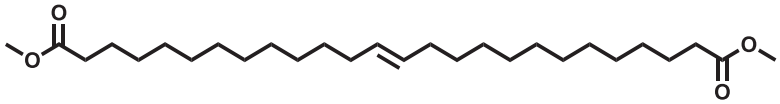
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 5.40 – 5.30 (m, 2H, CH=CH), 3.66 (s, 6H, 2 *CH*$_3$OCO), 2.30 (t, *J* = 7.5 Hz, 4H, 2 $CH_3O(CO)CH_2$), 2.02 – 1.90 (m, 4H, 2 $CH_{2\ backbone}$), 1.68 – 1.54 (m, 4H, 2 $CH_{2\ backbone}$), 1.38 – 1.20 (m, 16H, 8 $CH_{2\ backbone}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.4, 130.4, 51.5, 50.8, 34.2, 32.6, 29.7, 29.4, 29.3, 29.2, 29.2, 27.4, 27.0, 25.0.

HRMS (FAB) of [$C_{20}H_{36}O_4H^+$]: calculated: 341.2686, found: 341.2688.

IR (ATR platinum diamond): 2923.1, 2852.5, 1736.9, 1434.8, 1361.2, 1243.9, 1195.1, 1164.2, 1018.1, 968.2, 851.9, 724.3, 578.9, 437.5.

Dimethyl (E)-hexacos-13-enedioate **30** derived from FAME **6**



White solid, 26% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 5.41 – 5.35 (m, 2H, CH=CH), 3.66 (s, 6H, 2 *CH*$_3$OCO), 2.30 (t, *J* = 7.5 Hz, 4H, 2 $CH_3O(CO)CH_2$), 2.01 – 1.90 (m, 4H, 2 $CH_{2\ backbone}$), 1.68 – 1.54 (m, 4H, 2 $CH_{2\ backbone}$), 1.38 – 1.21 (m, 32H, 16 $CH_{2\ backbone}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.3, 130.3, 51.4, 34.10, 32.6, 29.6, 29.6, 29.6, 29.5, 29.4, 29.2, 29.1, 24.9.

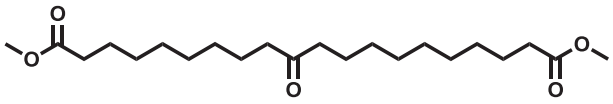
HRMS (FAB) of [$C_{28}H_{52}O_4H^+$]: calculated: 453.3938, found: 453.3938.

IR (ATR platinum diamond): 2915.7, 2847.1, 1736.9, 1460.7, 1434.5, 1382.1, 1324.2, 1277.3, 1251.3, 1222.6, 1195.6, 1170.7, 1072.3, 1027.3, 993.0, 957.1, 882.7, 772.8, 729.3, 719.2, 410.3.

(II) Wacker oxidation of diesters

4.00 mmol (1.00 eq.) diester (**28**, **29**, **30**) were dissolved in 24 mL of *N,N*-dimethylacetamide - deionized water (9:1 v/v). Subsequently, 2.5 mol% palladium(II) chloride were added and the reaction mixture was stirred in a high pressure reactor system for 24 hours at 70 °C and 10 bar of oxygen pressure. The crude reaction mixture was extracted with *n*-heptane (3 x 10 mL) and the combined organic phases were washed with water and brine, dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified by flash column chromatography (*n*-hexane/ ethyl acetate gradient 95:5 to 4:1).

Dimethyl 10-oxoicosanedioate (+ regioisomers) **31**



White solid, 70% yield.

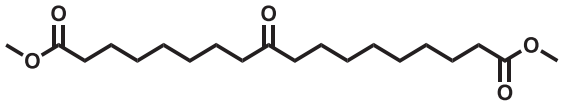
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.66 (s, 6H, 2 CH_3OCO), 2.35 (t, *J* = 7.5 Hz, 4H, CH_2(CO)CH_2), 2.26 (t, *J* = 7.5 Hz, 4H, 2 $CH_3O(CO)CH_2$), 1.65 – 1.44 (m, 8H, 4 CH_2 $_{backbone}$), 1.38 – 1.21 (m, 18H, 9 CH_2 $_{backbone}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 211.7, 174.4, 174.3, 51.5, 42.9, 42.8, 34.2, 34.1, 29.4, 29.3, 29.3, 29.3, 29.2, 29.2, 29.1, 25.0, 25.0, 23.9, 23.9.

HRMS (FAB) of [$C_{22}H_{40}O_5H^+$]: calculated: 385.3061, found: 385.3060.

IR (ATR platinum diamond): 2913.8, 2847.1, 1735.0, 1707.4, 1461.9, 1435.5, 1413.9, 1377.2, 1330.0, 1287.9, 1252.1, 1209.3, 1168.9, 1114.5, 1044.0, 1019.4, 980.4, 964.3, 883.6, 842.4, 754.7, 745.3, 729.2, 719.6, 680.1, 587.0, 504.6, 433.5.

Dimethyl 9-oxooctadecanedioate (+ regioisomers) **32**



White solid, 69% yield.

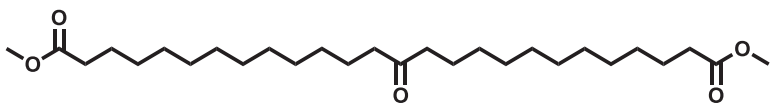
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.66 (s, 6H, 2 CH_3OCO), 2.36 (t, J = 7.5 Hz, 4H, $CH_2(CO)CH_2$), 2.28 (t, J = 7.5 Hz, 4H, 2 $CH_3O(CO)CH_2$), 1.66 – 1.46 (m, 8H, 4 CH_2 $_{backbone}$), 1.38 – 1.21 (m, 14H, 7 CH_2 $_{backbone}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 211.5, 174.3, 174.2, 51.4, 42.7, 42.7, 34.0, 34.0, 29.2, 29.1, 29.0, 29.0, 28.9, 24.9, 24.8, 23.8, 23.7.

HRMS (FAB) of [$C_{20}H_{36}O_5H^+$]: calculated: 357.2636, found: 357.2637.

IR (ATR platinum diamond): 2913.8, 2846.7, 1736.2, 1705.9, 1462.2, 1434.5, 1412.8, 1378.3, 1304.7, 1261.8, 1213.5, 1168.6, 1112.6, 1029.2, 986.4, 965.1, 881.9, 814.0, 758.2, 730.1, 720.2, 701.0, 680.3, 586.5, 413.6.

Dimethyl 13-oxohexacosanedioate (+ regioisomers) **33**



White solid, 62% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.66 (s, 6H, 2 *CH_3*OCO), 2.37 (t, *J* = 7.5 Hz, 4H, *CH_2*(CO)*CH_2*), 2.29 (t, *J* = 7.5 Hz, 4H, 2 $CH_3O(CO)CH_2$), 1.66 – 1.47 (m, 8H, 4 CH_2 backbone), 1.38 – 1.21 (m, 30H, 15 CH_2 backbone).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 211.6, 174.3, 51.4, 42.8, 34.1, 29.5, 29.5, 29.4, 29.2, 29.2, 29.1, 24.9, 23.8.

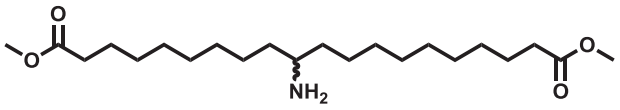
HRMS (FAB) of [$C_{28}H_{52}O_5H^+$]: calculated: 469.3888, found: 469.3890.

IR (ATR platinum diamond): 2914.3, 2846.7, 1737.1, 1709.0, 1461.4, 1434.7, 1412.8, 1379.4, 1316.9, 1288.4, 1257.7, 1229.9, 1199.0, 1171.4, 1117.6, 1052.7, 991.4, 975.8, 883.0, 768.3, 729.0, 719.2, 410.3.

(III) Reductive amination of ketone diester

2.00 mmol (1.00 eq.) keto-diester (**31**, **32**, **33**), 8.00 mmol (4.00 eq.) ammonium acetate and 1.00 mmol (1.00 eq.) ammonium chloride were dissolved in 15 mL ethanol. Subsequently, 20.0 wt% Raney®-Nickel were added and the reaction mixture was stirred in a high pressure reactor system for 24 hours at room temperature/or 70 °C and 30 bar of hydrogen. Afterwards, the catalyst was filtered off and the crude reaction mixture was washed with water and brine. The water phase was extracted with dichloromethane (3 x 10 mL) and the combined organic phases were dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified by flash column chromatography ($CHCl_3$/MeOH/Et_3N gradient 98:1:1 to 94:5:1).

Dimethyl 10-aminoicosanedioate (+ regioisomers) **34**



White solid, 92% yield.

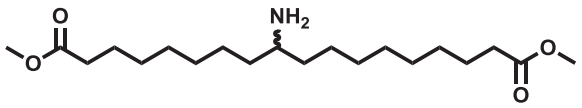
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.29 (bs, 2H, NH_2), 3.63 (s, 6H, 2 *CH*$_3$OCO), 2.85 – 2.71 (m, 1H, *CH*-NH_2) 2.26 (t, *J* = 7.5 Hz, 4H, 2 $CH_3O(CO)CH_2$), 1.65 – 1.16 (m, 30H, 15 $CH_{2\ backbone}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.4, 174.3, 51.5, 51.4, 35.8, 34.2, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.2, 26.6, 25.8, 25.0.

HRMS (FAB) of [$C_{22}H_{43}NO_4H^+$]: calculated: 386.3265, found: 386.3264.

IR (ATR platinum diamond): 2922.0, 2849.5, 1731.7, 1604.6, 1516.6, 1469.6, 1434.9, 1379.2, 1301.4, 1267.9, 1234.5, 1198.9, 1164.8, 1098.1, 1047.5, 1004.6, 973.9, 884.9, 851.5, 826.4, 786.6, 720.5, 582.0, 469.1.

Dimethyl 9-aminooctadecanedioate (+ regioisomers) **35**



White solid, 85% yield.

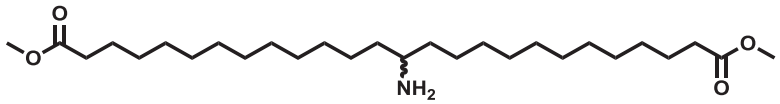
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 5.27 (bs, 2H, NH_2), 3.65 (s, 6H, 2 *CH*$_3$OCO), 3.00 – 2.76 (m, 1H, *CH*-NH_2), 2.28 (t, *J* = 7.5 Hz, 4H, 2 $CH_3O(CO)CH_2$), 1.66 – 1.18 (m, 26H, 13 $CH_{2\ backbone}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.4, 51.5, 51.5, 37.5, 34.2, 29.9, 29.7, 29.7, 29.5, 29.3, 29.2, 26.2, 25.0.

HRMS (FAB) of [$C_{20}H_{39}NO_4H^+$]: calculated: 358.2952, found: 358.2950.

IR (ATR platinum diamond): 2922.8, 2850.2, 1730.8, 1605.3, 1515.3, 1468.6, 1433.9, 1379.6, 1320.5, 1278.7, 1241.6, 1201.6, 1161.3, 1093.0, 1040.7, 975.6, 883.1, 830.0, 722.3, 444.0, 407.3.

Dimethyl 13-aminohexacosanedioate (+ regioisomers) **36**



White solid, 70% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 5.64 (bs, 2H, NH_2), 3.66 (s, 6H, 2 *CH_3*OCO), 2.78 – 2.65 (m, 1H, *CH*-NH_2), 2.28 (t, *J* = 7.5 Hz, 4H, 2 $CH_3O(CO)$*CH_2*), 1.67 – 1.54 (m, 4H, 2 $CH_{2\ backbone}$), 1.49 – 1.18 (m, 38H, 20 $CH_{2\ backbone}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.4, 51.5, 51.5, 37.5, 34.2, 29.9, 29.7, 29.7, 29.5, 29.3, 29.2, 26.2, 25.0.

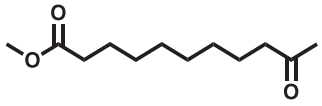
HRMS (FAB) of [$C_{28}H_{55}NO_4H^+$]: calculated: 470.4204, found: 470.4206.

IR (ATR platinum diamond): 2914.6, 2848.2, 1731.5, 1469.7, 1436.4, 1379.9, 1296.7, 1270.8, 1245.6, 1217.8, 1193.4, 1164.8, 991.3, 883.9, 718.8.

Chapter 4.2.4 Catalytic oxyfunctionalization of Methyl 10-undecenoate for the synthesis of step-growth polymers

Synthesis of Methyl 10-oxoundecanoate **38**

2.00 g (10.1 mmol, 1.00 eq.) methyl 10-undecenoate **37** were dissolved in 30 mL of *N,N*-dimethylacetamide - deionized water (9:1 v/v) and then transferred into a 100 mL Teflon reaction tube. Subsequently, 45.0 mg (0.25 mmol, 2.5 mol%) palladium(II) chloride were added and the reaction mixture was stirred in a high pressure reactor system for 24 hours at 50 °C and 10 bar of oxygen. The crude reaction mixture was extracted with *n*-heptane (3 × 10 mL) and the combined organic phases were washed with water and brine, dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified by flash column chromatography (*n*-hexane/ ethyl acetate 4:1 v/v).



Colorless liquid, 74% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.66 (s, 3H, CH_3OCO), 2.40 (t, *J* = 7.4 Hz, 2H, CH_2COCH_3), 2.29 (t, *J* = 7.5 Hz, 2H, CH_3OCOCH_2), 2.12 (s, 3H, CH_3), 1.57 (dt, *J* = 14.2, 7.1 Hz, 4H, 2 CH_2), 1.28 (bs, 8H, 4 CH_2).

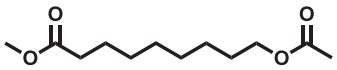
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 209.3, 174.3, 51.7, 43.7, 34.1, 29.9, 29.1, 29.1, 29.1, 29.1, 24.9, 23.8.

HRMS (FAB) of [$C_{12}H_{22}O_3H^+$]: calculated: 215.1642, found: 215.1642.

IR (ATR platinum diamond): 2929.3, 2855.9, 1735.6, 1714.7, 1435.7, 1358.6, 1194.7, 1167.2, 1101.6, 1063.3, 1012.7, 880.6, 719.9, 595.7, 432.6.

Synthesis of methyl 9-acetoxynonanoate **39**

428 mg (2.00 mmol, 1.00 eq.) **38** were dissolved in 3.0 mL dichloromethane and then cooled in an ice bath to 0 °C. Subsequently, 673 mg (3.00 mmol, 1.50 eq., 77.0 wt%) 3-chloroperbenzoic acid were added and the reaction mixture was stirred for one hour at room temperature and then 16 hours at 50 °C. The crude reaction mixture was washed with water and brine, the water phase was extracted with ethyl acetate (3 × 10 mL) and the combined organic phases were dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified by flash column chromatography (*n*-hexane/ ethyl acetate 4:1 v/v) to afford methyl 9-acetoxynonanoate **39** as colorless liquid in 92% yield (426 mg).



^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 4.04 (t, *J* = 6.7 Hz, 2 H, CH_2OOCCH_3), 3.66 (s, 3 H, CH_3OCO), 2.29 (t, *J* = 7.5 Hz, 2 H, $OOCCH_2$), 2.04 (s, 3 H, CH_3), 1.60 (2 dt, *J* = 14.2, 7.1 Hz, 4 H, 2 CH_2), 1.30 (bs, 8 H, 4 $CH_{2,\ backbone}$).

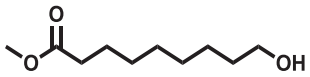
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.3, 171.3, 64.6, 51.7, 34.1, 29.2, 29.1, 29.1, 28.6, 25.9, 24.9, 21.0.

HRMS (FAB) of [$C_{12}H_{22}O_4H^+$]: calculated: 231.1591, found: 231.1591.

IR (ATR platinum diamond) [cm^{-1}]: 2930.1, 2855.6, 1734.1, 1435.5, 1364.6, 1232.8, 1169.6, 1104.6, 1033.8, 846.0, 725.3, 633.9, 606.4, 426.0.

Synthesis of methyl 9-hydroxynonanoate **40**

720 mg (3.10 mmol, 1.00 eq.) **39** were dissolved in 5.0 mL methanol. Subsequently, three drops of concentrated sulfuric acid were added and the reaction mixture was stirred for five hours under reflux. The crude mixture was washed with sodium hydrogencarbonate solution, brine and water. The water phase was extracted with ethyl acetate (3 × 10 mL) and the combined organic phases were dried over sodium sulfate and evaporated to dryness to afford methyl 9-hydroxynonanoate **40** as colorless liquid in quantitative yield (> 99%, 590 mg).



^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.65 (s, 3 H, *CH*$_3$OCO), 3.62 (t, *J* = 6.7 Hz, 2 H, *CH*$_2$OH), 2.29 (t, *J* = 7.5 Hz, 2 H, OOC*CH*$_2$), 1.57 (dt, *J* = 14.2, 7.1 Hz, 4 H, 2 CH_2), 1.49 (s, 1 H, OH), 1.30 (bs, 8 H, 4 $CH_{2,\ backbone}$).

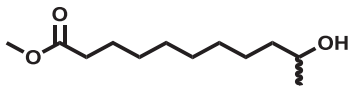
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.5, 63.0, 51.6, 34.2, 32.8, 29.3, 29.3, 29.1, 25.7, 25.0.

HRMS (FAB) of [$C_{10}H_{20}O_3$]: calculated: 188.1412, found: 188.1407.

IR (ATR platinum diamond) [cm^{-1}]: 3352.9, 2926.8, 2854.1, 1736.0, 1435.8, 1361.8, 1196.6, 1169.7, 1101.2, 1053.5, 881.1, 724.1, 588.7, 437.4.

Synthesis of methyl 10-hydroxyundecanoate **41**

2.00 g (9.34 mmol, 1.00 eq.) **38** were dissolved in 20 mL dichloromethane – methanol (9:1 v/v). Subsequently, 177 mg (4.67 mmol, 0.50 eq.) sodium borohydride were added and the reaction mixture was stirred over night at room temperature. The crude mixture was washed with sodium hydrogencarbonate solution, brine and water. The water phase was extracted with dichloromethane (3 × 5 mL) and the combined organic phases were dried over sodium sulfate and evaporated to dryness to afford 10-hydroxyundecanoate **41** as colorless liquid in quantitative yield (> 99%, 2.01 g).



^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.85 – 3.72 (m, 1 H, *CH*OH), 3.66 (s, 3 H, *CH$_3$*OCO), 2.30 (t, *J* = 7.5 Hz, 2 H, CH_2), 1.68 – 1.55 (m, 2 H, CH_2), 1.53 – 1.33 (m, 5 H, 2 CH_2, OH), 1.29 (bs, 8 H, 4 $CH_{2\ backbone}$), 1.18 (d, *J* = 6.2 Hz, 3 H, CH_3).

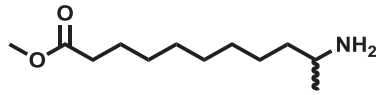
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.4, 68.1, 51.5, 39.3, 34.1, 29.6, 29.4, 29.2, 29.2, 25.8, 25.0, 23.5.

HRMS (FAB) of [$C_{12}H_{24}O_3H^+$]: calculated: 217.1798, found: 217.1798

IR (ATR platinum diamond) [cm^{-1}]: 3381.5, 2924.9, 2853.3, 1737.4, 1435.8, 1369.6, 1196.2, 1168.9, 1105.7, 1064.8, 1012.8, 940.6, 838.6, 722.7, 583.9.

Synthesis of 10-aminoundecanoate **42**

15.0 mmol (1.00 eq.) **38**, 4.59 g (59.6 mmol, 4.00 eq.) ammonium acetate and 0.80 g (15.0 mmol, 1.00 eq.) ammonium chloride were dissolved in 25 mL ethanol. Subsequently, 20.0 wt% Raney®-Nickel were added and the reaction mixture was stirred in a high pressure reactor system for 24 hours at room temperature and 30 bar of hydrogen. Afterwards, the catalyst was filtered off and the crude reaction mixture was washed with water and brine. The water phase was extracted with dichloromethane (3 x 10 mL) and the combined organic phases were dried over sodium sulfate and evaporated to dryness.



White solid, T_m = 97 °C, 95% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.90 (bs, 2H, NH_2), 3.64 (s, 3H, *CH*$_3$OCO), 3.34 – 3.18 (m, 1H, *CH*NH_2), 2.28 (t, *J* = 7.5 Hz, 2H, OC*CH*$_2$), 1.83 – 1.67 (m, 1H, *CH*$_2$CH), 1.65 – 1.49 (m, 3H, *CH*$_2$CH, OCCH$_2$*CH*$_2$), 1.42 – 1.32 (m, 2H, *CH*$_2$CH$_2$CH), 1.37 (d, *J* = 6.5 Hz, 3H, CH_3), 1.27 (bs, 8H, 4 CH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.3, 51.5, 48.5, 35.0, 34.1, 29.2, 29.2, 29.2, 29.1, 25.6, 25.0, 18.7.

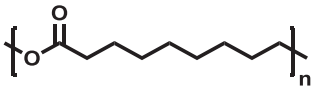
HRMS (FAB) of [$C_{12}H_{25}NO_2H^+$]: calculated: 216.1958, found: 216.1958.

IR (ATR platinum diamond): 2926.7, 2852.9, 1731.3, 1611.8, 1520.6, 1467.3, 1426.7, 1393.8, 1366.6, 1327.7, 1291.3, 1259.8, 1202.3, 1165.7, 1131.9, 1037.0, 1003.6, 970.4, 882.0, 751.3, 721.8, 519.3, 478.7, 415.0.

General procedure for the synthesis of polyester

200 mg AB-monomer (**40** or **41**) and 1.00 mol% titanium(IV) isopropoxide were added into a 10 mL round bottom flask equipped with a magnetic stir bar and then dissolved in 1.0 mL tetrahydrofuran. Afterwards, the reaction mixture was stirred in an oil bath for two hours at 120 °C, thus the solvent evaporated. Subsequently, vacuum was applied and the reaction mixture was stirred for 24 hours at 120 °C. Afterwards, the crude polymer was dissolved in THF and added dropwise into cold methanol, the precipitated polymer was filtered off and dried in vacuum (Further tested reaction conditions are listed in Table 16).

Polyester **PE-9** derived from hydroxy-ester **40**

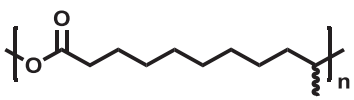


White solid, T_m = 72 °C, 90% yield.

^{1}H-NMR: (300 MHz, $CDCl_3$) δ/ppm: 4.02 (t, *J* = 6.1 Hz, 2 H, CH_2OOC), 3.64 (s, 3 H, CH_3OOC), 2.26 (t, *J* = 7.1 Hz, 2 H, OOCCH_2), 1.59 (bs, 5 H, 2 CH_2, OH), 1.29 (s, 8 H, 4 $CH_{2,\ backbone}$).

IR (ATR platinum diamond) [cm^{-1}]: 2926.5, 2850.4, 1728.6, 1465.5, 1416.6, 1366.0, 1329.0, 1295.9, 1252.5, 1213.6, 1177.0, 1114.1, 1073.7, 959.9, 756.5, 722.4, 476.2.

Polyester **PE-10** derived from hydroxy-ester **41**



Colorless viscous liquid, T_g = -57 °C, 76% yield.

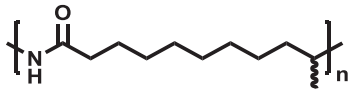
^{1}H-NMR: (300 MHz, $CDCl_3$) δ/ppm: 4.92 – 4.79 (m, 1 H, CH), 3.62 (s, 3 H, *CH_3*OOC), 2.21 (t, *J* = 7.5 Hz, 2 H, OOC*CH_2*), 1.64 – 1.47 (m, 2 H, CH_2), 1.46 – 1.35 (m, 5 H, 2 CH_2, OH), 1.24 (bs, 8 H, 4 $CH_{2,\ backbone}$), 1.18 – 1.11 (m, 3 H, CH_3).

IR (ATR platinum diamond) [cm^{-1}]: 2924.8, 2854.1, 1729.0, 1461.7, 1376.4, 1337.4, 1244.0, 1176.0, 1128.4, 1101.3, 1072.1, 1025.5, 982.7, 944.1, 855.0, 723.5, 591.9, 426.8.

General procedure for the synthesis of polyamide

433 mg (2.00 mmol, 1.00 eq) **42** and 14.0 mg (5.00 mol%) 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) were added into a 10 mL round bottom flask equipped with a magnetic stir bar and then heated in an oil bath from 120 °C with an increase of temperature of 20 °C each hour until 200 °C were reached. Subsequently, vacuum was applied and the reaction mixture was stirred for additional five hours at 200 °C. Afterwards, the polymer was dissolved in hexafluoroisopropanol (HFIP) and added dropwise into diethyl ether at room temperature, the precipitated polymer was filtered off and dried in vacuo. (Further tested reaction conditions are listed in Table 16).

Polyamide **PA-10** derived from amino-ester **42**



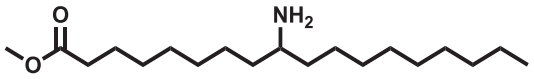
Black solid, T_g = -21 °C, T_m = 148 °C, 78% yield.

^{1}H-NMR: (300 MHz, CD_3OD) δ/ppm: 4.69 – 4.52 (m, 1H, NH), 3.90 – 3.69 (m, 1 H, *CH*NH_2), 2.36 – 2.01 (t, *J* = 6.4 Hz, 2 H, OC*CH_2*), 1.62 – 1.14 (m, 14 H, 7 $CH_{2,\ backbone}$), 1.05 (d, *J* = 6.5 Hz, 3 H, CH_3).

IR (ATR platinum diamond) [cm^{-1}]: 3272.5, 2924.9, 2853.8, 1633.7, 1544.5, 1455.1, 1375.0, 1284.2, 1261.7, 1199.7, 1176.9, 1134.5, 1100.6, 892.4, 839.1, 799.3, 720.3, 684.2, 614.5, 518.5, 463.6.

Chapter 4.2.5 Synthesis of dimer fatty acid methyl esters by catalytic and reductive amination: efficient route to polyamides

Methyl 9(10)-aminosterate **46** (see procedure of amino-ester synthesis before)



Brown oil, >99% yield.

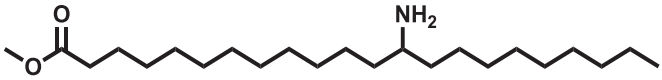
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.85 (bs, 2H, NH_2), 3.63 (s, 3H, *CH*$_3$OCO), 3.16 – 3.02 (m, 1H, *CH*NH_2), 2.26 (t, *J* = 7.5 Hz, 2 H, OC*CH*$_2$), 1.75 – 1.10 (m, 30H, 15 CH_2), 0.84 ((t, *J* = 6.7 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.3, 52.6, 51.5, 34.1, 32.7, 31.9, 29.7, 29.5, 29.4, 29.4, 29.3, 29.2, 29.2, 29.1, 25.4, 25.0, 22.7, 14.2.

HRMS (FAB) of [$C_{19}H_{39}NO_2H^+$]: calculated: 314.3054, found: 314.3052.

IR (ATR platinum diamond): 2921.5, 2852.4, 1738.1, 1606.2, 1516.5, 1457.7, 1435.3, 1375.9, 1194.6, 1168.6, 1013.8, 879.4, 753.7, 721.8, 646.7, 432.4.

Methyl 13(14)-aminodocosanoate **47** (see procedure of amino-ester synthesis before)



Brown oil, >99% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 6.55 (bs, 2H, NH_2), 3.66 (s, 3H, *CH*$_3$OCO), 2.99 – 2.86 (m, 1H, *CH*NH_2), 2.28 (t, *J* = 7.5 Hz, 2H, OC*CH*$_2$), 1.68 – 1.15 (m, 38H, 19 CH_2), 0.88 (t, *J* = 6.7 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.4, 52.0, 51.5, 34.2, 33.7, 32.0, 32.0, 29.7, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 25.6, 25.1, 22.8, 14.2.

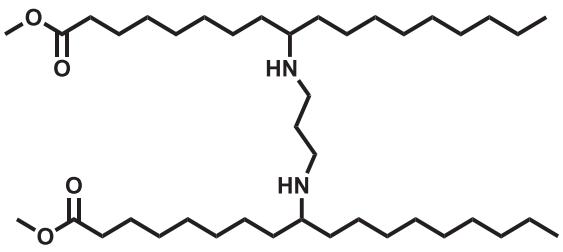
HRMS (FAB) of [$C_{23}H_{47}NO_2H^+$]: calculated: 370.3679, found: 370.3682.

IR (ATR platinum diamond): 2921.3, 2852.1, 1740.2, 1607.6, 1523.7, 1463.6, 1375.8, 1195.3, 1169.7, 1012.9, 721.7.

General procedure for the synthesis of dimer FAMEs using diamines

6.30 mmol (2.10 eq.) methyl 9(10)-oxosterate **7** and 3.00 mmol (1.00 eq) diamine (**44a-g**) were dissolved in 6.0 mL dichloroethane and then stirred for 30 minutes at room temperature. Subsequently, 9.45 mmol (1.50 eq./oxo-FAME) were added and the reaction mixture was stirred for 24 hours at room temperature. The crude reaction mixture was washed with water and brine, the water phase was extracted with dichloromethane (3 x 10 mL) and the combined organic phases were dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified by flash column chromatography ($CHCl_3$/MeOH/Et_3N) to afford the dimer FAMEs **45a-g**.

Dimethyl 9,9'-(propane-1,3-diylbis(azanediyl))distearate (+ regioisomers) **45a**



Yellowish solid, T_m = 54 °C, 80% yield.

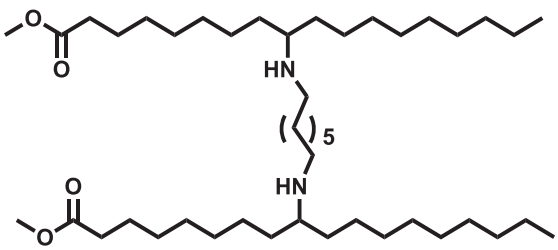
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.65 (s, 6H, 2 *CH*$_3$OCO), 3.00 – 2.79 (m, 6H, 3 $CH_{2,\ propane\ chain}$), 2.74 – 2.54 (m, 2H , 2 *CH*NH_2), 2.28 (t, *J* = 7.5 Hz, 4H, 2 OC*CH*$_2$), 1.98 (s, 2H, 2 NH),1.87 – 1.54 (m, 12H, 6 CH_2), 1.44 – 1.18 (m, 44H, 22 CH_2), 0.86 (t, *J* = 6.6 Hz, 6H, 2 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.4, 174.3, 59.70, 51.5, 43.3, 34.2, 34.1, 31.9, 31.9, 30.1, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 29.2, 29.1, 29.0, 28.9, 25.5, 25.5, 25.4, 25.0, 24.9, 24.9, 22.7, 22.7, 14.2.

HRMS (FAB) of [$C_{41}H_{82}N_2O_4H^+$]: calculated: 667.6347, found: 667.6350.

IR (ATR platinum diamond): 2922.5, 2851.0, 2774.7, 173.7, 1599.4, 1466.3, 1435.2, 1376.7, 1167.1, 1113.7, 1049.2, 1013.2, 880.8, 722.0, 649.6, 590.1, 489.3.

Dimethyl 9,9'-(heptane-1,7-diylbis(azanediyl))distearate (+ regioisomers) **45b**



Yellowish solid, T_m = 60 °C, 76% yield.

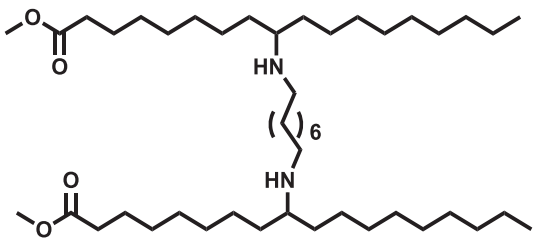
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.64 (s, 6H, 2 *CH*$_3$OCO), 2.92 – 2.79 (m, 2H, 2 *CH*NH), 2.74 (t, *J* = 6.6 Hz, 4H, 2 *CH*$_2$NH), 2.28 (t, *J* = 7.5 Hz, 4H, 2 OC*CH*$_2$), 1.98 – 1.52 (m, 16H, 8 CH_2), 1.94 (s, 2H, 2 NH), 1.44 – 1.18 (m, 50H, 25 CH_2), 0.86 (t, *J* = 6.6 Hz, 6H, 2 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.3, 174.2, 58.8, 51.4, 45.7, 34.1, 34.0, 31.9, 31.88, 30.9, 30.7, 29.8, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 29.3, 29.2, 29.1, 29.1, 28.9, 27.8, 25.6, 25.5, 24.9, 24.9, 22.7, 22.6, 14.1.

HRMS (FAB) of [$C_{45}H_{90}N_2O_4H^+$]: calculated: 723.6973, found: 723.6975.

IR (ATR platinum diamond): 2922.6, 2851.1, 2714.3, 1737.8, 1579.7, 1464.5, 1375.7, 1299.5, 1168.4, 1011.0, 881.0, 776.4, 724.9, 590.1, 434.9.

Dimethyl 9,9'-(octane-1,8-diylbis(azanediyl))distearate (+ regioisomers) **45c**



Yellowish solid, T_m = 61 °C, 93% yield.

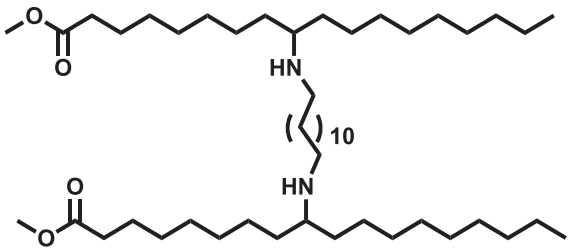
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.65 (s, 6H, 2 *CH*$_3$OCO), 3.03 – 2.91 (m, 2H, 2 *CH*NH), 2.86 (t, *J* = 6.6 Hz, 4H, 2 *CH*$_2$NH), 2.28 (t, *J* = 7.5 Hz, 4H, 2 OC*CH*$_2$), 1.93 (s, 2H, 2 NH), 1.92 – 1.15 (m, 68H, 34 CH_2), 0.86 (t, *J* = 6.6 Hz, 6H, 2 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.3, 174.2, 58.5, 51.5, 45.0, 34.1, 34.1, 34.0, 31.9, 31.9, 30.3, 30.2, 30.2, 30.2, 29.7, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 29.3, 29.3, 29.3, 29.1, 29.1, 29.1, 29.0, 27.9, 26.1, 25.8, 25.6, 25.5, 25.0, 24.9, 22.7, 22.7, 14.1.

HRMS (FAB) of [$C_{46}H_{92}N_2O_4H^+$]: calculated: 737.7130, found: 737.7128.

IR (ATR platinum diamond): 2923.3, 2852.6, 1737.1, 1560.2, 1464.1, 1435.5, 1375.8, 1249.4, 1196.0, 1164.6, 1115.4, 1015.3, 842.5, 723.0, 649.2, 595.4, 434.0.

Dimethyl 9,9'-(dodecane-1,12-diylbis(azanediyl))distearate (+ regioisomers) **45d**



Yellowish solid, T_m = 63 °C, 84% yield.

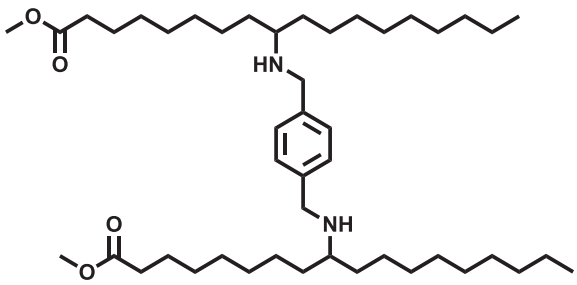
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.65 (s, 6H, 2 *CH*$_3$OCO), 3.03 – 2.90 (m, 2H, 2 *CH*NH), 2.82 (t, *J* = 6.6 Hz, 4H, 2 *CH*$_2$NH), 2.28 (t, *J* = 7.5 Hz, 4H, 2 OC*CH*$_2$), 2.03 – 1.53 (m, 16H, 8 CH_2), 2.00 (s, 2H, 2 NH), 1.45 – 1.18 (m, 60H, 30 CH_2), 0.86 (t, *J* = 6.6 Hz, 6H, 2 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.2, 174.1, 58.2, 51.3, 45.0, 34.0, 33.9, 33.9, 31.8, 31.8, 31.7, 30.1, 30.0, 29.5, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 29.2, 29.2, 29.1, 29.0, 29.0, 28.9, 28.8, 28.3, 28.1, 27.7, 26.8, 25.6, 25.4, 25.3, 25.3, 24.8, 24.8, 24.7, 22.6, 22.6, 14.0.

HRMS (FAB) of [$C_{50}H_{100}N_2O_4H^+$]: calculated: 793.7756, found: 793.7758.

IR (ATR platinum diamond): 2918.4, 2850.8, 2737.7, 1739.5, 1601.8, 1455.1, 1435.1, 1376.4, 1247.2, 1195.0, 1168.7, 990.4, 880.0, 722.4, 612.1, 447.7.

Dimethyl 9,9'-((1,4-phenylenebis(methylene))bis azanediyl))distearate (+ regioisomers) **45e**



Yellowish solid, T_m = 60 °C, 30% yield.

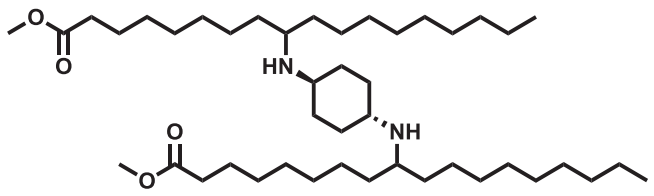
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 8.17 – 7.88 (m, 4H, 4 CH), 3.66 (bs, 4H, 2 CH_2), 3.64 (s, 6H, 2 *CH_3*OCO), 2.80 – 2.67 (m, 2H, 2 *CH*NH), 2.28 (t, *J* = 7.5 Hz, 4H, 2 OC*CH_2*), 1.97 (s, 2H, 2 NH), 1.66 – 1.50 (m, 12H, 6 CH_2), 1.35 – 1.15 (m, 44H, 22 CH_2), 0.86 (t, *J* = 6.6 Hz, 6H, 2 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.4, 174.3, 132.6, 130.3, 56.7, 51.5, 48.3, 34.2, 34.1, 34.1, 32.0, 31.9, 31.9, 30.9, 30.9, 29.7, 29.6, 29.5, 29.5, 29.5, 29.4, 29.4, 29.3, 29.3, 29.2, 29.1, 25.3, 25.0, 25.0, 23.0, 22.7, 22.7, 14.2.

HRMS (FAB) of [$C_{46}H_{84}N_2O_4H^+$]: calculated: 729.6504, found: 729.6504.

IR (ATR platinum diamond): 2924.5, 2854.1, 2676.8, 1739.3, 1583.6, 1523.1, 1459.0, 1436.5, 1376.4, 1247.8, 1197.1, 1169.2, 1112.0, 1021.5, 835.9, 722.6, 582.4.

Dimethyl 9,9'-(((1r,4r)-cyclohexane-1,4-diyl)bis(azanediyl))distearate (+ regioisomers) **45f**



Yellowish solid, T_m = 52 °C, 6% yield.

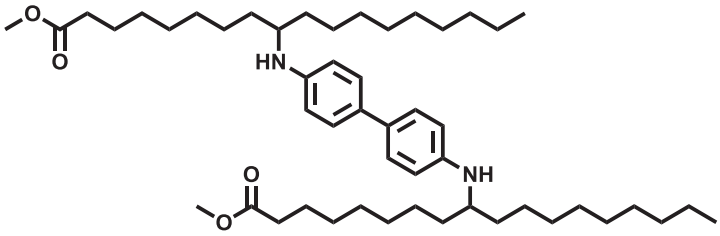
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.62 (s, 6H, 2 *CH*$_3$OCO), 2.85 – 2.58 (m, 4H, 4 *CH*NH), 2.26 (t, *J* = 7.5 Hz, 4H, 2 OC*CH*$_2$), 2.18 – 2.01 (m, 4H, 4 CH_2), 1.91 (s, 2H, 2 NH), 1.64 – 1.15 (m, 60H, 34 CH_2), 0.86 (t, *J* = 6.6 Hz, 6H, 2 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.2, 174.1, 55.2, 53.4, 51.3, 34.0, 34.0, 32.0, 31.8, 31.8, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 29.2, 29.2, 29.1, 29.0, 29.0, 25.6, 25.5, 25.5, 24.9, 24.8, 22.63, 22.6, 14.0.

HRMS (FAB) of [$C_{44}H_{86}N_2O_4H^+$]: calculated: 707.6660, found: 707.6659.

IR (ATR platinum diamond): 2920.5, 2850.7, 1739.2, 1636.3, 1545.1, 1455.5, 1435.3, 1400.0, 1364.0, 1315.6, 1195.7, 1169.4, 112.3, 1011.9, 721.4, 651.4.

Dimethyl 9,9'-([1,1'-biphenyl]-4,4'-diylbis(azanediyl))distearate (+ regioisomers) **45g**



Yellowish solid, T_m = 46 °C, 5% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 7.33 (d, *J* = 8.4 Hz, 4H, 4 CH), 6.59 (d, *J* = 8.0 Hz, 4H, 4 CH), 3.66 (s, 6H, 2 *CH*$_3$OCO), 3.38 – 3.26 (m, 2H, 2 *CH*NH), 2.29 (t, *J* = 7.5 Hz, 4H, 2 OC*CH*$_2$), 2.04 (s, 2H, 2 NH), 1.67 – 1.16 (m, 56H, 28 CH_2), 0.87 (t, *J* = 6.6 Hz, 6H, 2 CH_3).

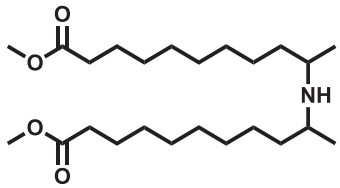
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.4, 174.4, 157.0, 127.2, 127.1, 113.4, 113.3, 107.2, 53.2, 51.5, 42.9, 35.0, 34.2, 32.0, 29.9, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 29.2, 29.1, 27.2, 26.0, 26.0, 25.9, 25.0, 24.0, 23.9, 22.8, 14.2. HRMS (FAB) of [$C_{50}H_{84}N_2O_4H^+$]: calculated: 777.6504, found: 777.6505.

IR (ATR platinum diamond): 3002.5, 2923.6, 2852.8, 1737.2, 1503.5, 1462.8, 1436.0, 1436.7, 1319.4, 1304.91281.5, 1247.8, 1179.1, 1110.6, 1014.5, 810.4, 722.8, 646.4, 518.8, 436.7.

Synthesis of fully renewable dimer FAMEs

10.0 mmol (1.05 eq.) keto-FAME and 9.50 mmol (1.00 eq) amino-FAME were dissolved in 20.0 mL dichloroethane and then stirred for 30 minutes at room temperature. Subsequently, 14.2 mmol (1.50 eq./amino-FAME) were added and the reaction mixture was stirred for 1 - 7 days at room temperature. The crude reaction mixture was washed with water and brine, the water phase was extracted with dichloromethane (3 x 10 mL) and the combined organic phases were dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified by flash column chromatography ($CHCl_3$/MeOH/Et_3N) to afford the dimer FAMEs **48a-f**.

Dimethyl 10,10'-azanediyldiundecanoate (C22) **48a**



White solid, T_m = 56 °C, 93% yield.

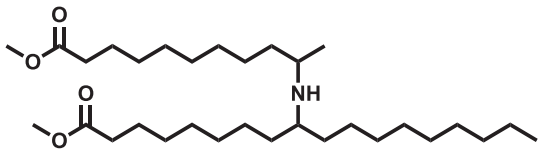
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.62 (s, 6H, 2 *CH_3*OCO), 2.75 (dt, *J* = 12.3, 6.1 Hz, 2H, 2 *CH*CH_3), 2.26 (t, *J* = 7.5 Hz, 4H, 2 OC*CH_2*), 1.87 (s, 1H, 1 NH), 1.64 – 1.50 (tt, *J* = 14.4, 7.2 Hz, 4H, 2 CH_2), 1.50 – 1.42 (m, 2H, 2 CH_2), 1.37 – 1.16 (m, 22H, 12 CH_2), 1.07 (d, *J* = 6.9 Hz, 3H, CH_3), 1.05 (d, *J* = 6.9 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.3, 51.4, 50.2, 50.1, 36.5, 35.9, 34.1, 29.7, 29.7, 29.4, 29.2, 29.1, 26.1, 26.0, 24.9, 19.8, 19.4.

HRMS (FAB) of [$C_{50}H_{84}NO_4H^+$]: calculated: 414.3578, found: 414.3580.

IR (ATR platinum diamond): 2922.3, 2852.3, 2730.1, 1735.9, 1472.1, 1436.9, 1378.3, 1307.5, 1271.2, 1254.5, 1164.7, 1032.9, 983.5, 917.5, 881.0, 753.5, 725.9, 566.1, 491.8, 435.9.

Methyl 9-((11-methoxy-11-oxoundecan-2-yl)amino)octadecanoate
(+ regioisomers) (C29) **48b**



Brownish oil, 82% yield.

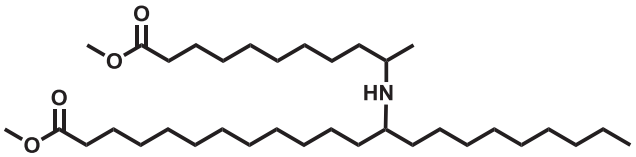
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.66 (s, 6H, 2 *CH_3*OCO), 2.70 – 2.41 (m, 2H, 2 CH), 2.29 (t, *J* = 7.5 Hz, 4H, 2 OC*CH_2*), 1.68 – 1.52 (m, 4H, 2 CH_2), 1.44 – 1.17 (m, 39H, 19 CH_2, NH), 1.00 (d, *J* = 6.1 Hz, 3H, *CH_3*CH), 0.87 (t, *J* = 6.6 Hz, 3H, 2 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.4, 54.5, 51.5, 50.4, 37.6, 34.8, 34.4, 34.2, 32.0, 30.1, 30.1, 29.9, 29.9, 29.8, 29.7, 29.5, 29.4, 29.4, 29.3, 29.2, 26.2, 25.9, 25.6, 25.0, 22.8, 21.0, 14.2.

HRMS (FAB) of [$C_{31}H_{61}NO_4H^+$]: calculated: 512.4673, found: 512.4675.

IR (ATR platinum diamond): 2922.9, 2852.8, 1739.8, 1460.6, 1435.6, 1365.3, 1244.0, 1195.7, 1168.2, 1114.2, 1016.2, 879.5, 722.7, 433.8.

Methyl 13-((11-methoxy-11-oxoundecan-2-yl)amino)docosanoate
(+ regioisomers) (C33) **48c**



Brownish oil, 69% yield.

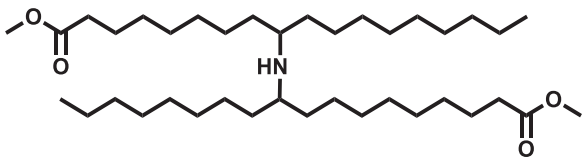
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.65 (s, 6H, 2 *CH*$_3$OCO), 2.70 – 2.44 (m, 2H, 2 CH), 2.29 (t, *J* = 7.5 Hz, 4H, 2 OC*CH*$_2$), 1.94 (s, 1H, NH), 1.67 – 1.51 (m, 4H, 2 CH_2), 1.45 – 1.15 (m, 46H, 23 CH_2), 1.10 (d, *J* = 6.6 Hz, 3H, *CH*$_3$CH$_{isomer}$), 0.99 (d, *J* = 6.1 Hz, 3H, *CH*$_3$CH$_{isomer}$), 0.87 (t, *J* = 6.6 Hz, 3H, 2 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.5, 174.4, 54.6, 51.5, 50.4, 37.7, 34.9, 34.4, 34.2, 32.0, 30.1, 30.1, 29.9, 29.8, 29.7, 29.6, 29.4, 29.4, 29.4, 29.3, 27.8, 26.2, 26.0, 25.6, 25.1, 22.8, 21.1, 14.2.

HRMS (FAB) of [$C_{35}H_{69}NO_4H^+$]: calculated: 568.5299, found: 568.5301.

IR (ATR platinum diamond): 2922.2, 2852.4, 1740.5, 1462.3, 1435.7, 1369.2, 1243.8, 1195.5, 1168.3, 1113.5, 1015.0, 879.5, 722.0, 610.7, 436.4.

Methyl 10-((1-methoxy-1-oxooctadecan-9-yl)amino)octadecanoate
(+ regioisomers) (C36) **48d**



Brownish oil, 70% yield.

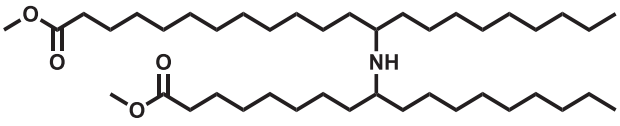
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.65 (s, 6H, 2 CH_3OCO), 2.95 – 2.78 (m, 2H, 2 CH), 2.29 (t, J = 7.5 Hz, 4H, 2 $OCCH_2$), 1.97 (s, 1H, NH), 1.92 – 1.52 (m, 12H, 6 CH_2), 1.45 – 1.16 (m, 44H, 22 CH_2), 0.87 (t, J = 6.6 Hz, 6H, 2 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.3, 174.2, 56.8, 51.5, 34.2, 34.1, 31.9, 31.9, 31.2, 31.2, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 29.2, 29.1, 26.1, 26.0, 25.9, 25.0, 24.9, 22.7, 14.2.

HRMS (FAB) of [$C_{38}H_{75}NO_4H^+$]: calculated: 610.5769, found: 610.5767.

IR (ATR platinum diamond): 2922.6, 2852.9, 1740.2, 1461.8, 1435.4, 1367.5, 1243.7, 1195.5, 1168.3, 1113.8, 1015.9, 879.4, 722.2, 609.5, 435.4.

Methyl 13-((1-methoxy-1-oxooctadecan-9-yl)amino)docosanoate
(+ regioisomers) (C40) **48e**



Brownish oil, 73% yield.

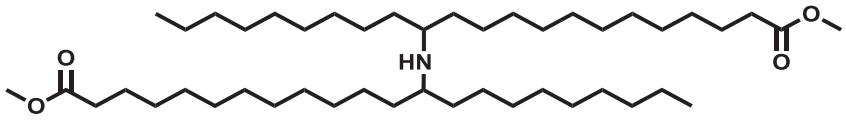
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.65 (s, 6H, 2 *CH_3*OCO), 2.83 – 2.66 (m, 2H, 2 CH), 2.29 (t, *J* = 7.5 Hz, 4H, 2 OC*CH_2*), 1.96 (s, 1H, NH), 1.75 – 1.53 (m, 12H, 6 CH_2), 1.42 – 1.18 (m, 52H, 26 CH_2), 0.87 (t, *J* = 6.6 Hz, 6H, 2 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.4, 174.3, 56.2, 56.1, 51.5, 34.2, 34.2, 34.1, 32.3, 32.0, 31.9, 29.8, 29.7, 29.7, 29.7, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.3, 29.3, 29.2, 29.2, 25.9, 25.0, 25.0, 25.0, 22.7, 22.7, 14.2.

HRMS (FAB) of [$C_{42}H_{83}NO_4H^+$]: calculated: 666.6395, found: 666.6393.

IR (ATR platinum diamond): 2922.2, 2852.6, 1739.9, 1583.2, 1462.4, 1435.6, 1363.2, 1247.3, 1195.5, 1169.3, 1114.7, 1014.6, 878.9, 721.8, 598.3, 436.2.

Dimethyl 13,13'-azanediyldidocosanoate (+ regioisomers) (C44) **48f**



Brownish oil, 76% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 3.64 (s, 6H, 2 *CH_3*OCO), 2.72 – 2.53 (m, 2H, 2 CH), 2.27 (t, *J* = 7.5 Hz, 4H, 2 OC*CH_2*), 1.95 (s, 1H, NH), 1.66 – 1.41 (m, 12H, 6 CH_2), 1.37 – 1.16 (m, 60H, 25 CH_2), 0.87 (t, *J* = 6.6 Hz, 6H, 2 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 174.4, 55.6, 51.5, 34.2, 32.0, 32.0, 29.9, 29.7, 29.6, 29.4, 29.4, 29.4, 29.3, 25.9, 25.1, 22.8, 14.2.

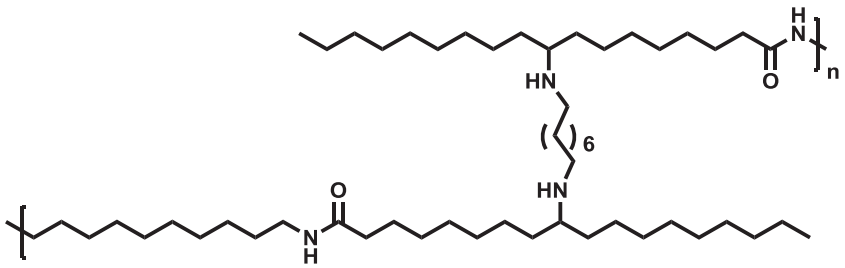
HRMS (FAB) of [$C_{46}H_{91}NO_4H^+$]: calculated: 722.7021, found: 722.7022.

IR (ATR platinum diamond): 2921.5, 2852.1, 1740.9, 1583.1, 1463.4, 1435.7, 1363.9, 1195.1, 11169.1, 1115.2, 1016.1, 879.0, 721.6, 584.1, 419.6.

Synthesis of polyamides from dimer FAMEs

0.50 mmol (1.00 eq) dimer FAME, 86.1 mg (0.50 mmol, 1.00 eq) 1,10-diaminodecane and 3.60 mg (5.00 mol%) 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) were added into a 10 mL round bottom flask and heated from 100 °C with an increase of temperature of 20 °C each hour until 180 °C were reached. Subsequently, vacuum was applied and the reaction mixture was stirred for additional two hours at 180 °C. Afterwards, the polymer was dissolved in hexafluoroisopropanol (HFIP) and added dropwise into diethyl ether at room temperature, the precipitated polymer was filtered off and dried in vacuo.

Polyamide **P1** derived from dimer FAME **45b**.

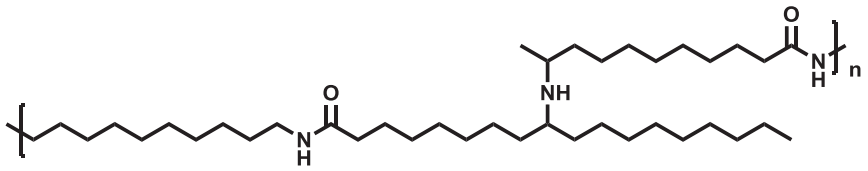


Brownish solid, 85% yield, T_g = 9 °C, T_m = 161 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 6.00 (s, 2H, *HN*CO), 3.28 – 2.88 (m, 10H, 2 CH, 2 *CH*$_2$NHCO, 2 *CH*$_2$NHCH), 2.16 (t, *J* = 7.5 Hz, 4H, 2 *CH*$_2$CONH), 1.80 – 1.10 (m, 84H, 42 $CH_{2,\ backbone}$), 0.84 (bs, 6H, 2 CH_3).

IR (ATR platinum diamond): 3258.1, 2922.3, 2851.9, 1639.5, 1551.7, 1464.6, 1375.8, 1261.0, 1200.1, 1173.6, 1131.9, 925.4, 886.2, 798.2, 720.6, 596.1, 517.6, 408.2.

Polyamide **P2** derived from dimer FAME **48b**.

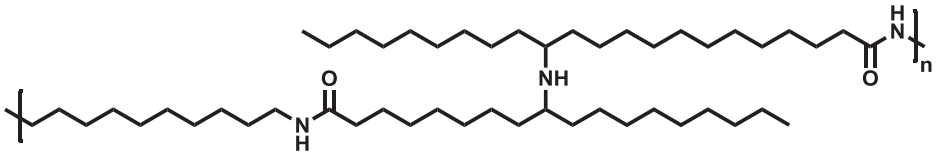


Brownish solid, T_g = -4°C ,T_m = 106 °C, 92% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 6.00 (s, 2H, *HN*CO), 3.39 – 3.11 (m, 6H, 2 CH, 2 *CH_2*NHCO), 2.67 (s, 1H, *NH*CH), 2.21 (t, *J* = 7.4 Hz, 4H, 2 *CH_2*CONH), 1.85 – 1.05 (m, 61H, 29 $CH_{2,\ backbone}$, 1 *CH_3*CH), 0.89 (bs, 3H, CH_3).

IR (ATR platinum diamond): 3309.5, 2922.7, 2851.9, 1670.2, 1633.4, 1537.6, 1468.0, 1432.5, 1374.9, 1284.1, 1260.7, 1206.5, 1178.6, 1122.9, 1100.3, 1048.6, 955.0, 892.2, 836.3, 802.6, 722.4, 684.4, 596.1, 517.1, 465.2.

Polyamide **P3** derived from dimer FAME **48e**.



Brownish solid, T_g = -16 °C, T_m = 70 °C, 88% yield.

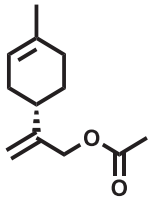
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 6.14 (s, 2H, *HN*CO), 3.73 (s, 1H, *NH*CH), 3.39 – 3.11 (m, 4H, 2 CH, *CH_2*NHCO), 2.27 (t, *J* = 7.5 Hz, 4H, 2 *CH_2*CONH), 1.90 – 1.10 (m, 80H, 40 $CH_{2,\ backbone}$), 0.93 (bs, 6H, 2 CH_3).

IR (ATR platinum diamond): 3306.3, 2921.5, 2852.6, 1636.4, 1542.1, 1465.0, 1373.6, 1200.9, 1174.5, 1130.3, 831.1, 799.8, 720.6, 593.1.

Chapter 4.2.6 Acetoxylation of limonene

0.20 g (*S*)-(-)-limonene **50** (1.47 mmol) were dissolved in 1.5 mL DMSO and 1.5 mL acetic acid. Additionally, 0.16 g *p*-benzoquinone (1.47 mmol, 1.0 eq), 0.25 g molecular sieves (3Å), and 29.0 mg *n*-tetradecane (0.15 mmol, 10.0 mol%) as internal standard were added and the mixture was stirred for five minutes at 50 °C. Then, 13.2 mg palladium(II) acetate (0.06 mmol, 4.0 mol%) was added and the mixture was stirred for 24 hours at 50 °C. The crude reaction mixture was washed with water, sodium hydrogen carbonate and brine, dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified by column chromatography (hexane/ ethyl acetate 95:5) to afford an orange-yellow liquid. The product was obtained as a mixture of the major product **51** and small amounts of the by-products (enantiomers **52** and **53** as well as **54** and **55**).

(*S*)-2-(4-methylcyclohex-3-en-1-yl)allyl acetate **51**



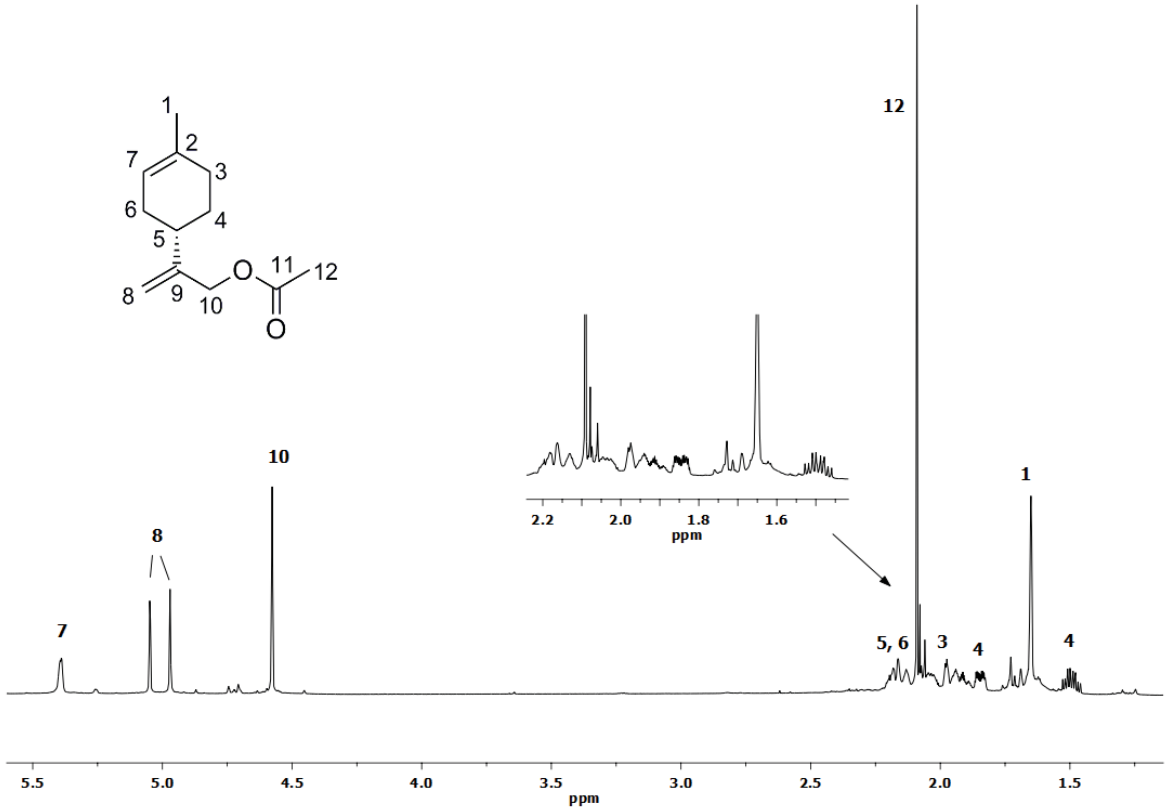
Orange-yellow liquid, 52% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm 5.41-5.28 (m, 1H, CH, ^{7}), 5.05 (s, b, 1H, CH_2, ^{8}), 4.97 (s, b, 1H, CH_2, ^{8}), 4.58 (s, b, 2H, CH_2, ^{10}), 2.28-2.12 (m, 1H, CH, ^{5}), 2.13-1.98 (m, 2H, CH_2, ^{6}), 2.12-1.88 (m, 2H, CH_2, ^{3}), 2.09 (s, 3H, CH_3, ^{12}), 1.96-1.82 (m, 1H, CH_2, ^{4}), 1.65 (s, 3H, CH_3, ^{1}), 1.53-1.46 (m, 1H, CH_2, ^{4}).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 170.9, 148.4,.133.9, 120.4, 111.1, 66,3, 37.2, 31.2, 30.5, 28.0, 23.5, 21.1.

SEC/ESI-MS of [$C_{12}H_{18}O_2Na^+$]: calculated: 217.12, found: 217.08.

IR (ATR platinum diamond): 2916.1, 1736.6, 1646.3, 1436.7, 1370.8, 1220.5, 1149.6, 1097.1, 1022.8, 967.2, 912.3, 797.4, 759.1, 604.0, 523.1, 429.8.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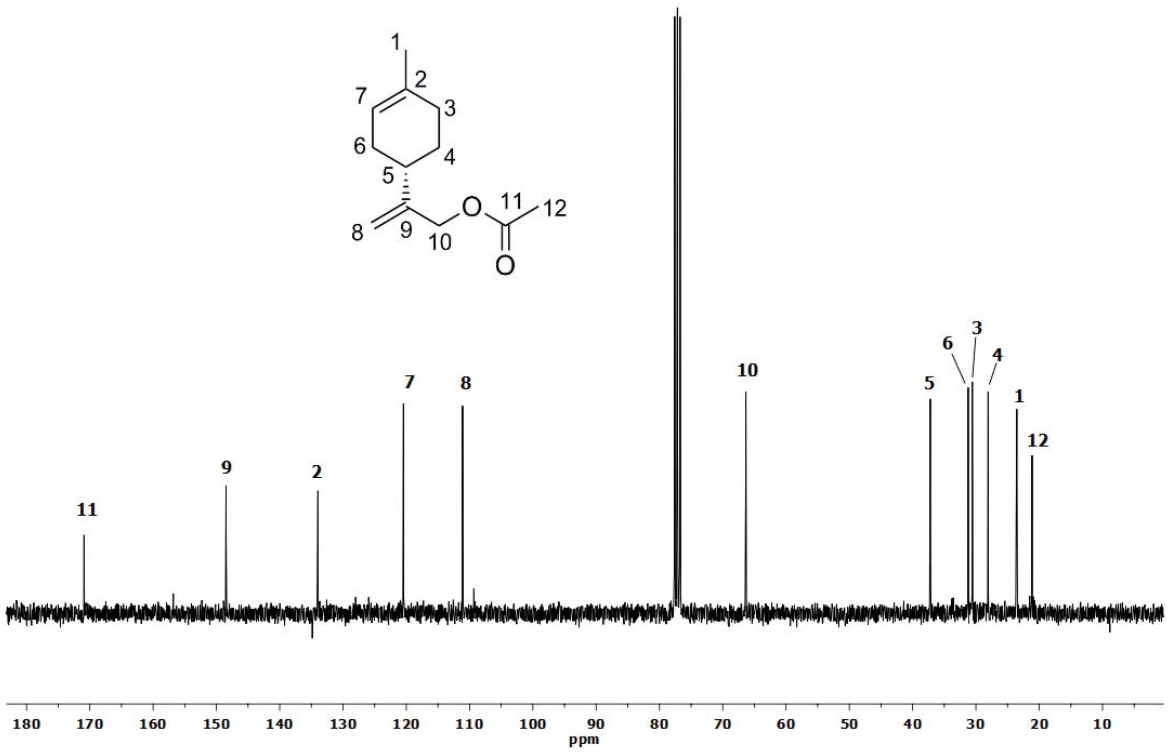
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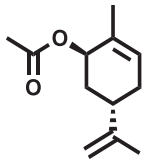
Acetoxylation of (*S*)-(-)-limonene at the internal double bond:

(5S)-2-methyl-5-(pro-1-en-2-yl-)cyclohex-2-en-1-yl acetate **52** (+ regioisomer **53**):



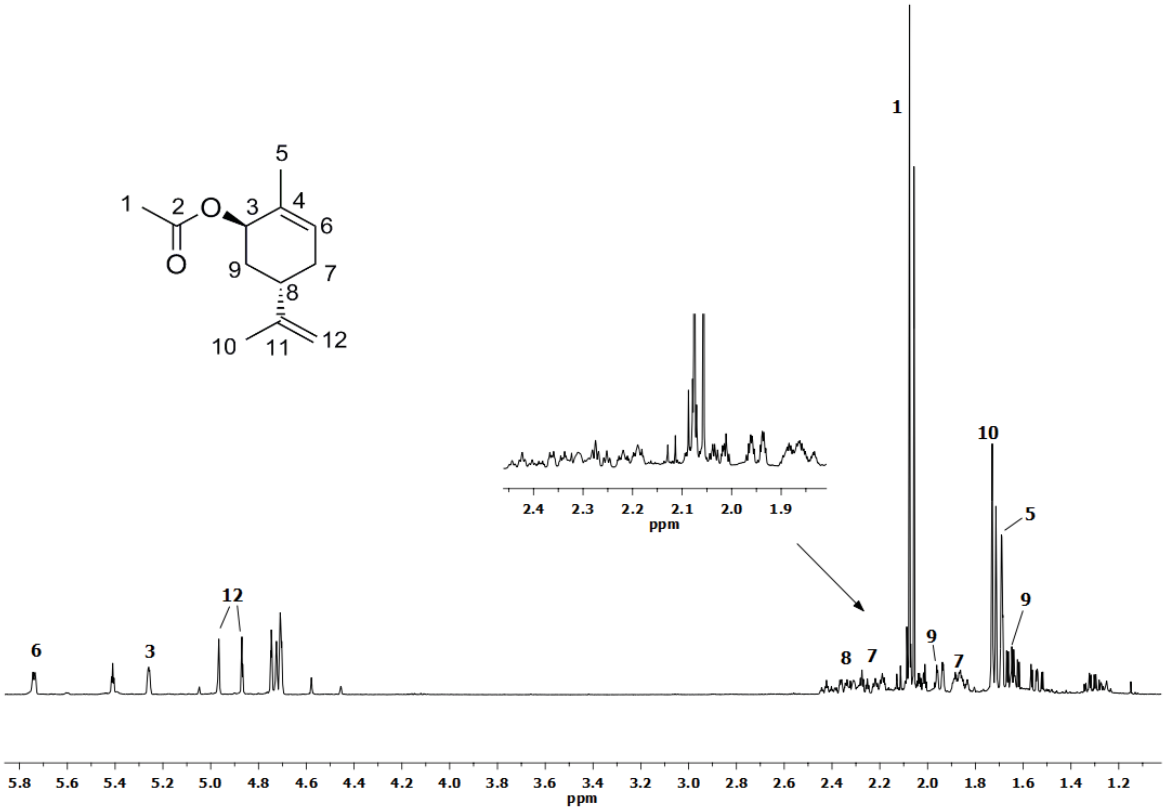
0.20 g (1.47 mmol, 1.0 eq) S-(-)-limonene **1** was dissolved in 2.0 ml dimethylacetamide and 2.0 ml acetic acid. Additionally 0.16 g (1.47 mmol, 1.0 eq) *p*-benzoquinone and 0.25 g molecular sieve (3 Å) were added and the mixture was stirred for five minutes at 50 °C. Then, 13.2 mg (0.06 mmol, 4.0 mol%) of palladium(II) acetate was added and the mixture was stirred for 24 hours at 50 °C. The crude mixture was washed with water, sodium hydrogen carbonate and brine, dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified *via* column chromatography (hexane/ ethyl acetate 95:5) to afford a light yellow liquid in 54 % yield (154 mg). The obtained product represented a mixture of the enantiomeric products **52** and **53** as well as **54** and **55**, and furthermore a small amount of by-product **51**.

^{1}H NMR: (600 MHz, $CDCl_3$) δ/ppm 5.75-5.72 (m, 1H, CH, ^{6}), 5.26 (t, *J* = 3.1 Hz, 1H, CH, ^{3}), 4.97 (t, *J* = 1.7 Hz, 1H, CH_2, ^{12}), 4.87 (t, *J* = 1.8 Hz, 1H, CH_2, ^{12}), 2.35 - 2.29 (m, 1H, CH, ^{8}), 2.24 - 2.20 (m, 1H, CH_2, ^{7}), 2.08 (s, 3H, CH_3, ^{1}), 1.97 - 1.93 (m, 1H, CH_2, ^{9}), 1.90 - 1.84 (m, 1H, CH_2, ^{7}), 1.73 (s, 3H, CH_3, ^{10}), 1.70 - 1.68 (m, 3H, CH_3, ^{5}), 1.67 - 1.64 (m, 1H, CH_2, ^{9}).

^{13}C NMR: (75 MHz, $CDCl_3$) δ/ppm 171.0, 148.9, 131.0,128.0, 112.6, 70.8, 35.9, 33.8, 31.0, 21.5, 20.9, 20.8.

SEC/ESI-MS of [$C_{12}H_{18}O_2Na^+$]: calculated: 217.12, found: 217.08.

IR (ATR platinum diamond): 2935.4, 1733.2, 1643.7, 1437.8, 1368.0, 1232.2, 1149.9, 1073.6, 1045.4, 1016.1, 965.5, 950.6, 911.1, 887.8, 807.6, 673.6, 609.2, 538.0, 469.4, 437.0.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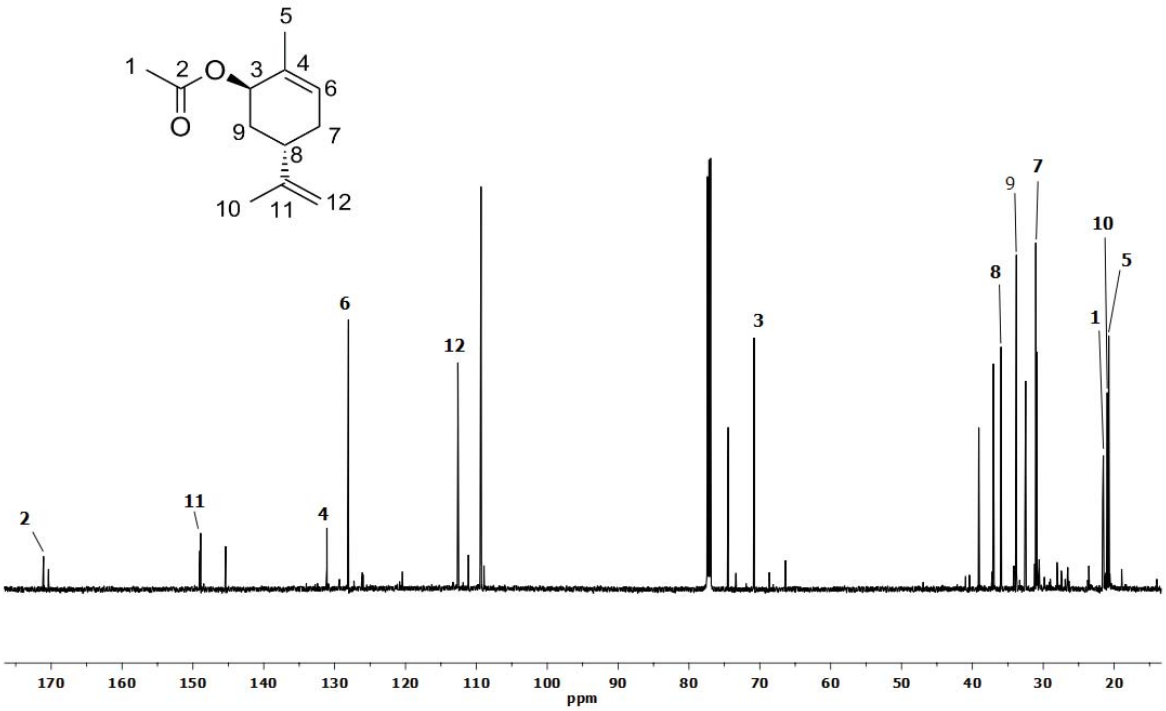
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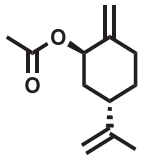
ppm

Acetoxylation of (*S*)-(-)-limonene at the internal double bond:

(*5S*)-2-methylene-5-(prop-1-en-2-yl)cyclohexyl acetate **54** (+ regioisomer **55**):



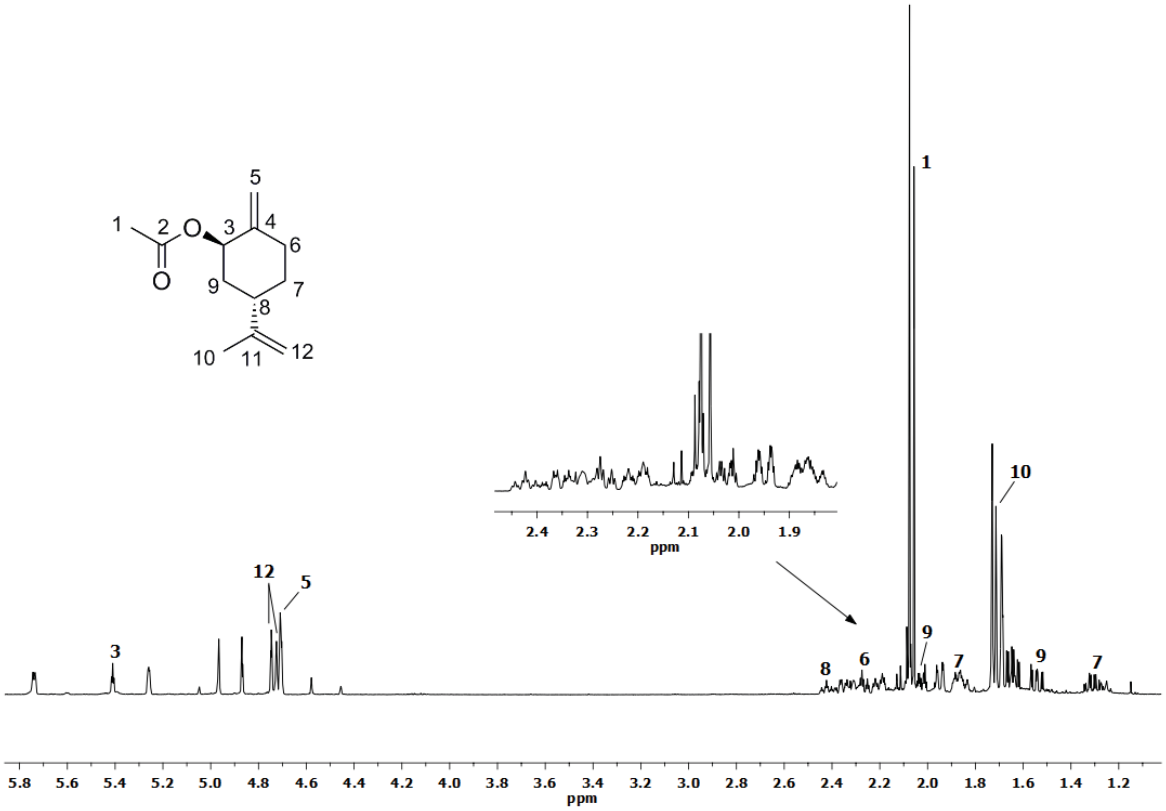
0.20 g (1.47 mmol, 1.0 eq) S-(-)-limonene **1** was dissolved in 2.0 ml dimethylacetamide and 2.0 ml acetic acid. Additionally 0.16 g (1.47 mmol, 1.0 eq) *p*-benzoquinone and 0.25 g molecular sieve (3 Å) were added and the mixture was stirred for five minutes at 50 °C. Then, 13.2 mg (0.06 mmol, 4.0 mol%) of palladium(II) acetate was added and the mixture was stirred for 24 hours at 50 °C. The crude mixture was washed with water, sodium hydrogen carbonate and brine, dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified *via* column chromatography (hexane/ ethyl acetate 95:5) to afford a light yellow liquid in 54 % yield (154 mg). The obtained product represented a mixture of the enantiomeric products **52** and **53** as well as **54** and **55**, and furthermore a small amount of by-product **51**.

^{1}H NMR: (600 MHz, $CDCl_3$) δ/ppm 5.41 (t, *J* = 3.1 Hz, 1H, CH, ^{3}) 4.76 - 4.74 (m, 1H, CH_2, ^{12}), 4.73 - 4.71 (m, 1H, CH_2, ^{12}), 4.71 - 4.69 (m, 2H, CH_2, ^{5}), 2.45 - 2.39 (m, 1H, CH, ^{8}), 2.39 - 2.35 (m, 1H, CH_2, ^{6}), 2.29 - 2.26 (m, 1H, CH_2, ^{6}), 2.06 (s, 3H, CH_3, ^{1}), 2.05 - 2.00 (m, 1H, CH_2, ^{9}), 1.90 - 1.84 (m, 1H, CH_2, ^{7}), 1.71 (s, 3H, CH_3, ^{10}), 1.57 - 1.51 (m, 1H, CH_2, ^{9}), 1.35 - 1.26 (m, 1H, CH_2, ^{7}).

^{13}C NMR: (75 MHz, $CDCl_3$) δ/ppm 170.3, 149.0, 145.2, 109.3, 109.3, 74.4, 39.1, 37.0, 32.5, 30.9, 21.3, 21.0.

SEC/ESI-MS of [$C_{12}H_{18}O_2Na^+$]: calculated: 217.12, found: 217.08.

IR (ATR platinum diamond): 2935.4, 1733.2, 1643.7, 1437.8, 1368.0, 1232.2, 1149.9, 1073.6, 1045.4, 1016.1, 965.5, 950.6, 911.1, 887.8, 807.6, 673.6, 609.2, 538.0, 469.4, 437.0.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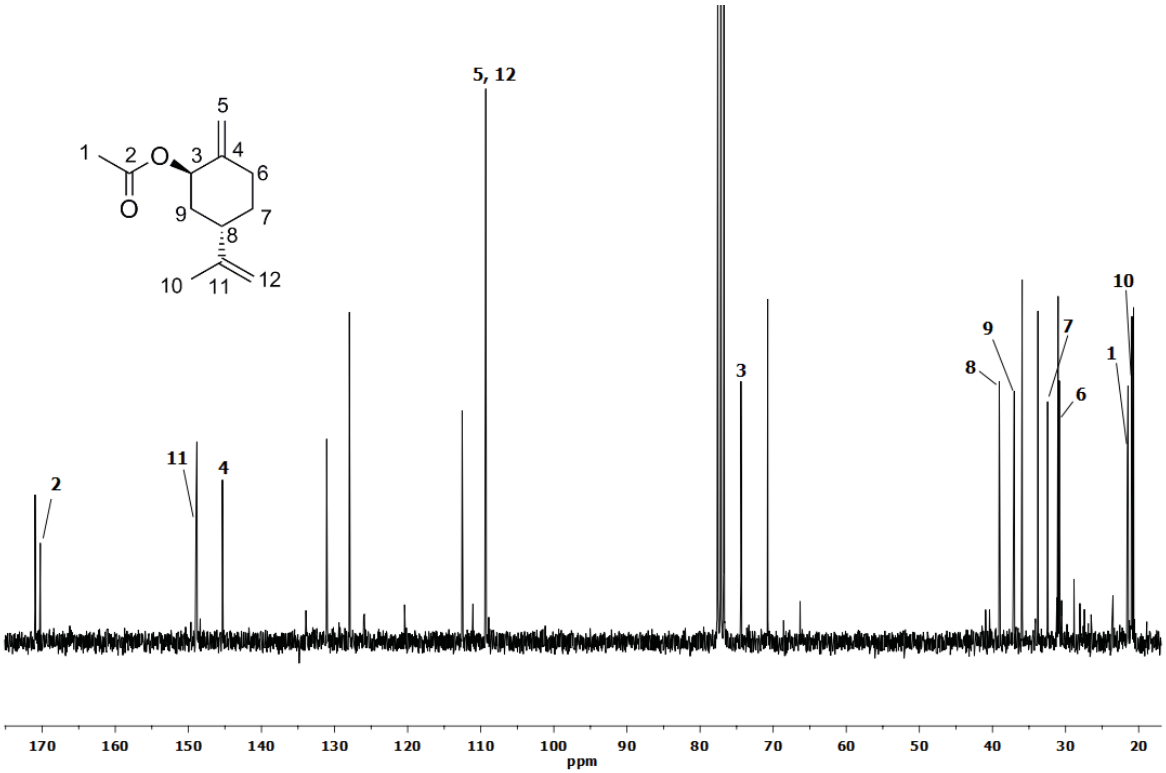
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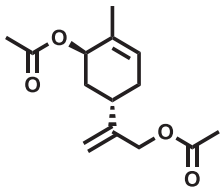
ppm

Additional acetoxylation of the terminal acetoxylated (*S*)-(-)-limonene 51:

2-((*1S*)-5-acetoxy-4-methylcyclohex-3-en-1-yl)allyl acetate **56** (+enantiomer **57**)



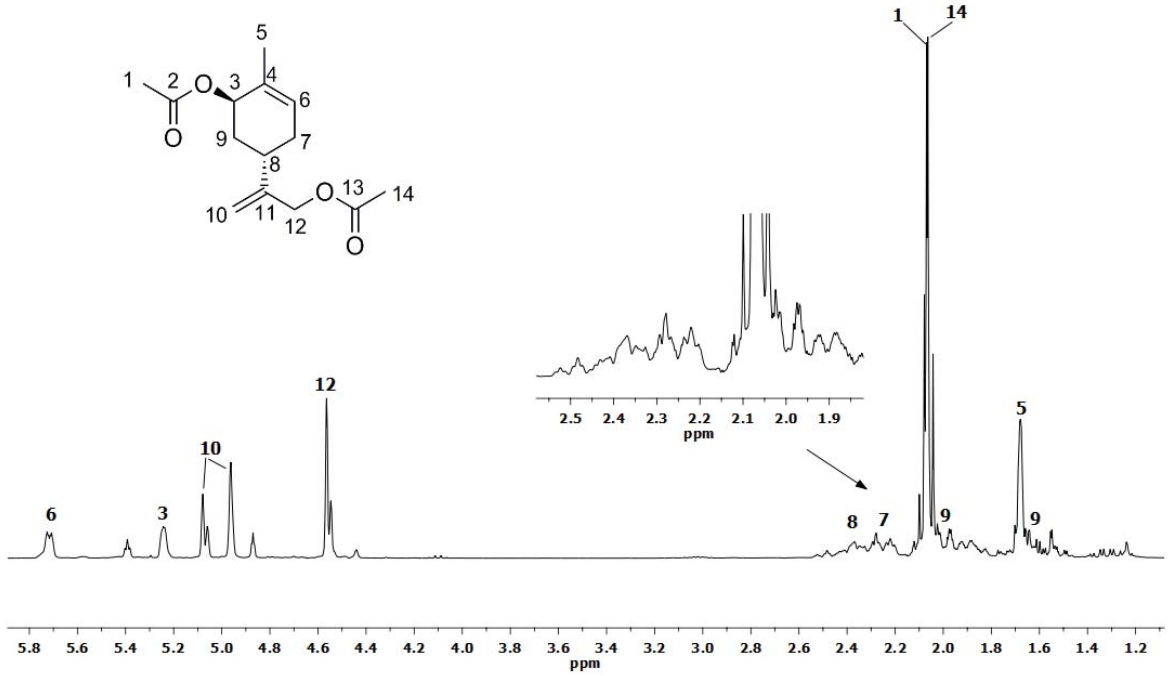
0.20 g (1.03 mmol, 1.0 eq.) **2**, 29.3 mg (0.05 mmol, 5.0 mol%) iron(II) phthalocyanine, 22.7 mg (0.21 mmol, 20 mol%) hydroquinone, 42.2 mg (0.52 mmol, 0.5 eq) sodium acetate were dissolved in 3.0 ml acetic acid and stirred for five minutes at 60 °C. Subsequently 11.6 mg (0.05 mmol, 5.0 mol%) palladium(II) acetate was added and the mixture was stirred for 5 days at 60 °C. The crude mixture was washed with water, sodium hydrogen carbonate and brine, dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified *via* column chromatography (hexane/ ethyl acetate 95:5) to afford a yellow liquid in 37 % yield (95.0 mg). The obtained product represented a enantiomeric mixture of **56** and **57** as well as **58** and **59.**

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 5.75 - 5.68 (m, 1H, CH, ^{6}), 5.27 - 5.21(m, 1H, CH, ^{3}), 5.08 (s, 1H, CH_2, ^{10}), 4.96 (s, 1H, CH_2, ^{10}), 4.56 (s, 2H, CH_2, ^{12}), 2.43 - 2.30 (m, 1H, CH, ^{8}), 2.29 - 2.19 (m, 2H, CH_2, ^{7}), 2.07 (s, 3H, CH_3, ^{1}), 2.06 (s, 3H, CH_3, ^{14}), 2.04 - 1.95 (m, 1H, CH_2, ^{9}), 1.69 - 1.64 (m, 1H, CH_2, ^{9}), 1.68 (s, b, 3H, CH_3, ^{5}).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 170.9, 170.7, 147.2, 131.2, 127.5, 112.0, 70.4, 66.2, 33.9, 32.2, 31.2, 21.4, 21.0, 20.6.

EI-MS: calculated: 252.14; found: 252.13.

IR (ATR platinum diamond): 2935.2, 1730.2, 1649.5, 1438.0, 1368.7, 1224.6, 1155.0, 1097.4, 1025.0, 953.7, 911.3, 836.5, 807.9, 605.0, 549.4, 469.9, 437.8.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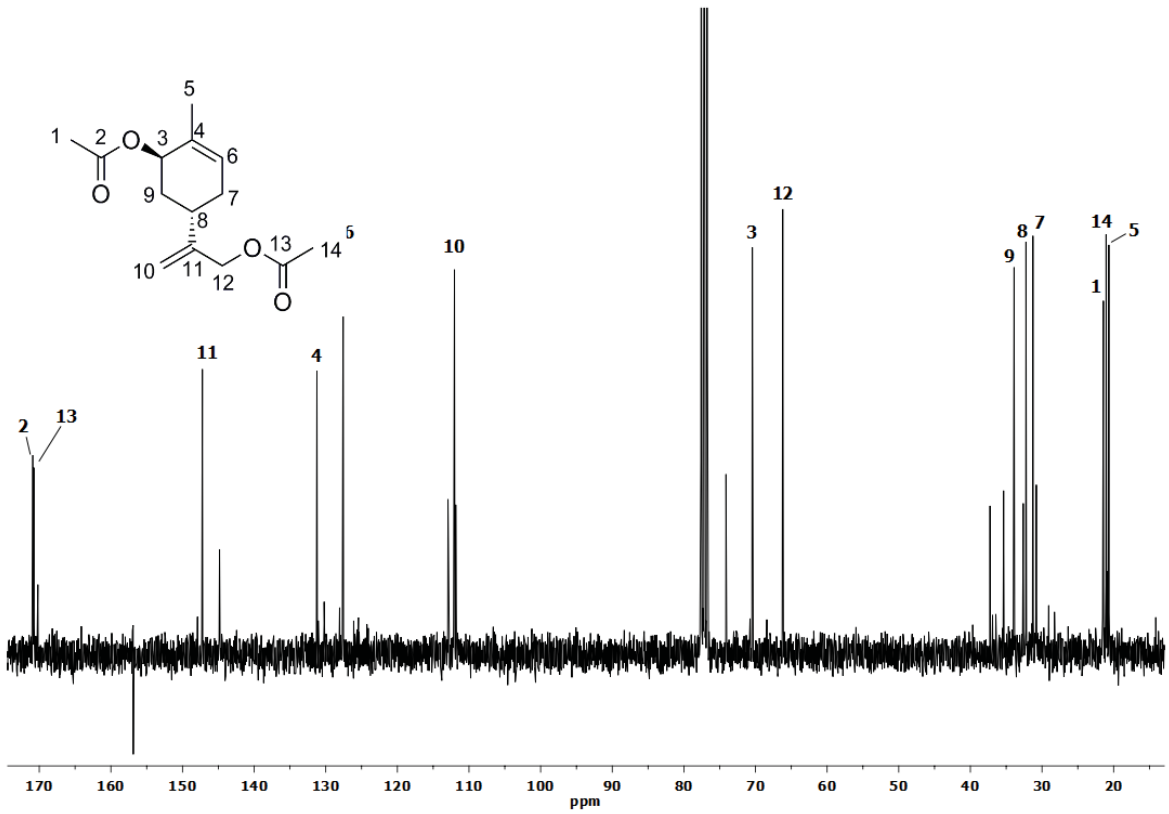
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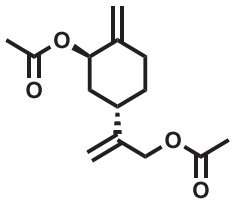
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm

Additional acetoxylation of the terminal acetoxylated (*S*)-(-)-limonene 51:

2-((*1S*)-3-acetoxy-4-methylenecyclohexyl)allyl acetate **58** (+ enantiomer **59**):

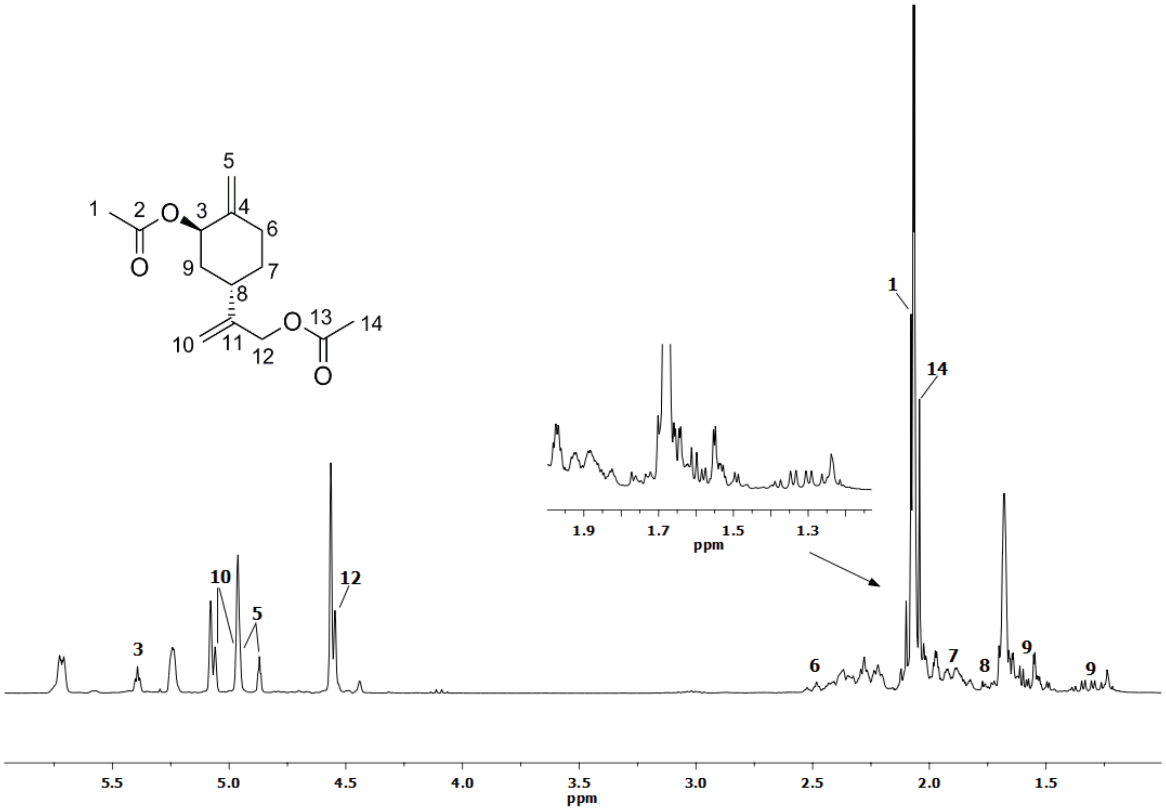


^{1}H NMR: (300 MHz, $CDCl_3$) δ/ppm 5.39 (t, J = 3.0 Hz, 1H, CH, ^{3}), 5.06 (s, 1H, CH_2, ^{10}), 4.96 (s, 1H, CH_2, ^{10}), 4.96 (s, 1H, CH_2, ^{5}), 4.86 (s, b, 1H, CH_2,^{5}), 4.54 (s, 2H, CH_2, ^{12}), 2.54 - 2.43 (m, 2H, CH_2, ^{6}), 2.08 (s, 3H, CH_3, ^{1}), 2.04 (s, 3H, CH_3, ^{14}), 1.94 - 1.82 (m, 2H, CH_2, ^{7}), 1.78 - 1.69 (m, 1H, CH, ^{8}), 1.62 - 1.51 (m, 1H, CH_2, ^{9}), 1.40 - 1.24 (m, 1H, CH_2, ^{9}).

^{13}C NMR: (75 MHz, $CDCl_3$) δ/ppm 170.8, 170.2, 147.3, 144.8, 112.9, 111.8, 74.1, 66.1, 37.3, 35.4, 32.6, 30.8, 21.5, 20.8.

EI-MS: calculated: 252.14; found: 252.13.

IR (ATR platinum diamond): 2935.2, 1730.2, 1649.5, 1438.0, 1368.7, 1224.6, 1155.0, 1097.4, 1025.0, 953.7, 911.3, 836.5, 807.9, 605.0, 549.4, 469.9, 437.8.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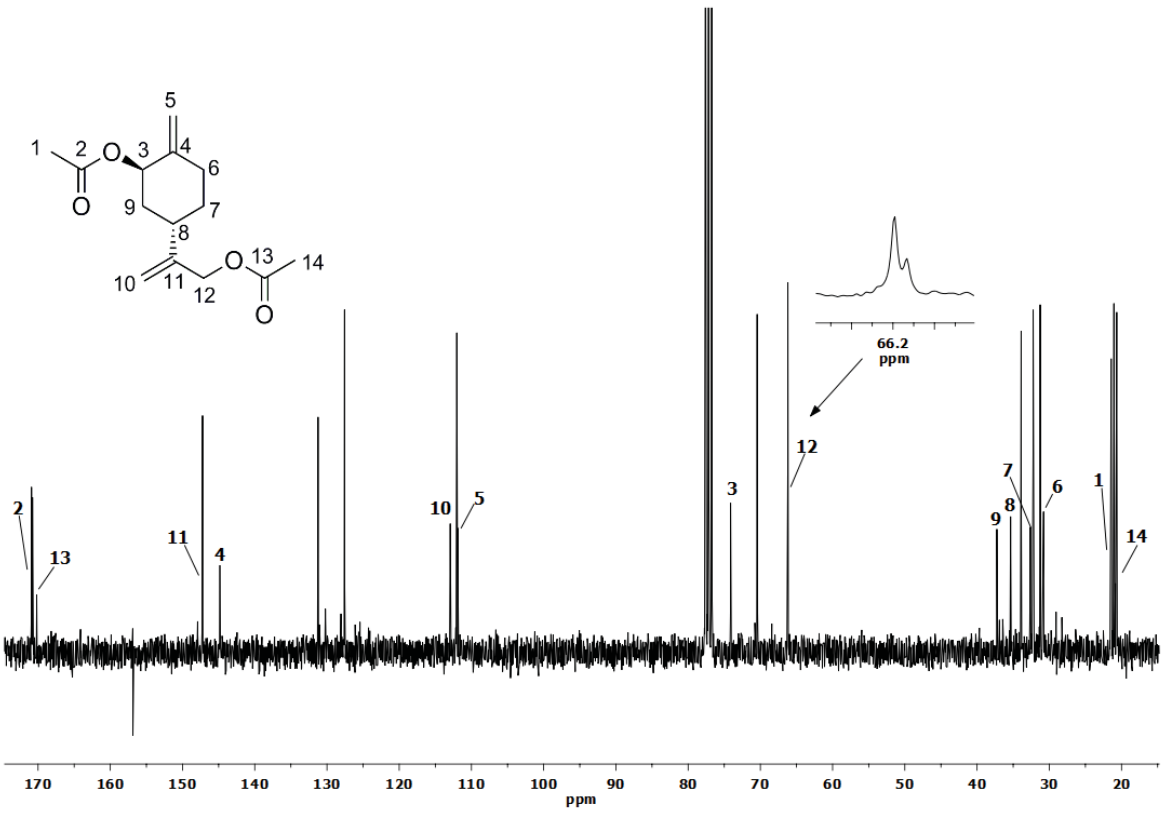
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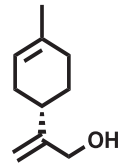
7
8
9
10
11
12
13
14
O
O
66.2
ppm
12
2
13
11
4
10
5
3
7
6
8
9
1
14
170
160
150
140
130
120
110
100
ppm
90
80
70
60
50
40
30
20

Chapter 4.2.7 Polyacrylates from limonene by catalytic acetoxylation and multi-component reaction

Synthesis of allylic alcohol derived from 51

0.50 g (2.57 mmol) of **51** and 18.0 mg (0.13 mmol, 0.05 eq) of TBD were dissolved in 30 ml methanol and stirred under reflux conditions for 6 hours at 90 °C. After cooling down to room temperature, the reaction mixture was washed with water, sodium hydrogen carbonate and brine, dried over sodium sulfate and evaporated to dryness. Afterwards, the crude product was purified *via* column chromatography (hexane/ ethyl acetate 8:2) to afford a deep orange liquid in 94 % yield (369 mg). The obtained product represented a mixture of the major product **60** and a small amount of by-products **61** and **62**.

(*S*)-2-(4-methylcyclohex-3-en-1-yl)prop-2-en-1-ol **60**



^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 5.41 - 5.36 (s, b, 1H, CH, ^{7}), 5.04 (s, 1H, CH_2), 4.89 (s, 1H, CH), 4.12 (s, 2H, CH_2), 2.23 - 2.04 (m, 2H, CH_2), 2.05 - 1.91 (m, 2H, CH_2), 1.94 - 1.88 (m, 1H, CH), 1.83 - 1.76 (m, 1H, CH_2), 1.64 (s, 3H, CH_3), 1.57 - 1.41 (m, 1H, CH_2), 0.85 (s, b, 1H, OH).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 153.7, 133.9, 120.5, 107.9, 65.2, 36.9, 31.4, 30.6, 28.3, 23.5.

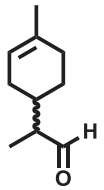
EI-MS of [$C_{10}H_{16}O$] calculated: 152.12, found: 152.2.

IR (ATR platinum diamond): 3347.0, 2915.7, 1708.4, 1645.4, 1436.5, 1374.6, 1167.5, 1017.2, 960.5, 894.6, 797.7, 564.8.

Synthesis of aldehyde derived from 60

98.3 mg (0.14 mmol, 0.07 eq) palladium hydroxide on carbon were suspended in 14.0 mL toluene and stirred under an hydrogen atmosphere for 30 minutes at room temperature. Subsequently, 304 mg (2,00 mmol, 1.00 eq) **60** dissolved in 6.00 mL toluene were added to the pre-activated catalyst and stirred for further 16 hours at room temperature. Afterwards, the crude product was purified *via* column chromatography (hexane/ ethyl acetate 9:1) to afford a colorless liquid.

2-(4-methylcyclohex-3-en-1-yl)propanal **63**



Colourless liquid, 72 % yield based on allylic alcohol ratio determined by GC-MS measurement using an internal standard (80 % terminal allylic alcohol **60**)

^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm 9.64 (d, *J* = 2.4 Hz, 1H, CH-*CHO*), 5.35 - 5.31 (m, 1H, C-*CH*-CH_2), 2.30 - 2.22 (m, 1H, CH_3-*CH*-CHO), 2.05 - 1.83 (m, 2H, CH-*CH_2*-CH), 1.98 - 1.83 (m, 1H, CH_2-*CH*-CH_2), 1.82 - 1.70 (m, 1H, C-*CH_2*-CH_2), 1.74 - 1.63 (m, 1H, C-*CH_2*-CH_2), 1.61 (s, 3H, *CH_3*-CH), 1.40 - 1.30 (m, 1H, CH_2-*CH_2*-CH), 1.38 - 1.25 (m, 1H, CH_2-*CH_2*-CH), 1.05 (d, *J* = 6,8 Hz, 3H, *CH_3*-CH).

^{13}C-NMR (126 MHz, $CDCl_3$) δ/ppm: 205.8; 134.2; 120.0; 51.1; 34.4; 30.2; 27.4; 25.5; 23.6; 10.4.

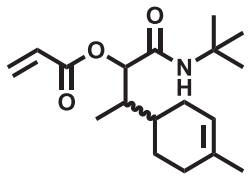
HRMS (FAB) of [$C_{10}H_{16}O$]: calculated: 152.1201, found: 152.1196.

IR (ATR platinum diamond): 3408.0; 2920.1; 1718.9; 1450.3; 1375.3; 1152.2; 1016.3; 913.1; 841.1; 798.2; 756.8; 525.1; 430.7; 402.5.

Synthesis of acrylate monomers *via* Passerini reaction (P-3CR)

608 mg (4.00mmol, 1.0 eq) **63** and 317 µL (4.40 mmol, 1.10 eq) acrylic acid **64** were dissolved in 4.0 mL dichloromethane. Subsequently, the respective isocyanide **65a-e** (1.10 eq) was added and the reaction mixture was stirred for 24 hours at room temperature. The crude product was evaporated to dryness and further purified *via* column chromatography (hexane/ ethyl acetate 8:2).

1-(*tert*-Butylamino)-3-(4-methylcyclohex-3-en-1-yl)-1-oxobutan-2-yl acrylate **66a**



Colorless viscous liquid, 72 % yield.

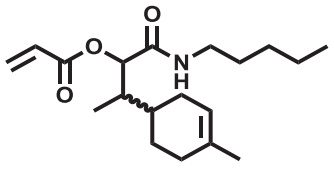
^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm: 6.50 – 6.42 (m, 1 H, CH_2-*CH*-CO), 6.21 – 6.13 (m, 1H, *CH_2*-CHCO), 5.96 – 5.88 (m, 1H, *CH_2*-CHCO), 5.79 – 5.69 (m, 1H, *NH*$_{isomers}$), 5.42 (s, 1 H, O-*CH*$_{isomers}$), 5,36 – 5,26 (m, 2H, C-*CH*-CH_2, O-$CH_{isomers}$), 5.09 (d, *J* = 6.1 Hz, 1H, O-$CH_{isomers}$), 5.06 (d, *J* = 6.3 Hz, 1H, O-$CH_{isomers}$), 2.11 – 1,96 (m, 2H, CH-*CH*-CH, CH-*CH_2*-CH), 1.98 – 1.83 (m, 3H, CH-*CH_2*-CH, C-*CH_2*-CH_2), 1.84 – 1.65 (m, 2H, CH_2-*CH_2*-CH), 1,60 (s, 3H, C-*CH_3*), 1.43 – 1.13 (m, 1H, CH-*CH*-CH_2), 1.33 (s, 9H, 3 C-*CH_3*), 0.96 – 0.85 (m, 3H, $CH_{3isomers}$).

^{13}C NMR (126MHz, $CDCl_3$) δ/ppm: 169.2, 165.0, 133.9, 132.1, 127.9, 120.8, 76.6, 51.4, 39.8, 35.3, 30.6, 28.7, 28.7, 28.7, 27.8, 25.0, 23.5, 11.8.

HRMS (FAB) of [$C_{18}H_{29}NO_3H^+$]: calculated: 308.2220, found: 308.2218.

IR (ATR platinum diamond): 3302.7, 2965.6, 2914.0, 1730.6, 1655.5, 1558.7, 1520.5, 1451.7, 1402.8, 1363.1, 1259.6, 1222.2, 1188.2, 1090.9, 1039.9, 982.1, 912.1, 808.3, 761.5, 646.2, 514.8, 429.7.

3-(4-Methylcyclohex-3-en-1-yl)-1-oxo-1-(pentylamino)butan-2-yl acrylate **66b**



Colorless viscous liquid, 70 % yield.

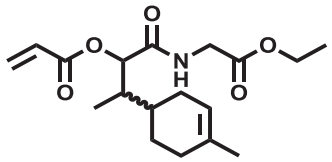
^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm: 6.50 – 6.43 (m, 1H, CH_2-*CH*-CO), 6.22 – 6.13 (m, 1H, *CH_2*-CHCO), 6.08 – 5.97 (m, 1H, *$NH_{isomeres}$*), 5.96 – 5.89 (m, 1H, *CH_2*-CHCO), 5.49 (s, 1H, O-$CH_{isomers}$), 5.42 (s, 1H, O-$CH_{isomers}$), 5.35 – 5.28 (m, 1H, C-*CH*-CH_2), 5.22 – 5.16 (m, 2H, 2 O-$CH_{isomers}$), 3.32 – 3.16 (m, 2H, *NCH_2*), 2.12 – 1.96 (m,2H,CH-*CH*-CH, CH-*CH_2*-CH), 1.98 – 1.83 (m, 3H, 2 CH-*CH_2*-CH, C-*CH_2*-CH_2), 1.84 – 1.66 (m, 2H, CH_2-*CH_2*-CH), 1.59 (s, 3H, C-*CH_3*), 1.51 – 1.43 (m, 2 H, NCH_2- *CH_2*), 1.43 – 1.14 (m, 1H, CH-*CH*-CH_2), 1.34 – 1.19 (m, 4H, 2 CH_2-*CH_2*-*CH_2*-CH_3), 0.96 – 0.83 (m, 3H, CH-*CH_3*$_{isomers}$), 0.89 – 0.83 (m, 3H, CH_2-*CH_3*).

^{13}C NMR (126 MHz, $CDCl_3$) δ/ppm: 169.9, 165.1, 134.2, 132.3, 127.8, 120.7, 76.6, 40.0, 39.3, 35.5, 30.6, 29.3, 29.0, 27.9, 27.1, 23.5, 22.3, 14.0, 11.8.

HRMS (FAB) of [$C_{19}H_{31}NO_3H^+$]: calculated: 322.2377, found: 322.2377.

IR (ATR platinum diamond): 3303.6, 2957.6, 2923.1, 1728.7, 1651.4, 1534.0, 1437.4, 1403.7, 1377.8, 1292.5, 1256.4, 1176.8, 1087.7, 1046.2, 981.6, 911.3, 807.4, 729.3, 430.8.

1-((2-Ethoxy-2-oxoethyl)amino)-3-(4-methylcyclohex-3-en-1-yl)-1-oxobutan-2-yl acrylate **66c**



Colorless viscous liquid, 70 % yield.

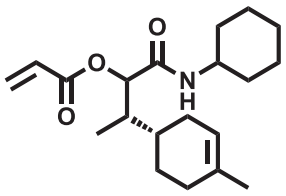
^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm: 6.59 – 6.51 (m, 1H, *NH*$_{isomers}$) 6.52 – 6.45 (m, 1H, CH_2-*CH*-CO), 6.23 – 6.15 (m, 1H, *CH*$_2$-CHCO), 5.97 – 5.90 (m, 1H, *CH*$_2$-CHCO), 5.57 (d, *J* = 2.6 Hz, 1H, O-CH$_{isomers}$), 5.48 (d, *J* = 2.7 Hz, 1H, O-CH$_{isomers}$), 5.35 – 5.28 (m, 1H, C-*CH*-CH_2), 5.29 (d, *J* = 6.0 Hz, 1H, O-CH$_{isomers}$), 5.27 (d, *J* = 6.2 Hz, 1H, O-CH$_{isomers}$), 4.21 – 4.16 (q, *J* = 5.0 Hz, 2H, O-*CH*$_2$-CH_3), 4.20 – 3.89 (m, 2H, *NCH*$_2$), 2.11 – 1.96 (m, 2H, CH-*CH*-CH, CH-*CH*$_2$-CH), 1.98 – 1.83 (m, 3H, 2 CH-*CH*$_2$-CH, C-*CH*$_2$-CH_2), 1.84 – 1.65 (m, 2H, CH_2-*CH*$_2$-CH), 1.60 (s, 3H, C-*CH*$_3$), 1.43 – 1.13 (m, 1H, CH-*CH*-CH_2), 1.26 (t, *J* = 5.0 Hz, 3H, CH_2-*CH*$_3$), 1.02 – 0.89 (m, 3H, CH-CH$_{3isomers}$).

^{13}C NMR (126 MHz, $CDCl_3$) δ/ppm: 170.4, 169.7, 164.9, 134.2, 132.4, 127.7, 120.7, 76.4, 61.7, 41.2, 40.2, 35.6, 30.5, 27.8, 26.5, 23.5, 14.2, 11.9.

HRMS (FAB) of [$C_{18}H_{27}NO_5$ H^+]: calculated: 338.1962, found: 338.1962.

IR (ATR platinum diamond): 3306.9, 2914.0, 1729.1, 1664.5, 1525.7, 1440.7, 1404.2, 1374.8, 1255.3, 1175.1, 1026.0, 982.3, 807.3, 670.6.

1-(Benzylamino)-3-(4-methylcyclohex-3-en-1-yl)-1-oxobutan-2-yl acrylate **66d**



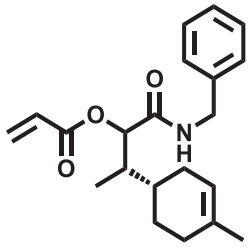
Colorless viscous liquid, 67 % yield.

^{1}H-NMR (300 MHz, $CDCl_3$) δ/ppm: 7.38 - 7.21 (m, 5H, 5 *CH*$_{arom}$), 6.53 – 6.42 (m, 1H, CH_2-*CH*-CO), 6.34 - 6.22 (m, 1H, *NH*$_{isomers}$), 6.24 - 6.10 (m, 1H, *CH*$_2$-CHCO), 5.96 – 5.87 (m, 1H, *CH*$_2$-CHCO), 5.59 (s, 1H, O-CH$_{isomers}$), 5,51 (s, 1H, O-CH$_{isomers}$), 5.38 - 5.26 (m, 3H, C-*CH*-CH_2, 2 O-CH$_{isomers}$), 4.60 - 4.37 (m, 2H, NH-*CH*$_2$-CH), 2.11 – 1,96 (m, 2H, CH-*CH*-CH, CH-*CH*$_2$-CH), 1.98 – 1.83 (m, 3H, 2 CH-*CH*$_2$-CH, C-*CH*$_2$-CH_2), 1.84 – 1.65 (m, 2H, CH_2-*CH*$_2$-CH), 1,63 (s, 3H, C-*CH*$_3$), 1.43 – 1.13 (m, 1H, CH-*CH*-CH_2), 1.01 – 0.89 (m, 3H, CH-*CH*$_3$ isomers).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 170.1, 165.0, 138.0, 133.9, 132.4, 128.8, 127.8, 127.7, 127.7, 127.6, 127.6, 120.3, 76.6, 43.3, 40.0, 35.5, 30.6, 30.5, 27.2, 23.5, 12.0.
HRMS (FAB) of [$C_{21}H_{27}NO_3$ H^+]: calculated: 342.2064 found: 342.2062.

IR (ATR platinum diamond): 3304.0, 2913.6, 1726.3, 1653.9, 1527.8, 1496.0, 1452.8, 1403.7, 1292.6, 1255.3, 1175.0, 1045.2, 981.2, 911.4, 806.8, 726.4, 696.6, 486.9, 431.1.

1-(Cyclohexylamino)-3-(4-methylcyclohex-3-en-1-yl)-1-oxobutan-2-yl acrylate **66e**



Colorless solid, 69 % yield.

^{1}H-NMR: (300 MHz, $CDCl_3$) δ/ppm 6.53 – 6.43 (m, 1H, CH_2-*CH*-CO), 6.26 - 6.13 (m, 1H, *CH_2*-CHCO), 5.98 – 5.89 (m, 1H, *CH_2*-CHCO), 5.87 - 5.71 (m, 1H, *$NH_{isomers}$*), 5.50 (d, *J* = 2.6 Hz, 1H, O-$CH_{isomers}$), 5.41 (d, *J* = 2.7 Hz 1H, O-$CH_{isomers}$), 5.38 - 5.29 (m, 1H, C-*CH*-CH_2), 5.21 - 5.14 (m, 2H, O-$CH_{isomers}$), 3.88 - 3.71 (m, 1H, CH_2-*CH*-CH_2), 2.14 – 1.96 (m, 2H, CH-*CH*-CH, CH-*CH_2*-CH), 1.98 – 1.83 (m, 3H, 2 C, CH-*CH_2*-CH, C-*CH_2*-CH_2), 1.84 – 1.65 (m, 2H, CH_2-*CH_2*-CH), 1.75 - 1.58 (m, 2H, 2 CH-*CH_2*-CH_2), 1.61 (s, 3H, C-*CH_3*),1.45 - 1.28 (m, 4H, 2 CH-*CH_2*-CH_2), 1.43 – 1.13 (m, 1H, CH-*CH*-CH_2), 1.32 - 1.16 (m, 2H, CH_2-*CH_2*-CH_2), 1.24 - 1.06 (m, 2H, 2 CH_2-*CH_2*-CH_2), 0.98 – 0.86 (m, 3H, CH-$CH_{3\ isomers}$).

^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 169.0, 165.0, 134.0, 132.4, 127.9, 120.8, 76.6, 48.0, 40.0, 35.6, 33.1, 33.0, 30.6, 30.1, 27.3, 25.5, 24.9, 24.8, 23.5, 11.8.

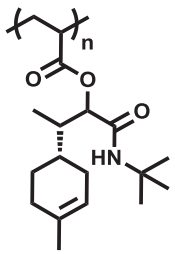
HRMS (FAB) of [$C_{21}H_{27}NO_3$ H^+]: calculated: 334.2377 found: 334.2376.

IR (ATR platinum diamond) 3293.7, 2925.5, 2853.1, 1727.4, 1649.7, 1534.3, 1448.9, 1403.6, 1375.6, 1293.2, 1251.8, 1179.9, 1097.5, 1046.1, 981.4, 911.4, 890.5, 807.3, 635.7, 429.7.

Polymerization of acrylate monomers

250 mg of the corresponding acrylate monomer **66a**-**e** and 1.0 mol% AIBN were dissolved in 1.0 mL ethyl acetate. Then, the reaction mixture was degassed with argon for 10 min and the polymerization was performed at 70 °C for 6 hours. Subsequently, the solution was added dropwise into cold diethyl ether. The precipitated polymer was separated by filtration and dried in vacuum to obtain polyacrylates **P4-8**.

Polymer **P4**

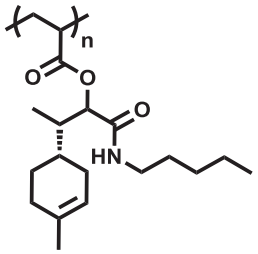


Colorless solid, T_g = 134 °C, 95 % yield.

^{1}H-NMR: (300 MHz, $CDCl_3$) δ/ppm: 6.95 - 6.12 (br, 1H, NH), 5.45 - 4.80 (m, 2H, C-*CH*-CH_2, O-$CH_{isomers}$), 2.78 - 2.16 (m, 1H, CH backbone), 2.18 - 1.12 (m, 10H, 2 CH, 4 CH_2),1.68 (s, 3H, CH_3),1.34 (s, 9H, 3 CH_3), 0.95 - 0.78 (m, 3H, $CH_{3\ isomers}$).

IR (ATR platinum diamond) 2964.3, 1734.5, 1682.8, 1519.8, 1454.2, 1392.7, 1364.9, 1223.1, 1154.7, 998.4, 798.7, 737.6, 690.5, 506.1.

Polymer **P5**

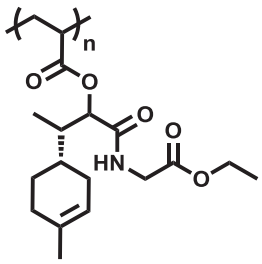


Colorless solid, T_g = 105 °C, 92 % yield.

^{1}H-NMR: (300 MHz, $CDCl_3$) δ/ppm:7.10 - 6.25 (br, 1H, NH),5.40 - 4.85 (m, 2H, C-*CH*-CH_2, O-$CH_{isomers}$), 3.45 - 2.80 (m, 2H, N-*CH_2*), 2.75 - 2.16 (m, 1H, CH backbone), 2.18 - 1.35 (m, 11H, CH, 5 CH_2), 1,61 (s, 3H, CH_3), 1.37 - 1.16 (m, 5H, CH, 2 CH_2), 0.98 - 0.78 (m, 6H, 2 CH_3);.

IR (ATR platinum diamond) 3321.9, 2927.8, 2858.8, 1735.7, 1657.0, 1534.2, 1445.8, 1378.0, 1151.6, 986.3, 913.1, 845.0, 797.3, 728.0, 527.6, 457.5.

Polymer **P6**

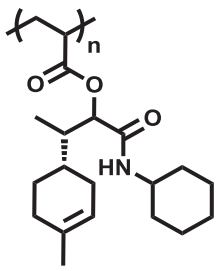


Colorless solid, T_g = 86 °C, 75 % yield.

^{1}H-NMR: (300 MHz, $CDCl_3$) δ/ppm:7.45 - 6.55 (br, 1H, NH),5.40 - 4.85 (m, 2H, C-*CH*-CH_2, O-$CH_{isomers}$), 4.27 - 3.65 (m, 4H, 2 CH_2), 2.85- 2.16 (m, 1H, CH backbone), 2.18 - 1.40 (m, 9H, CH, 5 CH_2), 1,61 (s, 3H, CH_3), 1,45 - 1.12 (s, 4H, CH, CH_3), 1.05 - 0.85 (m, 3H, CH_3).

IR (ATR platinum diamond) 3337.0, 2833.8, 1734.7, 1670.6, 1540.1, 1437.8, 1374.6, 1193.8, 1152.7, 1021.7, 913.8, 858.3, 797.1, 474.2, 430.2.

Polymer **P7**

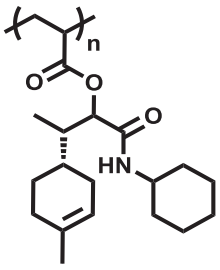


Colorless solid, T_g = 117 °C, 74 % yield.

^{1}H-NMR: (300 MHz, $CDCl_3$) δ/ppm: 7.35 - 6.95 (m, 5H, 5 CH_{arom}), 7.05 - 6.05 (br, 1H, NH), 5.40 - 4.85 (m, 2H, C-*CH*-CH_2, O-$CH_{isomers}$), 4.55 - 3.75 (m, 2H, CH_2), 2.78 - 2.16 (m, 1H, CH backbone), 2.18 - 1.05 (m, 10H, 2 CH, 4 CH_2),1.68 (s, 3H, CH_3), 0.95 - 0.65 (m, 3H, $CH_{3\ isomers}$).

IR (ATR platinum diamond) 2920.9, 1733.9, 1653.9, 1558.3, 1522.2, 1455.7, 1434.6, 1242.2, 1155.8, 1067.8, 1028.6, 738.5, 697.4, 600.5, 508.2, 484.4, 419.1.

Polymer **P8**



Colorless solid, T_g = 143 °C, 83% yield.

^{1}H-NMR: (300 MHz, $CDCl_3$) δ/ppm: 7.10 - 6.05 (br, 1H, NH), 5.45 - 4.80 (m, 2H, C-*CH*-CH_2, O-$CH_{isomers}$), 3.95 - 3.50 (m, 1H, CH), 2.85 - 2.15 (m, 1H, CH backbone), 2.18 - 1.40 (m, 11H, CH, 7 CH_2), 1,61 (s, 3H, CH_3), 1,45 - 0.95 (m, 9H, CH, 7 CH_2), 1.05 - 0.78 (m, 3H, $CH_{3\ isomers}$).

IR (ATR platinum diamond) 2929.9, 2854.0, 1734.1, 1683.4, 1669.9, 1653.6, 1558.5, 1540.1, 1521.7, 1507.9, 1449.2, 1375.0, 1152.8, 983.6, 891.3, 844.3, 762.1, 544.1, 427.7.

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7.1 List of abbreviations

ADMET	acyclic diene metathesis
AIBN	2,2′-azobis(2-methylpropionitrile)
ATM	atom transfer mediator
CG	coordinating groups
CM	cross-metathesis
DBU	1,8-diazabicyclo(5.4.0)undec-7-ene
DFA	dimer fatty acids
DMA	dimethylacetamide
DMF	dimethylformamide
DMSO	dimethylsulfoxide
DSC	differential scanning calorimetry
ETM	electron transfer mediator
FAMEs	fatty acid methyl esters
FG	functional group
FTIR	Fourier transform infrared spectroscopy
GC	gas chromatography
GC-MS	gas chromatography - mass spectrometry
HFIP	hexafluoroisopropanol
HG-II	Hoveyda-Grubbs II
HOAc	acetic acid
HOSO	high oleic sunflower oil
HQ	hydroquinone
kDA	kilo Dalton

m-CPBA	*m*-chloroperbenzoic acid
MCR	multi component reaction
MPV-reduction	Meerwein-Ponndorf-Verley-reduction
MS	mass spectrometry
MS/MS	Mass-spectrometry/mass-spectrometry
NIPU	non-isocyanide-polyurethane
NMR	nuclear magnetic resonance
OA	oxidation agent
P-3CR	Passerini Three Component Reaction
p-BQ	*p*-benzoquinone
PE	polyethylene
PEG	Polyethylene glycol
PS	polystyrene
PU	polyurethane
PVC	polyvinylchloride
RA	reductive amination
RCM	ring-closing metathesis
ROMP	ring-opening metathesis polymerization
ROP	ring-opening-polymerization
SEC	size exclusion chromatography
SM	self-metathesis
TBD	1,5,7-triazabicyclo[4.4.0]dec-5-ene
TH	transfer hydrogenation
THF	tetrahydrofuran
TLC	thin layer chromatography

TPP	tetraphenylporphyrin
UCST	upper critical solution temperature
Ugi-4CR	Ugi four component reaction
UV	ultra violet
WO	Wacker oxidation
wt%	weight percent

7.2 List of tables

7.3 List of schemes

7.4 List of figures

8 Appendix

8.1 List of Publications

1) M. von Czapiewski, O. Kreye, H. Mutlu, M. A. R. Meier, *Eur. J. Lipid Sci. Technol.* **2013**, 115, 76–85.
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5) M. von Czapiewski, M. A. R. Meier, *Macromol. Chem. Phys.* **2017**, 218, 1700153.
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