ARTICLE

Terpenes and Terpenoids: How can we use them?

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As one of the twelve fundamental principles of green chemistry, the employed feedstocks in chemical processes received substantial attention over the past decades. These efforts can, for a large part, be attributed to Werpy's list of top-value added chemicals from biomass from 2004.[1] The conventional fossil-based feedstocks are both depleting and damaging to the environment. This has led to the transition from the petroleum-based chemicals to more renewable, bio-based platform chemicals. The terpenes and terpenoids are a group of bio-based compounds well known throughout the scientific community. Although much is known about their acquirement from natural feedstocks, there is a shortage on comprehensive overviews of the chemistry that these compounds have been used for. Herein, we provide a full comprehensive overview of the reported chemistry with terpenes while specifically highlighting their reactivity. Fifteen of the most common and useful mono-terpenes and terpenoids are discussed, followed by a list of the remaining known compounds belonging to this group. The fifteen compounds that are discussed in more detail have been employed in a vast amount of chemical transformations with different applications including: polymerizations, total syntheses, chiral reagents/auxiliaries, pharmaceuticals, and chemical conversion to other useful bio-based chemicals. We believe that the presented chemistry in this work will provide chemists with a useful tool that should facilitate and stimulate the search for more sustainable, renewable and environmental friendly starting points for novel synthesis routes.

1. Introduction

In the last three decades, scientists have given much attention to the development of environmentally more attractive chemical processes. The collective terms that chemists have come to use to describe the goal of this trend are "green chemistry", "sustainable technology" or ''circular chemistry''.[2–5] Slootweg *et al.* divided green chemistry into twelve fundamental principles (Table 1. The 12 principles of Cio Chemistry

).[5] These principles serve as a powerful guide towards the development of sustainability in both industry and research laboratories. They aid chemists to address sustainability right from the start in the design of (new) molecules, catalysts and reactions to meet the societal challenges that we face. Many innovations have been brought to society after the introduction of green chemistry; such as boat paint without tin or fire extinguishers without freons.[6] Over the past decades, scientists have become more concerned with the employed feedstocks for their syntheses. Before the emergence of green chemistry, the main source of chemicals was the non-renewable petroleum industry. This fossil feedstock has been and continues to be depleted rapidly for both chemical products (*i.e.* synthetic textiles, plastics, surfactants, dyes and pigments, agrichemicals, pharmaceuticals, cosmetics and cleaning products) and energy production. Moreover, the resulting greenhouse emissions have long been the subject of environmental impact concerns. Therefore, scientists have turned to the use of more renewable sources for both fuel and material. The main other source of chemicals that our planet has to offer is biomass. This source is sustainable as it keeps the carbon-cycle (and other cycles) closed and is merely limited by the efficiency of photosynthesis.[7] It comprises the material made available to us by living organisms (e.g. crops, food, wood, agricultural residues, etc.). The transition from fossil-based sources of chemicals to biomass as a renewable feedstock is crucial for the preservation of our planet and life as we know it.[4,8] The main employed feedstocks for biorefineries comprise arable crops (e.g. cereals, oilseeds), biomass crops (e.g. perennial lignocellulosic crops), biowaste (e.g. agricultural and forestry residues, food, and municipal wastes), and algae.[9] These sources can all potentially provide the platform chemicals required for the production of most of the chemical products we utilize in our daily lives. In 2004, Werpy *et al*. – while working for the US Department of Energy (US DOE) – reported the identification of the twelve most valuable building blocks that could be derived from carbohydrate feedstocks.[1] This report caused a strong increase in the research and development of platform molecules. Six years after the report of the US DOE, Bozell *et al*. updated the list of the potential target structures owing to the considerable progress that had been made over the years.[10] Furthermore, as the original list merely included the chemicals made available from carbohydrate feedstocks, a second volume was released that comprised the chemicals derivable from lignin.[11] Platform chemicals can be categorized based on the required feedstock for obtaining them: polysaccharides (cellulose, hemicellulose, chitin, starch, inulin, etc.), lignin, and extracts (triglycerides, terpenes, pigments, etc.). Over the years, many

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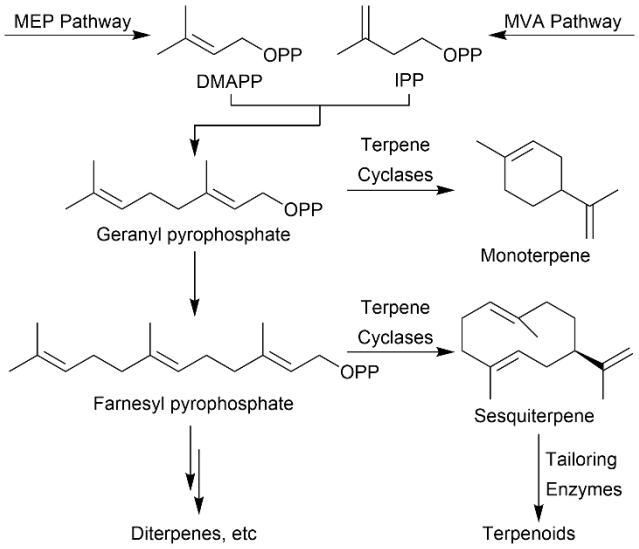
reviews have extensively covered the conversion of the known biomass feedstocks to all the important platform chemicals of these

categories and their subsequent transformation to bio-based chemicals. [7,10,12–23] In contrast, there is a strong shortage of reviews that provide a comprehensive and clear overview of the applications and performed chemistry of all the involved bio-based/platform chemicals. This is particularly the case for certain bio-based structures such as terpenes and terpenoids. Terpenes have a basic (cyclo)aliphatic structure composed of isoprene units, whereas terpenoids are modified terpenes that include added oxygen atoms and they have methyl groups displaced or removed. Along with considerable structural diversity, these compounds contain double bonds with varying reactivity, making them easy to functionalize and exceedingly adaptable. In their biosynthesis, the five-carbon isoprene units are first connected, providing a linear chain (Scheme **1**).[24] This can be done in a head-to-tail fashion for the lower terpenes or include one head-to-head condensation for the higher terpenes. Then, the linear chain is transformed into a wide range of complex cyclic skeletons via a series of carbocationic ring cyclizations and rearrangements, either mediated/catalyzed by enzymes (terpene cyclases) or even spontaneous. A final modification by tailoring enzymes then affords the useful terpenoid derivatives, which are decorated with a range of functional groups. Terpenes can be classified into different categories based on the amount of isoprene units that they comprise: monoterpenes (C_{10}), sesquiterpenes (C_{15}), and diterpenes (C_{20}) comprise two, three and four isoprene units, respectively.[24,25] Existing reviews merely encompass certain aspects of their usage (e.g.; polymerization chemistry, redox chemistry).[26,27] Additionally, the terpene family has found many applications in the chemical community and their use encompasses a vast selection of chemical transformations (e.g. total syntheses, chiral reagents/auxiliaries, pharmaceuticals).[28–39] With that in mind, the aim of this review is to provide a comprehensive overview of the diverse chemical transformations involving terpenes, with a particular emphasis on their reactivity. Many studies have been reported that incorporate terpenes as starting points or intermediates in their appropriate syntheses.[40] The following sections discuss numerous bio-based terpenes along with examples of their employment in syntheses on small or industrial scale. As a result of the large quantity of available terpenes, this report merely discusses the most common and useful mono-terpenes and terpenoids and makes a selection of the most relevant examples for their use in synthesis.

The 12 principles of Cio Chemistry
1. Collect and use waste
2. Maximize atom circulation
3. Optimize resource efficiency
4. Strive for energy persistence
5. Enhance process efficiency
6. No out-of-plant toxicity
7. Target optimal design
8. Assess sustainability
9. Apply ladder of circularity
10. Sell service not product
11. Reject lock-in
12. Unify industry and provide coherent policy framework



Scheme 1 Route for the biosynthesis of terpenes. MVA: mevalonic acid pathway, MEP: 2-C-erythrithol-4-phosphate pathway.

Table 1. The 12 principles of Cio Chemistry

2. Terpenes and Terpenoids

2.1 Isoprene

Isoprene **1** is the simplest and one of the more common terpenes. This olefin occurs naturally in the environment and is emitted from living organisms such as plants and even humans. It has been estimated that approximately 400 million tonnes are produced by foliar emission alone.[41] It can be obtained in various ways including a fermentation method that also employs biomass feedstocks (e.g. glucose). [42]

Isoprene contains a butadiene functionality of which the reactivity can be exploited for numerous synthetic purposes. Mother nature utilized it for the synthesis of natural rubber, which displays

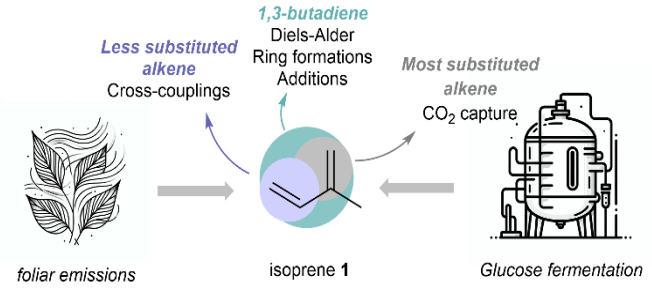
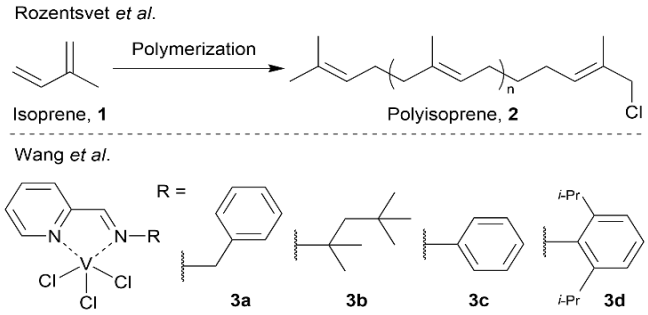


Figure 1. Isoprene's functional groups and procedence

unique structures and features. In that respect, synthetic polyisoprene **2** has been synthesized in numerous ways (Figure 1).

One example by the group of Rozentsvet *et al*. involves the cationic polymerization utilizing a $TiCl_4$/acid catalyst system (Scheme 2). This afforded structures with various molecular functionalities in excellent yields.[43,44] The cationic polymerization method employed here demonstrates the nucleophilic character of the diene system that can be

exploited. Other vanadium(III)-based catalytic systems **3a-d** have also been published that could be used for the polymerization of isoprene (Scheme 2).[45] These complexes have various electronic and steric properties because of slight changes in the iminopyridine bidentate ligands. One of these,



Scheme 2 Cationic polymerization of isoprene by Rozentsvet *et al*. and the vanadium-based catalysts employed by Wang *et al*. for isoprene polymerization.

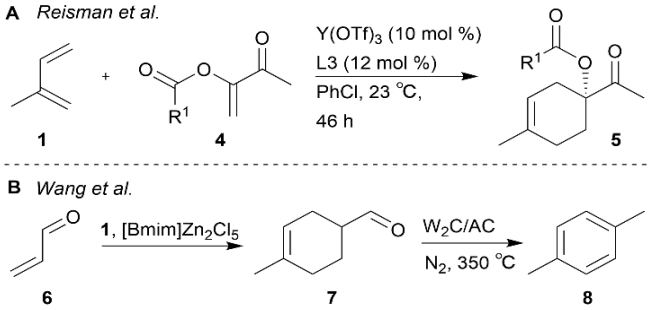
3c, displayed a high *cis*-selectivity and could provide high molecular weight polymers. Isoprene is also utilized for the synthesis of copolymers.[41]

Aside from polymerizations, chemists have frequently employed isoprene **1** in small molecules synthesis. Butadiene compounds are well known in organic synthesis as substrates for cycloaddition reactions. In the case of isoprene, multiple groups have employed it as one of the model substrates for the Diels-Alder ring formation, both in batch and flow setups.[46–48] We will discuss two examples in more detail. Very recently, Reisman *et al*. published an enantioselective Yttrium-catalysed Diels-Alder reaction with α-acyloxy enones **4** for the synthesis of chiral oxidized cyclohexene derivatives **5** (Scheme 3A).[48] They were able to utilize their method to selectively produce (—)-terpinen-4-ol, a key intermediate in the synthesis of the BASF herbicide cinmethylin. The authors envisioned the other products to be valuable chiral building blocks for terpene synthesis. Another report, by Wang *et al*., discussed a very atom-economical synthesis of *p*-xylene **8**, an indispensable chemical building block in industry (Scheme 3B) With acrolein 6 as the dienophile, these two bio-based building blocks were coupled to afford 4-methyl-3-cyclohexene-1-carbonylaldehyde **7**, which would sequentially undergo a dehydroaromatization-hydrodeoxygenation cascade to form the desired arene **8**. This process could be performed with numerous terpenes containing conjugated dienes, thus providing a means of attaining valuable aromatic structures that circumvents the need for the petrol industry.[47]

Another reaction type reported with isoprene was reported by Chen *et al*. who discussed the [3+3] annulation of this terpene with 3-hydroxycoumarins **9** (Scheme 4).[49] This reaction is particularly interesting as the use of a Brønsted or Lewis acid mainly resulted in pyranochomones **9a** and pyranocoumarins **9b**, respectively. An additional reagent-dependent reaction with isoprene was presented by the same group earlier that year.[50] It involved the installation of prenyl or reverse-prenyl groups onto the 3'-position of indoles, thus providing a method for the synthesis of a diverse set of natural indole alkaloids. Therein, the employed transition metal (TM) hydride (i.e. Rh-H or Pd-H) was the deciding factor for product formation. Other more earth-abundant metals like nickel have also afforded prenylations with benzimidazoles.[51]

There are also additions that rely on the nature of the ligand for a regioselective functionalization of isoprene. For example, the nickel-catalyzed Mizoroki-Heck reaction reported by Chen *et al*. (Scheme 5A).[52] that yields linear product **10**; or the cobalt-catalyzed regiodivergent hydrosilylation that produces 2,1 (**11a**) or 4,1 **11b** hydrosilylation via a cobalt-isoprene complex **1-Co** (Scheme 5B).[53] Similar reactivity has been exploited for the construction of 2,3-dihydrobenzofuranes, an important building block for the synthesis of pharmaceuticals and natural products,using a Heck/Tusji-Trost reaction.[54]

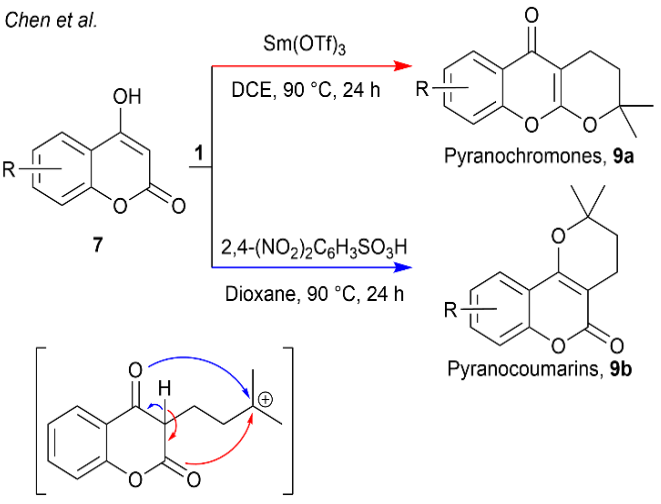
Isoprene has also been employed in Multi-Component Reactions. Remarkable examples are the Co(III)-catalyzed



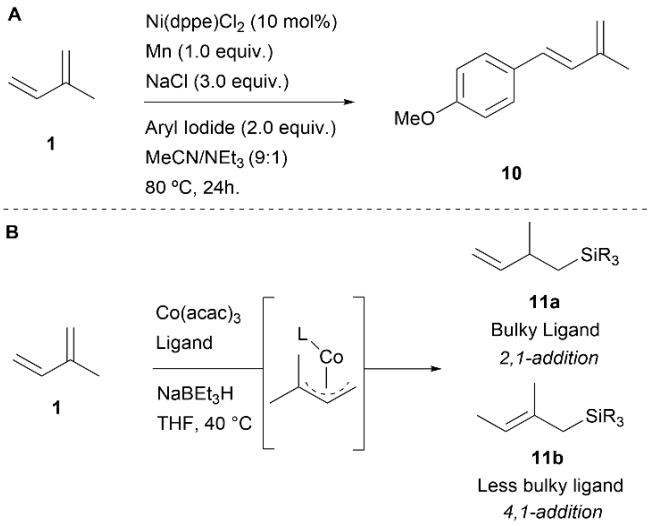
Scheme 3 A. Enantioselective Diels-Alder reaction with alpha-acyloxy enones for chiral cyclohexene derivative synthesis. B. Zinc mediated Diels-Alder reaction with acrolein in the synthesis towards p-xylene.

assembling of isoprene with N-(2-pyrimidyl) indoles **12** and formaldehyde to obtain homoallylic alcohols **12a** (Scheme 6A)[55]. This 1,4-addition is dictated by a series of cobalt hydride eliminations, hydride insertions and a final six-membered ring transition state with formaldehyde **13** and the cobalt.

Yet another example is the non stereoselective cobalt/photoredox 1,2-amino oxygenation that yields quaternary carbon centers as in **14a** (Scheme 6B).[56] The

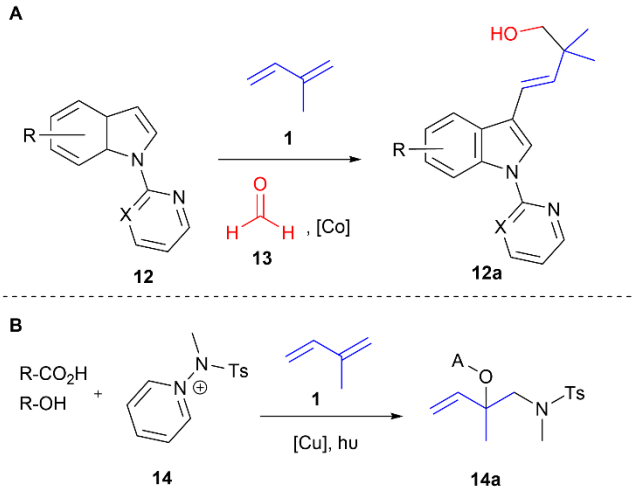


Scheme 4 Reagent dependent synthesis of pyranochromones and pyranocoumarins.



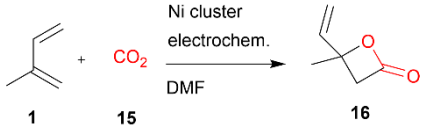
Scheme 2 A. Nickel-catalyzed Mizorok-Heck reaction. B. Cobalt-Catalyzed regiodivergent hydosilylation

1,2-addition is rationalized via radical additions, which involve the formation of an stable tertiary radical in isoprene.



Scheme 3 A. MCR Cobalt-catalyzed obtention of homoallylic alcohols. B. Cupper-catalyzed synthesis of quarternary centers by means of 1,2-amino oxygenation

The last example uses this isoprene **1** for CO_2 **15** capture in a 1,2-addition fashion. The authors employ an electrocatalytic approach to yield β-propiolactones **16** (Scheme 7), which are interesting building blocks for numerous applications (e.g. ROP polymerization).[57] They also use *o*-cimene **47** in their scope.



Scheme 4 Electrocatalytical CO_2 capture for the formation of β propiolactones

2.2 Tullipalin A (α-Methylene-γ-butyrolactone)

Structurally related to isoprene and belonging to the class of terpenoids is an exceedingly useful compound: tulipalin A **17**, also commonly known as α-methylene-γ-butyrolactone **17** (MBL). This MBL is mainly found in tulips and as the ring structure is known to be an essential building block for natural products, it is a well-studied monomer in the organic synthesis community.[28,29,58] Recently, the group of Fors *et al.* published the large-scale synthesis of **17** utilizing another bio-derived compound as starting material: itaconic acid **18** (IA)[59]. IA is a bio-renewable feedstock obtained by the fermentation of biomass. Indeed MBL features two chemically reactive moieties; a Michael-acceptor, and a lactone ring (Figure 2A). The former provides **17** with a reactivity similar to acrylate compounds and as we will see, this moiety and the lactone ring can both be employed for polymerization reactions. Furthermore, MBL displays structural features similar to methyl methacrylate **19**, a petroleum-based compound which is often used as monomer in polymerization reactions (Figure 2B).[28,29]

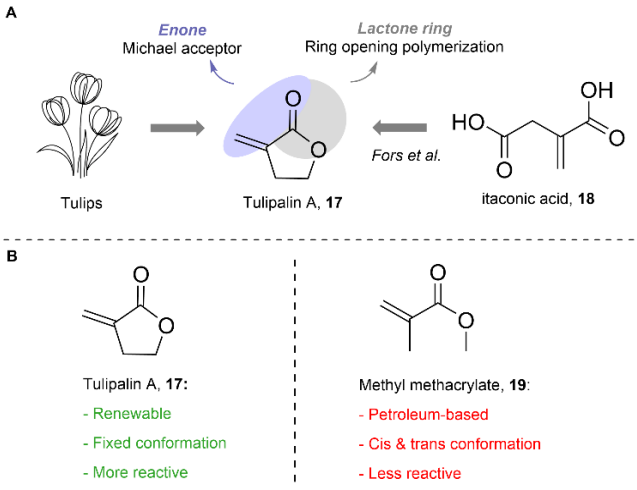
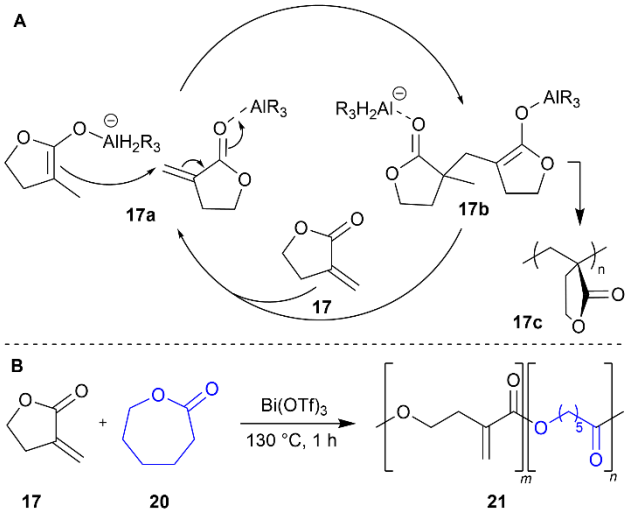


Figure 2 A. Tulipalin A's functional groups and sources. B. Comparison of the chemical structures of Tulipalin A (MBL) and methyl methacrylate.

The replacement of **19** with MBL **17** is motivated by its renewability and fixed conformation. Polymerization using MBL as a building block can be achieved by numerous radical-based methods including controlled radical polymerization (i.e. atom transfer radical polymerization).[29] Compared to **19**, MBL displays a higher reactivity when subjected to polymerization initiated by radical intermediates. This behavior is likely a consequence of both the more planar structure and the exocyclic C=C double bond in MBL. [28,29]

Aside from radical-based polymerization, MBL polymers have also been synthesized by different polymerization methods such as; group-transfer polymerization, photo-copolymerization, reversible addition-fragmentation chain-transfer polymerization, and controlled anionic polymerization (Scheme 8A). [28,29,59] The resulting polymers of these methods all still contain the intact lactone rings **17d**. The first known polymerization involving a ring-opening mechanism was reported by Ritter *et al*. who described the ring-opening co-polymerization (ROCOP) of MBL with ε-caprolactone **20** utilizing a Bi(III)-catalyst (Scheme 8B).[60] The resulting polymer **21** was

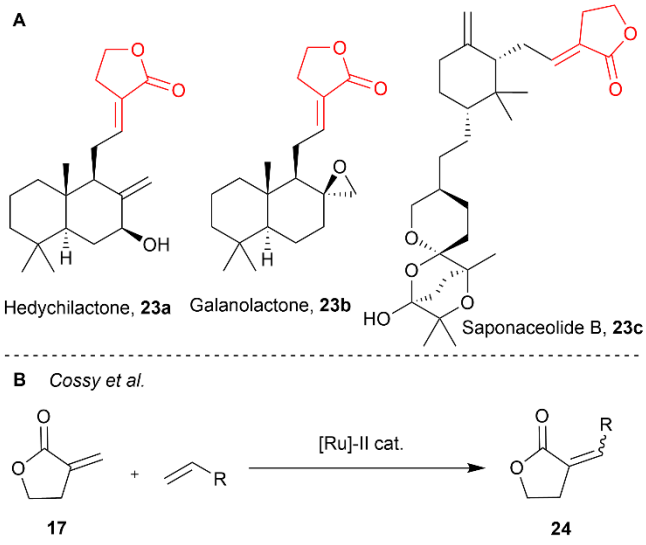
subsequently cross-linked affording an elastic and transparent material with shape memory.



Scheme 5 A. Controlled anionic polymerization of MBL utilizing aluminium catalyst as reported by Zhu et al. B. ROCOP of MBL and ε-caprolactone.

Alongside the polymerizations described above, other interesting applications involving **17** have been described in literature. The α-alkylidene-γ-butyrolactone group is present in a wide range of biologically active natural products (**23a-c**) (Scheme **9**A).[61] Therefore, it was synthetically incorporated in final (natural)-products. A well-known reaction that is one of the most valuable methods for C-C bond formations is olefin-metathesis. To facilitate introduction of MBL **17** in natural products, the group of Cossy *et al*. reported novel conditions for the stereoselective metathesis reaction of MBL **17** with numerous olefin reactants (Scheme 9B). Contrary to other reports, they use additives that minimize the formation of an undesired isomerized byproduct. [61]

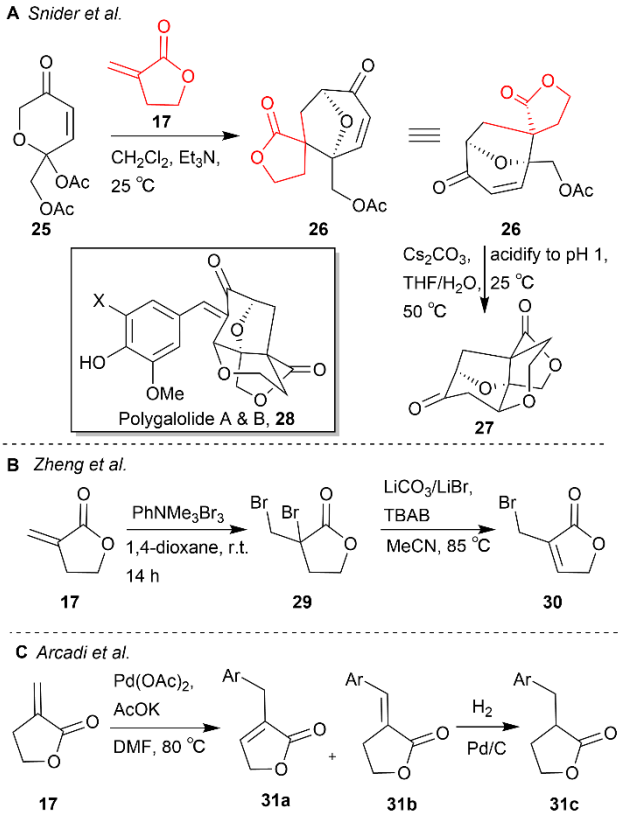
Next to the above-mentioned natural products containing MBL **17**, other natural products can also be synthesized where this functionality is not present in the final structure but is incorporated in intermediates during the total synthesis. For



Scheme 7 A. Natural compounds containing MBL in their structure. B. Methathesis reaction with MBL developed by Cossy et al.

example, various reports have employed **17** in order to attain polygalolides A & B. In 2006, Snider *et al*. reported the two-step synthesis of key intermediate **27** by means of a stereo- and regiospecific [5+2] cycloaddition reaction (Scheme 10A).[62] The remaining synthesis from **27** to form polygalolides A & B **28** has previously been reported by Hashimoto *et al*.[63] while Suga *et al*. later reported an improved Pd-catalyzed [5+2] cycloaddition with **17** to provide key intermediate **27**.[64]

MBL can also be transformed to other useful building blocks for subsequent use in alternative chemical transformations. For example, Zheng *et al*. described the synthesis of irreversible indole derivatives as LSD1 inhibitors.[30] Therein, MBL **17** was first brominated to **29** and a subsequent elimination provided the required bromolactone **30** (Scheme **10**B). This synthesis both provides examples of how MBL can functionalized and how, through **30**, it can conveniently be installed in target compounds by means of the Barbier reaction. Multiple other studies have reported variations of the latter reaction with **30**. [30,65–79] Compound **30** has also been utilized for other transformations such as; the synthesis of butenolide-containing dicarbamates[80], Suzuki cross-coupling reactions[81], nucleophilic substitutions[82], and bioreduction using ene-reductases.[83] Arcadi *et al*. reported an additional method for the facile installation of **17** in other structures. By means of the Heck reaction, they were able to couple a diverse set of aryl groups to MBL **17**, thus furnishing a useful method for the incorporation of this versatile compound, obtaining compounds

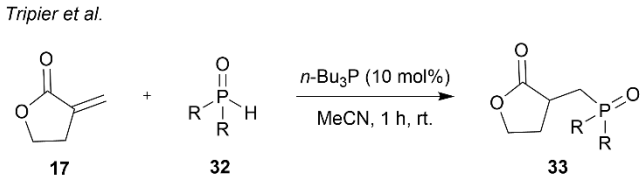


Scheme 6 A. Synthesis of polygalolide A & B intermediate 23 from 15 by means of a [5+2] cycloaddition reaction. B. Synthesis route for the installation of MBL on indole derivatives by means of a bromination and the subsequent Blaise reaction. C. Pd-catalyzed reductive arylation

31a-c (Scheme 10C).[84] It must be mentioned that Genet *et al.* published a similar reaction with MBL **17** a year prior where they performed the Heck-type reaction with arene diazonium salts.[48]

As mentioned before, MBL **17** also contains a Michael acceptor moiety, which has been exploited by numerous groups. For example, Salin and Islamov reported numerous phophine-catalyzed Michael-additions to **17** with PPh_3 and diethyl malonate, thus offering an economical and practical strategy for the functionalization of this sustainable bioactive compound.[85,86] Another reaction by Tripier *et al*. reported the synthesis of (oxo-)cyclam and (oxo-) homocyclen bifunctional chelating agents (known for their coordination properties) utilizing **17** (Scheme 11).[87] Therein, a ring-opening with **17** provided the cyclized C-functionalized structures bearing an EtOH group. This group was subsequently modified for other purposes. There is also work from Shu e*t. al.* regarding the synthesis of 2-piperidinones in one step via a [1+2+3] strategy.[88]

2.3 Myrcene



Scheme 8 Conditions for the phosphorus-catalyzed Michael addition to MBL.

The first natural monoterpene discussed herein is β-myrcene **34**. Although not an economically beneficial process, **34** can be attained by extraction from numerous plant oils (e.g. wild thyme, ylang-ylang, bay). It is, however, produced on a mass scale by the pyrolysis of β-pinene (discussed below).[89] Myrcene contains an isopropylidene group, which has a significant role in cyclization reactions. Moreover, it contains a highly active 1,3-diene moiety comparable to that in isoprene. As can be expected from this similarity, β-myrcene displays comparable reactivity to isoprene and has been employed in similar transformations. Owing to the diene in **34**, it has been employed for the synthesis of a large variety of compounds with different applications in pharmaceuticals, flavors, fragrances, vitamins and cosmetics (Figure 3).[89]

For over half a century, organic and polymer chemists have developed reaction conditions for the polymerization of myrcene **34**. One of the first reports emerged in 1960 and since then, many more publications reported novel methodologies for the polymerization of this compound.[90] A popular approach involves stereoselective polymerization reactions utilizing metal complexes. The choice of metal-catalyst is the deciding factor

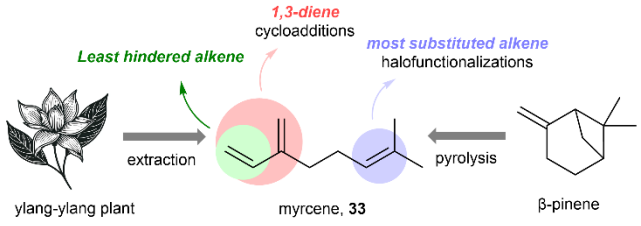
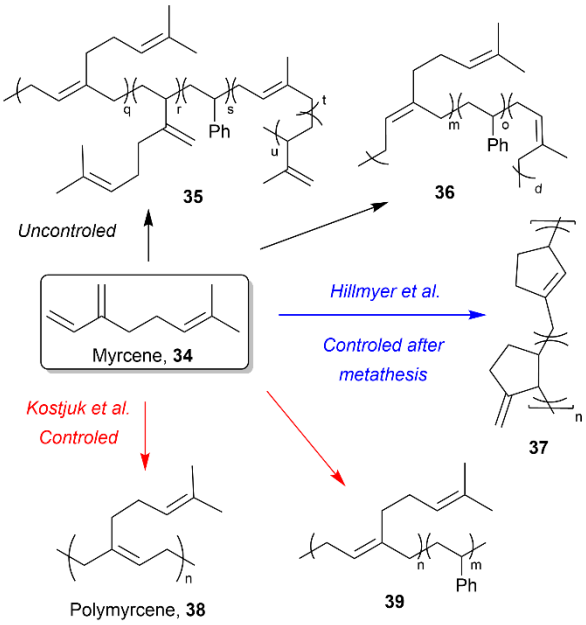


Figure 3. Myrcene's functional groups and sources

for the structure of the obtained polymer. The use of a neodymium borohydride-based catalyst activated by $[CPh_3][B(C_6F_5)_4]$[91] or *n*-butylethylmagnesium[92], for example, mainly results in the formation of *cis*-1,4-poly(β-myrcene). In contrast, employment of dichloro-1,4,-dithiabutanediyl-2,2'-bis[4,6-bis(2-phenyl-2-propyl)phenoxy] titanium[93] or lanthanum-based catalytic complexes[94] results in *trans*-1,4-poly(β-myrcene). Additionally, when neodymium borohydride is used in combination with *n*-butylethylmagnesium[92], or a lutetium-based catalyst, 3,4-poly(β-myrcene) **38** is formed (Scheme 12).[95] Furthermore, studies have also provided various methods for the copolymerization of **34** with other substrates (*e.g* styrene) to obtain novel structures **35** and **36** with different properties, although without selectivity (Scheme 12).[90,94,96] Finally, Hillmyer *et al*. have synthesized polymers with internal five-membered rings **37** from myrcene **34** by means of a ring closing metathesis and subsequent radical, anionic, or cationic polymerization, in a more selective fashion.[97] One of the more recent reports, by Kostjuk *et al*., involved the controled cationic polymerization of myrcene **34** utilizing a lewis acid surfactant combined complex (LASC) made by reacting ytterbium chloride and sodium dodecylbenzenesulfonate surfactant.[90] Therein, they showed that this relatively novel class of metal catalysts can efficiently initiate cationic polymerization.[98] Not only could the use of this LASC provide poly(β-myrcene) **38**, but it also afforded copolymers with styrene **39** with high molecular weights and single glass transition temperatures (T_g). The stereoselective polymerization of β-myrcene was achieved via the coordinative mechanism using catalytic complexes of different metals (Scheme **12**). [90]

Multiple studies have investigated myrcene's reactivity to access other (than polymer) valuable target molecules. In 2013, Behr *et al*. reported the Ru-catalyzed co-dimerization of **34** with methyl methacrylate **18** (Scheme 12).[99] Co-dimerization is a great method to obtain functionalized longer chain alkenes in a

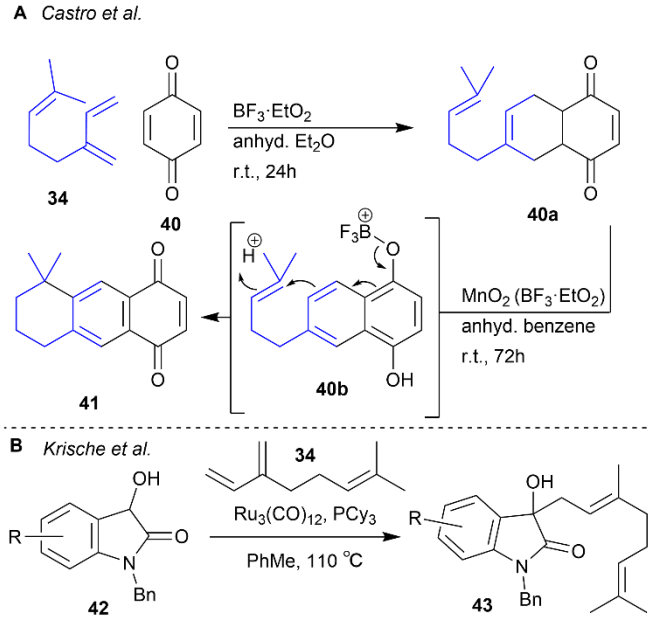


Scheme 9 Various polymerization strategies with myrcene.

single step. This study provided novel C_{13}-ester co-dimers for the flavor and fragrance industries. Moreover, under the same reaction conditions, numerous by-products were also formed through other pathways i.e., dimerization, isomerization, and the Diels-Alder reaction.[99]

Numerous studies have also included variations of the Diels-Alder reaction with the 1,3-diene moiety in **34** and *p*-benzoquinone **40.** For example, Castro *et al*. reported the synthesis of antifungal terpenyl-1,4-naphtoquinones and 1,4-anthracenediones **41**. After the cycloaddition with myrcene, the hydroquinone intermediate **40a** is oxydized again in presence of $BF_3{\cdot}EtO_2$ to obtain a boron enolate **40b** that attacks the double bond of the tail of myrcene (**Error! Reference source not found.**A).[100,101] This can be used for inserting two rings in an enone with one substrate, in two steps.[46]

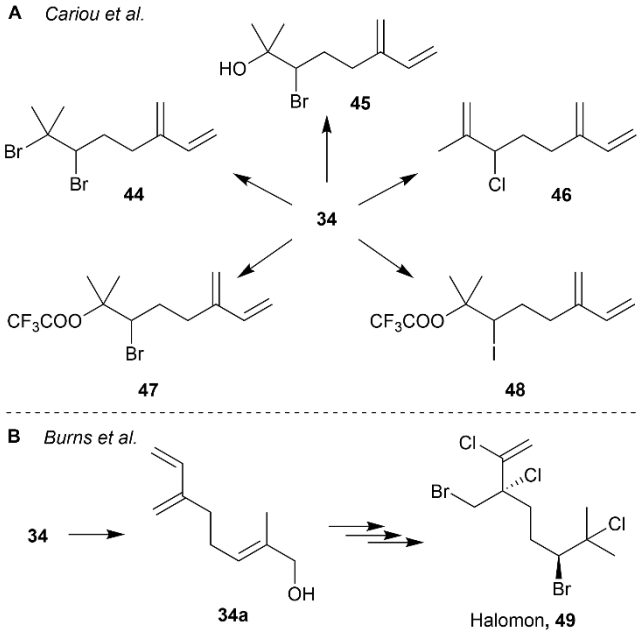
Related to the previously discussed co-dimerization reaction, other studies have utilized the diene of myrcene in slightly different alkylation strategies. For instance, Krische *et al*., developed the regioselective Ru-catalyzed hydrohydroxyalkylation of numerous dienes (e.g., myrcene and isoprene) without the formation of stoichiometric oxidants by the reaction of 3-hydroxy-2-oxindoles **42** with myrcene **34** (**Error! Reference source not found.**B). [102,103] Moreover, an asymmetric cyclopropanation with carbenes has been reported with myrcene (regioselective with 92% ee) and other terpenes ((+)-nopadiene and parthenolide). [104]



Scheme 10 A: Synthesis of antifungal terpenyl-1,4-naphtoquinones. B: Ru-catalyzed hydrohydroxyalkylation by reaction of 3-hydroxy-2-oxindoles with myrcene **34**.

Owing to the large structural diversity of halogenated compounds present in nature, much attention is devoted to the development of halogenation reactions of terpenoid feedstock. In that respect, Cariou *et al*. reported five different iodine(III)-mediated halo-functionalyzation reactions of myrcene **34** and numerous derivatives utilizing different hypervalent iodine(III) reagents and halide salts.[105] They reported conditions for selective dibromination (**44**), bromohydroxylation (**45**), chlorination (**46**), bromo(trifluoro)acetoxylation (**47**) and iodo(trifluoro)acetoxylation (**48**)reactions (Scheme 14A). Due to the increased nucleophilic character of the isopropylidene double bond, it can selectively undergo these transformations without affecting the conjugated double bonds.

Furthermore, regarding halogenation reactions, Hirama *et al*. published the three-step total synthesis of racemic Halomon **49** (47% yield), an antitumor agent containing five halogen atoms on an acyclic carbon chain, which was obtained via halogenations with poor regioselectivity and stereoselectivity that resulted in several by-products.[106] More recently, Burns *et al*. reported the selective and scalable synthesis (3.4 g scale) of



Scheme 11 A: Various halogenation reactions with myrcene 36 B: Selective synthesis of Halomon **49** from **34**

this compound starting from a myrcene-derived compound **34a**. The chlorinations we mostly done with a chiral titanium complex that allowed the selective synthesis, although the yield is still low (15%) and multiple steps are required. (Scheme 14B).[107] Further expanding the examples discussed previously, we refer to Behr and Johnen who published an extensive review on the known chemical transformations and applications of myrcene.[89]

2.4 Ocimene

Another monoterpene and an isomer of myrcene is β-ocimene **51**. This compound is a common structure present in floral scents of a large variety of plant species. It can be obtained through the thermal cracking of α-pinene, but, as it can isomerize to alloocimene **57** under high temperatures, the pure form is obtained through the pyrolysis of linalyl acetate **50**. [89] Furthermore, the central double bond of this terpene results in two stereoisomers, (*Z*) and (*E*), the latter of which is both more abundant and thermally stable. [89,108] The structure and reactivity of this compound are very similar to that of myrcene,

however, since one of the double bonds is located in the internal potion, regioselective transformations are more challenging (**Error! Reference source not found.**).

Similar to the previously discussed terpenes, ocimene **51** has

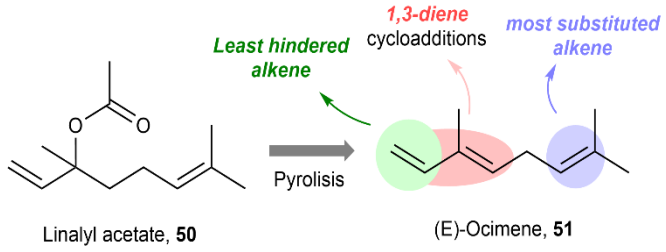
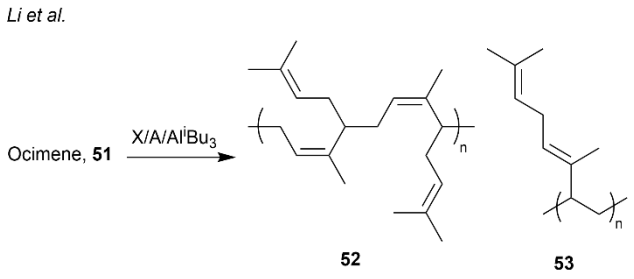


Figure 4. (E)-Ocimene functional groups and most common source

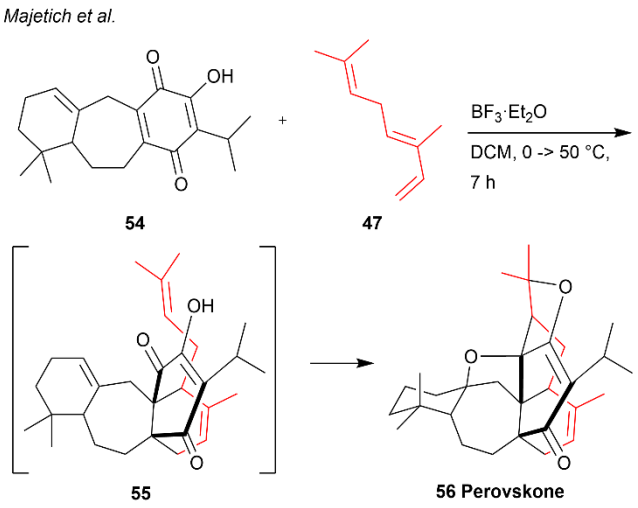
also been a building block in polymerization chemistry. Recently, Li *et al*. was the first one to report the polymerization of ocimene **51** utilizing the rare-metal dialkyl complexes with boranes and Al^iBu_3 (Scheme 15).[109] On one hand, the choice of metal had a crucial role on the regioselectivity; Sc complexes yielded primarly compound **52**, while the others (i.e.: Lu, Y, Dy) resulted in **53**. On the other hand, the employed cyclopentadienyl ligands had a significative change in the stereoselectivity of both polymers, switching between cis and trans.



Scheme 12 Polymerization of ocimene utilizing metal dialkyl complexes (X), and activator (A) and Al^iBu_3.

Another polymerization of ocimene **51** was reported with the same titanium complex described in the previous section for the stereoselective polymerization of myrcene and provided *trans*-1,4-poly(β-ocimene).[93] Additionally, the study showed the possibility for the synthesis of copolymers with styrene in an extended range of compositions including microstructural features.

Aside from the polymer chemistry reported with ocimene **51**, various studies utilized this building block for the synthesis and construction of complex ring systems. In 2011, Majetich *et al*. reported the total synthesis of (+)-perovskone **56** starting from the natural product vanillin and 1,2,4-trimethoxybenzene **54**, respectively.[27] In the synthesis of the pure enantiomer, they developed a key reaction with (*E*)-β-ocimene and $BF_3{\cdot}Et_2O$ that resulted in the formation of four rings, five bonds, and six stereocenters (Scheme 16). The reaction was initiated by a Diels-Alders ring formation after which the Prins reaction took place to form the remaining rings.[31] Similar to this study,



Scheme 13 Synthesis of (±)-perovskone utilizing ocimene **51** as one of the key building blocks.

Majetich *et al.*, Liu *et al*., and Gao *et al*. reported total syntheses of (+)-silvadione A and boli vianine, perovskones, hydrangenone, and hydrangenone B.[110–112] Interestingly, the total synthesis of biolivianine started from verbenone, a monoterpenoid that is discussed later in section 2.14.

2.5 Alloocimene

Another terpene isomer of myrcene and ocimene is alloocimene **57**. Like the other isomers, this compound is found in numerous plant oils (e.g., basil, bay, cannabis, and thyme), however, it is ordinarily obtained from the thermal isomerization of α-pinene.[113] The structure of **57** is certainly similar to myrcene and ocimene, but the key difference is that the three double bonds in this tri-ene are all conjugated, resulting in a distinct reactivity (Figure 5).

Multiple studies have reported polymerizations of

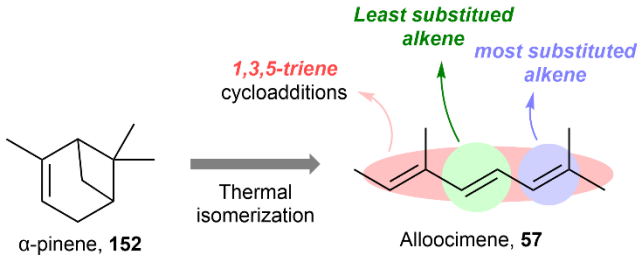
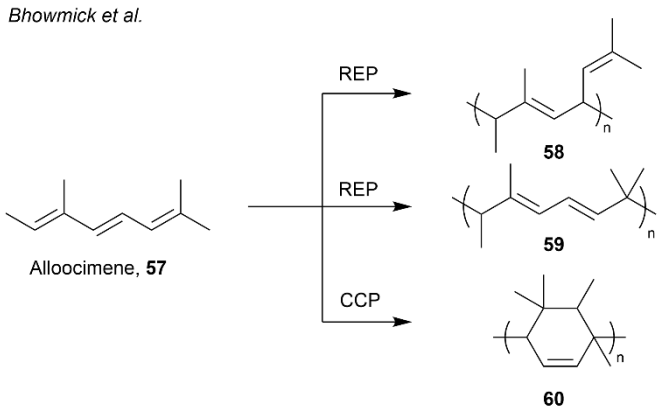


Figure 5. Alloocimene functional groups and source

alloocimene **57** by various methods. In this context, Marvel *et al*. described the first cationic homo-polymerizations of this terpene to yield amorphous polymers with high T_g values.[114,115] More recently, Puskas *et al*. reported the living carbocationic copolymerization of isobutylene with alloocimene using an $AlCl_3/H_2O$ initiating system, resulting in the formation of high molecular weight diblock polymers with thermoplastic properties.[116] Later, the same group also reported the synthesis of triblock and tetrablock copolymers based on the same two monomers using this two-phase living carbocationic system.[117]

Finally, Bhowmick *et al*. published a green synthesis of poly(allo-ocimene) **58**-**60** by means of a redox emulsion polymerization (**Error! Reference source not found.**).[118]

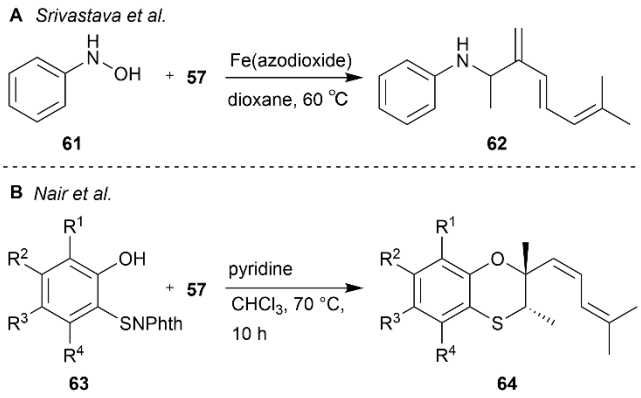
Aside from the polymerization reactions described above,



Scheme 14 Products of alloocimene polymerization by various methods: redox emulsion polymerizaton (REP), cationic cyclo-polymerization (CCP).

allo-ocimene **57** has also been used in other (in)organic reactions. One of the more recent examples, published by Srivastava *et al*. in 2014, reported a novel iron-catalyzed C-H amination reaction that employed the use of arylhydroxylamines **61** (Scheme 18A).[119] This was the first method capable of selective allylic amination on substituted 1,3-dienes and can be very useful for the functionalization of other known bio-derived dienes such as **62**. The selectivity of the reaction originates from the preference of one of the dienes to form a η^2 complex with Fe, which leaves the other alkene available for amination. Tamaru *et al*. reported a different example which involved the stereo- and regioselective homoallylation of aldehydes and ketones with 1,3-dienes utilizing $Ni(acac)_2$ and triethylborane/diethylzinc.[120] The latter are employed as reducing agents that deliver hydrides to the diene substrate resulting in a homo-allyl anion, which then react with these carbonyl-containing moieties. Next to **57,** this reaction also tolerates other terpenes with conjugated double bonds, such as isoprene and myrcene.

Similar to previously mentioned studies and owing to the conjugated unsaturations in alloocimene **57**, numerous studies



Scheme 15 A: Selective Fe-catalyzed allylic amination reaction with allocimene. B: General depiction of the cycloaddition of alloocimene to form 1,4-oxathiane rings.

investigated cycloaddition reactions with this terpene. For example, Plemenkov *et al*., published a Diels-Alder reaction of allo-omicene with maleic and citraconic anhydrides to afford novel terpenoids.[121] A different type of cycloaddition was reported by Nair *et al*. where they reacted *ortho*-thioquinones **63** with alloocimene **57** to afford 1,4-oxathiane rings, such as **64** (Scheme **18**B).[122]

2.6 Geraniol

Geraniol **65** is a linear monoterpene (two isoprene units) alcohol (terpenoid) which can be found in oils from various fragrant plants (e.g., lemongrass or rose), however, it is only produced in limited amounts via plant extraction resulting in a hampered market growth.[123] Nowadays, it can be produced through biosynthesis from yeast and bacterial species that show geraniol synthase expression. In that respect, the highest reported production of geraniol **65** was published in 2017 by means of *Saccharomyces cerevisiae*, which also expresses arsenyl diphosphate synthase, and can provide geraniol **65** in 1.68 g/L.[124] Furthermore, geraniol **65** has been shown to contain numerous pharmacological attributes; anti-microbial, antioxidant, antitumor, and anti-inflammatory activity.[125] With regard to the structure, geraniol contains two internal double bonds, one of which is part of an allylic alcohol functionality (Figure 6).

Like many others, this acyclic terpene has been utilized for the synthesis of polymers. For example, Worzakowska *et al.*

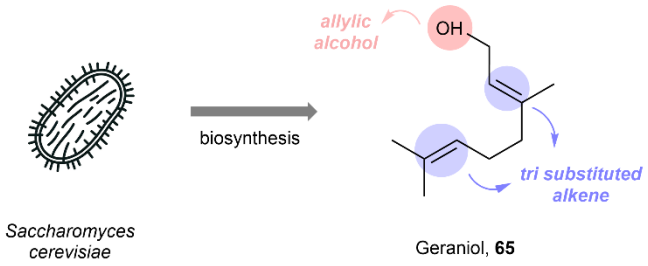
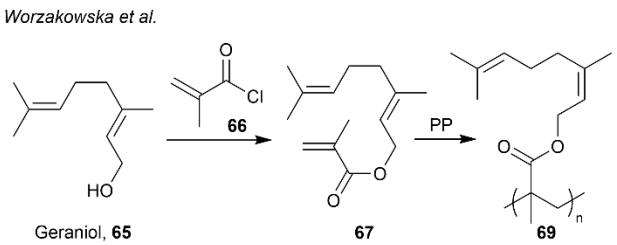
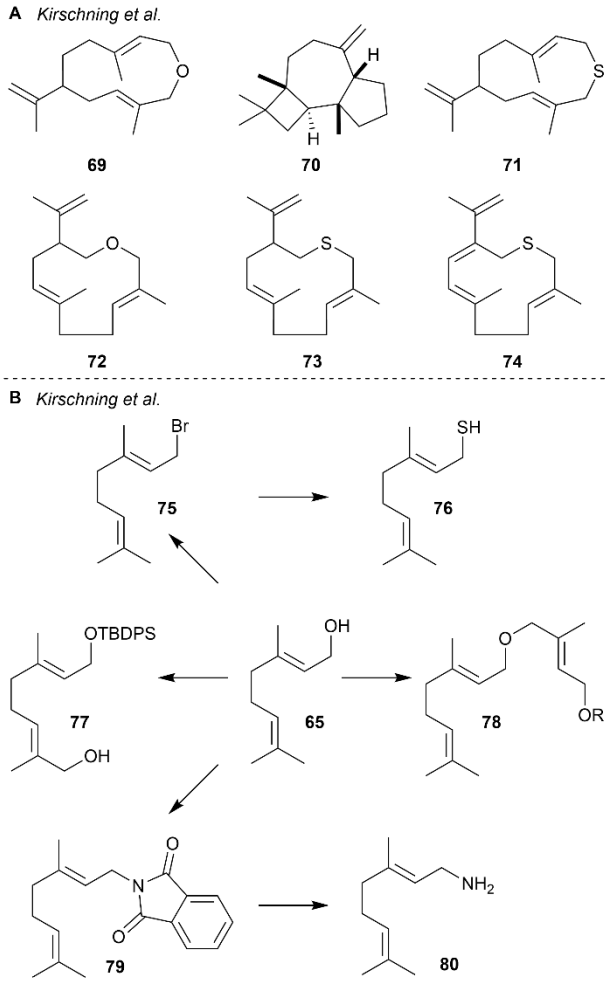


Figure 6. Geraniol's functional groups and source

published the synthesis of branched terpene methacrylate polymers **68** by means of photo-induced polymerization (Scheme 19).[126] Therein, geraniol **65** and an acid chloride **66** were reacted under basic conditions to furnish geranyl methacrylate monomers (among others).[127,128] These could sequentially be polymerized utilizing UV light, thus furnishing novel structures that showed resistance to basic, acidic and thermal environments. [126]



Scheme 16 Light-driven synthesis of branched terpene methacrylate polymers from geraniol through geranyl methacrylate monomers.



Scheme 17 A: Six non-natural macrocyclic terpenes synthesized by biotransformations with terpene cyclases. B: Various reactions performed with geraniol leading to a variety of products. Reactions include: Appel reaction, thiolation, substitution, amine installation, and diol formation.

Other studies have also devoted their attention to the transformation of geraniol in order to obtain further useful building blocks. The synthesis of six non-natural macrocyclic terpenes **69-74** was reported by Kirschning *et al*. including multiple biotransformation reactions catalysed by numerous terpene cyclases (Scheme 20A).[32] They employed geraniol in the synthesis of several farnesyl pyrophosphate derivatives that would subsequently be utilized as substrates for the enzymatic transformations. The various biomimetic reactions performed with geraniol in their article included; the Appel reaction (**75**) and subsequent thiolation (**76**), diol formation (**77**), nucleophilic substitution by the alcohol moiety (**78**) and amine installation (**80**) (Scheme 20B). Additional transformations for geraniol reported by other groups covered: oxidation of the alcohol to the aldehyde[129] and carboxylic acid[130], cyclopropanation[131], and epoxide formation.[132] Utilizing geranyl-epoxides, Hall *et al*. reported the synthesis of vicinal diols by means of the biotransformation with epoxide hydrolases.[133]

2.7 Limonene

Limonene **81** is one of the more abundant and useful bio-derived monoterpenes known. The main reasons are that this cyclic monoterpene is present in most plants and that it can be extr acted from citrus fruits and waste products thereof (e.g. oran ge peels from the juice industry).[134] Moreover, it comprises two separate functionalizable double bonds in its structure.[40] Both the (*R*) and (*S*), enantiomers of limonene, can be extracted from different sources in the environment, but as the former ((*R)*-limonene) is more abundant, most studies have employed the use of that enantiomer (**Error! Reference source not found.**).[40,135]

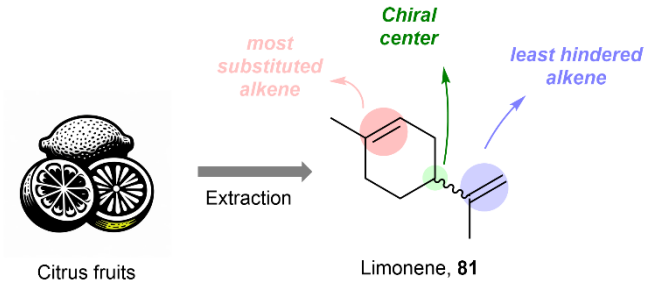
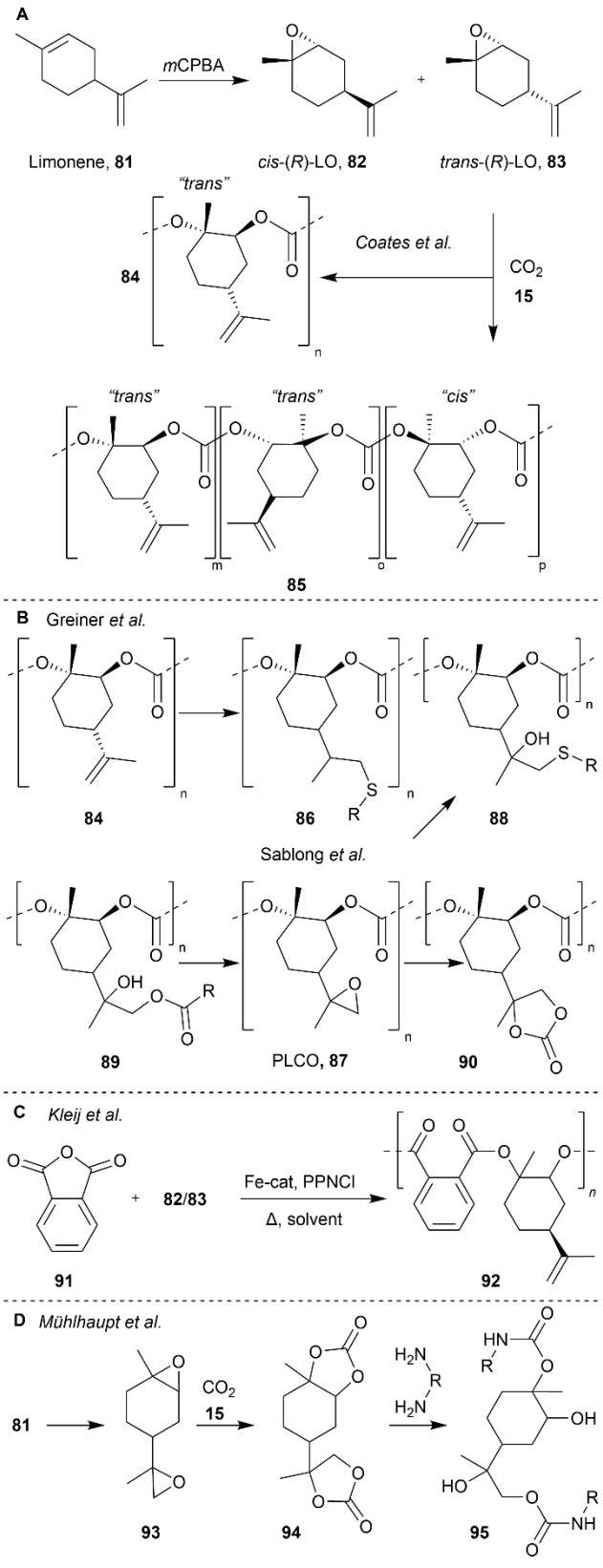


Figure 7. Limonene's functional groups and sources

Many research groups have devoted their energy to the development of polymers based on **81**. A known method for the synthesis of polycarbonates is through ring opening polymerization (ROP) of the respective epoxides. Accordingly, several studies have reported the selective oxidation of **81** to limonene oxide (LO, **82**-**83**).[136,137] Bégué *et al.* attributed the regioselectivity of their oxidation reaction to the difference in activation and substitution pattern of the double bonds. To date, two separate methods established catalytic conditions for the polymerization of this compound with CO_2 providing poly(limonene carbonate) (PLC) (**Error! Reference source not found.**A). The first was reported by Coates *et al*. and involved a β-diiminate zinc complex capable of stereo-selectively affording PLC **84** with *trans-(R)*-LO **83**.[138] Interestingly, the reaction failed when utilizing the *cis*-diastereomer. Later Greiner *et al*. reported improvements on these conditions (**Error! Reference source not found.**B).[139] The second method was reported by Kleij *et al*. who employed a nucleophilic co-catalyst (PPN-halides) alongside an aluminum catalyst.[140] In contrast to the work of Coates *et al*. [138] , these conditions could copolymerize both *cis*- and the *trans-(R)*-LO furnishing polymers with high stereoregularity. Building on this work, the same catalyst was employed for the coplymerization of LO/cyclohexane oxide/CO_2 polymers.[141] Another report utilized these same monomers along with the catalyst reported by Coates *et al.* for the synthesis of block copolymers.[142]

Aside from the PLCs, there are also reports of limonene-based polyesters and polyurethanes. With respect to the former, Stockman *et al*. reported the synthesis of hydroxyl acids and limonene-based diols for the creation of numerous polyesters with high number average molecular weights (M_n).[143] Another study by Kleij *et al*. described the ring opening copolymerization of several terpene-based epoxides, including LO, with phthalic anhydride (PA, **91**) (**Error! Reference source**

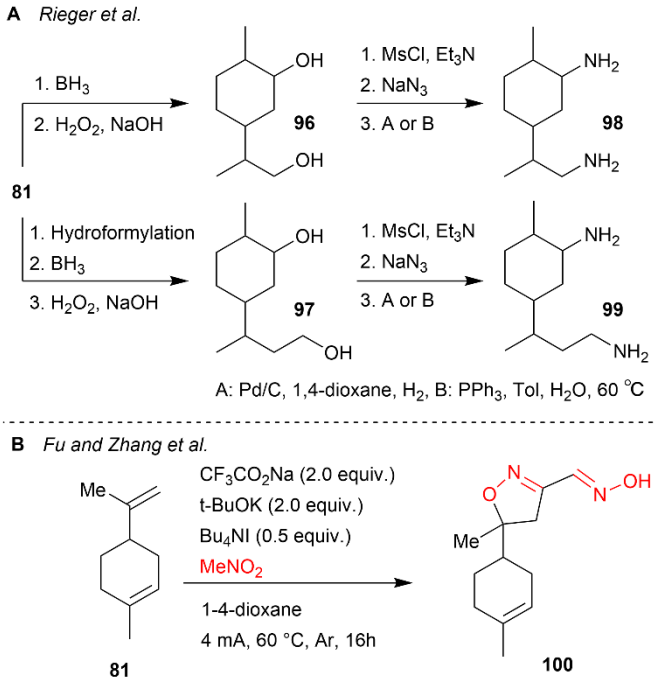


Scheme 18 A: Epoxidation of limonene and subsequent copolymerization with CO_2 affording poly(limonene carbonate). B: Examples of functionalization reactions of limone-carbonate polymers. C: Copolymerization of limonene oxide and phthalic anhydride. D: Synthesis of poly-hydroxyurethanes through limonene dicarbonate.

not found.C) and naphthalic anhydride (NA).[144] In contrast, Mühlhaupt *et al*. reported the synthesis of limonene-based non-isocyanate poly-hydroxyurethanes utilizing limonene dicarbonate (LDC, **93**).[145] This synthesis involved the initial transformation of LDO to LDC utilizing CO_2 and tetrabutyl ammonium chloride, and the sequential polymerization of LDC with an alkyl diamine (**Error! Reference source not found.**D). Another example of the synthesis of such polymers is that of Firdaus and Meier, who reported the polycondensation of diols and limonene-based dicarbamate monomers to furnish poly(hydroxyurethanes).[146] Therein, they also reported the synthesis of limonene-based polyamides.

An interesting transformation of limonene **81** that Rieger *et al*. reported can be employed for the installation of alcohols and amines at unsaturated bonds in terpenes. They functionalized **81** to afford limonene-CHO by means of a Rh-catalyzed hydroformylation.[134] Subsequently, obtained the diols **96,97** of this product and limonene through hydro-boration-oxidation. Moreover, these diols could be converted to their respective diamines **98-99** by two similar fully optimized routes that both proceed through an azide moiety (Scheme 22 A). Moreover, a recent study discussed the catalytic ability of dehydroaromatization of terpenes affording aromatic hydrocarbons where the employed palladium-based catalyst was highly active, selective, and recyclable.[147]

Recently, Fu and Zhang *et al*. reported the use of limonene **81** for the (*E*)-selective synthesis of isoxazoline aldoximes like **100**. The addition takes place selectively on the exocyclic double bond of limonene The novelty of this reaction is the use of electrochemistry for the activation of nitromethane (Scheme 22B).[148]



Scheme 19 A: Synthetic route for the conversion of limonene to its respective diol and diamines. B: (E)-selective synthesi s of isoxazoline aldoximes

2.8 Carvone

The cyclic monoterpene carvone **101** is a bio-derived product that can be found naturally in spearmint (≥51% of the oil), dill (40%-60% of the seed oil) and caraway (50%-70% of the oil).[149,1 50] Therefore, it can be produced by simple extraction of these plant oils, but also by chemical synthesis and biotechnological synthesis. In 2006, Carvalho *et al*. published a review on the various known methods for the production of carvone **101** along with its diverse applications as; flavor and fragrance, antimicrobial agent, biochemical environmental indicator, potato sprouting inhibitor, and as building block.[150] The structure of carvone **101** is similar to limonene **81**. The only difference is the enone moiety in the ring, which facilitates the access of all positions on the cyclohexane ring. [150] **(Error! Reference source not found.**).

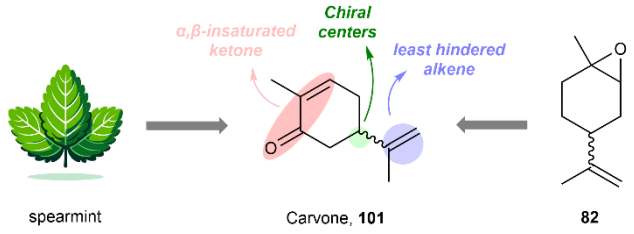
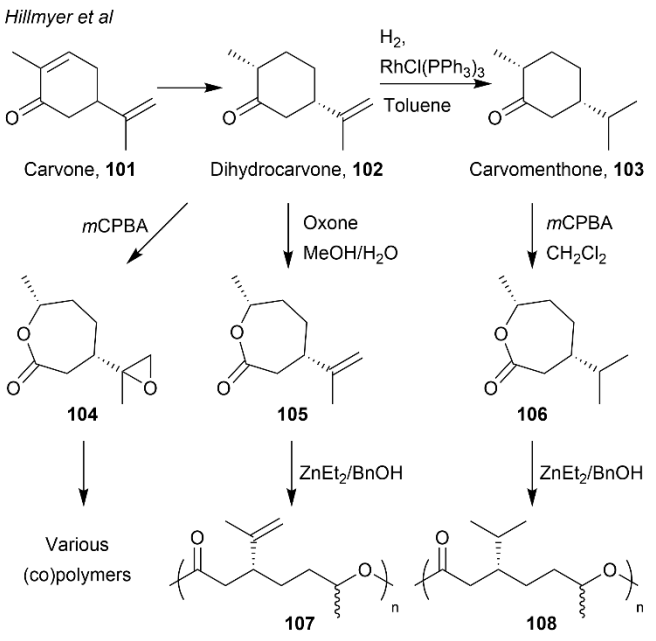
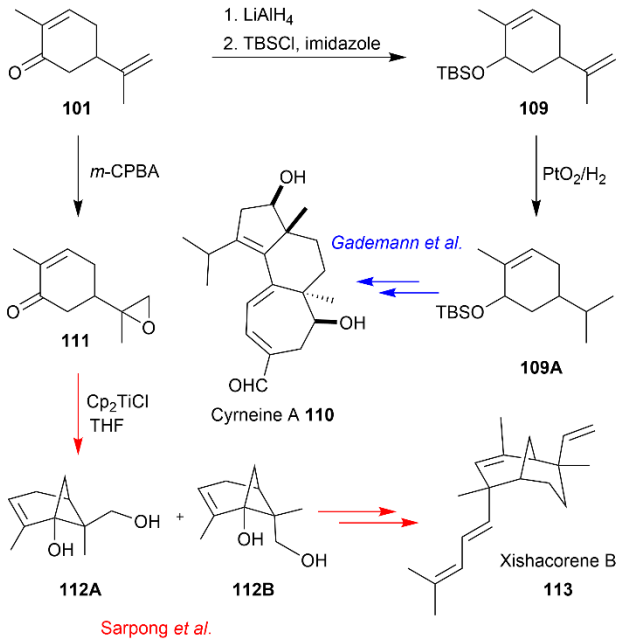


Figure 8. Carvone's functional groups and sources

Multiple reports utilized carvone **101** as a precursor for other terpene monomers that could subsequently be employed for the synthesis of polymers. A little over a decade ago, Hillmyer *et al.* explained that the hydrogenation of carvone **101** provides dihydrocarvone (DC) **102**.[151] This compound can sequentially be oxidized to an epoxylactone, which is in turn used in ROPs as multifunctional cross-linker and monomer (Scheme 23). Two years later, the same group reported the synthesis of carvomenthide **106** and dihydrocarvide **105** starting from carvomenthone **102** and **103**, respectively, by means of Baeyer-Villiger oxidation reactions. [149] Subsequently, they performed ROPs, utilizing diethyl zinc and benzyl alcohol, to afford aliphatic polyesters with low T_g values (Scheme 23). These conditions were also employed for the synthesis of copolymers, which were subsequently functionalized at the alkene side-groups to form epoxides or employed for radical-induced crosslinking. [149] With regards to the latter, they were able to attain cross-linked gels with the use of dithiols. Finally, the authors reported the copolymerization of dihydrocarvide and ε-caprolactone **20** to afford materials with cross-linked networks that showed good shape-memory properties (**107** and **108**).[58]



Scheme 21 Synthesis route of the conversion of carvone to derived terpenoids and their subsequent polymerization by means of a Baeyer-Villiger oxidation and sequential ROP.

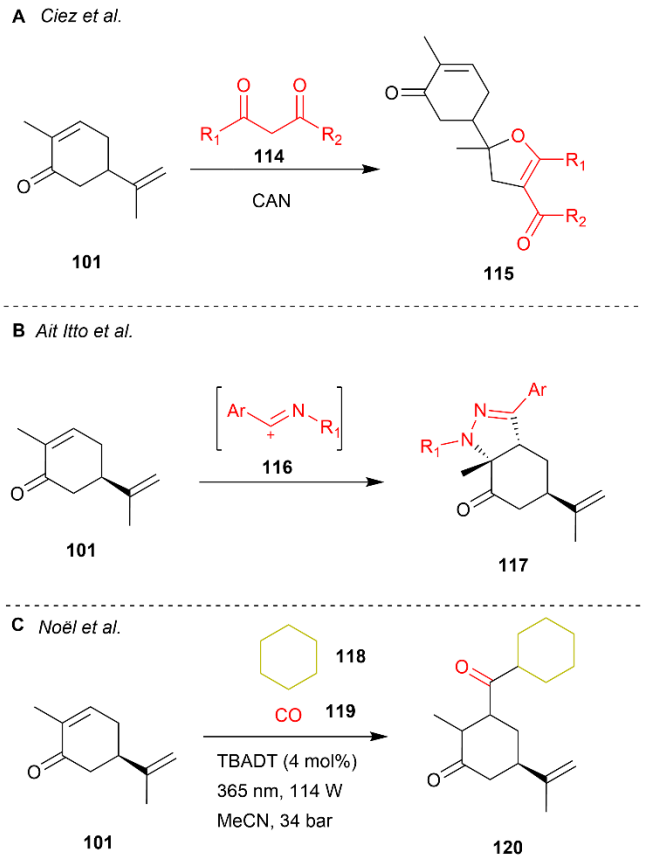


Scheme 20 Various chemical conversions from carvone.

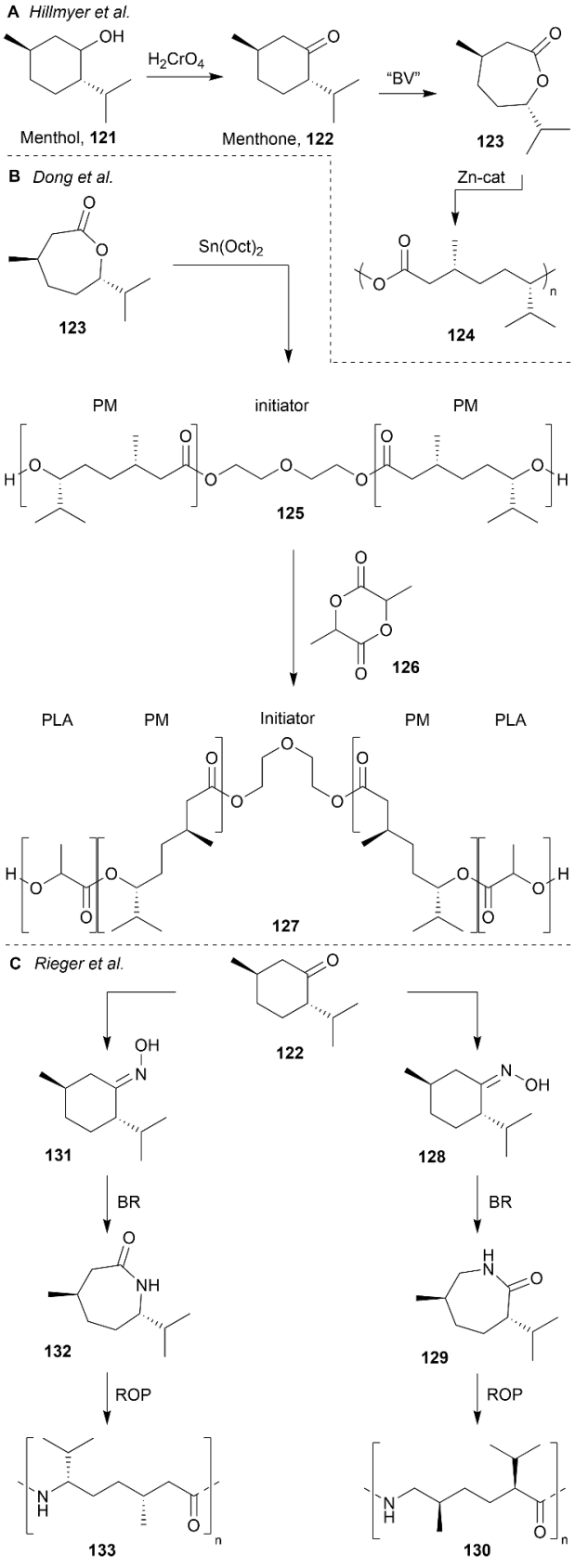
Besides polymerization reactions, many studies reported the use of carvone **101** a s starting material for the synthesis of natural products.[152] In that respect, Gademann *et al*. reported the total synthesis of cyrneine A **110** where the first steps involved reduction of the carbonyl, protection of the resulting alcohol and hydrogenation of the exocyclic double bond. This last step shows that it is possible to selectively reduce by means of using PtO_2. The remaining route included three reductions and a carbene rearrangement (Scheme 24).[153] In 2006, Bermejo *et al*. developed a Ti(III)-promoted radical cyclization for the conversion of the epoxyenone of carvone to bridged bicyclic diols.[154] As the authors demonstrated, these products are useful for the synthesis of numerous diols. Further building on this work, Sarpong *et al*. reported two separate studies involving TM-mediated C-C bond cleavage, and the synthesis of natural product-like scaffolds utilizing a Pd-catalyzed C-C cross-coupling from **111**, respectively.[155,156] The same group later applied the latter concept to the total synthesis of xishacorene B **113** (Scheme 24).[157]

The group Ciez *et al*. reported an additional chemical transformation (**Error! Reference source not found.**A) wherein they utilized ceric ammonium nitrate (CAN) for various oxidative free radical cycloadditions of C-H acids with numerous terpenes and terpene like structures (e.g. α-pinene, norbornene, camphene, nopol, and carvone).[158] Two of the reacting substrates, α-pinene and nopol, reacted stereoselectively when reactions took place at their endocyclic double bonds. Reactions with the other terpenes afforded a mixture of enantiomers.

Carvone **101** has on multiple occasions been employed for the development of biologically active compounds. A report of Dong *et al*. focuses on the synthesis of carvone and limonene derivatives with antiproliferative effect in prostate cancer cells.[154] Therein, they functionalized the isopropylene group in carvone **101** with various nucleophiles to generate a small library. In other work, by Lochyński *et al*., they synthesized numerous monoterpenoids containing nitrogen functionalities with different terpene starting materials (e.g. menthone, fenchone, pulegone, β-cyclocitral, **102**, and carvone **101**).[159] Finally, Ait Itto *et al*. synthesized a series of isoxazoles **116** and pyrazoles **117** from carvone for the study towards cytotoxicity against various cancer cell lines.[33] They reacted nitrile oxides and nitrilimines with carvone resulting in a 1,3-dipolar cycloaddition with high peri- and regioselectivity (**Error! Reference source not found.**B). The selectivity therein was



Scheme 22 A. Oxidative radical cyclization of C-H acids with carvone. B. Synthesis of isoxazoles and pyrazoles from **116** by 1,3-dipolar cycloaddition. C. HAT-mediated carbonylation with CO in flow.



Scheme 26. A. Oxidation of carveol affording various epoxides. B. Regioselective ring-opening and O-acylation / sulfonylation of carveol. C. Beckmann rearrangement of the oxime derivatives of **122.**

speculated to be the result of the fundamental difference in reactivity of the two double bonds, one being endocyclic, trisubstituted and conjugated, and the other di-substituted, exocyclic and does not have an electron withdrawing group. Finally, Noël *et al*. reported the carbonylation of carvone **101** via a photocatalytic and HAT-mediated activation of carbon monoxide **119** to obtain carbonyl **120** (**Error! Reference source not found.**C).[160]

2.9 Menthol

Menthol **121** is well known for its use in the flavor and fragrance industry. Currently, the worldwide production is around 34 000 metric tons per year, with the share of synthetic menthol now being about 60%. It can be found in several members of the mint p lant family *Labiatae*, particularly in members of the *Mentha* family (e.g. spearmint, corn mint, and peppermint).[157] Menthol is a monocyclic terpenoid with three chiral centers on its cyclohexane ring, resulting in numerous isomers. Of the available isomers, *L*-menthol (or (*1R,2S,5R*)-menthol) is the most abundant in plant-based sources. Moreover, this is also the isomer responsible for the peppermint fragrance and flavor and, as opposed to the other isomers, it generates a cooling effect when applied to the skin.[157] As the whole structure of menthol **121** is saturated, the only moiety that can be utilized for its reactivity is the secondary alcohol. The chirality of the structure, however, can be exploited for stereoselective synthesis (**Error! Reference source not found.**).

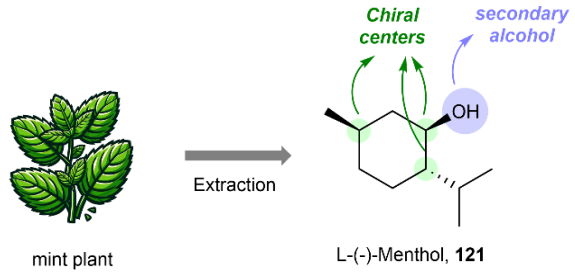
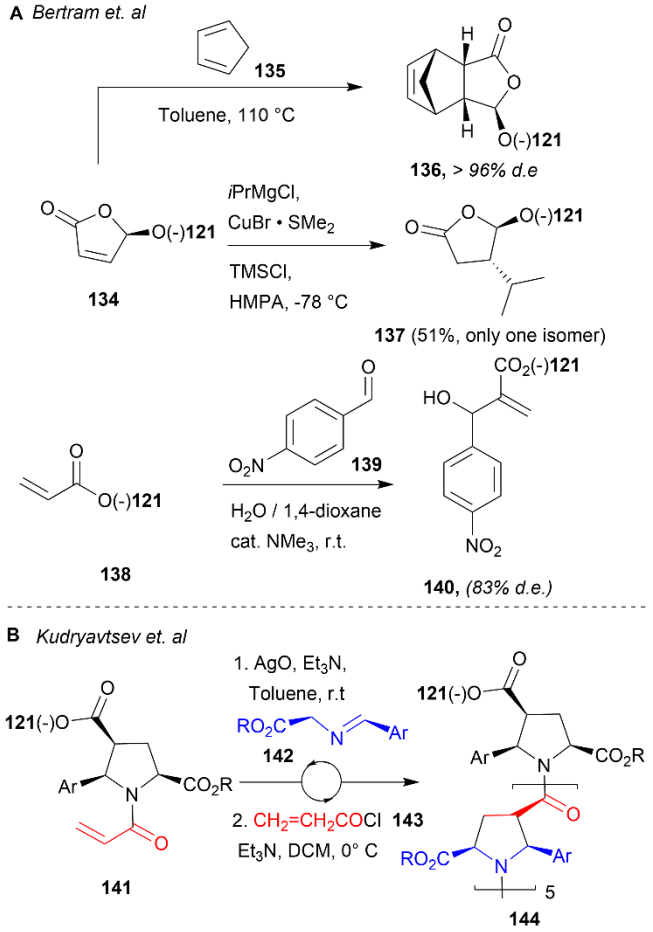


Figure 9. Menthol's functional group and source

There have been various reports in polymer synthesis that involve the use of *L*-menthol **121** as starting material. For example, Hillmyer *et al*. reported the oxidation of **121** to (–)-menthone **122**, an intermediate well suited for a subsequent Baeyer-Villiger oxidation to provide menthide **123** (Scheme 26A).[161] This substituted caprolactone **123** is an important building block for polyesters and polyamides and the oxidation is a replacement for the fossil based analogue.

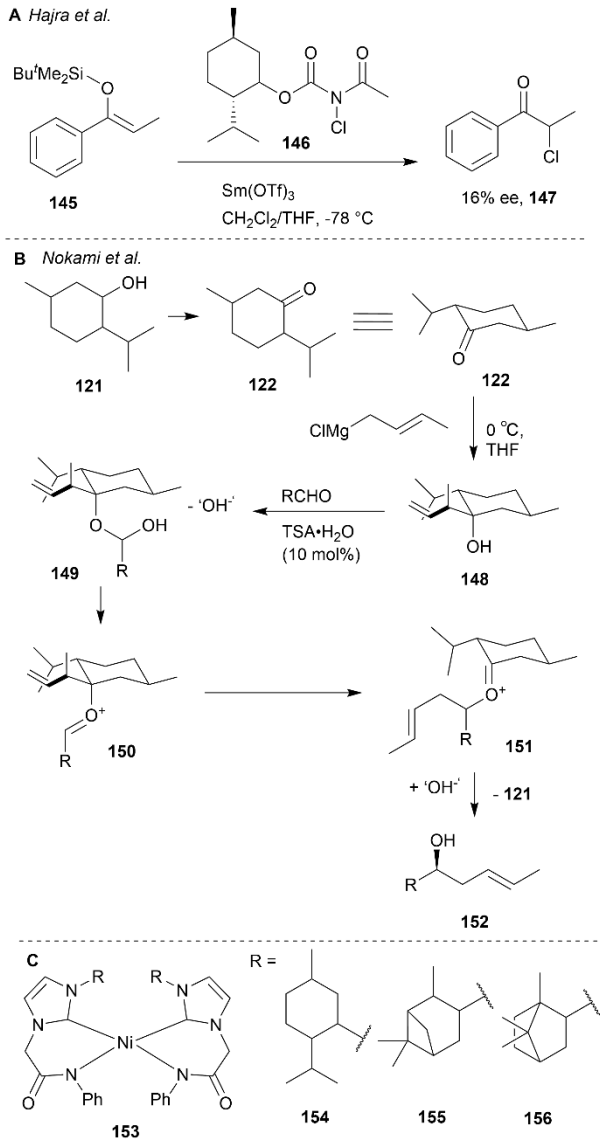
Similar to the discussed studies in the previous sections, **123** was subjected to a ROP reaction, but now by means of a zinc-alkoxide catalyst to afford aliphatic poly(menthide) (PM) **124**.These polymers were later used by Dong *et al.* in the synthesis of triblock copolymers in order to attain novel materials to be employed for various uses.[162] Along with PM, the initial block copolymer comprised poly(lactide) (PLA) and was of the ABA-type to form PLA-PM-PLA **127** (Scheme 26B). Other studies later reported improvements on this synthesis; the switch to a greener oxidant (i.e. oxone) [162] , a more facile purification by crystallization, and a one-pot synthesis with tin octanoate as catalyst for both reactions. [158,162] Finally, researchers prepared another triblock copolymer with poly(α-methylene-γ-butyrolactone) (PMBL) as opposed to PLA.[159] Similar to the studies described above, *L*-menthol **121** was also converted to lactams, which were subsequently converted to novel polyamides through ROP. The group of Rieger *et al*. were the first to publish the synthesis of two types of polyamides-6 (**130,133**) by means of the anionic or acid catalyzed ROP of the two caprolactam precursors **129** and **132**. They attained these starting materials through a Beckmann rearrangement of the oxime derivatives of **122** (Scheme 26C).[163] The resulting lactams **129** and **132** were separated by column chromatography. The chiral information in the chain can result in



Scheme 27. A: Numerous stereoselective synthesis with menthol as a chiral organocatalyst. B: Stereoselective synthesis of β-proline hexamers

stereocomplexes in the polymers to provide interesting properties. As mentioned above, the chiral nature of *L*-menthol **121** can be exploited for stereoselective synthesis. Numerous groups have utilized this concept and employed *L*-menthol **121** as chiral auxiliary.[164] Like the use of chiral menthyloxy furanone **134** as a dienophile for Diels–Alder reactions (**136**) with cyclopentadiene (**135**), or for Michael additions to obtain **137** (Scheme 27A). It has also been used in Baylis-Hillman reactions, like the addition of p-nitrobenzaldehyde **139** to menthyl acrylate **138** in aqueous dioxane gave the allylic alcohol **140**. More examples can be found in the

review by Bertram *et al.*[164] Kazmaier *et al*. had previously reported a similar approach for the synthesis of pretubulysin, a biosynthetic precursor of tubulysin.[165] The group of Kudryavtsev *et al*. reported another example of the use of *L*-menthol as a chiral auxiliary.[166] They were capable of stereoselective synthesis of β-proline hexamers **144** through asymmetric cycloadditive oligomerization (Scheme 27B). In addition to these syntheses where **121** is employed as chiral auxiliary, other studies have utilized the chirality of this terpenoid for the creation of selective reagents. For example, Hajra *et al*. developed *N*-chloroimidodicarbonate (**146**) capable of enantioselective chlorination of silyl enol ethers (from **145** to **147**) , although only with a 16% ee (**Error! Reference source not found.**A).[167] Furthermore, Nokami *et al*. developed allyl transfer reactions for the asymmetric crotonylation of aldehydes (**Error! Reference source not found.**B).[34] Therein, the both enantiomers of the chiral crotyl-donors were synthesized by the Grignard reaction with (+)- or (-)-**121**, which were obtained from the oxidation of **121**.



Scheme 23. A: enantioselective chlorination of silyl enol ethers. B: asymmetric crotonylation of aldehydes. C. Ni-based bifunctional catalysts with terpene-based ligands

This process involved reagents that were both easy to handle and environmentally friendly. The group of Willis *et al*. adopted this approach in their stereoselective synthesis of the tetrahydropyran core of polycarvernoside A.[168] Another example, reported by Ghosh *et al*., describes an asymmetric Michael addition reaction under base-free conditions.[169] To that end, they applied a nickel-based bifunctional catalyst **153** with N-heterocyclic carbene (NHC) ligands obtained from menthol **154**, pinene **155** and camphor **156** (Scheme 28C). Although all of these complexes were successful in catalyzing the reaction, only **154** proved capable of significant chiral induction (75% *ee*).

2.10 Carveol

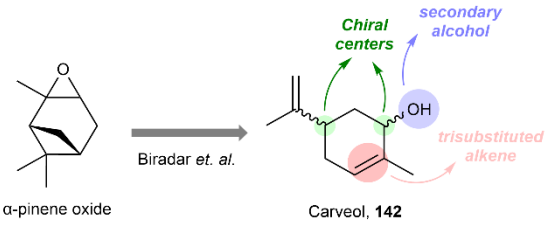
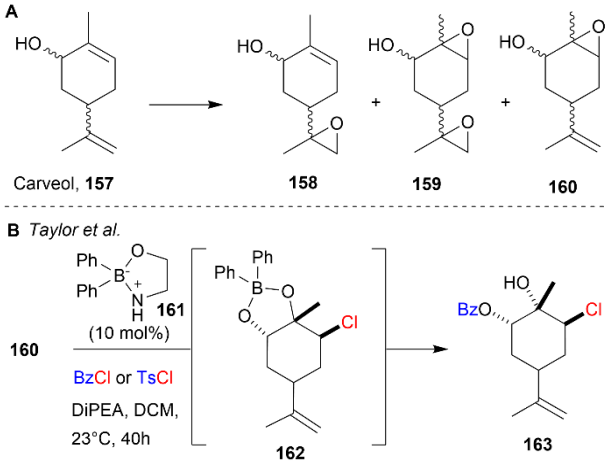


Figure 10. Carveol functional groups and source

A well-known monoterpenoid that is closely related to carvone **101** is carveol **157**. This compound has shown to contain pharmacologically beneficial properties. Moreover, *trans*-carveol is known to exert a chemo-preventive effect on carcinogenesis in various tumor rodent models. [170,171] It is also highly important in the chemical industry as orange essence food, perfumery, and flavor adduct. Over the years the synthesis of **157** has been performed in numerous ways from different starting materials (e.g. limonene, α-pinene).[170–175] One of the more recent examples was reported by Biradar *et al*., who developed the synthesis of a novel phosphonate functionalized Brønsted acid for the catalysis of the isomerization of α-pinene oxide to *trans*-carveol.[170] The same group reported a more selective sulfonic acid functionalized carbon catalyst for this synthesis.[176] With regards to the structure of carveol **157** it is very similar to carvone **101,** with the exception of the alcohol moiety. Owing to this difference, the endocyclic double bond is not



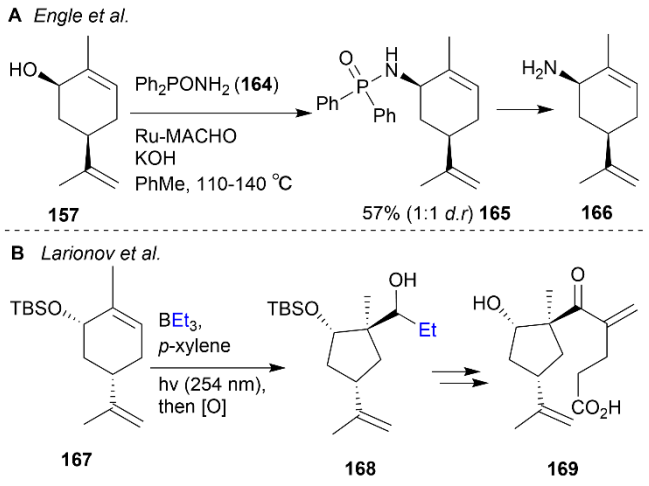
Scheme 24 A. Oxidation of carveol affording various epoxides. B. Regioselective ring-opening and O-acylation / sulfonylation of carveol.

electronpoor. Hence different strategies have to be applied to differentiate between the two double bonds. Like *L*-menthol **121**, the chiral information of carveol can also be utilized as a chiral auxiliary. However, *L*-menthol **121** is often favored as a chiral auxiliary due to the presence of a large isopropyl group adjacent to the hydroxyl group and the absence of reactive double bonds (Figure 10).

Similar to what was described previously for other terpenes, carveol **157** can also be oxidized to the corresponding carveol (di)oxide **158-160** (**Error! Reference source not found.**A), with poor selectivity.[177,178] To our knowledge, there has not been a report on the polymerization of this compound similar to those described for the previous terpenes. Interestingly, Taylor *et al*. reported the chloroacylation/chlorosulfoxination of 2,3-epoxy alcohols using a boronic acid derived catalyst **161** (**Error! Reference source not found.**B).[179] The chlorohydrin **163** can be used to introduce the epoxide only on the endocyclic double bond.

An additional modification of carveol is the installment of a phosphinic (thio)amide group at the position of the alcohol, reported by Engle *et al.* .[180] This method employs Ru-MACHO, a transfer hydrogenation catalyst that dehydrogenates the alcohol to the carbonyl and, after attack from the phosphinic amide, subsequently hydrogenates the formed imine. Phosphinic amides **165** have found numerous applications in materials, agrochemicals, medicines, etc. [180] Moreover, they are ideal intermediates for the synthesis of amines by cleaving the N-P bond. In the case of carveol, the primary amine **166** could be a useful moiety for further synthesis (**Error! Reference source not found.**A).

In addition to the reactions described above, there have been various reports that involve carveol **157** as intermediate and/or starting point for the synthesis of natural products. For example, Bermejo *et al*. reported the synthesis of (+)-ampullicin and (+)-isoampullicin[181] while Lee *et al*. published alkylidene carbene insertions which were utilized for the synthesis of platansimycin.[182] Next to these interesting reports, carveol **157** was used by Zografos *et al*. to synthesize germacrane and guaiane sesquiterpenes.[183] Finally, Larionov *et al*. reported the photoinduced carboborative ring contraction of a variety of terpenoids (**Error! Reference source not found.**B).[35] Initial attack of the alkene on boron results in a tertiary carbocation, which subsequently induces the rearrangement that results in ring contraction, alkylation and oxidation with air. The group successively applied this method to the synthesis of artalbic acid **169** starting from TBS-protected carveol **167**.



Scheme 25 A. Phosphinic amide instalment on carveol and subsequent N-P bond cleavage resulting in the primary amine. B. Synthesis of artalbic acid **169** from carveol through a key photoinduced carboborative ring contraction.

2.11.1 α-Pinene

α-Pinene **170** is found as a major component (45-97%) in turpentine oil. The latter is acquired from conifers in around 350.000 tons per year. It is commonly used for the production of flavors, pine-oil, resins, and fragrances and contains various other terpenes: β-pinene **171** (0.5-28%), limonene **81**, camphene **172** and 3-carene **173** (**Error! Reference source not found.**A).[184] α-Pinene **170** contains a CH_2-bridged six-membered ring with a trisubstituted C-C double bond and it has a four-membered ring. The alkene is the main reactive functional group in the structure and because of the bridged system, **170** has shown reactivity resembling allyl species. One can also fragment the four-membered ring for various chemical conversions (**Error! Reference source not found.**).

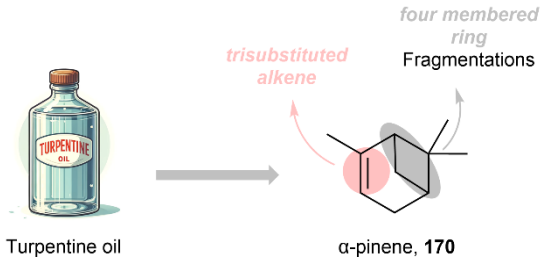


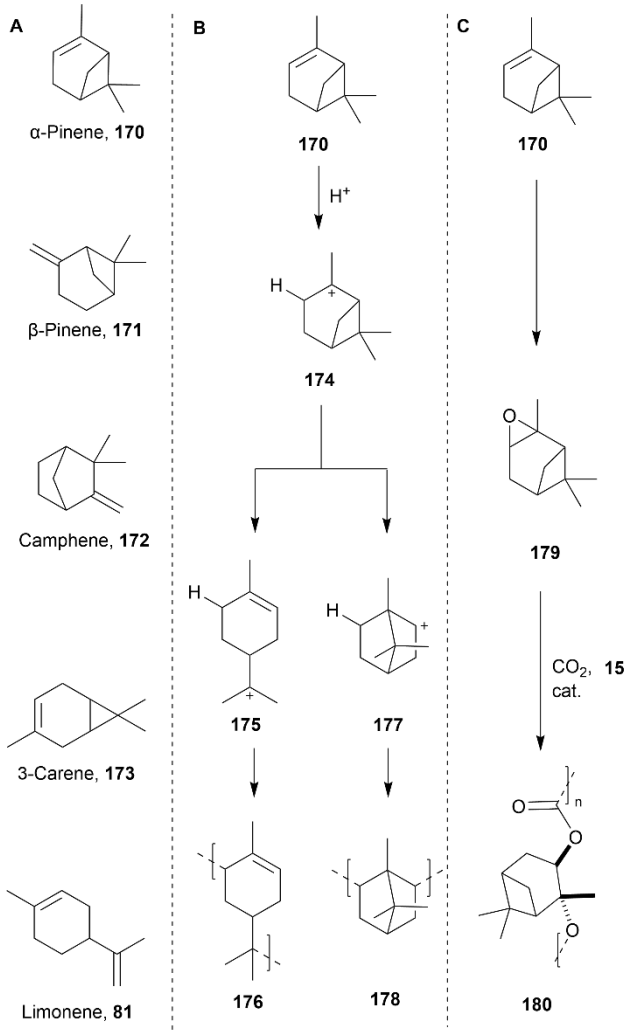
Figure 11. α-Pinene functional groups and source

Although the large steric hindrance caused by the substituents makes the polymerization of this compound into high weight polymers difficult. However, effective polymerization can be achieved by utilization of strong Lewis acids BF_3 or $AlCl_3$.[184,185] Interesting is the approach by Yu *et al.* who further improved the quality of such polymerizations utilizing ionic liquids (Scheme 31B).[186]

The scope of applications of α-pinene is greatly expanded by its transformation into more easily polymeriz able structures. Similar to what was discussed for limonene, it can be epoxidized to form α- pinene oxide **179** (APO)), which has a strong structural resemblance to cyclohexene oxide. Cyclic epoxides such as these are useful for the synthesis of polycarbonates by reaction with CO_2.[187] To our knowledge, there has thus far only been one report that involved a ROP reaction with α-pinene oxide and CO_2 for the synthesis of poly-(α-pinene carbonate) **180** (**Error! Reference source not found.**C). Therein, Shan *et al*. utilized a binary catalyst that included a Cr^{III}(salen) complex and bis(triphenylphosphine)iminium chloride ([PPN]Cl).[188]

A photo-initiated cationic polymerization that employs **179** in combination with arylsulfonium salts and was reported by Crivello *et al.* (**Error! Reference source not found.**A). This example shows that with the use of APO the carbocation **182** allows ring-opening of the four-membered ring resulting in carbocation **183** with a double bond that polymerizes into **184**. In contrast, a similar type of ring-

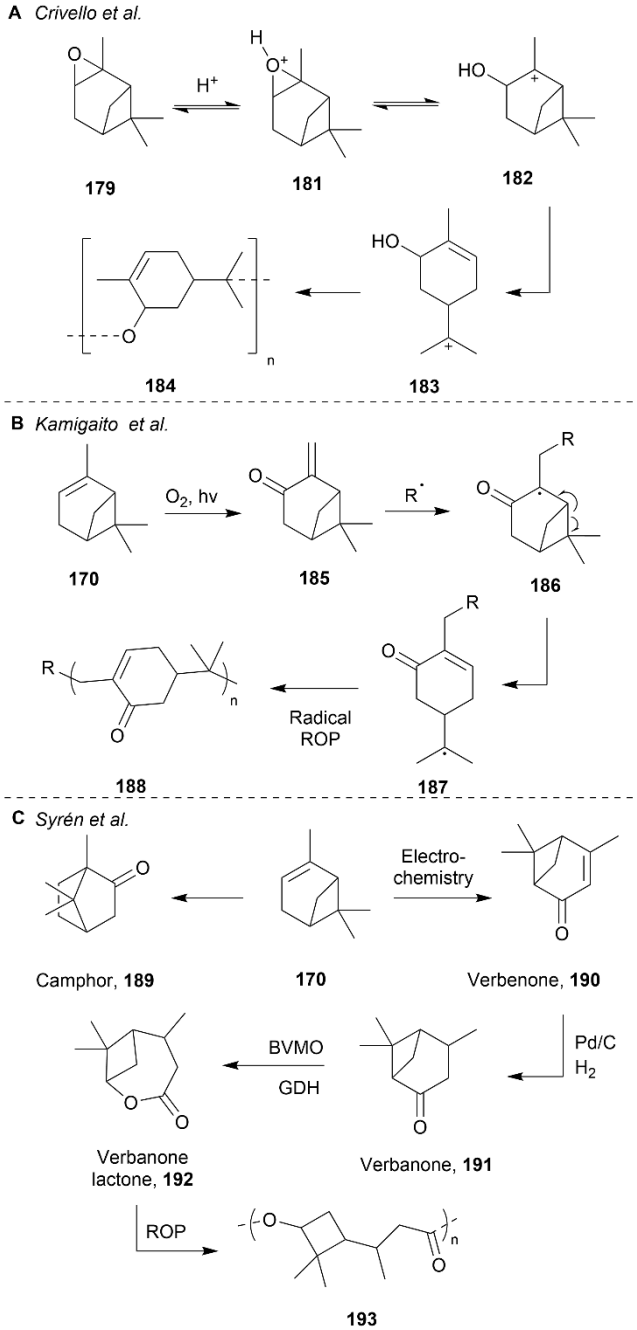
opening is not possible for LO, which is why different polymers would be obtained. Furhermore, **179** can also be reacted with multifunctional epoxide and oxetane monomers functioning as reactive diluent.[189] Finally, the copolymerization of APO with glutaric anhydride was reported that employed the use of salen complexes in a tandem synthesis of polyesters.[190]



Scheme 27 A. Terpenes found in terpentine oil. B. **.** α-Pinene polymerization in ionic liquids. C. Synthesis of α-pinene oxide (APO) and its subsequent copolymerization with CO_2.

Another monomer that can be obtained from the conversion of α-pinene is pinocarvone **185**. In 2016, Kamigaito *et al*. reported such a conversion by photooxidation with singlet oxygen. Pinocarvone was then polymerized by selective radical ROP to provide distinctive polymers containing conjugated ketones **188** (**Error! Reference source not found.**B).[191] As the synthesized polymers still contained the reactive α,β-unsaturated ketones, it was shown that they could be further functionalized (e.g. conjugate addition, reduction). Finally, methyl acrylate or n-butyl acrylate were shown to react with **185** for the successful synthesis of block copolymers.[191]

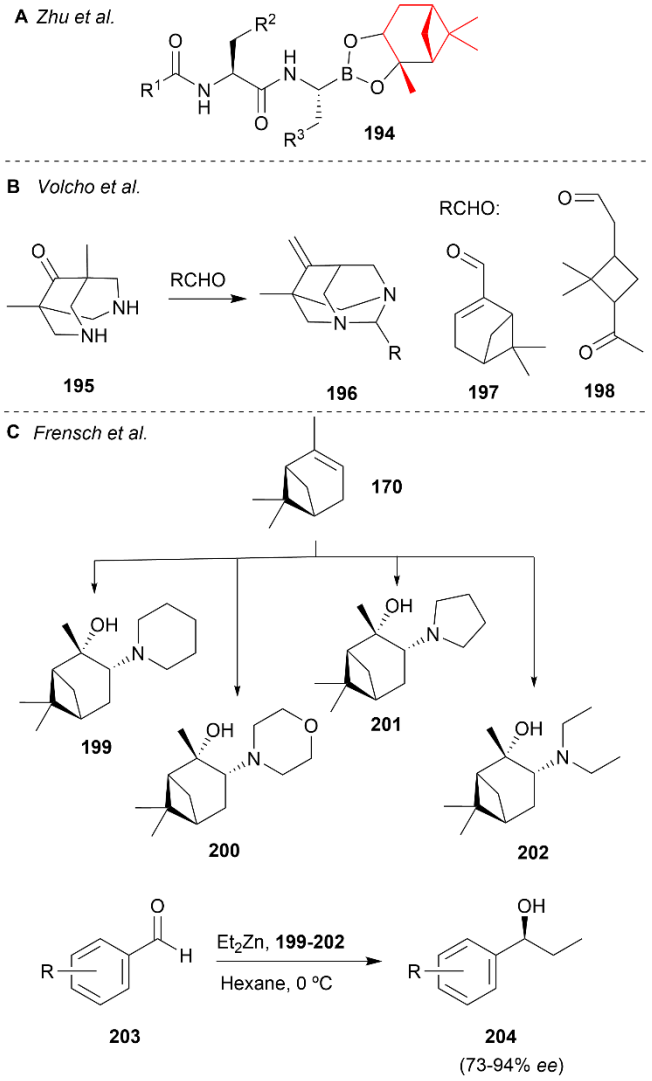
α-Pinene **170** can also be used as precursor for the synthesis of other terpenes. One example is camphor **189**, a monoterpene that will be discussed in more detail later. Its synthesis commences with a Wagner-Meerwein rearrangement, followed by the formation of bornyl acetate. Subsequently, this is hydrolyzed and oxidized to obtain camphor **189.**[192] Another compound that can be synthesized from α-pinene is (–)-verbenone **190** (also discussed later) as was demonstrated by Syrén *et al*. They achieved this through an electrochemical oxidation and the resulting (-)-verbenone was sequentially utilized in the synthesis of a pinene-derived polyester



Scheme 26 A. The photo-initiated cationic polymerization of APO. B. Photochemical oxidation of α-pinene **152** to pinocarvone **110** and the sequential selective radical ROP. C. Transformation of α-pinene to other useful terpenoids: camphor and verbenone. The latter can be further converted to the lactone form and subsequently polymerized.

using a bio-catalytic Baeyer-Villiger mono-oxygenase to verbanone lactone **192** and a successive ROP (**Error! Reference source not found.**C).[193] Additionally, Sieber *et al*. reported the successful ROP of various lactams derived from α-pinene **170**for the synthesis of

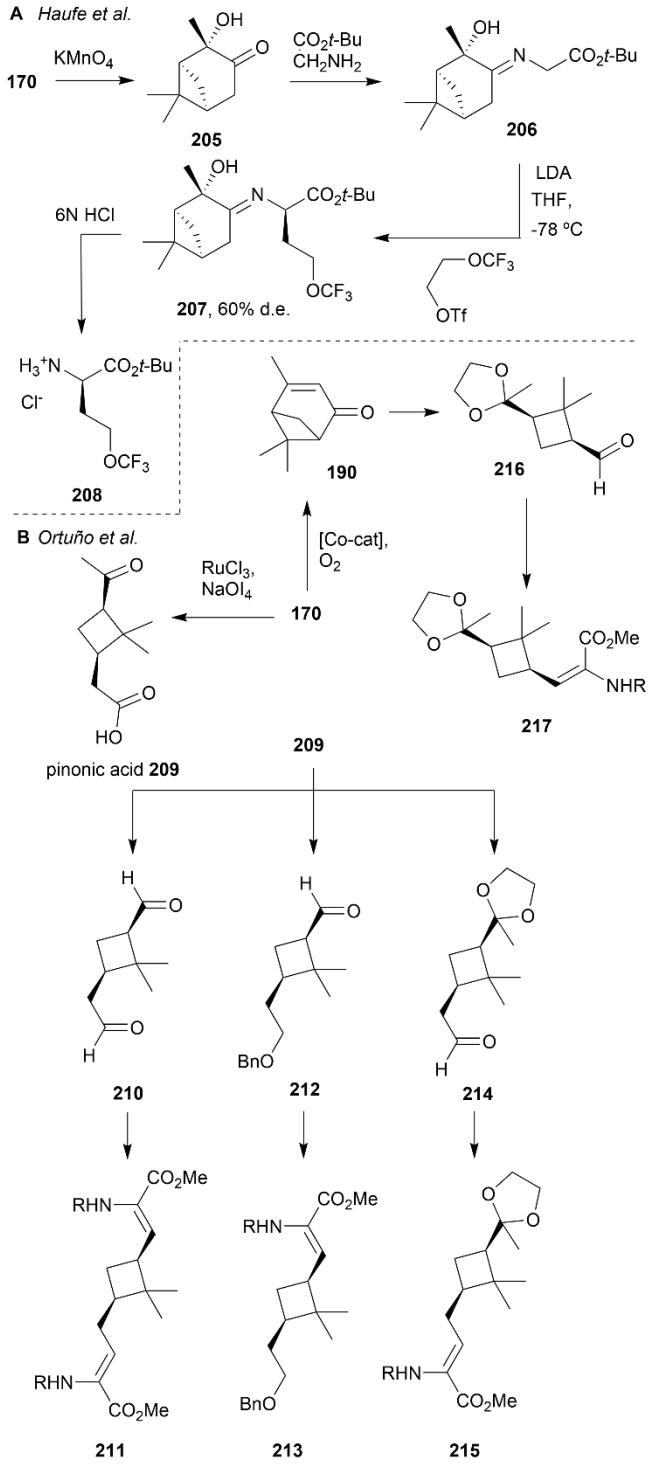
polyamides.[194] These are merely a selection of examples and a large variety of further reports involving the transformations of α-pinene **170** to other terpenes can be found in literature.[195–205]



Scheme 33 A: General structure of dipeptidyl boronate proteasome inhibitors containing α-pinene scafold. B: Example condensation reaction of diazaadamantane derivatives with α-pinene derived structures. C. Synthesis of α-pinene-based chiral ligands for stereoselective addition reactions to aldehydes.

Next to the above discussed polymer syntheses starting from α-pinene **170**, multiple publications have reported its involvement in the synthesis of pharmaceutically relevant compounds. For example Zhu *et al*., have made dipeptidyl boronate proteasome inhibitors (**194**) of which the structures contain α-pinene **170** (Scheme 33A) fragments.[206] Similarly, Volcho *et al*. combined diaza-adamantane **195** and monoterpenoid moieties for the investigation of the analgesic activities of their constructs (Scheme 33B).[36] They could react a variety of monoterpene-derived aldehydes with dimethylbispidinone to obtain the desired compounds. Along with (+)- and (–)-α-pinene, (–)-myrtenal, citral, citronellal, (–)-verbenone, (–)-nopol, and APO were also included as starting materials in this study. Aldehydes **197** and **198** were obtained from α-pinene **170** through oxidation with tert-butyl hydroperoxide and SeO_2, and through ozonolysis, respectively.

Another useful feature that **170** offers is its chirality. Multiple groups have previously exploited this property for stereoselective synthesis. The report of Frensch *et al*., for example, describe the



Scheme 34 A. Stereoselective synthesis of non-natural amino acids as reported by Haufe et al. B. Synthesis of a range of chiral cyclobutane synthons from α-pinene.

synthesis of novel chiral ligands **199-202** derived from **170** to facilitate the stereoselective addition of diethylzinc to aldehydes **203** to afford secondary chiral alcohols **204** (Scheme 33C).[37] Next to this, Loginov *et. al.* also reported the use of α-pinene **170** as a chiral ligand

in a planar rhodium complex.[207] Another example is that of Haufe *et al*., who reported the use of **170** as chiral auxiliaries for the selective synthesis of the first unprotected CF_3O-containing unnatural α-amino acid (Scheme 34A).[208] The used auxiliaries were first applied by Yamada *et al*. in their asymmetric synthesis of α-amino acids.[209]

Similar to the work by Syrén *et al*. discussed above, numerous other studies have focused on the development of synthetic strategies from **170** to afford cyclobutane derivatives. One of the first examples of such chemistry was reported by Burgess *et al.*,[210] who presented an enantio-divergent synthesis of 1,3-cyclobutane amino acids. This way, both enantiomers of the product were obtained from the same stereoisomer of **170**.

A year later, Ortuño *et al*. published the synthesis of cyclobutane dehydro amino acids from (+)-α-pinene through stereoselective Wittig-Horner condensations.[211] The same group later reported a follow-up article where they discussed the synthesis of other cyclobutane species from α-pinene **170** through both (–)-verbenone **190** and pinonic acid **209** (Scheme 34B).[212] These two intermediates are accessible by allylic oxidation and double bond oxidation, respectively. These versatile reactive specieswere in turn also utilized to create other cyclobutane dehydro amino acids **211, 213** and **215**.

Aside from these studies, recently other groups have also inspected the synthesis of cyclobutane derivatives from a related terpenoid, namely myrtenal.[213]

2.11.2 β-Pinene

β-Pinene **171** can, as mentioned previously, be obtained from turpentine oil. It is structurally very similar to α-pinene **170** with the exception of its exocyclic double bond. This makes it sterically more accessible and consequently allows for a more facile polymerization (Figure 12). Similar to what was described for **170**, β-pinene **171** can also be converted into other useful structures. The following paragraphs discuss several examples of such compounds, but is not intended to be comprehensive.

An example synthesis where β-pinene **171** was converted to other useful structures was published by Jones *et al*., who reported a four-step process starting from nopinone **216**, to form isopropyl ε-caprolactone **219**, a product that used to be obtained from the petrochemical industry (Scheme 35).[214] Similar caprolactones have been shown before *e.g.* from carvone (Scheme 23) or from *L*-menthol (Scheme 26).

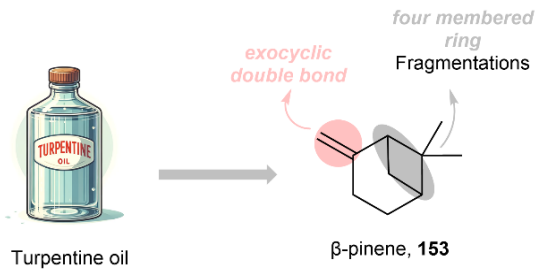
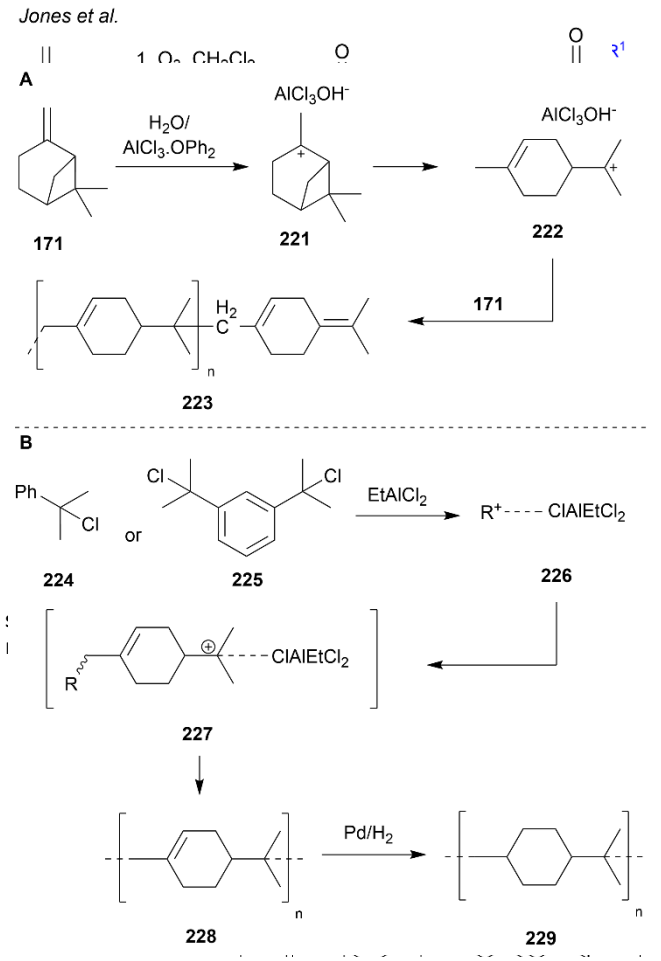


Figure 12. β-pinene functional groups and source

They proceeded to perform a ROP with this product by the employment of two different zirconium aminophenolate complexes. Furthermore, they were also able to perform a one-pot copolymerization with lactic acid providing copolymers with diverse structures. Other examples of useful transformations of β-pinene are the formation of linear myrcene and α-methyl-*p*-methyl styrene through pyrolysis and dehydrogenation.[215] These two monomers were employed by Hillmyer *et al*. for the synthesis of triblock copolymers.



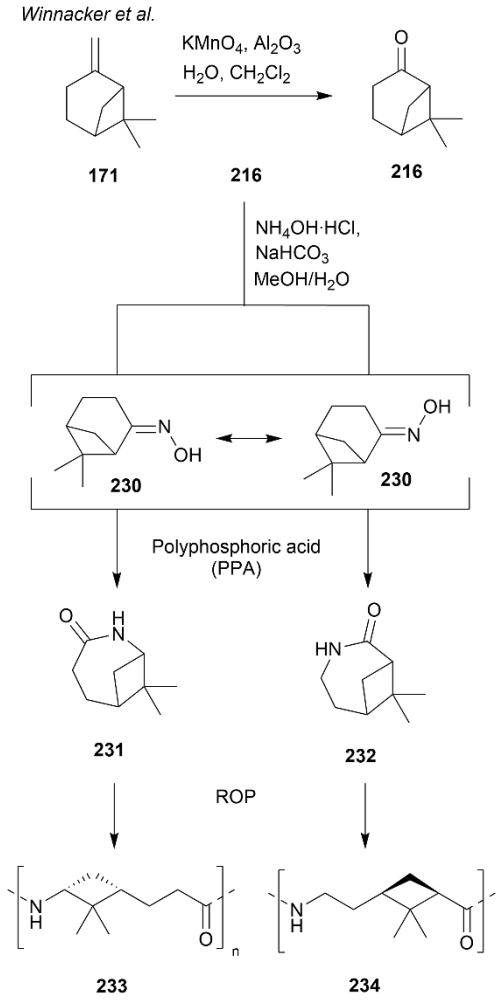
Scheme 36 Polymerization of β-pinene by cationic polymerization (**A** & **B**) including a controlled living cationic polymerization (**B**).

Scheme 38 A. Opening of the four membered ring of β-pinene via a Ritter-like reaction. Further functionalization of the amines for a hybrid library of compounds for screening strategies. B. Synthetic approach of Robustadial A & B key precursors from β-pinene.

The general method employed for the polymerization of β-pinene **171** is cationic ROP of the four-membered ring with tertiary carbocation intermediates. Several chemists report significant improvements for these reactions. As initially Lewis acids were utilized for the polymerizations, a significantly improved method was later reported utilizing an $AlCl_3$ etherate catalyst (Scheme 36A).[216] The enhanced functioning can be explained either by the Lewis acid being stronger upon formation of dimeric counterions, or by suppression of chain transfer reactions through the formation of a weakly nucleophilic counterion. An additional set of improved conditions for the synthesis of poly-β-pinene rely on Lewis acid catalyst $EtAlCl_2$ and $Et_3Al_2Cl_3$. These conditions were applied for the

polymerization of another terpene, namely phellandrene. A further enhancement was later reported where a living cationic polymerization, a controlled polymerization technique, was described by the use of RCl/$EtAlCl_2$/Et_2O (Scheme 36B).[217] Moreover, niobium pentahalides and TaF_5 have proven useful for β-pinene **171** polymerization at room temperature.

A useful class of polymers are the polyamides. The group of Winnacker *et al.* reported a β-pinene based synthesis of such polyamides in 2017 (Scheme 37).[218] The initial oxidation of β-pinene **171** to form nopinone **216** and subsequent Beckmann rearrangment through the respective regioisomeric oximes furnished lactams **231** and **232** in a 5:1 ratio, respectively. These could be separated by column chromatography and were finally subjected to cationic ROP. It was later reported that these polymers could also be formed from the lactams by anionic ROP mediated by use of a strong base (e.g. KO*t*Bu, NaH) and the employment of benzoylated lactams.[219] The stereo information of the monomers is transferred to the formed



Scheme 37 Synthesis of polyamides from β-pinene by ROP from the respective lactams. PPA: polyphosphoric acid.

polyamides, providing them with intriguing properties (e.g. high thermal stability, high melting points).

Aside from the polymerization reactions with β-pinene **171** discussed in the previous paragraphs, other groups employed this terpene as substrate for an alternative chemical transformation: the

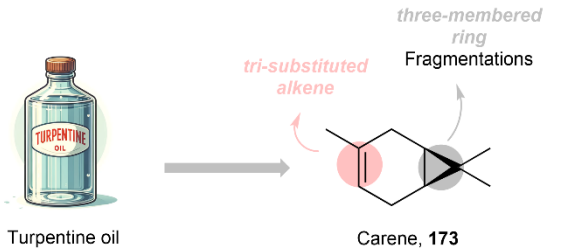
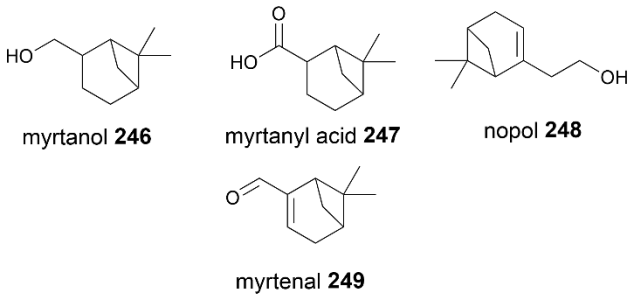


Figure 13. Carene's functional groups and source

Ritter reaction. More specifically, Schreiber *et al*. have utilized β-pinene **171** in a convergent synthesis of a series of small molecules (Scheme 38A).[220] They performed a mercury(II)-mediated Ritter reaction, similar to that initially developed by Delpech and Khuong-Huu, for the synthesis of a sub-library of structures, which was in turn utilized for the creation of a hybrid library of compounds (**240**) that was applied in screening.[220,221] In the first step, the ring opening is caused by the mercury triflate, which allows the nitrile to attack the quaternary carbon. This is followed by a reduction with $NaBH(OAc)_3$ and further functionalization of the amine. The group of Williams later investigated this bridged Ritter reaction in more detail by varying the nitrile substituents resulting in different reactivities and, in doing so, attained structural diversity.[222]

In addition to the Ritter reaction, various articles discuss the use of **171** in formal and total syntheses. For example, Hoffmann *et al*. reported the stereoselective synthesis of key precursors of robustadials A and B **244-245** starting from (*S*)-(–)-β-pinene in high overall yields (Scheme 38B).[223] They were able to access the tetracyclic skeletons of the targets efficiently in one step via a tandem Knoevenagel condensation followed by a hetero Diels-Alder reaction. Similar chemistry was later published by Chiba *et al*., who utilized **171** for the synthesis of euglobal-G3 and -G4, which are naturally occurring phloroglucinol-monoterpene adducts, through a biomimetic cycloaddition.[224] In 2002, Kobayashi and William disclosed their synthetic methods towards tetrahydrocannabinols wherein they employed **171** as building block.[225]

Not only is **171** useful as building block for synthetic purposes, but it can also readily be converted to other bio-based chemicals (e.g. terpenoids, terpenes). We have already seen that it is applied to the synthesis of myrcene. β-Pinene **171** is also commonly used for the synthesis of nopol **248**, a bicyclic primary alcohol known for its applications in pesticides and fine chemicals using the Prins reaction with formaldehyde.[226] Moreover, Shang *et al*. have reported the conversion of **171** to myrtanol **249** and successive oxidation to



Scheme 39 Conversion to other bio-based chemicals from **171**.

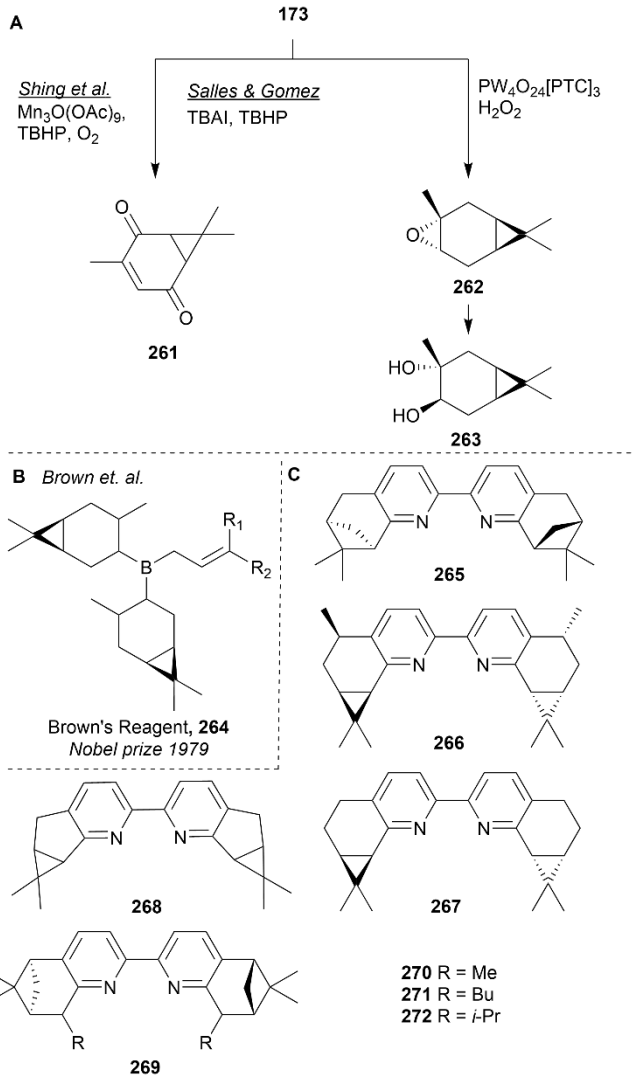
myrtanyl acid **247**.[227] They subsequently synthesized 26 derivatives containing acylthiourea or amide groups to inspect their antitumor activity on various cancer cell lines. Finally, El Houssame *et al*. reported the oxidation of various terpenes wherein **171** was also converted to myrtanal **249** [228] and Fret *et. al.* have used the latter for the formation of nopadiene (Scheme 39). Copolymerization of that with β-myrcene efficiently provided a biobased thermoplastic elastomer.[229]

2.12 Carene

3-Carene **173** is yet another bicyclic monoterpene that, as mentioned above, can be found in turpentine oil, but it can also be synthesized from the pinenes through isomerization.[27] Its structure includes a fused bicyclic 6-3 membered ring system which makes it a chiral compound. As will be explained later, the chirality can be exploited for asymmetric synthesis. The most reactive groups of this compound are the three-membered ring and the double bond in the six-membered ring. The majority of conversions with **173** start by altering the latter position (Figure **13**).

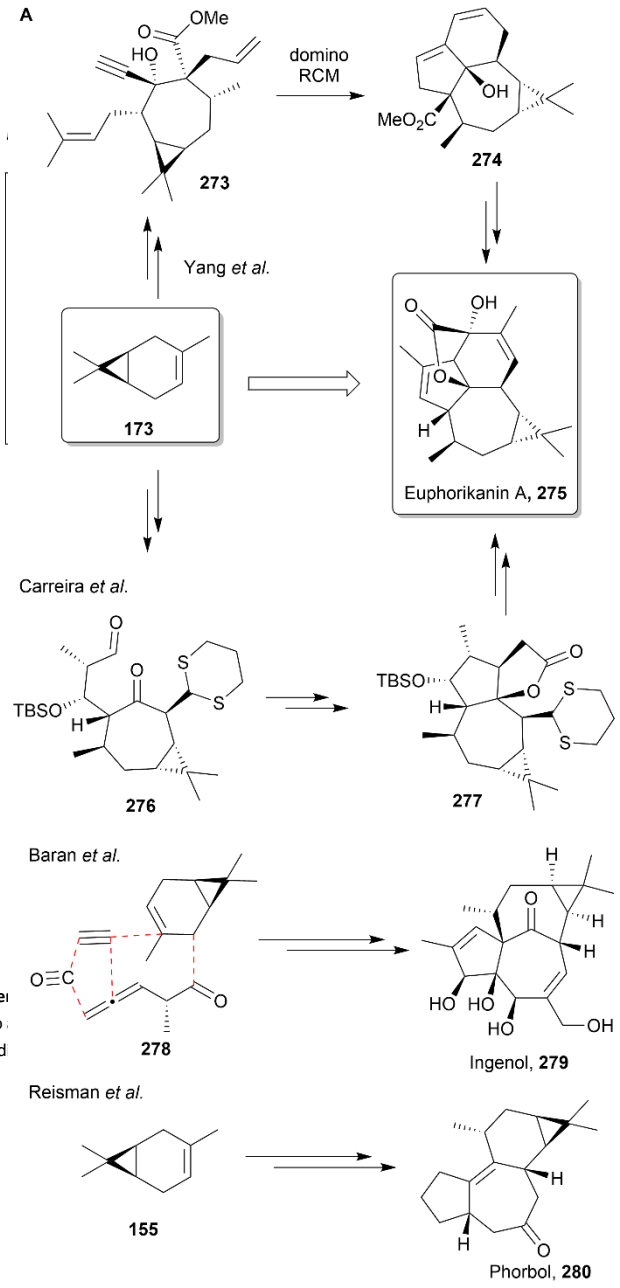
In the past, numerous polymers have been synthesized which employed **173** as starting material. The conversion of both α-pinene and 3-carene to β- and ε-lactams was reported by Sieber *et al*., for example (**Error! Reference source not found.**).[194,230] They developed a [2+2] cycloaddition reaction with chlorosulfonyl isocyanate **250**. On the other hand, ε-lactam **255** was obtained by a successive regioselective hydroboration, oxidation to the ketone **253**, oxime formation **254**, and Beckmann rearrangement with TsCl in basic media. Subsequent subjection of the lactams to anionic ROP provided various polyamides (**252** and **256**). Owing to the bulky sidechains, these polymers have very intriguing characteristics (i.e.: high impact strength, mechanical resistance and superior thermal properties), which are a novelty for terpene-based polyamides. Another polymerization by Kleij *et al*., mentioned previously for LO, employed carene oxide (CAO) in a copolymerization with phtalic anhydride. [144]

Other studies have focused on the conversion of **173** into different useful building blocks. Recently, for example, Sidorenko *et al*. reported the isomerization of both α-pinene and 3-carene to useful other terpenes (e.g. 2-carene, camphene, limonene).[231] These isomerization reactions utilized numerous acid-treated clays as catalysts like montmorillonite, illite, and kaolinite. Another publication that also employed these two terpenes, involved the synthesis of keto acids or methyl esters depending on the solvent (**Error! Reference source not found.**).[232] The terpenes were first subjected to ozonolysis and a subsequent reduction with 4-hydroxybenzohydrazide provided the final cyclopropane- and cyclobutane-containing products **258** and **260,** respectively. Finally, Fülöp *et al*. reported the conversion of **173** into a series of novel cyclic β-amino acids and derivatives thereof.[233] These chiral structures were postulated to be useful as building blocks or auxiliaries in asymmetric synthesis of potential pharmacons.



Scheme 42 A. Various reports involving the oxidation of 3-carene. B. Structure of the allyldialkylborane stereoselective allylation reagent reported by Brown *et al*. C. 2,2-bipyridine ligands for Cu-catalysed asymmetric allylic oxidation and cyclopropanation.

Over the years, green oxidation methodologies have gained much interest. In that respect, Salles and Gomes reported a TM-free approach – with tetrabutylammonium iodide (TBAI) and TBHP – that proved effective for allylic and benzylic oxidations in water to provide products with nitriles, amides and ketone moieties.[234] They were able to oxidize **173** to the diketone **261** using this methodology, which was an extension of the work from Shing *et al*, who had already reported conditions to afford the diketone **261** (**Error! Reference source not found.**A).[235] Their manganese(III)acetate catalyzed allylic oxidation to enones displayed high regioselectivity and chemoselectivity. A more recent report by Bull et al. discussed a novel method for the catalytic solvent-free epoxidation of various biorenewable terpenes.[236] The tungsten-based polyoxometalate catalyzed reaction merely requires aqueous H_2O_2 as oxidant and is capable of providing LO, APO, and 3-carene oxide **262** on a multigram scale. The formed epoxides could be hydrolyzed to provide the respective anti-diols **263** using a heterogeneous acid catalyst.



Scheme 43 Numerous studies involving total and formal syntheses starting from 3-carene.

As briefly mentioned above, another feature of **173** that has proven useful in numerous studies is its chirality. In 1984, Brown *et al*. published their novel method for the enantioselective allylation of aldehydes for the synthesis of chiral homoallylic alcohols.[237,238] They explored numerous terpene-based chiral allyldialkylborane compounds for this transformation and found **264** to be the superior auxiliary (**Error! Reference source not found.**B), Due to the rigid six-membered transition state observed with boron, steric interactions between the axial ligands and the allyl group are minimized, leading to an excellent stereocontrol. Another study that exploited the chirality of **173** was reported by Malkov *et al*., who designed and synthesized novel chiral 2,2-bipyridine ligands **265-272** for copper-catalyzed asymmetric allylic oxidation and cyclopropanation (**Error! Reference source not found.**C).[38] The chiral nature of the ligands originated from numerous terpenes that were incorporated into the structure (e.g. α-pinene, β-pinene, 3-carene, and 2-carene). Copper complexes derived from these ligands were used for the allylic oxidation of cyclic olefins and displayed high reaction rates along with a good enantioselectivity of up to 82% *ee*. Cyclopropanation reaction were also performed with up to 76% *ee* and 75-99% *de*.

Several natural terpenoids contain similar skeletal features to **173**, therefore it is not surprising that this terpene is used as a building block in natural product synthesis. Particularly the dimethyl substituted cyclopropane can often be found in natural products. The first example that we discuss here is that of euphorikanin A, a diterpenoid comprising a highly congested tetracyclic carbon skeleton. Last year, the group of Yang *et al*. published their synthesis of the skeleton of this compound, which included a key domino ring-closing metathesis reaction.[239] Starting from **173**, the researchers synthesized a dienyne building block **273,** which would subsequently be subjected to the metathesis reaction. More recently, Carreira *et al*. published the total synthesis of euphorikanin A **275**, which also started from **173**, but with the initial steps being slightly different (**Error! Reference source not found.**).[240]

Another natural compound that was synthesized from **173** is ingenol **279**. This structure contains numerous challenging features and since it was first reported in 1968, multiple groups have invested in the development of its synthesis.[39,241] The group of Baran *et al*. reported a concise total synthesis of ingenol **279** in merely 14 steps. Starting from **173**, their approach included a Pauson-Khand reaction and a pivotal Pinnacol rearrangement (**Error! Reference source not found.**). [39] A final example in which this terpene was employed as building block, is that of Reisman *et al*.[242] They reported the synthesis of a 4-alkyne-1-ol compound from **173**, which was sequentially subjected to a tandem anionic 5-exo-dig cyclization/Claisen rearrangement to provide the tetracyclic core of phorbol **280** (**Error! Reference source not found.**).

Another field in which the utilization of **173** has been fruitful is medicinal chemistry. For example, Singh *et al*., used this and other

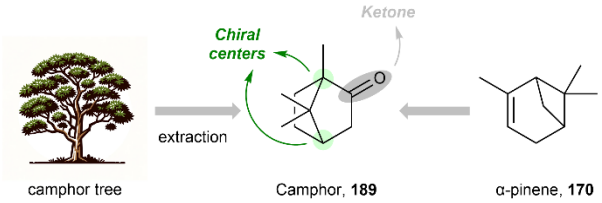
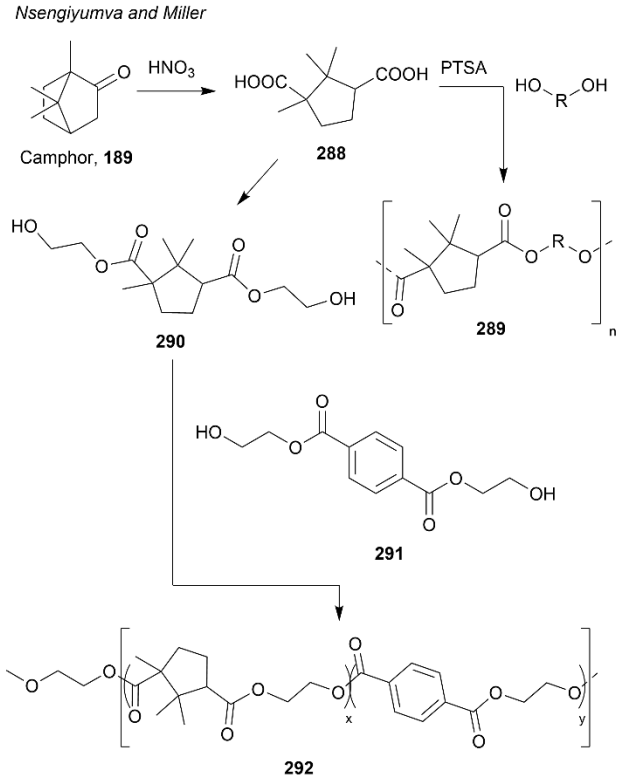


Figure 14. Camphor's functional group and sources

terpenes (i.e. α-pinene, β-pinene, camphene) as building block for the synthesis of euglobal G1-G4 and various analogues thereof (**Error! Reference source not found.**).[243] These compounds were tested for antibacterial, antifungal, antileishmanial, and antimalarial activity and multiple compounds demonstrated promising results. In another study, by Bolli *et al*., novel $S1P_1$ receptor antagonists were synthesized and investigated for the treatment of relapsing remitting multiple sclerosis. These showed improved stability and potency, which was attributed to a higher selectivity and affinity.[244] The five-membered rings **281** and **282** are obtained after oxidative cleavage of the double bond and a posterior Claisen condensation. The

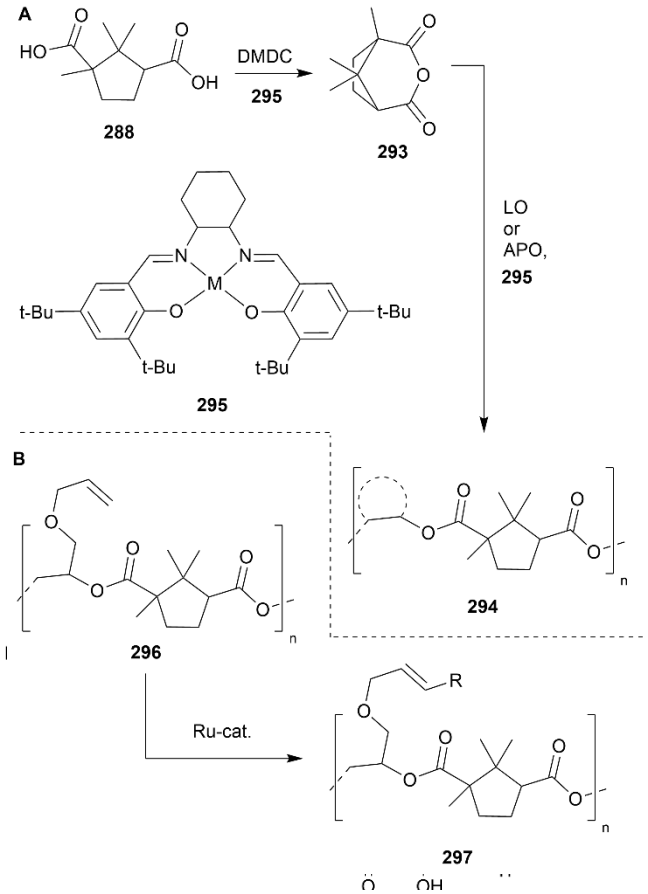


Scheme 45 Polycondensation and copolymerization of various diols made from camphor through camphoric acid.

researchers designed and synthesized pyrazole and thiophene containing compounds **281-284,** which could be made from **173** (**Error! Reference source not found.**). Finally, via allylic C-H functionalization, Duan *et al*. studied a series of (*Z*)- and (*E*)-3-caren-5-one oxime sulfonates **285-286,** which were all obtained from **173** (**Error! Reference source not found.**).[245] They investigated the antifungal activities of these compounds and found numerous active hits against various strains of fungi. There is also reported the use of acylimidazoles for acylation of the allylic position. [246]

2.13 Camphor

It has been mentioned that camphor **189** is a cyclic monoterpene that can be obtained either by extraction from the camphor tree or from the conversion of α-pinene **170** through a Wagner-Meerwein rearrangement, acid-catalyzed oxidation and hydrolysis. Although



Scheme 46 A. Syntheses of copolymers utilizing camphor and a TM-Salen complex. B. Sequential functionalization reactions.

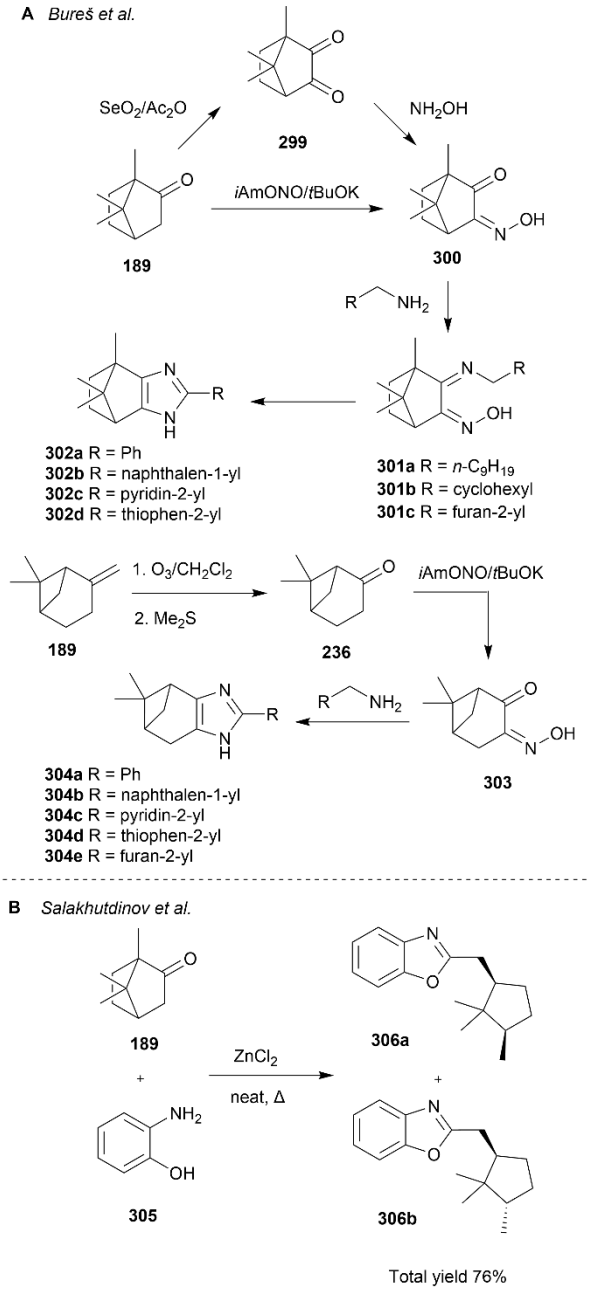
Scheme 44 Conversion of 3-carene to various reported medicinally relevant compounds.

the conversion of α-pinene is more reliable in terms of purity and scalability, it is more expensive. Then again, some industries, such as fragances and healthcare, benefit from the impurities that come with the extraction process.[192] Camphor is produced in over 30000 tons annually, where the production is mainly performed in China and India. The structure of **189** contains a ketone. Therefore, it can be reduced to two stereoisomeric alcohols (i.e. borneol and isoborneol). Furthermore, the structure contains two asymmetric carbons resulting in the existence of two isomers: (–)- and (+)-**189** (**Error! Reference source not found.**).[192]

Like many of the terpenes discussed in the previous sections, **189** has been utilized for the synthesis of polymers. In 2019, the synthesis of polyesters based on this terpene were described by Nsengiyumva and Miller.[247] In their synthesis, camphor was oxidized to camphoric acid **288**, which could subsequently be subjected to a

polycondensation reaction with numerous diols utilizing *p*-toluenesulfonic acid (PTSA) as catalyst (**Error! Reference source not found.**). The same article discussed the copolymerization of bis(hydroxyethyl) camphorate **290** – derived from camphoric acid **288** – and bis(hydroxyethyl) terephthalate **291**, which resulted in polymers with interesting thermal properties **292** (**Error! Reference source not found.**).

Another polymerization of camphor-derived compounds was published by Thomas *et al*.[190] They reported the Salen-complex



Scheme 47 A. Synthesis of imidazole and imino-oxime ligands based on β-pinene and camphor. B. Synthesis of benzoxazoles from camphor an substituted anilines.

mediated synthesis of cyclic anhydrides using dicarboxylic acids. The anhydrides could sequentially be copolymerized by addition of an epoxide in a one-pot fashion where the same catalyst **295** is utilized for both steps. Thus, they converted camphoric acid **288** to camphoric anhydride **293**, which was then copolymerized with LO or APO to **294**. A later study employed this methodology for the post-modification of the provided polyesters (**Error! Reference source not found.**A).[248] Therein, various olefins were coupled to the polymers by ruthenium-based cross-metathesis reactions (**Error! Reference source not found.**B). Finally, Strößer and Williams were capable of synthesizing triblock copolymers with **273**.[249]

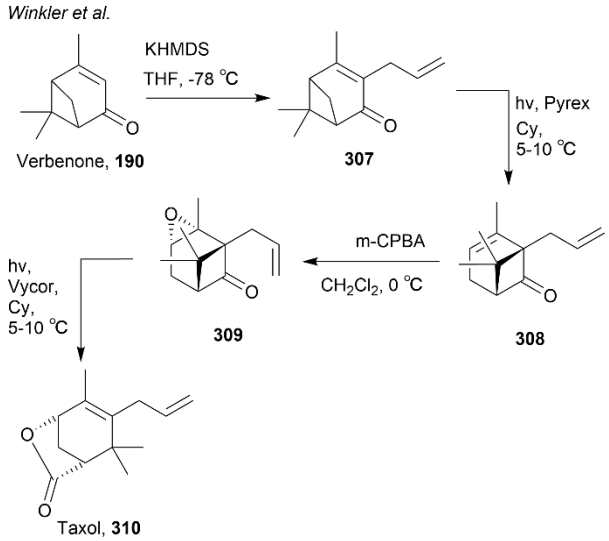
Like other previously discussed terpenes, camphor has also been employed in the synthesis of terpene derived ligands. Bureš *et al*. developed a novel route for the synthesis of imidazole (**302a-d, 304a-e**) and ligands from different terpenes *i.e.* camphor and β-pinene (**Error! Reference source not found.**A).[250] The authors in turn used these compounds for the copper catalysed assymetric Henry reaction. It is interesting to notice how the enantioselectiviy can differ by using the mentioned terpenes (29% *ee* for the S with **302c** and 32% *ee* for the R with **304c**). Finally, camphor-based Schiff base tridentate ligands have also been developed and proved to be useful for catalyzing the enantioselective addition of phenyl acetylene to aldehydes.[251] This reaction provided a way to access both (*R*)- and (*S*)-propargylic alcohols in excellent yields (91-99%) and enantioselectivities (82-91% *ee*). Various other applications have been found for **189**. An interesting study by Lewis *et al.* reports on the use of a camphorsulfonyl-group as recyclable chiral auxiliary.[252] Moreover, derivatives of **189** have been applied for medicinal purposes in attempts to uncover inhibitors of filoviruses.[253] In a fascinating recent publication, Salakhutdinov *et al*. reported the synthesis of benzoxazoles by reacting substituted anilines **305** with camphor-like ketones (**Error! Reference source not found.**B).[254] Therein, the initially expected imines were merely intermediates before the subsequent ring-opening reactions took place towards the products **306a-b**. In a preceding publication, Nowicka-Scheibe reported a similar method for the synthesis of benzoxazoles under aerobic conditions.[255] Benzoxazoles are known to exhibit important biological activities, so these procedures provided chemists with a method of obtaining these invaluable compounds.

2.14 Verbenone

An additional member of the bicyclic terpenoids that was described in previous sections is verbenone **190**. This compound and verbenol – the alcohol form of **190** – have been utilized as anti-aggregation and aggregation pheromones, respectively, and can both be employed as insecticide.[256] Moreover, (–)-verbenone plays an important role in the food industry as flavoring agent. In the past, many studies have focused on the bioconversion of α-pinene to afford this compound utilizing various methods (e.g. bacteria, fungi,

and plant cell suspension cultures). The reactivity is very similar to that of carvone **101**, except for the now present four membered ring. This ring can be an interesting source for reactivity that has been previously discussed for other terpenes, but is also important when considering undesired side reactivity (**Error! Reference source not found.**).[256,257]

Aside from these methods, numerous studies have developed synthetic approaches towards **190**. We have already discussed an example of this by Syrén *et al*. (**Error! Reference source not found.**B) They demonstrated the electrochemical oxidation of α-pinene towards **190**, a method initially developed by Baran *et al*. for allylic oxidation.[193,258] Another option for allylic oxidation of α-pinene toward **190** is that of the previously discussed study by Shing *et al* (Scheme B).[235]

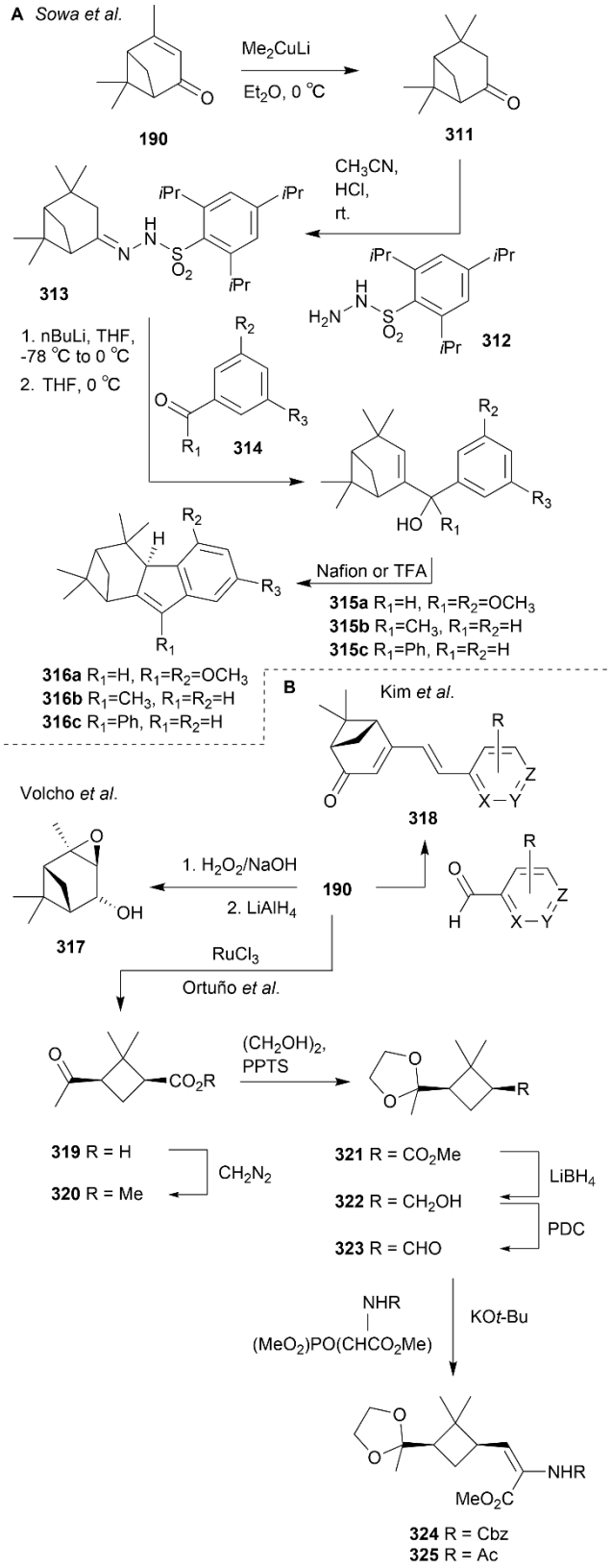


Scheme 48 A. Synthesis of a taxol subunit from verbenone **190**.

Owing to the chiral nature of this terpenoid, it has also been utilized in numerous asymmetric syntheses. Winkler *et al.*, for example, reported the synthesis of a ring subunit of taxol **310**, a compound well-known to have anticancer activity (**Error! Reference source not found.**).[259] They performed a variety of transformations including: an allylation, photochemical rearrangement, epoxidation and a final photochemically-mediated rearrangement.

Additionally, **190** has also been employed in the synthesis of *verbindenes* **315a-c** (i.e. verbenone-based chiral indenes).[260] Sowa *et al*. utilized these compounds as metallocene ligands for the TM-mediated catalysis of asymmetric reactions (**Error! Reference source not found.**A).

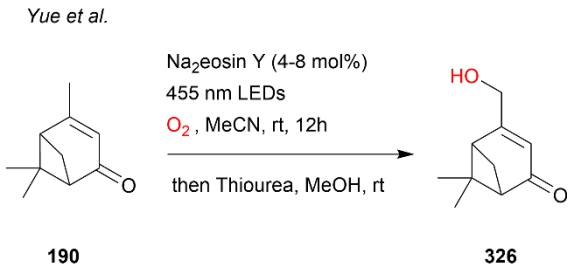
Aside from the above-mentioned reactions, additional transformations of verbenone to useful intermediates/products have been reported. Volcho *et al*. have reported the epoxidation of **190** for the synthesis and study of potentially analgesic compounds (**Error! Reference source not found.**A).[261] Another study, by Ortuño *et al.*, involved the synthesis of functionalized cyclobutane derivatives by means of the oxidative cleavage of α-pinene and **190** (**Error! Reference source not found.**B).[212] The authors later employed the provided cyclobutanes for the synthesis of dehydro amino acids. Finally, Kim *et al*. reported the synthesis of a series of



Scheme 49 A. Synthesis of "verbindene" ligands from verbenone **190** for asymmetric B. Various synthetic conversions and uses which utilize verbenone

verbenone derivatives as potential anti-oxidant, anti- excitotoxic, and anti-ishemic agents (**Error! Reference source not found.**B).[262] They attained the products **318** by a vinylogous aldol condensation with **190** and various aromatic aldehydes.

Additionally, photocatalytc allylic hydroxylation of the enone in **190** to alcohol **326** is presented in the work from Yue *et al*. (Scheme **50**). They also report the use of other terpenoids such as myrtenal **249**, isophorone **358** or piperitone **359**.[263]



Scheme 50 Photocatalytic allylic hydroxylation.

2.15 Additional Terpenes & Terpenoids

The previous sections discuss the most common mono-terpenes and terpenoids along with reported examples of how to exploit their reactivity. While there are many more known structures belonging to this class of compounds, their reactivity is either underexpored or overlaps with the previously discussed terpenes and terpenoids.

A list of the remaining mono-terpenes and terpenoids is provided below, along with the most common way of obtaining them (Figure **16**, Table 1). We have utilized a color-based classification system to rank the compounds in three categories: price (P), synthesis (S) and natural abundance (NA). For the price, we checked three important chemical suppliers in Europe (Merck, Doug Discovery and Combi Blocks) and chose the cheapest option.

Regarding the natural abundance, we assigned color code gren to compounds that have a reported extraction (*e.g.* essential oils, bacteria or plants) in the mg/Kg range were assigned green. Compounds of which the concentrations have been reported in plants/oils, but have not been isolated from these sources, were classified as yellow. The red color is for compounds with no reported natural abundance.

For the synthesis, compounds with a reported biosynthesis or chemical syntheses with an overall yield above 60% are green. The ones with the chemical synthesis with a total yield between 20-60% were assigned yellow; and red for the ones with total yields lower than 20%.

We assigned the color code green to compounds with the price ranging from 0-500 €/Kg for synthesis grade compounds (>96%). The yellow color was assigned to thoses with a price range of 500-4000 €/Kg; and the red color for compunds with prices higher than 4000 €/kg

The following paragraphs discuss a few example compounds. Sobrerol **343** is very expensive (red, 27.000 €/Kg) and has reported abundance (green, 12 mg/kg). This terpenoid, although having a reported bio-conversion by the mold *Aspergillus Niger* from α-pinene, it is not classified as green since it is just a minor by-product in that process (3%). [264]

Camphene **326** (25 €/Kg) and Isoborneol **327** (123 €/Kg) are both cheap (green) but have no natural abundance (red), yet their synthesis (yellow) from α-pinene (i.e. through a Wagner-Meerwein rearrangement) is quite facile, which explains the low price. It is worth mentioning that in both cases there are multiple reports that describe small amounts (3-7%) of these compounds in different plants. However, these percentatges are based on data that is not being corrected by a response factor; therefore, its natural abundance is classified as yellow.

There are two cases where price and synthesis are well correlated. These are Thujone **335** (60000 €/Kg) and umbellulone **336** ($2*10^9$ €/Kg), classified as red in both categories. The former has a reported enantioselective synthesis with a 35% yield over three steps, but in a very small scale (46 mg of final product). [265] This makes it a very inefficient process for industry (red), resulting in a high price. A one-step synthesis was reported for umbellulone **336** from thymol **353**, which is a cheap starting material (80 €/Kg). However, the process has an 8% yield (red), which makes it also very inefficient for industry.[266] However, with the current technologies available, it would likely be possible to increase the efficiency [267]

Compound	Nr.	Production/ natural occurrence	P	NA	S	Ref.
Camphene	**326**	Isomerization of α-pinene		112		204
Nopinone	**216**	Oxidative cleavage of β-pinene				268
Isoborneol	**327**	Plant oils/ Isomerization of camphene/ carvone reduction				269,270
Borneol	**328**	Plant oils/ carvone reduction		34		269,270
Verbenol	**329**	Bioconversion of α-pinene				271,272
Eucalyptol	**330**	Extraction of essential oils		52		273,274
Myrtenol	**347**	β-pineneoxide rearrangement				275–277
Myrtanyl acid	**261**	myrtanol oxidation				278
Myrtenal	**249**	β-pineneoxide rearrangement				275–277
Pinocarvone	**331**	Plant oils/ conversion of α-pinene and β-pinene				191,279–281
α-Thujene	**332**	Extraction of essential oils/ synthesized from thujone				282,283
β-Thujene	**333**	synthesized from thujone				282,284
Sabinene	**334**	Biosynthesis				285
Thujone	**335**	Extraction of essential oils				286–288
Umbellulone	**336**	Extraction of essential oils				289
γ-Terpinene	**337**	Extraction of essential oils/ bioconversion of glycerol/ α-pinene isomerization				290,291
α-Terpinene	**338**	α-pinene isomerization				291–293
β-Terpinene	**339**	Extraction of essential oils				294,295
Terpinolene	**340**	α-pinene conversion or limonene isomerization				296–298
α-Phellandrene	**341**	Extraction of essential oils				299
β-Phellandrene	**342**	Extraction of essential oils/ biosynthesis				300–302
Sobrerol	**343**	Bioconversion/isomerization/hydrolysis of α-pinene		12		303–307
Terpineol	**344**	Plant oils/ (bio)conversion of α-pinene or limonene				308,309
Perillyl alcohol	**345**	Plant oils/ (bio)chemical conversion limonene				310–312
Thioterpineol	**346**	Extraction of numerous fruits/ conversion from terpineol				313–315
Hinokitiol	**347**	Plant oils/ Chemical conversion from limonene among others/ bioproduction				316–319
Ascaridole	**348**	Photocatalytic α-terpinene oxidation/ plant oils				320–323
p-Cymene	**349**	Transformation limonene, 1,8-cineole, or perrilyl alcohol/ Essential oils				324–326
m-cymene	**350**	Plant oils				327–329
o-cymene	**351**	Plant oils				328–330
Carvacrol	**352**	Plant oils/ transformation of carvone, or p-menthene glucosides		1		331–334
Thymol	**353**	Extraction of essential oils		1		333,335,336
(*R*,*S*-)Linalool	**354**	Plant oils/ biosynthesis/ Chemical synthesis		7.9		337–342
(*E*,*Z*-)Citral	**355**	Plant oils/ oxidation geraniol/ Chemical synthesis				343–347
Nerol	**356**	Plant oils/ biosynthesis/ hydrogenation of citral				348,349
Citronellol	**357**	Plant oils/ Hydrogenation citral, geraniol, nerol/ Biosynthesis				350–355
Isophorone	**358**	Calcium carbide catalysed acetone condensation/ Plants		100		356,357
Piperitone	**359**	Plant oils				358

Table 1 Overview of the production and natural occurrence of various known mono-terpenes and terpenoids. Each compound has been color-coded with red (poor), yellow (moderate), and green (good) for the following categories; price (P) from three important chemical suppliers in Europe (Sigma Aldrich, Doug Discovery and Combi Blocks), synthesis (S), and natural abundance (NA) in mg/Kg of extracted compound.

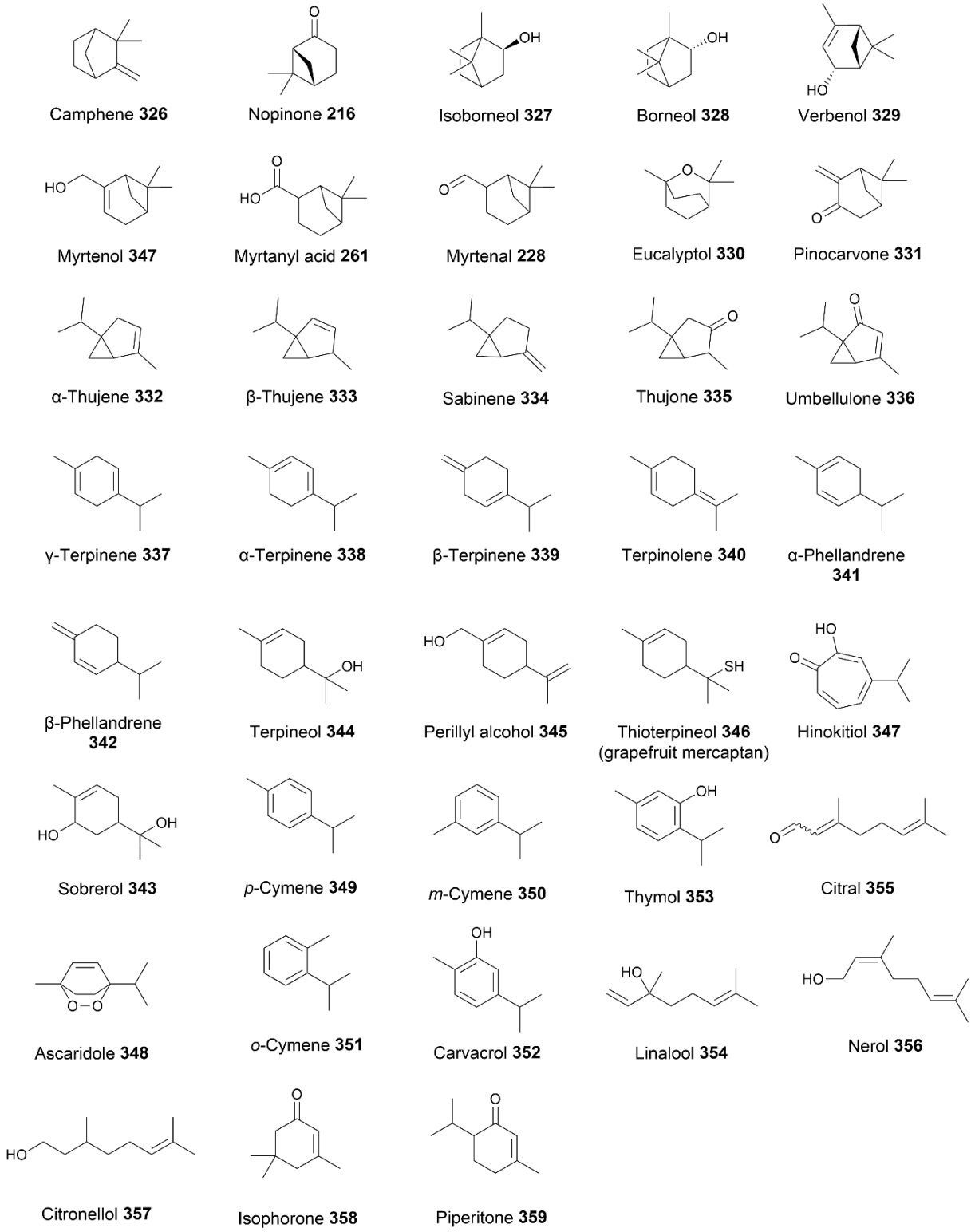


Figure 16 Additional known mono-terpenes and terpenoids

Conclusions

The aim of this review is to provide a clear comprehensive overview of the known bio-based terpenes and terpenoids and report how to exploit their reactivity. In that respect, 15 of the most common and abundant mono-terpenes and terpenoids have been discussed in the order of their increasing structural complexity.

The discussed terpenes and terpenoids have their own distinct reactivity and properties resulting in a multitude of chemical conversions (*e.g.* reductions/oxidations, olefin metathesis, allylic oxidation, and cycloadditions). Many of the terpenes and terpenoids contain multiple double bonds, which can be chemoselectively functionalized in some cases. For example, the majority of the reported functionalizations of myrcene **34** happen in the most substituted double bond. Another case is the hydrogenation of the endocyclic double bond in carvone **101**, which is done using sodium dithionite. The epoxidation of limonene with *m*CPBA is also a selective process, which only affects the endocyclic double bond. These unsaturations served as ideal handles in many different reactions.

Furthermore, many reports have utilized the bio-based terpenes in this report as monomers in a large variety of polymerization reactions. Therein, many of the cyclic terpenes/terpenoids could be subjected to ROP, often via initial oxidation and subsequent lactone or lactam formation by means of the Baeyer-Villiger oxidation or Beckmann rearrangement, respectively. This chemistry is strongly comparable to the use of caprolactam, a compound well-known for its use in nylon synthesis. This is merely one of the examples where this review has demonstrated the applicability of terpenes/terpenoids as substitutes for conventional fossil-based chemicals. Another example is that of tullipalin A. Many regard this compound as the renewable analog of petrol-based methyl methacrylate **21** and it offers numerous benefits aside from the renewability.

Multiple structures in this report include a 1,3-diene functionality, making them ideal substrates for Diels-Alder reactions to provide cyclohexane rings that can be seen as an alternative to BTX (a fossil feedstock) derived chemicals, like xylene. Many studies employed these compounds as building blocks for the synthesis of other platform chemicals. In that respect, the pinenes have proven highly useful by not only being a diverse source of platform molecules, but also of other less abundant terpenes. For example, geraniol has shown similar value by being biochemically converted into six non-natural terpenes. Aside from these conversions, numerous chemists have utilized the terpenes as building blocks in total syntheses of natural products, such as polygalolides A & B, euphorikanin A, Halomon, etc. Moreover, they have also been utilized for the fabrication of pharmaceutically active compounds. Various groups constructed entire libraries for drug screening using terpenes/terpenoids as starting points.

Finally, one of the major benefits terpenes have offered is their chiral nature and so their applicability in asymmetric synthesis. Consequently, numerous studies have utilized chiral terpenes and terpenoids (e.g. menthol, α,β-pinene, and carene) for different asymmetric strategies (i.e. as chiral auxiliaries, reagents, and ligands).

By showing the capabilities and limitations of the chosen terpenes and terpenoids, we hope this compendium serves for the upcoming research in the use of bio-based terpenes/terpenoids in novel chemical transformations. Specially in the obtention of fuctional molecules for materials with chiral characteristics. We would like to point out the potential of the underexplored terpenes in *Figure 16* for this purpose.

Author Contributions

The authors confirm contribution to the paper as follows: Conceptualization of idea: J.M.S.; Writing – original draft: J.H.; Writing – draft editing and finalizing: D.F.M.S.; Writing – review and editing: J.H., D.F.M.S., J.M.S., R.V.A.O.; Acquiring funding: R.V.A.O.

Conflicts of interest

There are no conflicts to declare.

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