SAINT PETERSBURG STATE UNIVERSITY

Lotsman Kristina Aleksandrovna

NUCLEOPHILIC ADDITION OF PHOSPHINOXIDES AND ALCOHOLS TO ACETYLENE GENERATED *in situ* FROM CALCIUM CARBIDE

Thesis
for the degree of candidate of chemistry sciences
Scientific specialty 1.4.3. Organic chemistry

Translation from Russian

Academic supervisor:
Doctor of Science in Chemistry
Rodygin Konstantin Sergeevich

Saint Petersburg
2024

TABLE OF CONTENTS

INTRODUCTION 4
CHAPTER 1. LITERATURE REVIEW 12
  1.1. Nucleophilic addition reactions to acetylene 13
    1.1.1. Superbasic medium 13
    1.1.2. Nucleophiles in addition reactions to acetylene 15
  1.2. Calcium carbide as *in situ* source of acetylene 27
    1.2.1. Reactions of nucleophilic addition to acetylene generated *in situ* from calcium carbide 29
    1. 2.2. Application areas of nucleophilic addition reactions to acetylene generated *in situ* from calcium carbide 31
  1.3. Conclusion from the literature review 32
CHAPTER 2. RESULTS AND DISCUSSION 34
  2.1. Selection of research objects 34
  2.2. Obtaining phosphine ligands such as 1,2-bis(phosphine)ethanes from phosphine oxides and calcium carbide 35
    2.2.1. Addition of phosphine oxides to acetylene generated *in situ* from calcium carbide 37
    2.2.2. Preparation of deuterium-labeled 1,2-bis(phosphine oxide)ethanes 41
    2.2.3. Preparation of 1,2-bis(phosphine)ethanes and their use as ligands 45
  2.3. Using the reaction of nucleophilic addition of alcohols to acetylene from calcium carbide for the cyclic production of acetaldehyde 50
    2.3.1. Vinylation 51
    2.3.2. Devinylation 53
    2.3.3. General vinylation-devinylation sequence 63
  2.4. Using the reaction of nucleophilic addition of alcohols to acetylene from calcium carbide for the cyclic production of polymers 69
    2.4.1. Preparation of monomers based on natural alcohols and calcium carbide 70
    2.4.2. Preparation of polymers based on synthesized vinyl ethers 73
    2.4.3. Thermal properties of polymers based on vinyl ethers of terpene alcohols 76

2.4.4. Pyrolysis of polymers based on vinyl ethers of terpene alcohols 77
2.4.5. Recycling of polymers based on vinyl ethers of terpene alcohols 87
2.4.6. Using the resulting polymers to production of material for 3D printing 89
CHAPTER 3. EXPERIMENTAL SECTION 106
3.1. Materials and instruments 106
3.2. Synthesis of initial phosphine oxides 109
3.3. Synthesis and characterization of 1,2-bis(phosphine oxide)ethanes 111
3.4. Synthesis and characterization of 1,2-bis(phosphine)ethanes 117
3.5. Synthesis and characterization of complexes with the obtained 1,2-bis(phosphine)ethanes 119
3.6. Acetaldehyde synthesis 121
3.7. Synthesis and characterization of vinyl ethers of terpene alcohols 123
3.8. Synthesis and characterization of polymers 127
3.9. Polymer pyrolysis 129
3.10. Obtaining material for 3D printing from the obtained polymers 130
CONCLUSION 132
LIST OF ABBREVIATIONS 133
ACKNOWLEDGMENTS 135
REFERENCES 136

INTRODUCTION

The relevance of the field of research and the degree of its development. Acetylene is a large-scale organic synthesis reagent. In the last century, many technological processes were based on acetylene, which have now been replaced by cheaper and safer processes based on ethylene, propylene and other hydrocarbon raw materials. In the last few years, in connection with the transition of the world community to sustainable chemistry and the circular economy, it has increasingly been suggested that there will be a return to acetylene as a “building block”, which can be obtained from renewable raw materials - coal.

Nucleophilic addition reactions to acetylene are a well-studied tool for introducing a vinyl group into the molecules of many nucleophiles. Often, these reactions are used to obtain a variety of monomers, but there are also works in which, using these reactions, the carbon chain is complicated, heterocyclic compounds and other compounds are obtained that were previously impossible to obtain in one step. Despite the large number of works devoted to the reactions of nucleophilic addition to acetylene, gaseous acetylene has significant disadvantages, such as explosion hazard, flammability, the use of special expensive equipment for working under pressure, difficulties in storage and transportation. All these disadvantages significantly limit the use of acetylene and make its use unsafe.

Calcium carbide is a convenient, safe and affordable source of acetylene. Currently, of particular interest is carrying out reactions with acetylene through the generation of acetylene directly during the reaction (*in situ*) from calcium carbide and water. This approach makes it possible to reduce the pressure in the system due to the slow hydrolysis of calcium carbide, the solubility of the resulting acetylene and its consumption during the reaction. However, at the same time, the formation of calcium hydroxide during hydrolysis, as well as changes in other reaction parameters, can affect the course of the process, which requires additional optimization of the conditions and study of reaction mechanisms. The possibility of introducing labels of deuterium and carbon-13 through varying the conditions of hydrolysis of calcium carbide, as well as easy dosing of the resulting acetylene, makes it possible to selectively modify the resulting product, which provides great advantages for carrying out reactions with *in situ* generation of acetylene compared to the direct use of acetylene gas.

Currently, many nucleophilic addition reactions have been carried out with *in situ* generation of acetylene from calcium carbide, including with O-, S-, N-nucleophiles to obtain the corresponding vinyl derivatives. However, to date, the use of this reaction has been limited exclusively to the production of monomers for the purpose of further polymerization.

The purpose and tasks of the thesis. The aim of this work was to expand the areas of application of the nucleophilic addition reaction to acetylene generated *in situ* from calcium carbide, by the example of reactions with phosphine oxides and alcohols.

To achieve this goal, the following tasks were solved:

1. Development and optimization of a method for producing deuterium-labeled and unlabeled 1,2-bis(phosphine oxide)ethanes from phosphine oxides and calcium carbide.
2. Synthesis of phosphine ligands from the resulting phosphine oxides.
3. Synthesis of nickel and palladium complexes with the resulting ligands.
4. Development, optimization and scaling up of a method for producing deuterium-labeled and unlabeled acetaldehyde through a sequence of vinylation and devinylation reactions of alcohols.
5. Synthesis of vinyl ethers of natural alcohols using calcium carbide and production of polymers based on them.
6. Study of the physical and thermal properties of the resulting polymers.
7. Pyrolysis of the resulting polymers based on terpene alcohols and the use of their decomposition products for the re-synthesis of polymers.
8. Using the resulting polymers to create a recyclable material for 3D printing.

The scientific novelty of the work lies in the development of new areas of application of nucleophilic addition reactions to acetylene generated *in situ* from calcium carbide: synthesis of deuterium-labeled and unlabeled phosphine compounds ligands, the cyclic method for producing acetaldehyde, as well as polymer materials from renewable raw materials.

Theoretical and practical significance of the work:

1. Development of new approaches to the synthesis of phosphine ligands from calcium carbide and phosphine oxides.
2. Development of new methods for obtaining deuterium-labeled phosphine ligands using calcium carbide.
3. Development of a method for alcohols vinylation by calcium carbide without a solvent.
4. Use of a variety of alcohols to synthesize acetaldehyde using a sequence of vinylation-devinylation reactions.
5. Development of a method for producing polymers from renewable raw materials: natural alcohols and calcium carbide.
6. Study of the thermal properties of the resulting polymers.
7. Study of the pyrolysis products of the resulting polymers and the mechanism of their formation.
8. Development of a method for processing the resulting polymers through pyrolysis with recycling of the resulting alcohol.
9. Using the resulting recyclable polymers from renewable raw materials to obtain material for 3D printing.

Structure and content of the thesis. The dissertation includes an introduction, literature review, discussion of results, experimental part and conclusion. The introduction reveals the relevance of the research, characterizes the degree of scientific development of the topic, defines the purpose and tasks of the work, and reveals the theoretical and practical significance. In accordance with the purpose of the thesis, the first part of the literature review is devoted to nucleophilic addition reactions to acetylene, the development of this reaction, the use of superbasic media and various nucleophiles used in this reaction. Due to the large number of disadvantages of using acetylene gas, the second part of the literature review is devoted to the use of calcium carbide in reactions as *in situ* source of acetylene. This part discusses the main differences between the use of calcium carbide and acetylene, and also presents the development of the nucleophilic addition reaction to acetylene with *in situ* generation from calcium carbide. It has been shown that the scope of this reaction is limited to the production of monomers for further polymerization.

The discussion of the results is divided into 3 main parts, each of which is devoted to a separate new direction in the use of nucleophilic addition reactions to acetylene generated *in situ* made of calcium carbide. The first part is devoted to the preparation of the 1,2-bis(phosphine)ethane type structure ligands from calcium carbide and phosphine oxides. This part discusses the optimization of the conditions for their preparation, the scope of the reaction, the preparation of deuterium-labeled ligands, as well as their use for synthesis of complexes with metal salts. The second part is devoted to the cyclic production of acetaldehyde from calcium carbide and various alcohols using a sequence of vinylation-devinylation reactions. This part discusses the optimization of both components of the process, the production of deuterium-labeled acetaldehyde, and the scaling of the reaction. The third part of the discussion of the results is devoted to the production and processing of polymers from renewable raw materials - natural alcohols and calcium carbide. In this part of the work, the sequence of obtaining polymers, their thermal properties are considered, the products of pyrolysis of polymers are studied, and the possibility of resynthesizing polymers from pyrolysis products is shown. In conclusion, scaling of vinylation and polymerization was carried out, and the possibility of using the resulting polymers to produce material for 3D printing was shown.

The experimental part outlines the methods of conducting experiments on the synthesis of substances, pyrolysis of polymers and the production of materials for 3D printing, as well as a description of the physical properties and spectral characteristics of the compounds obtained during the work.

Methodology and research methods. To study the structure of the compounds obtained during the work, modern physicochemical methods of analysis were used: ^{1}H, ^{13}C, ^{31}P, ^{2}H NMR spectroscopy, high-resolution mass spectrometry with electrospray ionization, gas chromatography-mass spectrometry (GC-MS) . For some complexes of the obtained ligands with metals, the structure was additionally confirmed using X-ray diffraction. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to study the thermal properties. Gel permeation chromatography (GPC) was used to determine the molecular weight of the polymers. Pyrolysis of polymers was carried out using a pyrolysis installation with further detection of the resulting products by GC-MS.

Degree of reliability and approbation of the research. The provisions presented in the work for defense are scientifically substantiated and reliably confirmed by experimental results. All physical and chemical measurements were carried out using modern certified equipment in the Science Park of St. Petersburg State University (Magnetic Resonance Research Centre, Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre, Thermogravimetric and Calorimetric Research Centre, Interdisciplinary Center for Nanotechnology, Center for Innovative Technologies of Composite Nanomaterials).

The materials of the dissertation work were presented at the following conferences: all-Russian scientific conference “Markovnikov Readings: Organic Chemistry from Markovnikov to the Present Day”, January 17–20, 2020, MSU Krasnovidovo Boarding House (oral and poster presentation); all-Russian scientific conference “Markovnikov readings: organic chemistry from Markovnikov to the present day”, October 8–11, 2021, Sochi (oral presentation); Scientific conference-school “New horizons of catalysis and organic chemistry”, May 19-20, 2022, IOC, Moscow (poster presentation); all-Russian scientific conference “Markovnikov readings: organic chemistry from Markovnikov to the present day”, September 16–21, 2022, Loo, Sochi (oral report); The Sixth International Scientific Conference “Organic Chemistry Inorganic and Coordination Chemistry Physical and Colloidal Chemistry”, September 26-30, 2022, Moscow (poster presentation); all-Russian conference with international participation “Ideas and legacy of A.E. Favorsky in organic chemistry”, July 3-6, 2023, St. Petersburg (oral report).

The work was carried out with the financial support of the Russian Science Foundation 21-73-20003, as well as a mega-grant from SPbSU (Pure ID: 92285019).

Based on the dissertation materials, 4 articles were published in journals indexed in the WoS and Scopus databases, as well as abstracts of 7 reports at national and international scientific conferences and school conferences.

Articles published based on the results of the dissertation:

1. Lotsman, K.A. Atom-economical synthesis of 1,2-bis(phosphine oxide)ethanes from calcium carbide with straightforward access to deuterium- and ^{13}C-labeled bidentate phosphorus ligands and metal complexes / K.A. Lotsman, K.S. Rodygin, I. Skvortsova, A.M. Kutskaya, M.E. Minyaev, V.P. Ananikov // Org. Chem. Front. – 2023. – Vol. 10. – No. 4. – P. 1022-1033.
2. Rodygin, K.S. Calcium Carbide Looping System for Acetaldehyde Manufacturing from Virtually any Carbon Source / K.S. Rodygin, K.A. Lotsman, V.P. Ananikov // ChemSusChem. – 2020. – Vol. 13. – No. 14. – P. 3679-3685.
3. Metlyaeva, S.A. Biomass- and calcium carbide-based recyclable polymers / S.A. Metlyaeva, K.S. Rodygin, K.A. Lotsman, D.E. Samoylenko, V.P. Ananikov // Green Chem. – 2021. – Vol. 23. – No. 6. – P. 2487-2495.
4. Lotsman, K.A. Syntheisis of Divinyl Ether from 5-Hydroxymethylfurfural (5-HMF) and Calcium Carbide / K.A. Lotsman, K.S. Rodygin // Russ. J. Gen. Chem. – 2022. – Vol. 92. – No. 11. – P. 2507-2510.

Main scientific results:

1. Lotsman, K.A. Atom-economical synthesis of 1,2-bis(phosphine oxide)ethanes from calcium carbide with straightforward access to deuterium- and ^{13}C-labeled bidentate phosphorus ligands and metal complexes / K.A. Lotsman, K.S. Rodygin, I. Skvortsova, A.M. Kutskaya, M.E. Minyaev, V.P. Ananikov // Org. Chem. Front. – 2023. – Vol. 10. – № 4. – P. 1022-1033.

A method has been developed for the synthesis of both labeled and unlabeled deuterium phosphine ligands using the reaction of nucleophilic addition of phosphine oxides to acetylene generated *in situ* from calcium carbide. It was shown that the synthesized ligands can be used to obtain palladium and nickel complexes.

The candidate carried out the optimization and synthesis of all ligands, both labeled and unlabeled with deuterium, the starting phosphine oxides, the reduction of the resulting 1,2-bis(phosphine oxide)ethanes, as well as the synthesis of complexes with metals. The candidate independently analyzed all NMR and mass spectra. The candidate interpreted the data obtained and prepared the initial draft of the publication.

2. Rodygin, K.S. Calcium Carbide Looping System for Acetaldehyde Manufacturing from Virtually any Carbon Source / K.S. Rodygin, K.A. Lotsman, V.P. Ananikov // ChemSusChem. – 2020. – Vol. 13. – № 14. – P. 3679-3685.

A cyclic method for the production of acetaldehyde has been developed using a sequence of reactions of vinylation of alcohols with the help of calcium carbide and hydrolysis of the resulting vinyl ethers in an acidic medium with complete recycling of products without the use of solvents.

The candidate optimized both stages of the acetaldehyde production process, product capture methods, and scaled up hydrolysis. The candidate independently analyzed all NMR spectra. The candidate carried out an interpretation of the data obtained, as well as an analysis of literary sources. The candidate was directly involved in writing the publication.

3. Metlyaeva, S.A. Biomass- and calcium carbide-based recyclable polymers / S.A. Metlyaeva, K.S. Rodygin, K.A. Lotsman, D.E. Samoylenko, V.P. Ananikov // Green Chem. – 2021. – Vol. 23. – № 6. – P. 2487-2495.

A method has been developed for the synthesis and processing of polymers from renewable raw materials: natural alcohols and calcium carbide. It has been shown that the resulting polymers decompose during pyrolysis to the original alcohols and the corresponding carbonyl compounds, which can be used to regenerate alcohol and re-produce polymers based on it.

The candidate carried out the synthesis of vinyl ethers and polymers together with student S.A. Metlyaeva. The candidate analyzed all GC-MS data, identified the main products of polymer pyrolysis and proposed mechanisms of their formation. The candidate independently carried out pyrolysis of polymers in a quartz tube, analyzed the resulting products, restored the resulting reaction mixture, and used the resulting alcohol to resynthesize polymers. The candidate investigated the thermoplastic properties of polymers. The candidate participated in writing the publication.

4. Lotsman, K.A. Syntheisis of Divinyl Ether from 5-Hydroxymethylfurfural (5-HMF) and Calcium Carbide / K.A. Lotsman, K.S. Rodygin // Russ. J. Gen. Chem. – 2022. – Vol. 92. – № 11. – P. 2507-2510.

A method has been developed for the synthesis of 2,5-bis(hydroxymethyl)furan divinyl ether, obtained from renewable 5-(hydroxymethyl)furfural, using the nucleophilic addition reaction of the corresponding alcohol to acetylene generated *in situ* from calcium carbide. It was shown that the synthesized ether can be used to obtain a cross-linked polymer.

The candidate carried out all synthetic procedures, including the synthesis of 2,5-di(hydroxymethyl)furan and its divinyl ether, as well as the preparation of a cross-linked polymer. The candidate independently analyzed all the data received, searched for literary sources and prepared the first draft of the publication.

Main findings of the dissertation to be defended:

1. Development of a method for the synthesis of 1,2-bis(phosphine) ethane ligands through the reaction of nucleophilic addition of phosphine oxides to acetylene generated *in situ* from calcium carbide.

2. Development of a method for producing deuterium-labeled 1,2-bis(phosphine) ethane ligands.

3. Development of a cyclic method for the production of acetaldehyde through a sequence of reactions of nucleophilic addition of alcohols to acetylene generated *in situ* from calcium carbide, and hydrolysis of the resulting vinyl ether.

4. Development of a cyclic method for producing polymers from renewable raw materials through the reaction of nucleophilic addition of natural alcohols to acetylene generated *in situ* from calcium carbide.

5. Patterns of pyrolysis of the resulting polymers.

6. Creation of materials for 3D printing from synthesized polymers.

CHAPTER 1. LITERATURE REVIEW

Acetylene is a large-scale industrial reagent. Due to its unsaturated structure, this hydrocarbon was a key building block on which industry was founded in the first half of the 20th century [1]. Later, many reactions involving acetylene were replaced by cheaper technologies based on ethylene, propylene and other hydrocarbon feedstocks. However, currently, due to the transition to sustainable development and a circular economy, it is increasingly suggested that there will be a reverse transition to acetylene as a key renewable raw material obtained from coal [2, 3] or methane [4], which makes acetylene chemistry again in demand and relevant today.

A huge contribution to the development of acetylene chemistry was made by such famous scientists as Kucherov M.G., Favorsky A.E., Reppe V.Yu., Shostakovsky M.F., as well as the current scientific supervisor of the Irkutsk Institute of Organic Chemistry, academician Trofimov B.A. Thanks to the works of these great scientists, many reactions involving acetylene became famous. In general, the chemistry of acetylene can be divided into several main areas (Figure 1.1), among which we can highlight the addition reactions of nucleophilic (nucleophilic addition reactions) and electrophilic reagents (electrophilic addition reactions) to acetylene, ethinylation reactions (introduction of an acetylene fragment), cycloaddition (preparation of aromatic and heterocyclic compounds), carbonylation (reactions with carbon monoxide), condensation and polymerization (production of dimers, oligomers and polymers of acetylene).

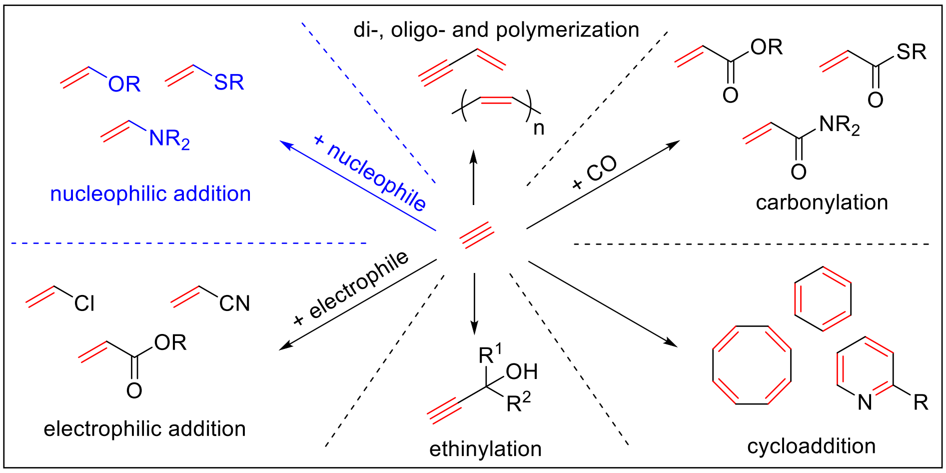
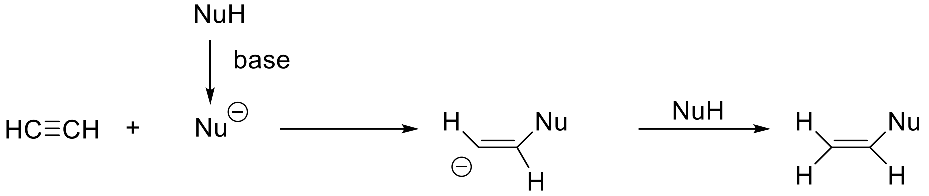


Figure 1.1. Main directions of acetylene chemistry

As can be seen from the Figure 1.1, the rich chemistry of acetylene allows one to obtain a wide variety of important products of organic synthesis during various transformations. In this dissertation research, we limited ourselves to the study and application of only nucleophilic addition reactions to acetylene.

1.1. Nucleophilic addition reactions to acetylene

Nucleophilic addition reactions to acetylene are reactions in which a nucleophilic species, often generated by a base, is added to an acetylene molecule (Scheme 1.1). These reactions are called vinylation reactions due to the introduction of the corresponding fragment into the molecule.

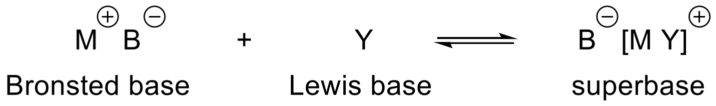


Scheme 1.1. General mechanism of nucleophilic addition to acetylene

For most of the 20th century, nucleophilic addition reactions to acetylene were carried out in the presence of alkalis, which was accompanied by the use of high temperatures and pressure. An example is the work of Reppe V.Yu. and Favorsky A.E. on the synthesis of vinyl ethers [5, 6]. Currently, superbasic media have been used for nucleophilic addition reactions to acetylene, which has made it possible to soften the reaction conditions [3, 7].

1.1.1. Superbasic medium

A superbase can be defined as a complex base consisting of a strong Brønsted base and a Lewis base that can specifically bind an alkali metal cation, thereby exposing an anion in a weakly anion-binding medium [8]. In general, this concept is depicted in Scheme 1.2, which is essentially a mirror image of the concept of superacidity. The scientific group of B.A. Trofimov has been actively developing and applying the concept of superbasicity since 1977 [9].

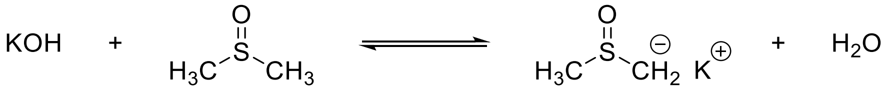


M = Li, Na, K, Rb, Cs;
B = carbanion, H, OH, OR, NH_2, NR_2;
Y = ethers (polyethers), amines (polyamines), NH_3, cryptands, sulfoxides, sulfones, amides, phosphine oxides, etc.

Scheme 1.2. Superbase concept

Carbanions, hydroxyl, alkoxides, and amines can act as superbase anions. And the complex-forming ligands for the cation (ion pair separators) are usually electron-donating dipolar aprotic solvents (DMSO, DMF and others), amines, ammonia, polyethers and other compounds that can selectively bind metal cations. Systems with a Hammett acidity function (*H_*) higher than 18.5 were classified as superbases [10].

The most accessible, studied and convenient is the superbasic KOH-DMSO system. The upper limit of the basicity of such a system is set by the acidity of DMSO (pKa = 35.1), while usually, if measures are not taken to remove water released during the formation of dimsilpotassium, then the acidity does not exceed 32 (on the *H_* scale) (Scheme 1.3). When the water content in DMSO is reduced to 25%, the system enters the superbasicity region (*H_* > 20). A further decrease in the water concentration in the system leads to increase in *H_* to 30–32 (for 99% DMSO).



Scheme 1.3. Formation of dimsilpotassium in KOH-DMSO medium

An interesting feature of this system is its self-adjustment (maintaining basicity at the same level due to water absorption). Since the concentration of dissolved KOH in DMSO is low (about 0.04 mol/L), the medium is a heterogeneous system with a solid alkali. Therefore, as water is released during the reaction, the solid phase can absorb excess water. Moreover, as the superbase is consumed in the reaction, the KOH concentration can also be replenished from the solid phase. From this point of view, the KOH-DMSO system resembles a phase-transfer catalytic system with anion transfer [8].

Superbasic systems are used to generate anions, including carbanions, and carry out elimination reactions. With their help, it is possible to deprotonate even thiophene and furan rings with subsequent splitting of the resulting carbanions to acetylene derivatives [8]. With acetylene, superbasic medium are used both for nucleophilic addition reactions to acetylene and for reactions of nucleophilic addition of acetylene (ethynylation) and triple bond migration reactions [9, 11]. Using a superbasic medium in nucleophilic addition reactions to acetylene, it was possible to vinylate methanol at atmospheric pressure in the liquid phase, involve allyl alcohol in the reaction, vinylate secondary acetylene alcohols, as well as chemo- and regioselectively vinylylate oximes and amidoximes, which can act as C-, N- and O-nucleophiles [7]. Many of these reactions were previously considered impossible or went very poorly.

Recently, a new generation of superbasic systems CsF-MOH-DMSO (M = Li, Na, K) has been developed. These systems showed higher vinylation activity acetoxime and polyhydric alcohols, which increased the yields of the corresponding products by 20–80% when the reaction temperature was reduced by 10 °C [10, 12]. The increased activity of these superbases is explained by the formation of CsOH, which is more basic than KOH, due to a shift in equilibrium towards the formation of poorly soluble fluorides (Scheme 1.4) [9].

$$\mathrm{CsF} + \mathrm{MOH} \rightleftharpoons \mathrm{CsOH} + \mathrm{MF}$$

$$\mathrm{M} = \mathrm{Li, Na, K}$$

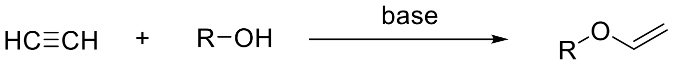
Scheme 1.4. Formation of CsOH in the CsF-MOH-DMSO system

Thus, carrying out reactions in superbasic medium allows one to significantly soften the conditions for carrying out reactions of nucleophilic addition to acetylene. Next, the most used nucleophiles in these reactions will be discussed.

1.1.2. Nucleophiles in addition reactions to acetylene

1.1.2.1. O-nucleophiles. Historically, the first type of nucleophiles, using which nucleophilic addition reactions to acetylene were discovered, are O-nucleophiles, namely alcohols. This reaction was first discovered by A.E. Favorsky in

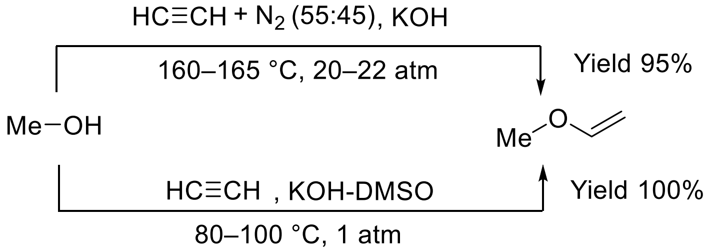
1888, but acquired practical significance only in the late 30s of the 20th century, mainly due to the systematic work of A.E. Favorsky's student - M.F. Shostakovsky and the emergence of demand for the products of this reactions [13]. Currently, the reaction of alcohols with acetylene is a convenient and widespread method for the synthesis of the corresponding vinyl ethers (Scheme 1.5). In industry, this method is widely used to obtain valuable monomers, for example, butyl vinyl ether, from which the world-famous antiseptic "Vinilin" (Shostakovsky balm) is obtained by polymerization.



Scheme 1.5. Preparation of vinyl ethers

A large variety of alcohols have been involved in nucleophilic addition reactions with acetylene. The general reaction mechanism corresponds to the mechanism presented in Scheme 1.1, where Nu = OR. The rate of vinylation depends on the nature of the alcohol and for aliphatic alcohols it decreases greatly in the order primary > secondary > tertiary. Vinylation of aromatic alcohols requires more stringent conditions: higher temperatures, more alkali and water. In this case, water prevents the polymerization of the resulting vinyl ethers and increases the rate of vinylation by increasing the amount of aryloxide ions [14].

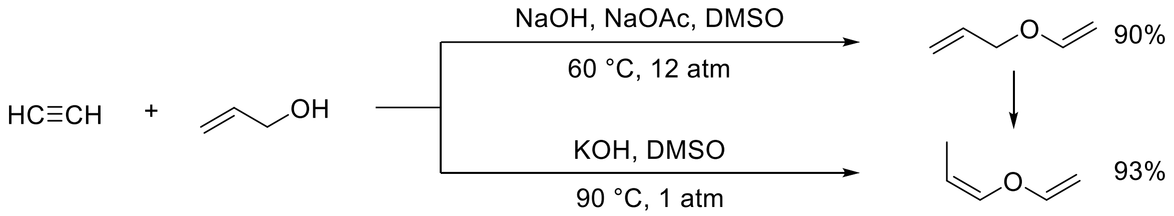
The use of superbasic conditions in reactions with alcohols made it possible to significantly soften the reaction conditions. For example, a comparison of reaction conditions for the vinylation of methanol in the presence of KOH and in the superbasic medium KOH -DMSO is presented in Scheme 1.6.



Scheme 1.6. Comparison of methanol vinylation conditions in a superbasic medium with conditions using KOH

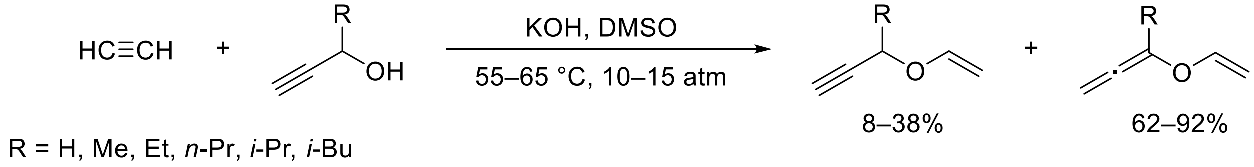
It can be noted that in a superbasic medium the product yield becomes quantitative, while the reaction temperature decreases by 60 °C and the pressure drops from 20 to 1 atmosphere [11].

The use of superbasic systems made it possible to involve allylic alcohols, which were previously considered unreactive, into the reaction. Depending on the process conditions, different products are obtained (Scheme 1.7). When vinylation allyl alcohol in a NaOH-NaOAc-DMSO medium and a pressure of 12 atmospheres, the product is vinyl ether of allyl alcohol, which quickly isomerizes into Z-1-propenyl vinyl ether. The latter product is also formed directly when the reaction is carried out in the KOH-DMSO system at atmospheric pressure [3].



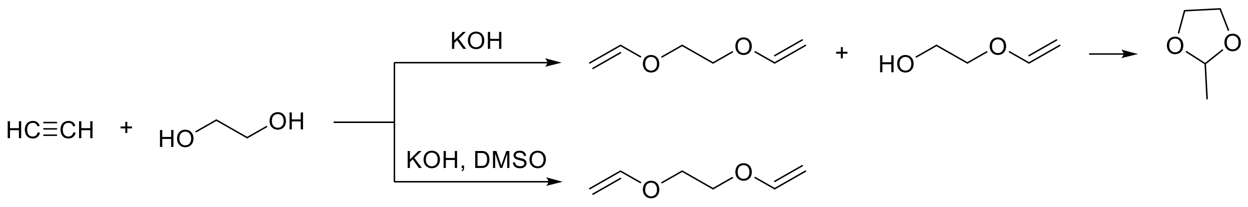
Scheme 1.7. Reaction of acetylene with allyl alcohols

Superbasic conditions also allowed for vinylation of propargyl alcohols (Scheme 1.8). In this case, depending on the substituent, the ratio of the products (vinyl ether of acetylene alcohol and the product of prototropic isomerization) changes, but the main one is the isomerization product [3, 15].

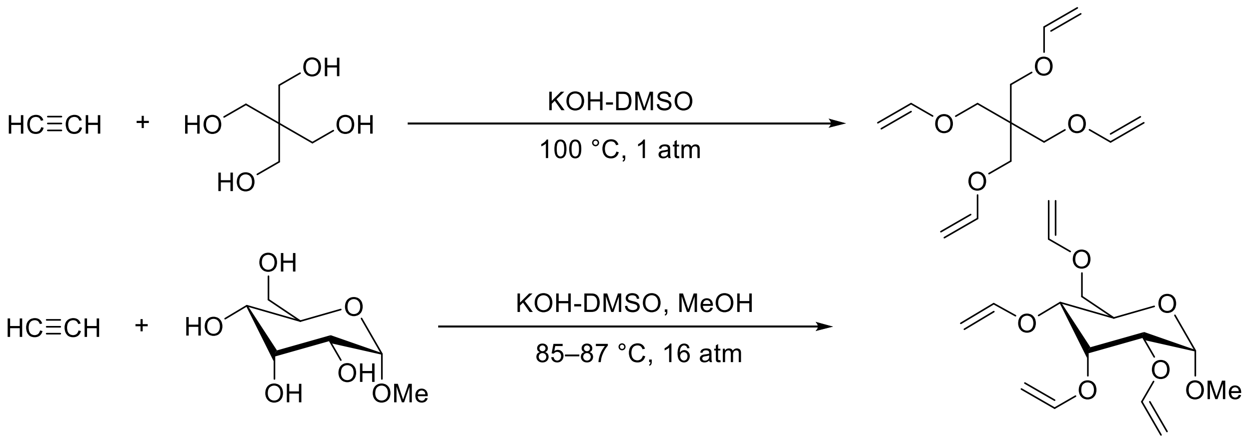


Scheme 1.8. Reaction of acetylene with propargyl alcohols

For a long time, it was difficult to obtain polyvinyl ethers of polyhydric alcohols due to their tendency to form internal acetals (Scheme 1.9) [11]. However, when carrying out the reaction in superbasic medium, it was possible to obtain ethylene glycol divinyl ether, as well as other polyvinyl ethers, including pentaerythritol [10] and glucose [16] (Scheme 1.10).

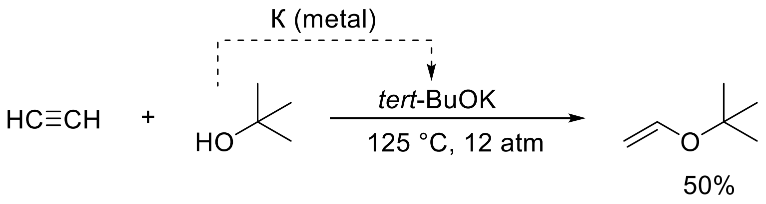


Scheme 1.9. Reaction of acetylene with ethylene glycol



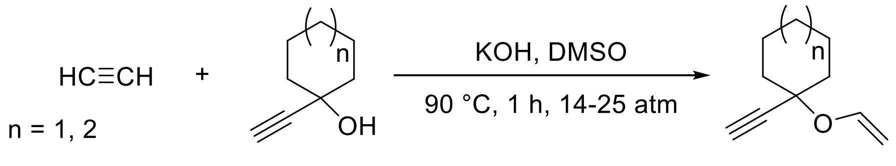
Scheme 1.10. Reaction of acetylene with polyhydric alcohols

The production of vinyl ethers of tertiary alcohols requires special conditions due to their lower reactivity compared to primary and secondary alcohols. For example, for vinylation *of tert*-butyl alcohol, potassium *tert*-butoxide generated *in situ* from potassium metal and *tert*-butyl alcohol (Scheme 1.11) [17].



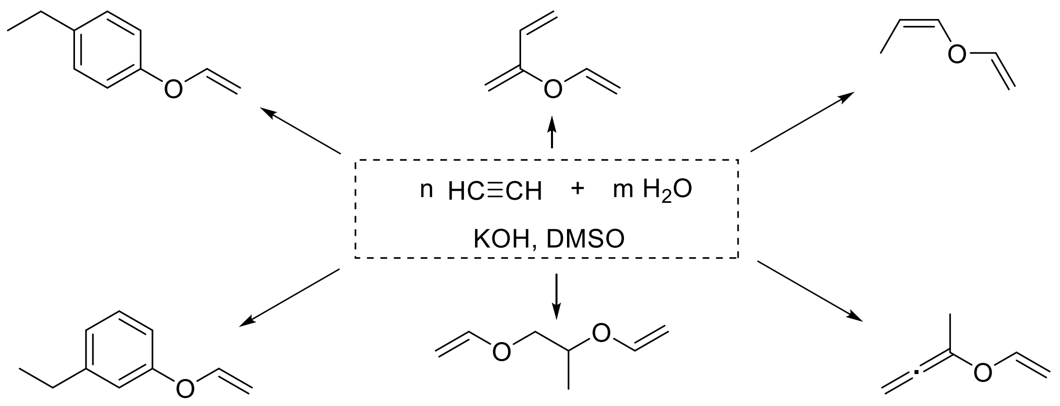
Scheme 1.11. Reaction of acetylene with tertiary alcohol

It is also known to obtain vinyl ethers of tertiary propargyl alcohols (Scheme 1.12). The yields in this reaction do not exceed 40% [18].



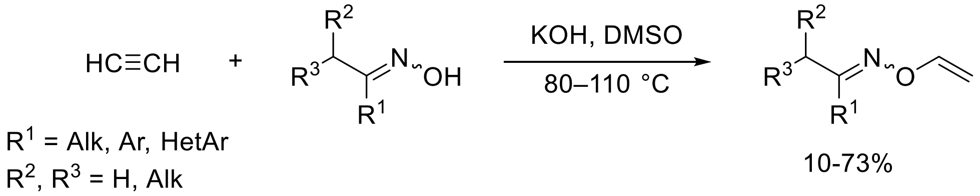
Scheme 1.12. Reaction of acetylene with tertiary propargyl alcohols

In addition to various alcohols, water can act as an O-nucleophile in the nucleophilic addition reaction to acetylene. In this case, instead of the expected ether, other products are formed, united by the general name “hydration polymerization of acetylene” (Scheme 1.13) [3].

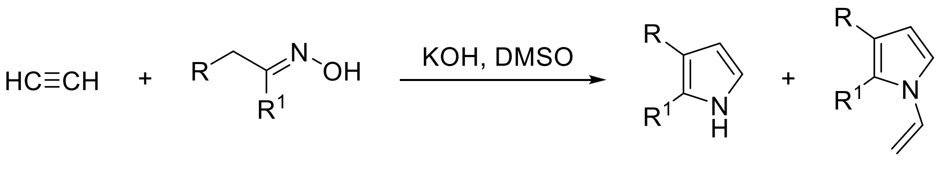


Scheme 1.13. Nucleophilic addition of water to acetylene

Other well-studied O-nucleophiles used in nucleophilic addition reactions to acetylene are oximes (Scheme 1.14). It is noteworthy that when using ketoximes containing at least one CH_2 group in the *α*-position to the oxime functional group, pyrroles are formed as a reaction product (Trofimov reaction) (Scheme 1.15) [3].

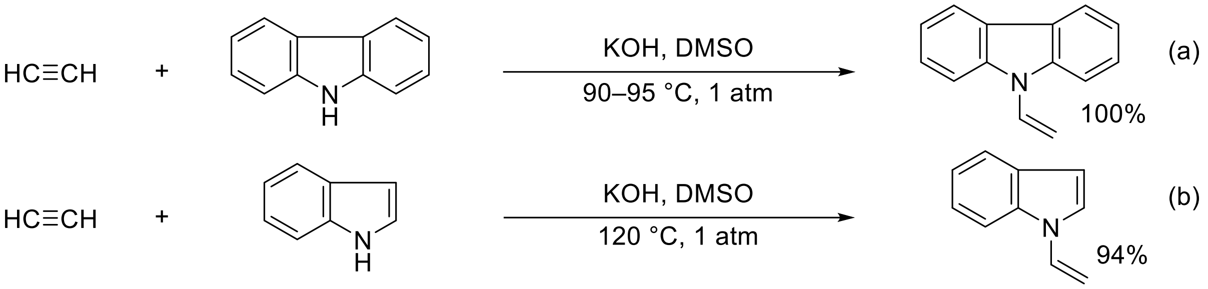


Scheme 1.14. Reaction of acetylene with oximes



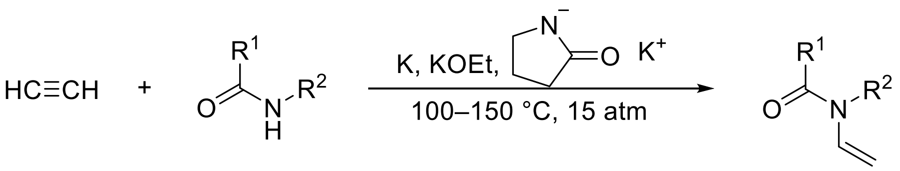
Scheme 1.15. Preparation of pyrroles from acetylene and ketoximes

1.1.2.2. N-nucleophiles. Historically, the reaction of nucleophilic addition to N-nucleophiles is associated with the works of Reppe V.Yu., in which N-vinyl derivatives of indole and carbazole were obtained [19]. The methodology for vinylation of N-nucleophiles was similar to the preparation of vinyl ethers: the corresponding heterocycle and acetylene were heated in a closed vessel under pressure in the presence of an alkali in a solvent (cycloalkanes or ethylene glycol). This methodology was later improved by using superbasic medium. Currently, processes have been developed for the production of important N-vinyl monomers - carbazole and indole at atmospheric pressure (Scheme 1.16) [11, 20]. Polymers based on these monomers are widely used to create fiber optic materials.



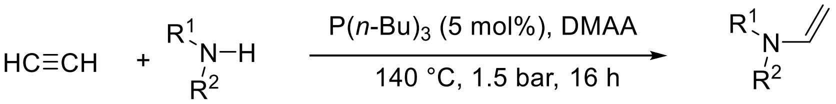
Scheme 1.16. Modern methods for the preparation of N-vinyl derivatives of carbazole (a) and indole (b)

A valuable industrial monomer is also N-vinylpyrrolidone, the polymer of which is widely used in medicine. In 1943, a technique was developed for the vinylation of lactams, including pyrrolidone, which is still used today (Scheme 1.17) [14, 21]. In this method, the base was formed *in situ* from potassium metal or for N-phenylacetamide, potassium ethoxide was used.



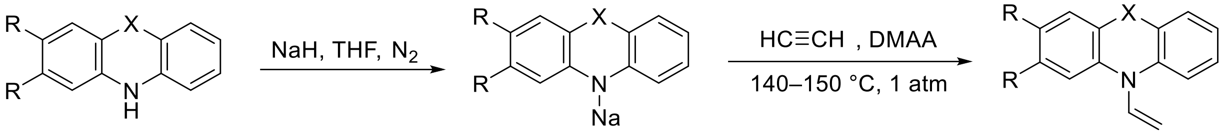
Scheme 1.17. Interaction of acetylene with lactams

To obtain N-vinyl derivatives of heterocyclic compounds, organocatalysis with phosphines was also used (Scheme 1.18) [22]. The key advantage of this method is the absence of high pressure in the system and the applicability of the reaction to a wide range of heterocyclic compounds.



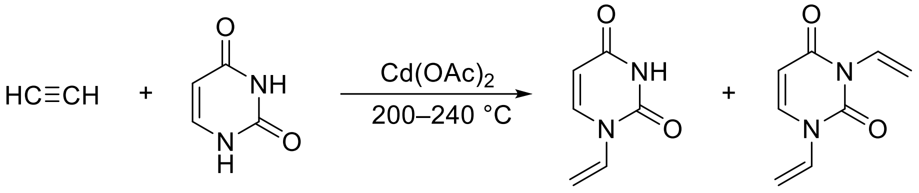
Scheme 1.18. Preparation of N-vinyl derivatives using phosphine catalysis

Sodium hydride can be used as a base for vinylation of diarylamines (Scheme 1.19) [23]. The reaction is carried out at atmospheric pressure, but in the first stage of the reaction hydrogen is released, which can pose a hazard during the reaction.



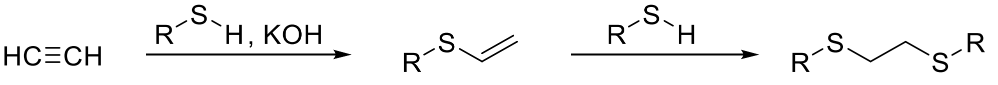
Scheme 1.19. Reaction of acetylene with diarylamines

To carry out vinylation of uracil, slightly basic cadmium acetate was used (Scheme 1.20) [24]. The reaction products are mono- and di-N-vinyl derivatives, and the yield of the mixture reaches 43%.



Scheme 1.20. Vinylation of uracil

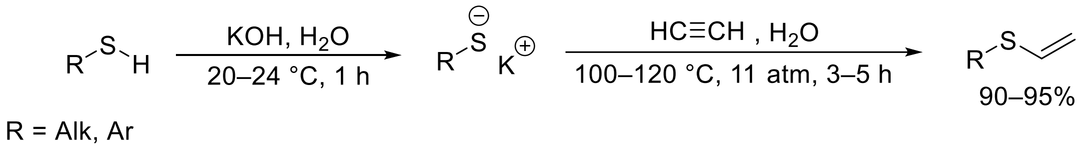
1.1.2.3. S-nucleophiles. The corresponding thiols are mainly used as S-nucleophiles, and in this case S-vinyl derivatives are formed [14]. The mechanism is similar to that presented in Scheme 1.1., where Nu = SR. Because sulfur is a stronger nucleophile than oxygen and nitrogen, reaction conditions with acetylene are usually milder than for O- and N-nucleophiles. However, it is worth considering that at temperatures above 100 °C, the resulting S-vinyl derivatives are prone to tarring, so the reaction is carried out at lower temperatures. Due to the high reactivity of S-nucleophiles, further addition of a thiol to the resulting S-vinyl derivative is possible (Scheme 1.21). To reduce the amount of double addition product, excess acetylene is used, as well as solvents in which acetylene is highly soluble (for example, DMSO and DMF) [25].



Scheme 1.21. Addition of thiols to acetylene

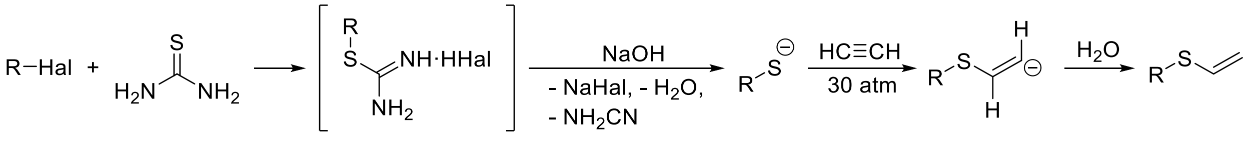
It was also assumed that the product of the double addition of a thiol to acetylene is formed *via* a radical pathway due to the presence of air in the system. This was confirmed by an experiment in which vinyl thioether was mixed in air with a thiol, and the reaction proceeded with the formation of their addition product against Markovnikov's rule [26]. Therefore, to reduce the amount of double addition product, it is necessary to carry out the reaction in the absence of air in the system.

To synthesize vinyl thioethers in Shostakovsky's works, the following process conditions were used: temperature 70–90 °C, solvent – dioxane, pressure – 30 atm, KOH as a base [25]. Under these conditions, the yields of vinylation products were 60–76%. Later, vinylation of thiols began to be carried out in an aqueous-alkaline medium using a large excess of alkali (Scheme 1.22) [27].



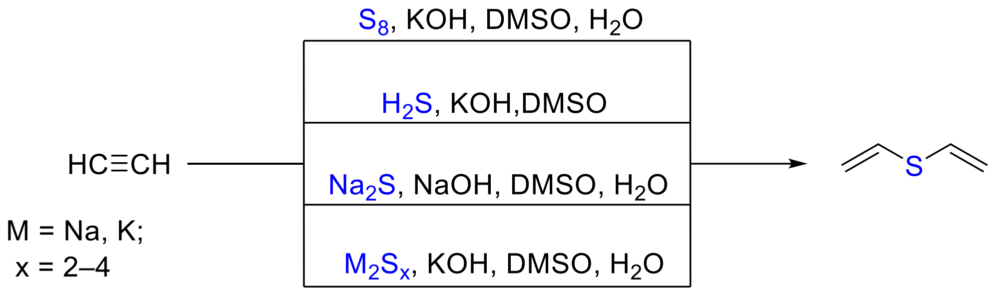
Scheme 1.22. Addition of metal thiolates to acetylene

Notably, the reaction between alkyl or aryl halides and thiourea can be used to generate the thiolate anion [28]. In this case, the reaction mechanism (Scheme 1.23) includes *in situ* formation of isothiouronium salt. In an alkaline medium, this salt breaks down into the corresponding thiolate anion and cyanamide. Next, interaction with acetylene occurs *via* the mechanism of nucleophilic addition. A wide range of vinyl thioethers have been synthesized using this methodology.



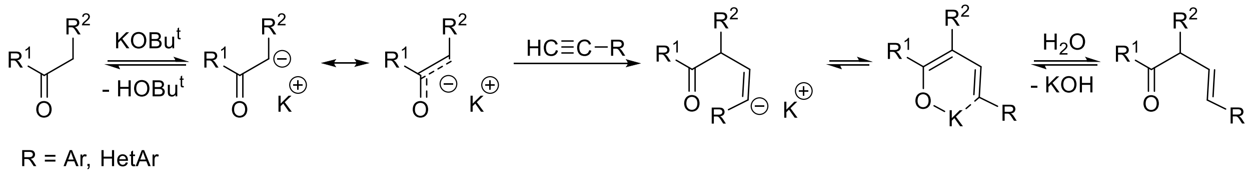
Scheme 1.23. Use of thioureas and halides to generate the thiolate anion and react with acetylene

Elemental sulfur, hydrogen sulfide, and potassium and sodium sulfides can also act as S-nucleophiles in nucleophilic addition reactions to acetylene [14, 29, 30]. In all cases, the reaction leads to divinyl sulfide (Scheme 1.24) and proceeds through the formation of the corresponding sulfur-containing anion, after which two acetylene molecules are sequentially added to the anion.



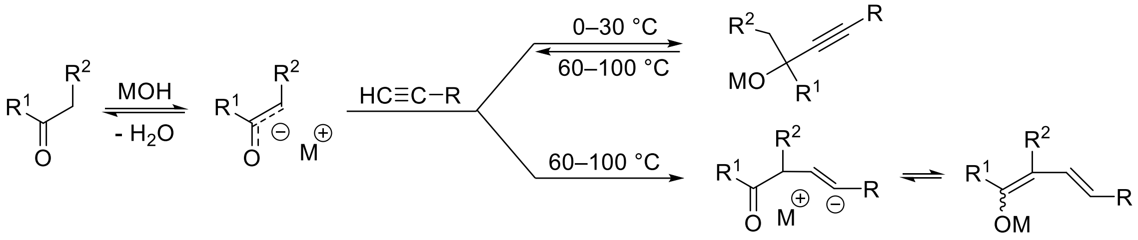
Scheme 1.24. Preparation of divinyl sulfide from acetylene

1.1.2.4. C-nucleophiles. Relatively newer (compared to the addition of O-, S-, N-nucleophiles) are the reactions of addition of anions to acetylene with charge localization on the carbon atom [7]. Ketones having hydrogen atoms in the *α*-position to the carbonyl group can be used as C-nucleophiles [31]. The interaction of such compounds with substituted acetylenes in a superbasic medium leads to the formation of *β*,*γ*-unsaturated ketones at elevated temperatures (Scheme 1.25) [32, 33].



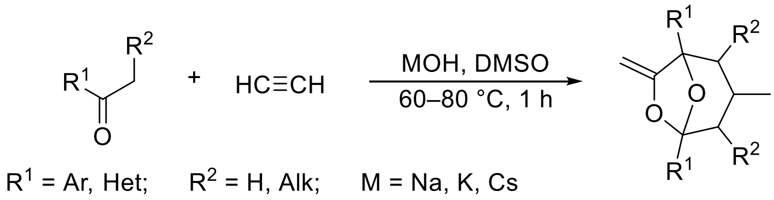
Scheme 1.25. Interaction of substituted acetylenes with ketones at elevated temperatures

It can be noted that this reaction occurs under the same conditions as the Favorsky reaction (formation of acetylene alcohols). However, unlike the Favorsky reaction, the nucleophilic addition to acetylene is irreversible, therefore, with increasing temperature, the product of the Favorsky reaction decomposes to the starting compounds (retro-Favorsky reaction), which enter into the C-vinylation reaction (Scheme 1.26) [32].



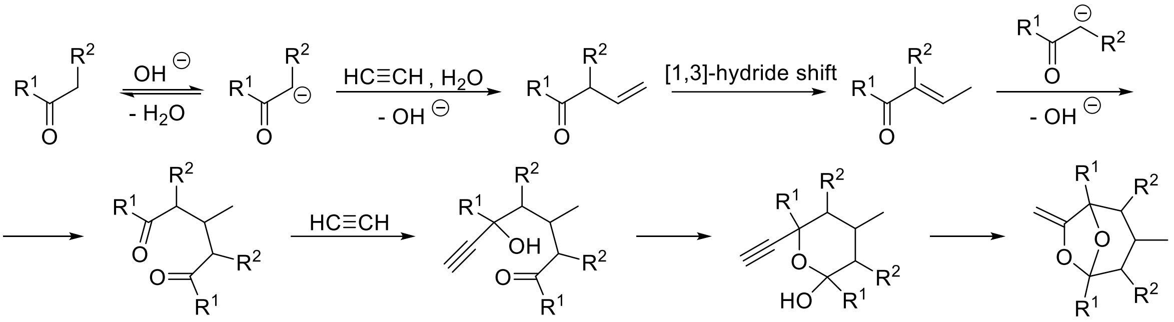
Scheme 1.26. Reaction direction of acetylenes with ketones depending on temperature

When carrying out this reaction with acetylene, the formation of products of a more complex structure is observed. In the first, the product from two ketone and two acetylene molecules was formed in a superbasic medium at a temperature of 60–80 °C and an pressure of 12 atm (Scheme 1.27) [34]. Product yields were up to 84%.



Scheme 1.27. Reaction of acetylene with ketones in a superbasic medium

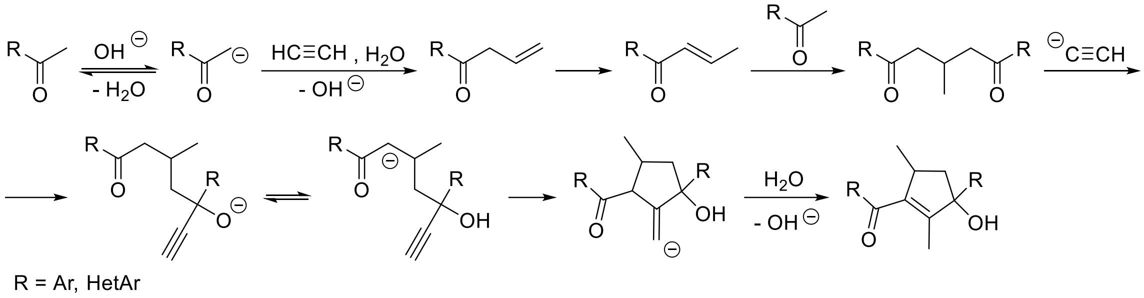
The authors of the work present the mechanism with Scheme 1.28. At the first stage of this process, a carbanion, formed from the initial ketone under the influence of a superbasic medium, is added to acetylene.



Scheme 1.28. Reaction mechanism

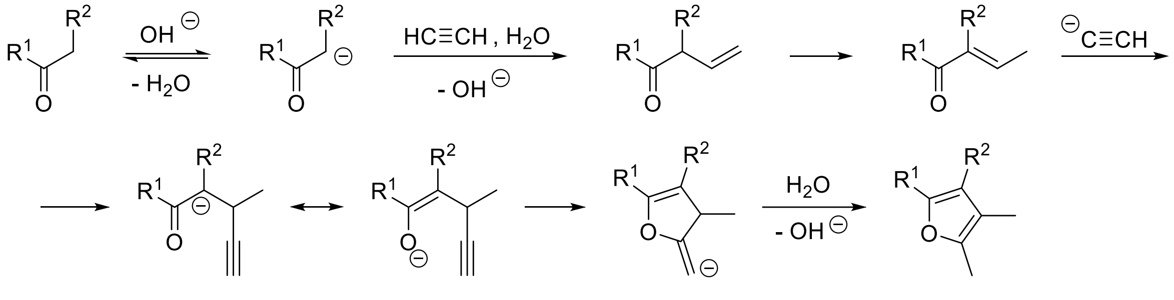
With methyl aryl ketones, in reaction with acetylene, a product of a different structure is formed (Scheme 1.29), also consisting of two ketone molecules and two acetylene molecules. The reaction begins with the nucleophilic addition of a carbanion, formed from a ketone, to acetylene. The reaction is carried out in a superbasic

KOH-DMSO medium at a temperature of 70 °C with a large excess of acetylene (12–14 atm). Product yields was 51–63% [35].



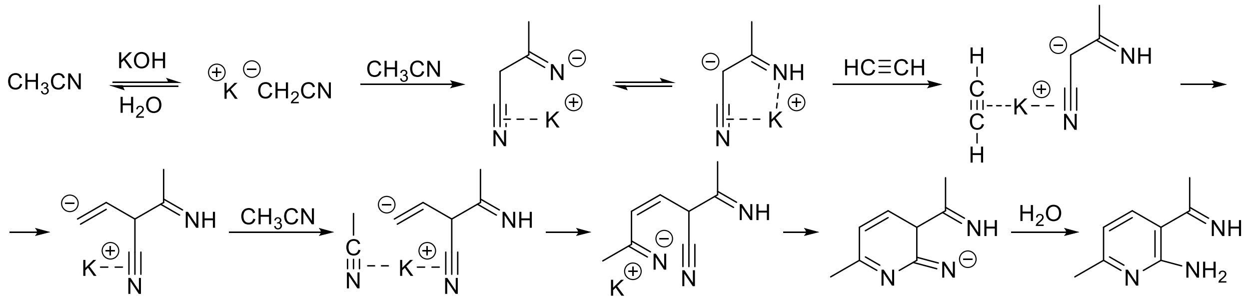
Scheme 1.29. Preparation of cyclopentenols from ketones and acetylene

Additionally, when ketones interact with acetylene, the formation of substituted furans is possible (Scheme 1.30) [36]. The reaction is carried out in a KOH-DMSO medium at a temperature of 90 °C and a pressure of 10 atm for 15 minutes. Product yields are up to 86%. The reaction mechanism is similar to the previous ones, however, after the [1,3]-hydride shift, the acetylide anion is added.



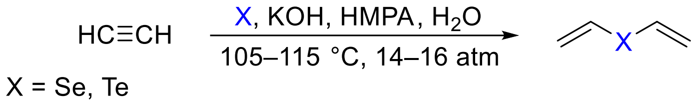
Scheme 1.30. Preparation of furans from acetylene and ketones

An example in which another C-nucleophile is used instead of a ketone is the synthesis of pyridine from acetylene and acetonitrile under superbasic conditions [37]. According to the mechanism presented by the authors of the article, one of the stages is the nucleophilic addition of a C-nucleophile to acetylene (Scheme 1.31).



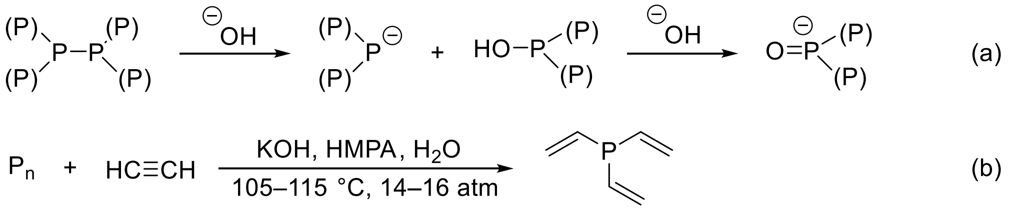
Scheme 1.31. Reaction of acetonitrile with acetylene

1.1.2.5. Other nucleophiles. In addition to the main O-, S-, N- and C-nucleophiles, to which many studies of reactions with acetylene are devoted, there are rare examples of addition reactions with other nucleophiles. Examples of such reactions can be the interaction under superbasic conditions of acetylene with elemental selenium and tellurium (Scheme 1.32) [38]. These reactions proceed in a similar way with elemental sulfur and lead to the formation of the corresponding divinyl derivative. The yield of the product with selenium is 60%, and with tellurium - 100%. In these reactions, the role of the superbase is not limited to catalysis; it also acts as a reagent and participates in the redox disproportionation of selenium and tellurium.



Scheme 1.32. Interaction of acetylene with elemental selenium and tellurium under superbasic conditions

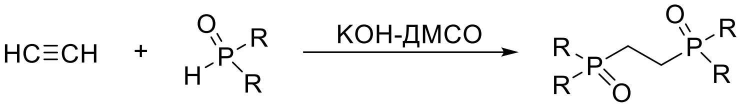
Elemental phosphorus (red and white) can also act as a nucleophile, since the P-P bond is easily cleaved under the influence of superbasic conditions to form phosphides and phosphinite anions, which can then attach to electrophiles (Scheme 1.33, a) [9]. This reaction is well known for substituted acetylenes and proceeds with the formation of the corresponding trivinyl derivatives. However, with acetylene this product is formed only in trace amounts (10%) (Scheme 1.33, b) [39].



Scheme 1.33. Reaction of elemental phosphorus with acetylene in a superbasic medium

Reactions with phosphine oxides and phosphines as P-nucleophiles for addition to acetylene are also known. It is noteworthy that the product of this reaction is not a vinyl derivative, but the product of the double addition of the corresponding nucleophile to acetylene (Scheme 1.34). This reaction was first carried out in the

1980s under phase-transfer catalysis conditions, passing acetylene through the reaction mixture [40]. Later, the addition reaction of phosphine oxides to acetylene was repeated under different conditions: superbasic (KOH-DMSO) [41] and using *tert* -BuOLi as a base in THF [42], in all cases the same double addition product of the nucleophile was formed in high yield.



Scheme 1.34. Reaction of acetylene with phosphine oxides

Thus, when considering the nucleophiles used in the addition reaction to acetylene, the most studied reactions are O-, S-, N-vinylation, during which the corresponding vinyl derivatives are formed. Recently, reactions with C-nucleophiles, which are of interest from the point of view of self-organization of simple molecules into complex structures, have attracted much attention. Notably, reactions with other nucleophiles – elemental sulfur, selenium, tellurium and phosphorus lead to addition products of several acetylene molecules. Reactions with phosphine oxides end with the formation of the product of double addition of a nucleophile to acetylene.

1.2. Calcium carbide as *in situ* source of acetylene

Despite the active development of acetylene chemistry, the use of acetylene gas is accompanied by significant disadvantages that significantly limit the scope of its application (Figure 1.2) [43]. Among the main disadvantages are the risk of explosion, flammability, difficulties with storage and transportation, the use of special expensive equipment for working under pressure, and, as a result, special safety precautions. Due to these disadvantages, many acetylene-based technologies were later replaced by technologies using safer and more readily available resources. Also, a big disadvantage of acetylene from the point of view of modern chemistry, aimed towards sustainable development, is the non-renewability of the main raw materials from which acetylene is obtained (petroleum). Due to these disadvantages of acetylene gas, interest has recently increased in the use of calcium carbide as *in situ* source of acetylene.

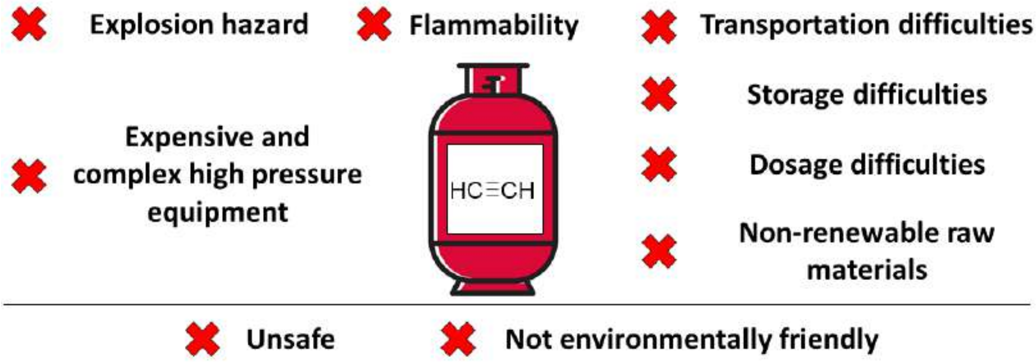


Figure 1.2. Disadvantages of using acetylene gas

Calcium carbide is called “solid acetylene”, and unlike acetylene from a gas cylinder, it is non-explosive, non-flammable, and can be worked with in laboratory containers for working under low pressure [44]. Storage, transportation and work with calcium carbide is not difficult and does not require special safety precautions. Since calcium carbide is solid, it is easy to dose and an equimolar amount of acetylene generated *in situ* (that is, directly in the reaction mixture), without creating high pressure. Due to the fact that calcium carbide can be obtained from almost any carbon source [45], including waste and biomass, it can be considered a renewable raw material [46]. Thus, calcium carbide is a convenient, safe and environmentally friendly source of acetylene, meeting modern requirements for “sustainable development”.

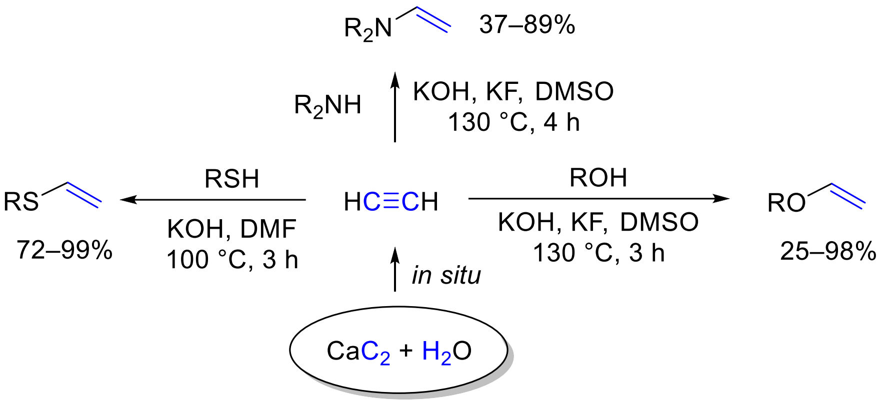
It is worth noting that the use of calcium carbide *in situ* introduces its own characteristics into the vinylation reaction, which are not present when using acetylene from a cylinder. Firstly, the release of acetylene during the hydrolysis of calcium carbide in DMSO or DMF (solvents that readily dissolve both water and the resulting acetylene) occurs slowly. This allows acetylene to react and be consumed as it is formed, without thereby creating large pressures in the system [43]. Secondly, during the hydrolysis of calcium carbide, calcium hydroxide is formed, which is also a base and can contribute to the reaction. Thirdly, it was shown that the addition of potassium fluoride can affect the yield of the resulting vinyl ether, which may be due both to the direct participation of the fluoride anion in the vinylation mechanism, and to the etching and renewal of the calcium hydroxide surface covering the during the reaction, still unreacted calcium carbide [47]. All these features allow us to conclude that reactions using calcium carbide with the generation of acetylene *in situ* are different from those that use acetylene from a cylinder, and therefore require separate optimization of conditions and study of reaction mechanisms and products.

In addition to the mentioned features, reactions with calcium carbide have greater flexibility in terms of modification of the resulting products. Thus, the use of D_2O, instead of H_2O during the hydrolysis of calcium carbide allows the generation of acetylene-d_2, which can undergo further transformations, retaining the deuterium mark. In addition, the use of ^{13}C-calcium carbide allows the introduction of a ^{13}C label through the generation of $^{13}C_2$-acetylene. And the use of a combined approach (D_2O and ^{13}C-calcium carbide) opens up access to the production of $^{13}C_2$-acetylene-d_2 and corresponding compounds containing both labels at once. Each of these approaches has been actively studied by our research group recently [48-53]. Another possibility of flexible modification using calcium carbide can be achieved due to the ability to dose the desired amount of acetylene during the reaction. Using this feature, it is possible to introduce the required number of vinyl groups into a molecule with several reaction centers [47].

Therefore, the use of calcium carbide as *in situ* source of acetylene opens up great opportunities, both from a safety and environmental point of view, and from the point of view of product modification.

1.2.1. Reactions of nucleophilic addition to acetylene generated *in situ* from calcium carbide

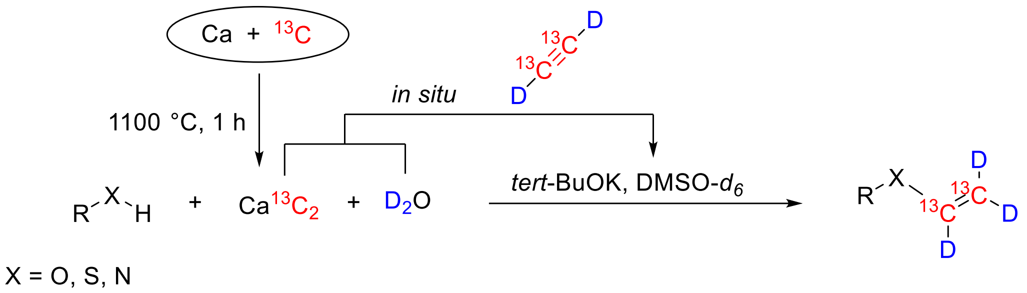
Our laboratory is actively studying reactions with calcium carbide. For the nucleophilic addition reaction under superbasic conditions, methods have been developed for the vinylation of thiols [54, 55], amines [56] and alcohols [47], including carbohydrates [57] and natural alcohols [58, 59], as well as disulfides and diselenides [60], using *in situ* generation of acetylene from calcium carbide. The general approach to vinylation of the corresponding O-, S-, N-nucleophiles is shown in Scheme 1.35. In all cases, the yields of the corresponding vinyl derivatives are quite high (up to 99%).



Scheme 1.35. Methods for obtaining vinyl derivatives from O-, S-, N-nucleophiles and calcium carbide, developed by our scientific group

Other scientific groups are also actively developing the use of calcium carbide [61, 62]. For nucleophilic addition reactions to acetylene generated *in situ* from calcium carbide, methods have been developed for the vinylation of alcohols [63], including aromatic [64] and polyhydric [65]. In these reactions, Cs_2CO_3 is often used as a base. Also, using calcium carbide, a method for vinylation of methanol in water has been developed [66]. An interesting reaction is vinylation epoxides and aryl ethers, accompanied by cleavage of the C-C bond [67]. Methods for the vinylation of primary aromatic amides [68] and sulfonamides have been developed in the reactions of calcium carbide with N-nucleophiles [69].

Calcium carbide has also been used to produce deuterium [50], carbon-13 [51] or doubly labeled (deuterium and carbon-13) [53] vinyl derivatives (Scheme 1.36). To introduce the deuterium label, the reaction is carried out in DMSO-d_6 and D_2O is used instead of H_2O to hydrolyze calcium carbide. In this case, the degree of deuterium inclusion (DI) is usually 95–99%. Since the reaction is carried out in the basic medium, labile protons, including those in the initial nucleophiles (at the O-H, S-H and N-H bonds), are also replaced by deuterium. To introduce the ^{13}C-label, calcium carbide is synthesized separately in a tube furnace from carbon-13 and calcium at 1100 °C, and then a further vinylation reaction is carried out with the resulting calcium carbide-$^{13}C_2$.

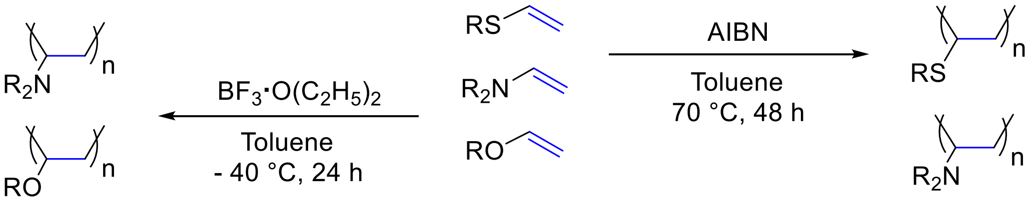


Scheme 1.36. Introduction of deuterium or carbon-13 ladels by calcium carbide (using the example of introducing both tags simultaneously)

Therefore, the use of calcium carbide as *in situ* source of acetylene in nucleophilic addition reactions allows one to safely obtain the corresponding O-, S-, N-vinyl derivatives with a controlled amount of vinyl groups, and also, if necessary, introduce deuterium and carbon-13 labels.

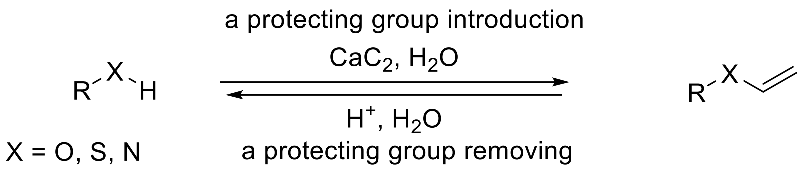
1. 2.2. Application areas of nucleophilic addition reactions to acetylene generated *in situ* from calcium carbide

Currently, most reactions of nucleophilic addition to acetylene from calcium carbide are used to obtain monomers for the further synthesis of polymers of both linear and network structure [70]. For vinyl ethers, cationic polymerization is usually used, for S-vinyl derivatives, radical polymerization is used, and for N-vinyl derivatives, both polymerization mechanisms are realized. Our scientific group has developed methods for the polymerization of the resulting O-, S-, N-vinyl derivatives [56, 57] (Scheme 1.37), including those labeled with carbon-13 [51] and D [50].



Scheme 1.37. The main methods of polymerization of O-, S-, N-vinyl derivatives (on the left - cationic polymerization, on the right - radical)

In addition to the synthesis of polymers, vinylation reactions with calcium carbide can be used to introduce a protecting group that is stable under basic conditions and can be easily removed by acid hydrolysis [71] (Scheme 1.38).



Scheme 1.38. Using the reaction of nucleophilic addition to acetylene through calcium carbide to introduce a protecting group

Thus, the use of nucleophilic addition reactions to acetylene generated *in situ* from calcium carbide, is currently limited to the production of polymers and the use of a protecting (vinyl) group for the introduction.

1.3. Conclusion from the literature review

An analysis of the literature showed that the chemistry of acetylene, discovered and widely studied back in the last century, is now again experiencing its renaissance (Figure 1.3). The use of superbasic medium allowed many reactions with acetylene to be carried out under much milder conditions. And the use of calcium carbide as *in situ* source of acetylene has opened up great opportunities both from a safety point of view and from the point of view of the development of chemical technology in the “sustainable development” paradigm. Due to the peculiarities of the formation of acetylene generated *in situ* from calcium carbide, these reactions may differ significantly from reactions carried out with acetylene gas. Therefore, this area requires separate study, both from the standpoint of optimizing conditions and using existing syntheses, and from the standpoint of reaction mechanisms.

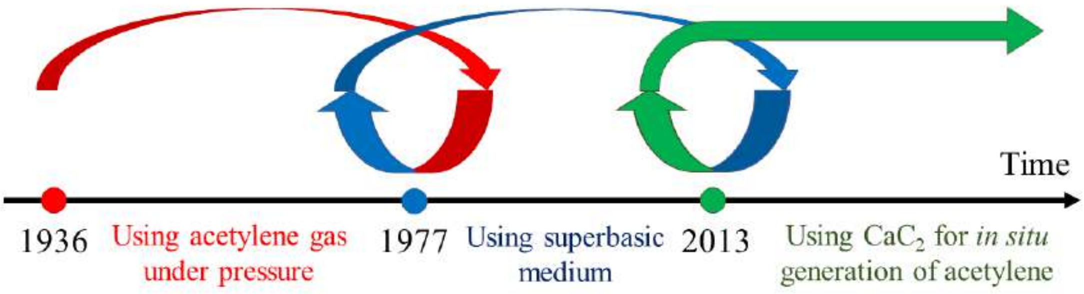


Figure 1.3. Cyclical development of nucleophilic addition reactions to acetylene

Nucleophilic addition reactions to acetylene in a superbasic environment are a widely studied method for the preparation of various vinyl derivatives. Many of these reactions have now been successfully transferred to calcium carbide. However, to date, the scope of application of such reactions is limited to the production of monomers for further polymerization. Therefore, the goal of this work was to expand the areas of application of nucleophilic addition reactions to acetylene from calcium carbide.

CHAPTER 2. RESULTS AND DISCUSSION

2.1. Selection of research objects

To expand the scope of applicability of nucleophilic addition reactions to acetylene generated *in situ* from calcium carbide, 3 main directions were chosen: the use of the reaction with phosphine oxides for the synthesis of phosphorus ligands (1); the use of reactions with alcohols for the cyclic production of acetaldehyde (2) and polymer materials from renewable raw materials (3). In accordance with each area of use, this section of the dissertation research is divided into corresponding subchapters (2.2–2.4).

Calcium carbide was chosen as a source of acetylene because it is a cheap, accessible and safe reagent. In addition, unlike explosive acetylene gas, calcium carbide is easy to dose and there is no need for specialized laboratory equipment (autoclaves) since most laboratory techniques can be carried out in low-pressure laboratory vessels. By varying the hydrolysis conditions of calcium carbide, it is possible to introduce deuterium or carbon-13 labels into the product molecule, which can be useful in the preparation of substances used to study reaction mechanisms or in the synthesis of drugs. Additionally, calcium carbide can be produced from many carbon sources, including waste, making it renewable. Since the topic of renewability is one of the key topics in some sections of this work, the choice of calcium carbide instead of acetylene was important.

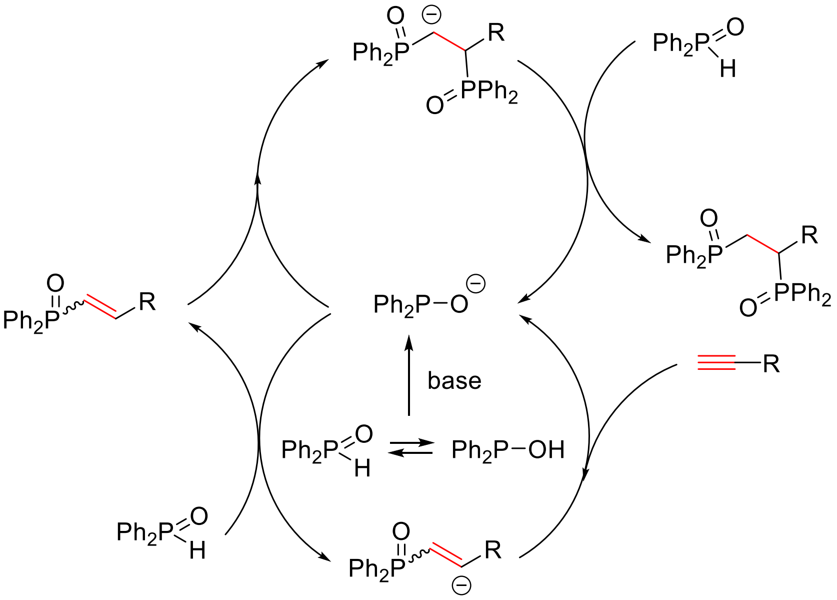
In subchapter 2.2. the addition of phosphine oxides to acetylene from calcium carbide is considered as a method for creating 1,2-bis(phosphine) ethane ligands and complexes based on them. This reaction has not been studied for calcium carbide, so it was chosen for the current study. Unlike other reactions of nucleophilic addition to acetylene, the reaction with phosphine oxides proceeds with the formation not of a vinyl derivative, but of a double addition product of a nucleophile. This feature could potentially be exploited to produce widely sought-after phosphorus ligands. Phosphine oxides are safer raw materials for the production of phosphine ligands than phosphines themselves, so phosphine oxides were used in the reaction. In this work, available aromatic and aliphatic phosphine oxides, obtained using Grignard reagents obtained from the corresponding bromides and diethyl phosphite or by oxidation of the corresponding phosphines, were used for addition to acetylene.

In subchapter 2.3. the use of the reaction of nucleophilic addition of alcohol to acetylene generated from calcium carbide in the absence of a solvent to create a cyclic method for the synthesis of acetaldehyde is shown. Acetaldehyde was chosen as the object of study, since it is a large-scale organic synthesis reagent used to obtain heterocyclic compounds, as well as other large-scale substances and materials. Cheap and available alcohols of various structures, including di- and triatomic ones, were chosen as alcohols for the vinylation reaction.

In the final subchapter 2.4. the reaction of the nucleophilic addition of natural alcohols to acetylene generated from calcium carbide is used to create a cyclic method for the production and processing of polymers from renewable raw materials. Available terpene alcohols, alcohols used in the perfume industry, and the so-called platform-compound 5-hydroxymethylfurfural (5-HMF) were selected as natural alcohols.

2.2. Obtaining phosphine ligands such as 1,2-bis(phosphine)ethanes from phosphine oxides and calcium carbide

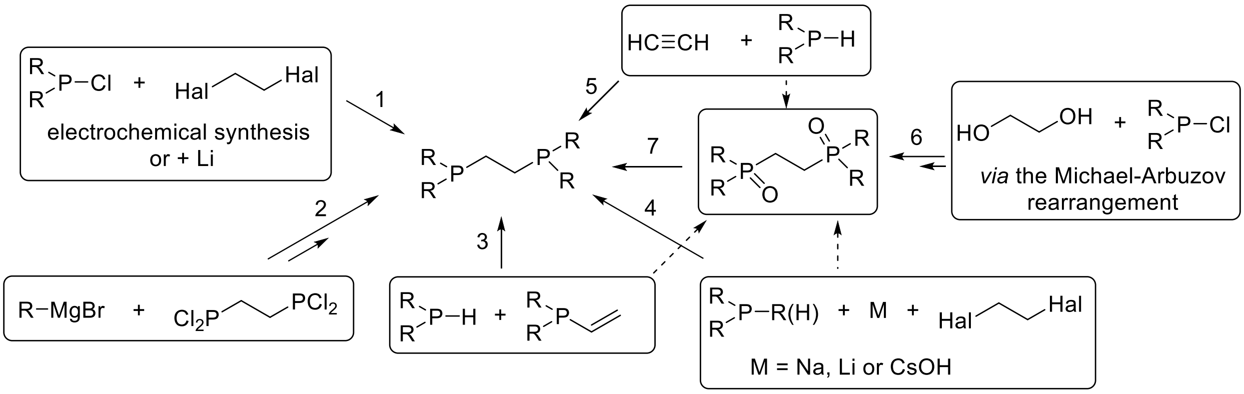
As shown in the literature review, most nucleophilic addition reactions to acetylene occur in a superbasic medium to form the corresponding vinyl compounds (O-, S-, or N-). These reactions have been well studied for both acetylene gas from a cylinder (carried out in an autoclave) and calcium carbide (*in situ* generation of acetylene). Other important nucleophiles are phosphine oxides. The interaction of acetylene gas with phosphine oxides was previously studied by other scientific groups [41, 42, 72, 73]. It is noteworthy that in all cases, instead of the formation of the corresponding vinyl derivative, the product of the double addition of phosphine oxide to acetylene is formed. It was suggested in [73] that double addition under superbasic conditions may be due to the electron-withdrawing effect of the phosphine oxide group, which facilitates the addition of the nucleophile. At the same time, it was suggested that a radical mechanism for this reaction is possible [42]. However, carrying out the reaction in the presence of a radical trap (TEMPO) showed that the reaction also proceeds with a high yield of the double addition product. Therefore, the authors of the work came to the conclusion that the radical mechanism is not the main one and proposed a mechanism based on nucleophilic addition (Scheme 2.1).



Scheme 2.1. The mechanism of interaction of diphenylphosphine oxide with alkynes, proposed in [42]

Since the methods for carrying out the reaction of acetylene generated *in situ* from calcium carbide, with phosphine oxides is unknown, and potentially this reaction may be the key to the synthesis of the corresponding phosphine oxides ligands, one of the objectives of this research was to study the interaction of calcium carbide with phosphine oxides and develop a method for obtaining phosphine ligands.

For comparison, ligands of a similar structure (such as 1,2-(bisphosphine)ethanes) were previously obtained using the following methods (Scheme 2.2). The approach 1 is electrochemical synthesis from the corresponding 1,2-dihaloethane and (diorgano)phosphine chloride [74] or synthesis from the same reagents and lithium [75]. Recently, method (approach 2) has been proposed, which consists of reacting a Grignard reagent with the corresponding phosphine dichlorides [76]. Phosphine ligands can also be prepared by the addition of phosphine to the corresponding P-vinyl derivative (approach 3) [77]. The most used is approach 4, based on the alkylation of phosphine with 1,2-dihaloethane in the presence of an alkali metal (often sodium or lithium) [78, 79], recently CsOH has been used instead of the metal and the reaction has been carried out with R_2PH [80, 81]. Also, as was shown in the literature review, the reaction for producing phosphine compounds is known ligands through the interaction of phosphines with acetylene (approach 5). In approaches 3, 4 and 5, instead of phosphines, the corresponding phosphine oxides are also used (arrows indicated by dotted lines in the Scheme) [42]. The desired phosphine oxide can also be prepared by reacting ethylene glycol with phosphine chloride *via* the Michael-Arbuzov rearrangement of the resulting intermediate (approach 6) [82]. Reduction of the resulting phosphine oxide also provides access to 1,2-bis(phosphine)ethanes (approach 7). It is worth noting that most of these reactions are not addition reactions, that is, they are not atom-efficient, which leads to the formation of a large amount of waste.



Scheme 2.2. Known approaches to 1,2-bis(phosphine)ethanes preparation

The preparation of deuterium-labeled 1,2-bis(phosphine)ethanes is limited to only one known preparation method (approach 4 of Scheme 2.2) [78]. In this method, triphenylphosphine reacts with sodium and 1,2-dibromoethane-d_4.

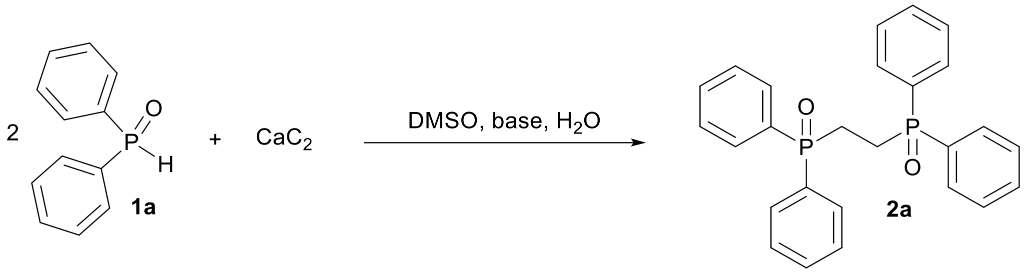
Thus, in the course of this chapter, the task was set to develop a universal method for the preparation of phosphine ligands of the DPPE type, both labeled and unlabeled with deuterium from calcium carbide and phosphine oxides.

2.2.1. Addition of phosphine oxides to acetylene generated *in situ* from calcium carbide

To optimize the nucleophilic addition reaction to acetylene generated *in situ* from calcium carbide, available diphenylphosphine oxide was selected (Table 2.1).

As a starting point, we took the superbasic conditions previously used by our research group to carry out vinylation reactions of alcohols using calcium carbide [47].

Table 2.1. Reaction optimization of phosphine oxide with calcium carbide [a]



Entry	Solvent	Base	T, °C	Time, h	Conversion, [b] mol%
1	DMSO	KOH, [c] KF [d]	100	1	21
2	DMSO	-	25	1	0
3	DMSO	-	50	1	2
4	DMSO	-	80	1	14
5	DMSO	-	130	1	96
6	Toluene	-	100	1	11
7	Chloroform	-	100	1	3
8	Dioxane	-	100	1	6
9	DMSO	-	130	2	99
10 [e]	DMSO	-	130	2	81
11	DMSO	KOH [c]	100	1	20
12	DMSO	KF [d]	100	1	60
13	DMSO	*tert*-BuOK [d]	100	1	20
14	DMSO	KF [d]	25	1	27
15	DMSO	KF [d]	25	16	100

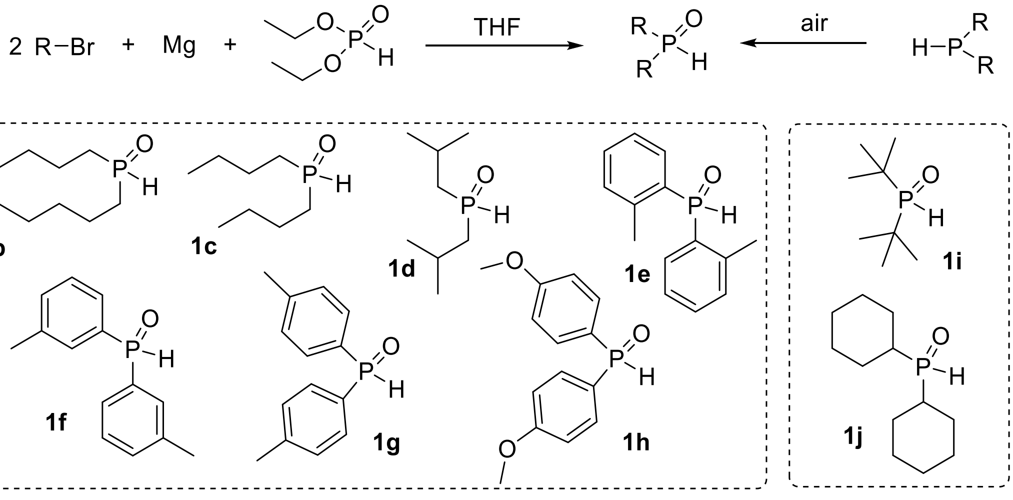
[a] Reaction conditions: 64 mg (1 mmol) calcium carbide, 50 mg (0.25 mmol) diphenylphosphine oxide, base, 0.5 ml solvent and 36 µl (2 mmol) water were placed in an 8 ml pressure tube. The cap was screwed on and the reaction mixture was stirred at the temperature and time specified in the table. [b] The conversion of phosphine oxide to the product is indicated, determined from the ratio of the corresponding signals in the ^{31}P NMR spectra. [c] 0.28 mmol. [d] 0.3 mmol. [e] 2 ml DMSO.

Carrying out the reaction under standard superbasic conditions resulted in product **2a** (entry 1), as in previous work by other scientific groups. It is noteworthy that no P- or O-vinyl compound was detected during the reaction, even in trace amounts. In an attempt to find the conditions under which the corresponding vinyl compounds are formed, the temperature conditions of the process were varied in DMSO (entries 2–5) and other solvents were used (entries 6–8) without adding bases. No vinyl compound was detected, but it turned out that product **2a** can be formed without the use of additional bases in any of the tested solvents. Apparently, calcium hydroxide, formed during the hydrolysis of calcium carbide during the reaction, acts as a base and its basicity is sufficient to promote the reaction with phosphine oxide **1a**. The best conversion of compound **1a** to **2a** during the reaction for 1 hour was achieved in DMSO at 130 °C (96%, entry 5). By increasing the reaction time to 2 hours, the conversion became 99% (entry 6). With an increase in the amount of solvent by 4 times, the conversion dropped significantly (to 81%, entry 7).

Entries 11–13 showed that the highest conversion was achieved using potassium fluoride (60%, entry 12). The use of this base made it possible to start the reaction already at room temperature. Thus, in 1 hour, a conversion of 27% was achieved (entry 13), and in 16 hours, complete conversion was achieved (entry 14).

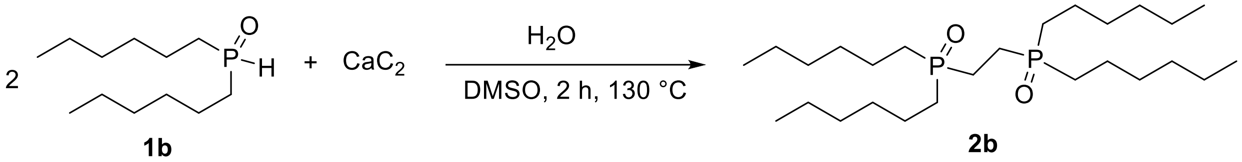
Thus, it has been shown that the use of calcium carbide as *in situ* acetylene source allows to react with diphenylphosphine oxide both without a base at 130 °C (2 hours) and with potassium fluoride at room temperature (16 hours). In both cases, a conversion more than 99% was observed.

To study this reaction with other phosphine oxides, a series of aliphatic and aromatic phosphine oxides were synthesized (Scheme 2.3). The synthesis was carried out by the interaction of Grignard reagents obtained from the corresponding bromides and magnesium with diethyl phosphite according to the methods [83-85] (for phosphine oxides **1b**–**1h**) or by oxidation of the corresponding phosphines in air according to the method [86] (for phosphine oxides **1i**–**1j**).



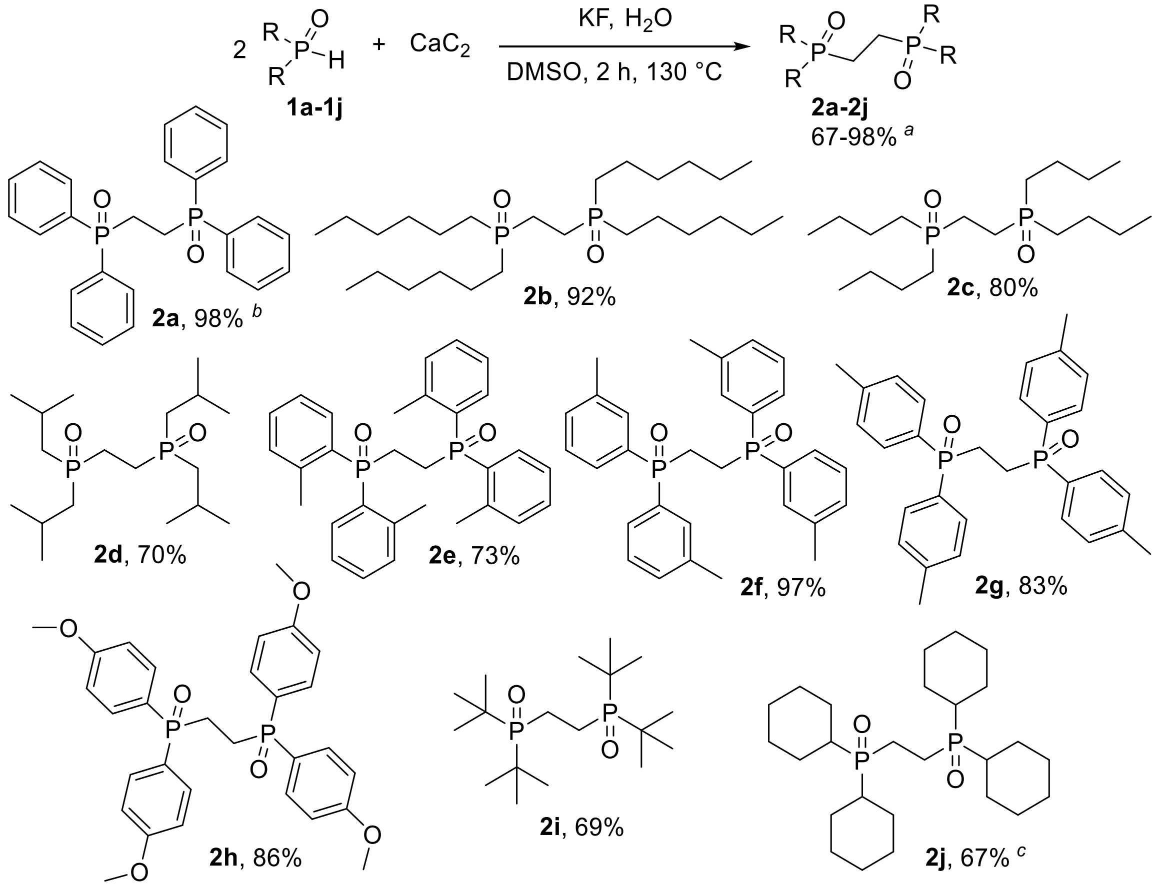
Scheme 2.3. Preparation of phosphine oxides **1b**–**1j**

When transferring optimal conditions to other phosphine oxides, in particular aliphatic phosphine oxide **1b** (Scheme 2.4), it turned out that the reaction did not proceed without a base.



Scheme 2.4. Reaction between calcium carbide and phosphine oxide **1b**

Varying the bases for this reaction showed that the best, as in the case of phosphine oxide **1a** turned out to be potassium fluoride (98% conversion when the reaction was carried out for 2 hours at 130 °C). Therefore, these are the conditions that were applied when establishing the scope of the reaction (Scheme 2.5).



[a] Isolated yield; [b] Obtained under the reaction conditions from the table 2.1 (entry 9);
[c] The reaction was carried out for 12 hours.

Scheme 2.5. Scope of the reaction

As in the case of phosphine oxide **1a**, the interaction of other phosphine oxides (**1b**–**1j**) with calcium carbide did not lead to the formation of a vinyl compound. Aliphatic phosphine oxides (**1b**–**1d, 1i**) reacted in high yields of 69–92%. It can be noted that as the length of the carbon chain decreased and as it branched in the starting phosphine oxide, the product yields decreased. In the case of aromatic substrates, the highest yields were observed for unsubstituted **1a** (98%) and *meta*-substituted phosphine oxide **1f** (97%). Moreover, all aromatic substrates reacted with a yield of more than 73%. Reaction with phosphine oxide **1j**, containing cyclohexyl substituents, was more difficult and a yield of 67% was achieved in 12 hours.

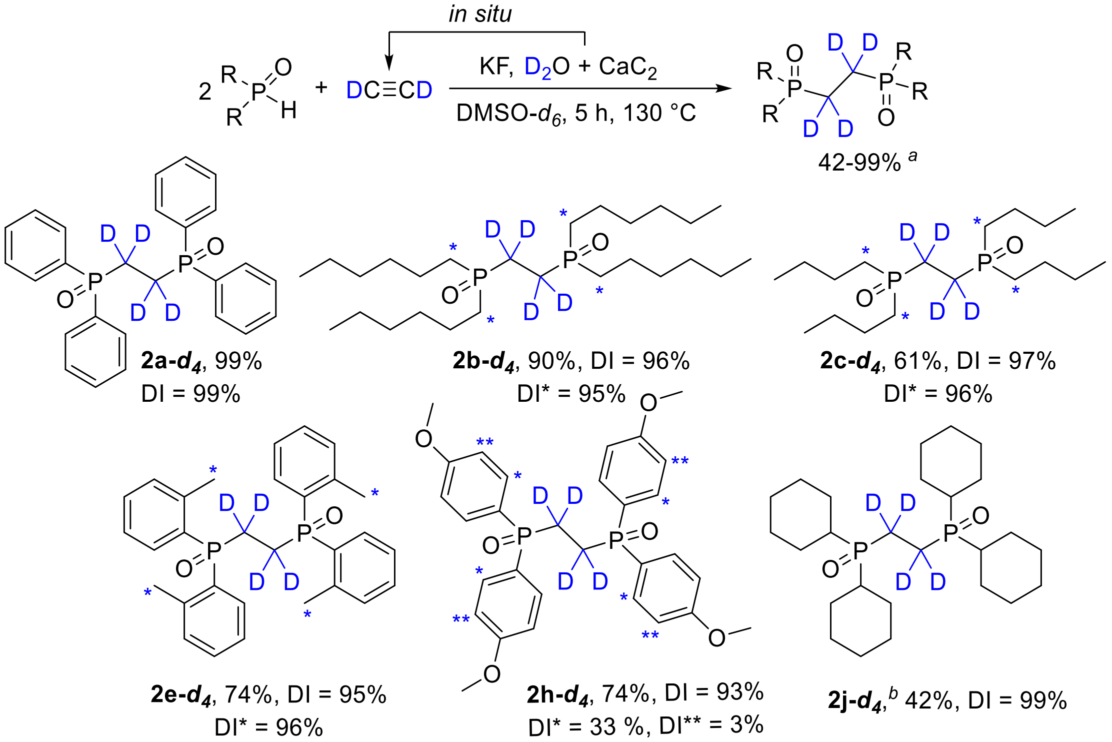
Thus, it is shown that the developed procedure can be used for the synthesis of both aliphatic and aromatic 1,2- bis(phosphine oxide)ethanes. The corresponding products were obtained in high isolated yields (67–98%). It has been established that the reaction of diphenylphosphine oxide with calcium carbide occurs even in the absence of an additional base.

2.2.2. Preparation of deuterium-labeled 1,2-bis(phosphine oxide)ethanes

One of the advantages of using calcium carbide as a source of acetylene (instead of using an acetylene gas) is the ability to introduce deuterium or ^{13}C labels *via* the use of different hydrolysis conditions. In this study, the task was to develop a method for introducing a deuterium label into the resulting 1,2-bis(phosphine oxide)ethanes.

To obtain deuterium-labeled ligands, several phosphine oxides were selected and their interaction with acetylene-d_2 generated *in situ* from calcium carbide and D_2O in DMSO-d_6. Since reactions with acetylene-d_2 usually take longer, the reaction was carried out for 5 hours (Scheme 2.6). The presence of a base, which converted the phosphine oxide to the salt, ensured that further conditions (deuterated solvent and water) led to a product containing 4 deuterium atoms in the ethane fragment.

For this reaction, the same patterns were observed as for the reaction for the production of non-deuterated compounds. Thus, product **2a-*d₄*,** as in the case of non-deuterated compound **2a**, was formed quantitatively. The long chain substrate **1b** reacted with acetylene-d_2 better than the shorter aliphatic chain substrate **1c.** Substituted aromatic phosphine oxides **1e** and **1h** reacted in the same yield of 74%. Product **2j-*d*$_4$** formed the slowest and in 15 hours the yield reached 42%. In general, the yields of the deuterated products were slightly lower (42–90%) than the non-deuterated ones, except for product **2a-*d*$_4$**.



Blue asterisks indicate protons that were additionally replaced by deuterium during the reaction.
[a] Isolated yield; [b] The reaction was carried out for 15 hours.

Scheme 2.6. Preparation of 1,2-bis(phosphine oxide)ethanes-d_4

For all products, the degree of deuterium incorporation (DI) was also determined (by the decrease in the signals of the corresponding protons in the ^{1}H NMR spectra). In general, for all compounds the DI for the ethane fragment was 93–99%, which indicates the almost complete inclusion of 4 deuterium atoms in this fragment. Interestingly, when DMSO-d_6 was used as a solvent in the reaction, some labile protons in the product molecules were also replaced by deuterium (marked with blue asterisks in Scheme 2.6). In some cases, such protons were replaced almost completely: in fact, in products **2b-*d*$_4$** and **2c-*d*$_4$** contained 12 deuterium atoms, and **2e-*d*$_4$** contained 16 deuterium atoms. Therefore, for these compounds, the notation **2b-*d*$_{12}$,** **2c-*d*$_{12}$** and **2e-*d*$_{16}$** was subsequently used. In the case of compound **2h-*d*$_4$,** only partial substitution of aromatic protons by deuterium was observed. The amount of deuterium in these compounds was also confirmed by mass spectrometry data, and their location by ^{2}H NMR spectroscopy data.

To study the effect of deuteration conditions on the yield and DI of the resulting products, as well as to reduce the consumption of deuterium solvent (DMSO-*d*$_6$), deuteration conditions were optimized (Table 2.2).

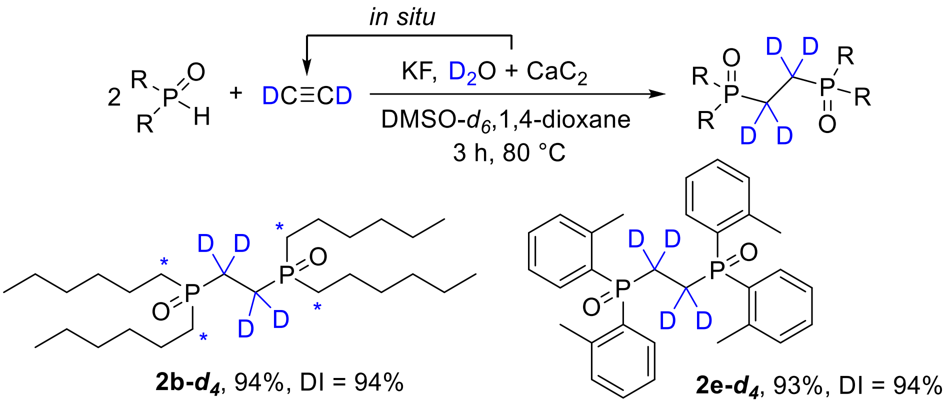
Table 2.2. Optimization of deuteration conditions (by the example of obtaining compound **2a-*d*$_4$**) [a]

Entry	DMSO- *d*$_6$, ml	1,4-dioxane, ml	T, °C	Time, h	Conversion, mol%	DI, %
1	0.5	-	130	5	100	99
2	0.5	-	80	5	100	97
3	0.5	-	80	3	100	98
4	0.5	-	50	3	100	95
5	0.5 [b]	-	80	3	97	23
6	-	0.5	80	3	85	93
7	0.2	0.3	80	3	90	97
8	0.1	0.4	80	3	95	95
9	0.05	0.45	80	3	100	94
10 [c]	0.05	0.45	80	3	88	92

[a] Reaction conditions: 64 mg (1 mmol) calcium carbide, (50 mg, 0.25 mmol) diphenylphosphine oxide, 17 mg (0.3 mmol) potassium fluoride, DMSO-*d*$_6$ and/or 1,4-dioxane (columns 2 and 3) and 80 µl (4 mmol) D_2O was placed in an 8 ml pressure tube. The tube was closed and the reaction mixture was stirred at the time specified in the table. The resulting mixture was analyzed by ^{1}H NMR spectroscopy (conversion and DI (after product extraction)). [b] Non-deuterated DMSO. [c] 40 µl D_2O.

Varying the reaction temperature and time (entries 1–4) using only DMSO-*d*$_6$ as solvent showed that stirring at 80 °C for 3 hours was optimal. Under these conditions, complete conversion was achieved and the DI was 98%. Further reduction of temperature to 50 °C was not practical due to the marked decrease in DI (entry 4). When the reaction was carried out in non-deuterated DMSO (entry 5), a strong decrease in DI was observed (up to 23%). To reduce the amount of DMSO-*d*$_6$ used, a recently discovered approach using 1,4-dioxane as a diluent for the deuteration reaction was tried [87]. When using only 1,4-dioxane (entry 6), a decrease in conversion was observed, but when adding DMSO-*d*$_6$ (entries 7–9), it increased. It is noteworthy that as the amount of DMSO-*d*$_6$ decreased, the conversion increased and became quantitative, but at the same time, DI gradually began to decrease. The optimal ratio from the point of view of reducing the amount of DMSO-d_6 was 1:9 (DMSO-d_6 to 1,4-dioxane, respectively), that is, 50 μl of DMSO-d_6 was sufficient to carry out the reaction (entry 9). It should be noted that D_2O was taken in a twofold excess (entries 1–9), since the stoichiometric amount of D_2O resulted in lower conversion and DI (entry 10).

These conditions were also used to obtain compounds **2b-d_{12}** and **2e-d_{16}**, in which the replacement of labile protons with deuterium was observed (Scheme 2.7).



2b-d_4, 94%, DI = 94%
DI* = 95%

2e-d_4, 93%, DI = 94%

Blue asterisks indicate protons that were additionally replaced by deuterium during the reaction

Scheme 2.7. Use of optimal deuteration conditions for the synthesis of compounds **2b-d_4** and **2e-d_4**

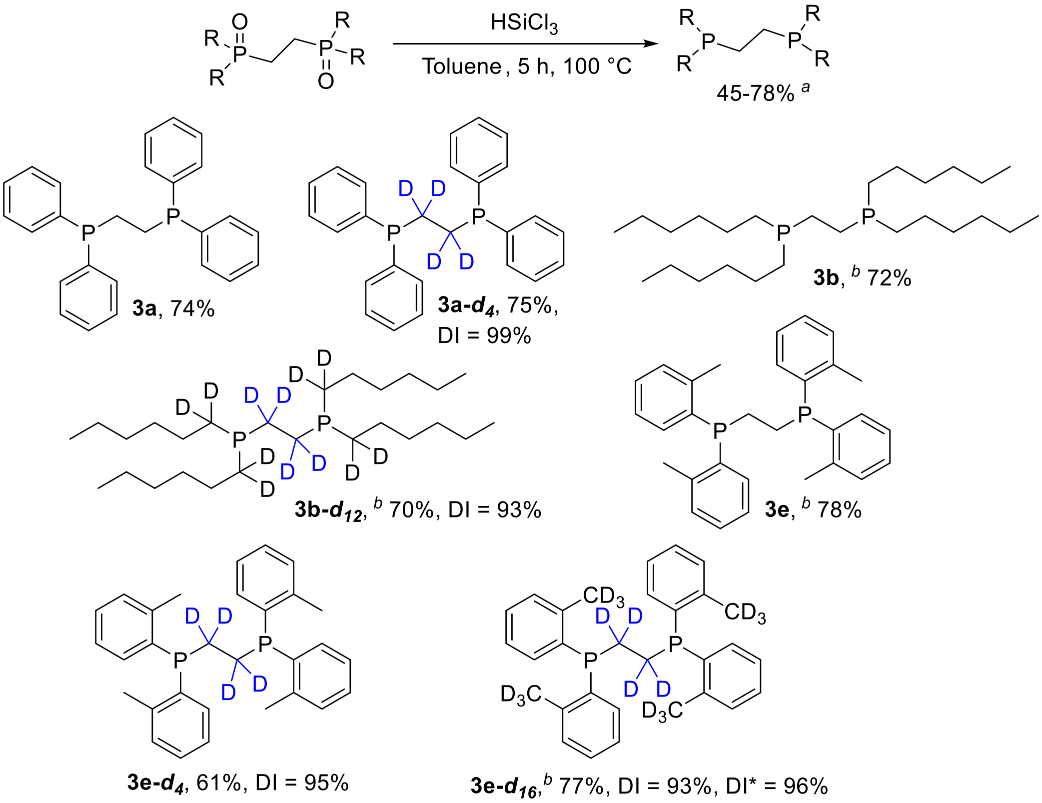
It turned out that in the case of an aromatic compound, the conditions obtained (Table 2.2, entry 9) were applicable, and the corresponding product was formed with a yield 93% and a DI 94%. It is noteworthy that under these conditions only the product **2e-d_4** was formed (instead of d_{16}), that is, the labile protons of the methyl groups in the *ortho*-position of the aromatic ring were not replaced by deuterium. However, in the case of using an aliphatic substrate, more stringent conditions were required and the deuterated product **2b-d_4** (DI 94%, yield 94%) was formed only when the amount of DMSO-d_6 was increased to 0.2 ml (per 0.3 ml of 1,4-dioxane) and carrying out the reaction at 130 °C for 5 hours. In the resulting product, labile protons were also almost completely replaced by deuterium.

Thus, a procedure for the preparation of deuterated 1,2-bis(phosphine oxide)ethanes was developed. The corresponding products were obtained both in

DMSO-d_6 with a yield 42–99% and DI 93–99%, and in a mixture of DMSO-d_6 with 1,4-dioxane. The amount of deuterium included in the product can be changed by changing the ratio of deuterated to non-deuterated solvent. In the case of aromatic phosphine oxides, 10% DMSO-d_6 is sufficient to carry out the reaction.

2.2.3. Preparation of 1,2-bis(phosphine)ethanes and their use as ligands

Often, phosphorus (III) compounds rather than phosphorus (V) compounds are used as ligands for the preparation of complex used in catalysis and other fields. An example of this is the compound closest to those obtained in this study – 1,2-bis(diphenylphosphino)ethane (DPPE), which is actively used as a ligand in the synthesis of palladium, nickel, cobalt and other complexes used as catalysts. Therefore, in the final stage of this part of the study, some of the resulting 1,2-bis(phosphine oxide)ethanes were reduced and used as ligands to obtain complexes with palladium and nickel salts. For reduction, a modified method was used [88] (Scheme 2.8).



3a, 74%

3a-*d*4, 75%, DI = 99%

3b, [b] 72%

3b-*d*12, [b] 70%, DI = 93%

3e, [b] 78%

3e-*d*4, 61%, DI = 95%

3e-*d*16, [b] 77%, DI = 93%, DI* = 96%

[a] Isolated yield; [b] *The reaction was carried out for 15 hours.*

Scheme 2.8. Preparation of 1,2-bis(phosphine)ethanes

Regardless of the presence of deuterium in the starting phosphine oxide molecule, reduced products of similar structure were obtained with almost identical preparative yields. In the case of compounds **3a** and **3a-*d₄*,** the yield was 75%. However, in the case of aliphatic substrates, the reaction time was increased to obtain the target products (**3b** and **3b-*d₁₂***) with a yield 70%. In the case of substrates **3e**, **3e-*d₄*** and **3e-*d₁₆***, the conditions were also varied, and in 5 hours the yield for **3e-*d₄*** was 61%, and when the reaction was carried out for 15 hours – 78% for **3e** and **3e-*d₁₆***. In all cases, the deuterium label was retained and the DI was not changed. Thus, the reduction technique for the resulting phosphine oxides was shown to work well for both deuterium-labeled and non-deuterium-labeled substrates.

For compound **3a-*d₄***, crystals were obtained and X-ray diffraction analysis (XRD) was performed (Figure 2.1). The molecular structure of **3a-*d₄*** is isomorphic to previously described polymorphic modifications **3a** [89].

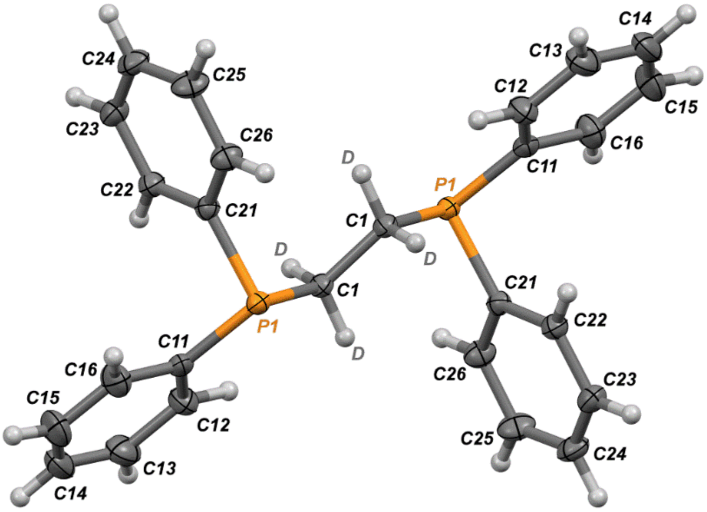
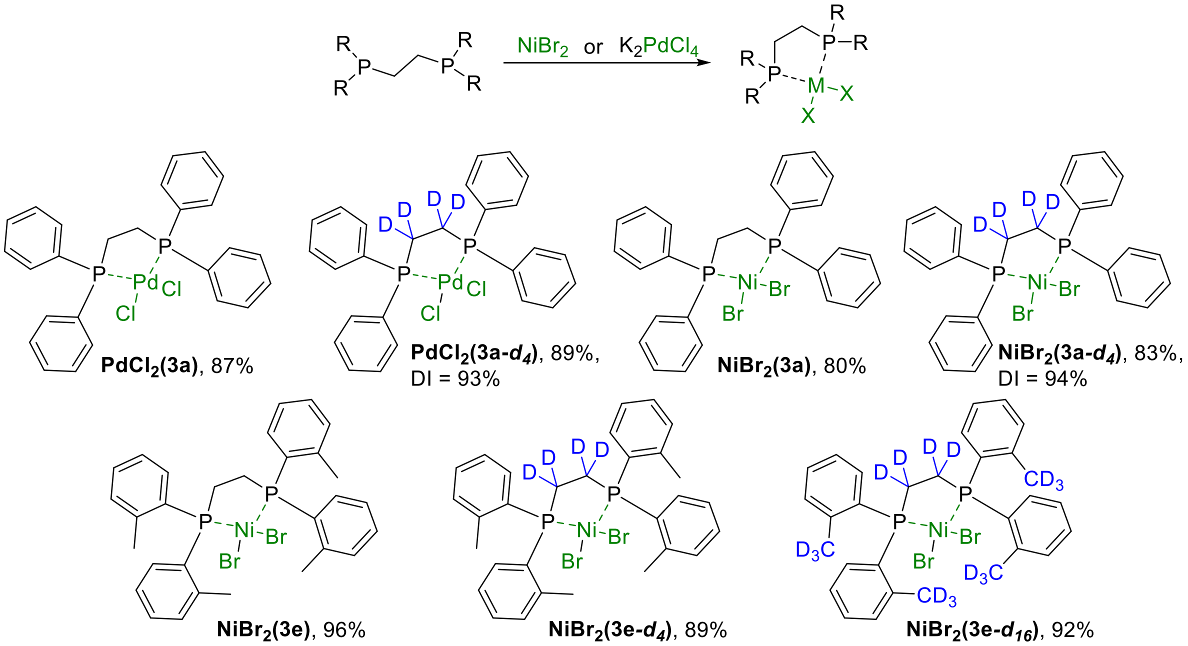


Figure 2.1. Structure of compound **3a-*d₄***

Complexes with synthesized ligands were obtained with nickel and palladium salts. Thus, complexes with $NiBr_2$ were obtained according to the method [90] from anhydrous $NiBr_2$, and complexes with $PdCl_2$ were obtained according to the method [91] from K_2PdCl_4 (Scheme 2.9).



Scheme 2.9. Preparation of Ni (II) and Pd (II) complexes with synthesized ligands

In all cases, ligands containing deuterium formed complexes with the same structure as ligands without deuterium. The yields of the corresponding complexes were approximately the same: for complexes **3a** and **3a-d_4** with $PdCl_2$ – 87–89%, c $NiBr_2$ – 80–83%, for **3e, 3e-d_4** and **3e-d_{16}** c $NiBr_2$ – 89–96%. For complexes soluble in chloroform (all except complexes with deuterated and non-deuterated ligand **3e**) it was shown that the deuterium label was maintained and the DI did not change significantly. The structure of the resulting complexes, soluble in chloroform, was confirmed by ^1H and ^{31}P NMR spectroscopy and mass spectrometry data. For complexes **$PdCl_2$(3a-d_4)** (Figure 2.2), **$NiBr_2$(3a)** and **$NiBr_2$(3a-d_4)** (Figure 2.3), **$NiBr_2$(3e)**, **$NiBr_2$(3e-d_4)** and **$NiBr_2$(3e-d_{16})** (Figure 2.4) crystals were obtained, which were studied using X-ray diffraction. The structure of the rest of the resulting fine-crystalline powders for each of the compounds fully corresponded to the structures established using X-ray diffraction, which was confirmed by X-ray diffraction data.

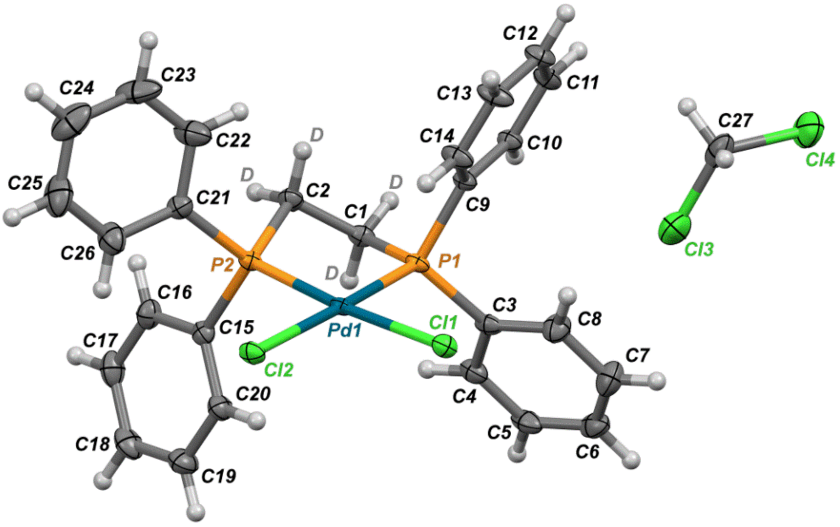


Figure 2.2. Structure of the **PdCl$_2$(3a-*d*$_4$)** complex

The structure of **PdCl$_2$(3a-*d*$_4$)**·CH$_2$Cl$_2$ (Figure 2.2) is isostructural to the previously described non-deuterated structure of **PdCl$_2$(3a)**·CH$_2$Cl$_2$ [92].

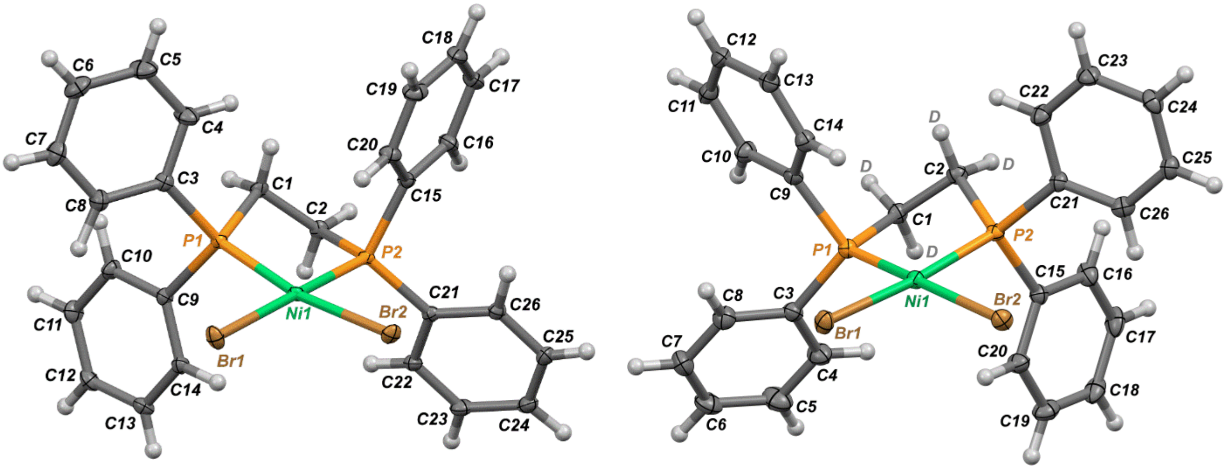


Figure 2.3. Structures of the **NiBr$_2$(3a)** and **NiBr$_2$(3a-*d*$_4$)** complexes

The crystal structures of **NiBr$_2$(3a)** and **NiBr$_2$(3a-*d*$_4$)** (Figure 2.3) are also isostructural. Conformations of the **NiBr$_2$(3a)** complex (Figure 2.3, left) and the **PdCl$_2$(3a-*d*$_4$)** complex (Figure 2.2) turned out to be very similar.

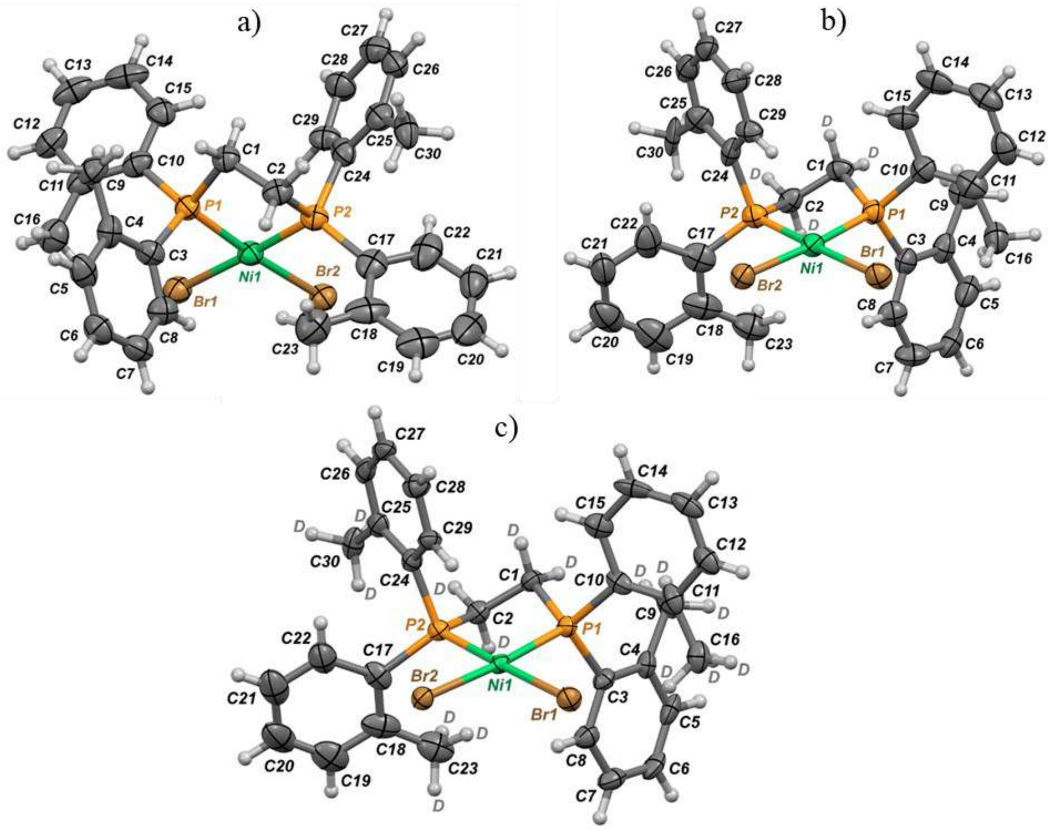


Figure 2.4. Structures of **NiBr$_2$(3e)** (a), **NiBr$_2$(3e-d_4)** (b) and **NiBr$_2$(3e-d_{16})** (c) complexes

The complexes **NiBr$_2$(3e)**, **NiBr$_2$(3e-d_4)** and **NiBr$_2$(3e-d_{16})** (Figure 2.4) were isostructural. These complexes crystallized as multidomain crystals of space group $P2_1$ with two symmetrically nonequivalent molecules having similar conformations.

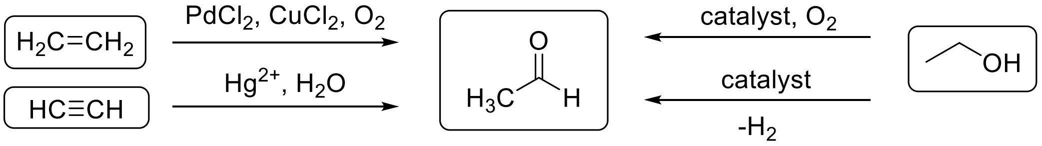
Thus, comparison of deuterated and non-deuterated complexes confirmed their crystal structure. Using these complexes as an example, as well as ligands **3a** and **3a-d_4** it was shown that the introduction of deuterium into the ligand molecule does not affect the structure and packaging of the resulting complexes in the crystal.

At the end of this subchapter, we can conclude that a universal method for the synthesis of both deuterated and non-deuterated ligands, based on the reaction of nucleophilic addition of phosphine oxides to acetylene generated *in situ* from calcium carbide. Using the example of several obtained ligands, the possibility of synthesizing complexes with the obtained ligands containing deuterium was shown. The results obtained in this chapter were published in a peer-reviewed scientific journal [93].

2.3. Using the reaction of nucleophilic addition of alcohols to acetylene from calcium carbide for the cyclic production of acetaldehyde

The next task of this study was to find the applicability of previously developed methods for vinylation of alcohols using calcium carbide to create cyclic processes for the production of important large-scale substances. Acetaldehyde was chosen as such a large-capacity compound. It is known that hydrolysis of vinyl ethers under acidic conditions leads to the formation of alcohol and acetaldehyde in quantitative yield [94]. Therefore, the idea was to capture acetaldehyde and recycle the alcohol and thus obtain a closed cycle for the production of acetaldehyde. For the first time, the preparation of acetaldehyde using such a vinylation-devinylation sequence was proposed by V.Yu. Reppe [95]. Also, in the works of Soviet chemists one can find references to the study of this process [13]. However, this sequence was never widely used due to the use of explosive acetylene gas as the vinylation agent.

Alternative methods for producing acetaldehyde, used in different countries (depending on the availability of raw materials), are ethylene oxidation ("Wacker process") [96, 97], direct hydration of acetylene [98-100], as well as oxidation [101-106] and dehydrogenation [107-109] of ethanol (Scheme 2.10). Acetylene hydration and the Wacker process require catalysis by heavy metals and are based on non-renewable raw materials, which are significant disadvantages from the point of view of the concept of the development of chemical technology in the "sustainable development" paradigm. Ethanol, as well as another type of raw material, representing a new actively developing direction, is lactic acid (decarbonylation reaction is used for the synthesis of acetaldehyde [110-112]) - can be obtained from biomass and are therefore considered renewable. However, this process requires a certain type of biomass, the quantity of which may be limited in different countries. Ethanol-related processes also use metal catalysis.



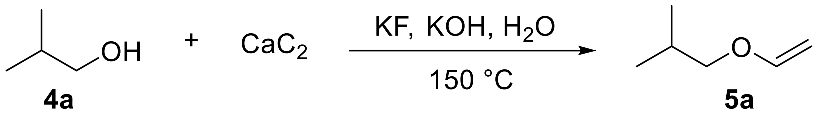
Scheme 2.10. Main raw materials and methods for acetaldehyde production

In this dissertation, the goal was to develop a scheme for producing acetaldehyde from calcium carbide without the use of solvents, with complete recycling of alcohol and other substances used.

2.3.1. Vinylation

Standard methods for producing vinyl ethers typically use DMSO as a solvent (to create superbasic medium). But in the case of waste-free production, it is not suitable because of its partial decomposition under reaction conditions, which makes its complete recycling impossible. Therefore, we investigated the possibility of carrying out the vinylation reaction without using a solvent.

Isobutyl alcohol (**4a**) was chosen as a model substrate because it and its vinyl ether (**5a**) are cheap, commercially available reagents. The reaction (Scheme 2.11) was carried out in a pressure reactor equipped with a pressure gauge.



Scheme 2.11. Vinylation of alcohol **4a**

Reagents were loaded into the reactor in the quantities given in Table 2.3, in the following sequence: calcium carbide, potassium fluoride, alkali, alcohol, water. The reactor was tightly closed and the reaction mixture was stirred at a temperature of 150 °C. The reaction mixture was then filtered and the yield of vinyl ether was determined using ^{1}H NMR spectroscopy (based on 85% CaC_2 (purity of calcium carbide taken, determined volumemetrically)). The yield was calculated by the formula:

$$\eta = \frac{i_{v.e.}((m_f - n \cdot 74.12) + n \cdot 100.16)}{n(i_{v.e.} \cdot 100.16 + i_{alc.} \cdot 74.12)} \cdot 100\%$$

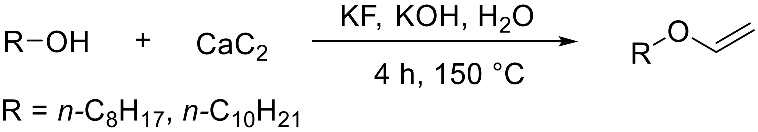
where $i_{v.e.}$ – the value of the integral in the ^{1}H NMR spectrum corresponding to one IBVE proton; $i_{alc.}$ – value of the integral in the ^{1}H NMR spectrum corresponding to one isobutanol proton; n – the theoretical number of moles of IBVE (based on the number of moles of acetylene released); m_f – the actual weight of alcohol taken to carry out the reaction.

Table 2.3. Vinylation reaction conditions and product yields

Entry	CaC_2, g	**4a**, ml	Mole ratio $CaC_2 : H_2O : KF : KOH$	Time, h	η, wt%
1	2.5	3.6	1 : 3 : 0 : 0.3	4	0
2	2.5	3.6	1 : 3 : 0.45 : 0. 3	4	3
3	5	7.2	1: 2:2:0.5	4	35
4	5	7.2	1 : 2 : 0 : 0.5	4	16
5	5	7.2	1: 2:1:0.5	4	2 6
6	5	7.2	1: 2:1.5:0.5	4	38
7	5	7.2	1: 3:1.5:0.5	4	31
8	5	7.2	1 : 1.5 : 1.5 : 0.5	4	42
9	5	12	1 : 1.5 : 1.5 : 0.5	4	19
10	5	7.2	1 : 1.5 : 1.5 : 0.5	6	63
11	5	7.2	1 : 1.5 : 1.5 : 0.5	10	74
12	5	7.2	1 : 1.5 : 1.5 : 0.5	13	79
13	5	7.2	1 : 1.5 : 1.5 : 0.5	15	7 0

When using 2.5 g of CaC_2, the pressure in the system did not exceed 5 bar, and for 5 g the pressure rose to 10–15 bar. It is likely that insufficient pressure is responsible for the lower product yields in entries 1 and 2 compared to other entries. When using the usual ratios of vinylation reagents (except for calcium carbide, which is taken in a 1:1 ratio to alcohol) (entry 3), the calculated yield of vinyl ether was 35%. Without the use of potassium fluoride, the yield decreased to 16% (entry 4), however, with a gradual increase in its loading to 1.5 mol KF per 1 mol CaC_2, the yield increased to 38% (entries 5 and 6). An excess of water reduced the yield to 31% (entry 7), and a deficiency, on the contrary, increased it to 42% (entry 8). When using excess alcohol, the yield decreased to 19% (entry 9). Varying the time showed that the highest yield (79%) was achieved when the reaction was carried out for 13 hours (entries 10–13). Thus, the optimal conditions for vinylation were the molar ratio of CaC_2:H_2O:KF:KOH equal to 1:1.5:1.5:0.5, reaction duration 13 hours at a temperature of 150 °C.

For further hydrolysis, the reaction mixture after filtration was washed with water to remove remaining inorganic substances and hydrolyze the resulting alcoholate, and the aqueous layer was separated from the ether layer (containing vinyl ether and the corresponding alcohol). The resulting vinyl ether is very volatile, so the inorganic precipitate was not further washed with other solvents, since this would make it difficult to isolate the ether from these solvents (hexane or diethyl ether) during evaporation. Due to this, a small amount of vinyl ether, which is insoluble in water, remained on the sediment solids, which reduced the amount of ether released. This problem did not arise with other alcohols whose vinyl ethers were not as volatile. For example, when vinylation of octanol and decanol (Scheme 2.12).



Scheme 2.12. Vinylation of alcohols **4b** and **4c**

Vinylation octanol (**4b**) and decanol (**4c**) were carried out according to the optimal ratios found for vinylation of alcohol **4a** for 4 hours at 150 °C. Since the boiling points of the corresponding vinyl ethers and alcohols differ significantly from the boiling point of hexane, the precipitate after filtration was washed with this solvent and then with water to more completely isolate the vinyl ether. The organic layer was dried with Na_2SO_4 and the solvent was evaporated under reduced pressure. Yields calculated using a formula similar to that used for **5a** were 39% for vinyl ether **5b** and 33% for **5c**, i.e., slightly lower than for vinyl ether **5a** obtained under the same conditions (42%).

Thus, a solvent-free vinylation procedure was developed, which was subsequently used in the vinylation-devinylation reaction sequence.

2.3.2. Devinylation

2.3.2.1. Determination of optimal hydrolysis conditions. The next step towards the production of acetaldehyde was the optimization of the conditions for the hydrolysis of vinyl ether. Commercially available vinyl ether **5a** was chosen to carry out the reaction. Hydrolysis was carried out in the absence of a solvent by mixing the ether with a solution of sulfuric acid. At the first stage, the optimal time and temperature of hydrolysis was determined (Table 2.4). The reaction was carried out by mixing vinyl ether with a 2% solution of H_2SO_4 (a 4-fold excess of water relative to vinyl ether was used).

As a result of the analysis of the spectra, a product of the interaction of alcohol with vinyl ether was observed. As it turned out, this product (acetal) was formed under the reaction conditions, but was hydrolyzed in the same way as vinyl ether, with the formation of acetaldehyde (Scheme 2.13). Therefore, for further calculations of the conversion of vinyl ether to alcohol, the acetal content in the spectrum was recalculated to the content of vinyl ether and alcohol. In this regard, conversion **5a** was calculated using the following formula:

$$Conv = \frac{C\ alc_{\%mol}}{C\ alc_{\%mol} + C\ vin_{\%mol}} \cdot 100\%,$$

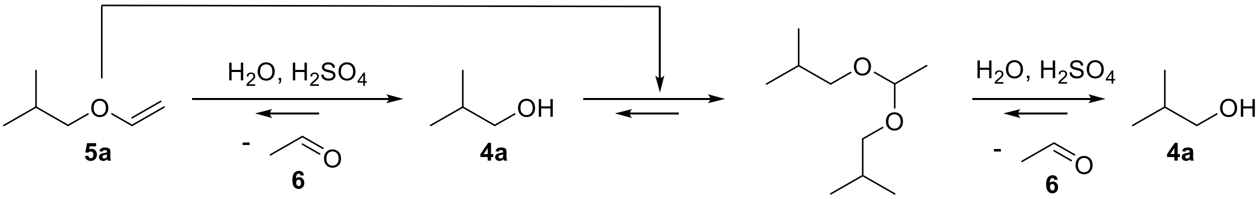
$$C\ vin_{\%mol} = C\ vin1_{\%mol} + C\ acetal_{\%mol}$$

$$C\ alc_{\%mol} = C\ alc1_{\%mol} + C\ acetal_{\%mol}$$

$$C\ vin1_{\%mol} = \frac{vin_{mol}}{total_{mol}} \cdot 100\%, \qquad C\ alc1_{\%mol} = \frac{alc_{mol}}{total_{mol}} \cdot 100\%$$

$$C\ acetal_{\%mol} = \frac{acetal_{mol}}{total_{mol}} \cdot 100\%$$

where vin_{mol}, alc_{mol}, $acetal_{mol}$ and $total_{mol}$ is the number of moles of vinyl ether, alcohol, acetal and total, respectively, determined from the spectrum.



Scheme 2.13. Vinyl ether hydrolysis products **5a**

Table 2.4. Optimization of conditions for hydrolysis of vinyl ether **5a**

The reaction was carried out at 25 °C													
Time, min	0	30	60	90	120	150	180	210	240	270	300	day	
Vinyl ether, %	100	92	91	91	90	85	80	78	64	62	48	0	
Acetaldehyde, %	0	3	3	3	2	4	5	5	10	10	16	20	
Alcohol, %	0	4	5	6	9	11	14	18	23	24	26	43	
Acetal, %	0	0	1	1	0	0	1	0	4	4	10	37	
Vinyl ether when taking into account acetal, %	100	92	92	92	90	85	81	78	68	65	58	37	
Alcohol when taking into account acetal, %	0	4	7	7	9	11	15	18	27	28	36	80	
Conversion, %	0	4	7	7	9	11	16	19	28	30	38	68	
The reaction was carried out at 50 °C													
Time, min	0	30	60	90	120	150	180	210	240	270	300	330	360
Vinyl ether, %	100	89	79	47	0	0	0	0	0	0	0	0	0
Acetaldehyde, %	0	4	8	19	36	29	30	26	25	27	22	23	24
Alcohol, %	0	5	10	13	48	56	56	57	57	58	61	61	62
Acetal, %	0	2	4	21	16	15	15	18	18	15	17	16	15
Vinyl ether when taking into account acetal, %	100	91	82	69	16	15	15	18	18	15	17	16	15
Alcohol when taking into account acetal, %	0	8	13	34	64	71	71	74	75	73	78	77	76
Conversion, %	0	8	14	33	80	83	83	81	81	83	82	83	84
The reaction was carried out at 80 °C													
Time, min	0	30	60	105	120	150	180	210	240	270	300	330	360
Vinyl ether, %	100	59	0	0	0	0	0	0	0	0	0	0	0
Acetaldehyde, %	0	10	23	12	11	11	8	7	6	6	5	6	5
Alcohol, %	0	14	59	74	77	80	82	8	86	88	89	91	92
Acetal, %	0	17	18	13	12	9	9	10	8	7	7	3	4
Vinyl ether when taking into account acetal, %	100	76	18	13	12	9	9	10	8	7	7	3	4
Alcohol when taking into account acetal, %	0	31	77	88	89	90	92	93	94	94	95	94	95
Conversion, %	0	29	81	87	88	91	91	91	92	92	94	97	96

The reaction was carried out at 100 °C									
Time, min	0	30	60	90	120	150	180	210	240
Vinyl ether, %	100	0	0	0	0	0	0	0	0
Acetaldehyde, %	0	25	5	1	1	0	0	0	0
Alcohol, %	0	34	93	97	98	99	100	100	100
Acetal, %	0	42	3	2	2	1	1	0	0
Vinyl ether when taking into account acetal, %	100	42	3	2	2	1	1	0	0
Alcohol when taking into account acetal, %	0	75	95	99	99	100	100	100	100
Conversion, %	0	64	98	98	99	99	100	100	100

According to Table 2.4, as well as the graph of changes in conversion over time at different temperatures (Figure 2.5), it is noticeable that the reaction took place fastest at 100 °C (after 60 minutes the conversion quickly reached 97% and then slowly rose to 100%). The temperature was found to be unsuitable due to the boiling point of the original vinyl ether being above the boiling point (83 °C). And as a consequence, it is impossible to simultaneously distill off the resulting acetaldehyde at a given temperature.

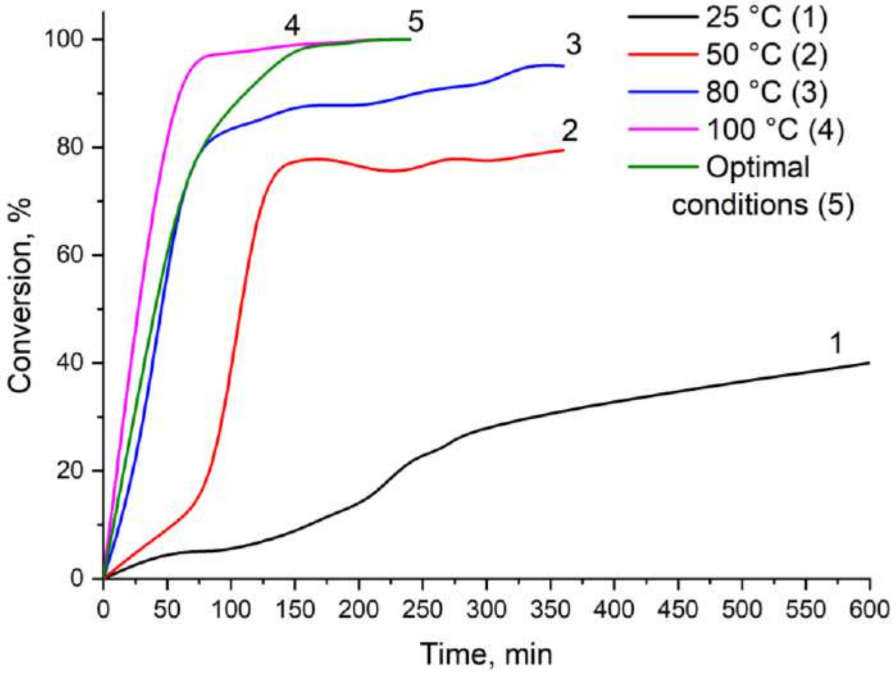


Figure 2.5. Change in the conversion of vinyl ether **5a** over time during hydrolysis at different temperatures

At 80 °C, a sharp increase in conversion also occurred during the first hour (up to 81%), then its level slowly increased to 96% (within 6 hours). At 50 °C the reaction was even slower and a rapid increase in conversion was observed within 2 hours (up to 80%) and then increased slightly to 84% (over 6 hours). At room temperature the reaction did not reach completion and after 24 hours the conversion was 68%. Based on these observations, it was decided to carry out the reaction for the first hour at 80 °C, and then, when the reaction mixture contains mainly the corresponding alcohol, increase the temperature to 100 °C until the reaction is complete. The data obtained as a result of such an experiment are presented in Table 2.5 and

Figure 2.5 (green line). It can be seen that complete conversion was achieved in a total reaction time of 3.5 hours.

Table 2.5. Carrying out the vinylation reaction under optimal conditions (heating to 80 °C for an hour, then to 100 °C)

Time, min	0	30	60	90	120	150	180	210	240
Vinyl ether, %	100	74	0	0	0	0	0	0	0
Acetaldehyde, %	0	8	20	14	5	1	0	0	0
Alcohol, %	0	14	59	75	89	98	99	100	100
Acetal, %	0	4	21	11	6	1	1	0	0
Vinyl ether when taking into account acetal, %	100	78	21	11	6	1	1	0	0
Alcohol when taking into account acetal, %	0	18	80	86	95	99	100	100	100
Conversion, %	0	19	79	89	94	99	99	100	100

Having optimized the temperature and reaction time, the next parameter was the acid concentration. To determine the best concentration, the reaction was carried out at 80 °C for 2 hours with a **5a**:water ratio of 1:4 (Table 2.6). An appropriate sulfuric acid solution was used as a water source.

Table 2.6. Determining the optimal concentration of sulfuric acid solution

Acid concentration, wt%	Content **5a** including acetal, %	Content **4a** including acetal, %	Conversion **5a**, %
0.01	100	0	0
0.1	81	25	24
1	29	63	69
2	12	89	88
3	17	84	83
4	19	87	82
5	14	88	87

According to the table, when using highly dilute solutions of sulfuric acid (0.01%), the reaction did not proceed (there were no signals of reaction products in the spectrum after 4 hours). As the acid concentration increased, the conversion increased and reached its maximum when using a 2% H_2SO_4 solution (88%). It can be concluded that the optimal acid concentration for this reaction was 2wt%.

The optimal ratio of water to vinyl ether was determined at 100 °C using a 2% sulfuric acid solution (Table 2.7). The reaction was carried out for 45 minutes.

Table 2.7. Determining the optimal ratio of ether to water

Ether:water ratio	1:1	1:2	1:4
Vinyl ether, %	0	1	0
Acetaldehyde, %	1	0	2
Alcohol, %	95	98	94
Acetal, %	4	1	4
Vinyl ether when taking into account acetal, %	2	2	2
Alcohol when taking into account acetal, %	97	98	96
Conversion, %	98	98	98

Based on the presented data, we can conclude that no matter what excess of water is taken in relation to vinyl ether, the conversion practically did not change and amounted to 98%.

Thus, the optimal hydrolysis conditions were found and used further: 2% sulfuric acid solution, water to ether ratio 4 to 1, heating to 80 °C for 1 hour, then to 100 °C for 2.5 hours.

2.3.2.2. Acetaldehyde capture. As can be seen from these optimization tables, the acetaldehyde content in the mixture was very low, because during the reaction the vinyl ether easily escaped from the reaction zone (bp. 20 °C). This may be advantageous in terms of carrying out the hydrolysis reaction since the reaction is at equilibrium, but complete capture of acetaldehyde, especially when carrying out the reaction in small quantities, was difficult. Therefore, various acetaldehyde capture methods were investigated by distilling acetaldehyde from the reaction system directly during the reaction, carried out at 80 °C for 2 hours. Depending on the temperature and tightness of the system, different data were obtained.

When collected in a U-shaped tube cooled to -5 °C, 0.32 g of acetaldehyde was obtained (purity 69 wt%). The yield in terms of pure product was 33%. Along with acetaldehyde, alcohol and vinyl ether were captured, and the acetaldehyde content in the organic layer of the reaction mixture was 2%. An option was also tested with the supply of argon through the system to completely remove acetaldehyde. In this case, it was also captured in a U-shaped tube cooled to -5 °C. In this case, significantly more product was obtained (0.88 g), but the purity was significantly lower

(13wt%). The yield in terms of pure product was only 17%, since a lot of vinyl ether evaporated along with acetaldehyde.

A 4-fold supply of vinyl ether to a 4-fold excess of a 2% sulfuric acid solution was also tested. In this case, acetaldehyde was distilled into a test tube cooled to -20 °C. As a result of the experiment, 3 ml (2.71 g) of acetaldehyde (purity 67wt%) was obtained. The yield in terms of pure product was 67%. The residual content of acetaldehyde in the organic layer of the reaction mixture was 3%.

We also tried trapping acetaldehyde in a tube filled with water cooled in an ice bath. In this case, the reaction was carried out by refluxing for 45 minutes at 100 °C, then replacing the reflux condenser with a stopper and distilling the contents through a silicone hose into a tube with water. The aqueous layer was then analyzed using ^{1}H NMR spectrometry. It was discovered that the trapped acetaldehyde in the water trimerized and formed paraldehyde. In addition, a small amount of alcohol was distilled into water. The disadvantage of this procedure was that only a small part of the acetaldehyde was captured.

Thus, it was shown that the most effective way to capture acetaldehyde was by distillation into a tube cooled to -20 °C, with several feeds of vinyl ether **5a**.

Continuing to work in this direction, we simulated continuous supply conditions in order to evaluate the process dynamics and solve the problem of acetaldehyde accumulation in the reaction mixture. Several different temperature conditions were tested and the best results are presented below. Hydrolysis was carried out by adding 4 times 2 ml (15.4 mmol) of ether **5a** to 1.2 ml of a 2% sulfuric acid solution. When adding each portion, the reaction mixture was first stirred for 1.5 hours at 80 °C so that most of the vinyl ether reacted, then the reaction mixture was heated to 100 °C to complete the reaction and remove all acetaldehyde. Acetaldehyde was collected in a tube cooled to -20 °C. The amount of acetaldehyde released is presented on the graph (Figure 2.6).

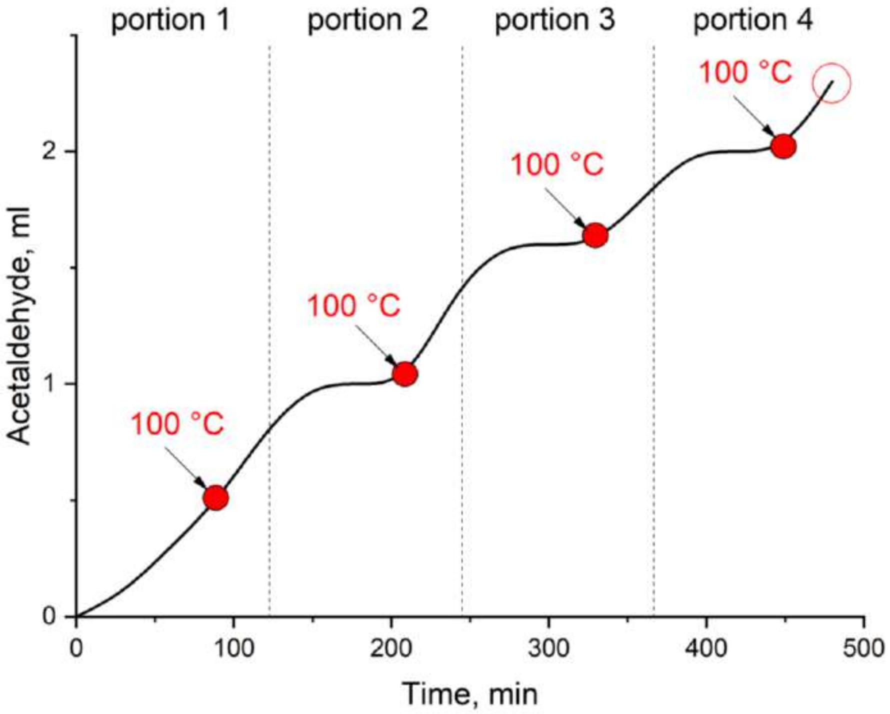


Figure 2.6. The release of acetaldehyde in dynamics (red dots mark the places where heating to 100 °C began)

It is noticeable from the graph that in the first two feeds, acetaldehyde was released almost continuously, and then active release was observed only when heated to 100 °C and a new portion of the reagent was added. This indicates that acetaldehyde accumulated in the reaction mixture until it was heated to 100 °C. This assumption is also confirmed by analysis of the composition of the organic layer of the reaction mixture. The graph of the concentration of acetaldehyde in the organic layer of the reaction mixture (Figure 2.7) shows that with the addition of each new portion, the acetaldehyde content decreased and reached 0% when the last portion was added and heated to 100 °C.

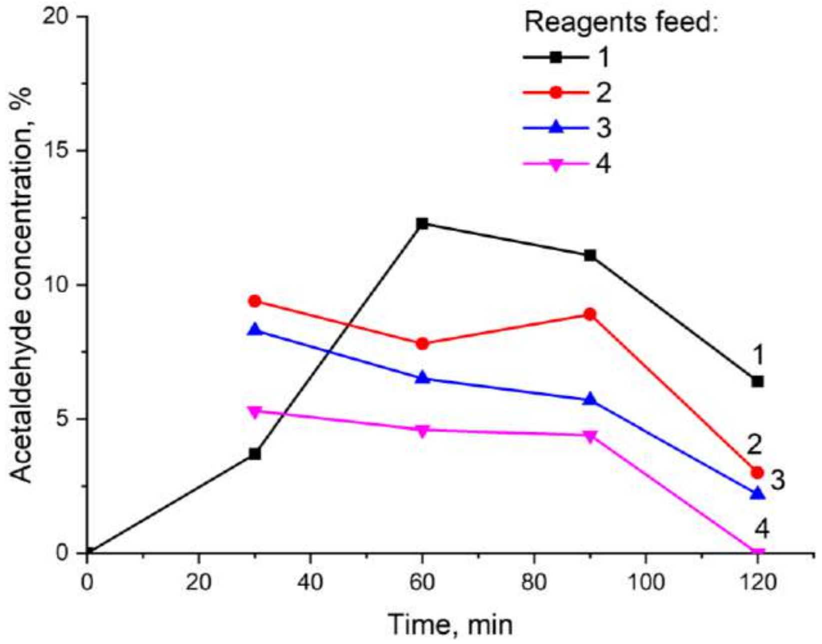
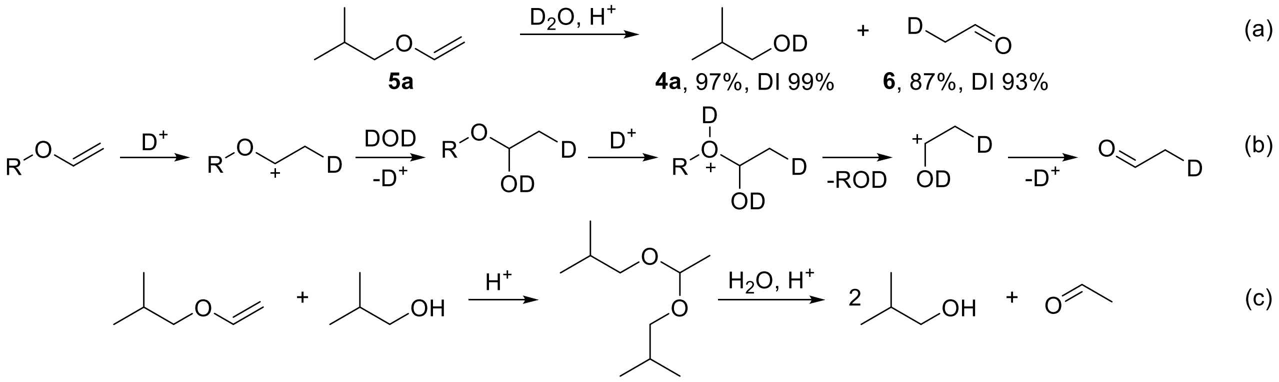


Figure 2.7. Dependence of the acetaldehyde content in the organic layer of the reaction mixture on time and number of reagent feeds

After 4 feeds (full consumption of water), 2.3 ml of acetaldehyde was obtained with a purity of 83 wt%, which corresponded to a yield of 56%. Since no acetaldehyde remained in the organic layer of the reaction mixture, and the vinyl ether conversion was 93%, it is obvious that losses occurred when using a distillation system of too large a volume and its not being completely sealed; this problem was solved further at the scaling stage. By lowering the cooling temperature of the tube in which acetaldehyde was captured, it was possible to increase the isolated yield to 74%.

2.3.2.3. Reaction mechanism. The mechanism of hydrolysis is widely discussed in the literature [94, 113-115]. To confirm this mechanism, hydrolysis was carried out using D_2O (Scheme 2.14). The resulting deuterated alcohol and acetaldehyde (Scheme 2.14, a) corresponded to those obtained earlier in the literature when the reaction was carried out in an NMR tube in $CDCl_3$ using a ruthenium catalyst [116]. It is worth noting that during the hydrolysis of vinyl ethers, the resulting alcohol reacted with unreacted vinyl ether to form an acetal in an acidic medium (Scheme 2.14, b). The resulting acetal also hydrolyzed under the reaction conditions to form alcohol and acetaldehyde. The overall mechanism, based on the obtained reactions a and b, is presented under the letter c.



Scheme 2.14. Mechanism of vinyl ether hydrolysis

The reaction with heavy water opened the way to the production of deuterated alcohol and acetaldehyde. Acetaldehyde is a key building block in the preparation of various compounds, including heterocycles, and the use of labeled acetaldehyde provides great opportunities for the synthesis of labeled heterocycles used in the creation of drugs [117]. Until now, acetaldehyde-2-*d* was obtained only by hydrolysis in an NMR tube with $CDCl_3/D_2O$ using a ruthenium catalyst [116] and from a vinyl ether [118], and deuterated alcohols were obtained by H/D exchange with a large excess of D_2O for three cycles [119, 120]. Using the method described in this study makes it possible to simultaneously obtain two deuterated compounds, **6-*d*** and alcohol **4a-*d*,** using simple hydrolysis of compound **5a**.

2.3.3. General vinylation-devinylation sequence

2.3.3.1. Use of alcohol 4a in the vinylation-devinylation sequence. During the hydrolysis reaction and during the vinylation reaction, no formation of reaction by-products was observed, which allows complete recycling of the alcohol. In addition, it is not necessary to separate the vinyl ether from the alcohol after the vinylation. This mixture can be used immediately for hydrolysis. To confirm this hypothesis, hydrolysis of the vinyl ether obtained under the conditions of entry 8 (Table 2.3) was carried out. The reaction was carried out under optimal hydrolysis conditions for pure ether **5a**.

The graph (Figure 2.8) shows that, as in the case of the hydrolysis of pure **5a**, the conversion (relative) increased sharply in the first 60 minutes, and then the growth slowed down, and after 3 hours the conversion reached 93% (the actual alcohol content in the reaction mixture after the reaction was 98%). Thus, we were convinced that both reactions proceeded quite smoothly, and after hydrolysis, only the resulting alcohol remained in the organic layer.

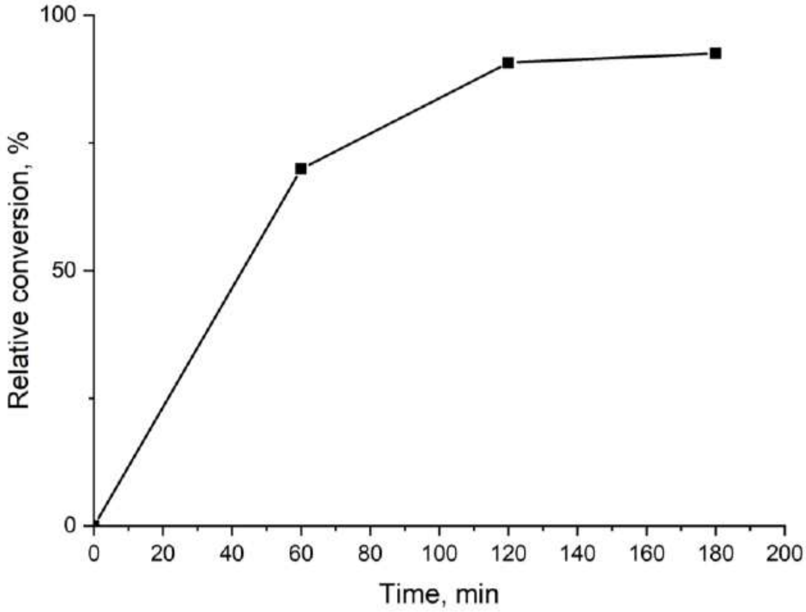
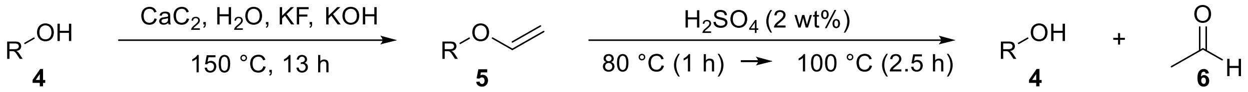


Figure 2.8. Relative change in conversion **5a** (the initial ratio of alcohol to ether in the initial mixture is taken as 0%)

To close the cycle of acetaldehyde production, the organic part of the reaction mixture remaining after hydrolysis was separated and vinylated with a new portion of calcium carbide. Since the organic layer at the end of hydrolysis was the original alcohol, the secondary vinylation was successful and resulted in a similar yield of vinyl ether. We subsequently tested the ring closure of the entire vinylation-devinylation sequence in the same reaction mixture. The alcohol was vinylated under basic conditions according to the developed procedure; the mixture was filtered, washed with water and devinylated under acidic conditions, followed by distillation of acetaldehyde. The mixture was then used in a second round of the vinylation- devinylation sequence. The total amount of acetaldehyde collected sequentially was twice that of a single cycle. Thus, the possibility of using alcohol **4a** in the cyclic production of acetaldehyde was demonstrated.

2.3.3.2. Using different alcohols in sequence. In order to increase the alcohol conversion and obtain more acetaldehyde, other alcohols were tried in the vinylation-devinylation reaction sequence (Table 2.8). A number of available alcohols of different structures were chosen as substrates. The use of polyols to produce more acetaldehyde from the same number of moles of alcohol has also been explored.

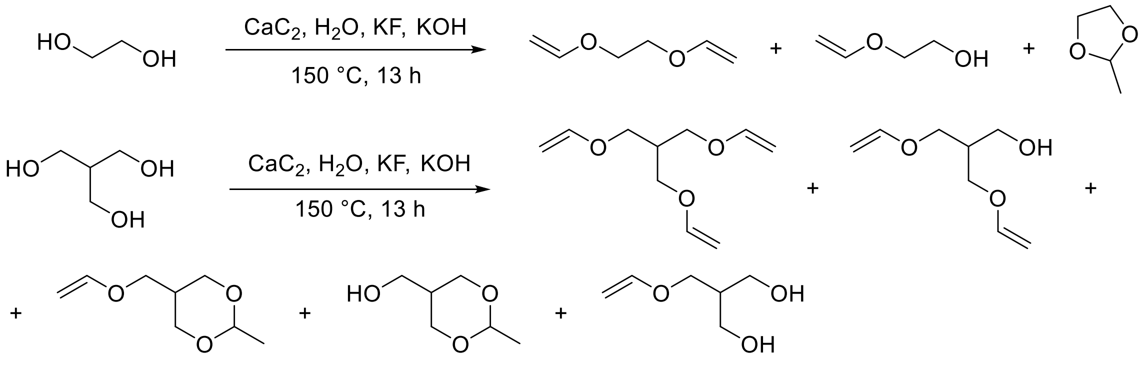
Table 2.8. Variation of alcohols in the sequence of vinylation reactions and subsequent hydrolysis of the product [a]



Entry	Alcohol	Vinylation	Devinylation	
		Conversion **4**, wt%	Relative conversion **5**, wt%	Yield **6**, wt%
1	*i*-Butanol (**4a**)	79	100	79
2	*n*-Octanol (**4b**)	78	71	55
3	*n*-Decanol (**4c**)	56	43	24
4	*n*-Butanol (**4d**)	61	85	52
5	*i*-Amyl alcohol (**4e**)	85	84	71
6	Menthol (**4f**)	11	100	11
7	Benzyl alcohol (**4g**)	35	100	35
8	Ethylene glycol (**4h**)	- [b]	- [c]	3 [d]
9	1,10-decanediol (**4i**)	68	89	61 (23 [d])
10	Glycerol (**4j**)	- [b]	- [c]	16 [d]

[a] Calculation of the conversion of alcohol in the vinylation and vinyl ether in the hydrolysis was carried out by ^{1}H NMR spectra, based on the theoretical ratio of alcohol to vinyl ether, taking into account the excess of alcohol and acetals, converting mol% to wt%. The total yield of acetaldehyde is indicated by multiplying the yields of each step. [b] Analysis of the spectra is complicated by the complex composition of products of similar structure (Scheme 2.13). [c] Under the reaction conditions, partial resinization occurred, so the conversion of vinyl ether to alcohol was not taken into account for the yield of acetaldehyde. [d] Isolated yield.

From the data in the table, it can be seen that in the absence of a solvent, alcohols with an aliphatic structure (**4a**-**4e**, **4i**), especially containing a branched fragment (**4a** and **4e**), were best vinylated. In the case of menthol, hydrolysis was much worse, presumably due to the crystalline structure at room temperature (the remaining compounds are liquids). In the case of benzyl alcohol (**4g**), low vinylation conversion was also observed. Vinylation of ethylene glycol and glycerol led to a mixture of products of complex composition (Scheme 2.15), which made it difficult to determine the conversion using the method used for other compounds.



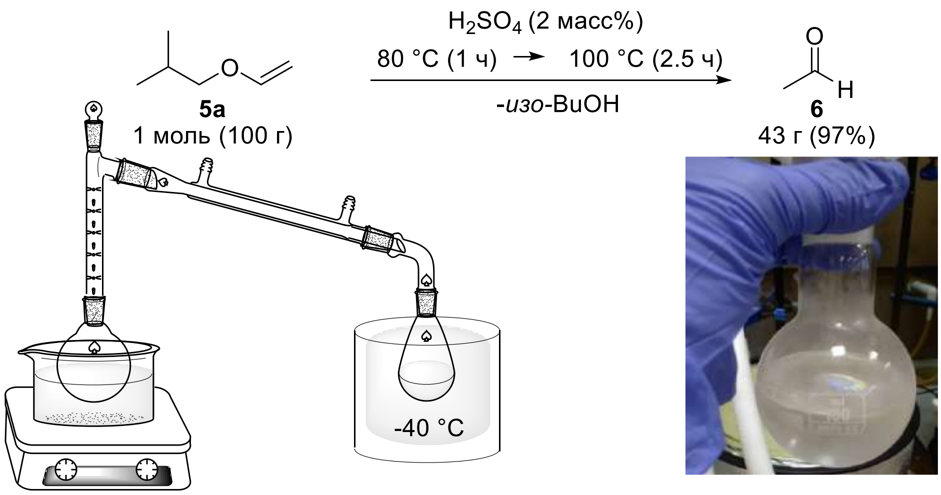
Scheme 2.15. Vinylation products for **4h** and **4j** alcohols

Hydrolysis of the mixture obtained after vinylation occurred in most cases in high yields, quantitatively for some compounds (entries 1, 6, 7). It was noted that when using alcohols with a long aliphatic chain (entries 2 and 3), hydrolysis proceeded much worse, apparently due to poor mixing of the mixture with water. It is worth noting that **4h** and **4j**, on the contrary, are highly soluble in water, which made it difficult to separate them from the reaction mixture during vinylation and hydrolysis. In addition, hydrolysis of mixtures obtained by vinylation of these alcohols produced small amounts of resins, making it impossible to completely recycle them and determine hydrolysis conversion in the manner used for other compounds.

Comparison of the total acetaldehyde yield based on the two steps showed that the best substrate for the vinylation-devinylation reaction sequence was alcohol **4a** (acetaldehyde yield after two steps 79%), alcohol **4e** (yield 71%) or **4i** (yield 61%).

2.3.3.3. Scaling. Having a large vinylation reactor makes it possible to synthesize large amounts of vinyl ether. However, in our laboratory we are limited to using a 50 mL pressure reactor. Therefore, the scalability of the procedure was shown only on the hydrolysis of the resulting vinyl ether. To do this, hydrolysis of 1 mol (100 g) of vinyl ether **5a** was carried out according to the developed procedure in a simple distillation unit shown in Figure 2.9. Larger loads greatly simplified the isolation procedure and increased the amount of product collected. To further complete the reaction, the acetaldehyde collected from the first preparation and containing unreacted vinyl ether was re-added to the aqueous layer and the reaction was repeated. After the second cycle, 43 g (97%) of **6** with a purity of 99% were obtained.

Given the absence of by-products, if necessary, the yield can be increased to quantitative levels under industrial conditions.



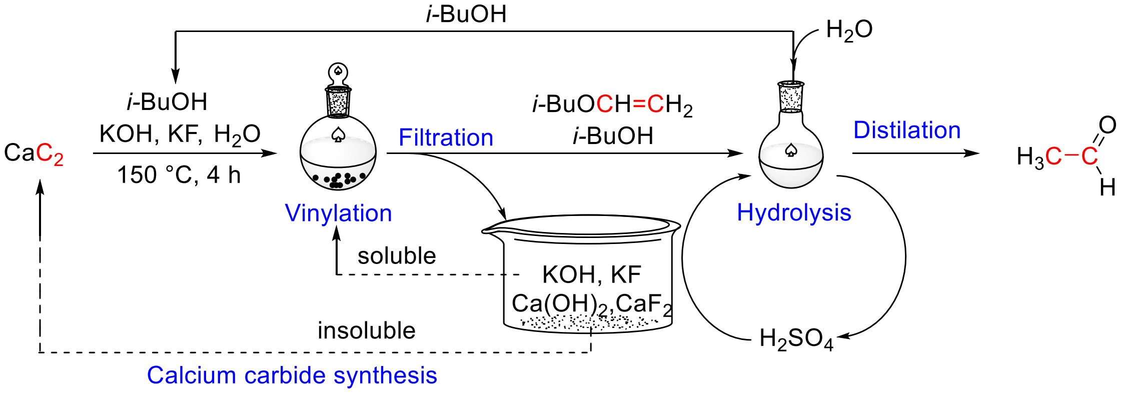
5a
1 моль (100 г)

6
43 г (97%)

Figure 2.9. Scheme of equipment for obtaining **6** on a 1 mol scale

Thus, by scaling up the hydrolysis of vinyl etper, it was possible to significantly increase theisolated yield of acetaldehyde (97% in the gram procedure *vs* 67% in optimization experiments).

2.3.3.4. General sequence including inorganic reagents. In the previous parts, the vinylation and devinylation procedures were described in detail from the point of view of alcohol recycling, and in general the sequence can be represented as follows (Scheme 2.16).



Scheme 2.16. General procedure for cyclic production of acetaldehyde

According to the scheme, calcium carbide, alcohol, water, alkali and potassium fluoride reacted in one reactor to form vinyl ether. The resulting mixture of alcohol and vinyl ether, after filtering and washing from alkali, was hydrolyzed with water in the presence of sulfuric acid to form the original alcohol and acetaldehyde. Acetaldehyde was distilled from the reactor during the reaction. A heterogeneous mixture remained in the reactor, consisting of an aqueous solution of acid and pure alcohol, which were separated and reused at the appropriate stages.

Inorganic reagents can theoretically also be recovered from the precipitate formed during the vinylation step. According to the proposed Scheme 2.16, the residue after filtration and washing with water consisted of two parts: a liquid aqueous part containing alkali and the remains of unreacted potassium fluoride, and a solid residue, insoluble in water, which is a mixture of calcium hydroxide and calcium fluoride formed during the hydrolysis of carbide calcium [47]. The water can be evaporated from the liquid part and the dry alkali and potassium fluoride can be used again at the vinylation stage. The solid residue can be used for the synthesis of calcium carbide and the regeneration of potassium fluoride, according to the reactions presented in Scheme 2.17. Any biomass, coal, and even waste can be used as a carbon source for the synthesis of calcium carbide [121].

$$
\begin{array}{lcll}
Ca(OH)_2 & \xrightarrow{600\ ^\circ C} & CaO + H_2O & (1) \\
CaF_2 + H_2O & \xrightarrow{800\ ^\circ C} & CaO + 2\ HF & (2) \\
HF + KOH & \longrightarrow & KF + H_2O & (3) \\
CaO + 3\ C & \xrightarrow{1900\ ^\circ C} & CaC_2 + CO & (4) \\
2\ CO + O_2 & \longrightarrow & 2\ CO_2 & (5) \\
CaO + CO_2 & \longrightarrow & CaCO_3 & (6)
\end{array}
$$

Scheme 2.17. Sequence of reactions for the regeneration of KF and CaC_2

Thus, in this part of the study, a fully cyclic method for the production of acetaldehyde was developed, based on the sequence of vinylation-devinylation reactions. The advantages of the proposed method include complete recycling of the process, availability and low cost of starting materials. The results obtained in this chapter were published in a peer-reviewed scientific journal [122].

2.4. Using the reaction of nucleophilic addition of alcohols to acetylene from calcium carbide for the cyclic production of polymers

The developed method for the cyclic production of acetaldehyde prompted us to create another cyclic process, which is based on the reaction of the nucleophilic addition of alcohols to acetylene - the production of polymers. Currently, most polymer materials are obtained from non-renewable raw materials, the main ones being ethylene, propylene and styrene, extracted from oil [123]. In fact, such polymers are disposable because after use they are difficult to decompose into original monomers suitable for re-polymerization. Thus, according to data for 2015, about 60% of all plastics produced by humanity are thrown away and accumulate in the environment [124]. In this regard, the problem of obtaining recyclable polymer materials from renewable raw materials has recently become particularly urgent, as evidenced by the avalanche-like growth of publications devoted to this topic.

There are several approaches to the production of renewable polymers, the main of which is the use of biomass as a raw material for their production [123]. The advantages of using biomass are its availability, low cost and, as mentioned earlier, renewability. Biomass can act as a source of monomers, for example, eugenol, pinene, myrcene, limonene. In this case, the compound already contains a double bond or a ring through which polymerization subsequently occurs. Examples of such reactions include the polymerization of β-pinene [125], myrcene [126] and alloocymene [127]. However, after using these polymers, the problem remains related to the complexity of processing.

Another direction of using biomass to produce polymers is the modification of its components in order to obtain monomers with other functional groups, through which further polymerization occurs. Examples of such reactions include modification of limonene for further ring-opening polymerization [128], protection of the hydroxyl group of eugenol [129], and modification of β-pinene and other terpenes with thiols [130] for further polymerization. Modification of a natural compound often involves multi-step syntheses and complex reagents, which in many cases are not renewable.

In this section of the dissertation, attention is paid to the renewability of calcium carbide, as the key to the production of polymers from renewable raw materials, for which terpene alcohols were also used. In the course of the research presented in this subchapter, the goal was to develop a cyclic method for producing polymers from renewable raw materials, and, consequently, materials based on them.

2.4.1. Preparation of monomers based on natural alcohols and calcium carbide

Available terpene alcohols were selected as natural alcohols: menthol (**4f**), borneol (**4k**), fenchol (**4l**); natural alcohols common in perfumery: citronellol (**4m**), javanol (**4n**), myrtanol (**4o**) and rosafen (**4p**), as well as 5-HMF (**4q**) (Figure 2.10).

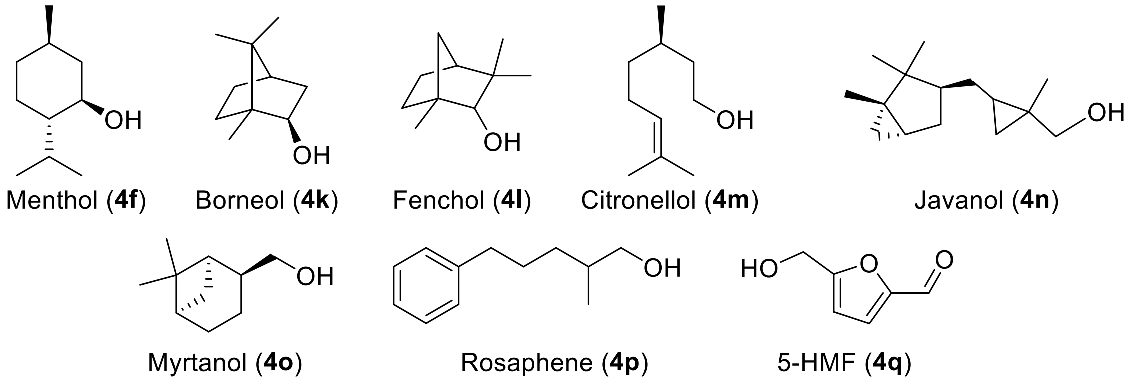
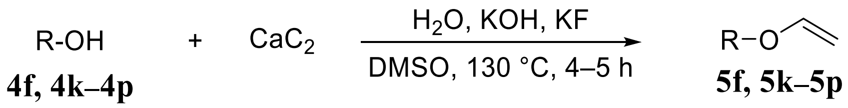


Figure 2.10. Natural alcohols selected for research

For vinylation of natural alcohols **4f, 4k–4p** (Scheme 2.18) using calcium carbide, we used a technique previously developed [47]. In this procedure, the reaction is typically carried out in pressure tubes using a loading of 2 mmol calcium carbide per 8 ml tube. In this case, the reaction of addition of acetylene to alcohols is often carried out under superbasic conditions, for which the DMSO-KOH-KF system has proven to work well for the vinylation of alcohols using calcium carbide. By slightly modified the ratios of the reagents and increasing the reaction time to 4–5 hours, was achieved high isolated yields of the resulting vinyl ethers (Table 2.9).



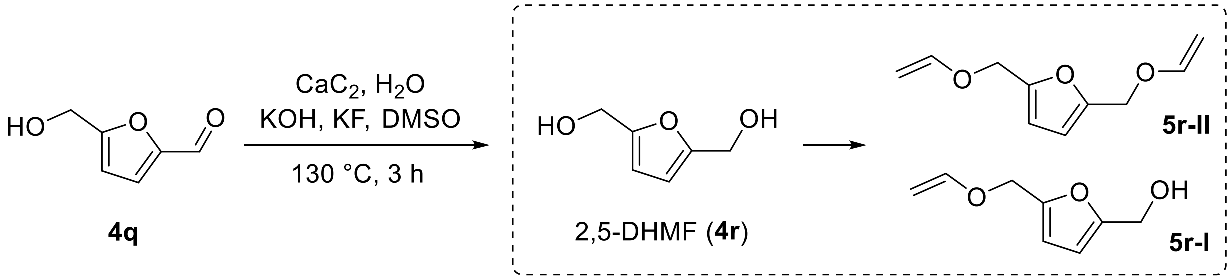
Scheme 2.18. Vinylation of natural alcohols **4f**, **4k–4p**

Table 2.9. Vinyl ether **5f**, **5k**–**5p**

Vinyl ether	Reaction time, h	Isolated yield, %
Menthol (**5f**)	5	87
Borneol (**5k**)	4	75
Fenchol (**5l**)	4	92
Citronellol (**5m**)	4	93
Javanol (**5n**)	4	88
Myrtanol (**5o**)	4	82
Rosafene (**5p**)	5	88

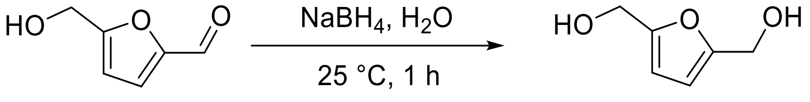
It is worth noting that under rather severe vinylation conditions, the double bond in the structure of vinyl ether **5m** was retained (no resinization was observed), which was confirmed by ^{1}H NMR spectrometry data and a high yield of the product. Vinyl ether **5n** was obtained as a mixture of two isomers, with the same ratio as the original alcohol **5**, which was confirmed by GC-MS and ^{1}H NMR spectrometry data. The structure of all obtained vinyl ethers **5f**, **5k**–**5p** was confirmed by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry data.

When using this method for alcohol **4q**, it turned out that in a superbasic medium this alcohol was reduced to 2,5-di(hydroxymethyl)furan (2,5-DHMF) (**4r**), which then reacted with acetylene formed from calcium carbide (Scheme 2.19). According to ^{1}H NMR and GC-MS, under the reaction conditions a mixture of products was formed, mainly consisting of alcohol **4r** and mono- and divinyl ethers **5r**.



Scheme 2.19. Transformations of 5-HMF under vinylation conditions

An analysis of the literature showed that the reduction of compound **4q** to **4r** apparently occurred *via* the Cannizzaro reaction, which occurs in the presence of an alkali [131]. Optimization of vinylation conditions did not lead to the desired vinyl ether **5q**, but opened the way to di- and mono-vinyl ethers **5r**. Due to the large number of by-products from the transformation of alcohol **4q** under superbasic conditions, it was decided to obtain alcohol **4r** separately by well-known method [132]. Thus, alcohol **4r** was obtained by reducing alcohol **4q** in water with $NaBH_4$ (Scheme 2.20). After extraction and removal of the solvent, the product yield was 69%.



4q **4r**

Scheme 2.20. Preparation of diol **4r**

Having obtained alcohol **4r**, the conditions for its vinylation were optimized (Table 2.10). Since it is difficult to stop the reaction at the stage of formation of mono-vinyl ether, the main goal was to obtain divinyl ether **5r-II**.

Table 2.10. Optimization of conditions for obtaining **5r-II** [a]

Entry	Base	T, °C	t, h	CaC_2:**4r** ratio	Conversion **4r**, %	Selectivity **5r**, [b] %	Selectivity **5r-II**, %	Yield **5r-II**, %
1	KOH	100	1	4:1	98	61	53	52
2	*t* - BuOK	100	1	4:1	92	63	52	48
3	KF	100	1	4:1	39	100	17	7
4	KF, KOH	100	1	4:1	98	73	59	58
5	-	100	1	4:1	0	-	-	0
6	KF	130	1	4:1	94	91	61	57
7	KF	80	1	4:1	3	100	0	0
8	KF	25	1	4:1	0	-	-	-
9	KF	100	3	4:1	71	100	39	28
10	KF	100	6	4:1	97	93	73	71
11	KF	100	14	4:1	100	45	45	45
12	KF	100	6	5:1	100	66	66	66
13	KF	100	6	6:1	100	80	78	78

[a] Selectivity, conversion and yield determined by GC-MS; [b] Selectivity for the formation of mono- and divinyl ethers **5r**, %.

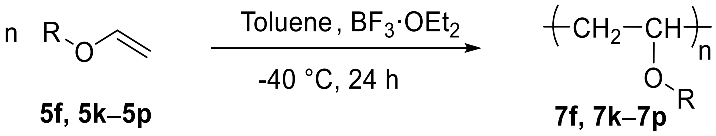
When using alkali and potassium *tert*-butoxide (entries 1 and 2), a high conversion of **4r** was achieved, but the selectivity for the formation of vinyl ethers was low (61–63%). At the same time, when using potassium fluoride (entry 3), high selectivity for the formation of vinyl ethers was achieved, but low conversion of the starting alcohol. To increase conversion, a mixture of KF and KOH was used (entry 4), however, the selectivity of the reaction in this system decreased (to 73%), so further conditions were varied using KF as a base. As expected, without a base (entry 5) the reaction did not occur.

Varying temperature conditions (entries 6–8) showed that increasing the temperature to 130 °C led to the formation of by-products, which reduced the selectivity of the reaction (up to 91%). At the same time, a decrease in temperature led to a significant drop in the rate of the process (**4r** conversion decreased from 17% at 100 °C to 3% at 80 °C and to 0% at room temperature, respectively). Increasing the reaction duration led to an increase in conversion (entries 9–11), while the optimal conversion-selectivity ratio was achieved when the reaction was carried out for 6 hours (entry 10). Increasing the calcium carbide loading (entries 12–13) led to an increase in the yield of divinyl ether **5r-II**. Thus, under optimal conditions for vinylation (entry 13) (KF as a base, the ratio of CaC_2 to alcohol **4r** was 6:1, 6 hours at 100 °C), a yield of **5r-II** 78% was achieved.

Thus, a series of vinyl ethers of natural alcohols was obtained in high yields (75-93%). Once obtained, all vinyl ethers were purified by column chromatography, dried over CaH_2 and distilled *in vacuo* using the Kugelrohr system (vacuum short distillation) to remove traces of parent alcohols and water that inhibit cationic polymerization.

2.4.2. Preparation of polymers based on synthesized vinyl ethers

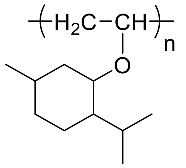
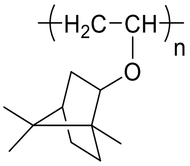
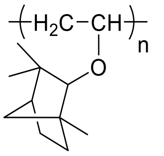
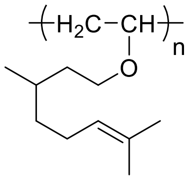
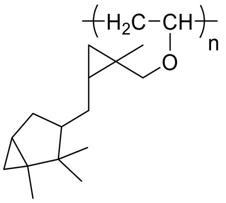
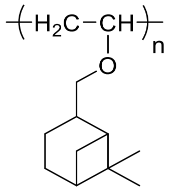
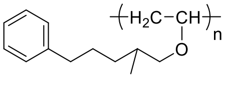
2.4.2.1. Linear polymers based on monovinyl ethers of terpene alcohols. After thorough purification, the vinyl ethers of natural alcohols were subjected to cationic polymerization using a standard procedure using boron trifluoride etherate as an initiator (Scheme 2.21). Since polymerization is sensitive to traces of water and oxygen, all glassware (Schlenk flasks, syringes, stirrer arms) were first thoroughly dried in an oven (110 °C), and also additionally heated with a hairdryer in a vacuum on the Schlenk line, and then filled with argon. Pre-dried and argonized toluene was used, which was taken in an argon flow. The temperature during polymerization was maintained using a cryostat.



Scheme 2.21. Polymerization of vinyl ethers **5f, 5k–5p**

Vinyl ethers **5f**, **5k**–**5p** were polymerized at -40 °C. After preparation, the polymers were reprecipitated 3 times with methanol from a solution in chloroform and dried in a vacuum at 40 °C for 48 h. The yields and characteristics of the obtained polymers (aggregate state and molecular weight) are presented in Table 2.11.

Table 2.11. Characteristics of polymers **7f**, **7k**–**7p**

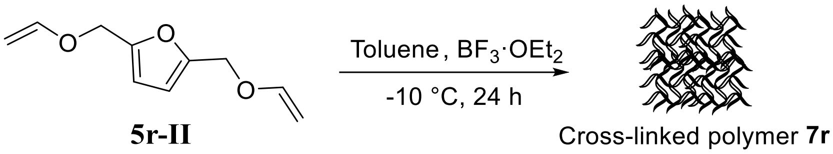
Entry	Polymer	Structure	Yield, %	Aggregation state	Mn (g/mol)	Mw (g/mol)	D
1	Polyvinyl - menthol **(7f)**		76	Solid	5.04×10^4	8.50×10^4	1.69
2	Polyvinyl - borneol (**7k**)		81	Solid	5.54×10^4	7.08×10^4	1.28
3	Polyvinyl - fenchol (**7l**)		74	Solid	1.29×10^4	2.57×10^4	1.98
4	Polyvinyl - citronellol (**7m**)		85	Viscous liquid	3.35×10^4	5.38×10^4	1.61
5	Polyvinyl - javanol (**7n**)		71	Solid	6.20×10^3	1.12×10^4	1.82
6	Polyvinyl - myrtanol (**7o**)		82	Solid	2.10×10^4	4.3×10^4	2.02
7	Polyvinyl - rozafene (**7p**)		72	Viscous liquid	5.01×10^4	6.28×10^4	1.25

It can be noted that most of the resulting polymers were solids. Polymers containing aliphatic groups without rings (for example, **7m**, **7p**) were viscous liquids. The resulting polymers were highly soluble in organic solvents such as THF and methylene chloride, which made it possible to determine their molecular weights by GPC. The molecular weight of all polymers was in the range of 0.6–5.5 × 10^4 g/mol, and the dispersity (Đ) was 1.25–2.02.

It is noteworthy that the polymers after isolation were exclusively polymerization products at the O-vinyl group. In the ^{1}H NMR spectra there were no signals for the formation of polymers obtained *via* other double bonds (polymer **7m)**, and the molecular weight distribution was monomodal. Also, no ring opening or rearrangement products were observed under polymerization conditions.

Thus, a series of polymers with a linear structure were obtained from mono-vinyl ethers of natural alcohols in yields of 71–85%.

2.4.2.2. Cross-linked polymers based on divinyl ether. Divinyl ether **5r-II** was also subjected to cationic polymerization under the same conditions as indicated above for mono-vinyl ethers. It turned out that ether **5r-II** crystallized at this temperature and did not readily enter into further polymerization, so the reaction temperature was increased to -10 °C. Under optimized reaction conditions, divinyl ether was converted to cross-linked polymer **7r** in 71% yield (Scheme 2.22).



Scheme 2.22. Polymerization of divinyl ether **5r-II**

This polymer turned out to be insoluble in organic solvents, which made it difficult to analyze using NMR and GPC methods. This property is characteristic of cross-linked polymers.

2.4.3. Thermal properties of polymers based on vinyl ethers of terpene alcohols

For polymers **7f**, **7k**–**7p**, the limits of temperature stability of the polymer were determined by thermogravimetric analysis (TGA). According to TGA data (Figure 2.11), all synthesized polymers completely decomposed at 450–500 °C (the weight of the solid residue was 0.05–3.4%). Polymer **7f** began to decompose at 300 °C (small drop in weight up to about 380 °C (up to 5%) and a sharp drop in weight after (99%)) and was one of the most stable polymers, along with polymers **7m**, **7n** and **7p**. For these polymers, a small drop in weight was also observed up to 300 °C (less than 3%) and a sharp drop after 350 °C (**7m** and **7n**) and 370 °C (**7p**) (up to 97–99%). For the polymer **7k**, two stages of decomposition were observed: the first at 170–220 °C (5% weight loss) and the second after 400 °C (99% weight loss). The thermal stability of polymer **7l** was the lowest: up to 170 °C the polymer lost about 4% in weight, then when heated to 250 °C another 5%, up to 300 °C – the total loss was 15%, and then after 320 °C it was observed a sharp drop in weight to 99%. Polymer **7o**, in turn, apparently due to solvent residue, lost 5% of its weight when heated to 120 °C, and a significant drop was observed after 360 °C (up to 99%). Thus, for most polymers, decomposition began at 120–299 °C with a weight loss of 3–5%, then at higher temperatures (after 320–400 °C) it reached 97–99%.

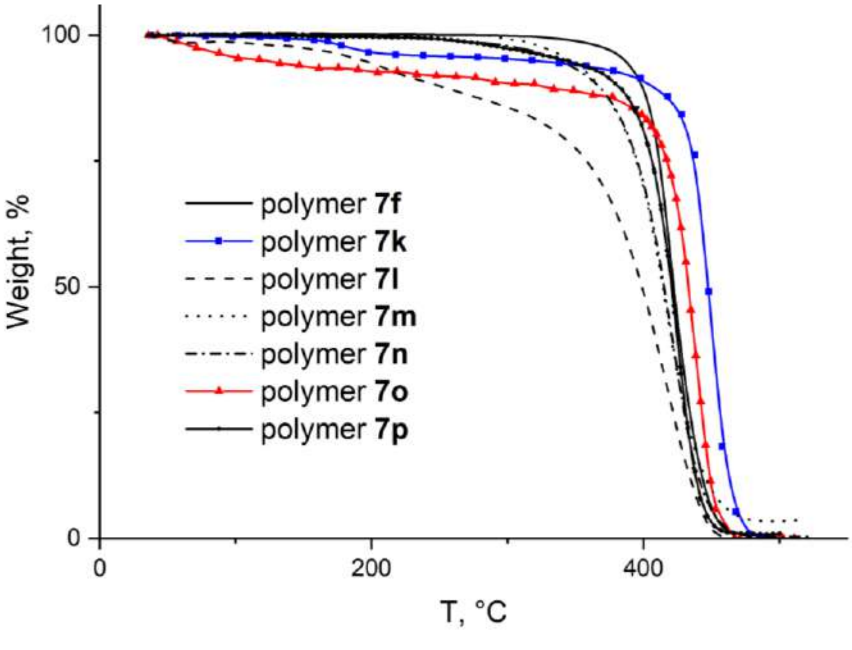


Figure 2.11. Curves of TGA for polymers **7f**, **7k**–**7p**

An interesting feature of the obtained polymers was their thermoplasticity, which is a characteristic feature of polymers with a polyethylene chain. The possibility of repeated softening-hardening was studied using the example of polymer **7o** with a molding temperature of about 120 °C. The selected polymer was heated to a specified temperature, after which it was softened and shaped into various shapes, shown in Figure 2.12.

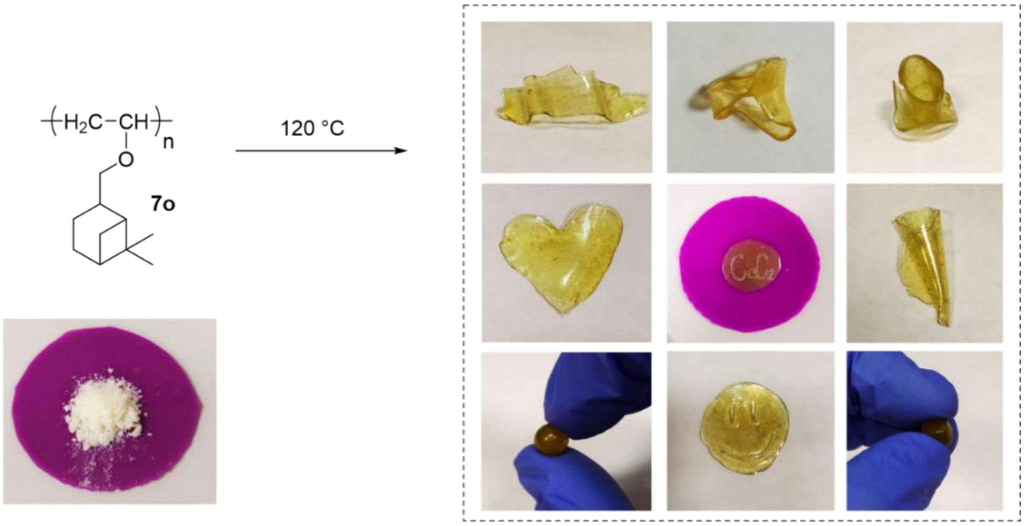


Figure 2.12. Thermoplastic properties of polymer **7o**

After cooling, the polymer solidified, maintaining its shape. This procedure was performed multiple times (up to 10 times), after which the polymer was analyzed using GPC to determine its molecular weight. It turned out that the molecular weight distribution remained almost the same, from which we can conclude that it is possible to subject the polymer to multiple temperatures without destroying its structure. This property served as the basis for further research on a number of polymers as filaments for 3D printing (see Chapter 2.4.6).

Thus, it was shown that some of the synthesized polymers have thermoplastic properties. Most of the synthesized polymers were stable up to 300 °C and completely decomposed at 450–500 °C. To make it possible to further process these polymers, their decomposition products were studied.

2.4.4. Pyrolysis of polymers based on vinyl ethers of terpene alcohols

To identify the decomposition products of polymers **7f**, **7k**–**7p** when heated above 300 °C, pyrolysis of the polymers **7f**, **7k**–**7p**, as well as the corresponding alcohols **4f**, **4k**–**4p** and vinyl ethers **5f**, **5k**–**5p** was carried out. Pyrolysis was carried out in an argon atmosphere in a special pyrolysis unit connected to a GC-MS analyzer used to identify the pyrolysis products.

Terpene alcohols, in particular **4f**, **4l**, **4p**, were resistant to pyrolysis at 300 °C (Table 2.12). Alcohols **4k** and **4n** were only slightly degraded. However, during the pyrolysis of **4m** and especially **4o** at 300 °C, a large amount of pyrolysis products was observed; in the case of **4m**, the main alcohol still remained, and in the case of **4o**, the main product was a compound whose structure could not be determined (content – 40%).

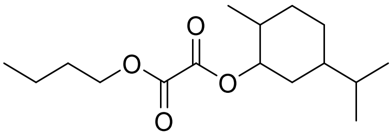
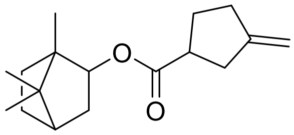
Table 2.12. Products of pyrolysis of alcohols at 300 °C

Alcohol	Alcohol content, %	Other pyrolysis products [a]
4f	100	-
4k	94	5% (*iso*-borneol)
4l	100	-
4m	63	8% [b]
4n	97	-
4o	16	12% (glycerol tricaprylate), 40% [b]
4p	100	-

[a] Products whose content in the mixture is more than 5% are indicated. [b] The product could not be identified.

Vinyl ethers of terpene alcohols, on the contrary, turned out to be unstable under pyrolysis conditions at 300 °C, as evidenced by the large number of pyrolysis products and, in most cases, the complete absence of the original vinyl ether (Table 2.13). The main product of pyrolysis **5f** and **5p** was squalene, also with lower concentrations the formation of glycerol tricaprylate and the corresponding alcohol was observed. In the case of **5k** and **5m** the main product was alcohol: *iso*-borneol and citronellol, respectively; the by-product, as for compounds **5n** and **5o**, was the corresponding acetate, and the original vinyl ether also remained**.** All vinyl ethers had their own by-products, which were generally lower in content.

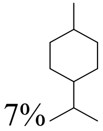
Table 2.13. Products of pyrolysis of vinyl ethers at 300 °C

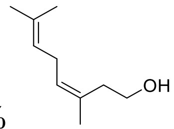
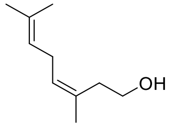
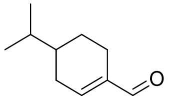
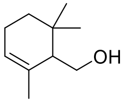
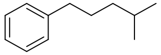
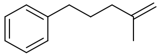
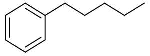
Vinyl ether	Content in the mixture after pyrolysis, %					
	Alcohol	V.E.	Acetate	Glycerotricaprylate	Squalene	Other[a]
5f	6	-	-	27	26	10%  18%[b]
5k	4 + 41(*iso*-borneol)	-	8	-	-	9%[b], 5% (ketone)
5m	41	-	12	-	-	12% (formate)
5n	17	26	47	-	-	-
5o	21	16	9	-	-	37% 
5p	4	-	-	6	77	-

[a] Products whose content in the mixture is more than 5% are listed. [b] The product could not be identified.

Based on the TGA data, the following pyrolysis temperatures were chosen for the pyrolysis of polymers: 300, 350, 400 and 450 °C. Tube furnace pyrolysis of some polymers was also performed (**7f**, **7k** and **7o**). Depending on the temperature used, the composition of the polymer pyrolysis products changed (Table 2.14).

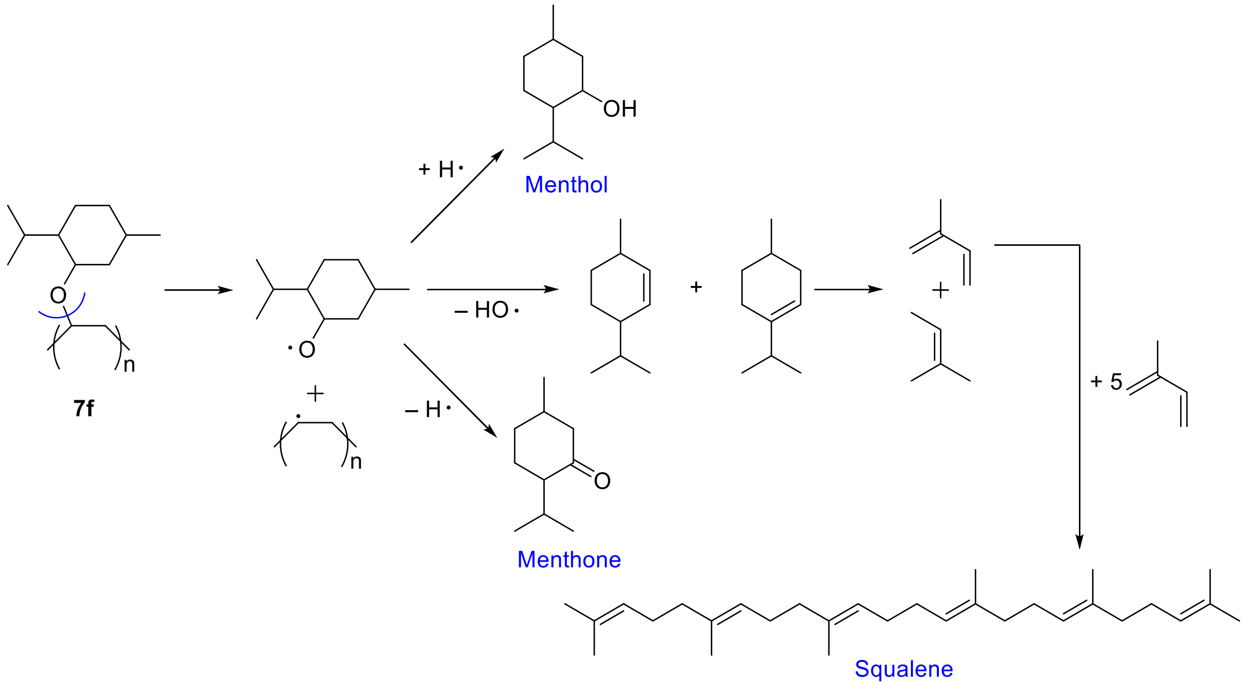
Table 2.14. Products of polymer pyrolysis **7f**, **7k–7p** at 300–450 °C

Main Products	T, °C				Pyrolysis in a tube
	300	350	400	450	
7 f					
Alcohol, %	73	87	73	57	73
Ketone, %	1	8	20	21	10
Squalene, %	26	3	8	2	-
Other [a]	-	-	-	 7%	16% [b]
7k					
Alcohol, %	4	4	15	37	36
Ketone, %	5	21	47	59	47
Toluene, %	84	62	26	1	16
Squalene, %	4	11	–	2	-
Other [a]	3% (camphene)	-	12% [b]	-	-
7l					
Alcohol, %	pyrolysis does not occur	pyrolysis does not occur	25	26	-
Ketone, %			44	52	-
Acetaldehyde,%			20	-	-
Other [a]			-	-	-
7m					
Alcohol, %	76	66	52	49	-
Aldehyde, %	10	27	35	32	-
Squalene, %	7	3	5	-	-
Other [a]	8% [b]	-	-	-	-
7n					
Alcohol, %	86	59	62	56	-

Aldehyde, %	3	8	12	13	-
Toluene, %	2	1	-	-	-
Squalene, %	4	7	-	-	-
Other [a]	-	12% [b]	 9%	5% [b], 7% 	-
7o					
Alcohol, %	67	67	45	28	54
Aldehyde, %	2	21	13	9	4
Toluene, %	21	-	10	10	-
Other [a]	-	10% 	-	-	17% 
7p					
Alcohol, %	56	48	48	37	-
Aldehyde, %	44	37	35	39	-
	-	7	11	14	-
	-	2	4	7	-
	-	-	1	3	-
Squalene, %	-	3	-	-	-
Other [a]	-	-	-	-	-

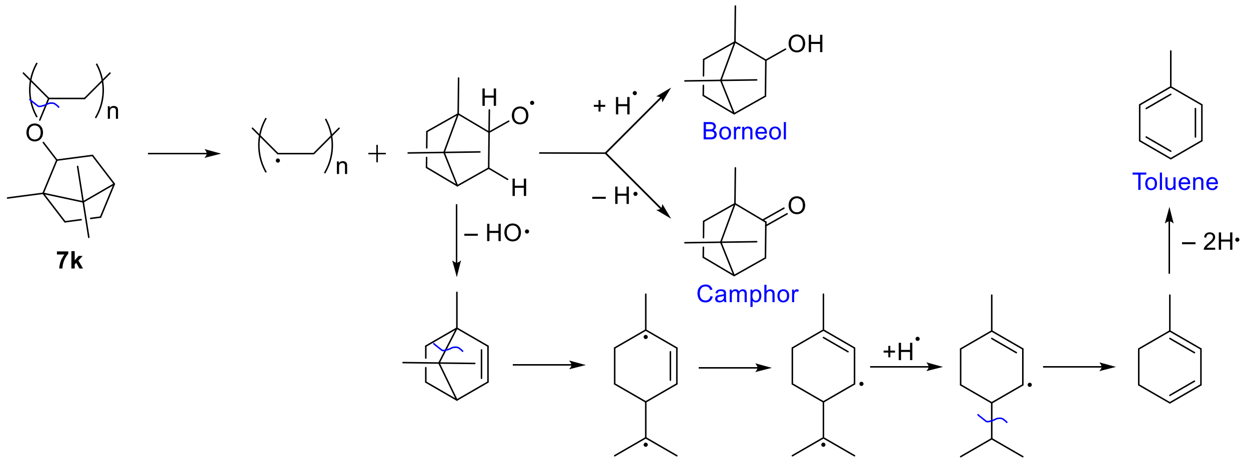
[a] Products whose content in the mixture is more than 5% are listed. [b] The product could not be identified.

In the case of pyrolysis of polymer **7f**, the main products were menthol, menthone and squalene (Scheme 2.23), and the content of alcohol and squalene decreased with increasing temperature, while the content of ketone increased. During pyrolysis in a tube, the main product was also alcohol (73%), which was confirmed by ^{1}H NMR spectroscopy data.



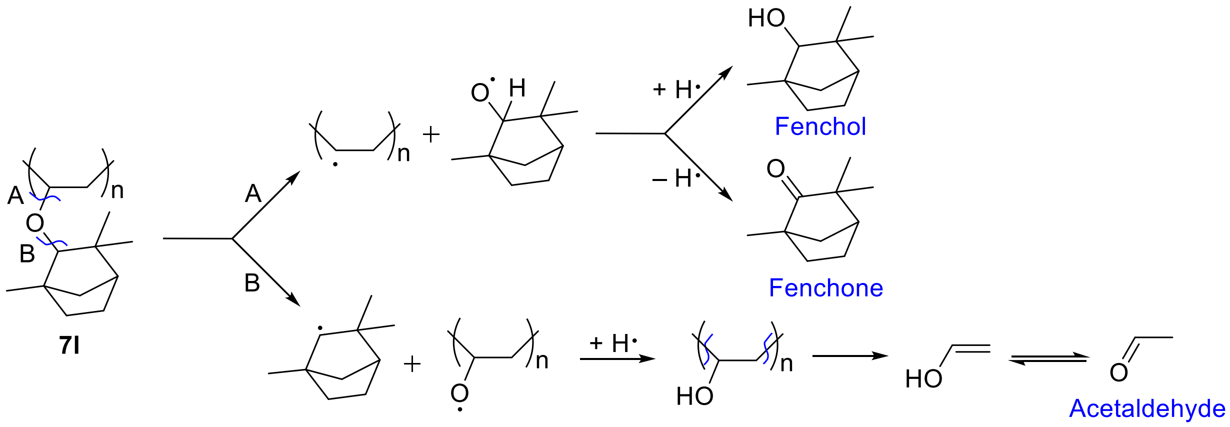
Scheme 2.23. Proposed mechanism of pyrolysis of polymer **7f**

The main products of pyrolysis of polymer **7k** were borneol, camphor and toluene (Scheme 2.24). It is possible that toluene was initially contained in the polymer, since it was a solvent during polymerization. It can be noted that with increasing pyrolysis temperature, the toluene content in the mixture decreased, while borneol and camphor increased. This may be due to the fact that at low temperatures pyrolysis only began and a significant contribution was made by the evaporation of toluene, which could be contained in the initial polymer. Pyrolysis in the tube led mainly to alcohol and ketone; in the ^{1}H and ^{13}C NMR spectra, signals were observed mainly from alcohol, and there were no signals from toluene.



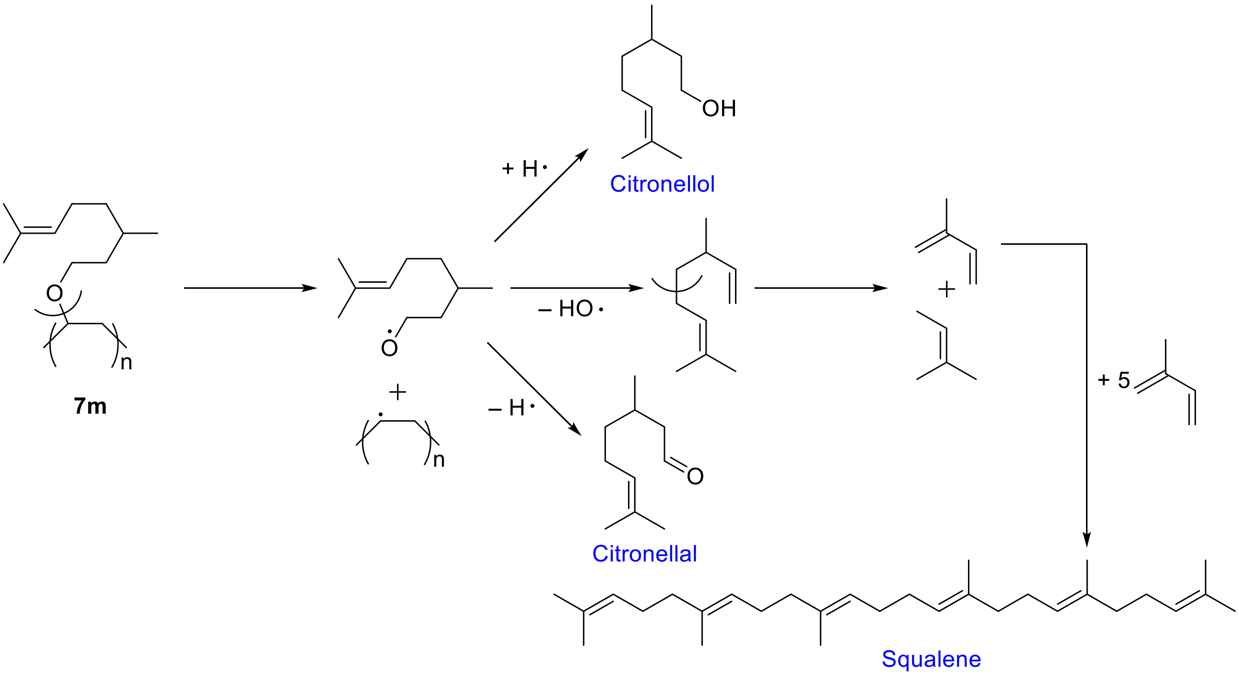
Scheme 2.24. Proposed mechanism of polymer **7k** pyrolysis

During the pyrolysis of polymer **7l**, in contrast to other polymers, the formation of acetaldehyde was observed at 350 °C; at lower temperatures, pyrolysis did not occur. When the temperature increased above 400 °C, pyrolysis led mainly to fenchol and fenchone (Scheme 2.25); with increasing temperature, the content of both products increased significantly.



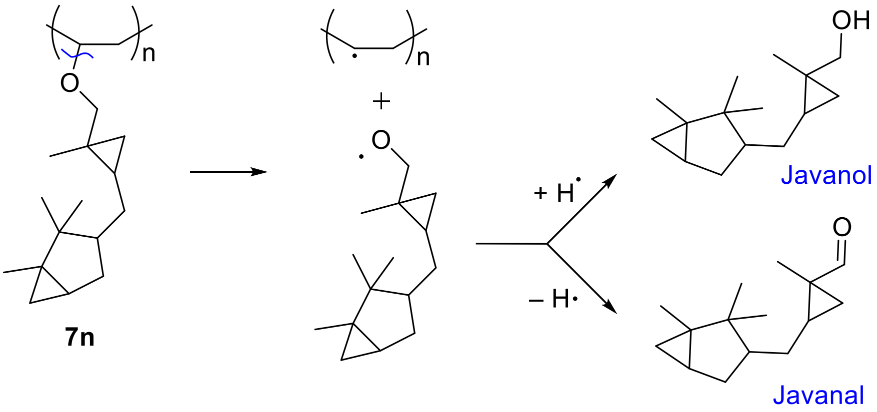
Scheme 2.25. Proposed mechanism of polymer **7l** pyrolysis

Pyrolysis of polymer **7m** led to a smaller amount of the main products - citronellol and citronellal (Scheme 2.26), while the alcohol content decreased with increasing temperature, and the aldehyde content increased. The formation of small amounts of squalene was also observed.



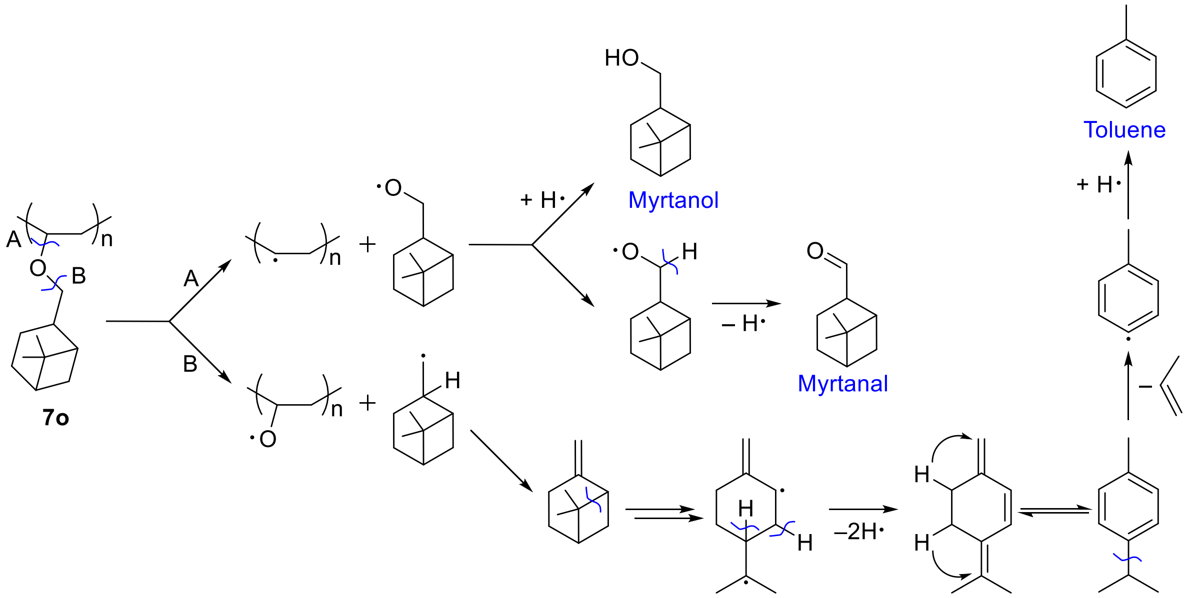
Scheme 2.26. Proposed mechanism of polymer **7m** pyrolysis

Pyrolysis of polymer **7n** proceeded mainly with the formation of javanol (Scheme 2.27); the content of aldehyde and other products was significantly lower.



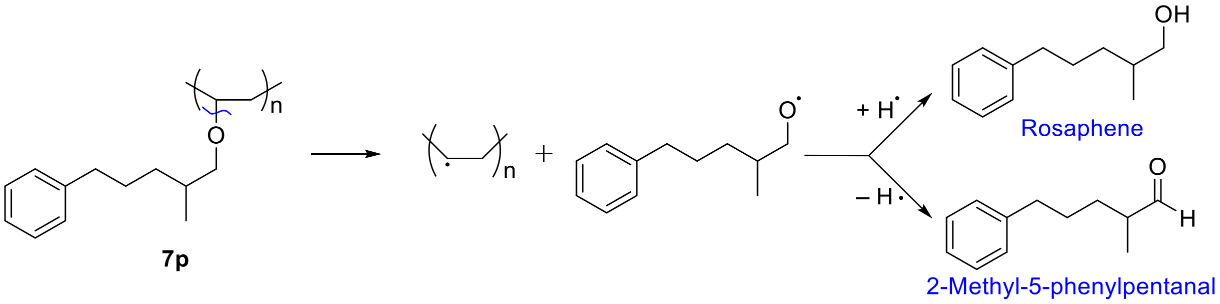
Scheme 2.27. Proposed mechanism of polymer **7n** pyrolysis

In the pyrolysis of polymer **7o**, the main products were myrtanol, myrtanal and toluene (Scheme 2.28). Toluene, as in the case of polymer **7k**, could be present in the polymer initially after polymerization and not be a pyrolysis product. The content of alcohol, aldehyde and toluene decreased with increasing temperature, while the number of by-products increased (a large number of peaks with an area of less than 5% were observed in the mass spectra). Pyrolysis in the tube resulted mainly in myrtanol (53%).



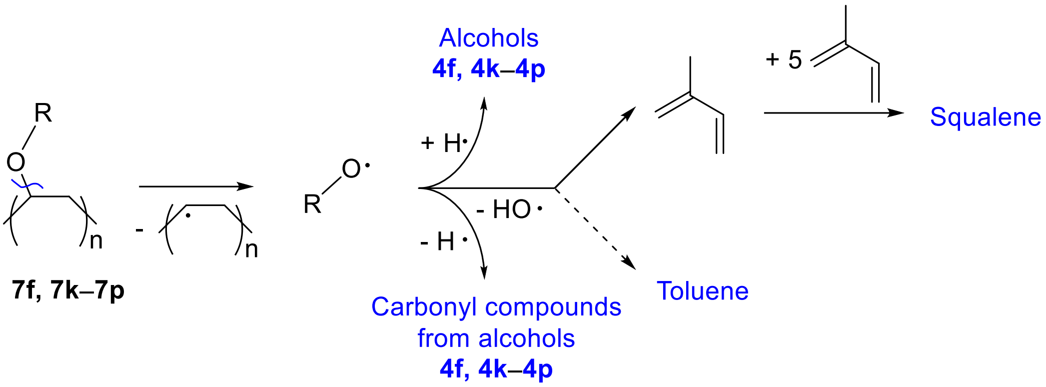
Scheme 2.28. Proposed mechanism of polymer **7o** pyrolysis

During the pyrolysis of polymer **7p**, the formation of rosapfene and its corresponding carbonyl compound was observed (Scheme 2.29). As the pyrolysis temperature increased, the alcohol and aldehyde content decreased, while the content of by-products increased.



Scheme 2.29. Proposed mechanism of polymer **7p** pyrolysis

Thus, the main products of pyrolysis of polymers **7f**, **7k**–**7p** were the initial alcohol and the corresponding aldehyde or ketone, depending on whether it was a primary or secondary alcohol (Scheme 2.30). In many cases, squalene or toluene (which may have been present in the polymer initially) was also formed. It can be noted that for polymers **7f**, **7m**–**7o** alcohol was predominantly formed, and for **7k** and **7l** – ketone (Table 2.15). In this case, the alcohol–carbonyl compound ratio, as well as their total content, strongly depended on the pyrolysis temperature.



Scheme 2.30. Main products of polymer **7f**, **7k–7p** pyrolysis

Table 2.15. The main products of pyrolysis of synthesized polymers at different temperatures

Polymer	T, °C	Alcohol, %	Carbonyl compound, %	Total content of alcohol and carbonyl compound, % [b]
7f	300	67	2	69
	350	80	12	92
	400	73	20	93
	450	57	21	78
7k	300	4	5	9
	350	4	6	10
	400	15	47	62
	450	37	59	96
7l	350	5	17	22
	400	17	60	77
	450	26	52	78
7m	300	76	6	82
	350	66	27	93
	400	52	35	87
	450	49	32	81
7n	300	86	3	89
	350	59	8	67
	400	62	12	74
	450	56	13	69
7o	300	64	4	68
	350	67	21	88
	400	45	13	58
	450	38	9	47
7p	300	56	44	100
	350	48	37	85
	400	48	35	83
	450	37	39	76

Since pyrolysis in a pyrolysis installation is carried out in small quantities (several mg), the work also carried out pyrolysis of the resulting polymers in large volumes (20–100 mg) in a quartz tube. The tube was connected in series with traps into which pyrolysis products were captured. The tube was placed in a tube furnace preheated to 750 °C, and the reaction products were analyzed using ^{1}H NMR and GC-MS. Polymers **7f**, **7k** and **7o** were chosen for tube pyrolysis. The reaction products are presented in Table 2.16.

Table 2.16. Products of pyrolysis of selected polymers in a tube furnace according to GC-MS data

Polymer	Alcohol, %	Carbonyl compound, %	Total content of alcohol and carbonyl compound, %
7f	73	10	83
7k	36	47	83
7o	53	4	57

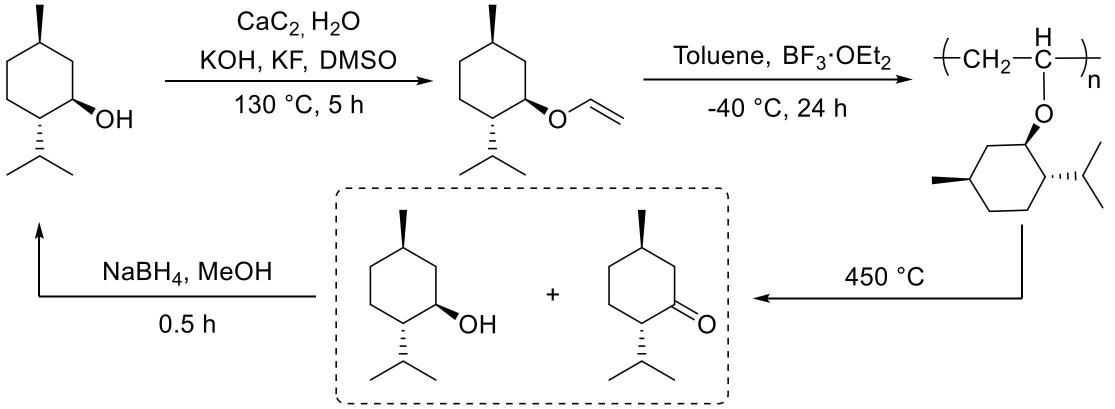
Despite the fact that the total content of the carbonyl compound and alcohol during pyrolysis in the tube turned out to be slightly lower than in the pyrolytic installation (possibly due to the higher temperature in the furnace), we were able to isolate this mixture. Subsequently, an experiment was even carried out with a large amount of polymer **7f** at a lower temperature (450 °C), in which it was possible to obtain a mixture of menthol and menthone with a preparative yield of 76%. This confirmed the formation of the starting alcohols and their corresponding carbonyl compounds during the pyrolysis of the synthesized polymers.

Thus, it was shown that the main products of pyrolysis of polymers **7f**, **7k**–**7p** were the corresponding starting terpene alcohols and their carbonyl compounds. The total content of alcohol and carbonyl compound in the mixture after pyrolysis ranged from 78 to 100% according to GC-MS. The discovered patterns make it possible to create a closed cycle for the production and decomposition of polymers based on terpene alcohol.

2.4.5. Recycling of polymers based on vinyl ethers of terpene alcohols

The final stage of this part of the work was the return of the original alcohols back to the polymer production cycle. In order to return more alcohol to the system, the resulting mixture of carbonyl compound and alcohol can be reduced to pure alcohol. To confirm this hypothesis, the standard procedure for the reduction of alcohols with sodium borohydride was used in the work. Having worked out the reduction procedure on pure camphor, the conditions were transferred to a mixture of camphor and borneol, and then to the mixture obtained after pyrolysis of the polymer **7k**. Thus, it was possible to successfully restore the mixture obtained after pyrolysis of polymer **7k** to the original alcohol used in the preparation of the same polymer.

In order to confirm the processability of the synthesized polymers, a full cycle of synthesis, decomposition and re-synthesis of polymers was carried out using the example of polymer **7f** (Scheme 2.31).



Scheme 2.31. Full cycle of polymer recycling using example **7f**

At the initial stage, vinyl ether **5f** was obtained with a yield after purification and distillation of 87%. The resulting vinyl ether was then polymerized; after reprecipitation and drying, the yield of polymer **7f** was 76%. The resulting polymer was pyrolyzed in a quartz tube at 450 °C, after which the liquid fraction was collected, which was mainly a mixture of menthol and menthone (mixture yield 76%). Next, the resulting mixture was reduced with sodium borohydride to obtain menthol with an isolated yield of 98%. Thus, alcohol **4f** was returned to the polymerization cycle. After re-vinylation of the resulting menthol and further polymerization, it was possible to re-obtain polymer **7f** with the same characteristics.

Thus, the possibility of pyrolysis of the polymer to the starting alcohol and carbonyl compound was demonstrated. Reduction of this mixture opened the way to re-producing a polymer with the same characteristics as the original one. The entire path of the so-called “cyclic assembly and disassembly” of synthesized polymers was demonstrated using the example of a menthol-based polymer.

2.4.6. Using the resulting polymers to production of material for 3D printing

Since some of the resulting polymers, in addition to being recyclable, also turned out to be thermoplastic, we decided to explore the possibility of using them to create a material for making objects. 3D printing was chosen as a method for production of objects, since this method allows you to create complex objects without waste, which accompany methods based on the removal of excess material (subtractive methods). To create objects using 3D printing, various technologies are used, one of which is fused modeling deposition modeling (FDM). In this technology, material in the form of a filament (thread of a certain diameter 1.75 mm) is fed into a heated nozzle of a 3D printer, where it is softened and applied layer by layer to the surface of the printing table, thereby creating a pre-modeled object. Despite the fact that this technology is now actively developing, there are only a few industrial filaments that meet the principles of “sustainable development”, namely the use of renewable raw materials and the possibility of recycling. Therefore, the polymers obtained in this work could potentially be used as a sustainable filament.

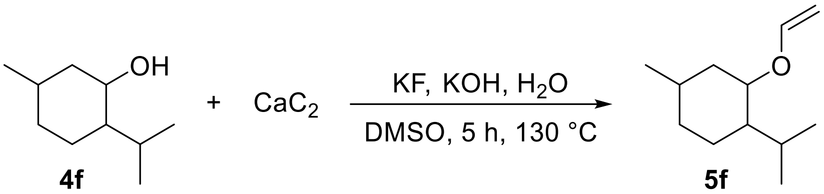
To stretch filament for 3D printing, you can use a single-screw extruder of a suitable diameter. In this case, in addition to optimal temperature conditions, it is necessary to create internal pressure due to the excess of the supplied material. In our laboratory, previous experiments have shown that loading 15–20 g of polymer material is optimal for drawing a rod with a diameter of 1.75 mm. Since the available polymerization and vinylation methods, including those used in this work, are not designed to obtain such an amount of product, to obtain filament from the resulting polymers, the problem of scaling up the synthesis of polymers and vinyl ethers was first solved.

2.4.6.1. Optimization of vinyl ether production for large volumes. To obtain the filament, the 3 most accessible solid thermoplastic polymers **7f, 7k, 7l**, obtained above, were selected. To optimize vinylation scaling, the available terpene alcohol **4f** was selected.

Among the works using calcium carbide in the synthesis of vinyl ethers of terpene alcohols, three main approaches can be distinguished. The first is to carry out the reaction in a glass pressure tube. This approach is the most used in laboratory practice and has proven itself well for carrying out reactions with 1 mmol of alcohol (for 8 ml tubes with a carbide load of 128 mg). The lab also used method for a homemade 50 mL glass reactor made from a 15 mL pressure tube. In this method, the alcohol loading was 8 mmol with a carbide loading of 1.5 g. However, these reactors could not withstand a carbide loading of more than 1.5–2 g, and therefore further scaling is possible only by increasing the number of parallel syntheses. Also, this approach is accompanied by high consumption of solvents used in the extraction and purification of vinyl ether. Another option for carrying out the vinylation reaction using calcium carbide is to carry out the reaction using special cartridges [133]. However, in the case of using menthol during vinylation, the conversion was only 22%, apparently due to the lack of tightness of the system and, as a consequence, the removal of acetylene from the reaction zone and the lack of pressure in the system. A third option is to carry out the reaction without adding solvent in a steel pressure reactor (the approach used in the synthesis of acetaldehyde described in Chapter 2.3). In this case, there was no superbasic medium usually used in reactions of nucleophilic addition to acetylene (for which DMSO or DMF is usually used as a solvent). When menthol was used in this system, its conversion was also quite low (10%). Based on the advantages and disadvantages of each method, we decided to develop a more universal method for producing vinyl ethers in large quantities with lower solvent consumption.

When optimizing the scale-up of the vinyl etper synthesis (Table 2.17), the reaction was carried out in a 60 mL steel pressure reactor equipped with a pressure gauge to avoid creating too high a pressure in the system. The conditions used in the reaction of 1.2 g of menthol in a homemade pressure flask were chosen as a basis.

Table 2.17. Optimization of conditions for the menthol vinylation reaction in a steel reactor [a]



Entry	**4f**, g (mmol)	CaC_2, [b] g (mmol)	Mole ratio **4f** : CaC_2 : KF : KOH : H_2O	Conversion, [c] mol%
1	1.2 (7.8)	1.5 (23)	1 : 3 : 1.2 : 1.1 : 6	55
2	4.5 (29)	5.8 (90)	1 : 3 : 1.2 : 1.1 : 6	68
3	4.5 (29)	5.8 (90)	1 : 3 : 2.4 : 1.1 : 7	40
4	4.5 (29)	4.8 (75)	1 : 2.5 : 2.4 : 1.1 : 7	59
5	4.5 (29)	3.8 (58)	1 : 2 : 1.2 : 1.1 : 4.7	63
6 [d]	4.5 (29)	3.8 (58)	1 : 2 : 1.2 : 1.1 : 4.7	68
7 [e]	4.5 (29)	3.8 (58)	1 : 2 : 1.2 : 1.1 : 4.7	69

[a] Reaction procedure: KF, CaC_2, menthol, KOH, 30 ml DMSO were loaded into the reactor and water was carefully added. The reaction mixture was stirred for 3 hours at 130 °C. [b] The loading of pure calcium carbide is indicated based on a carbide purity of 75%. [c] The conversion was determined from the ^1H NMR spectrum based on the ratio of the signals of vinyl ether and alcohol. [d] The reaction time was increased to 20 hours. [e] The reaction was carried out in a commercially available 100 mL pressure flask.

Under the initial reaction conditions in a steel reactor (entry 1), the menthol conversion was 55%. To reduce the consumption of reagents used in isolation, the alcohol load was increased to 4.5 g and the loads of other reagents, except the solvent, were proportionally increased (the same amount of DMSO (30 ml) was used). Under these conditions (entry 2), conversion increased to 68%. An increase in conversion is usually also facilitated by an increase in the loading of potassium fluoride; for example, in [47] a 2-fold excess of KF in relation to CaC_2 was used. However, in this case (entry 3), doubling the KF amount, on the contrary, led to a decrease in conversion to 40%. When the loading of CaC_2 was reduced (from 1:3 to 1:2.5 mole ratio of alcohol to carbide), an increase in conversion to 59% was observed (entry 4). An even greater reduction in carbide loading to a ratio of 1:2, as well as a return to the original ratio of KF (entry 5), further increased the conversion (up to 63%). Increasing the reaction time only slightly increased menthol conversion (entry 6). Since under the conditions of entry 5 the lowest reagents consumption was used and high conversion was observed, these conditions were taken as optimal. Under these conditions, the pressure in the system did not exceed 4 atm, therefore an additional experiment was carried out not in a steel autoclave, but in a commercially available 100 ml pressure flask. This flask withstood the experimental conditions, and the alcohol conversion even increased slightly (up to 69%). Thus, it was shown that optimal reaction conditions can be safely transferred to standard laboratory glassware.

The further procedure for isolation and purification also was optimized, since it was wanted to reduce the reagent consumption. It was observed that many vinyl ethers of terpene alcohols partially escaped with hexane upon solvent evaporation, possibly due to the formation of an azeotrope. This problem also needed to be solved. It was suggested that the starting alcohol could be removed directly at the isolation stage *via* the formation of the corresponding alcoholate, without resorting to column chromatography later. To test this hypothesis, after the experiment, the mixture from Table 2.19 was extracted with different solvents, and then these solutions were washed with alkali solutions of various concentrations (Table 2.18).

Table 2.18. Study of the possibility of removing alcohol when isolating vinyl ether from the reaction mixture [a]

Entry	Extractant	Alkali solution	Wight isolated **5f**	Purity, %
1	Pentane	5% KOH	563 mg	77
2		10% KOH	587 mg	77
3		25% KOH	503 mg	77
4		40% KOH	603 mg	77
5	Diethyl ether	5% KOH	310 mg	64
6		10% KOH	361 mg	64
7		25% KOH	319 mg	64
8		40% KOH	398 mg	64
9	Hexane	5% KOH	413 mg	67
10		10% KOH	600 mg	68
11		25% KOH	391 mg	68
12		40% KOH	646 mg	64
13 [b]	Pentane	Brine	-	70
14 [b]	Pentane	10% KOH	4.82 g	71

[a] Entries 1–12: The reaction mixture from entry 1 from Table 2.19 was used. The reaction mixture was divided into 3 parts, after which each part was extracted with pentane (entries 1–4), diethyl ether (entries 5–8) or hexane (entries 9–12), respectively (4 × 10 ml). Then each series was divided into 4 equal parts and washed with a KOH solution of a given concentration (3 × 10 ml), brine, dried over Na_2SO_4 and the solvent was evaporated. [b] The reaction mixture from entry 2 from Table 2.19 was used.

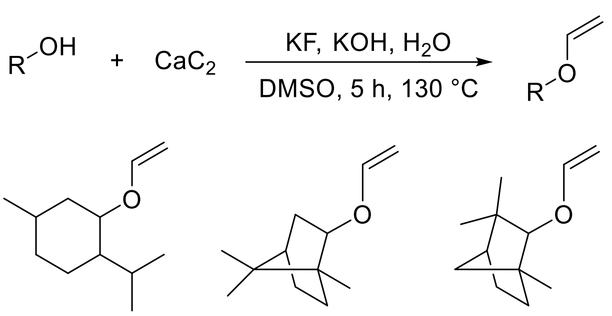
It turned out that the purity of the isolated ether was practically independent of the alkali concentration, but strongly depended on the choice of extractant. Thus, when using diethyl ether, the lowest purity of the isolated vinyl ether was observed, while its color was dark brown and the darkest of the series (entries 5–8). When using hexane (entries 9–12), a slight increase in purity was observed, but at the same time, based on the weight of the isolated ether, it was determined that after drying a significant amount of hexane remained, which was difficult to distill from the mixture under reduced pressure, since solvent vapors began to be captured along with is a vinyl ether. The best results were shown by using pentane for extraction (entries 1–4), since after evaporation there were no solvent signals in the spectra, and the highest purity of 77% was achieved.

We decided to check whether the use of alkali for washing affects the purity of the released vinyl ether. To do this, the reaction mixture obtained after entry 2 (Table 2.19) was extracted with pentane and washed with saturated salt solution, after which it was additionally washed with a 10% alkali solution. It turned out that the cleanliness remained the same in both cases. Thus, it was concluded that washing with an alkali solution did not even partially clear the mixture of alcohol.

Having tested this hypothesis, we decided to try to purify the mixture after isolation through the formation of an alcoholate using a reaction with sodium metal. For the experiment, 2 options were chosen: without solvent and with dilution of vinyl ether with pentane. In both cases, after adding finely chopped sodium metal, the mixture was left at room temperature overnight, after which the mixture was filtered through Celite, washed with pentane and the solvent was evaporated. Analysis of the spectra showed no changes in purity. Thus, it was shown that the use of sodium metal also did not lead to the formation of alcoholate from menthol. An analysis of the literature showed that this alcoholate using metallic sodium is formed only when they are boiled in THF for 40 hours with a yield of 60% [134]. Thus, the method for producing alcoholates was not suitable for chemical purification of the mixture.

Less consumptive options in terms of the substances used were also tested: vacuum distillation with a reflux condenser and steam distillation. Vacuum distillation was accompanied by large losses inside the distillation system. Analysis of the fractions showed that the purity of the distilled vinyl ether was the same as before distillation in all fractions collected. The same results were obtained with steam distillation, in which the mixture was also distilled without purification. In this regard, the bestoption was purification by column chromatography on deacidified silica gel with pentane as an eluent. If necessary, unreacted menthol can be washed from the column using a more polar solvent such as diethyl ether.

Thus, a less consumptive method was developed (since the same solvent amount was used for large reagents loads, the solvent consumption for extraction decreased by 5 times). This method allowed the preparation of **5f** on a scale of about 3.5 g at a time in commercially pressure flasks.



5f 3.5 g (65%)
5k 4.4 g (82%)
5l 4.6 g (85%)

Scheme 2.32. Preparation of vinyl ethers **5f**, **5k** and **5l** on a 3–5 g scale

This method has also been successfully applied to the preparation of vinyl ethers of other available terpene alcohols, borneol and fenchol (Scheme 2.32), used for polymerization. The preparative yield of vinyl ethers was 65–85%.

2.4.6.2. Optimization of polymerization scaling. The next step towards a filament for 3D printing from polymers was the synthesis of approximately 20 g of each polymer. Polymerization can be carried out with small loads to obtain the required polymer amount, but this is accompanied by a large time and resources consumption. Therefore, polymerization scaling was carried out. A key characteristic for further filament extrusion was forming temperatures, which is influenced by the molecular weight distribution, therefore the influence of polymerization conditions on these factors was studied during scaling by the example of **5k** ether (Table 2.19).

Table 2.19. Scaling of **5k** polymerization and characteristics of the resulting polymers [a]

Entry	**5k**, g (mmol)	Toluene, [b] ml	Initiator concentration, mmol/ml	T, °C	Time, h	Yield **7k**, g (%)	Mn, g/mol (× 10^4)	Mw, g/mol (× 10^4)	D	T_{form}, [c] °C
1	0.27 (1.5)	0.5+0.5	0.06	-40	24	0.24 (90%)	3.91	4.04	1.03	220
2	0.54 (3)	0.5+0.5	0.06	-40	24	0.51 (95%)	2.02	6.26	2.83	220
3	1.08 (6)	0.5+0.5	0.06	-40	24	1.04 (96%)	4.16	6.71	1.62	220
4	0.27 (1.5)	1+0.5	0.06	-40	24	0.26 (96%)	2.98	5.72	1.92	220
5	0.54 (3)	1+0.5	0.06	-40	24	0.50 (92%)	3.86	6.11	1.58	220
6	1.08 (6)	2+2	0.06	-40	24	0.98 (90%)	3.04	6.27	2.06	220
7	0.27 (1.5)	0.5+0.5	0.24	-40	24	0.23 (83%)	3.15	4.86	1.54	220
8	0.54 (3)	0.5+0.5	0.24	-40	24	0.51 (94%)	2.96	4.85	1.64	220
9	0.54 (3)	1+0.5	0.06	-20	24	0.44 (82%)	1.03	3.31	3.20	220
10	0.54 (3)	1+0.5	0.06	rt	24	0.40 (75%)	0.73	1.57	2.15	200
11	0.54 (3)	1+0.5	0.06	-40	6	0.48 (89%)	3.07	4.52	1.47	220
12	0.54 (3)	1+0.5	0.06	-40	4	0.46 (85%)	2.88	4.59	1.59	220
13	3.24 (12)	6+3	0.06	-20	24	3.24 (99%)	1.73	4.11	2.37	220
14	3.24 (12)	6+3	0.06	-40	24	3.24 (99%)	2.65	4.37	1.65	220
15	3.24 (12) [d]	6+3	0.06	-40	24	2.81 (87%)	0.51	1.48	2.90	200
16	Polymer after 3-fold molding of the polymer obtained in experiment 3						4.05	7.80	1.93	220

[a] Polymerization procedure: **5k** and toluene was placed in a prepared Schlenk flask under argon flow. The flask was then sealed with a septum and cooled to the temperature indicated in the Table. After this, the initiator solution was added dropwise while cooling and stirring. The reaction mixture was stirred at the temperature and for the time indicated in the Table. After the reaction was completed, 20 mL of methanol was added to the flask to precipitate the polymer. The polymer was reprecipitated from toluene with methanol twice and then dried in a vacuum oven at 40°C for 2 days. [b] The amount of toluene is indicated for the monomer solution and the initiator solution (through the + sign). [c] The approximate forming temperature is indicated, determined by the visual softening of the polymer when heated to the specified temperature. [d] Vinyl ether was used without purification by column chromatography.

Carrying out the reaction under standard conditions resulted in a 90% yield of polymer **7k** with Đ = 1.03 at $M_w = 4.04 \times 10^4$ g/mol (entry 1). At this molecular weight, the molding temperature was 220 °C. With increasing monomer loading, M_w increased along with Đ, but the forming temperature remained virtually unchanged (entries 2–3). Reducing the monomer concentration (2-fold dilution) (entries 4–5) did not significantly affect the molecular weight distribution and forming temperature. However, it promoted more thorough and stable mixing than that observed in concentrated solutions from entries 2 and 3. With a proportional increase in loadings relative to entry 1 (entry 6), the polymer was obtained with the same yield and forming temperature, but with higher dispersity. When the initiator concentration increased by 4 times, a slight decrease in molecular weights was observed (entries 7 and 8), which did not affect the polymer forming temperature. Varying the polymerization temperature showed that with increasing temperature, the yield, molecular weight, and forming temperature gradually decreased (entries 9–10), which was especially noticeable when room temperature was used. As the polymerization duration decreased, the yield decreased slightly, although the properties of the polymer remained the same (entries 11–12). A proportional increase in reagents relative to entries 9 and 5 led to an increase in yields (entries 13 and 14, respectively) without changing the forming temperature. The use of a lower purity monomer (vinyl ether was not purified by column chromatography) (entry 15) resulted in a significant reduction in molding temperature and polymer yield. It is noteworthy that after 3 cycles of softening-hardening of the polymer, the molecular weight distribution remained virtually unchanged (entry 16).

Thus, it was shown that the polymerization temperature and monomer purity had the greatest influence on the molecular weight and, as a consequence, on the forming temperature. The decrease in molecular weight was also affected by an increase in the initiator concentration, but the forming temperature did not change significantly. Optimization of polymerization scaling resulted in a quantitative polymer yield of **7k** (3.2 g) (entry 14), while the forming temperature (220 °C) was the same as when the reaction was carried out under standard conditions.

The conditions found were used for the polymerization of other vinyl ethers (**5f** and **5l**) (Table 2.20).

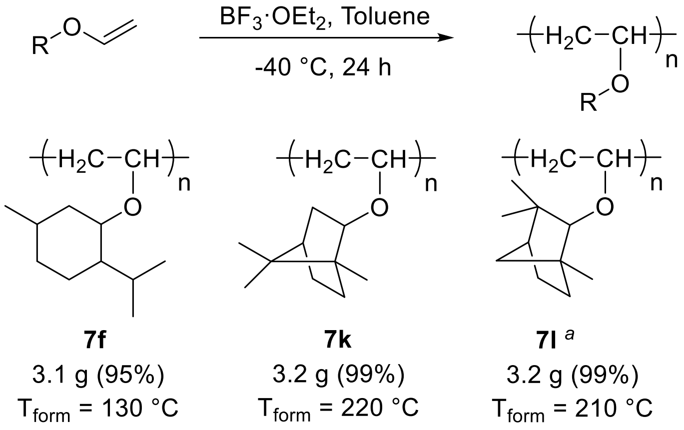
Table 2.20. The influence of polymerization conditions on the molecular weight distribution and forming temperature of polymers **1b** and **3b** [a]

Entry	Monomer, g (mmol)	Toluene, [b] ml	T, °C	Yield, mg (%)	Mn, g/mol (× 10^4)	Mw, g/mol (× 10^4)	D	T form, [c] °C
1	**5l**, 0.54 (3)	1+0.5	-40	0.54 (99%)	4.66	5.49	1.17	> 270 [d]
2	**5l**, 0.54 (3)	1+2	-40	0.43 (85%)	2.98	3.79	1.27	> 270 [d]
3	**5l**, 0.54 (3)	1+0.5	25	0.41 (81%)	1.12	1.73	1.54	205
4	**5l**, 3.24 (12)	6+3	25	3.24 (99%)	1.33	1.82	1.37	210
5	**5f,** 0.27 (1.5)	0.5+0.5	-40	0.25 (92%)	1.08	2.73	2.51	130
6	**5f**, 3.24 (12)	6+3	-40	3.08 (95%)	2.49	5.74	2.30	130

[a] The polymerization procedure is the same as in Table 2.21. The initiator concentration was 0.06 mmol/ml. [b] The amount of toluene is indicated for the monomer solution and the initiator solution (through the + sign). [c] The approximate forming temperature is indicated, determined by the visual softening of the polymer when heated to the indicated temperature. [d] When heated above the specified temperature, the polymer turns black.

The use of optimal conditions for the polymerization of vinyl ether **7l** at small loadings (entry 1) led to a quantitative yield of polymer with a narrow molecular weight distribution. However, it turned out that such a polymer did not soften up to 270 °C; at a higher temperature it turned black. To obtain a softening polymer **7l** it was necessary to reduce the molecular weight and for this purpose the patterns found for polymer **7k** were used. The first approach (entry 2) was to increase the initiator loading, which slightly reduced the molecular weight and yield of the polymer, but did not lead to softening of the polymer. In the second variant (entry 3), polymerization was carried out at room temperature, which led to a decrease in molecular weight and the ability to mold the polymer at 205 °C, although the yield was also lower. A proportional increase in loadings relative to entry 3 (entry 4) resulted in a polymer in quantitative yield with a narrower molecular weight distribution and a forming temperature of 210 °C.

Under standard polymerization conditions of **7f** (entry 5), a polymer with a forming temperature of 130 °C was obtained. Under optimal conditions (entry 6), the yield and molecular weight of the polymer increased slightly, but the forming temperature remained the same.



7f
3.1 g (95%)
T_{form} = 130 °C

7k
3.2 g (99%)
T_{form} = 220 °C

7l [a]
3.2 g (99%)
T_{form} = 210 °C

[a] Polymerization was carried out at 25 °C

Scheme 2.33. Scaling polymerization

Thus, optimization of polymerization scaling made it possible to obtain polymers **7f**, **7k** and **7l** (about 3 g at a time) with different softening temperatures (130–220 °C) and high isolated yields (95–99%) (Scheme 2.33). These methods were used to produce 20 g of polymers (parallel syntheses), which were subsequently used for filament extrusion.

2.4.6.3. Thermal properties of the polymers. For all synthesized polymers, TGA and DSC were recorded (Figure 2.13) to determine decomposition temperatures and first-order phase transitions (glass transition and melting temperatures).

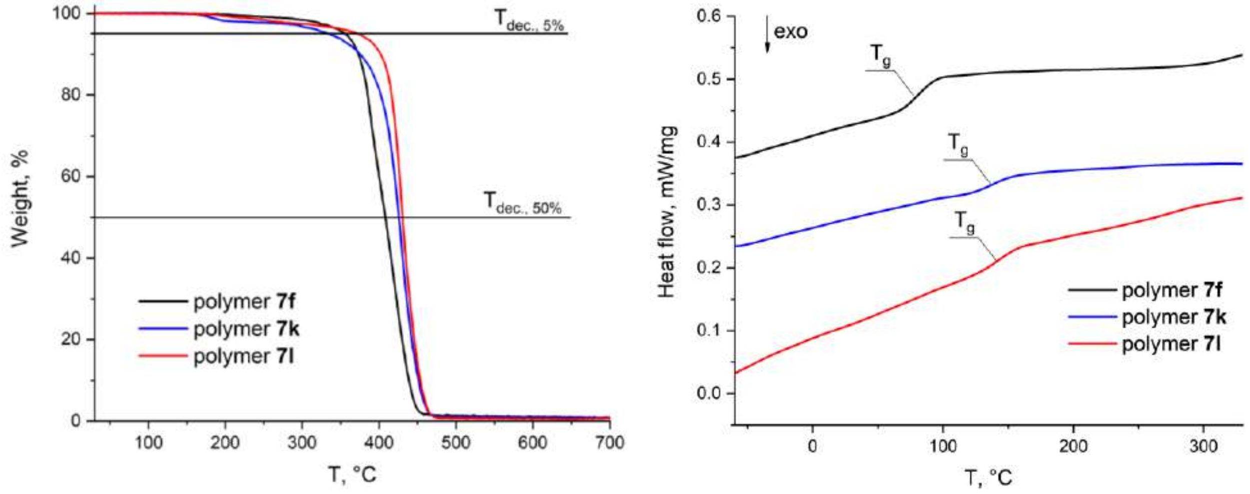


Figure 2.13. TGA and DSC curves for polymers **7f**, **7k** and **7l**

According to TGA data (Figure 2.13 (left)), the decomposition temperatures of 5 wt% of the polymer were 356 °C for **7f** , 372 °C for **7k** and 335 °C for **7l** . The decomposition temperatures of 50 wt% of the polymer were 408 °C for **7f** , 430 °C for **7k** and 425 °C for **7l** . In this case, significant decomposition ended at 460 °C for **7f** and 470 °C for **7k** and **7l** (residue weight less than 1%).

According to DSC (Figure 2.13 (right)), all polymers had glass transition temperatures: 83 °C for **7f**, 145 °C for **7k** (weak effect) and 140 °C for **7l** (weak effect).

The softening temperatures of the synthesized polymers were also determined using thermomechanical analysis (TMA) (Figure 2.14). According to the graph, all polymers had softening temperatures. Polymer **7f** began to soften at a temperature of 87 °C , **7k** – 125 °C , and **7l** – 132 °C.

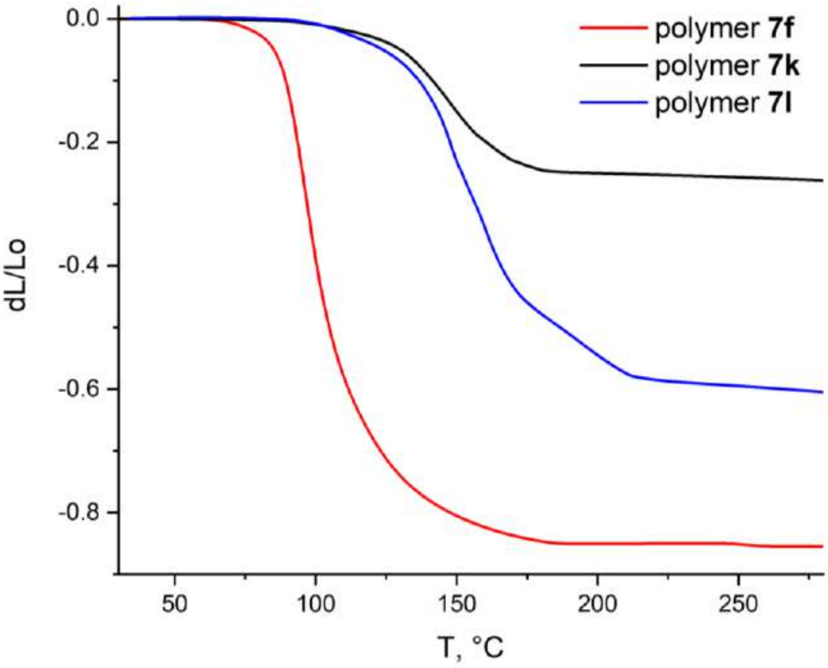


Figure 2.14. TMA curves for polymers **7f**, **7k** and **7l**

Thus, it was shown that all synthesized polymers are stable up to 300 °C, and the softening temperature is much lower (87–132 °C). This indicates the possibility of thermal molding of polymers without destruction.

2.4.6.4. Adding plasticizers to the resulting polymers. The next step was to obtain filament from the synthesized polymers. To obtain filaments, the polymers were passed through a special single-screw extruder equipped with a nozzle with an outlet diameter of 1.75 mm. All polymers have been successfully extruded filaments with a diameter of 1.6 to 1.8 mm. Extrusion temperatures were: 120 °C, 190 °C and 225 °C for polymers **7f**, **7k** and **7l** respectively. It is noteworthy that the polymer **7f** filament was transparent, unlike the others.

All filaments were quite brittle after cooling to room temperature, which made it difficult to use these materials directly in a 3D printer with metal pressure rollers (the filament would crack after feeding the material). To increase flexibility and reduce brittleness, it was decided to add a plasticizer to the resulting materials. Considering that the main advantage of these polymers was their disassembly into the original alcohol or its corresponding carbonyl compound, it was extremely important to find a plasticizer that would not violate the “assembly-disassembly” concept. The products of polymer decomposition during pyrolysis, the original alcohols and carbonyl compounds, were chosen as such potential plasticizers that satisfy this principle (Table 2.21).

Table 2.21. Physical properties of potential plasticizers

Entry	Polymer	Plasticizer	m.p., °C	b.p., °C
1	**7f**	Menthol	36–38 (racemic)	212
2	**7f**	Mentone	- 6	207
3	**7k**	Borneol	206	210
4	**7k**	Camphor	179	204
5	**7l**	Fenchol	39–45 (racemic)	203
6	**7l**	Fenchone	5	191

Important characteristics influencing the choice of plasticizer are the solubility of the polymer in the plasticizer, its boiling point and state of aggregation at ambient temperature. In the case of polymer **7f**, both menthol and menthone can be used as plasticizers. For polymer **7k**, both potential plasticizers are solid at ambient temperature and their boiling point is below the molding temperature of the corresponding polymer, which may lead to the removal of plasticizer from the polymer during operation. For polymer **7l,** both potential plasticizers also have a boiling point close to the molding temperature of the polymer. Therefore, the most promising was the use of a mixture of polymer **7f** with menthol and menthone.

Mixing of polymer **7f** with menthol or menthone was carried out by stirring in the melt at a temperature of 100–130 °C until a homogeneous mixture was obtained (Table 2.22).

Table 2.22. The influence of the plasticizer on the forming temperature and physical properties of the polymer **7f**

Entry	Plasticizer	Plasticizer concentration, [a] wt%	Material	T $_{form}$, °C	Properties after cooling
1	Menthol	9 (+10%)	PMVE +M1-10	120	Fragile
2	Menthol	17 (+20%)	PMVE +M1-20	110	Fragile
3	Menthol	23 (+30%)	PMVE +M1-30	100	Increased flexibility
4	Menthol	29 (+40%)	PMVE +M1-40	90	Increased flexibility
5	Menthol	33 (+50%)	PMVE +M1-50	90	Increased flexibility
6	Menton	9 (+10%)	PMVE +M2-10	120	Fragile
7	Menton	20 (+30%)	PMVE +M2-30	60	Increased flexibility
8	Menton	29 (+40%)	PMVE +M2-40	25	Viscous
10	Menton	33 (+50%)	PMVE +M2-50	25	Viscous

[a] The amount of menthol added to the polymer in wt% is indicated in parentheses.

In all cases, when adding a plasticizer, the forming temperature of the mixture of relatively pure polymer decreased. A decrease in brittleness was observed when adding a plasticizer in an amount of more than 20 wt% to the polymer weight. In the case of using menthone, when more than 40 wt% of plasticizer was added to the polymer, the composite became viscous already at room temperature. The PMVE+M1-30 material was chosen for further research due to its greatest flexibility and forming temperature with the smallest amount of added plasticizer.

Thus, adding 30% menthol to polymer **7f** increased the flexibility of the polymer, allowing it to be used in 3D printing. A filament with a diameter of 1.6–1.8 mm based on the PMVE+M1-30 material, suitable for further 3D printing, was extruded at 75 °C (Figure 2.15). It is noteworthy that the thread retained good flexibility, transparency and ease of spinning after cooling to 35–40 °C.

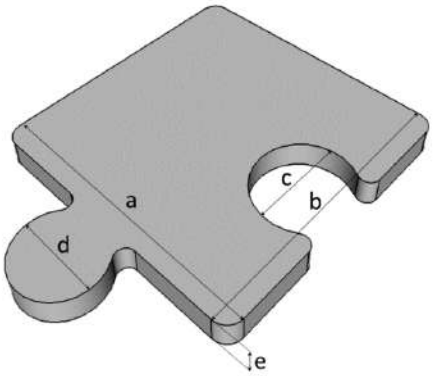
Figure 2.15. Filament from PMVE+M1-30 material

2.4.6.5. Production of objects from polymer materials by 3D printing. The filament obtained at the previous stage was used directly in a 3D printer with FDM printing technology. Having determined the optimal temperature conditions for printing with this material, a series of objects were successfully printed at a temperature of 125 °C (Figure 2.16).

Figure 2.16. Objects printed on a 3D printer from PMVE+M1-30 material

Remarkably, objects adhered well to the glass surface without the need for additional adhesives or coatings typically used in 3D printing. Printed objects were easily removed without damage from the heating surface at a temperature of 40 °C. The versatility of the PMVE+M1-30 filament was demonstrated when printing both hollow and monolithic objects. A puzzle-shaped object was used to determine the changes in size of the object after 3D printing relative to the specified dimensions (Table 2.23). For comparison, commercially available plastics for 3D printing, PLA and PETG, were chosen due to the similarity of their characteristics with the resulting material. The comparison took into account changes in both external and internal dimensions of the object.

Table 2.23. Comparison of the dimensions of a part printed from PMVE+M1-30 with similar parts printed from PETG and PLA



Size	Set size, mm	Size of part printed from various materials, mm					
		PMVE +M1-30	Δ, %	PETG	Δ, %	PLA	Δ, %
a	23.4	23.6	1	23.4	0	24.3	4
b	23.4	23.7	1	23.4	0	24.3	4
e	1.8	1.7	-6	1.5	-17	1.5	-17
c	8	7.5	-6	7.6	-5	6.9	-14
d	7	7.1	1	6.9	-1	7.9	13
		∑ = ± 3 %		∑ = ± 5%		∑ = ± 10%	

For the resulting material for dimensions of about 23 mm, the deviations were minimal and amounted to 1% deviation from the theoretical dimensions. For medium-sized areas (7–8 mm), the deviation ranged from 1% to 6%, and for smaller areas (2 mm) it reached 6%. Thus, the calculated average deviation was only 3%. In comparison, using commercially available materials such as PTEG and PLA to print puzzle-shaped objects resulted in average deviations of 5% and 10%, respectively.

To assess the layers sintering quality during printing, the sample was divided in half and the fracture surface was examined by SEM. In the SEM images (Figure 2.17), there is a noticeable absence of obvious boundaries between the top and side layers (photos 1 and 2), which indicates good sintering of the layers during printing. However, it is very difficult to completely eliminate air inclusions from a part due to the printing technology, so there were still rare voids in the object (photo 3), which inevitably arose due to air entrapment during the printing process. However, most of the printed objects had an almost monolithic internal structure, which is quite difficult to achieve using conventional 3D plastics (PLA, ABS, PETG, Nylon, etc.).

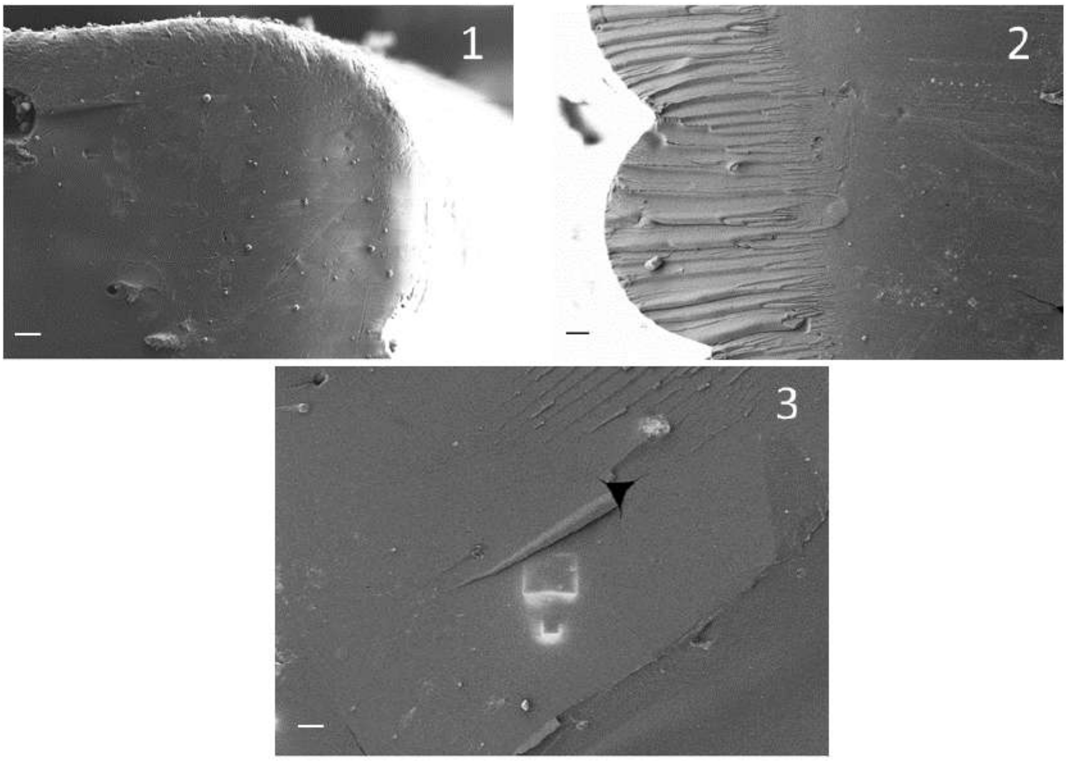


Figure 2.17. SEM photographs of the inside of an object printed from PMVE+M1-30 material

Objects printed from PMVE+M1-30 material can be subjected to post-treatment with a solvent (THF or CH_2Cl_2) to effectively eliminate external interlayer boundaries. Due to the transparency of this material, such post-processing opens up access to printing transparent monolithic objects.

Thus, the possibility of using the recyclable PMVE+M1-30 material in 3D printing was demonstrated. Printing was carried out at a lower printing temperature (125 °C) compared to commercial plastics for 3D printing (220–240 °C). However, no signs of thermal destruction of the material during printing were observed. This filament demonstrated good layer sinterability and high adhesion to glass, as well as low shrinkage, similar to commercial 3D printing plastics.

In conclusion of this subchapter, it can be summarized that a method for producing recyclable (through the assembly-disassembly cycle) polymers has been developed. The possibility of obtaining a material based on the synthesized polymers for use in 3D printing was demonstrated. The results obtained in this chapter have been published in peer-reviewed scientific journals [135, 136].

CHAPTER 3. EXPERIMENTAL SECTION

3.1. Materials and instruments

Calcium carbide (granular, particle size 0.1–1 mm, 75%), isobutyl bromide (99%), anhydrous palladium (II) chloride (59%Pd), isobutyl vinyl ether (99%), menthol (99%), (–)-borneol (97%) and fenchyl alcohol (≥96%) were purchased from Sigma-Aldrich. 4-Bromotoluene (99%), 0.5 M (10 wt%) solution of di-*tert*-butylphosphine in hexane, citronellol (95%) and boron trifluoride etherate (48% BF_3) were purchased from Acros Organics. 2-Bromotoluene (99%) and 3-bromotoluene (98%) were purchased from Macklin. 4-Bromanisole (99%) and 1,10-decanediol (98%) were purchased from Alfa Aesar. *n*-Butyl bromide (99%), dicyclohexylphosphine (98%), diethyl phosphite (99%), diphenylphosphine oxide (97%), nickel(II) bromide anhydrous (99%), magnesium (shavings) were purchased from Chemical Line, abcr GmbH&Co, Energy-chemical, Bide Pharmatech Ltd. and "Ruskhim" respectively. *cis*-Myrtanol, javanol and rosapfene were purchased from a local perfume company and tested by ^{1}H NMR and GC-MS before use. Decanol (pure grade), octanol (pure grade) and isoamyl alcohol (pure grade) were purchased from the Reakhim company. *iso*-Butanol (pure grade), *n*-butanol (analytical grade), ethylene glycol (analytical grade), glycerol (analytical grade), potassium hydroxide (reagent grade) and 2-aqueous potassium fluoride (analytical grade) were purchased from the Vekton company. Before use, potassium fluoride was calcined at 160 °C, stirring occasionally, and ground in a mortar. Potassium hydroxide was ground in a mortar before use. THF was purified from peroxides by treatment with ferrous sulfate, then with potassium hydroxide, after which it was boiled and distilled in the sodium/benzophenone system in an argon atmosphere. Toluene was distilled over sodium under argon and stored over 4 Å molecular sieves. Standard laboratory methods were used to purify and absolute the organic solvents and reagents used [137]. K_2PdCl_4 was obtained from $PdCl_2$ and KCl according to a well-known method [138]. 2,5-di(hydroxymethyl)furan was prepared according to a previously described procedure [132]. Menthone was obtained from menthol according to the method [139].

NMR spectra were recorded on Bruker spectrometers Avance DPX 400 and Bruker Avance III 500 (400, 101 or 126, 162 and 61 or 77 MHz for ^{1}H, ^{13}C, ^{31}P and ^{2}H spectra, respectively); solvents: $CDCl_3$ or D_2O. Data were processed using MestReNova NMR data processing software (version 6.0.2). Chemical shifts are given in parts per million (ppm) and measured relative to the residual proton signals in the ^{1}H NMR spectra δ_H 7.26 ppm ($CHCl_3$), δ_H 4.79 ppm (H_2O), signals of the solvent carbon atom in the ^{13}C NMR spectra δ_C 77.2 ppm ($CDCl_3$), deuterium signals in the ^{2}H NMR spectra δ_D 7.26 ppm ($CDCl_3$) or 85% H_3PO_4 in the ^{31}P NMR spectra δ_P 0.0 ppm. The degree of DI was calculated using ^{1}H NMR spectroscopy by decreasing the signal intensity of the corresponding hydrogen atom. Spin-spin interaction constants (SSICs) in proton spectra (Hz) are measured in the first order approximation. The multiplicity of signals is given according to the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, d.d = doublet of doublets, d.t = doublet of triplets, m = multiplet, br = broadened signal. Mass spectra were recorded on a Bruker instrument micrOTOF with electrospray ionization (ESI). The reaction mixtures were analyzed on a chromatography-mass spectrometer combining a PerkinElmer gas-liquid chromatograph Clarus 680 (GC) and Clarus SQ 8T mass spectrometric detector (MS). The stationary phase was an ELITE-5ms capillary column 30 m × 0.25 mm × 0.25 µm. GC-MS coupled with a pyrolyzer was carried out using a QP2010 Ultra Shimadzu system; multi-charge pyrolyzer EGA/PY 3030D (Frontier Lab). Capillary columns Rtx 5ms (30 m × 0.25 mm × 0.25 µm; Restek) and HP 5ms (60 m × 0.32 mm × 0.25 µm; Agilent), He carrier gas (high purity, grade 6.0).

X-ray diffraction analysis was performed at 100 K for compound **3a-*d₄*** on a diffractometer Xtalab Supernova with HyPix3000 X-ray Cu Kα detector for **$NiBr_2$(3a), $NiBr_2$(3a-*d₄*), $NiBr_2$(3e)**, **$NiBr_2$(3e-*d₄*)**, **$NiBr_2$(3e-*d₁₆*), $PdCl_2$(3a-*d₄*)** on a diffractometer Rigaku Synergy S with HyPix6000 (**$PdCl_2$(3a-*d₄*)**) or HyPix6000HE (rest) detector using Mo Kα (**$NiBr_2$(3a)**) or Cu Kα (rest) X-rays. The structures were solved by direct methods using SHELX T [140] and refined by the least squares method using SHELXL-2018 [141] integrated into the OLEX2 package [142]. All atoms, except hydrogen, were considered anisotropically.

Molar masses and polydispersity indices of the polymers were measured using gel permeation chromatography (GPC) in THF at 40 °C (flow rate = 1.0 mL/min) compared to polystyrene standards. GPC was performed using a Shimadzu LC-20 modular system equipped with an MZ-Gel GPC column SDplus 10E3A (8 mm × 300 mm) and a differential refractive index detector RID-20A. The setup was calibrated using commercially available polystyrene standards with a narrow molecular weight distribution (0.5–1000 kDa, Polymer Laboratories). Chromatograms were processed using Shimadzu LC Solution software. Before analysis, polymer samples were dissolved in THF (2 mg/ml) and filtered through a polyvinylidene difluoride filter (0.45 μm, 13 mm).

The thermal and decomposition characteristics of the materials were determined by thermogravimetric analysis (TGA) carried out on a NETZSCH STA 449 F3 Jupiter apparatus, in the temperature range from 25 to 700 °C with a heating rate of 10 K/min with an argon flow rate of 50 ml/min. Differential scanning calorimetry (DSC) measurements were carried out using a NETZSCH STA 449 F3 Jupiter system. DSC analysis was carried out in an argon atmosphere from -80 to 300 °C (data recording for the second heating cycle). During the heating scan, a heating rate of 10 K/min was used. The glass transition temperature (Tg) was determined as the temperature at half the height of the glass transition heat capacity step. The softening temperature of the polymers was determined by thermomechanical analysis (TMA) carried out on a Netzsch TMA 402 F1 Hyperion apparatus in the temperature range from 25 to 300 °C with a heating rate of 3 K/min in a helium stream at a flow rate of 100 ml/min.

Column chromatography was performed on Loba silica gel Chemie PVT. LTD. 60-200 mesh. To purify vinyl ethers, silica gel was preliminarily deacidified with a 2% solution of triethylamine in hexane. Macherey–Nagel plates were used for thin layer chromatography (TLC) Xtra Sil G/UV$_{254}$, detection was carried out under UV light.

Vinylation in the synthesis of acetaldehyde and scale-up of vinylation to produce materials was carried out in a SITEC high-pressure reactor made from

Hastelloy. Trapping of acetaldehyde and polymerization of vinyl ethers was carried out while cooling to -20–(-40) °C using a LOIP FT-311-80 cryostat. Before polymerization, all used glassware was dried at 110 °C. The Schlenk flasks in which polymerization was carried out were additionally heated to 110 °C in vacuum to remove traces of water, after which they were cooled and filled with argon.

Filament suitable for 3D printing was extruded from the synthesized polymers using a Wellzoom single-screw extruder. Printing was carried out on a Creality 3D printer Ender 3 with "direct" filament feed. Digital models were created using FreeCAD 0.19. Ultimaker software was used to generate the corresponding G-code from the 3D model Cura v 4.6.1.

3.2. Synthesis of initial phosphine oxides

Method 1. The procedure was carried out in an argon atmosphere. 367 mg (15.1 mmol) of magnesium turnings were placed in a 25 ml Schlenk flask. The flask was heated in vacuum to remove traces of water, filling it with argon after cooling. Then a few iodine crystals were added and heated until violet vapors were released. After cooling to room temperature, a solution of the corresponding bromide (15.1 mmol) in 2 ml of anhydrous THF was added dropwise with stirring. In some cases, strong heating was observed, in which case the flask was cooled in an ice bath. The reaction mixture was stirred at 65 °C for 15 hours. The solution acquired a grayish tint. After this, the mixture was cooled to 0 °C and a solution of 593 µl (4.6 mmol) of diethyl phosphite in 2 ml of anhydrous THF was slowly added dropwise and vigorously stirring. The reaction mixture was stirred for 2 hours at room temperature. Then 10 ml of 0.1 N HCl solution was added to the mixture, stirred until the layers separated, and the mixture was filtered through Celite. The organic layer was separated, the aqueous layer was further extracted with CH_2Cl_2 (3 × 10 ml). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated. The resulting products were purified in different ways: phosphine oxides **1b** and **1c** recrystallized from hexane; phosphine oxides **1d** and **1g** were purified using silica gel column chromatography (eluent: diethyl ether : methanol (97:3) for **1d** and methylene chloride : methanol (40:1–20:1) for **1 g**) [83] .

Method 2. The procedure was carried out in an argon atmosphere. A 25 ml Schlenk flask was loaded with 0.345 g (14.2 mmol) of magnesium turnings, 10 ml of anhydrous THF and several iodine crystals, and then heated until violet iodine vapor was formed. Then, after cooling the mixture to room temperature, 2.5 g (14.2 mmol) of 2-bromotoluene was added dropwise with vigorous stirring. The reaction mixture was refluxed for 30 minutes. After this, the mixture was cooled to 0 °C and a solution of 554 μl (4.3 mmol) of diethyl phosphite in 2 ml of anhydrous THF was added slowly dropwise and vigorously stirring. The reaction was continued for 2 hours at room temperature. Then, 10 ml of 0.1 N HCl solution was slowly added to the mixture at 0 °C, followed by additional stirring for 20 min. After this, 10 ml of MTBE was added to the reaction mixture and stirred for 5 minutes. The organic layer was decanted, and 15 ml of methylene chloride was added to the remaining gel and stirred for 5 minutes. The resulting mixture was filtered through a pad of Celite and washed with methylene chloride. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated. The resulting oil was ground with hexane to obtain a pure product [84].

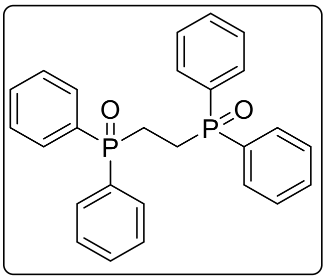
Method 3. The procedure was carried out in an argon atmosphere. A 25 ml Schlenk flask was loaded with 0.3 g (12.6 mmol) of magnesium turnings, 5 ml of anhydrous THF and several iodine crystals, and then heated until violet iodine vapor was formed. Then, after cooling the mixture to room temperature, a solution of 12.6 mmol of the corresponding bromide in 5 ml of anhydrous THF was added dropwise with vigorous stirring. If the reaction with bromide did not start spontaneously, then the reaction mixture (with a small amount of bromide) was briefly heated (until the start of the reaction, which is noticeable by the strong heating of the mixture), and then cooled to room temperature and the remainder of the bromide solution was added. The reaction mixture was stirred at room temperature for 1 hour. Once complete, the mixture was cooled to 0 °C and a solution of 491 μL (3.8 mmol) of diethyl phosphite in 2 mL of anhydrous THF was slowly added dropwise with vigorous stirring. The reaction was continued to stir for 2 hours at room temperature. Then 10 ml of 10% $NaHCO_3$ solution was slowly added to the mixture at 0 °C and stirred for 20 minutes. The resulting mixture was filtered and extracted with ethyl acetate (3 × 10 ml). The organic layer was dried over $MgSO_4$ and the solvent was evaporated. The resulting product was further purified using silica gel column chromatography (eluent: methylene chloride : methanol (99:1 for **1f** or 40:1–20:1 for **1h**)) [85].

Method 4. Phosphine (5 mmol) was stirred without solvent in air at room temperature for 15 hours. The resulting product was purified by column chromatography on silica (eluent: diethyl ether : methanol (97:3)) for **1i** or by trituration with hexane for **1j** [86].

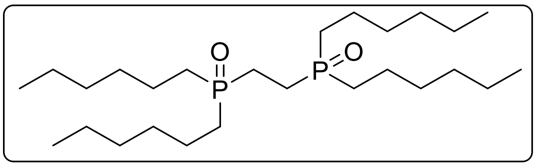
3.3. Synthesis and characterization of 1,2-bis(phosphine oxide)ethanes

Method 1. Phosphine oxide (0.25 mmol), potassium fluoride (17 mg, 0.3 mmol), calcium carbide (64 mg, 1 mmol) and DMSO (0.5 ml) were placed into an 8 ml pressure tube, and water (36 µl, 2 mmol) was carefully added. Then the tube was hermetically sealed and the mixture was stirred at 130 °C for 2 hours. After cooling to room temperature, the mixture was filtered, the liquid portion was diluted with water (2 ml), extracted with methylene chloride (3 × 2 ml), treated with brine (3 × 2 ml) and the organic layer was dried over Na_2SO_4. After removal of the solvent, the crude product was washed with cold diethyl ether (3 × 0.5 ml).

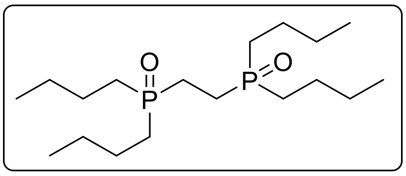
Method 2. Phosphine oxide (0.5 mmol), potassium fluoride (35 mg, 0.6 mmol), calcium carbide (128 mg, 2 mmol) and DMSO-d_6 (1 ml) (or a mixture of 0.05 ml of DMSO-d_6 and 0.45 ml of dioxane) were placed into an 8 ml pressure tube, and 80 µl (4 mmol) D_2O was carefully added. Then the tube was hermetically sealed and the mixture was stirred at 130 °C for 5 hours. After cooling to room temperature, the mixture was filtered, the liquid portion was diluted with water (2 ml), extracted with methylene chloride (3 × 2 ml), treated with brine (3 × 2 ml) and the organic layer was dried over Na_2SO_4. After evaporation of the solvent, the crude product was washed with cold diethyl ether (3 × 0.5 ml).



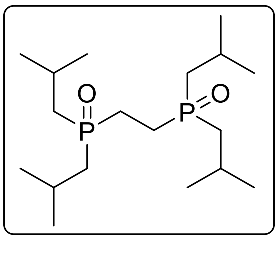
Ethane-1,2- diylbis(diphenylphosphine oxide) (2a) [143]. Synthesized by method 1. Yield 105 mg (98%), white powder, m.p. 272–273 °C. ^{1}H NMR (400 MHz, $CDCl_3$), *δ*, ppm: 2.51 (d, *J* = 2.2 Hz, 4H), 7.43 (t, *J* = 7.2 Hz, 8H), 7.50 (t, *J* = 7.2 Hz, 4H), 7.62 – 7.76 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$), *δ*, ppm: 21.0 – 22.7 (m), 128.9 (t, *J* = 5.9 Hz), 130.9 (t, *J* = 4.8 Hz), 131.3 – 132.9 (m), 132.2. ^{31}P NMR (162 MHz, $CDCl_3$), *δ*, ppm: 32.5.



Ethane-1,2-diylbis(dihexylphosphine oxide) (2b) [144]. Synthesized by method 1. Yield 106 mg (92%), white powder, m.p. 163–164 °C. ^{1}H NMR (400 MHz, $CDCl_3$), *δ*, ppm: 0.76 – 0.97 (m, 12H), 1.20 – 1.35 (m, 16H), 1.34 – 1.45 (m, 8H), 1.47 – 1.63 (m, 8H), 1.62 – 1.81 (m, 8H), 1.90 (d, *J* = 2.1 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$), *δ*, ppm: 14.1, 19.5 – 20.6 (m), 21.9, 22.5, 27.5 – 28.8 (m), 31.0 (t, *J* = 7.0 Hz), 31.4. ^{31}P NMR (162 MHz, $CDCl_3$), *δ*, ppm: 48.4. HRMS (ESI), m/z: $[M+H]^+$ calculated for $C_{26}H_{57}O_2P_2^+$ 463.3828; found 463.3830.

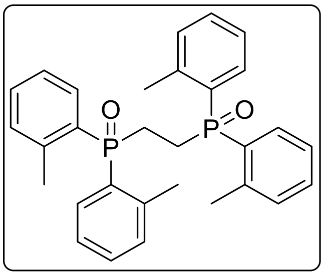


Ethane-1,2-diylbis(dibutylphosphine oxide) (2c) [145]. Synthesized by method 1. Yield 70 mg (80%), white powder, m.p. 173–174 °C. ^{1}H NMR (400 MHz, $CDCl_3$), *δ*, ppm: 0.90 (t, *J* = 7.2 Hz, 12H), 1.31 – 1.45 (m, 8H), 1.46 – 1.59 (m, 8H), 1.60 – 1.80 (m, 8H), 1.89 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$), *δ*, ppm: 13.7, 19.1 – 20.7 (m), 23.9, 24.3 (t, *J* = 7.1 Hz), 27.1 – 28.6 (m). ^{31}P NMR (162 MHz, $CDCl_3$), *δ*, ppm: 48.7. HRMS (ESI), m/z: $[M+H]^+$ calculated for $C_{18}H_{41}O_2P_2^+$ 351.2576; found 351.2578.

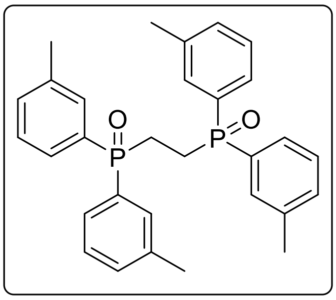


Ethane-1,2-diylbis(di-*iso*-butylphosphine oxide) (2d) [146]. Synthesized by method 1. Yield 61 mg (70%), white powder, m.p. 155–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$), *δ*, ppm: 1.08 (d, *J* = 6.6 Hz, 12H), 1.09 (d, *J* = 6.6 Hz, 12H), 1.58 – 1.70 (m, 8H), 1.92 (d, *J* = 2.4 Hz, 4H), 2.02 – 2.21 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$), *δ*, ppm: 21.4 – 22.9 (m), 23.8 (t, *J* = 1.7 Hz), 24.8 – 25.2 (m), 37.4 – 39.2 (m). ^{31}P NMR

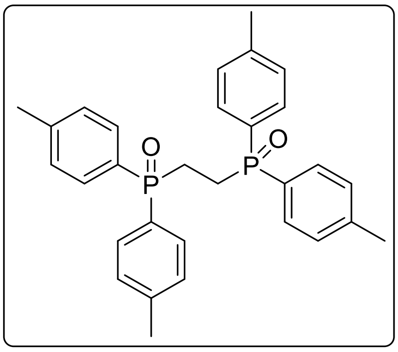
(162 MHz, $CDCl_3$), δ, ppm: 46.4. ^{31}P NMR (162 MHz, $CDCl_3$), δ, ppm: 48.7. HRMS (ESI), m/z: $[M+H]^+$ calculated for $C_{18}H_{41}O_2P_2^+$ 351.2576; found 351.2577.



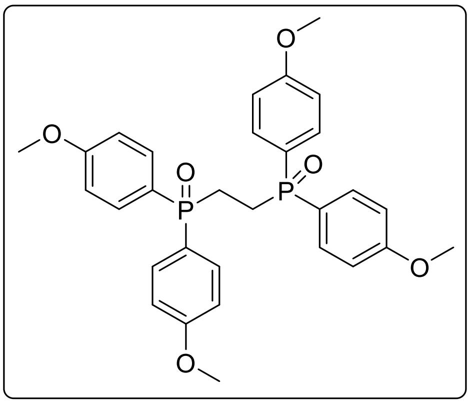
Ethane-1,2-diylbis(di-*ortho*-tolylphosphine oxide) (2e). Synthesized by method 1. Yield 89 mg (73%), white powder, m.p. 228–233 °C. ^1H NMR (400 MHz, $CDCl_3$), δ, ppm: 2.23 (s, 12H), 2.63 (d, *J* = 2.4 Hz, 4H), 7.17 (d, *J* = 7.4 Hz, 4H), 7.20 – 7.32 (m, 4H), 7.39 (t, *J* = 7.5 Hz, 4H), 7.62 – 7.78 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$), δ, ppm: 20.4 – 21.6 (m), 21.2 (t, *J* = 2.0 Hz), 125.9 (t, *J* = 5.9 Hz), 129.7 – 131.5 (m), 131.8 – 132.5 (m), 141.8 (t, *J* = 4.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$), δ, ppm: 34.6. HRMS (ESI), m/z: $[M+H]^+$ calculated for $C_{30}H_{33}O_2P_2^+$ 487.1950; found 487.1953.



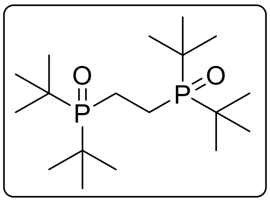
Ethane-1,2-diylbis(di-*meta*-tolylphosphine oxide) (2f). Synthesized by method 1. Yield 118 mg (97%), white powder, m.p. 174–178 °C. ^1H NMR (400 MHz, $CDCl_3$), δ, ppm: 2.33 (s, 12H), 2.49 (s, 4H), 7.27 – 7.32 (m, 8H), 7.42 – 7.47 (m, 4H), 7.53 – 7.56 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$), δ, ppm: 21.5, 21.7 – 22.5 (m), 127.8 (t, *J* = 4.8 Hz), 128.8 (t, *J* = 6.2 Hz), 131.4 (t, *J* = 4.6 Hz), 131.5 – 132.7 (m), 132.9, 138.9 (t, *J* = 5.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$), δ, ppm: 32.9. HRMS (ESI), m/z: $[M+H]^+$ calculated for $C_{30}H_{33}O_2P_2^+$ 487.1950; found 487.1950.



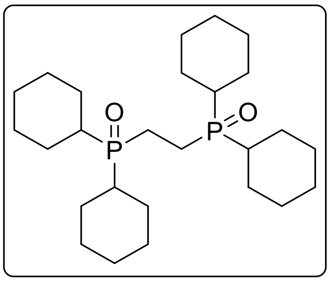
Ethane-1,2-diylbis(di-*para*-tolylphosphine oxide) (2g). Synthesized by method 1. Yield 101 mg (83%), white powder, m.p. 237–238 °C. ^1H NMR (400 MHz, $CDCl_3$), δ, ppm: 2.34 (s, 12H), 2.46 (s, 4H), 7.09 – 7.28 (m, 8H), 7.44 – 7.69 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$), δ, ppm: 21.7, 21.2 – 23.3 (m), 128.5 – 129.1 (m), 129.6 (t, *J* = 6.0 Hz), 130.9 (t, *J* = 4.8 Hz), 142.5. ^{31}P NMR (162 MHz, $CDCl_3$), δ, ppm: 33.1. HRMS (ESI), m/z: $[M+Na]^+$ calculated for $C_{30}H_{32}O_2P_2Na^+$ 509.1770; found 509.1770.



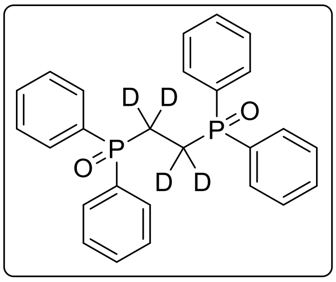
Ethane-1,2-diylbis(bis(4-methoxyphenyl) phosphine oxide) (2h) [147]. Synthesized by method 1. Yield 118 mg (86%), white powder, m.p. 179–180 °C. ^{1}H NMR (400 MHz, $CDCl_3$), *δ*, ppm: 2.41 (s, 4H), 3.79 (s, 12H), 6.91 (d, *J* = 7.5 Hz, 8H), 7.39 – 7.75 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$), *δ*, ppm: 20.0 – 23.9 (m), 55.4, 114.4 (t, *J* = 6.3 Hz), 121.9 – 125.1 (m), 132.7 (t, *J* = 5.2 Hz), 162.5. ^{31}P NMR (162 MHz, $CDCl_3$), *δ*, ppm: 32.7. HRMS (ESI), m/z: $[M+H]^+$ calculated for $C_{30}H_{33}O_6P_2^+$ 551.1747; found 551.1747.



Ethane-1,2-diylbis(di-*tert*-butylphosphine oxide) (2i) [146]. Synthesized by method 1. Yield 60 mg (69%), white powder, m.p. 134–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$), *δ*, ppm: 1.18 – 1.29 (m, 36H), 2.01 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$), *δ*, ppm: 13.7 – 14.6 (m), 26.6, 35.6 – 36.6 (m). ^{31}P NMR (162 MHz, $CDCl_3$), *δ*, ppm: 60.7. HRMS (ESI), m/z: $[M+H]^+$ calculated for $C_{18}H_{41}O_2P_2^+$ 351.2576; found 351.2579.

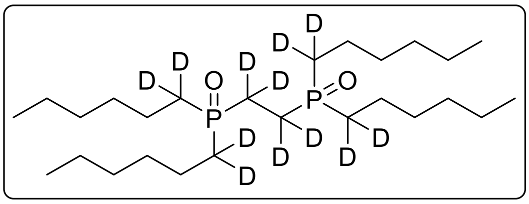


Ethane-1,2-diylbis(dicyclohexylphosphine oxide) (2j) [82]. Synthesized by method 1. Yield 76 mg (67%), white powder, m.p. 184–188 °C. ^{1}H NMR (400 MHz, $CDCl_3$), *δ*, ppm: 1.10 – 1.47 (m, 10H), 1.46 – 2.23 (m, 14H). ^{13}C NMR (101 MHz, $CDCl_3$), *δ*, ppm: 14.8 – 16.2 (m), 25.8 (d, *J* = 22.0 Hz), 26.0, 26.5 – 27.0 (m), 35.8 – 37.5 (m). ^{31}P NMR (162 MHz, $CDCl_3$), *δ*, ppm: 51.8. HRMS (ESI), m/z: $[M+H]^+$ calculated for $C_{26}H_{49}O_2P_2^+$ 455.3202; found 455.3201.

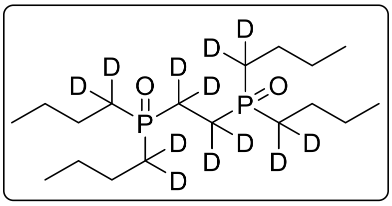


(Ethane-1,2-diyl-*d₄*)bis(diphenylphosphine oxide) (2a-*d₄*). Synthesized by method 2. Yield 107 mg (99%), white powder, m.p. 264–266 °C. ^{1}H NMR (400 MHz, $CDCl_3$), *δ*, ppm: 7.44 (t, *J* = 7.1 Hz, 8H), 7.47 – 7.57 (m, 4H), 7.57 – 7.82 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$), *δ*, ppm: 19.9 – 22.1 (m), 128.9 (t, *J* = 5.7 Hz), 130.8 (t, *J* = 4.4 Hz), 131.1 – 133.1 (m), 132.1. ^{31}P NMR (162

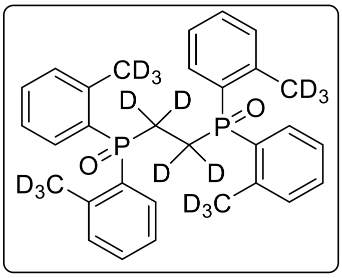
MHz, CDCl$_3$), *δ*, ppm: 32.5. ^{2}H NMR (77 MHz, CHCl$_3$), *δ*, ppm: 2.48 (s). HRMS (ESI), m/z: [M+H]$^+$ calculated for $C_{26}H_{21}D_4O_2P_2^+$ 435.1575; found 435.1575.



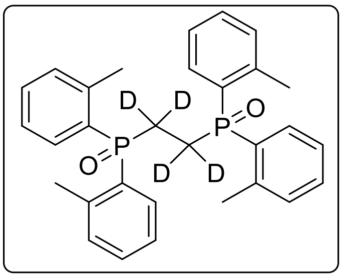
(Ethane-1,2-diyl-d_4)bis(bis(hexyl-1,1-d_2)-phosphine oxide) (2b-d_{12}). Synthesized by method 2. Yield 107 mg (90%), white powder, m.p. 163–164 °C. ^{1}H NMR (400 MHz, CDCl$_3$), *δ*, ppm: 0.65 – 1.02 (m, 12H), 1.06 – 1.43 (m, 24H), 1.50 (s, 8H). ^{13}C NMR (101 MHz, CDCl$_3$), *δ*, ppm: 14.1, 18.0 – 20.2 (m), 21.6, 22.5, 26.5 – 28.6 (m), 30.8 (t, *J* = 6.8 Hz), 31.4. ^{31}P NMR (162 MHz, CDCl$_3$), *δ*, ppm: 48.3. ^{2}H NMR (61 MHz, CHCl$_3$), *δ*, ppm: 1.66 (s, 8D), 1.83 (s, 4D). HRMS (ESI), m/z: [M+Na]$^+$ calculated for $C_{26}H_{44}D_{12}O_2P_2Na^+$ 497.4394; found 497.4389.



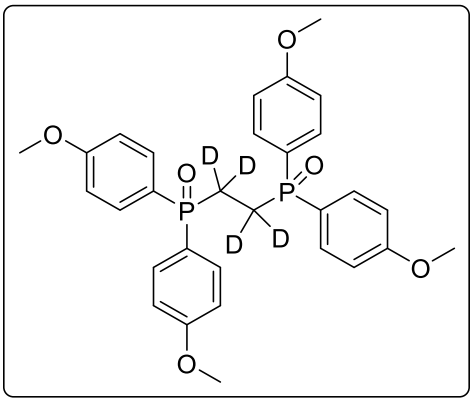
(Ethane-1,2-diyl-d_4)bis(bis(butyl-1,1-d_2)-phosphine oxide) (2c-d_{12}). Synthesized by method 2. Yield 55 mg (61%), white powder, m.p. 174–175 °C. ^{1}H NMR (400 MHz, CDCl$_3$), *δ*, ppm: 0.77 – 0.93 (m, 12H), 1.28 – 1.41 (m, 8H), 1.45 (s, 8H). ^{13}C NMR (101 MHz, CDCl$_3$), *δ*, ppm: 13.6, 18.0 – 20.1 (m), 23.6, 24.0 – 24.4 (m), 26.2 – 28.1 (m). ^{31}P NMR (162 MHz, CDCl$_3$), *δ*, ppm: 48.5. ^{2}H NMR (77 MHz, CHCl$_3$), δ, ppm: 1.65 (s, 8D), 1.83 (s, 4D). HRMS (ESI), m/z: [M+H]$^+$ calculated for $C_{18}H_{29}D_{12}O_2P_2^+$ 363.3330; found 463.3329.



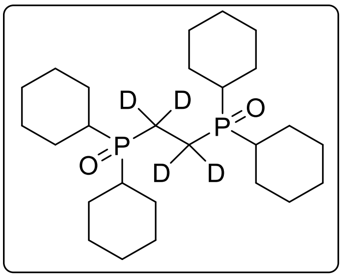
(Ethane-1,2-diyl-d_4)bis(bis(2-(methyl-d_3)phenyl)phosphine oxide) (2e-d_{16}). Synthesized by method 2. Yield 93 mg (74%), white powder, m.p. 228–233 °C. ^{1}H NMR (400 MHz, CDCl$_3$), *δ*, ppm: 7.17 (d, *J* = 7.1 Hz, 4H), 7.23 – 7.31 (m, 4H), 7.34 – 7.49 (m, 4H), 7.72 (d.d, *J* = 12.7, 6.8 Hz, 4H). ^{13}C NMR (101 MHz, CDCl$_3$), *δ*, ppm: 20.0 – 20.8 (m), 125.9 (t, *J* = 5.9 Hz), 129.9 – 131.4 (m), 132.0 – 132.2 (m), 141.6. ^{31}P NMR (162 MHz, CDCl$_3$), *δ*, ppm: 34.5. ^{2}H NMR (61 MHz, CHCl$_3$), *δ*, ppm: 2.18 (s, 12D), 2.60 (s, 4D). HRMS (ESI), m/z: [M+H]$^+$ calculated for $C_{30}H_{17}D_{16}O_2P_2^+$ 503.2944; found 503.2949.



(Ethane-1,2-diyl-d_4)bis(di-*ortho*-tolylphosphine oxide) (2e-d_4). Synthesized by method 2. Yield 98 mg (80%), white powder, m.p. 226–230 °C. ^{1}H NMR (400 MHz, $CDCl_3$), *δ*, ppm: 2.23 (s, 12H), 7.17 (d, *J* = 7.4 Hz, 4H), 7.22 – 7.31 (m, 4H), 7.39 (t, *J* = 7.5 Hz, 4H), 7.71 (d.d, *J* = 13.0, 6.6 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$), *δ*, ppm: 20.9 – 22.0 (m), 125.9 (t, *J* = 5.8 Hz), 129.7 – 131.4 (m), 131.7 – 132.8 (m), 141.7 (t, *J* = 4.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$), *δ*, ppm: 34.5. ^{2}H NMR (77 MHz, $CHCl_3$), δ, ppm: 2.61 (s). HRMS (ESI), m/z: $[M+Na]^+$ calculated for $C_{30}H_{28}D_4O_2P_2Na^+$ 513.2021; found 513.2018.



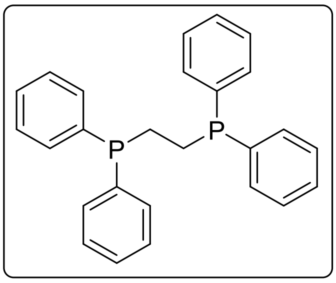
(Ethane-1,2-diyl-d_4)bis(bis(4-methoxyphenyl) phosphine oxide) (2h-d_4). Synthesized by method 2. Yield 102 mg (74%), white powder, m.p. 181–182 °C. Signal intensities may differ from theoretical due to partial deuteration at *the ortho* positions of the aromatic ring. ^{1}H NMR (400 MHz, $CDCl_3$), *δ*, ppm: 3.78 (s, 12H), 6.90 (d, *J* = 7.4 Hz, 5H), 7.57 (s, 8H). ^{13}C NMR (101 MHz, $CDCl_3$), *δ*, ppm: 21.5 – 22.1 (m), 55.4, 114.2 – 114.5 (m), 122.3 – 124.8 (m), 132.2 – 133.2 (m), 162.5. ^{31}P NMR (162 MHz, $CDCl_3$), *δ*, ppm: 32.8. ^{2}H NMR (61 MHz, $CHCl_3$), *δ*, ppm: 2.40 (s, 4D), 6.96 (s, 2D), 7.63 (s, 1D). HRMS (ESI), m/z: $[M+Na]^+$ calculated for $C_{30}H_{25}D_7O_6P_2Na^+$ 580.2004; found 580.1975.



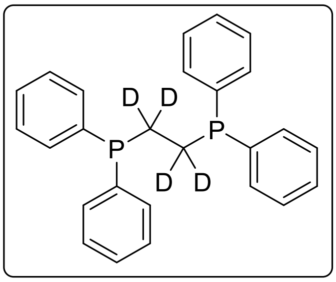
(Ethane-1,2-diyl-d_4)bis(dicyclohexylphosphine oxide) (2j-d_4) [148]. Synthesized by method 2. Yield 48 mg (42%), white powder, m.p. 198–199 °C. ^{1}H NMR (400 MHz, $CDCl_3$), *δ*, ppm: 1.09 – 1.45 (m, 20H), 1.56 – 2.03 (m, 24H). ^{13}C NMR (101 MHz, $CDCl_3$), *δ*, ppm: 13.3 – 16.1 (m), 25.7 (d, *J* = 23.6 Hz), 26.0, 26.2 – 27.4 (m), 34.9 – 38.4 (m). ^{31}P NMR (162 MHz, $CDCl_3$), *δ*, ppm: 50.8. ^{2}H NMR (77 MHz, $CHCl_3$), *δ*, ppm: 1.84 (s). HRMS (ESI), m/z: $[M+H]^+$ calculated for $C_{26}H_{45}D_4O_2P_2^+$ 459.3453; found 459.3454.

3.4. Synthesis and characterization of 1,2-bis(phosphine)ethanes

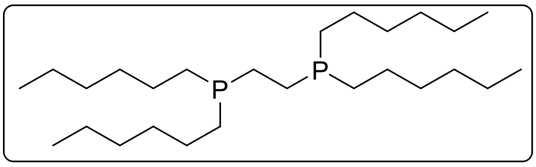
The reduction of the resulting phosphine oxides was carried out according to a modified procedure [88]. Phosphine oxide (1 mmol), toluene (3.5 ml) and $HSiCl_3$ (2 ml, 20 mmol) were loaded in a 50 ml pressure flask in an argon atmosphere, after which it was purged with argon and the lid was screwed on. The reaction mixture was stirred for 5 hours at 100 °C. After this, while cooling in an ice bath, 20 ml of 25% NaOH solution was carefully added, and the formation of white flakes and gas evolution were observed. The resulting mixture was left to stir overnight. The organic layer was then separated, the aqueous layer was extracted with diethyl ether (3 × 20 mL) and washed with brine (3 × 20 mL). The organic layers were combined, dried over $MgSO_4$ and solvent was evaporated. The resulting product was purified by column chromatography on silica gel (eluent: methylene chloride : methanol (80:1) for **3a**, methylene chloride for **3b** and **3e**).



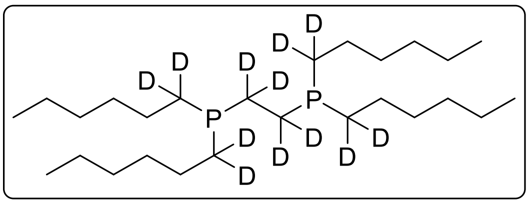
1,2-bis(diphenylphosphino)ethane (3a) [143]. Yield 295 mg (74%), white powder, m.p. 139–140 °C. ^1H NMR (400 MHz, $CDCl_3$), δ, ppm: 2.10 (t, J = 3.7 Hz, 4H), 7.22 – 7.46 (m, 20H). ^{31}P NMR (162 MHz, $CDCl_3$), δ, ppm: -12.5.



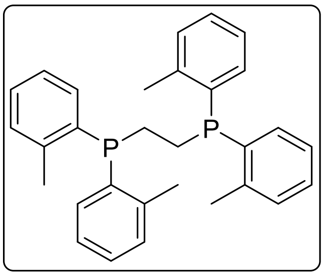
1,2-bis(diphenylphosphino)ethane-1,1,2,2-*d₄* (3a-*d₄*) [78]. Yield 302 mg (75%), white powder, m.p. 139–140 °C. ^1H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.28 – 7.41 (m, 20H). ^{13}C NMR (101 MHz, $CDCl_3$), δ, ppm: 22.2 – 24.0 (m), 128.6 (t, J = 3.0 Hz), 128.8, 132.9 (t, J = 9.3 Hz), 138.2 – 138.3 (m). ^{31}P NMR (162 MHz, $CDCl_3$), δ, ppm: -13.2. ^2H NMR (61 MHz, $CHCl_3$), δ, ppm: 2.08 (s). HRMS (ESI), m/z: $[M+H]^+$ calculated for $C_{26}H_{21}D_4P_2^+$ 403.1677; found 403.1677.



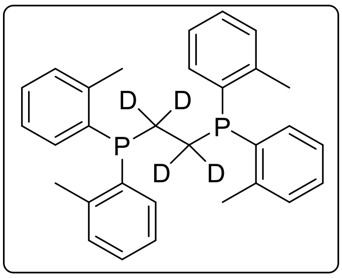
1,2-bis(dihexylphosphino)ethane (3b). Yield 46 mg (72%), yellow oil. ^1H NMR (400 MHz, $CDCl_3$), δ, ppm: 0.88 (t, J = 6.7 Hz, 12H), 1.07 – 1.83 (m, 44H). ^{13}C NMR (101 MHz, $CDCl_3$), δ, ppm: 14.2, 22.3 – 22.7 (m), 22.7, 26.0 (t, J = 6.3 Hz), 26.7 – 27.3 (m), 31.3 (t, J = 5.3 Hz), 31.7. ^{31}P NMR (162 MHz, CDCl$_3$), δ, ppm: -26.1. HRMS (ESI), m/z: [M+H]$^+$ calculated for $C_{26}H_{57}P_2^+$ 431.3930; found 431.3922.



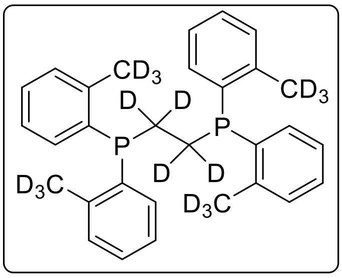
1,2-bis(bis(hexyl-1,1-*d$_2$*)-phosphino)ethane-1,1,2,2-*d$_4$* (3b-*d$_{12}$*). Yield 46 mg (70%), yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$), δ, ppm: 0.87 (t, J = 6.9 Hz, 12H), 1.11 – 1.65 (m, 32H). ^{13}C NMR (101 MHz, CDCl$_3$), δ, ppm: 14.2, 21.4 – 22.6 (m), 22.7, 25.6 – 25.9 (m), 25.9 – 26.4 (m), 31.2 – 31.3 (m), 31.7. ^{31} P NMR (162 MHz, CDCl$_3$), δ, ppm: -28.2. ^{2}H NMR (61 MHz, CHCl$_3$), δ, ppm: 1.36 (s, 8D), 1.69 (s, 4D). HRMS (ESI), m/z: [M+H]$^+$ calculated for $C_{26}H_{45}D_{12}P_2^+$ 443.4683; found 443.4677.



1,2-bis(di-*ortho*-tolylphosphino)ethane (3e) [149]. Yield 35 mg (78%), white powder, m.p. 150–152 °C. ^{1}H NMR (400 MHz, CDCl$_3$), δ, ppm: 2.06 (t, J = 4.4 Hz, 4H), 2.40 (s, 12H), 6.99 – 7.06 (m, 4H), 7.09 (t, J = 7.4 Hz, 4H), 7.12 – 7.18 (m, 4H), 7.18 – 7.25 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$), δ, ppm: 21.0 – 21.6 (m), 22.8 (d, J = 3.7 Hz), 126.2, 128.6, 130.2 (t, J = 2.3 Hz), 131.2, 136.3 – 136.7 (m), 142.3 – 142.8 (m). ^{31}P NMR (162 MHz, CDCl$_3$), δ, ppm: -33.6. HRMS (ESI), m/z: [M+H]$^+$ calculated for $C_{30}H_{33}P_2^+$ 455.2052; found 455.2051.



1,2-bis(di-*ortho*-tolylphosphino)ethane-1,1,2,2-*d$_4$* (3e-*d$_4$*). Yield 28 mg (61%), white powder, m.p. 147–152 °C. ^{1}H NMR (400 MHz, CDCl$_3$), δ, ppm: 2.41 (s, 12H), 6.99 – 7.05 (m, 4H), 7.09 (t, J = 7.4 Hz, 4H), 7.12 – 7.18 (m, 4H), 7.18 – 7.25 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$), δ, ppm: 21.1 – 21.6 (m), 126.2, 128.6, 130.0 – 130.4 (m), 131.2, 136.4 – 136.9 (m), 142.3 – 142.8 (m). ^{31}P NMR (162 MHz, CDCl$_3$), δ, ppm: -34.1. ^{2}H NMR (61 MHz, CHCl$_3$), δ, ppm: 2.02 (s). HRMS (ESI), m/z: [M+H]$^+$ calculated for $C_{30}H_{29}D_4P_2^+$ 459.2303; found 459.2302.

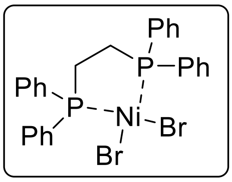


1,2-bis(bis(2-(methyl-*d₃*)phenyl)phosphino)ethane-1,1,2,2-*d₄* (3e-*d₁₆*). Yield 36 mg (77%), white powder, m.p. 151–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$), *δ*, ppm: 6.97 – 7.06 (m, 4H), 7.10 (t, $J = 7.4$ Hz, 4H), 7.12 – 7.18 (m, 4H), 7.18 – 7.25 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$), *δ*, ppm: 20.3 – 21.0 (m), 22.0 – 22.3 (m), 126.2, 128.6, 130.2, 131.2, 136.2 – 136.7 (m), 142.1 – 142.8 (m). ^{31}P NMR (162 MHz, $CDCl_3$), *δ*, ppm: -34.1. ^{2}H NMR (61 MHz, $CHCl_3$), *δ*, ppm: 2.03 (s, 4D), 2.38 (s, 12D). HRMS (ESI), m/z: $[M+H]^+$ calculated for $C_{30}H_{17}D_{16}P_2^+$ 471.3056; found 471.3061.

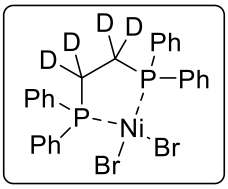
3.5. Synthesis and characterization of complexes with the obtained 1,2-bis(phosphine)ethanes

Method 1. $NiBr_2$ (82 mg, 0.375 mmol) was dissolved with heating in a minimal amount of methanol (3–4 ml). After this, the hot solution was added through a filter to a warm solution of 0.25 mmol of the ligand in 1 ml of toluene. At the same time, a change in the color of the solution from colorless to dark brown was observed. The resulting mixture was refluxed for 2 hours, during which time a red crystalline precipitate formed. After cooling to room temperature, the resulting precipitate was filtered, washed with methanol and dried in vacuum [90]. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a solvent (a mixture of methylene chloride and diethyl ether).

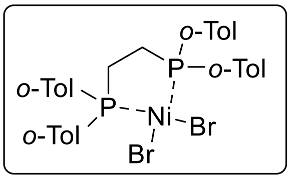
Method 2. K_2PdCl_4 (20 mg, 0.06 mmol) was dissolved at heating in DMF (1.25 ml). After this, the hot salt solution was added through a filter to a warm solution of 25 mg (0.063 mmol) of the ligand **3a** in 2 ml of methylene chloride, and a change in the color of the solution from colorless to yellow was observed. The resulting mixture was refluxed for 2 hours, and a white crystalline precipitate formed. After cooling to room temperature, the precipitate was filtered off, washed with water, diethyl ether and dried in vacuum [91]. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from methylene chloride.



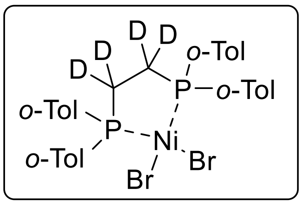
[1,2-bis(diphenylphosphino)ethane]dibromonickel (II) ($NiBr_2$(3a)) [90]. Synthesized by method 1. Yield 123 mg (80%), red crystals, decomposes above 280 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 2.06 – 2.16 (m, 4H), 7.50 (t, J = 6.9 Hz, 8H), 7.57 (t, J = 7.3 Hz, 4H), 7.94 – 8.03 (m, 8H). ^{31}P NMR (162 MHz, $CDCl_3$), δ, ppm: 65.6. HRMS (ESI), m/z: $[M-Br]^+$ calculated for $C_{26}H_{24}P_2NiBr^+$ 536.9863; found 536.9852.



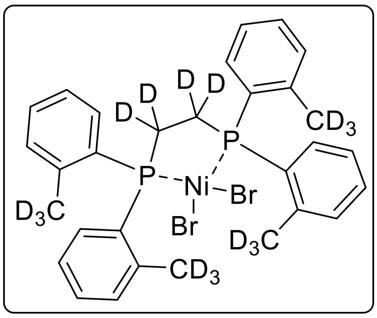
[1,2-bis(diphenylphosphino)ethane-1,1,2,2-*d$_4$*]dibromonickel (II) ($NiBr_2$(3a-*d$_4$*)). Synthesized by method 1. Yield 128 mg (83%), red crystals, decomposes above 280 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.50 (t, J = 7.4 Hz, 8H), 7.57 (t, J = 7.3 Hz, 4H), 7.90 – 8.08 (m, 8H). ^{31}P NMR (162 MHz, $CDCl_3$), δ, ppm: 65.0. HRMS (ESI), m/z: $[M-Br]^+$ calculated for $C_{26}H_{20}D_4P_2NiBr^+$ 541.0114; found 541.0100.



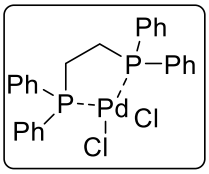
[1,2-bis(di-*ortho*-tolylphosphino)ethane] dibromonickel (II) ($NiBr_2$(3e)). Synthesized by method 1. Yield 162 mg (96%), red crystals, decomposes above 280 °C. Due to low solubility in organic solvents, it was not possible to record NMR and mass spectra. The experimental diffraction patterns of the resulting fine-crystalline powder completely coincide with the diffraction patterns modeled from single-crystalline data.



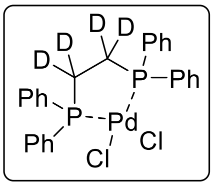
[1,2-bis(di-*ortho*-tolylphosphino)ethane-1,1,2,2-*d$_4$*]dibromo nickel (II) ($NiBr_2$(3e-*d$_4$*)). Synthesized by method 1. Yield 151 mg (89%), red crystals, decomposes above 280 °C. Due to low solubility in organic solvents, it was not possible to record NMR and mass spectra. The experimental diffraction patterns of the resulting fine-crystalline powder completely coincide with the diffraction patterns modeled from single-crystalline data.



[1,2-bis(bis(2-(methyl-*d$_3$*)phenyl)phosphino)ethane-1,1,2,2-*d$_4$*]dibromonickel (II) ($NiBr_2$(3e-*d$_{16}$*)). Synthesized by method 1. Yield 158 mg (92%), red crystals, decomposes above 280 °C. Due to low solubility in organic solvents, it was not possible to record NMR spectra and mass spectra. The experimental diffraction patterns of the resulting fine-crystalline powder completely coincide with the diffraction patterns modeled from single-crystalline data.



[1,2-bis(diphenylphosphino)ethane]dichloropalladium (II) ($PdCl_2$(3a)) [92]. Synthesized by method 2. Yield 30 mg (87%), white crystals, decomposes above 270 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 2.40 – 2.50 (m, 4H), 7.44 – 7.53 (m, 8H), 7.53 – 7.62 (m, 4H), 7.83 – 7.93 (m, 8H). ^{31}P NMR (162 MHz, $CDCl_3$), δ, ppm: 63.7. HRMS (ESI), m/z: $[M+Na]^+$ calculated for $C_{26}H_{24}P_2PdCl_2Na^+$ 596.9661; found 596.9672.



[1,2-bis(diphenylphosphino)ethane-1,1,2,2-*d*$_4$]dichloropalladium (II) ($PdCl_2$(3a-*d*$_4$)). Synthesized by method 2. Yield 31 mg (89%), white crystals, decomposes above 270 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.44 – 7.52 (m, 8H), 7.52 – 7.60 (m, 4H), 7.76 – 8.03 (m, 8H). ^{31}P NMR (162 MHz, $CDCl_3$), δ, ppm: 63.1. HRMS (ESI), m/z: $[M+Na]^+$, calculated for $C_{26}H_{20}D_4P_2PdCl_2Na^+$ 600.9913; found 600.9920.

3.6. Acetaldehyde synthesis

Optimization of alcohol 4a vinylation. Calcium carbide, potassium fluoride, calcium hydroxide, isobutyl alcohol was loaded in a 60 ml pressure reactor and water was carefully added (the amounts of reagents are indicated in Table 2.3). The reactor was closed and the mixture was stirred at 150 °C for 13 hours. After cooling to room temperature, the mixture was filtered and analyzed by ^{1}H NMR spectroscopy.

Optimization of hydrolysis 5a. 2% H_2SO_4 solution (1.1 ml, 61.6 mmol of water) was loaded into a two-neck flask equipped with a dropping funnel and an outlet connected to a receiving flask cooled to -20 °C. Then *iso*-butyl vinyl ether (2 ml, 15.4 mmol, ratio vinyl ether: water 1:4) was added dropwise, and the release of acetaldehyde was observed, which was immediately captured in the receiving flask. After adding the entire volume of vinyl ether, the mixture was further stirred at 80 °C for 1 hour, and then at 100 °C for 2.5 hours, during which time condensation of acetaldehyde was observed in the receiving flask. The isolated yield of **6** was 54%.

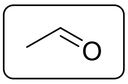
Stepwise hydrolysis 5a. It was carried out in a similar way to the previous method, equipment and loadings were the same. The receiving flask was replaced by a graduated tube cooled to -40 °C. The temperature regime was changed to stirring at 80 °C for 1.5 hours, and then at 100 °C for 0.5 hours. After this, the flask with the acid solution was cooled to 80 °C and a new portion of vinyl ether was added, stirring the mixture under the same temperature conditions. In total, the process of adding vinyl ether was carried out 4 times. The isolated yield of **6** was 74%.

Method 1 (general procedure for vinylation-devinylation of alcohols). Calcium carbide (5 g, 78 mmol), potassium fluoride (6.8 g, 117 mmol), potassium hydroxide (2.2 g, 39 mmol), alcohol (78 mmol, 39 mmol and 26 mmol for monohydric alcohols, diols and glycerol, respectively) were loaded in the pressure reactor and water (2.1 ml, 117 mmol) was carefully added. The reactor was closed and the mixture was stirred at 150 °C for 13 hours. After cooling to room temperature, the mixture was filtered using a Buchner funnel. The precipitate was washed with a solvent (hexane (Table 2.8, alcohols **4b**–**4c**, **4e**–**4f**), ethyl acetate (alcohols **4g**–**4j**) or heptane (alcohols **4a**, **4d**)). The organic layer was washed with brine (2 × 5 ml), dried over Na_2SO_4 and the solvent was removed *in vacuo* (except alcohols **4a**, **4d**). The conversion of alcohol to vinyl ether was determined by ^{1}H NMR spectroscopy.

The resulting mixture, without further purification, was added dropwise to a 2% H_2SO_4 solution (water : vinyl ether ratio 1:4) in a short-distance distillation unit, where the receiving flask was cooled to -40 °C. The mixture was stirred at 80 °C for 1 hour and then at 100 °C for 2.5 hours. During the entire reaction time, acetaldehyde condensed in the receiving flask. The organic layer located in the distillation flask was separated from the aqueous layer (except for alcohols **4h** and **4j**). For alcohols **4a** and **4d**, the solvent was removed under reduced pressure. The conversion of vinyl ether to acetaldehyde and alcohol was determined using ^{1}H NMR spectroscopy.

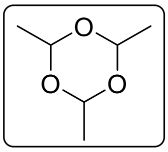
Method 2 (preparation of D-labeled compounds). Isobutyl vinyl ether (2 ml, 15.4 mmol) was added dropwise to 1.1 ml of a 2% solution of H_2SO_4 in D_2O (61.6 mmol D_2O, vinyl ether : water ratio 1:4) in a short-cut distillation unit, where the receiving flask was cooled to -40 °C. The mixture was stirred at 80 °C for 3 hours and then at 100 °C for 2 hours. The isolated yield of **6-*d*** was 87%. Alcohol **4a-*d*** was separated from the aqueous layer, the yield of **4a-*d*** was 97%. DI was 100% for **4a-*d*** and 93% for **6-*d***.

Method 3 (scaled hydrolysis of 5a). Isobutyl vinyl ether (130 ml, 1 mol) was added dropwise to 72.6 ml of 2% H_2SO_4 solution (4 mol water) in a simple distillation unit, where the receiving flask was cooled to -40 °C. The mixture was stirred at 80 °C for 1 hour and then at 100 °C for 2.5 hours (until distillation was completed). Next, the distillate containing a small amount of unreacted vinyl ether was re-hydrolyzed under the same conditions. The isolated yield of **6** after the second distillation was 43 g (97%).

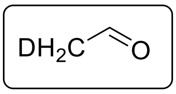


Acetaldehyde (6) [150]. Obtained by method 1 and 3 (yield 43 g (97%)), transparent colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 2.20 (d, $J = 2.9$ Hz, 3H), 9.79 (q, $J = 2.9$ Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ, ppm: 31.1, 200.0. MS (EI), m/z: $[M]^+$ calculated for $C_2H_4O^+$ 44; found 44.

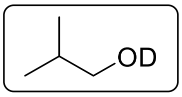
Acetaldehyde in aqueous solutions forms a trimer (paraldehyde).



Paraldehyde [151]. Colorless liquid. ^{1}H NMR (400 MHz, D_2O), δ, ppm: 1.37 (d, $J = 5.2$ Hz, 9H), 5.28 (q, $J = 5.2$ Hz, 3H).



Acetaldehyde-2-*d* (6-*d*) [152]. Obtained by method 2 (yield 0.6 g (87%)), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 2.14 – 2.22 (m, 2H), 9.80 (t, $J = 2.7$ Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ, ppm: 30.8 (t, $J = 19.6$ Hz), 200.1. ^{2}H NMR (61 MHz, toluene), δ, ppm: 2.10 (t, $J = 2.2$ Hz). MS (EI), m/z: $[M]^+$ calculated for $C_2H_3DO^+$ 45; found 45.



2-methylpropan-1-ol-*d* (4a-*d*) [153]. Obtained by method 2 (yield 1.1 g (97%)), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 0.89 (d, $J = 6.7$ Hz, 6H), 1.74 (n, $J = 6.6$ Hz, 1H), 3.37 (d, $J = 6.5$ Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$), δ, ppm: 19.0, 30.9, 69.7. ^{2}H NMR (61 MHz), δ, ppm: 5.09 (s).

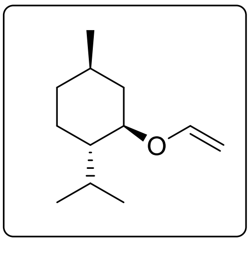
3.7. Synthesis and characterization of vinyl ethers of terpene alcohols

Method 1. Potassium fluoride (58 mg, 1.2 mmol), potassium hydroxide (56 mg, 1.2 mmol), alcohol (1 mmol), calcium carbide (192 mg, 3 mmol), DMSO (0.5

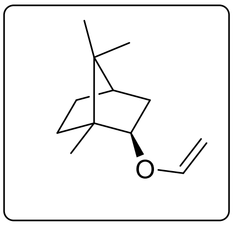
ml) were loaded in an 8 ml pressure tube, then water (108 μl, 6 mmol) carefully added and screwed on the cap. The reaction mixture was stirred for 4–5 hours at 130 °C. After cooling, the mixture was filtered, extracted with hexane (3 × 2 ml), then the organic layer was washed with brine (3 × 2 ml), dried over sodium sulfate and the solvent was removed under reduced pressure. Further purification was carried out using column chromatography on deacidified silica gel (eluent hexane or hexane : diethyl ether).

Method 2. 2,5-DHMF (32 mg, 0.25 mmol), potassium fluoride (44 mg, 0.3 mmol), calcium carbide (128 mg, 1.5 mmol), DMSO (0.5 ml) and water (54 μl, 3 mmol) were loaded in an 8 ml pressure tube. The tube was tightly closed with a lid and the mixture were stirred for 6 hours at 100 °C. After cooling, the reaction mixture was filtered through cotton wool and extracted with diethyl ether (4 × 2 ml). The ether layer was washed with brine (3 × 2 ml) and dried over Na_2SO_4, after which the solvent was evaporated. Pure divinyl ether was obtained using column chromatography on deacidified silica gel (a mixture of diethyl ether : hexane (1:60) was used as an eluent). For polymerization, divinyl ether was additionally dried over CaH_2 for 12 hours and distilled in vacuum at 70 °C (150 mbar).

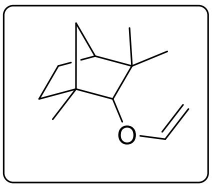
Method 3. Potassium fluoride (2.0 g, 35 mmol), potassium hydroxide (1.8 g, 31 mmol), terpene alcohol (30 mmol), calcium carbide (3.84 g, 60 mmol) and DMSO (30 ml) were placed in a 100 ml pressure flask, and then water (2.5 ml, 139 mmol) was slowly added. The flask was sealed and the mixture was stirred at 130 °C for 5 hours. After cooling, the mixture was filtered through a Buchner funnel, extracted with pentane (4 × 30 ml), treated with brine (3 × 30 ml) and the organic layer was dried over Na_2SO_4. After removal of the solvent, the product was purified by column chromatography on deacidified silica gel using pentane (or a pentane: ethyl acetate mixture) as eluent.



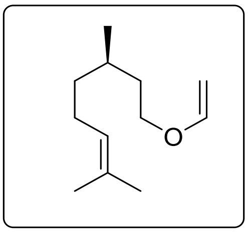
(1S,2R,4R)-1-isopropyl-4-methyl-2-(vinyloxy)cyclohexane (5f) [154]. Synthesized by method 1 (yield 158 mg (87%)) and method 3 (yield 3.5 g (65%)), colorless liquid. ^1H NMR (400 MHz, $CDCl_3$), *δ*, ppm: 0.78 (d, *J* = 7.0 Hz, 3H), 0.83 – 0.95 (m, 7H), 0.95 – 1.08 (m, 2H), 1.29 – 1.48 (m, 2H), 1.55 – 1.75 (m, 2H), 2.01 – 2.16 (m, 2H), 3.52 (d.t, J = 10.7, 4.3 Hz, 1H), 3.94 (d.d, J = 6.5, 1.3 Hz, 1H), 4.28 (d.d, J = 14.1, 1.3 Hz, 1H), 6.32 (d.d, J = 14.1, 6.5 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$), δ, ppm: 16.5, 20.9, 22.3, 23.7, 26.0, 31.6, 34.6, 41.0, 47.9, 80.0, 87.7, 151.5.



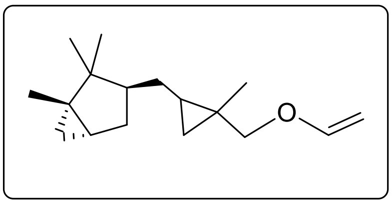
(1S,2S,4R)-1,7,7-trimethyl-2-(vinyloxy)bicyclo[2.2.1]heptane (5k) [47]. Synthesized by method 1 (yield 134 mg (75%)) and method 3 (yield 4.4 g (82%)), colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$), δ, ppm: 0.82 – 0.94 (m, 9H), 1.07 (d.d, J = 13.4, 3.3 Hz, 1H), 1.16 – 1.33 (m, 2H), 1.64 – 1.70 (m, 1H), 1.70 – 1.78 (m, 1H), 2.00 (m, 1H), 2.22 (m, 1H), 3.94 (d.d, J = 6.7, 1.3 Hz, 1H), 4.01 (d.d, J = 9.4, 2.4 Hz, 1H), 4.12 (d.d, J = 14.3, 1.3 Hz, 1H), 6.40 (d.d, J = 14.3, 6.7 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$), δ, ppm: 13.8, 19.0, 19.9, 26.9, 28.1, 36.5, 45.2, 47.9, 49.3, 84.0, 87.1, 152.0.



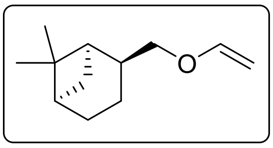
(1S,2R,4S)-1,3,3-trimethyl-2-(vinyloxy)bicyclo[2.2.1]heptane (5l) [155]. Synthesized by method 1 (yield 165 mg (92%)) and method 3 (yield 4.6 g (85%)), colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$), δ, ppm: 0.88 (s, 3H), 0.98 – 1.04 (m, 1H), 1.06 (s, 3H), 1.09 (s, 3H), 1.14 (d.d, J = 10.2, 1.2 Hz, 1H), 1.36 – 1.47 (m, 1H), 1.47 – 1.54 (m, 1H), 1.64 – 1.84 (m, 3H), 3.36 (d, J = 1.5 Hz, 1H), 3.90 (d.d, J = 6.5, 1.3 Hz, 1H), 4.26 (d.d, J = 14.1, 1.3 Hz, 1H), 6.32 (d.d, J = 14.1, 6.5 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$), δ, ppm: 19.8, 20.5, 26.1, 26.3, 31.0, 40.1, 41.5, 48.8, 49.2, 87.3, 92.7, 153.5.



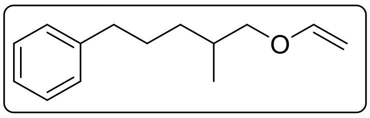
(R)-2,6-dimethyl-8-(vinyloxy)oct-2-ene (5m) [156]. Synthesized by method 1 (yield 170 mg (93%)), colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$), δ, ppm: 0.92 (d, J = 6.6 Hz, 3H), 1.13 – 1.24 (m, 1H), 1.30 – 1.40 (m, 1H), 1.41 – 1.53 (m, 1H), 1.53 – 1.65 (m, 4H), 1.66 – 1.77 (m, 4H), 1.87 – 2.12 (m, 2H), 3.64 – 3.77 (m, 2H), 3.97 (d.d, J = 6.8, 1.8 Hz, 1H), 4.17 (d.d, J = 14.3, 1.8 Hz, 1H), 5.02 – 5.18 (m, 1H), 6.46 (d.d, J = 14.3, 6.8 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$), δ, ppm: 17.8, 19.6, 25.6, 25.9, 29.7, 36.1, 37.3, 66.5, 86.3, 124.8, 131.4, 152.1. HRMS (ESI), m/z: [M]$^+$ calculated for $C_{12}H_{22}OAg^+$, 289.0716; found 289.0714.



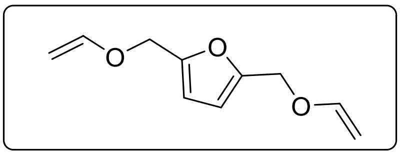
(1S,3R,5R)-1,2,2-trimethyl-3-(((1R,2R)-2-methyl-2-((vinyloxy)methyl)cyclopropyl)methyl)bicyclo[3.1.0]hexane (5n). Synthesized by method 1 (yield 218 mg (88%)) as a mixture of two isomers, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$), *δ*, ppm: -0.06 – -0.01 (m, 1H), 0.01 – 0.08 (m, 3H), 0.46 – 0.52 (m, 2H), 0.54 – 0.65 (m, 4H), 0.75 – 0.80 (m, 6H), 0.89 (s, 6H), 0.97 – 1.02 (m, 3H), 1.04 (s, 7H), 1.11 – 1.15 (m, 6H), 1.15 – 1.26 (m, 4H), 1.30 – 1.48 (m, 3H), 1.80 – 1.95 (m, 2H), 3.30 – 3.45 (m, 4H) , 3.93 – 3.96 (m, 2H), 4.09 – 4.19 (m, 2H), 6.45 – 6.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$), *δ*, ppm: 13.9, 14.0, 15.5, 16.1, 16.8, 17.3, 17.4, 17.4, 19.0, 19.6, 19.8, 20.0, 21.3, 21.7, 22.6, 22.7, 22.9, 28.9, 29.6, 31.3, 31.4, 32.4, 32.5, 41.2, 41.4, 44.8, 45.1, 77.5, 77.7, 86.0, 86.1, 152.3. HRMS (ESI), m/z: [M] $^+$ calculated for $C_{17}H_{28}OAg^+$, 355.1186; found 355.1194.



(1R,2S,5R)-6,6-dimethyl-2-((vinyloxy)methyl)bicyclo[3.1.1]heptane (5o). Synthesized by method 1 (yield 148 mg (82%)), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$), *δ*, ppm: 0.95 (d, *J* = 9.6 Hz, 1H), 0.99 (s, 3H), 1.20 (s, 3H), 1.37 – 1.56 (m, 1H), 1.81 – 2.05 (m, 5H), 2.30 – 2.50 (m, 2H), 3.58 – 3.66 (m, 2H), 3.95 (d.d, *J* = 6.8, 1.8 Hz, 1H), 4.15 (d.d, *J* = 14.3, 1.7 Hz, 1H), 6.46 (d.d, *J* = 14.3, 6.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), *δ*, ppm: 19.0, 23.5, 26.1, 28.1, 33.2, 38.7, 40.9, 41.5, 43.4, 73.1, 86.2, 152.3. HRMS (ESI), m/z: [M]$^+$ calculated for $C_{12}H_{20}OAg^+$, 287.0560; found 287.0571.



(4-methyl-5-(vinyloxy)pentyl)benzene (5p). Synthesized by method 1 (yield 180 mg (88%)), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$), *δ*, ppm: 0.96 (d, *J* = 6.7 Hz, 3H), 1.15 – 1.31 (m, 1H), 1.43 – 1.57 (m, 1H), 1.57 – 1.77 (m, 2H), 1.79 – 1.91 (m, 1H), 2.53 – 2.69 (m, 2H), 3.47 (d.d, *J* = 9.5, 6.6 Hz, 1H), 3.55 (d.d, *J* = 9.5, 6.0 Hz, 1H), 3.97 (d.d, *J* = 6.8, 1.7 Hz, 1H), 4.17 (d.d, *J* = 14.3, 1.7 Hz, 1H), 6.48 (d.d, *J* = 14.3, 6.8 Hz, 1H), 7.15 – 7.24 (m, 3H), 7.24 – 7.33 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$), *δ*, ppm: 17.1, 29.0, 33.1, 33.3, 36.3, 73.4, 86.2, 125.8, 128.4, 128.5, 142.7, 152.3. HRMS (ESI), m/z: [M] $^+$ calculated for $C_{14}H_{20}OAg^+$, 311.0565; found 311.0556.



2,5-bis((vinyloxy)methyl)furan (5r-II) [157]. Synthesized by method 2 (yield 27 mg (30%)), yellow liquid. ^{1}H NMR (400 MHz, CDCl$_3$), δ, ppm: 4.10 (d.d, $^3J_{HH}$ = 6.8, $^2J_{HH}$ = 2.3, 2H), 4.31 (d.d, $^3J_{HH}$ = 14.3, $^2J_{HH}$ = 2.3, 2H), 4.69 (s, 4H), 6.35 (s, 2H), 6.51 (d.d, $^3J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 6.8, 2H). ^{13}C NMR (101 MHz, CDCl$_3$), δ, ppm: 62.5, 87.9, 110.7, 151.0, 151.3.

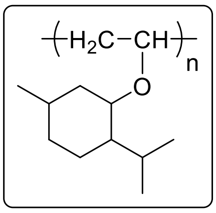
3.8. Synthesis and characterization of polymers

Before polymerization, all vinyl ethers were dried over calcium hydride and vacuum distilled using the “Kugelrohr” system (vacuum shortcut distillation).

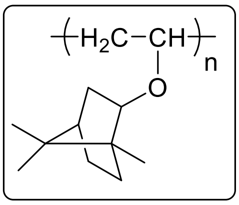
Method 1. Vinyl ether (1.5 mmol) and dry argonized toluene (0.5 ml) were loaded into a Schlenk flask pre-dried in vacuum in an argon atmosphere. The flask was sealed with a septum and stirred for 10 minutes at -40 °C. After this, 0.5 ml of a solution of the initiator in toluene (2 mol% boron trifluoride etherate). At this time, the solution turned yellow and thickened. The reaction mixture was stirred for 24 hours at -40 °C, after which 15 ml of methanol was added to precipitate the resulting polymer. The resulting white flakes were decanted, dried, and reprecipitated three times with methanol from a solution in chloroform. The resulting polymer was dried in vacuum at 40 °C for two days.

Method 2. Vinyl ether (135 mg, 0.75 mmol) and toluene (0.25 ml) were loaded into a Schlenk flask pre-dried in vacuum under an argon atmosphere. The flask was sealed with a septum and stirred for 10 minutes at -10 °C. After this, 0.3 ml of a solution of the initiator in toluene (2 mol% boron trifluoride etherate). At this time, the top of the solution immediately thickened (formation of a cross-linked polymer). The reaction mixture was stirred for 24 hours at -10 °C, after which methanol (10 ml) was added to precipitate the resulting polymer. The resulting white flakes were decanted and dried in vacuum at 40 °C for two days.

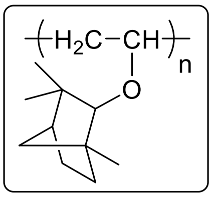
Method 3. Vinyl ether (12 mmol) and dry argonized toluene (6 ml) were loaded into a Schlenk flask pre-dried in vacuum under an argon atmosphere. The flask was sealed with a septum and stirred for 10 minutes at -20 °C. After this, 3 ml of a solution of initiator in toluene (2 mol% boron trifluoride etherate). At this time, the solution turned brown and thickened. The reaction mixture was stirred for 24 hours at -20 °C, after which the reaction mixture was poured into 25 ml of methanol to precipitate the resulting polymer. The precipitated polymer was filtered, dried, and reprecipitated three times with methanol from a solution in chloroform. The resulting polymer was dried in vacuum at 40 °C for two days.



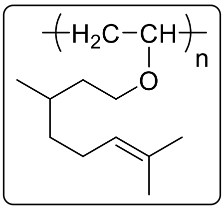
Polymer 7f [158]. Synthesized by method 1 (yield 140 mg (76%)) and method 3 (yield 3.1 g (95%)). White powder. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 0.52 – 1.09 (m, 12H), 1.13 (s, 1H), 1.34 (s, 1H), 1.63 (s, 3H), 1.90 – 2.33 (m, 2H), 2.80 – 4.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$), δ, ppm: 16.7, 21.6, 22.9, 23.6, 25.1, 31.8, 34.9, 41.3, 48.7, 68.1, 73.2.



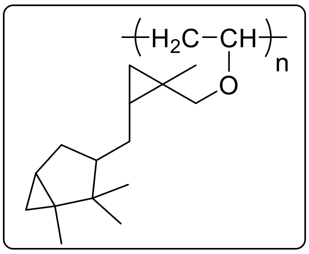
Polymer 7k [155]. Synthesized by method 1 (yield 146 mg (81%)) and method 3 (yield 3.2 g (99%)). White powder. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 0.84 (s, 9H), 0.97 – 1.52 (m, 4H), 1.54 – 1.90 (m, 3H), 2.09 (s, 2H), 3.10 – 3.88 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$), δ, ppm: 14.1, 19.2, 20.0, 26.9, 28.5, 36.7, 38.4, 41.5, 45.4, 47.8, 49.2, 49.6, 71.2, 79.8, 82.4.



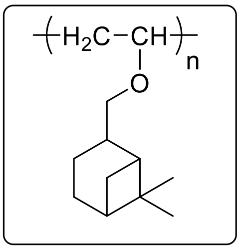
Polymer 7l [155]. Synthesized by method 1 (yield 133 mg (74%)) and method 3 (yield 3.2 g (99%)). White powder. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 0.57 – 2.14 (m, 18H), 3.10 (s, 1H), 3.67 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ, ppm: 20.9, 22.3, 26.4, 31.5, 39.6, 41.6, 48.9, 49.6, 74.6, 88.4.



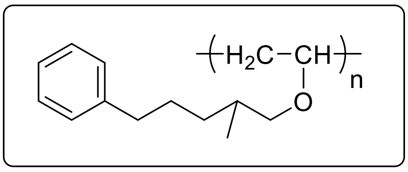
Polymer 7m. Synthesized by method 1 (yield 208 mg (85%)), colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 0.88 (d, J = 4.6 Hz, 3H), 1.00 – 1.22 (m, 1H), 1.22 – 1.43 (m, 2H), 1.41 – 1.72 (m, 10H), 1.70 – 2.10 (m, 3H), 3.23 – 3.67 (m, 3H), 4.97 – 5.16 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ, ppm: 17.8, 19.8, 25.6, 25.8, 29.9, 37.6, 38.9 – 40.6, 41.2 – 42.4, 66.6 – 68.6, 73.9, 124.0 – 125.7, 131.0.



Polymer 7n. Synthesized by method 1 (yield 176 mg (71%)). White powder. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: -0.21 – 0.08 (m, 2H), 0.34 – 0.62 (m, 3H), 0.64 – 0.81 (m, 3H), 0.81 – 1.26 (m, 12H), 1.26 – 1.52 (m, 2H), 1.52 – 1.71 (m, 1H), 1.71 – 1.98 (m, 2H), 2.86 – 3.66 (m, 3H).



Polymer 7o. Synthesized by method 1 (yield 149 mg (82%)). White powder. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 0.91 (d, J = 9.4 Hz, 1H), 0.97 (s, 3H), 1.18 (s, 3H), 1.35 – 1.61 (m, 2H), 1.69 – 2.11 (m, 6H), 2.13 – 2.45 (m, 2H), 3.05 – 3.72 (m, 3H).



Polymer 7p. Synthesized by method 1 (yield 147 mg (72%)), viscous white liquid. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 0.87 (s, 3H), 1.10 (s, 1H), 1.30 – 1.73 (m, 5H), 1.83 (s, 1H), 2.39 – 2.65 (m, 2H), 2.88 – 3.73 (m, 3H), 7.11 (t, J = 8.0 Hz, 3H), 7.21 (t, J = 7.2 Hz, 2H).

Cross-linked polymer 7r. Obtained from vinyl ether **5r-II** according to method 2. Yield 96 mg (71%), white powder. Insoluble in organic solvents.

3.9. Polymer pyrolysis

All operations were carried out in an argon atmosphere. The tube furnace was preheated to 750 °C. Then a sample of the polymer was placed in the far part of the quartz tube and the tube was pushed into the oven (in the case of polymers **7k** and **7o,** first, heated the end of the tube in which there was no sample, and then moved the tube further and heated the part with the sample).

Pyrolysis of polymer 7f: loading 25 mg, rapid heating to 415 °C, then heating to 650 °C for 5 minutes, then another 5 minutes to 720 °C, then very slowly increasing the temperature. During the first minutes, a yellow liquid appeared on the walls of the extended part of the tube and a small amount of white smoke was released. After 30 minutes of pyrolysis, the tube was removed and cooled. In the part of the tube that initially contained the sample, the substance was absent after pyrolysis. The liquid part was washed off with methylene chloride, the solvent was evaporated, and the mixture was analyzed by ^{1}H NMR and GC-MS.

Pyrolysis of polymers 7k and 7o: loading 20 mg, rapid heating to 745 °C, then very slowly increasing the temperature. During the first minutes, a yellow liquid appeared on the walls of the extended part of the tube and, in the case of polymer **7k**, a large amount of white smoke was observed. After 30 minutes of pyrolysis, the tube was removed and cooled. In the part of the tube that initially contained the sample, the substance was absent after pyrolysis. The liquid part was washed off with methylene chloride, the solvent was evaporated, and the mixture was analyzed by ^{1}H NMR and GC-MS.

Pyrolysis of polymer 7k (150 mg): pyrolysis was carried out at 400 °C in a quartz tube, on one side of which there was a continuous supply of argon, and on the other side it was connected in series with 3 traps: the first was cooled with ice, the second was filled with $CDCl_3$ (5 ml), third – C_6D_6 (1 ml). The polymer loading was 150 mg. After pyrolysis, a solid residue remained, insoluble in methylene chloride (3 mg). The liquid part from the first trap, combined with the part washed out of the tube with methylene chloride, after evaporation, was 117 mg. The contents of traps 2 and 3, as well as the part washed out with methylene chloride, were analyzed by ^{1}H and ^{13}C NMR, as well as GC-MS.

Pyrolysis of polymer 7f (300 mg): Pyrolysis was carried out at 450 °C in a quartz tube connected to argon and a trap, cooled to -40 °C by a cryostat. Polymer (300 mg) was loaded into the back of the tube, then the tube was placed in a pre-heated oven. Pyrolysis was carried out for 30 minutes. The liquid part (172 mg (yield 67% in terms of alcohol)) was washed out of the tube with methanol and used for further reduction. After pyrolysis, solid residue (31 mg, 10%) remained in the tube.

3.10. Obtaining material for 3D printing from the obtained polymers

Adding a plasticizer to a polymer. Polymer **7f** (10 g) was mixed in a mortar with 3 g of plasticizer (menthol or menthone). Then the mixture was placed in an oven heated to 100 °C, where the softened mixture was stirred until homogenized.

After cooling, the composite material was crushed to pieces of approximately 2 × 3 × 3 mm in size, suitable for an extruder.

Filament extrusion for 3D printing. Material in the form of small pieces (15–20 g) was passed through extruder heated to 75 °C (for a polymer **7f** composite with the addition of 30 wt% menthol) until a filament with a diameter of 1.6–1.8 mm without visible irregularities is obtained (usually 3 - 10 cycles).

3D printing. Printing with the resulting material was carried out by direct feeding of filament into the printer nozzle. Optimal printing conditions for polymer **7f** composite with the addition of 30 wt% menthol: layer thickness – 0.2 mm, printing temperature – 125 °C, heating surface temperature – 40 °C, airflow 60%, print head speed 10 mm/s.

CONCLUSION

Based on the work carried out, the following conclusions can be drawn:

1. The reaction of nucleophilic addition of phosphine oxides to acetylene from calcium carbide occurs both with and without the addition of a base;

2. Hydrolysis of calcium carbide with D_2O in the synthesis of phosphine compounds ligands allows the introduction of a deuterium label into the resulting 1,2-bis(phosphine oxide)ethane. By varying the ratio of DMSO-d_6 to dioxane, it is possible to introduce different numbers of deuterium atoms into the product. Reduction of the resulting phosphine oxide and subsequent complexation does not affect the deuterium label.

3. Alcohols vinylation with calcium carbide can occur in the solvent absence.

4. Pyrolysis of polymers obtained from vinyl ethers of terpene alcohols leads mainly to a mixture of the initial alcohol and the corresponding carbonyl compound. Reduction of this mixture allows the polymer to be re-obtained from the resulting alcohol with the same characteristics.

The following results were achieved in the dissertation work:

1. A method for the synthesis of both deuterium-labeled and unlabeled phosphine compounds ligands using the reaction of nucleophilic addition of phosphine oxides to acetylene generated *in situ* from calcium carbide has been developed;

2. A cyclic method for the production of acetaldehyde using the sequential reaction of alcohols vinylation by calcium carbide and hydrolysis of the resulting vinyl ethers in an acidic medium with complete recycling of products without the use of solvents has been developed;

3. A method for the synthesis and recycling of polymers from renewable raw materials: natural alcohols and calcium carbide has been developed. It has been shown that the resulting polymers can be used to produce material for 3D printing.

We can conclude that the main tasks of the dissertation research have been completed and the goal has been achieved. The results obtained may be useful for organic synthesis and the chemical industry.

LIST OF ABBREVIATIONS

2,5-DHMP − 2,5-di(hydroxymethyl)furan
3D − three-dimensional
5-HMF − 5-(hydroxymethyl)furfural
ABS − acrylonitrile butadiene styrene
Ac − acetyl
AIBN − azobisisobutyronitrile
Alk − alkyl
Ar − aryl
atm − atmosphere
b.p. − boiling temperature
Bu − butyl
D − dispersion
DI − deuterium incorporation
DMAA − dimethylacetamide
DMF − dimethylformamide
DMSO − dimethyl sulfoxide
DPPE − 1,2-bis(diphenylphosphino)ethane
DSC − differential scanning calorimetry
ESI − electrospray ionization
Et − ethyl
FDM − fused deposition modeling
g − gram
GC-MS − gas chromatography-mass spectrometry
GPC − gel permeation chromatography
h − hour
H_- − Hammett's acidity function
Het − heterocycle
HMPA − hexamethylphosphortriamide
l − liter
m.p. − melting temperature
M1 − menthol
M2 − mentone
Me − methyl
mg − milligram
min − minute
ml − milliliter
Mn − number average molecular weight
Mw − weight average molecular weight

NMR – nuclear magnetic resonance
Nu – nucleophile
PETG – polyethylene terephthalate glycol
Ph – phenyl
PLA – polylactide
PMVE – poly(vinyl ether of menthol)
Pr – propyl
RC – resource center
SEM – scanning electron microscope
SSIC – spin-spin interaction constant
TEMPO – (2,2,6,6-tetramethylpiperidin-1-yl)oxyl
tert – tertiary
TGA – thermogravimetric analysis
THF – tetrahydrofuran
TLC – thin layer chromatography
TMA – thermomechanical analysis
V.E. – vinyl ether
XRD – X-ray diffraction analysis
η – yield

ACKNOWLEDGMENTS

The dissertation work was carried out on the basis of the scientific laboratory of cluster catalysis of the Institute of Chemistry of St. Petersburg State University with financial support from the Russian Science Foundation (grant 21-73-20003) and St. Petersburg State University (Pure ID: 92285019).

The author expresses special gratitude to the head of the laboratory, Academician of the Russian Academy of Sciences, Ananikov V.P. for the opportunity to implement an important and interesting topic, motivation, creation of a special positive atmosphere and professional development, as well as to scientific supervisor, Doctor of Chemical Sciences, Rodygin K.S. for sharing the experience of writing articles and generating ideas, a thorough discussion of the results obtained, long scientific discussions and the opportunity to independently work on articles.

The author also expresses deep gratitude to his colleagues – Samoylenko D.E. for moral support, assistance in 3D printing, valuable advice and meaningful discussions, Metlyaeva S.A. for sharing experience in vinylation of terpene alcohols and creating a positive attitude, Ph.D. Minyaev M.E. for describing the XRD data, I. Skvortsova for co-authoring the article. Special thanks to Ph.D. Rozhkov A.V. for careful review of this work, valuable advice and moral support.

The dissertation author thanks his family and friends for their invaluable support, understanding and motivation throughout the entire period of scientific work.

The study of the obtained compounds was carried out at the Research Center “Magnetic resonance research methods”, “X-ray diffraction research methods”, “Methods for analyzing the composition of matter”, “Thermogravimetric and calorimetric research methods”, “Nanotechnologies”, “Innovative technologies of composite nanomaterials” of St. Petersburg State University.

The author expresses gratitude to all members of the scientific group of the scientific laboratory of cluster catalysis of the Institute of Chemistry of St. Petersburg State University for their fruitful joint work.

REFERENCES

1. Trotuş, I.T. Catalytic Reactions of Acetylene: A Feedstock for the Chemical Industry Revisited / I.-T. Trotuş, T. Zimmermann, F. Schüth // Chem. Rev. – 2014. – Vol. 114. – № 3. – P. 1761-1782. doi: 10.1021/cr400357r.

2. Schobert, H. Production of Acetylene and Acetylene-based Chemicals from Coal / H. Schobert // Chem. Rev. – 2014. – Vol. 114. – № 3. – P. 1743-1760. doi: 10.1021/cr400276u.

3. Trofimov, B.A. Reactions of Acetylene in Superbasic Media / B.A. Trofimov // Russ. Chem. Rev. – 1981. – Vol. 50. – № 2. – P. 138. doi: 10.1070/RC1981v050n02ABEH002551.

4. Bedenko, S.P. Modern Processes for Petrochemistry Based on Acetylene (A Review) / S.P. Bedenko, K.I. Dement'ev, A.L. Maximov // Pet. Chem. – 2022. – Vol. 62. – № 9. – P. 989-1026. doi: 10.1134/S0965544122090031.

5. Reppe, W. Vinylation. I. Vinyl ethers and vinyl esters / W. Reppe // Justus Liebigs Ann. Chem. – 1956. – Vol. 601. – №. – P. 84-111.

6. Shostakovskii, M.F. ADDITION OF ALCOHOLS AND MERCAPTANS / M.F. Shostakovskii, A.V. Bogdanova, G.I. Plotnikova // Russ. Chem. Rev. – 1964. – Vol. 33. – № 2. – P. 66. doi: 10.1070/RC1964v033n02ABEH001378.

7. Trofimov, B.A. Reactions of acetylenes in superbasic media. Recent advances / B.A. Trofimov, E.Y. Schmidt // Russ. Chem. Rev. – 2014. – Vol. 83. – № 7. – P. 600–619. doi: 10.1070/RC2014v083n07ABEH004425.

8. Trofimov, B.A. Superbasic medium in chemistry acetylene / B.A. Trofimov // J. Org. Chem. – 1986. – Vol. 22. – № 9. – P. 1991-2006.

9. Trofimov, B.A. Acetylene: new prospects of classical reactions / B.A. Trofimov, N.K. Gusarova // Russ. Chem. Rev. – 2007. – Vol. 76. – № 6. – P. 507-527. doi: 10.1070/RC2007v076n06ABEH003712.

10. Trofimov, B.A. Superbasic catalysts and reagents: concept, application, prospects / B.A. Trofimov // Modern Problem Org. Chem. – 2004. – Vol. 14. – P. 131.

11. Trofimov, B.A. Acetylene and its Derivatives in Reactions with Nucleophiles: Recent Advances and Current Trends / B.A. Trofimov // Curr. Org. Chem. – 2002. – Vol. 6. – № 13. – P. 1121-1162. doi: 10.2174/1385272023373581.

12. Trofimov, B.A. Synthesis and Thermal Stability of O-Vinylketoximes / B.A. Trofimov, A.b.I. Mikhaleva, A.M. Vasil'tsov, E.Y. Schmidt, O.g.A. Tarasova, L.V. Morozova, L.N. Sobenina, T. Preiss, J. Henkelmann // Synthesis. – 2000. – Vol. 2000. – № 8. – P. 1125-1132. doi: 10.1055/s-2000-6330.

13. Shostakovsky, M.F. Vinyl ethers / M.F. Shostakovsky. – Moscow: USSR Academy of Sciences, 1952. – 280 p.

14. Ledovskaya, M.S. Methods for the synthesis of O-, S- and N-vinyl derivatives / M.S. Ledovskaya, V.V. Voronin, K.S. Rodygin // Russ. Chem. Rev. – 2018. – Vol. 87. – № 2. – P. 167-191. doi: 10.1070/RCR4782.

15. Tarasova, O.A. Hydration trimerization of acetylene in superbasic media. IV. Vinyloxyalkynes, allenes and 1,3-dienes from aldehydes and acetylene in one preparative step / O.A. Tarasova, B.A. Trofimov, V.V. Keiko, S.V. Amosova // J. Org. Chem. – 1991. – Vol. 27. – № 6. – P. 1180-1183.

16. Trofimov, B.A. Direct vinylation of glucose derivatives with acetylene / B.A. Trofimov, L.N. Parshina, L.A. Oparina, A.P. Tantsyrev, Marina Y. Khil'ko, O.V. Vysotskaya, A.V. Stepanov, N.K. Gusarova, J. Henkelmann // Tetrahedron. – 2007. – Vol. 63. – № 47. – P. 11661-11665. doi: 10.1016/j.tet.2007.08.107.

17. Van Daalen, J.J. Chemistry of acetylenic ethers LII acetylenic tert. Butyl ethers and some other acetylenic ethers with branched alkyl groups: Some remarks concerning the preparation and the pyrolysis of acetylenic ethers / J.J. van Daalen, A. Kraak, J.F. Arens // Recl. Trav. Chim. Pays-Bas. – 1961. – Vol. 80. – № 8. – P. 810-818. doi: 10.1002/recl.19610800802.

18. Trofimov, B.A. Base-catalyzed O-vinylation of tertiary propargylic alcohols with acetylene: First examples / B.A. Trofimov, E.Y. Schmidt, E.V. Skital'tseva, I.A. Bidusenko, N.V. Zorina, A.I. Mikhaleva // Mendeleev Commun. – 2012. – Vol. 22. – № 2. – P. 62-63. doi: 10.1016/j.mencom.2012.03.002.

19. Pat.US2153993A. Production of N-vinyl Compounds / W. Reppe, E. Keyssner. - 1936.

20. Shmidt, E.Yu. Improved method for the synthesis of 1-vinylindole / E.Y. Shmidt, N.I. Protsuk, A.M. Vasil’tsov, A.V. Ivanov, A.I. Mikhaleva, B.A. Trofimov // Chem. Heterocycl. Comp. – 2013. – Vol. 49. – № 3. – P. 404-407. doi: 10.1007/s10593-013-1260-y.

21. Pat.US2317804A. N-vinyl lactams / W. Reppe, H. Kraikallz, O. Dornbelm, R. Sauerbier. - 1943.

22. Sitte, N.A. Phosphine-Catalyzed Vinylation at Low Acetylene Pressure / N.A. Sitte, M. Menche, P. Tužina, F. Bienewald, A. Schäfer, P. Comba, F. Rominger, A.S.K. Hashmi, T. Schaub // J. Org. Chem. – 2021. – Vol. 86. – № 18. – P. 13041-13055. doi: 10.1021/acs.joc.1c01807.

23. Lin, J.W.P. Synthesis, characterization, and polymerization of N-vinylarylamines / J.W.P. Lin // J. Polym. Sci. – 1979. – Vol. 17. – № 12. – P. 3797-3810. doi: 10.1002/pol.1979.170171201.

24. Stepanova, Z.V. New synthesis of 1-vinyl- and 1,3-divinyluracils / Z.V. Stepanova, G.G. Skvortsova, V.K. Voronov, A.V. Afonin // Chem. Heterocycl. Comp. – 1986. – Vol. 22. – № 4. – P. 469-470. doi: 10.1007/BF00542799.

25. Shostakovsky, M.F. Synthesis of sulfur compounds based on vinyl ethers and acetylene. Message 13. General method for the synthesis of thiovinyl ethers / M.F. Shostakovsky, E.N. Prilezhaeva // Izv. USSR Academy of Sciences Ser. Chem. – 1955. – № 5. – P. 906-912.

26. Shostakovsky, M.F. Synthesis of sulfur compounds based on vinyl ethers and acetylene. Message 10. Synthesis and some transformations of vinylethyl sulfide / M.F. Shostakovsky, E.N. Prilezhaeva, N.I. Uvarov // Izv. USSR Academy of Sciences Ser. Chem. – 1954. – № 3. – P. 526-534.

27. Gusarova, N.K. Highly efficient atom economical “green chemistry” synthesis of vinyl sulfides from thiols and acetylene in water / N.K. Gusarova, N.A. Chernysheva, S.V. Yas’ko, B.A. Trofimov // Russ. Chem. Bull. – 2013. – Vol. 62. – № 2. – P. 438-440. doi: 10.1007/s11172-013-0059-4.

28. Schneider, H.J. Vinyl Sulfides. I. A “One-Step” Synthesis from Halides / H.J. Schneider, J.J. Bagnell, G.C. Murdoch // J. Org. Chem. – 1961. – Vol. 26. – № 6. – P. 1980-1982. doi: 10.1021/jo01065a071.

29. Trofimov, B.A. Divinyl Sulfide: Synthesis, Properties, and Applications / B.A. Trofimov, S.V. Amosova // Sulfur reports. – 1984. – Vol. 3. – № 9. – P. 323-393. doi: 10.1080/01961778408082463.

30. Trofimov, B.A. Chalcogenation in Multiphase Superbase Systems / B.A. Trofimov // Sulfur reports. – 1992. – Vol. 11. – № 2. – P. 207-227. doi: 10.1080/01961779208046184.

31. Trofimov, B.A. Acetylenes in the Superbase-Promoted Assembly of Carbocycles and Heterocycles / B.A. Trofimov, E.Y. Schmidt // Acc. Chem. Res. – 2018. – Vol. 51. – № 5. – P. 1117-1130. doi: 10.1021/acs.accounts.7b00618.

32. Trofimov, B.A. Base-Catalyzed Stereoselective Vinylation of Ketones with Arylacetylenes: A New C(sp^3)-C(sp^2) Bond-Forming Reaction / B.A. Trofimov, E.Y. Schmidt, I.A. Ushakov, N.V. Zorina, E.V. Skital'tseva, N.I. Protsuk, A.I. Mikhaleva // Chem. Eur. J. – 2010. – Vol. 16. – № 28. – P. 8516-8521. doi: 10.1002/chem.201000227.

33. Trofimov, B.A. Transition-Metal-Free Superbase-Promoted Stereoselective α-Vinylation of Ketones with Arylacetylenes: A General Strategy for Synthesis of β,γ-Unsaturated Ketones / B.A. Trofimov, E.Y. Schmidt, N.V. Zorina, E.V. Ivanova, I.A. Ushakov // J. Org. Chem. – 2012. – Vol. 77. – № 16. – P. 6880-6886. doi: 10.1021/jo301005p.

34. Schmidt, E.Yu. Polycyclic bridgehead acetals with enol functionality: one-pot assembly from aliphatic ketones and acetylene in KOH/DMSO suspension / E.Y. Schmidt, I.A. Bidusenko, N.A. Cherimichkina, I.A. Ushakov, B.A. Trofimov // Tetrahedron. – 2016. – Vol. 72. – № 30. – P. 4510-4517. doi: 10.1016/j.tet.2016.06.010.

35. Schmidt, E.Yu. Base-Catalyzed Domino Cyclization of Acetylenes with Ketones to Functionalized Cyclopentenes / E.Y. Schmidt, B.A. Trofimov, I.A. Bidusenko,

N.A. Cherimichkina, I.A. Ushakov, N.I. Protzuk, Y.V. Gatilov // Org. Lett. – 2014. – Vol. 16. – № 15. – P. 4040-4043. doi: 10.1021/ol501881e.

36. Schmidt, E.Yu. Furans Conjugated with Bulky Aromatic Systems: One-Pot Synthesis from Ketones and Acetylene / E.Y. Schmidt, I.A. Bidusenko, N.A. Cherimichkina, I.A. Ushakov, T.N. Borodina, V.I. Smirnov, B.A. Trofimov // Chem. Eur. J. – 2015. – Vol. 21. – № 45. – P. 15944-15946. doi: 10.1002/chem.201503256.

37. Trofimov, B.A. Cyclooligomerization of Acetylene with Acetonitrile to 2-Amino-3-(1-iminoethyl)-6-methylpyridine in the System KOH-CH_3CN / B.A. Trofimov, A.G. Mal'kina, A.V. Afonin, I.A. Ushakov, V.V. Nosyreva, V.K. Bel'skii // Russ. J. Org. Chem. – 2003. – Vol. 39. – № 9. – P. 1358-1359. doi: 10.1023/B:RUJO.0000010229.95022.bd.

38. Trofimov, B.A. Reactions of triads Se_8-KOH-DMSO, Se_8-KOH-DMSO, Te-KOH-HMPA with acetylenes / B.A. Trofimov, S.V. Amosova, N.K. Gurasova, G.K. Musorin // Tetrahedron. – 1982. – Vol. 38. – № 5. – P. 713-718. doi: 10.1016/0040-4020(82)80214-7.

39. Trofimov, B.A. Elemental phosphorus–strong base as a system for the synthesis of organophosphorus compounds / B.A. Trofimov, T.N. Rakhmatulina, N.K. Gusarov, S.F. Malysheva // Russ. Chem. Rev. – 1991. – Vol. 60. – № 12. – P. 1360. doi: 10.1070/RC1991v060n12ABEH001152.

40. Khachatryan, R.A. Synthesis tertiary phosphines and phosphine oxides by reactions nucleophilic addition, application interfacial catalysts or superbasic medium / R.A. Khachatryan, S.V. Sayadyan, N.Yu. Grigoryan, M.G. Indzhikyan // J. Gen. Chem. – 1988. – Vol. 58. – № 11. – P. 2472-2478.

41. Gusarova, K.N. Competitive Deprotonation in Vicinal $O{=}SCH_2CH_2P{=}O$ Moieties / K.N. Gusarova, A.N. Chernysheva, N.S. Arbuzova, V.B. Maria, F.S. Malysheva, A.N. Belogorlova, A.I. Ushakov, M.N. Vitkovskaya, B.V. Kobychev, A.B. Trofimov // Lett. Org. Chem. – 2006. – Vol. 3. – № 9. – P. 720-722. doi: 10.2174/157017806778700097.

42. Yoshimura, A. An efficient base-catalyzed double addition of H-phosphine oxides to alkynes / A. Yoshimura, Y. Saga, Y. Sato, A. Ogawa, T. Chen, L.-B. Han

// Tetrahedron Lett. – 2016. – Vol. 57. – № 30. – P. 3382-3384. doi: 10.1016/j.tetlet.2016.06.079.

43. Rodygin, K.S. Calcium Carbide: Versatile Synthetic Applications, Green Methodology and Sustainability / K.S. Rodygin, M.S. Ledovskaya, V.V. Voronin, K.A. Lotsman, V.P. Ananikov // Eur. J. Org. Chem. – 2021. – Vol. 2021. – № 1. – P. 43-52. doi: 10.1002/ejoc.202001098.

44. Rodygin, K.S. Calcium Carbide: A Unique Reagent for Organic Synthesis and Nanotechnology / K.S. Rodygin, G. Werner, F.A. Kucherov, V.P. Ananikov // Chem. Asian J. – 2016. – Vol. 11. – № 7. – P. 965-976. doi: 10.1002/asia.201501323.

45. Rodygin, K.S. Towards Sustainable Carbon Return from Waste to Industry via C_2-Type Molecular Unit / K.S. Rodygin, K.A. Lotsman, D.E. Samoylenko, V.M. Kuznetsov, V.P. Ananikov // Int. J. Mol. Sci. – 2022. – Vol. 23. – № 19. – P. 11828. doi: 10.3390/ijms231911828.

46. Rodygin, K.S. Calcium-Based Sustainable Chemical Technologies for Total Carbon Recycling / K.S. Rodygin, Y.A. Vikenteva, V.P. Ananikov // ChemSusChem. – 2019. – Vol. 12. – № 8. – P. 1483-1516. doi: 10.1002/cssc.201802412.

47. Werner, G. A solid acetylene reagent with enhanced reactivity: fluoride-mediated functionalization of alcohols and phenols / G. Werner, K.S. Rodygin, A.A. Kostin, E.G. Gordeev, A.S. Kashin, V.P. Ananikov // Green Chem. – 2017. – Vol. 19. – № 13. – P. 3032-3041. doi: 10.1039/C7GC00724H.

48. Voronin, V.V. [3 + 2]-Cycloaddition of in Situ Generated Nitrile Imines and Acetylene for Assembling of 1,3-Disubstituted Pyrazoles with Quantitative Deuterium Labeling / V.V. Voronin, M.S. Ledovskaya, E.G. Gordeev, K.S. Rodygin, V.P. Ananikov // J. Org. Chem. – 2018. – Vol. 83. – № 7. – P. 3819-3828. doi: 10.1021/acs.joc.8b00155.

49. Ledovskaya, M.S. Calcium-mediated one-pot preparation of isoxazoles with deuterium incorporation / M.S. Ledovskaya, K.S. Rodygin, V.P. Ananikov // Org. Chem. Front. – 2018. – Vol. 5. – № 2. – P. 226-231. doi: 10.1039/C7QO00705A.

50. Ledovskaya, M.S. Direct Synthesis of Deuterium-Labeled O-, S-, N-Vinyl Derivatives from Calcium Carbide / M.S. Ledovskaya, V.V. Voronin, K.S. Rodygin, A.V. Posvyatenko, K.S. Egorova, V.P. Ananikov // Synthesis. – 2019. – Vol. 51. – № 15. – P. 3001-3013. doi: 10.1055/s-0037-1611518.

51. Ledovskaya, M.S. Efficient labeling of organic molecules using 13C elemental carbon: universal access to $^{13}C_2$-labeled synthetic building blocks, polymers and pharmaceuticals / M.S. Ledovskaya, V.V. Voronin, K.S. Rodygin, V.P. Ananikov // Org. Chem. Front. – 2020. – Vol. 7. – № 4. – P. 638-647. doi: 10.1039/C9QO01357A.

52. Ledovskaya, M.S. Calcium Carbide: From Elemental Carbon to Isotope-Economic Synthesis of $^{13}C_2$-Labeled Heterocycles / M.S. Ledovskaya, V.V. Voronin, N.R. Valov, D.E. Samoylenko // Chin. J. Chem. – 2023. – Vol. 41. – № 21. – P. 2810-2818. doi: 10.1002/cjoc.202300261.

53. Gyrdymova, Y.V. [^{13}C+D] Double Labeling with Calcium Carbide: Incorporation of Two Labels in One Step / Y.V. Gyrdymova, D.E. Samoylenko, K.S. Rodygin // Chem. Asian J. – 2023. – Vol. 18. – № 3. – P. e202201063. doi: 10.1002/asia.202201063.

54. Rodygin, K.S. An efficient metal-free pathway to vinyl thioesters with calcium carbide as the acetylene source / K.S. Rodygin, V.P. Ananikov // Green Chem. – 2016. – Vol. 18. – № 2. – P. 482-486. doi: 10.1039/C5GC01552A.

55. Rodygin, K.S. Calcium carbide as a convenient acetylene source in the synthesis of unsaturated sulfides, promising functionalized monomers / K.S. Rodygin, A.A. Kostin, V.P. Ananikov // Mendeleev Commun. – 2015. – Vol. 25. – № 6. – P. 415-416. doi: 10.1016/j.mencom.2015.11.004.

56. Rodygin, K.S. Vinylation of a Secondary Amine Core with Calcium Carbide for Efficient Post-Modification and Access to Polymeric Materials / K.S. Rodygin, A.S. Bogachenkov, V.P. Ananikov // Molecules. – 2018. – Vol. 23. – № 3. – P. 648. doi: 10.3390/molecules23030648.

57. Rodygin, K.S. A Green and Sustainable Route to Carbohydrate Vinyl Ethers for Accessing Bioinspired Materials with a Unique Microspherical Morphology / K.S.

Rodygin, I. Werner, V.P. Ananikov // ChemSusChem. – 2018. – Vol. 11. – № 1. – P. 292-298. doi: 10.1002/cssc.201701489.

58. Gyrdymova, Yu.V. Vinylation of Betulin with Calcium Carbide / Y.V. Gyrdymova, K.S. Rodygin // Dokl. Chem. – 2022. – Vol. 506. – № 2. – P. 211-215. doi: 10.1134/S0012500822700124.

59. Rodygin, K.S. Vinylation of Selected Terpenols with Calcium Carbide / K.S. Rodygin // Russ. J. Gen. Chem. – 2017. – Vol. 87. – № 12. – P. 2881-2883. doi: 10.1134/S1070363217120210.

60. Rodygin, K.S. Synthesis of vinyl thioethers and bis-thioethenes from calcium carbide and disulfides / K.S. Rodygin, Y.V. Gyrdymova, V.V. Zarubaev // Mendeleev Commun. – 2017. – Vol. 27. – № 5. – P. 476-478. doi: 10.1016/j.mencom.2017.09.015.

61. Teong, S.P. Calcium carbide and its recent advances in biomass conversion / S.P. Teong, Y. Zhang // J. Biores. Bioprod. – 2020. – Vol. 5. – № 2. – P. 96-100. doi: 10.1016/j.jobab.2020.04.002.

62. Zeng, F.-L. Recent Advances of Calcium Carbide in Organic Reactions / F.-L. Zeng, Q.-Y. Lv, X.-L. Chen, B. Yu // Curr. Chin. Chem. – 2021. – Vol. 1. – № 1. – P. 3-10. doi: 10.2174/2666001601999200817111836.

63. Matake, R. Synthesis of vinyl ethers of alcohols using calcium carbide under superbasic catalytic conditions (KOH/DMSO) / R. Matake, Y. Adachi, H. Matsubara // Green Chem. – 2016. – Vol. 18. – № 9. – P. 2614-2618. doi: 10.1039/C5GC02977E.

64. Rattanangkool, E. An Atom-Economic Approach for Vinylation of Indoles and Phenols Using Calcium Carbide as Acetylene Surrogate / E. Rattanangkool, T. Vilaivan, M. Sukwattanasinitt, S. Wacharasindhu // Eur. J. Org. Chem. – 2016. – Vol. 2016. – № 25. – P. 4347-4353. doi: 10.1002/ejoc.201600666.

65. Teong, S.P. Direct vinylation of natural alcohols and derivatives with calcium carbide / S.P. Teong, A.Y.H. Chua, S. Deng, X. Li, Y. Zhang // Green Chem. – 2017. – Vol. 19. – № 7. – P. 1659-1662. doi: 10.1039/C6GC03579E.

66. Parshina, L.N. Towards C1 chemistry: methanol vinylation by CaC_2 in water in the presence of potassium or sodium carbonates / L.N. Parshina, L.A. Oparina, N.K. Gusarova, B.A. Trofimov // J. Chem. Technol. Biotechnol. – 2019. – Vol. 94. – № 6. – P. 1945-1950. doi: 10.1002/jctb.5976.
67. Teong, S.P. Vinylation of Aryl Ether (Lignin β-O-4 Linkage) and Epoxides with Calcium Carbide through C−O Bond Cleavage / S.P. Teong, J. Lim, Y. Zhang // ChemSusChem. – 2017. – Vol. 10. – № 16. – P. 3198-3201. doi: 10.1002/cssc.201701153.
68. Zhang, Z. Selective N-Monovinylation of Primary Aromatic Amides Using Calcium Carbide as an Alkyne Source / Z. Zhang, F. Wen, H. Liu, Z. Li // ChemistrySelect. – 2022. – Vol. 7. – № 26. – P. e202201463. doi: 10.1002/slct.202201463.
69. Liao, H. N-vinylation of aromatic sulfonamides using calcium carbide as a concise solid alkyne source / H. Liao, Z. Li // Tetrahedron Lett. – 2023. – Vol. 120. – №. – P. 154445. doi: 10.1016/j.tetlet.2023.154445.
70. Kirillov, E. Recent advances in applications of vinyl ether monomers for precise synthesis of custom-tailored polymers / E. Kirillov, K. Rodygin, V. Ananikov // Eur. Polym. J. – 2020. – Vol. 136. – №. – P. 109872. doi: 10.1016/j.eurpolymj.2020.109872.
71. Voronin, V.V. Examining the vinyl moiety as a protecting group for hydroxyl (–OH) functionality under basic conditions / V.V. Voronin, M.S. Ledovskaya, K.S. Rodygin, V.P. Ananikov // Org. Chem. Front. – 2020. – Vol. 7. – № 11. – P. 1334-1342. doi: 10.1039/D0QO00202J.
72. Khachatryan, R.A. Synthesis of 1,2-bis(diphenylphosphino)ethane and 1,2-bis(diphenylphosphinyl)ethane from acetylene using phase-transfer catalysis or superbasic media / R.A. Khachatryan, S.V. Sayadyan, N.Y. Grigoryan, M.G. Indzhikyan // Arm. Khim. Zh. – 1986. – Vol. 39. – № 4. – P. 258-259.
73. Khachatryan, R.A. Synthesis of tertiary phosphines and phosphine oxides by nucleophilic addition reactions by using phase-transfer catalysts or a superbasic

medium / R.A. Khachatryan, S.V. Sayadyan, N.Y. Grigoryan, M.G. Indzhikyan // Russ. J. Gen. Chem. – 1988. – Vol. 58. – № 11. – P. 2472-2478.

74. Folest, J.C. Electrochemical synthesis of tertiary phosphine from organic halides and chlorophosphines / J.C. Folest, J.Y. Nedelec, J. Perichon // Tetrahedron Lett. – 1987. – Vol. 28. – № 17. – P. 1885-1886. doi: 10.1016/S0040-4039(00)96000-3.

75. Pat.CN104558030. A method for preparing bis(diphenylphosphino)alkane / X. Xuan, R. Liang, Y. Li, P. Zhao, Y. Cui. - 2015.

76. Vidal, A. Transmembrane Chloride Transport by Diphosphine-Pd(II) Complexes: Effect of the Ligand Geometry / A. Vidal, M. Tosolini, G. Balducci, P. Tecilla // Eur. J. Org. Chem. – 2022. – Vol. 2022. – № 44. – P. e202201121. doi: 10.1002/ejoc.202201121.

77. Bunlaksananusorn, T. t-BuOK-catalyzed addition phosphines to functionalized alkenes: a convenient synthesis of polyfunctional phosphine derivatives / T. Bunlaksananusorn, P. Knochel // Tetrahedron Lett. – 2002. – Vol. 43. – № 33. – P. 5817-5819. doi: 10.1016/S0040-4039(02)01177-2.

78. Bacci, M. Infrared spectra of $(C_6H_5)PCH_2CH_2P(C_6H_5)_2$ and $(C_6H_5)_2PCD_2CD_2P(C_6H_5)_2$ / M. Bacci // Spectrochim. Acta A Mol. Biomol. Spectrosc. – 1972. – Vol. 28. – № 11. – P. 2286-2289. doi: 10.1016/0584-8539(72)80205-8.

79. Pat.CN110041363. Preparation process of bis(diphenyl)phosphine / Q. Chen. - 2019.

80. Honaker, M.T. CsOH-promoted P-alkylation: a convenient and highly efficient synthesis of tertiary phosphines / M.T. Honaker, B.J. Sandefur, J.L. Hargett, A.L. McDaniel, R.N. Salvatore // Tetrahedron Lett. – 2003. – Vol. 44. – № 46. – P. 8373-8377. doi: 10.1016/j.tetlet.2003.09.117.

81. Honaker, M.T. A MILD AND EFFICIENT CsOH-PROMOTED SYNTHESIS OF DITERTIARY PHOSPHINES / M.T. Honaker, R.N. Salvatore // Phosphorus Sulfur Silicon Relat. Elem. – 2004. – Vol. 179. – № 2. – P. 277-283. doi: 10.1080/10426500490262261.

82. Baldwin, L. C. Synthesis of 1,2-bis[(diorgano)phosphino]ethanes *via* Michaelis–Arbuzov type rearrangements / L.C. Baldwin, M.J. Fink // J. Organomet. Chem. – 2002. – Vol. 646. – № 1. – P. 230-238. doi: 10.1016/S0022-328X(01)01431-0.

83. Krishnamurti, V. Siladifluoromethylation and Deoxo-trifluoromethylation of PV–H Compounds with $TMSCF_3$: Route to PV–CF_2– Transfer Reagents and P–CF_3 Compounds / V. Krishnamurti, C. Barrett, G.K.S. Prakash // Org. Lett. – 2019. – Vol. 21. – № 5. – P. 1526-1529. doi: 10.1021/acs.orglett.9b00381.

84. Busacca, C.A. A Superior Method for the Reduction of Secondary Phosphine Oxides / C.A. Busacca, J.C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei, C.H. Senanayake // Org. Lett. – 2005. – Vol. 7. – № 19. – P. 4277-4280. doi: 10.1021/ol0517832.

85. Zhang, D. Preparation of O-Protected Cyanohydrins by Aerobic Oxidation of α-Substituted Malononitriles in the Presence of Diarylphosphine Oxides / D. Zhang, M. Lian, J. Liu, S. Tang, G. Liu, C. Ma, Q. Meng, H. Peng, D. Zhu // Org. Lett. – 2019. – Vol. 21. – № 8. – P. 2597-2601. doi: 10.1021/acs.orglett.9b00569.

86. Rauhut, M.M. Oxidation of Secondary Phosphines to Secondary Phosphine Oxides1 / M.M. Rauhut, H.A. Currier // J. Org. Chem. – 1961. – Vol. 26. – № 11. – P. 4626-4628. doi: 10.1021/jo01069a102.

87. Voronin, V.V. Cycloaddition Reactions of in situ Generated C_2D_2 in Dioxane: Efficient Synthetic Approach to D_2-Labeled Nitrogen Heterocycles / V.V. Voronin, M.S. Ledovskaya, K.S. Rodygin, V.P. Ananikov // Eur. J. Org. Chem. – 2021. – Vol. 2021. – № 41. – P. 5640-5648. doi: 10.1002/ejoc.202101085.

88. Klingenberg, M.A. 1,4-Dihydrophosphinolines and their complexes with group 10 metals / M.A. Klingenberg, A.S. Bogachenkov, M.A. Kinzhalov, A.V. Vasilyev, V.P. Boyarskiy // New J. Chem. – 2016. – Vol. 40. – № 4. – P. 3336-3342. doi: 10.1039/C5NJ03038B.

89. Pelizzi, C. Crystal structures of two forms of 1,2-bis(diphenylphosphino)ethane / C. Pelizzi, G. Pelizzi // Acta Crystallogr. B. – 1979. – Vol. 35. – № 8. – P. 1785-1790. doi: 10.1107/S0567740879007779.

90. Van Hecke, G. R. Ditertiary Phosphine Complexes of Nickel. SpeCtral, Magnetic, and Proton Resonance Studies. A Planar-Tetrahedral Equilibrium / G.R. Van Hecke, W.D. Horrocks // Inorg. Chem. – 1966. – Vol. 5. – № 11. – P. 1968-1974. doi: 10.1021/ic50045a029.

91. Westland, A.D. 562. Five-co-ordinate palladium(II) and platinum(II) / A.D. Westland // J. Chem. Soc. – 1965. – P. 3060-3067. doi: 10.1039/JR9650003060.

92. Steffen, W.L. Crystal and molecular structures of dichloro[bis(diphenylphosphino)methane]palladium(II), dichloro[bis(diphenylphosphino)ethane]palladium(II), and dichloro[1,3-bis(diphenylphosphino)propane]palladium(II) / W.L. Steffen, G.J. Palenik // Inorg. Chem. – 1976. – Vol. 15. – № 10. – P. 2432-2439. doi: 10.1021/ic50164a025.

93. Lotsman, K.A. Atom-economical synthesis of 1,2-bis(phosphine oxide)ethanes from calcium carbide with straightforward access to deuterium- and ^{13}C-labeled bidentate phosphorus ligands and metal complexes / K.A. Lotsman, K.S. Rodygin, I. Skvortsova, A.M. Kutskaya, M.E. Minyaev, V.P. Ananikov // Org. Chem. Front. – 2023. – Vol. 10. – № 4. – P. 1022-1033. doi: 10.1039/D2QO01652D.

94. Kresge, A.J. The hydrolysis of ethyl vinyl ether. Part I. Reaction mechanism / A.J. Kresge, Y. Chiang // J. Chem. Soc. B. – 1967. – P. 53-57. doi:10.1039/J29670000053.

95. DE705273, Acetaldehyde / W. Reppe, H. Ufer. - 1941.

96. Keith, J.A. The Mechanism of the Wacker Reaction: A Tale of Two Hydroxypalladations / J.A. Keith, P.M. Henry // Angew. Chem. Int. Ed. – 2009. – Vol. 48. – № 48. – P. 9038-9049. doi: 10.1002/anie.200902194.

97. Stahl, S.S. Oxygenation of Nitrogen-Coordinated Palladium(0): Synthetic, Structural, and Mechanistic Studies and Implications for Aerobic Oxidation Catalysis / S.S. Stahl, J.L. Thorman, R.C. Nelson, M.A. Kozee // J. Am. Chem. Soc. – 2001. – Vol. 123. – № 29. – P. 7188-7189. doi: 10.1021/ja015683c.

98. Khan, M.M.T. Hydration of acetylene to acetaldehyde using $K[Ru^{III}(EDTA\text{-}H)Cl]_2H_2O$ / M.M.T. Khan, S.B. Halligudi, S. Shukla // J. Mol. Catal. – 1990. – Vol. 58. – № 3. – P. 299-305. doi: 10.1016/0304-5102(90)85019-E.

99. Wang, Q. A novel and effective Zn/PEI-MCM catalyst for the acetylene hydration to acetaldehyde / Q. Wang, M. Zhu, B. Dai, J. Zhang // Chin. Chem. Lett. – 2019. – Vol. 30. – № 6. – P. 1244-1248. doi: 10.1016/j.cclet.2019.03.049.

100. Yee, K.-K. Room-temperature acetylene hydration by a Hg(ii)-laced metal–organic framework / K.-K. Yee, Y.-L. Wong, M. Zha, R.Y. Adhikari, M.T. Tuominen, J. He, Z. Xu // Chem. Commun. – 2015. – Vol. 51. – № 54. – P. 10941-10944. doi: 10.1039/C5CC03943F.

101. Abdullahi, I. Partial oxidation of ethanol to acetaldehyde over surface-modified single-walled carbon nanotubes / I. Abdullahi, T.J. Davis, D.M. Yun, J.E. Herrera // Appl. Catal. – 2014. – Vol. 469. – №. – P. 8-17. doi: 10.1016/j.apcata.2013.09.027.

102. Chimentão, R.J. Oxidation of ethanol to acetaldehyde over Na-promoted vanadium oxide catalysts / R.J. Chimentão, J.E. Herrera, J.H. Kwak, F. Medina, Y. Wang, C.H.F. Peden // Appl. Catal. – 2007. – Vol. 332. – № 2. – P. 263-272. doi: 10.1016/j.apcata.2007.08.024.

103. Gong, J. Selective Oxidation of Ethanol to Acetaldehyde on Gold / J. Gong, C.B. Mullins // J. Am. Chem. Soc. – 2008. – Vol. 130. – № 49. – P. 16458-16459. doi: 10.1021/ja805303s.

104. Guan, Y. Selective oxidation of ethanol to acetaldehyde by Au−Ir catalysts / Y. Guan, E.J.M. Hensen // J. Catal. – 2013. – Vol. 305. – №. – P. 135-145. doi: 10.1016/j.jcat.2013.04.023.

105. Liu, P. Highly Efficient and Robust Au/$MgCuCr_2O_4$ Catalyst for Gas-Phase Oxidation of Ethanol to Acetaldehyde / P. Liu, E.J.M. Hensen // J. Am. Chem. Soc. – 2013. – Vol. 135. – № 38. – P. 14032-14035. doi: 10.1021/ja406820f.

106. Redina, E.A. Selective oxidation of ethanol to acetaldehyde over Au–Cu catalysts prepared by a redox method / E.A. Redina, A.A. Greish, I.V. Mishin, G.I. Kapustin, O.P. Tkachenko, O.A. Kirichenko, L.M. Kustov // Catal. Today. – 2015. – Vol. 241. – №. – P. 246-254. doi: 10.1016/j.cattod.2013.11.065.

107. Klinthongchai, Y. Synthesis, characteristics and application of mesocellular foam carbon (MCF-C) as catalyst for dehydrogenation of ethanol to acetaldehyde /

Y. Klinthongchai, S. Prichanont, P. Praserthdam, B. Jongsomjit // J. Environ. Chem. Eng. – 2020. – Vol. 8. – № 3. – P. 103752. doi: 10.1016/j.jece.2020.103752.

108. Ouyang, M. Atomically Dispersed Pd Supported on Zinc Oxide for Selective Nonoxidative Ethanol Dehydrogenation / M. Ouyang, S. Cao, S. Yang, M. Li, M. Flytzani-Stephanopoulos // Ind. Eng. Chem. Res. – 2020. – Vol. 59. – № 6. – P. 2648-2656. doi: 10.1021/acs.iecr.9b05202.

109. Sun, J. Direct Conversion of Bio-ethanol to Isobutene on Nanosized ZnxZryOz Mixed Oxides with Balanced Acid–Base Sites / J. Sun, K. Zhu, F. Gao, C. Wang, J. Liu, C.H.F. Peden, Y. Wang // J. Am. Chem. Soc. – 2011. – Vol. 133. – № 29. – P. 11096-11099. doi: 10.1021/ja204235v.

110. Katryniok, B. Highly efficient catalyst for the decarbonylation of lactic acid to acetaldehyde / B. Katryniok, S. Paul, F. Dumeignil // Green Chem. – 2010. – Vol. 12. – № 11. – P. 1910-1913. doi: 10.1039/C0GC00203H.

111. Tang, C. Sustainable production of acetaldehyde from lactic acid over the carbon catalysts / C. Tang, J. Peng, X. Li, Z. Zhai, H. Gao, W. Bai, N. Jiang, Y. Liao // Korean J. Chem. Eng. – 2016. – Vol. 33. – № 1. – P. 99-106. doi: 10.1007/s11814-015-0094-y.

112. Zhai, Z. Decarbonylation of Lactic Acid to Acetaldehyde over Aluminum Sulfate Catalyst / Z. Zhai, X. Li, C. Tang, J. Peng, N. Jiang, W. Bai, H. Gao, Y. Liao // Ind. Eng. Chem. Res. – 2014. – Vol. 53. – № 25. – P. 10318-10327. doi: 10.1021/ie500988q.

113. Chiang, Y. Vinyl ether hydrolysis. XII. Use of cis-trans isomerism to probe the reaction mechanism / Y. Chiang, A.J. Kresge, C.I. Young // Can. J. Chem. – 1978. – Vol. 56. – № 4. – P. 461-464. doi: 10.1139/v78-074.

114. Jones, D.M. The mechanism of vinyl ether hydrolysis / D.M. Jones, N.F. Wood // J. Chem. Soc. – 1964. – P. 5400-5403. doi: 10.1039/jr9640005400.

115. Chiang, Y. Vinyl ether hydrolysis. XXIX. 1-Methoxy-1,3-butadiene: reaction mechanism and implication for hydrolysis of the mutagen fecapentaene-12 / Y. Chiang, R. Eliason, G.H.X. Guo, A.J. Kresge // Can. J. Chem. – 1994. – Vol. 72. – № 7. – P. 1632-1636. doi: 10.1139/v94-205.

116. Serrano-Ruiz, M. Synthesis, reactivity and catalytic properties of the allenylidene [Ru(CCCPh$_2$)Cp(PTA)(PPh$_3$)](CF$_3$SO$_3$) (PTA = 1,3,5-triaza-7-phosphaadamantane) / M. Serrano-Ruiz, C. Lidrissi, S. Mañas, M. Peruzzini, A. Romerosa // J. Organomet. Chem. – 2014. – Vol. 751. – №. – P. 654-661. doi: 10.1016/j.jorganchem.2013.08.040.

117. Schmidt, C. First deuterated drug approved / C. Schmidt // Nat. Biotechnol. – 2017. – Vol. 35. – № 6. – P. 493-494. doi: 10.1038/nbt0617-493.

118. Capon, B. Generation of vinyl alcohol in solution and its slow conversion into acetaldehyde Generation of vinyl alcohol in solution and its slow conversion into acetaldehyde / B. Capon, D.S. Rycroft, T.W. Watson // J. Chem. Soc., Chem. Commun. – 1979. – № 16. – P. 724-725. doi: 10.1039/c39790000724.

119. Makowska, A. Isotope Effects on Miscibility of 1-Butyl-3-methylimidazolium Tetrafluoroborate with Butanols / A. Makowska, A. Siporska, J. Szydłowski // J. Phys. Chem. B. – 2006. – Vol. 110. – № 34. – P. 17195-17199. doi: 10.1021/jp0622987.

120. Milewska, A. Deuterium Isotope Effects on Miscibility Curves of Nitromethane + Pentanol and Nitromethane + Isobutanol / A. Milewska, J. Szydlowski // J. Chem. Eng. Data. – 1999. – Vol. 44. – № 3. – P. 505-508. doi: 10.1021/je980264p.

121. Rodygin, K.S. Towards Sustainable Carbon Return from Waste to Industry via C$_2$-Type Molecular Unit / K.S. Rodygin, K.A. Lotsman, D.E. Samoylenko, V.M. Kuznetsov, V.P. Ananikov // Int. J. Mol. Sci. – 2022. – Vol. 23. – № 19. – P. 11828. doi: 10.3390/ijms231911828.

122. Rodygin, K.S. Calcium Carbide Looping System for Acetaldehyde Manufacturing from Virtually any Carbon Source / K.S. Rodygin, K.A. Lotsman, V.P. Ananikov // ChemSusChem. – 2020. – Vol. 13. – № 14. – P. 3679-3685. doi: 10.1002/cssc.202000760.

123. Zhu, Y. Sustainable polymers from renewable resources / Y. Zhu, C. Romain, C.K. Williams // Nature. – 2016. – Vol. 540. – № 7633. – P. 354-362. doi: 10.1038/nature21001.

124. Geyer, R. Production, use, and fate of all plastics ever made / R. Geyer, J.R. Jambeck, K.L. Law // Sci. Adv. – 2017. – Vol. 3. – № 7. – P. e1700782. doi: 10.1126/sciadv.1700782.

125. Kukhta, N.A. Room temperature cationic polymerization of β-pinene using modified $AlCl_3$ catalyst: toward sustainable plastics from renewable biomass resources / N.A. Kukhta, I.V. Vasilenko, S.V. Kostjuk // Green Chem. – 2011. – Vol. 13. – № 9. – P. 2362-2364. doi: 10.1039/C1GC15593H.

126. Hilschmann, J. Bio-based polymyrcene with highly ordered structure via solvent free controlled radical polymerization / J. Hilschmann, G. Kali // Eur. Polym. J. – 2015. – Vol. 73. – P. 363-373. doi: 10.1016/j.eurpolymj.2015.10.021.

127. Sahu, P. Synthesis and Characterization of a Terpene-Based Sustainable Polymer: Poly-alloocimene / P. Sahu, P. Sarkar, A.K. Bhowmick // ACS Sustain. Chem. Eng. – 2017. – Vol. 5. – № 9. – P. 7659-7669. doi: 10.1021/acssuschemeng.7b00990.

128. Thomsett, M.R. New renewably-sourced polyesters from limonene-derived monomers / M.R. Thomsett, J.C. Moore, A. Buchard, R.A. Stockman, S.M. Howdle // Green Chem. – 2019. – Vol. 21. – № 1. – P. 149-156. doi: 10.1039/c8gc02957a.

129. Cheng, C. Renewable eugenol-based functional polymers with self-healing and high temperature resistance properties / C. Cheng, J. Li, F. Yang, Y. Li, Z. Hu, J. Wang // J. Polym. Res. – 2018. – Vol. 25. – № 2. – P. 57. doi: 10.1007/s10965-018-1460-3.

130. Firdaus, M. Terpene-Based Renewable Monomers and Polymers *via* Thiol-Ene Additions / M. Firdaus, L. Montero de Espinosa, M.A.R. Meier // Macromol. – 2011. – Vol. 44. – № 18. – P. 7253-7262. doi: 10.1021/ma201544e.

131. Subbiah, S. Direct transformation of 5-hydroxymethylfurfural to the building blocks 2,5-dihydroxymethylfurfural (DHMF) and 5-hydroxymethyl furanoic acid (HMFA) *via* Cannizzaro reaction / S. Subbiah, S.P. Simeonov, J.M.S.S. Esperança, L.P.N. Rebelo, C.A.M. Afonso // Green Chem. – 2013. – Vol. 15. – № 10. – P. 2849-2853. doi: 10.1039/C3GC40930A.

132. Kucherov, F.A. Efficient route for the construction of polycyclic systems from bioderived HMF / F.A. Kucherov, K.I. Galkin, E.G. Gordeev, V.P. Ananikov // Green Chem. – 2017. – Vol. 19. – № 20. – P. 4858-4864. doi: 10.1039/C7GC02211E.

133. Erokhin, K.S. 3D Printing to Increase the Flexibility of the Chemical Synthesis of Biologically Active Molecules: Design of On-Demand Gas Generation Reactors / K.S. Erokhin, E.G. Gordeev, D.E. Samoylenko, K.S. Rodygin, V.P. Ananikov // Int. J. Mol. Sci. – 2021. – Vol. 22. – № 18. – P. 9919. doi: 10.3390/ijms22189919.

134. Lochmann, L. Preparation of some alkoxides of alkali metals / L. Lochmann, J. Coupek, D. Lim // Collect. Czech. Chem. Commun. – 1970. – Vol. 35. – № 2. – P. 733-736. doi: 10.1135/cccc19700733.

135. Metlyaeva, S.A. Biomass- and calcium carbide-based recyclable polymers / S.A. Metlyaeva, K.S. Rodygin, K.A. Lotsman, D.E. Samoylenko, V.P. Ananikov // Green Chem. – 2021. – Vol. 23. – № 6. – P. 2487-2495. doi: 10.1039/D0GC04170J.

136. Lotsman, K.A. Syntheisis of Divinyl Ether from 5-Hydroxymethylfurfural (5-HMF) and Calcium Carbide / K.A. Lotsman, K.S. Rodygin // Russ. J. Gen. Chem. – 2022. – Vol. 92. – № 11. – P. 2507-2510. doi: 10.1134/S1070363222110378.

137. Armarego, W.L.F. Chapter 4 - Purification of Organic Chemicals in Purification of Laboratory Chemicals (Fifth Edition) / W.L.F. Armarego, C.L.L. Chai. - Butterworth-Heinemann: Burlington, 2003. - p. 80-388.

138. Feltham, R.D. Synthesis of new carbonyl complexes of palladium / R.D. Feltham, G. Elbaze, R. Ortega, C. Eck, J. Dubrawski // Inorg. Chem. – 1985. – Vol. 24. – № 10. – P. 1503-1510. doi: 10.1021/ic00204a020.

139. Kong, C. Control of the Chemoselectivity of Metal N-Aryl Nitrene Reactivity: C–H Bond Amination versus Electrocyclization / C. Kong, N. Jana, C. Jones, T.G. Driver // J. Am. Chem. Soc. – 2016. – Vol. 138. – № 40. – P. 13271-13280. doi: 10.1021/jacs.6b07026.

140. Sheldrick, G. SHELXT - Integrated space-group and crystal-structure determination / G. Sheldrick // Acta Crystallogr. A. – 2015. – Vol. 71. – № 1. – P. 3-8. doi: 10.1107/S2053273314026370.

141. Sheldrick, G. Crystal structure refinement with SHELXL / G. Sheldrick // Acta Crystallogr. C. – 2015. – Vol. 71. – № 1. – P. 3-8. doi: 10.1107/S2053229614024218.

142. Dolomanov, O.V. OLEX2: a complete structure solution, refinement and analysis program / O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann // J. Appl. Crystallogr. – 2009. – Vol. 42. – № 2. – P. 339-341. doi: 10.1107/S0021889808042726.

143. Laye, C. The Trityl-Cation Mediated Phosphine Oxides Reduction / C. Laye, J. Lusseau, F. Robert, Y. Landais // Adv. Synth. Catal. – 2021. – Vol. 363. – № 12. – P. 3035-3043. doi: 10.1002/adsc.202100189.

144. Mrochek, J.E. Bis-(disubstitutedphosphinyl)-alkanes—IV: Extraction of mineral acids, uranium (VI), and some lanthanides / J.E. Mrochek, C.V. Banks // J. Inorg. Nucl. Chem. – 1965. – Vol. 27. – № 3. – P. 589-601. doi: 10.1016/0022-1902(65)80265-2.

145. Maier, L. Organische Phosphorverbindungen XXXI. Ein einfaches Verfahren zur Herstellung von Alkylen- bzw. Arylen- bzw. diphosphiniten und von Bis-(dialkyl- und diaryl-phosphinyl)-alkanen / L. Maier // Helv. Chim. Acta. – 1968. – Vol. 51. – № 3. – P. 405-413. doi: 10.1002/hlca.19680510302.

146. Doyle, L.R. A Convenient Synthetic Protocol to 1,2-Bis(dialkylphosphino)ethanes / L.R. Doyle, A. Heath, C.H. Low, A.E. Ashley // Adv. Synth. Catal. – 2014. – Vol. 356. – № 2-3. – P. 603-608. doi: 10.1002/adsc.201300787.

147. Sinou, D. Synthesis of a Family of Triarylphosphanes with Fluorous Phase Affinity / D. Sinou, D. Maillard, G. Pozzi // Eur. J. Org. Chem. – 2002. – Vol. 2002. – № 2. – P. 269-275. doi: 10.1002/1099-0690(20021)2002:2<269::AID-EJOC269>3.0.CO;2-B.

148. Boehm, P. Mechanistic Investigation of the Nickel-Catalyzed Metathesis between Aryl Thioethers and Aryl Nitriles / P. Boehm, P. Müller, P. Finkelstein, M.A. Rivero-Crespo, M.-O. Ebert, N. Trapp, B. Morandi // J. Am. Chem. Soc. – 2022. – Vol. 144. – № 29. – P. 13096-13108. doi: 10.1021/jacs.2c01595.

149. Tchawou, A.A.S.W. Mechanism-Based Design and Optimization of a Catalytic Electrophilic Cyclopropanation without Diazomethane / A.A.S.W. Tchawou, M. Raducan, P. Chen // Organometallics. – 2017. – Vol. 36. – № 1. – P. 180-191. doi: 10.1021/acs.organomet.6b00531.

150. Diederich, P. Formation, stabilization and fate of acetaldehyde and higher aldehydes in an autonomously changing prebiotic system emerging from acetylene / P. Diederich, T. Geisberger, Y. Yan, C. Seitz, A. Ruf, C. Huber, N. Hertkorn, P. Schmitt-Kopplin // Commun. Chem. – 2023. – Vol. 6. – № 1. – P. 38. doi: 10.1038/s42004-023-00833-5.

151. Zhu, Z. Synthesis of 1,3,5-Trioxanes: Catalytic Cyclotrimerization of Aldehydes / Z. Zhu, J.H. Espenson // Synthesis. – 1998. – Vol. 1998. – № 04. – P. 417-422. doi: 10.1055/s-1998-2053.

152. Capon, B. Generation of vinyl alcohol in solution and its slow conversion into acetaldehyde / B. Capon, D.S. Rycroft, T.W. Watson // J. Chem. Soc., Chem. Commun. – 1979. – № 16. – P. 724-725. doi: 10.1039/C39790000724.

153. Reddy, G.R. Activation of Benzyl Aryl Carbonates: The Role of Cation−π Interactions / G.R. Reddy, A.S. Avadhani, S. Rajaram // J. Org. Chem. – 2016. – Vol. 81. – № 10. – P. 4134-4141. doi: 10.1021/acs.joc.6b00441.

154. Aoyama, H. Hydrolysis of Alkenyl Esters and Ethers Catalyzed by Metal Complexes / H. Aoyama, M. Tokunaga, S.-i. Hiraiwa, Y. Shirogane, Y. Obora, Y. Tsuji // Org. Lett. – 2004. – Vol. 6. – № 4. – P. 509-512. doi: 10.1021/ol036228j.

155. Watanabe, H. Stereoselective cationic polymerization of vinyl ethers by easily and finely tunable titanium complexes prepared from tartrate-derived diols: isospecific polymerization and recognition of chiral side chains / H. Watanabe, T. Yamamoto, A. Kanazawa, S. Aoshima // Polym. Chem. – 2020. – Vol. 11. – № 20. – P. 3398-3403. doi: 10.1039/D0PY00343C.

156. Kyasa, S.K. Synthesis of Ethers via Reaction of Carbanions and Monoperoxyacetals / S. Kyasa, R.N. Meier, R.A. Pardini, T.K. Truttmann, K.T. Kuwata, P.H. Dussault // J. Org. Chem. – 2015. – Vol. 80. – № 24. – P. 12100-12114. doi: 10.1021/acs.joc.5b02043.

157. Spiegelberg, B. Use of Iridium-Catalyzed Transfer Vinylation for the Synthesis of Bio-Based (bis)-Vinyl Ethers / B. Spiegelberg, H. Jiao, R. Grauke, C. Kubis, A. Spannenberg, A. Brandt, A. Taden, H. Beck, S. Tin, J.G. de Vries // Adv. Synth. Catal. – 2022. – Vol. 364. – № 7. – P. 1251-1263. doi: 10.1002/adsc.202101348.

158. Harada, N. Vinyl polymerization versus [1,3] O to C rearrangement in the ruthenium-catalyzed reactions of vinyl ethers with hydrosilanes / N. Harada, T. Nishikata, H. Nagashima // Tetrahedron. – 2012. – Vol. 68. – № 15. – P. 3243-3252. doi: 10.1016/j.tet.2012.02.025.