

Summary of Professional Accomplishments

Synthesis of alkenyl derivatives of organosilicon compounds by hydrosilylation of alkynes and 1,3-diynes

Adrian Franczyk



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W POZNANIU

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Table of contents

1. Personal data	2
2. Diplomas, degrees conferred in specific areas of science, including the name of the institution which conferred the degree, year of degree conferment, title of the Ph.D. dissertation	2
3. Information on employment in research institutes or faculties	3
4. Description of the scientific achievements	4
4.1. List of scientific articles describing scientific achievements	4
4.2. Introduction and aim of the research	12
4.3. Description of scientific achievements	17
4.5. References	40
5. Presentation of significant scientific activity carried out at more than one university, scientific or cultural institution, especially at foreign institutions	42
6. Information about teaching, organizational, and science achievements	44
6.1. Supervision of scientific works	44
6.2. Conducting teaching classes	44
6.3. Organization of events popularizing science	44
7. Apart from the information set out in 1-6 above, the applicant may include other information about his/her professional career, which he/she deems important	45

1. Personal data

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2. Diplomas, degrees conferred in specific areas of science, including the name of the institution which conferred the degree, year of degree conferment, title of the Ph.D. dissertation

- **Ph.D. in Chemical Sciences (17.10.2014)**

Adam Mickiewicz University,

Faculty of Chemistry (Poznan, Poland).

Title of Ph.D. dissertation:

"Mono- and bifunctional silsesquioxanes - synthesis and application in polymer composites", awarded by the Council of the Faculty of Chemistry

(Adam Mickiewicz University),

Supervisors:

Prof. Dr. Hab. Bogdan Marciniec,

Adam Mickiewicz University, Faculty of Chemistry
(Poznan, Poland),
Prof. Dr. Hab. Krzysztof Matyjaszewski,
Carnegie Mellon University, Department of Chemistry
(Pittsburgh, Pennsylvania, USA).

- **Master of Science in Chemistry (2008)**

Adam Mickiewicz University,
Faculty of Chemistry,
Field of study: Chemistry,

Title of master's dissertation:

“Silsesquioxyl and immobilized siloxyl rhodium(I) and iridium(I) complexes – synthesis, structure, catalytic activity”, awarded by the Council of the Faculty of Chemistry (Adam Mickiewicz University),

Supervisor:

Prof. Dr. Hab. Bogdan Marciniec,
Adam Mickiewicz University,
Faculty of Chemistry (Poznan, Poland).

3. Information on employment in research institutes or faculties

- 2015-until now – assistant professor, research position without teaching,
Adam Mickiewicz University,
Center for Advanced Technology (Poznan, Poland).
- 2012-2014 - senior technician,
Adam Mickiewicz University,
Faculty of Chemistry (Poznan, Poland).
- 2008-2014 – Ph.D. studies,
Adam Mickiewicz University,
Faculty of Chemistry (Poznan, Poland).

4. Description of the scientific achievements

4.1. List of scientific articles describing scientific achievements

H1. “*Hydrometallation of conjugated 1,3-diyne*”,

Jędrzej Walkowiak*, **Adrian Franczyk**, Jakub Szyling, Kinga Stefanowska,

in Encyclopedia of inorganic and bioinorganic chemistry, **2023**, pp. 1-35,
(DOI: 10.1002/9781119951438.eibc2831), (invited article).

Total citations = Scopus (0); Web of Science (0); Google Scholar (0).

Total citations without self-citations = Scopus (0); Web of Science (0); Google Scholar (0).

My contribution to the **H1** publication includes:

- participation in the development of the work concept;
- revision, analysis, and detailed description of scientific literature on hydrosilylation and hydrogermylation of conjugated 1,3-diyne;
- participation in the preparation and proofreading of the manuscript;
- assistance in preparing correspondence to the editor and reviewers.

H2. “*Directed cis-hydrosilylation of borylalkynes to borylsilylalkenes*”,

Kinga Stefanowska, Tomasz Sokolnicki, Jędrzej Walkowiak, Agnieszka Czapik,
Adrian Franczyk*,

Chemical Communications, **2022**, 58(86), 12046–12049, (DOI: 10.1039/D2CC04318A),
open access.

Article featured with graphic placed on the outside front cover
of the *Chemical Communications*.

IF₂₀₂₁ = 6,0; IF₂₀₂₂ = 4,9; IF^{5-yr}₂₀₂₁ = 5,9; IF^{5-yr}₂₀₂₂ = 4,9.

MEiN = 200 pts.

Total citations = Scopus (6); Web of Science (5); Google Scholar (6).

Total citations without self-citations = Scopus (2); Web of Science (2); Google Scholar (2).

My contribution to the **H2** publication includes:

- revision of scientific literature on the subject of research and its detailed analysis and description;
- development of a research hypothesis (originator of the research);
- developing the work concept;
- planning experiments;
- carrying out a part of experimental research in the field of synthesis, isolation and characterization of the obtained compounds and hydrosilylation process;
- solving research problems at the stage of performing experiments;
- interpretation of the obtained research results;
- preparation of the manuscript and participation in the preparation of supplementary materials;
- correspondence with the editor;
- discussion with reviewers;
- taking care of all stages related to the publication of the article.

H3. *“Synthesis of bifunctional disiloxanes: via subsequent hydrosilylation of alkenes and alkynes”*,

Jakub Szyling, Rafał Januszewski, Kamila Jankowska, Jędrzej Walkowiak, Ireneusz Kownacki, **Adrian Franczyk***,

Chemical Communications, **2021**, 57(37), 4504–4507, (DOI: 10.1039/D1CC01253C), open access.

Article featured with graphic placed on the outside back cover of the *Chemical Communications*.

$IF_{2021} = 6,0$; $IF_{2022} = 4,9$; $IF^{5\text{-yr}}_{2021} = 5,9$; $IF^{5\text{-yr}}_{2022} = 4,9$.

MEiN = 200 pts.

Total citations = Scopus (12); Web of Science (11); Google Scholar (12).

Total citations without self-citations = Scopus (7); Web of Science (6); Google Scholar (7).

My contribution to the **H3** publication includes:

- revision of scientific literature on the subject of research and its detailed analysis and description;
- development of a research hypothesis (originator of the research);
- developing the work concept;
- planning experiments;
- carrying out a part of experimental research in the field of synthesis, isolation and characterization of the obtained compounds and hydrosilylation process;
- solving research problems at the stage of performing experiments;
- interpretation of the obtained research results;
- preparation of the manuscript and participation in the preparation of supplementary materials;
- correspondence with the editor;
- discussion with reviewers;
- taking care of all stages related to the publication of the article.

H4. *“Synthesis of unsymmetrically and symmetrically functionalized disiloxanes via subsequent hydrosilylation of $C\equiv C$ bonds”*,

Jakub Szyling, Jędrzej Walkowiak, Agnieszka Czapik, **Adrian Franczyk***,

Scientific Reports, **2023**, 13, 10244 (DOI: 10.1038/s41598-023-37375-8), open access.

$IF_{2022} = 4,6$; $IF^{5\text{-yr}}_{2022} = 4,9$.

MEiN = 140 pts.

Total citations = Scopus (0); Web of Science (0); Google Scholar (0).

Total citations without self-citations = Scopus (0); Web of Science (0); Google Scholar (0).

My contribution to the **H4** publication includes:

- revision of scientific literature on the subject of research and its detailed analysis and description;
- development of a research hypothesis (originator of the research);
- developing the work concept;
- planning experiments;
- characterization of the obtained compounds and hydrosilylation process;
- solving research problems at the stage of performing experiments;
- interpretation of the obtained research results;
- participation in the preparation of the manuscript and supplementary materials;
- correspondence with the editor;
- discussion with reviewers;
- taking care of all stages related to the publication of the article.

H5. *“Synthesis of functional 3-buten-1-ynes and 1,3-butadienes with silsesquioxane moiety via hydrosilylation of 1,3-diynes”*,

Kinga Stefanowska, **Adrian Franczyk***, Jakub Szyling, Jędrzej Walkowiak*,

ChemCatChem, **2019**, *11*, 4848-4853 (DOI: 10.1002/cctc.201901082).

IF₂₀₁₉ = 4,8; IF₂₀₂₂ = 4,5; IF^{5-yr}₂₀₁₉ = 4,7; IF^{5-yr}₂₀₂₂ = 4,6.

MEiN = 100 pts.

Total citations = Scopus (15); Web of Science (14); Google Scholar (18).

Total citations without self-citations = Scopus (7); Web of Science (7); Google Scholar (8).

My contribution to the **H5** publication includes:

- revision of scientific literature on the subject of research and its detailed analysis and description;
- development of a research hypothesis (originator of the research);
- developing the work concept;
- planning experiments;
- characterization of the hydrosilylation process;
- solving research problems at the stage of performing experiments;
- interpretation of the obtained research results;
- participation in the preparation of the manuscript and supplementary materials;
- participation in correspondence with the editor;
- participation in discussions with reviewers;
- participation in the care of all stages related to the publication of the article.

H6. “Alkenyl-functionalized open-cage silsesquioxanes $(RSiMe_2O)_3R'_7Si_7O_9$: a novel class of building nanoblocks”,

Kinga Stefanowska, Jakub Szyling, Jędrzej Walkowiak, **Adrian Franczyk***,

Inorganic Chemistry, **2021**, 60(15), 11006–11013 (DOI: 10.1021/acs.inorgchem.1c00689), open access.

The article highlighted with graphics placed on the supplementary journal cover of the *Inorganic Chemistry*.

IF₂₀₂₁ = 5,4; IF₂₀₂₂ = 4,6; IF^{5-yr}₂₀₂₁ = 5,0; IF^{5-yr}₂₀₂₂ = 4,4.

MEiN = 140 pts.

Total citations = Scopus (12); Web of Science (11); Google Scholar (14).

Total citations without self-citations = Scopus (5); Web of Science (5); Google Scholar (6).

My contribution to the **H6** publication includes:

- revision of scientific literature on the subject of research and its detailed analysis and description;
- development of a research hypothesis (originator of the research);
- developing the work concept;
- planning experiments;
- carrying out a part of experimental research in the field of synthesis, isolation, and characterization of the obtained compounds and hydrosilylation process;
- solving research problems at the stage of performing experiments;
- interpretation of the obtained research results;
- preparation of the manuscript and participation in the preparation of supplementary materials;
- correspondence with the editor;
- discussion with reviewers;
- taking care of all stages related to the publication of the article.

H7. “*Selective hydrosilylation of alkynes with octaspherosilicate (HSiMe₂O)₈Si₈O₁₂”*,

Kinga Stefanowska, **Adrian Franczyk***, Jakub Szyling, Mikołaj Pyziak, Piotr Pawluć, Jędrzej Walkowiak*,

Chemistry - An Asian Journal, **2018**, 13(16), 2101-2108 (DOI: 10.1002/asia.201800726).

IF₂₀₁₈ = 3,7; IF₂₀₂₂ = 4,1; IF^{5-yr}₂₀₁₈ = 3,5; IF^{5-yr}₂₀₂₂ = 3,8.

MEiN = 100 pts.

Total citations = Scopus (21); Web of Science (20); Google Scholar (21).

Total citations without self-citations = Scopus (9); Web of Science (9); Google Scholar (9).

My contribution to the **H7** publication includes:

- revision of scientific literature on the subject of research and its detailed analysis and description;
- development of a research hypothesis (originator of the research);
- developing the work concept;
- planning experiments;
- characterization of the hydrosilylation process;
- solving research problems at the stage of performing experiments;
- interpretation of the obtained research results;
- participation in the preparation of the manuscript and supplementary materials;
- participation in correspondence with the editor;
- participation in discussions with reviewers;
- participation in the care of all stages related to the publication of the article.

H8. “*Functionalization of octaspherosilicate (HSiMe₂O)₈Si₈O₁₂ with buta-1,3-diyne by hydrosilylation*”,

Kinga Stefanowska, Jakub Nagórny, Jakub Szyling, **Adrian Franczyk***,

Scientific Reports, **2023**, *13*, 14314 (DOI: 10.1038/s41598-023-41461-2), open access.

IF₂₀₂₂= 4,6; IF^{5-yr}₂₀₂₂= 4,9.

MEiN = 140 pts.

Total citations = Scopus (0); Web of Science (0); Google Scholar (0).

Total citations without self-citations = Scopus (0); Web of Science (0); Google Scholar (0).

My contribution to the **H8** publication includes:

- revision of scientific literature on the subject of research and its detailed analysis and description;
- development of a research hypothesis (originator of the research);
- developing the work concept;
- planning experiments;
- characterization of the obtained compounds and hydrosilylation process;
- solving research problems at the stage of performing experiments;
- interpretation of the obtained research results;
- participation in the preparation of the manuscript supplementary materials;
- correspondence with the editor;
- discussion with reviewers;
- taking care of all stages related to the publication of the article.

Summary of indicators MEiN and IF for articles H2-H8:

Total number of MEiN points = 1020 pts.;

Average number of MEiN points = 146 pts.;

Total number of $IF_{2022} = 32,2$;

Total number of $IF^{5-yr}_{2022} = 32,4$;

Average number of $IF_{2022} = 4,6$;

Average number of $IF^{5-yr}_{2022} = 4,6$.

Corresponding author in 6 articles (**H2-H8**).

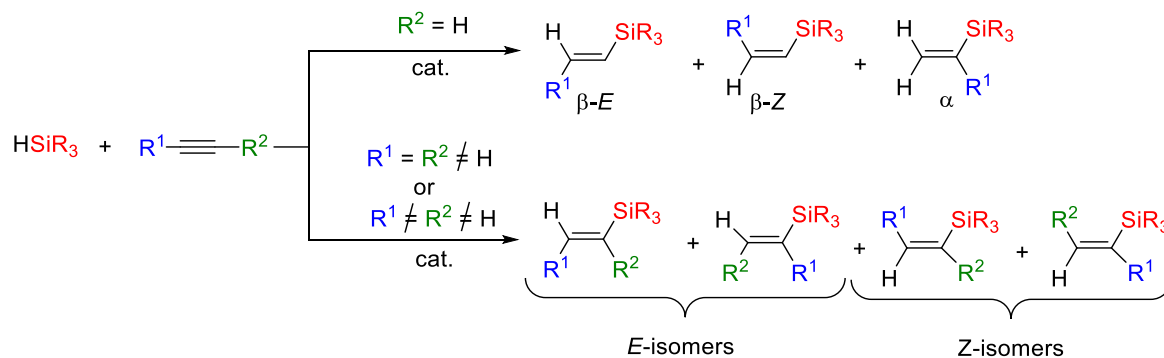
4.2. Introduction and aim of the research

This summary describes the achievements concerning the research included in articles **H1-H8**. All details are in the attached publications and supporting materials. The summary refers to the catalytic hydrosilylation of alkynes (terminal and internal) and 1,3-diyne (symmetrically and non-symmetrically disubstituted) with organosilicon compounds containing Si-H groups, with various structures and properties, such as silanes, siloxanes, silsesquioxanes, and spherosilicates.

The hydrosilylation process involves the addition of the Si-H bond to carbon-carbon, carbon-oxygen, carbon-nitrogen, nitrogen-nitrogen, or nitrogen-oxygen multiple bonds.¹⁻⁸ The first scientific publication on this reaction was published in 1947 by Sommer, who carried out the addition of trichlorosilane to 1-octene in the presence of a peroxide initiator (CH₃C(O)O)₂.⁹ The name of the process was given a little later by Chuck and Harold along with the first proposal of its mechanism.¹⁰⁻¹² A breakthrough in the development of hydrosilylation was the development of highly active Speier (H₂PtCl₆/*i*-PrOH)^{9, 13, 14} and later Karstedt (Pt₂(dvs)₃, dvs = 1,1,3,3-tetramethyl-1,3-divinyldisiloxane)¹⁵⁻¹⁷ catalysts. Thanks to them, this process has gained importance and has become the most effective and therefore the most widespread method of synthesizing silicon compounds, both laboratory and industrial. It currently leads to a rich family of organosilicon compounds, both molecular and macromolecular, which are widely used in almost every area of our lives.

The group of valuable compounds obtained by hydrosilylation includes alkenyl-derivatives of organosilicon compounds. They are obtained by the addition of Si-H bond to organic compounds containing a carbon-carbon triple bond (C≡C), such as alkynes¹⁸⁻²⁵, and 1,3-diyne^{1, 2, 26}. Hydrosilylation of these compounds, depending on the reaction conditions, reagents, and catalysts, makes it possible to obtain all isomers of Si-H addition to the C≡C bond, which is undoubtedly its greatest advantage. Conducting the process towards a specific product while eliminating the formation of others is extremely difficult and requires the appropriate selection of the catalyst and reaction conditions, which are usually strictly selected and unique for each set of reagents. Organosilicon compounds obtained in this way are important reagents, widely used in the synthesis of "*fine chemicals*" or advanced polymer materials.

Depending on the structure of the organosilicon and alkenyl groups, they may undergo various transformations, such as coupling with aryl and alkenyl halides, halodesilylation, desilylation and many others. In this case, the silyl group plays the role of the leaving functional



Scheme 1. Hydrosilylation of terminal and internal alkynes with organosilicon compounds containing Si-H bonds.

group and alkenyl derivatives of organosilicon compounds are considered intermediate products.²⁷⁻⁴¹

On the other hand, compounds in which silyl groups are part of the target systems, providing specific physicochemical and biological properties, can be used as monomers, coupling agents, initiators, or various types of additives in the preparation of polymeric materials, hybrid systems, and composites.⁴¹ These wide application possibilities of silyl-substituted alkenyl compounds, thanks to their reactivity in many chemical processes, as well as the influence on the properties of the obtained materials, determine the need to search for effective methods of their synthesis.

The first academic research describing the reaction between alkynes and silanes was published in 1958. The authors of this article carried out the addition of HSiCl_3 to terminal alkynes in the presence of a radical initiator or platinum deposited on activated carbon. In the first case, a product with the *Z* configuration of double bond was obtained, in the second, an isomer *E*.^{42, 43 44} Achievements in the area of hydrosilylation of alkynes have been described in reviews that summarize the catalytic systems based on transition metals and acid-base ones.¹⁸⁻²⁵ The vast majority are the former, as they are effective for a much wider range of reactants and lead to all possible isomers. From a review published in 2021 by the group of S-F Zhu²⁰, it appears that over 50 catalysts were used in the hydrosilylation of alkynes (containing metals such as Ti, Mn, Co, Fe, Ir, Cu, Rh, Pt, and others). Most of them were tested in the reaction of terminal alkynes with silanes, leading *via* syn-addition to the $\text{C}\equiv\text{C}$ bond to products with the $\beta\text{-E}$ configuration of double bond in which the silyl group is attached to a carbon atom with a larger number of hydrogen atoms (Scheme 1).

Much less research has been conducted on the synthesis of $\beta\text{-Z}$ and α isomers, or hydrosilylation of internal alkynes. The essence of the research carried out so far is very large

and constitutes a kind of flywheel for the further development of this area of chemistry, setting further challenges for researchers focusing on topics related to the hydrosilylation of $C\equiv C$ bonds. One of such challenges is to investigate the reactivity of previously undescribed sets of reagents (both alkynes and organosilicon compounds) in the presence of various catalytic systems, to ensure that the developed preparations work for a wide spectrum of reagents and lead to new compounds with well-defined and often diverse isomerization. In addition, synthetic methods should be easily accessible to a wide range of researchers and used on a wider scale, and the resulting products considered as attractive elements and building blocks with a wide range of applications.

The need to develop universal methods for the synthesis of alkenyl derivatives of organosilicon compounds results from, among others, recent achievements of research groups of S. Denmark and T. Hiyama, who independently demonstrated that substituents on the silyl group are crucial for the activity of silylarenes and alkenes in coupling reactions with aryl and alkenyl halides in the presence of palladium catalysts.^{28, 30-32, 34-37, 39, 40, 45} They found that trialkylsilyl groups are not very active or unreactive in this process, while dimethylbenzylsilyl groups can be activated in the presence of bases containing fluoride anions. In turn, derivatives with dimethylsilanol or siloxy groups react already in the presence of Me_3SiOK , KH , KOH , or Na_2CO_3 . Similarly, in the case of halodesilylation and desilylation processes, the influence of the structure of silyl groups on the efficiency of the process has been studied to a limited extent. Therefore, it seems most justified to search for new methods of synthesizing organosilicon compounds that work for a wide range of reagents and lead to a rich range of new substances with various structures and functionalization possibilities. A detailed examination of their reactivity will allow us to determine the real potential of alkenyl derivatives of organosilicon compounds as reagents in organic synthesis, as well as coupling agents and multifunctional building blocks. Siloxanes^{46, 47} and silsesquioxanes⁴⁸⁻⁵³ play an important role in these last two areas because they are characterized by a unique structure that determines the new properties of the obtained products. Silsesquioxanes, described by the general formula $(RSiO_{3/2})_n$, have a well-defined, three-dimensional, nanometric structure based on a silicon-oxygen skeleton to which organic groups are attached. They are of interest to many researchers, which is confirmed by a very large number of articles and patents. Most of the silsesquioxanes described in the literature were obtained by hydrosilylation of alkenes, while reactions with alkynes were negligible and usually led to mixtures of isomers.

A similar situation like in the case of hydrosilylation of alkynes occurs with the second group of compounds that are the subject of research herein presented, namely conjugated

1,3-diyne.^{1, 2, 26} The scientific literature describing the hydrosilylation of 1,3-diyne is much poorer than that concerning alkynes with numbers of about 20 articles.^{1, 2, 54-67} All reports have been summarized in article **H1**. The limited scope of current research results from the complexity of the research problem of selectively carrying out the process of functionalization of 1,3-diyne, in order to obtain a specific product. Hydrosilylation of symmetric 1,3-diyne can lead to four products of addition of the Si-H bond to one triple bond (two syn-addition isomers and two anti-addition isomers) and up to 9 products in the case of hydrosilylation of both triple bonds. When we consider the same transformations for non-symmetric 1,3-diyne, the numbers of products increase to 8 and 16, respectively. Additionally, depending on the type of organosilicon compound and 1,3-diyne, products such as allenes, cyclic products, and polymers (linear or cross-linked) can be formed as well. All this makes selectively obtaining the desired compound an extremely difficult challenge. However, the research described in the literature proves that this goal can be achieved through the appropriate selection of catalysts and reaction conditions. As indicated in publication **H1**, the most thoroughly explored area of hydrosilylation of 1,3-diyne is the syn-addition of the Si-H group to one C≡C bond.^{54, 55, 57-61, 65, 66} In this process, the SiR₃ group is attached to the carbon atom associated with the next C≡C group, and as a result (*E*)-2-silylbut-3-en-1-yne is obtained. So far, a wide spectrum of symmetrically and non-symmetrically substituted 1,3-diyne, silanes, and catalysts based on transition metals, i.e. Fe, Co, Rh, Ni, Pt, have been investigated. However, only one example of the syn-addition of the Si-H group, which leads to (*E*)-1-silylbut-3-en-1-yne, has been described. This compound was obtained as a result of the reaction of CH₃COOCH₂CC≡CC≡CCH₂OOCCH₃ with HSi(OSiMe₃)₃, catalyzed by a commercially available iridium catalyst [Ir(cod)Cl]₂.⁵⁶ The authors of these studies emphasized that the interaction of the 1,3-diyne ester group with the metal center had an impact on the formation of the mentioned isomer. On the other hand, in the literature, there are only two 2-silylbut-3-en-1-yne described which were obtained by anti-addition, in the presence of a ruthenium catalyst [Cp*Ru(MeCN)₃][PF₆].⁶³

The addition of Si-H to both triple bonds leading to silylated buta-1,3-diene has been studied to a much lesser extent.^{58, 59, 62, 64-66} As the literature indicates, it can be made stepwise as a result of the reaction of silylbut-3-en-1-yne with one equivalent of silane or directly as a result of the reaction of 1,3-diyne with two silane equivalents. The choice of the synthetic route depends on the selectivity with which 1,3-butadiene can be obtained using a specific set of reagents. Also in the case of addition to both C≡C bonds of 1,3-diyne, the syn-addition occurring in the presence of platinum catalysts has been most widely studied. The synthesis

of several compounds obtained by anti-addition using the $[\text{Cp}^*\text{Ru}(\text{MeCN})_3][\text{PF}_6]$ complex has also been described.⁶⁷

To sum up, the analysis of published research indicates that in the areas related to the hydrosilylation of alkynes and 1,3-diynes, many topics remain to be explored. They concern both the synthesis of compounds that could be used in organic synthesis and new systems in which the silyl group would remain in the structure of the final products and give them specific physicochemical properties. Taking into account the above information and the many years of tradition of the Poznan group of Professor Bogdan Marciniec in the field of silicon chemistry, the research goal was formulated, which was to develop highly efficient methods for the selective synthesis of new alkenyl derivatives of organosilicon compounds by hydrosilylation of alkynes and 1,3-diynes.

In this research, it was assumed that in addition to the acquired fundamental knowledge regarding the chemistry of the hydrosilylation process of alkynes and 1,3-diynes, taking into account the selection of catalysts leading to precisely defined products, the aim of the research would be to obtain and characterize new chemical compounds with typical and unconventional structure and isomerization, which they will constitute useful reagents (used in organic synthesis), coupling agents and multifunctional building blocks (dedicated to the construction of advanced macromolecules and hybrid materials). It was decided to achieve the above goals through research in the field of hydrosilylation of:

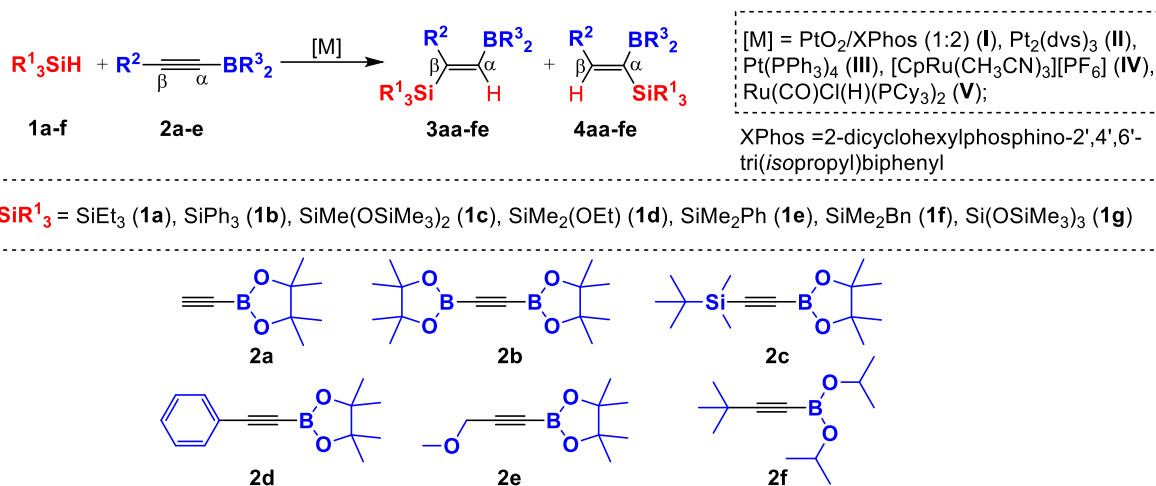
- borylalkynes with silanes HSiR_3 (**H2**);
- alkynes with functional disiloxanes $\text{R}^1\text{CH}_2\text{CH}_2\text{SiMe}_2\text{OSiMe}_2\text{H}$ (**H3**);
- internal alkynes with disiloxane $\text{HSiMe}_2\text{OSiMe}_2\text{H}$ (**H4**);
- alkynes and 1,3-diynes with functional disiloxanes $\text{R}^2\text{HC}=\text{C}(\text{R}^1)\text{SiMe}_2\text{OSiMe}_2\text{H}$ (**H4**);
- 1,3-diynes with monofunctional silsesquioxane $(\text{HSiMe}_2\text{O})(i\text{-Bu})_7\text{Si}_8\text{O}_{12}$ (**H5**);
- alkynes with trifunctional silsesquioxanes $(\text{HSiMe}_2\text{O})_3\text{R}'_7\text{Si}_7\text{O}_9$ (**H6**);
- alkynes (**H7**) and 1,3-diynes (**H8**) with octafunctional spherosilicate $(\text{HSiMe}_2\text{O})_8\text{Si}_8\text{O}_{12}$.

A detailed description of the research and the results obtained, constituting the scientific achievements that are the basis for this habilitation application, are described below in chapters: 4.3. Description of scientific achievements, and 4.4. Summary and conclusions.

4.3. Description of scientific achievements

Publication **H2** describes a highly efficient method for the synthesis of borylsilylalkenes by hydrosilylation of terminal and internal borylalkynes **2a-e** with silanes **1a-f**, catalyzed by complexes of platinum (PtO₂/XPhos, Karstedt catalyst, Pt(PPh₃)₄) and ruthenium (Ru(CO)Cl(H)(PCy₃)₂, [CpRu(CH₃CN)₃][PF₆]) (Scheme 2). Resulted products **3aa-fe** and **4aa-fe**, are important building blocks that can be gradually transformed using widely used processes such as Suzuki-Miyaura, Hiyama, Heck couplings, halodeborylation, halodesilylation, deborylation, desilylation, and others.⁶⁸ The preparation of this type of compounds has so far been described in the scientific literature using hydroboration of ethynyl silanes, borylsilylation of alkynes, and diborylation of ethynyl silanes. Taking into account the advantages of the hydrosilylation process, such as the availability of reagents and catalysts, tolerance for many functional groups, the possibility of conducting the process in an air atmosphere, in an almost unlimited spectrum of solvents, in a wide range of temperatures, and especially the potential to obtain all possible isomers of Si-H addition to C≡C, made attempts to use this process in the synthesis of borylsilylalkenes was justified. Structurally different reagents were selected for the study, and are presented in Scheme 2. They included both terminal and internal (symmetrically and non-symmetrically substituted) borylalkynes. Reagents with internal C≡C bonds had alkyl, aryl, boryl or silyl groups as the second substituent. Silanes with alkoxy, alkyl, and aryl groups were also used. This set of reagents allowed for the determination of the influence of their structure on the hydrosilylation process in the presence of individual catalysts.

Several catalysts based on transition metals such as Ru, Rh, Ir, and Pt have been tested in the hydrosilylation process, which were selected on the basis of literature reports, and preliminary research. The research carried out allowed for the selection of the most effective catalytic systems for each set of substrates (determining the highest possible efficiency of the desired products and selectivity of the reaction), process conditions, and isolation methods. It was observed that the catalyst formed *in situ* as a result of the reaction of platinum(IV) oxide with the XPhos ligand was selective for the reaction of terminal borylalkyne **2a** with triethylsilane (**1a**), 1,1,1,3,5,5,5-heptamethyltrisiloxane (**1c**), and benzyldimethylsilane (**1f**). These processes took place using an equimolar ratio of reagents, which is consistent with the issue of sustainable development aimed at rational management of reagents and simplifies the product separation procedures. As a result of the syn-addition



Scheme 2. Synthesis of borylsilylalkenes **3** and **4** by hydrosilylation of borylalkynes **2a-e** with silanes **1a-f** in the presence of platinum and ruthenium catalysts **I-V** (**H2**).

of the Si-H group to the C≡C bond, products **3** were obtained, with the *E* configuration of double bonds, in which the silyl group was attached to the β carbon atom (β-*E*). When comparing the obtained results with literature reports, it is worth emphasizing that one example of hydrosilylation of borylalkyne HC≡CB(MIDA) (where B(MIDA) - N-methylimidodiacetic boronic acid ester) with benzyldimethylsilane (**1f**) has been described so far, in which 1,5-fold excess of silane was used, and the process was carried out in the presence of a PtCl₂/XPhos catalyst.⁶⁹ As a result, the expected product was obtained with a yield of 91%. In our studies, we reproduced these conditions for the reaction of borate **2a** with silane **1f**. The analysis of the post-reaction mixture revealed the formation of several products. This confirmed that our proposed PtO₂-based system is more selective and more efficient for the reagents described above. However, for sterically hindered triphenylsilane (**1b**), the best results were obtained using an active Karstedt catalyst. In this case, it turned out to be highly selective and led to the efficient preparation of the target compound. The experiment conducted in the presence of PtO₂/XPhos generated a mixture of products, in which the second Si-H syn-addition isomer to the C≡C(α) bond was present. The catalytic activity of the ruthenium catalyst Ru(CO)Cl(H)(PCy₃)₂ in the reaction of borylalkyne **2a** with triethylsilane (**1a**) was also examined. As a result of the process carried out at room temperature, product **3aa** was selectively obtained. Also in this case, the selectivity of the process was higher than in the analogous experiment conducted in the presence of PtO₂/XPhos. Unfortunately, reactions with Ru(CO)Cl(H)(PCy₃)₂ and the remaining silanes **2a** were less effective due to the lower conversion of the reactants. Attempts to optimize the process conditions by increasing the temperature did not bring the intended result.

However, research on the activity of the $[\text{CpRu}(\text{CH}_3\text{CN})_3][\text{PF}_6]$ catalyst showed that the reaction of borylalkyne **2a** with silanes **1a** and **1b** leads to obtaining the second isomer syn-addition, in which the silyl group is attached to the α -carbon atom (products **4aa** and **4ba**). As a result, α (*gem*) isomers **4aa** and **4ab** were obtained. These results confirmed that careful selection of catalysts and conditions of the hydrosilylation process allows selectively obtaining β -*E* and α isomers of syn-addition by the uses of the same sets of substrates.

In the next stage of the research, hydrosilylation of internal borylalkynes **2b-e** containing a boryl, silyl, aryl, or alkyl group as a second substituent was carried out. In the reaction of diborylalkyne **2b** with silanes **1a-c** and **1f**, the best results were obtained for the $\text{Pt}(\text{PPh}_3)_4$ catalyst. The Karstedt catalyst was also effective, but only at room temperature, and attempts to use it at higher temperatures led to a decrease in selectivity and the formation of by-products, most likely as a result of the decomposition of borylalkyne **2b**.

Then, the reactivity of borylsilylalkyne **2c** was examined in the presence of the same catalytic systems. As a result, products **4** were obtained in which the silyl group derived from the silane was attached to the α -carbon atom, which was also bonded to the boryl group. Attempts to obtain the second syn-addition isomer in the presence of among others $[\text{CpRu}(\text{CH}_3\text{CN})_3][\text{PF}_6]$ were unsuccessful. The reactions resulted in a mixture of products, often with low conversion of the reactants.

For reactions with internal borylalkyne substituted with aryl (**2d**) and alkyl (**2e**) groups, the best results were obtained for Karstedt and $\text{Pt}(\text{PPh}_3)_4$ catalysts. By the syn-addition, products **4** were obtained in which the silyl group was attached to the α -carbon atom connected, to the boryl substituent. On the other hand, the use of the $[\text{CpRu}(\text{CH}_3\text{CN})_3][\text{PF}_6]$ catalyst for the addition of silanes **1c**, **f**, **g** to borylalkynes **2c** and **2d** resulted in the formation of the second syn-addition isomer **3**. For the reaction of borylalkyne **2e** with silanes **1c** and **1g**, a positive effect was observed of siloxy substituents on the selectivity of the process. In both cases, only **3ce** and **3ge** products were received.

As part of the research, borylalkyne **2f** containing isopropoxy groups in its structure was also tested. These types of ester groups are less stable than pinacol derivatives, hence their modification is more difficult. However, its hydrosilylation with triethylsilane (**1a**) turned out to be possible in the presence of the Karstedt catalyst, and as a result, the product **4af** was obtained in high yield.

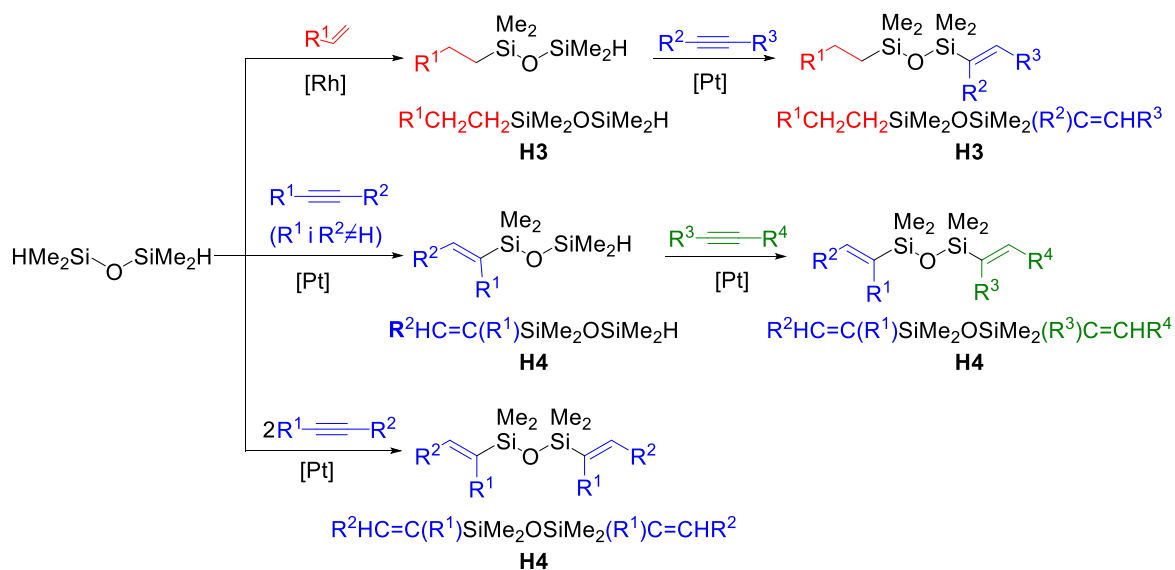
To summarize, the methods for the synthesis of borylsilylalkenes developed in publication **H2** using the hydrosilylation process made it possible to obtain and characterize a total of 29 borylsilylalkenes, including 25 that have not been described in the literature so far.

For five compounds **3ba**, **4ba**, **3bb**, **3fb**, and **6dc**, crystal structures were determined for the first time, which additionally and clearly emphasized the selectivity of the hydrosilylation process. So far, this is the widest group of such compounds obtained in one process, and at the same time the most diverse in terms of structure. It is worth emphasizing that some of them cannot be obtained using alternative synthesis methods described in the scientific literature.

The efficiency of tested catalysts in the reactions of individual sets of reagents was also determined. Thanks to their use, it was possible to obtain both isomers of Si-H syn-addition for terminal and internal C≡C bonds. PtO₂/XPhos and CpRu(CH₃CN)₃[PF₆] turned out to be the most effective systems for hydrosilylation of terminal borylalkynes, leading to products **3** and **4**, respectively. PtO₂/XPhos was, in turn, more selective than the PtCl₂/XPhos system described in the literature, in terms of tested reagents. However, the Karstedt catalyst proved to be effective in the synthesis of product **3ba** by the hydrosilylation with sterically expanded triphenylsilane (**1b**). In the analog reaction, the PtO₂/XPhos was less selective. Ru(CO)Cl(H)(PCy₃)₂ led to obtaining the desired product only in the reaction of borylalkyne **2a** with triethylsilane (**1a**). However, syn-addition reactions to internal triple bonds occurred effectively in the presence of Karstedt and Pt(PPh₃)₄ catalysts, leading selectively to products **4**. The CpRu(CH₃CN)₃[PF₆] catalyst for selected examples allowed obtaining the second syn-addition isomer (**3**). This selection of catalysts made it possible to obtain various isomers with high selectivity and efficiency. It is worth to underline that a detailed description of the hydrosilylation process taking into account such a wide spectrum of reagents, catalysts, and both syn-addition processes is rare in the scientific literature.

Compounds **3** and **4** described above are very useful reagents that can be modified through transformations typical of the boryl and silyl groups, and the hydrosilylation reaction ensures their effective synthesis. Moreover, the hydrosilylation process and the commercial reagents and catalysts used in it ensure that the synthesis methods are available to a wide range of researchers, repeatable, and possible to carry out on a larger scale. This is crucial considering their intended use for organic synthesis. It is worth noting that the research included in this publication is highlighted by a graphic presentation placed on the outside front cover of *Chemical Communications*.

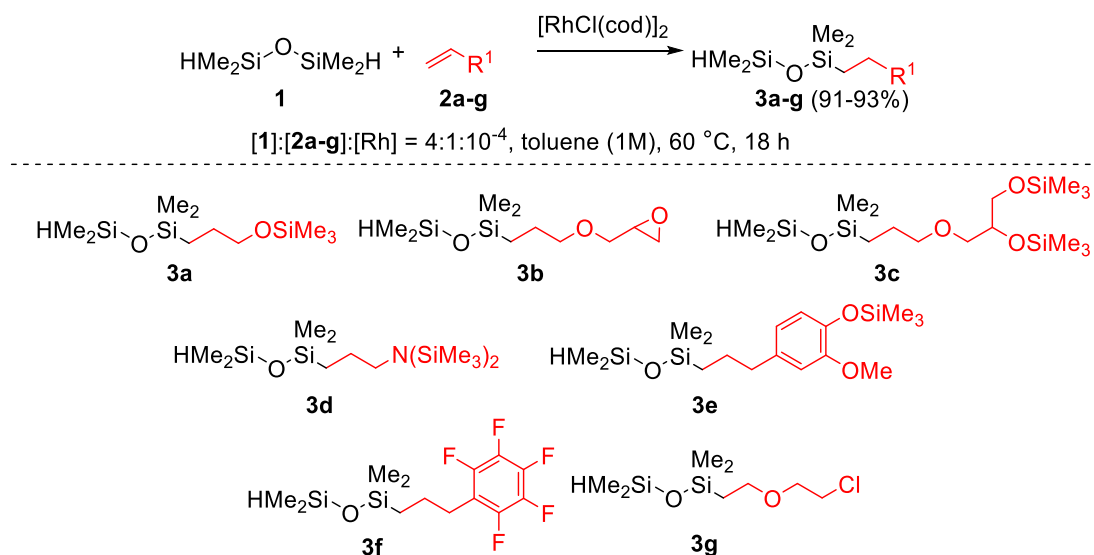
In publications **H3** and **H4**, research on the hydrosilylation of compounds containing C≡C bonds was continued. These articles describe the hydrosilylation of alkynes and 1,3-diynes with functional disiloxanes R¹CH₂CH₂SiMe₂OSiMe₂H and R²HC=C(R¹)SiMe₂OSiMe₂H, obtained as a result of hydrosilylation of alkenes or internal alkynes with 1,1,3,3-tetramethyldisiloxane (HSiMe₂OSiMe₂H, **1**) (Scheme 3). The unsymmetrical disiloxanes



Scheme 3. Synthesis of symmetrical and unsymmetrical disiloxanes by hydrosilylation of alkynes and 1,3-diynes with functional disiloxanes R¹CH₂CH₂SiMe₂OSiMe₂H, R²HC=C(R¹)SiMe₂OSiMe₂H, and 1,1,3,3-tetramethyldisiloxane (HSiMe₂OSiMe₂H) (**H3**, **H4**).

R¹CH₂CH₂SiMe₂OSiMe₂(R²)C=CHR³ and R²HC=C(R¹)SiMe₂OSiMe₂(R³)C=CHR⁴, containing alkyl and alkenyl groups, were obtained and characterized for the first time. In the publication **H4**, symmetrical disiloxanes R²HC=C(R¹)SiMe₂OSiMe₂(R¹)C=CHR² with the same two alkenyl groups were also obtained. The main goal of the work carried out was to develop a simple, direct, easy to repeat, and scale-up method for the synthesis of bifunctional disiloxanes (containing a wide range of reactive substituents), which can be used, among others, as coupling agents or multifunctional building blocks in the synthesis of hybrid materials.

In the first stage of the research, hydrosilylation of functional alkenes **2a-g** was carried out with 1,1,3,3-tetramethyldisiloxane (**1**) in the presence of a commercially available rhodium catalyst [RhCl(cod)]₂ (Scheme 4). As shown in previous studies, its use (in contrast to Karstedt or Wilkinson catalysts (RhCl(PPh₃)₃)) allowed the process to be carried out with excellent selectivity.^{70, 71} Syn-addition products of the Si-H group to the C=C bond were obtained, in which the silyl group was attached to the β-carbon atom. The best results were obtained when a four-fold excess of disiloxane **1** was used. This was necessary to selectively obtain product **3**, in which only one Si-H connection was converted. Unreacted disiloxane **1** was recovered as a result of its evaporation under vacuum. Using this methodology, seven R¹CH₂CH₂SiMe₂OSiMe₂H derivatives (**3a-g**) were obtained. In the case of alkenes **2a**, and **2c-e**, the hydroxyl and amino groups were blocked using chlorotrimethylsilane (TMSCl)

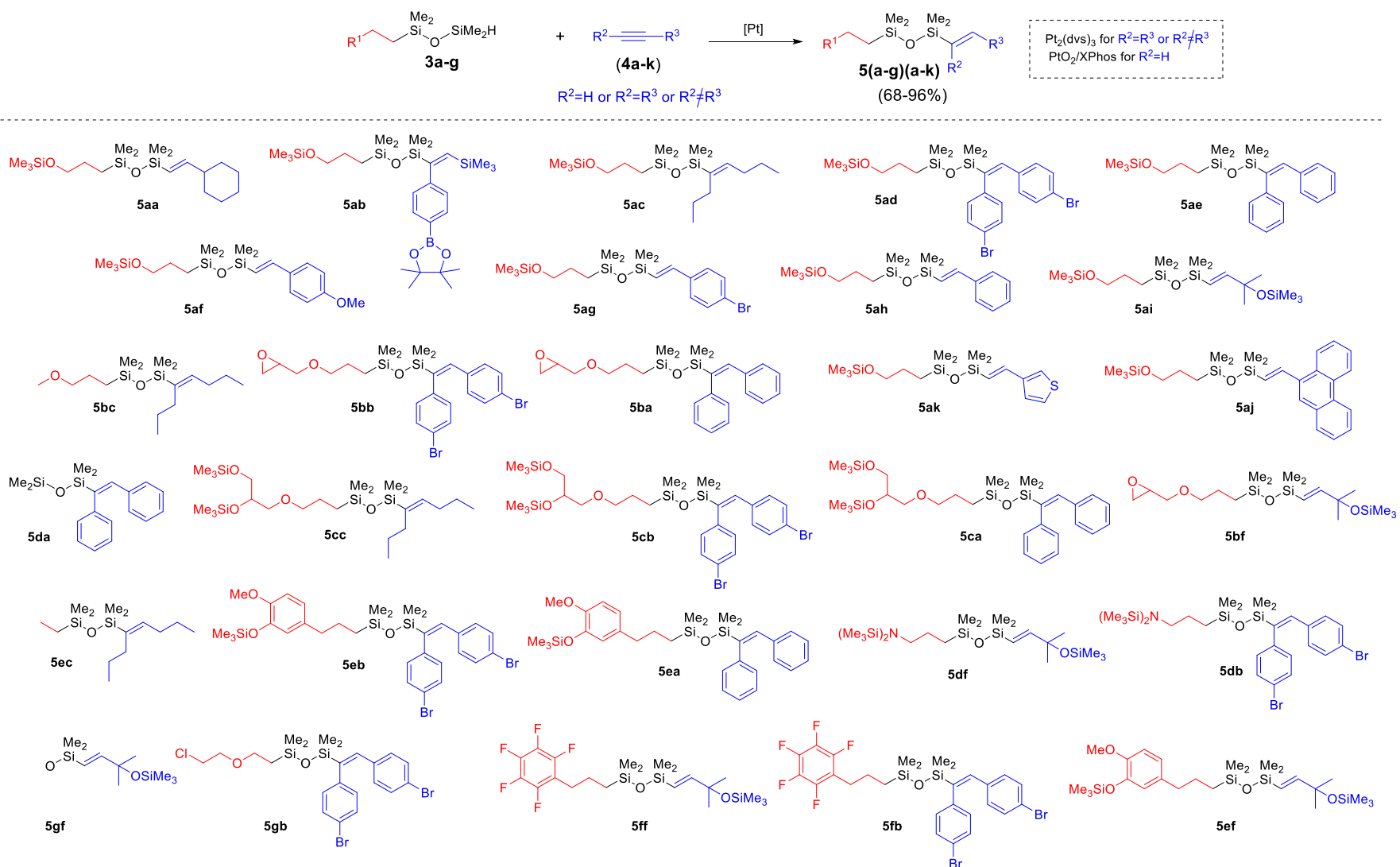


Scheme 4. Synthesis of disiloxanes $\text{R}^1\text{CH}_2\text{CH}_2\text{SiMe}_2\text{OSiMe}_2\text{H}$ (**3a-g**) by hydrosilylation of functional alkenes **2a-g** with 1,1,3,3-tetramethyldisiloxane (**1**) (**H3**).

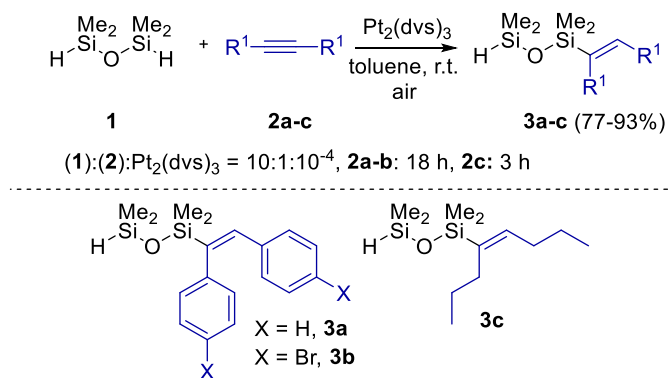
before the hydrosilylation process, as they deactivated the catalyst or caused the formation of by-products.

As part of process optimization, using the *in situ* FT-IR technique, which allows monitoring of the process in real-time, the influence of the structure of disiloxanes **3a-g** on the rate of hydrosilylation of diphenylacetylene (**4a**) in the presence of a Karstedt catalyst was examined. It was observed that the fastest consumption of siloxane took place for **3a** (2 hours), while for **3b** was the slowest (over 7 hours). For the remaining reagents, the reaction time was from 3 to 6 hours. This confirmed that the type of functional groups has a significant impact on the hydrosilylation process.

In the next step, the scope and limitations of the synthesis of bifunctional, unsymmetric derivatives $\text{R}^1\text{CH}_2\text{CH}_2\text{SiMe}_2\text{OSiMe}_2(\text{R}^2)\text{C}=\text{CHR}^3$ (**5**) obtained as a result of hydrosilylation of a wide group of internal and terminal alkynes (**4a-k**) (with diverse structure and functions) with disiloxanes **3a-g** (Scheme 5). Processes with internal alkynes were carried out in the presence of a Karstedt catalyst, while terminal ones were in the presence of $\text{PtO}_2/\text{XPhos}$. As a result of the experiments performed, products **5** with high efficiency were obtained. The library of the obtained products is summarized in Scheme 5. The possibility of obtaining such a significant number of structurally diverse products confirmed the tolerance of both catalysts used for a very wide range of functional substituents, clearly indicating the universality and usefulness of the hydrosilylation process in the field of modification of organic compounds containing $\text{C}\equiv\text{C}$ bonds.



Scheme 5. Synthesis of disiloxanes $R^1CH_2CH_2SiMe_2OSiMe_2(R^2)C=CHR^3$ (**5**) by hydrosilylation of alkynes **4a-k** with disiloxanes $R^1CH_2CH_2SiMe_2OSiMe_2H$ (**3a-g**) (**H3**).

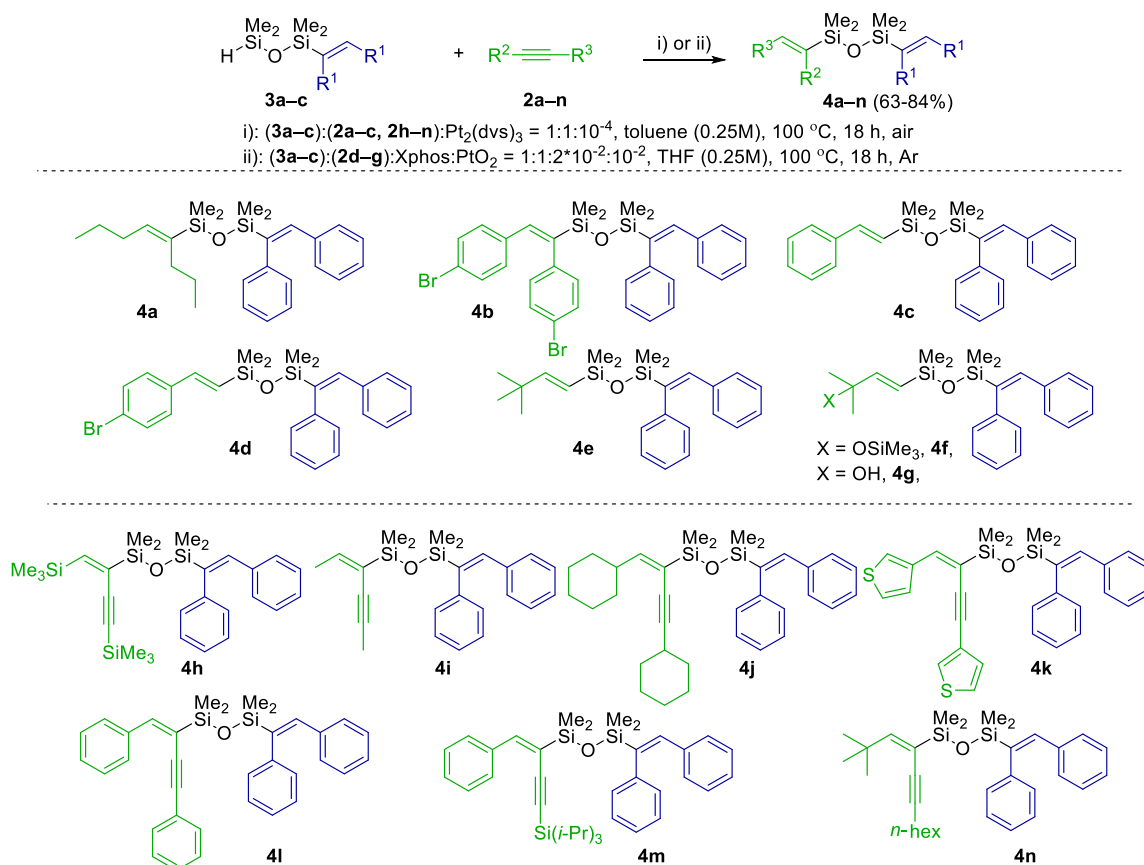


Scheme 6. Synthesis of disiloxanes $\text{R}^2\text{HC}=\text{C}(\text{R}^1)\text{SiMe}_2\text{OSiMe}_2\text{H}$ (**3a-c**) by hydrosilylation of internal alkynes **2a-c** with disiloxane **1** (**H4**).

The developed highly efficient synthesis methods allowed the preparation and characterization of 29 new, bifunctional, asymmetric derivatives $\text{R}^1\text{CH}_2\text{CH}_2\text{SiMe}_2\text{OSiMe}_2(\text{R}^2)\text{C}=\text{CHR}^3$ (**5**). The presence of unsaturated C=C bonds on one side of the siloxane and reactive species on the other makes these compounds very attractive building blocks with potential use as coupling agents or building blocks. Moreover, it is worth emphasizing that the obtained products $\text{R}^1\text{CH}_2\text{CH}_2\text{SiMe}_2\text{OSiMe}_2(\text{R}^2)\text{C}=\text{CHR}^3$ (**5**) are the only examples of compounds of this type described in the scientific literature, and the hydrosilylation process is the only method that has so far been used to obtain them. The research included in publication **H3** was distinguished by a graphic presentation placed on the outside back cover of *Chemical Communications*.

In publication **H4**, based on the same concept, the selective synthesis of unsymmetrical disiloxanes $\text{R}^2\text{HC}=\text{C}(\text{R}^1)\text{SiMe}_2\text{OSiMe}_2(\text{R}^3)\text{C}=\text{CHR}^4$ was carried out by gradual hydrosilylation of internal alkynes in the first step and alkynes (terminal or internal) or 1,3-dienes (symmetrically or non-symmetrically substituted) in the second using 1,1,3,3-tetramethyldisiloxane ($\text{HSiMe}_2\text{OSiMe}_2\text{H}$, **1**). The trials were carried out in the presence of Karstedt and $\text{PtO}_2/\text{XPhos}$ catalysts, previously proven in hydrosilylation reactions of alkynes and 1,3-dienes. As a result, a new family of unsymmetrical, bifunctional siloxanes containing two different alkenyl groups in the structure was obtained, which in turn provides even more possibilities for the use of these compounds in organic synthesis and materials chemistry.

Disiloxanes $\text{R}^2\text{HC}=\text{C}(\text{R}^1)\text{SiMe}_2\text{OSiMe}_2\text{H}$ (**3a-c**) (Scheme 6) were obtained by reacting internal alkynes **2a-c** with $\text{HSiMe}_2\text{OSiMe}_2\text{H}$ (**1**). It was observed that products of monofunctionalization were formed in high yields when a 10-fold excess of disiloxane **1** was used in the presence of a Karstedt catalyst, at room temperature. An excess of disiloxane was necessary to selectively obtain the intended product, because using a smaller amount of it led

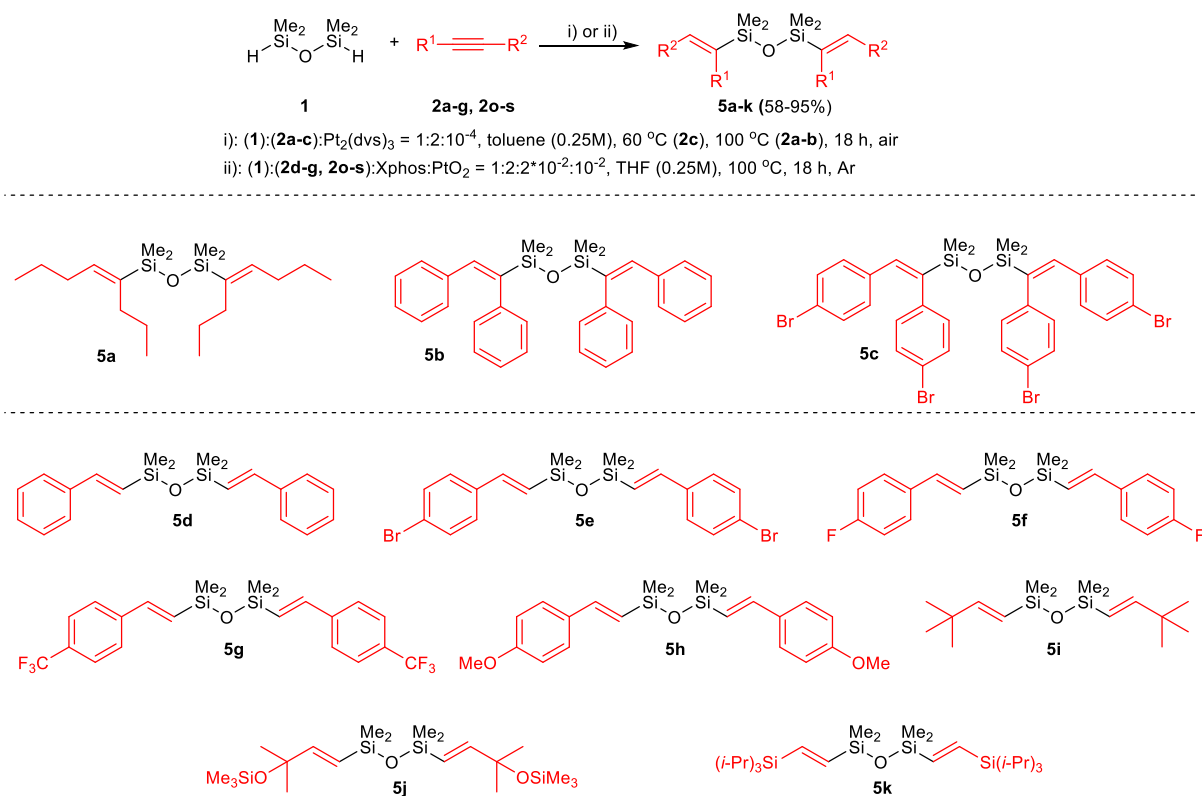


Scheme 7. Synthesis of disiloxanes $R^2HC=C(R^1)SiMe_2OSiMe_2(R^3)C=CHR^4$ (**4a-n**) by hydrosilylation of alkynes and 1,3-diynes **2a-n** with disiloxanes $R^2HC=C(R^1)SiMe_2OSiMe_2H$ (**3a-c**) (**H4**).

to the formation of products $R^2HC=C(R^1)SiMe_2OSiMe_2(R^1)C=CHR^2$ which resulted from the addition of both Si-H groups to two alkyne molecules. After completion of the reaction, excess disiloxane **1** was recovered using a high vacuum, while the pure product was isolated by filtration through silica gel. Disiloxanes **3a-c** have been prepared and characterized for the first time and served in the next stage of research as substrates in the synthesis of compounds **4a-n** (Scheme 7). It is worth adding that attempts were made to obtain analogous products by reacting disiloxane **1** with terminal alkynes, but they were unsuccessful.

In the next stage of the research, disiloxanes **3a-c** were reacted with a series of alkynes (terminal and internal) and 1,3-diynes (symmetrically and non-symmetrically disubstituted) (**2a-n**). Based on the experience of the research team and preliminary studies, reactions with internal alkynes and 1,3-diynes were carried out using a Karstedt catalyst, and with terminal alkynes in the presence of PtO₂/Xphos.

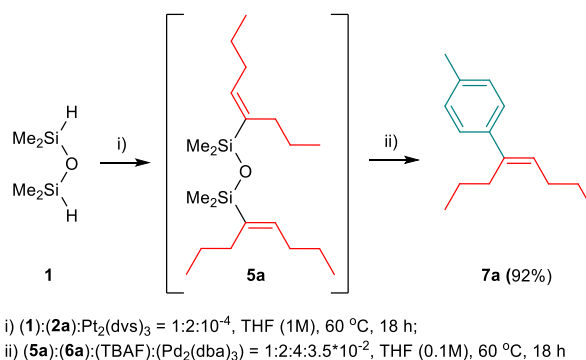
As a result, many new, non-symmetrical disiloxanes **4a-n** were synthesized, having two different alkenyl groups or one alkenyl and one enynyl group in their structure.



Scheme 8. Synthesis of disiloxanes $\text{R}^2\text{HC}=\text{C}(\text{R}^1)\text{SiMe}_2\text{OSiMe}_2(\text{R}^1)\text{C}=\text{CHR}^2$ (**5a-k**) by hydrosilylation of two equivalents of the same alkyne (**2a-g, 2o-s**) with disiloxane (**1**) (**H4**).

The use of the Karstedt catalyst in the synthesis of compounds **3a-c** and **4a-b, 4h-n**, by hydrosilylation of internal $\text{C}\equiv\text{C}$ bonds, allowed both stages of disiloxane modification to be performed in a one-pot manner, using the same portion of the catalyst. For this purpose, 4-octyne (**2c**) was reacted with a 10-fold excess of disiloxane **1** in the presence of this complex at room temperature. After 3 hours, complete conversion of alkyne **2c** was confirmed, and the excess disiloxane **1** was evaporated. Then 1,2-diphenylethyne (**2a**) and toluene were added and the mixture was heated to 100 °C. After 18 hours, product **4a** was obtained. The same experiment was performed to obtain product **4m**. However, in this case, the hydrosilylation of alkyne **2a** with disiloxane **1** was carried out in the first step at room temperature for 18 hours (as was done in the case of the two-step method). These experiments are an example of how detailed characterization of the application area of a given catalyst can influence the development of more sustainable preparation methods.

As part of the research, hydrosilylation of two molecules of the same alkyne with disiloxane **1** was also carried out to obtain symmetric compounds $\text{R}^2\text{HC}=\text{C}(\text{R}^1)\text{SiMe}_2\text{OSiMe}_2(\text{R}^1)\text{C}=\text{CHR}^2$ (**5a-k**) (Scheme 8). The present research was carried out to synthesize this type of disiloxane derivatives under optimized conditions to demonstrate



Scheme 9. One-pot synthesis of **7a** via hydrosilylation (i) and cross-coupling (ii) (**H4**).

the versatility of the hydrosilylation process in the synthesis of disiloxanes with alkenyl substituents. This also allowed us to supplement the range of known compounds with new examples. Undescribed products **5a** and **5c** and a known **5b**⁷² were obtained. For derivative **5b**, for the first time crystal structure was confirmed, which is the first example of a compound of this type reported to the Cambridge Structural Database (CSD). Also disiloxanes **5g**, **5j** and **5k**, obtained by reaction with terminal alkynes in the presence of PtO₂/Xphos, were obtained and characterized for the first time. Crystal structures have been determined for compounds **5e** and **5g**, which are the first ones reported to CSD.

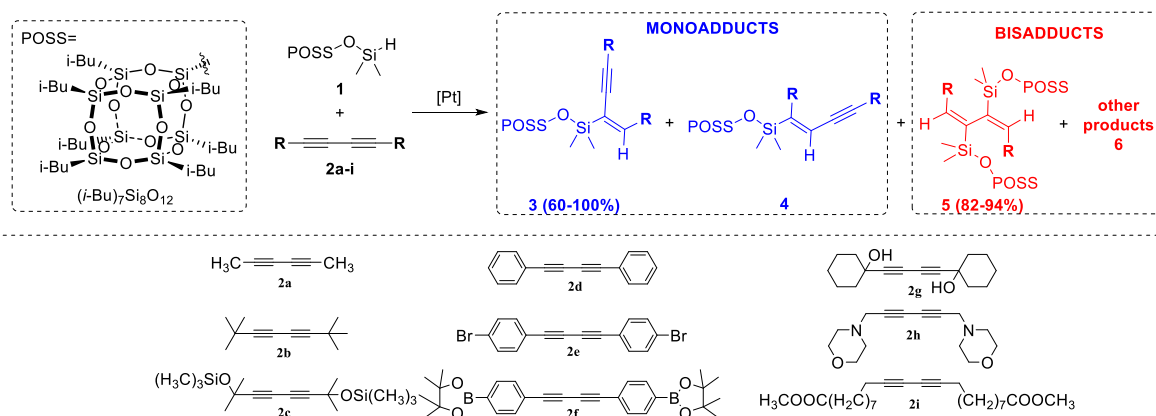
Obtaining symmetrical disiloxanes made it possible to demonstrate the potential use of compounds of this type in organic synthesis. Therefore, the reaction of disiloxane **5a** with 4-iodotoluene (**6a**) was carried out in the presence of a palladium catalyst Pd₂(dba)₃ (dba = dibenzylideneacetone) and TBAF (TBAF = tetrabutylammonium fluoride). As a result, the cross-coupling product of these reagents **7a** was obtained in 92% yield. A one-pot synthesis of **7a** was also performed *via* sequential hydrosilylation and coupling processes. The product was obtained with excellent selectivity (>99%) and the same high efficiency (92%) as observed when these processes are carried out in a one-pot manner (Scheme 9).

To sum up, in publication **H4**, as a result of hydrosilylation of internal alkynes with disiloxane **1** in the first step and alkynes (terminal or internal) and 1,3-diynes with disiloxanes **3a-c** in the second, 27 compounds were obtained, 21 of which were described for the first time (**3a-c**, **4a-n**, **5a**, **c**, **g**, **j**, **k**). In addition, the crystal structures of compounds **5b**, **5e**, and **5g** were determined, which are the only examples of compounds of this type reported to the Cambridge Structural Database. Using the example of disiloxane **5a**, the use of the described compounds in organic synthesis was presented. As a result of the reaction of this compound with 4-iodotoluene the cross-coupling product **7a** was obtained in 92% yield. This process was carried out by two-step synthesis with isolation of individual products, as well as the one-pot

method. The unsymmetrical disiloxanes $R^2HC=C(R^1)SiMe_2OSiMe_2(R^3)C=CHR^4$ described in publication **H4** are the first compounds of this type described in the literature, while the hydrosilylation process is the only method used in their synthesis. Moreover, the hydrosilylation process was used in the conducted research in the synthesis of symmetric disiloxanes $R^2HC=C(R^1)SiMe_2OSiMe_2(R^1)C=CHR^2$, confirming their usefulness also in the synthesis of this type of derivatives. The known range of compounds was supplemented with new examples, and the first crystal structures were determined for selected examples.

It is also worth emphasizing that the hydrosilylation of alkynes and 1,3-diynes with 1,1,3,3-tetramethyldisiloxane, carried out in the presence of Karstedt catalysts (for internal $C=C$ bonds) and $PtO_2/XPhos$ (for terminal $C\equiv C$ bonds), turned out to be the most versatile and tolerant method for many functional groups, leading to the richest family of functional disiloxanes. Another advantage of this method is that it uses commercially available reagents and catalysts.

Publication **H5** describes research on the hydrosilylation of 1,3-diynes, in which polyhedral oligosilsesquioxanes (POSS) were used as the silylating agent. POSS are attractive systems that arouse great interest in the world of science and industry. This is due to their unique structure, properties, and various areas of application. To explore their real potential, however, it is necessary to develop highly effective synthesis methods that allow obtaining a wide spectrum of derivatives with various structures and functions. Therefore, it seems justified to undertake research related to the preparation of their new derivatives, especially using such a versatile and direct synthesis method as the hydrosilylation process. This is why in this article we decided to check whether it is possible to perform selective functionalization of symmetric 1,3-diynes with silsesquioxane $(HSiMe_2O)(i-Bu)_7Si_8O_{12}$ (**1**) (Scheme 10). Although the target but-3-en-1-yne and 1,3-butadienes with a silsesquioxane moiety had not been obtained until the publication of this work, it is clear from literature reports that compounds containing conjugated unsaturated bonds, from the scientific point of view, they are extremely interesting systems and could be used in many areas of science, including those related to optoelectronics. Moreover, compounds of this type cannot be obtained by methods that have previously been used in the synthesis of alkenyl-substituted silsesquioxanes or silanes, such as silylation coupling, Wittig reactions, metathesis, or Heck coupling. Hence, the choice of hydrosilylation as a method of their synthesis is justified. As part of the work carried out in publication **H5**, 9 structurally diverse buta-1,3-diynes **2a-i** were examined in the presence of homogeneous and heterogeneous catalysts: Karstedt catalyst, $Pt(PPh_3)_4$, PtO_2 , and Pt/SDB .



Scheme 10. Hydrosilylation of one and both $\text{C}\equiv\text{C}$ bonds in symmetrical 1,3-diyne **2a-i** silsesquioxane $(\text{HSiMe}_2\text{O})(i\text{-Bu})_7\text{Si}_8\text{O}_{12}$ (**1**) (**H5**).

It was found that the selectivity of the hydrosilylation process strongly depended on the structure of 1,3-diyne. Hydrosilylation of sterically loaded diynes **2b**, **2c**, **2f** in the presence of Karstedt catalyst, using a stoichiometric amount of reagents, led to the formation of almost exclusively Si-H addition products to one $\text{C}\equiv\text{C}$ bond (**3b**, **3c**, **3f**, 91-100%).

Addition to both $\text{C}\equiv\text{C}$ bonds in the presence of the same catalyst occurred selectively only for diyne **2g**, while the formation of products **5b** and **5c** was not observed. However, hydrosilylation of buta-1,3-diyne **2a**, **2d**, **2e**, **2f**, **2h**, **2i** in the presence of Karstedt catalyst gave mixtures of addition products to one (**3**) and both (**5**) triple bonds, in which the former were obtained with selectivity 60-95%. For products **3a** and **3e**, higher selectivity was observed when the less active $\text{Pt}(\text{PPh}_3)_4$ catalyst was used. Heterogeneous PtO_2 and Pt/SDB catalysts showed similar efficiency to the Karstedt catalyst in the synthesis of compound **3f**.

In the next stage of the research, hydrosilylation of both $\text{C}\equiv\text{C}$ bonds was carried out with 1,3-diyne **2a**, **2d-i** to obtain buta-1,3-diene **5**. In these processes, the molar ratio of silsesquioxane **1** to diynes **2** was 2:1. The reactions were carried out in the presence of a Karstedt catalyst, which turned out to be the best system for all the tested reagents. The use of non-stoichiometric amounts of substrates was necessary only in reactions with 2,4-hexadiyne (**2a**). In this case, for the monoaddition, a 10-fold excess of diyne **2a** was necessary to eliminate the parallel formation of product **5a**. After complete consumption of silsesquioxane **1**, excess of diyne **2a** was removed from the post-reaction mixture by evaporating it in a vacuum. However, in the synthesis of bisadduct **5a**, it was necessary to use 2,3 equivalents of silsesquioxane **1**. Thanks to optimized synthesis conditions, both compounds were isolated and fully characterized.

To sum up, article **H5** describes for the first time a highly efficient method for the synthesis of new 3-buten-1-yne (**3**) and buta-1,3-dienes (**5**), containing polyhedral oligosilsesquioxane in their structure. The obtained products are hybrid compounds with a unique structure and the resulting physicochemical properties. They can undergo further transformations and become building blocks for more complex systems. In addition to reactive double and triple bonds, some of the obtained compounds have various functional groups, which indicates the potential of the described method.

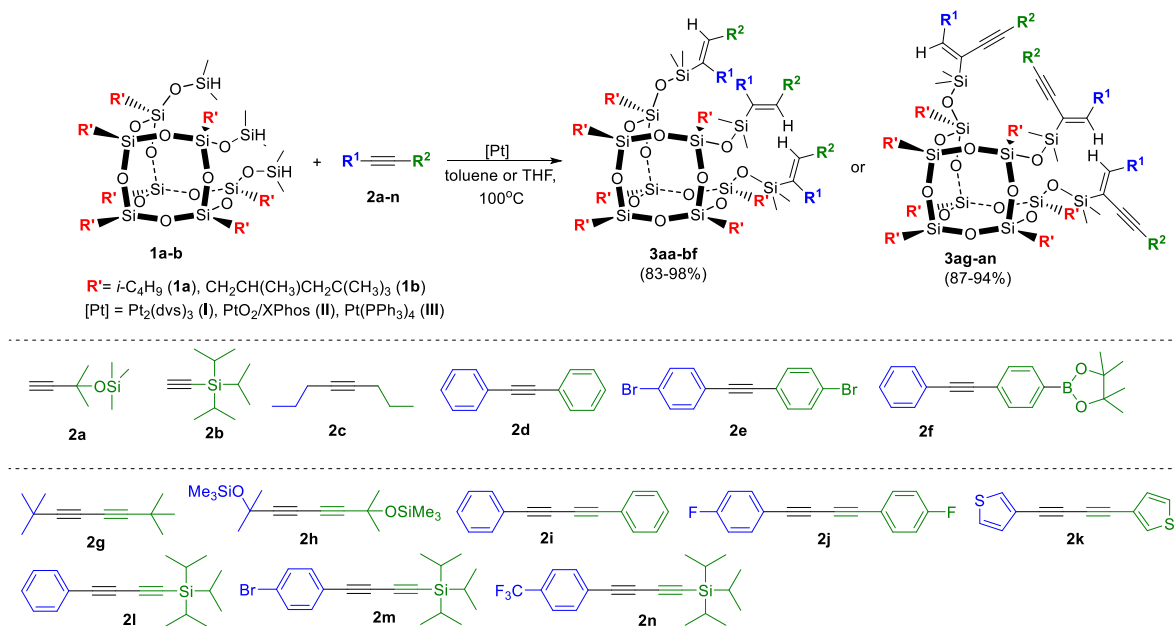
As a result of the work, 16 new compounds were obtained and characterized. It is worth emphasizing that to date these are the only examples of compounds of this type described in the scientific literature, and the process of hydrosilylation of 1,3-diynes is the only method of their synthesis.

In publication **H6**, research related to the chemistry of silsesquioxanes was continued. It describes the hydrosilylation of alkynes and 1,3-diynes with incompletely condensed oligosilsesquioxanes $(\text{HSiMe}_2\text{O})_3\text{R}'_7\text{Si}_7\text{O}_9$ (where $\text{R}' = i\text{-Bu}$ (**1a**), $i\text{-Oct}$ (**1b**)). As a result, many new compounds with the general formula $(\text{RSiMe}=\text{O})_3\text{R}'_7\text{Si}_7\text{O}_9$ (**3**) were obtained (Scheme 11), containing three alkenyl or enynyl groups in the structure.

Trifunctional silsesquioxanes $(\text{RSiMe}_2\text{O})_3\text{R}'_7\text{Si}_7\text{O}_9$ (IC-POSS) are based on a cubic silicon-oxygen core with one open corner. Therefore, on the one hand, they show properties similar to fully condensed polyhedral oligosilsesquioxanes, but on the other hand, they also have different properties. For example, IC-POSS is characterized by excellent thermal stability, similar to POSS, but due to the low symmetry of the molecules, their melting points are much lower. The lack of symmetry also limits their crystallinity, which makes them much better dispersed in polymer matrices compared to fully condensed POSS, which are more susceptible to aggregation.

Most of the IC-POSS described in the literature were obtained by hydrosilylation of alkenes, while the hydrosilylation of alkynes and 1,3-diynes has not been described so far, despite the enormous potential of this transformation compared to the modification of olefins, which results from the possibility of introducing 3, 6 or even more functional groups into the IC-POSS structure. Therefore, it was decided to undertake this research topic.

In the first step, the hydrosilylation of terminal alkynes **2a-b** was investigated with silsesquioxanes **1a-b** (differing in R substituents and therefore in physical properties) (Scheme 11). Hydrosilylation of **2a** with silsesquioxanes **1a-b** performed in the presence of Karstedt catalyst, it allowed to obtain products **3aa** and **3ba** with selectivity of 91 and 88%.



Scheme 11. Hydroosilylation of alkynes (**2a-f**) and 1,3-diyne (**2g-h**) with silsesquioxanes (HSiMe₂O)₃R'₇Si₇O₉ (where R' = *i*-Bu (**1a**), *i*-Oct (**1b**)) (**H6**).

The selectivity of **3aa** synthesis was improved to 97% when PtO₂/XPhos and Pt(PPh₃)₄ systems were used. Similar results were obtained using silsesquioxane **1b**. However, for the hydroosilylation of ethynyltri(*isopropyl*)silane (**2b**) and internal alkynes **2c-2f**, the most active Karstedt catalyst turned out to be the most effective.

Encouraged by the results of the hydroosilylation of alkynes, we carried out the hydroosilylation of symmetric and non-symmetric buta-1,3-diyne (**2g-n**). The challenge in this area of research was to selectively react one triple bond in 1,3-diyne and eliminate addition to the second bond, which would lead to oligomeric or cyclic systems. Hydroosilylation of 1,3-diyne **2g** and **2h** with silsesquioxane **1a** was carried out in the presence of Karstedt catalyst with stoichiometric amounts of reactants - [**1a**]:[**2g** or **2h**] = 1:3. It was found that in both cases the reaction led only to 1,2-syn-addition products of the Si-H group to one C≡C bond. In the case of reagents **2i-k**, product mixtures were obtained, in which addition products to both double bonds were observed. The solution was to use a 12-fold excess of 1,3-diyne and increase the concentration of the solution. Experiments conducted under such conditions led to the formation of monoaddition products **3ai-ak**, and **3bi** with high yields. The excess of 1,3-diyne used in the reaction was effectively removed by flash chromatography. However, in the case of tests with 1-silyl-4-aryl-1,3-diyne (**2l-n**), it was observed that the presence of silyl groups in the 1,3-diyne structure has a positive effect on the selectivity of the process. It caused that addition to the first triple bond (not substituted with a silyl group) occurred much more

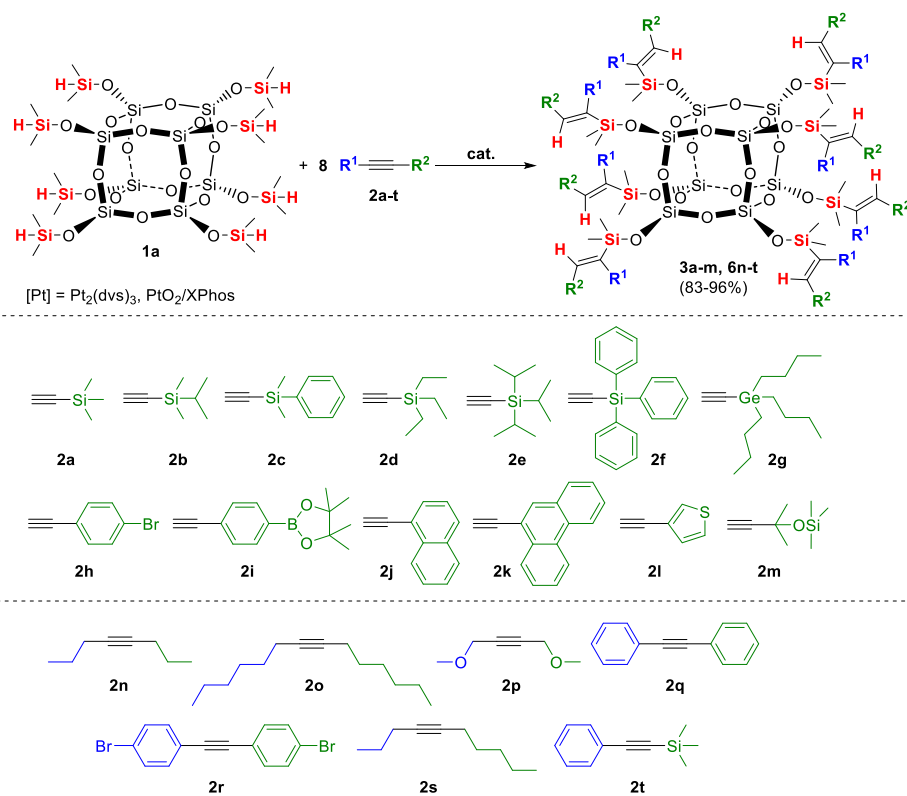
efficiently. The silyl group reduced the reactivity of the triple bond, with which it was associated. As a result, **3al-an** products were obtained with very good yields.

As part of the research, the thermal properties of most of the obtained products were determined, which were characterized using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results of DSC analysis carried out in the range from -50 to 100 °C showed that no thermal transformations were observed for all tested products. However, TGA analysis showed that the tested compounds are highly thermally stable. The most stable compound from the group containing alkenyl substituents was silsesquioxane **3ae** ($T_d^{5\%} = 355$ °C) and from the group containing enynyl substituents, silsesquioxane **3bi** ($T_d^{5\%} = 337$ °C). The lowest stability was demonstrated by compounds **3aa** ($T_d^{5\%} = 271$ °C), and **3ah** ($T_d^{5\%} = 200$), respectively.

In summary, the research resulted in 20 previously undescribed alkenyl compounds and enynyl derivatives of silsesquioxanes $(\text{RSiMe}_2\text{O})_3\text{R}'_7\text{Si}_7\text{O}_9$, which constitute a new class of nanometric building blocks. These compounds or their derivatives can be used in the preparation of advanced hybrid materials. They are the first examples of systems of this type described in the scientific literature. However, the hydrosilylation process is the only method used in their synthesis. The research included in publication **H6** was highlighted by a graphic presentation placed on the supplementary journal cover of the *Inorganic Chemistry*.

In the next stage of work, the hydrosilylation of alkynes and 1,3-diynes with octaspherosilicate $(\text{HSiMe}_2\text{O})_8\text{Si}_8\text{O}_{12}$ (**1a**) was investigated, and the obtained results were described in publications **H7** and **H8**. Polyhedral oligospherosilicates $(\text{RSiMe}_2\text{O})_8\text{Si}_8\text{O}_{12}$ (SPHS) are well-defined, nanometric hybrid compounds that are considered to be the smallest obtainable model silica particles. Their structure is based on the same silicon-oxygen, cubic core as polyhedral oligosilsesquioxanes, therefore they belong to the same family of compounds, although due to different synthesis methods and the fact that they contain silicon atoms connected to four oxygen atoms in their structure, they are isolated from this group and called spherosilicates. Compared to the previously discussed monofunctional $((\text{RSiMe}_2\text{O})\text{R}'_7\text{Si}_8\text{O}_{12})$ and trifunctional $((\text{RSiMe}_2\text{O})_3\text{R}'_7\text{Si}_7\text{O}_9)$ silsesquioxanes, SPHS have 8 identical R substituents, which determine their properties. In the case of the other two silsesquioxanes, they are defined by both R and R' substituents.

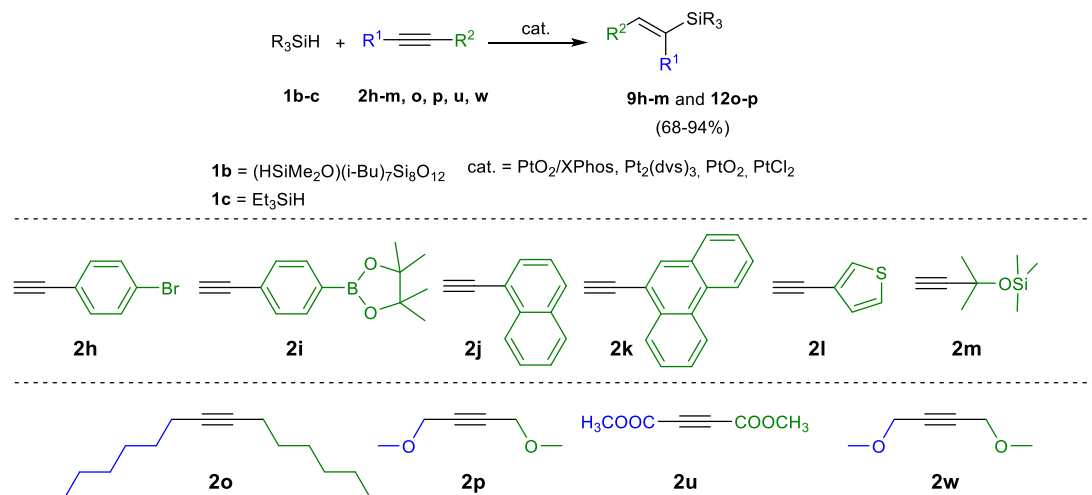
Only two spherosilicates are commercially available: $(\text{HSiMe}_2\text{O})_8\text{Si}_8\text{O}_{12}$ (**1a**) and $(\text{H}_2\text{C}=\text{CHSiMe}_2\text{O})_8\text{Si}_8\text{O}_{12}$. Among them, thanks to easy functionalization by hydrosilylation, $(\text{HSiMe}_2\text{O})_8\text{Si}_8\text{O}_{12}$ (**1a**) is much more widespread. The use of this compound in various areas of science has been described in over 400 articles and patents.



Scheme 12. Synthesis of alkenyl derivatives of spherosilicates **3a-m**, **6n-t** by hydrosilylation of alkynes **2a-t** with spherosilicate (HSiMe₂O)₈Si₈O₁₂ (**1a**) (**H7**).

Despite such a significant amount of research on systems obtained by hydrosilylation of alkenes, at the time of publication of this article, only three reports were known in the scientific literature describing the reduction of carbon-carbon triple bonds with spherosilicate (HSiMe₂O)₈Si₈O₁₂ (**1a**). In each case, mixtures of isomers were obtained in these studies.⁷³⁻⁷⁵ However, selected spherosilicates with monosubstituted alkenyl groups were synthesized, among others, by silylative coupling of spherosilicate (H₂C=CHSiMe₂O)₈Si₈O₁₂ with alkenes (styrene, 1-hexene, vinyltrimethylsilane, allyltrimethylsilane, vinyl ethers, 1-vinyl-2-pyrrolidinone, tert-butylvinyl sulfide).⁷⁶ This fact, in addition to the lack of effective procedures for hydrosilylation of alkynes with spherosilicate (HSiMe₂O)₈Si₈O₁₂ (**1a**), prompted us to undertake research related to the synthesis of new alkenyl derivatives of octaspherosilicates by hydrosilylation of alkynes (Scheme 12).

The research showed that the reactions of (HSiMe₂O)₈Si₈O₁₂ (**1a**) with terminal ethynyl silanes **2a-f** occur with high selectivity in the presence of a Karstedt catalyst. The crystal structure was determined for product **3a**. Then, derivatives containing germyl groups were examined. However, in the case of a reaction with tributylethynylgermane (**2g**) in the presence of the same catalyst, a mixture of isomers was obtained.



Scheme 13. Hydrosilylation of alkynes (**2h-m, o, p, u, w**) with silsesquioxane (**1b**), and triethylsilane (**1c**), (**H7**).

A change in the reaction method consisting of the gradual addition of germane **2g** at time intervals was successful and the assumed product was obtained with 96% selectivity. Hydrosilylation of alkyne **2h** was carried out in the same way, but in this case, the intended result was not achieved. Therefore, Pt(PPh₃)₄, PtO₂, PtCl₂/XPhos catalysts were tested. It was shown that their use also led to obtaining a mixture of products or incomplete conversion of the reactants. However, the selective formation of products for the terminal reactions of alkynes **2h-l** was ensured by the PtO₂/XPhos catalyst.

In the next step, hydrosilylation of disubstituted **2n-t** alkynes was carried out in the presence of the Karstedt catalyst, which led to the preparation of spherosilicates with disubstituted **6n-t** alkenyl groups. It is worth emphasizing that this group of compounds cannot be directly obtained by alternative methods described in the literature, such as silylation coupling, metathesis, Heck, or Wittig reactions.

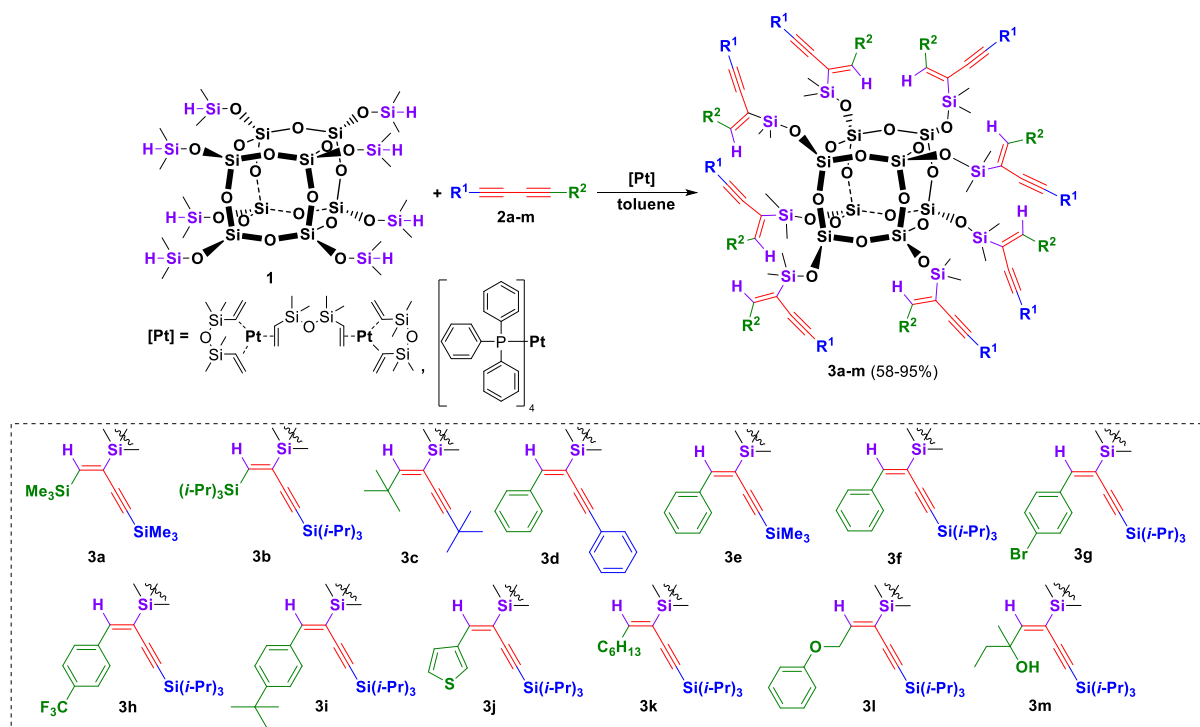
As part of the work, to simplify research on the selection of reaction conditions in the hydrosilylation of alkynes with octahydridospherosilicate (HSiMe₂O)₈Si₈O₁₂ (**1a**), optimizations were carried out for simpler models such as (HSiMe₂O)(i-Bu)₇Si₈O₁₂ (**1b**) and triethylsilane (**1c**) (Scheme 13). In this case, apart from the previously described catalytic systems, PtO₂ and PtCl₂ catalysts also turned out to be effective for the reaction of **1c** with **2u** and **2w**, respectively. These experiments became an excellent source of information about the hydrosilylation process of selected alkynes and also provided many previously undescribed compounds: **9h-m** and **12o-p**.

To sum up, in article **H7** comprehensive research on the hydrosilylation of a wide range of alkynes with spherosilicate (HSiMe₂O)₈Si₈O₁₂ (**1a**) was described for the first time.

The research determined the influence of the parameters and structure of the reactants on the efficiency of the process, which enabled the development of a comprehensive and selective method for the synthesis of 20 alkenyl derivatives of octaspherosilicates (**3a-m**, **6n-t**), including 18 for the first time. Moreover, the molecular structure of the compound was determined $(\text{Me}_3\text{Si}(\text{H})\text{C}=\text{C}(\text{H})\text{SiMe}_2\text{O})_8\text{Si}_8\text{O}_{12}$ (**3a**). This method is an excellent tool for the synthesis of branched compounds based on the cubic core of octafunctional spherosilicate. Additionally, 10 new compounds (**9h-m**, **12o-p**) were synthesized by hydrosilylation of alkynes with silsesquioxane $(\text{HSiMe}_2\text{O})(i\text{-Bu})_7\text{Si}_8\text{O}_{12}$ (**1b**) and triethylsilane (**1c**). The scope of use of platinum catalysts (Karstedt category, $\text{PtO}_2/\text{XPhos}$, PtO_2 , PtCl_2) in the above-described reactions of alkynes with organosilicon compounds (**1a-c**) was determined. As was the case with previous studies in reactions with internal alkynes, ethynyl silanes, and germaniums, the Karstedt catalyst turned out to be the most effective for the addition of Si-H to the terminal $\text{C}\equiv\text{C}$ bonds of $\text{PtO}_2/\text{XPhos}$. Using a PtO_2 catalyst, the product of hydrosilylation of the internal alkyne $\text{H}_3\text{COOCC}\equiv\text{CCOOCH}_3$ with triethylsilane (**1c**) was obtained. Analogous reactions with silsesquioxane $(\text{HSiMe}_2\text{O})(i\text{-Bu})_7\text{Si}_8\text{O}_{12}$ and spherosilicate $(\text{HSiMe}_2\text{O})_8\text{Si}_8\text{O}_{12}$ led to a complex mixture of products. The remaining catalysts were not active in this reaction. Whereas in the reaction of the internal alkyne $\text{ClCH}_2\text{C}\equiv\text{CCH}_2\text{Cl}$ with triethylsilane, the hydrosilylation product was obtained only in the presence of PtCl_2 . Analogous reactions with silsesquioxane $(\text{HSiMe}_2\text{O})(i\text{-Bu})_7\text{Si}_8\text{O}_{12}$ and spherosilicate $(\text{HSiMe}_2\text{O})_8\text{Si}_8\text{O}_{12}$ led to a complex mixture of products.

The achieved results in the area of hydrosilylation of alkynes made it possible to take up another challenge, which was the hydrosilylation of symmetrically and non-asymmetrically disubstituted buta-1,3-diyne (**2a-m**) with spherosilicate (**1**), in the presence of commercially available Karstedt and $\text{Pt}(\text{PPh}_3)_4$ catalysts. (Scheme 14). Research results regarding this aspect are described in publication **H8**. As a result of the work, compounds **3a-m** were obtained, with efficiencies ranging from 58-95%. They have double and triple bonds in their structure as well as other functional groups (e.g. Br, F, OH, SiR_3), making them highly desirable building blocks dedicated to the synthesis of advanced materials.

In the first step, hydrosilylation of symmetric 1,4-bis(trimethylsilyl)buta-1,3-diyne (**2a**) in the presence of Karstedt catalyst and $\text{Pt}(\text{PPh}_3)_4$ was investigated. It was observed that as the process temperature decreases, its selectivity increases. Product **3a** was obtained selectively in the presence of a higher concentration of $\text{Pt}(\text{PPh}_3)_4$ catalyst (40 °C, 72 hours) using 16 equivalents of 1,3-diyne **2a** relative to one equivalent of spherosilicate **1**.



Scheme 14. Synthesis of alkenyl-spherosilicates **3a-m** by hydrosilylation of 1,3-diyne **2a-m** with spherosilicate $(\text{HSiMe}_2\text{O})_8\text{Si}_8\text{O}_{12}$ (**1**), (**H8**).

The optimized conditions allowed for obtaining the desired product **3a** with very good insulation efficiency (80%). Similar reaction conditions were used for the hydrosilylation of 1,4-diphenylbut-1,3-diyne (**2d**). Hydrosilylation of the more sterically crowded 1,4-bis(tri(*isopropyl*)silyl)buta-1,3-diyne (**2b**) and 2,2,7,7-tetramethylocta-3,5-diyne (**2c**) proved to be less demanding. The use of a low concentration of Karstedt catalyst, the amount of reactants in the ratio $[\mathbf{1}]:[\mathbf{2b} \text{ or } \mathbf{2c}] = 1:8$, at a temperature of 100 °C, in a much shorter time (7 and 16 hours for 1,3-diyne **2b** and **2c**, respectively), the assumed products were obtained almost quantitatively.

Then, the hydrosilylation of a series of unsymmetrical buta-1,3-diyne **2e-2m** having a tri(*isopropyl*)silyl group in their structure was investigated. The trials were carried out in the presence of Karstedt's catalyst, with the reactant ratio $[\mathbf{1}]:[\mathbf{2}] = 1:8$, at a temperature of 100 °C. As a result, products **3e-m** were selectively obtained. The progress of the hydrosilylation process of the above reagents was monitored in real-time using *in situ* FT-IR spectroscopy (by tracking changes in the area of the 880-930 cm^{-1} band, assigned to the stretching vibrations of the Si-H bond).

The use of this analytical method was crucial to determine the time needed to achieve complete conversion of the reactants. It was observed that for 1,3-diyne **2k** the reaction ended after 5 hours and 40 minutes, while for **2j**, **2l**, and **2m**, 10-11 hours were required for complete

conversion. In the case of hydrosilylation of **2f**, the process was completed after 17 hours. Lower reaction rates (22-31 hours) were found for the hydrosilylation of diynes **2e**, **2g-i**. Kinetic plots obtained from *in situ* FT-IR measurements indicated that after the catalyst was added to the reaction mixture and heating, the reactants were consumed quickly (62-76%), after which the reaction rates decreased slightly due to the lower concentration of the reactants. Similar trends were observed for the hydrosilylation of 1,3-diynes **2b** and **2c**. However, the hydrosilylation of **2e** was characterized by a short initiation period. 40% of Si-H conversion was observed in just 33 minutes, followed by consumption of reactants at a similar rate for the rest of the process. The hydrosilylation of diynes **2f** and **2j** in the presence of Pt(PPh₃)₄ was also monitored. However, due to the steric hindrance of the catalyst structures and the reactants, the time needed to achieve full conversion of the Si-H bond was extended by 9 hours for 1,3-diyne **2f**, and 15 hours, and 30 minutes for **2j** compared to the same reactions carried out using the Karstedt catalyst.

Studies using the UV-Vis technique have shown that compounds **3d**, **3i**, **3j**, **3k**, **3m** absorb only in the UV range (200-400 nm), which is typical for molecules containing conjugated C-C bonds in their structure. The thermal properties of selected products were characterized using thermogravimetric analysis (TGA) performed in an inert atmosphere. It showed that the obtained products **3** are stable up to 300 °C. The highest stability was demonstrated by compounds **3k** ($T_d^{5\%} = 365$ °C), **3j** ($T_d^{5\%} = 360$ °C) and **3c** ($T_d^{5\%} = 357$ °C). A 10% of mass loss was observed for **3j** at 427°C and for **3c** and **3k** at 389°C. On the other hand, compound **3h** was identified as the least thermally stable ($T_d^{5\%} = 207$ °C). The sample residual for all analyses was in the range of 40-50%. The lowest residue was observed for compound **3m** and the highest for **3i** and **3k**.

To summarize, in paper **H8**, hydrosilylation of buta-1,3-diynes with octaspherosilicate **1** was investigated for the first time. As a result, 13 new octaspherosilicates **3a-m** with enynyl groups (58-95%) were successfully synthesized. So far, they are the only examples of systems of this type described in the scientific literature, and the hydrosilylation process is the only method used in their synthesis.

4.4. Summary and conclusions

The research described in this report on new methods for the synthesis of alkenyl derivatives of organosilicon compounds by hydrosilylation of alkynes and 1,3-dienes constitutes a significant contribution to the development of silicon chemistry. They contributed to the discovery of new areas of knowledge through the synthesis and characterization of previously undescribed areas in the scientific literature of chemical substances, through the Si-H syn-addition to C≡C bonds for a wide spectrum of reagents and determining the area of application of selected catalysts. Taking into account the development of the chemistry of silicon compounds and their applications in organic synthesis, as well as coupling agents and multifunctional building blocks, the development of methods for their synthesis leading to a wide spectrum of derivatives with various structures and functions significantly contributes to the full understanding of the applications of compounds of this type.

The achievements indicated in the presented works are:

1. Synthesis and characterization of the structure and properties (on selected examples) of over 164 alkenyl derivatives of organosilicon compounds, including 152 previously undescribed in the literature, of which crystal structures were determined for nine. Most of the obtained compounds are the only examples of this type of systems described in the literature, building new branches of their applications in organic and materials chemistry. Hydrosilylation process, characterized by high efficiency and productivity, was used in many cases of their synthesis for the first time and is often the only method for their obtaining. It is worth emphasizing that the synthesis methods developed as part of the research, based on commercially available reagents and catalysts, are simple, direct, and easy to repeat, and scale-up, tolerant to a very wide range of reactive substituents present in the structures of the reactants. This makes it useful for a wide range of researchers who can use the characterized products. in subsequent transformations in many areas of application.
2. Detailed characteristics of the hydrosilylation process of C≡C bonds in terms of syn-addition of:
 - HSiR₃ silanes to borylalkynes, in which, by selecting an appropriate catalyst, the silyl group was directed to the α or β carbon atom (**H2**);

- functional disiloxanes $R^1CH_2CH_2SiMe_2OSiMe_2H$ (obtained by hydrosilylation of alkenes) to alkynes (**H3**);
- 1,1,3,3-tetramethyl disiloxane ($HSiMe_2OSiMe_2H$) to internal alkynes (**H4**);
- functional disiloxanes $R^2HC=C(R^1)SiMe_2OSiMe_2H$ (obtained by hydrosilylation of internal alkynes) to alkynes and one $C\equiv C$ bond of 1,3-diyne (**H4**);
- silsesquioxane $(HSiMe_2O)(i-Bu)_7Si_8O_{12}$ to one and two $C\equiv C$ bonds of symmetrical 1,3-diyne (**H5**);
- silsesquioxanes $(HSiMe_2O)_3R'_7Si_7O_9$ to alkynes and to one $C\equiv C$ bond of 1,3-diyne (**H6**);
- spherosilicate $(HSiMe_2O)_8Si_8O_{12}$ to alkynes (**H7**) and to one $C\equiv C$ bond of 1,3-diyne (**H8**).
- silsesquioxane $(HSiMe_2O)(i-Bu)_7Si_8O_{12}$ and triethylsilane to alkynes (**H7**).

It is worth noting that the above-mentioned areas of the hydrosilylation of $C\equiv C$ bonds were examined in great detail and concerned a wide spectrum of reagents with various structures and functional groups in each part. Such a detailed presentation of the applications of this method is extremely rare in the scientific literature. The works published so far concerned narrow groups of compounds, for example, limited only to terminal alkynes or alkyl alkynes, and even one compound containing $C\equiv C$ and a silane. This makes it difficult to determine the potential and usefulness of such research. In contrast, publications **H2-H8** present a broad approach to the use of the hydrosilylation process in the synthesis of alkenyl derivatives of organosilicon compounds, using a wide spectrum of reagents, catalysts, and a comprehensive selection of reaction conditions. Thanks to this, it was possible to determine the area of effective application and limitations of hydrosilylation processes of unsaturated $C\equiv C$ bonds in alkynes and conjugated 1,3-diyne. This also resulted in the development of more optimal and sustainable methods (i.e. one-pot) synthesis of selected alkenyl derivatives of organosilicon compounds.

3. Determination of the areas of application of hydrosilylation catalysts for individual groups of compounds containing $C\equiv C$ bonds:

- it has been demonstrated that $PtO_2/XPhos$ is an effective catalyst for the hydrosilylation of a wide range of terminal alkynes with various functional groups. With its use reactions with all organosilicon compounds described in this report were successfully carried out.
- Karstedt catalyst was effective for Si-H addition to a wide spectrum of internal alkynes. It showed high selectivity in reactions with terminal ethynylsilanes and germananes. The expected products using it were obtained as a result of the reaction of terminal borylalkyne **2a** with triphenylsilane. Moreover, it was characterized by the highest

selectivity in hydrosilylation of one C≡C bond in 1,3-diynes with disiloxanes and silsesquioxanes. It was the only catalyst that could be used to obtain buta-1,3-dienes by hydrosilylation of both C≡C bonds with silsesquioxane (HSiMe₂O)(*i*-Bu)₇Si₈O₁₂. However, it turned out to be ineffective in the hydrosilylation of internal alkynes H₃COOCC≡CCOOCH₃ and ClCH₂C≡CCH₂Cl with triethylsilane.

- Pt(PPh₃)₄ was successfully used in the hydrosilylation of internal borylalkynes with silanes HSiR₃. It also worked well for selected examples of hydrosilylation of terminal alkynes, and one C≡C bond of 1,3-diynes with silsesquioxanes.

- using Ru(CO)Cl(H)(PCy₃)₂, the highest selectivity was achieved for the reaction of terminal borylalkyne **2a** with triethylsilane for the process carried out at room temperature;

- using a PtO₂ catalyst, the product of hydrosilylation of the internal alkyne H₃COOCC≡CCOOCH₃ with triethylsilane was obtained. Analogous reactions with silsesquioxane (HSiMe₂O)(*i*-Bu)₇Si₈O₁₂ and spherosilicate (HSiMe₂O)₈Si₈O₁₂ led to a complex mixture of products. The remaining catalysts were not active in this reaction;

- in the reaction of the internal alkyne ClCH₂C≡CCH₂Cl with triethylsilane, the hydrosilylation product was obtained only in the presence of PtCl₂. Analogous reactions with silsesquioxane (HSiMe₂O)(*i*-Bu)₇Si₈O₁₂ and spherosilicate (HSiMe₂O)₈Si₈O₁₂ led to a complex mixture of products.

- the activity of the [CpRu(CH₃CN)₃][PF₆] catalyst was characterized, which was the only catalyst among all tested in the hydrosilylation of borylalkynes that led to the Si-H syn-addition, directing the silyl group to the α atom in the case of terminal bonds and to the β atom in the case of C≡C internal bonds. Using the remaining platinum catalysts and Ru(CO)Cl(H)(PCy₃)₂, the second syn-addition isomer was obtained.

4.5. References

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5. Presentation of significant scientific activity carried out at more than one university, scientific or cultural institution, especially at foreign institutions

During my scientific career, I completed two research internships in foreign research units. The first internship in the period 04-07.2009 (4 months) was carried out in the group of Prof. Maria Rosario-Ribeiro at the Instituto Superior Tecnico, Dep. Engenharia Química e Biológica at the Universidade de Lisboa (Lisbon, Portugal), as part of the Lifelong Learning Program - Erasmus. During the internship, studies on the use of silsesquioxanes in ethylene polymerization were performed ("*Silsesquioxanes - application in ethylene polymerization*").

The second internship was in the period 01.2012-06.2012 (6 months), in the group of Prof. Krzysztof Matyjaszewski, at the Department of Chemistry, Carnegie Mellon University (Pittsburgh, United States), as part of the Ventures project awarded by the Foundation for Polish Science. The topic of performed work was "*The use of silsesquioxanes in the synthesis of modern hybrid polymers using the atom transfer radical polymerization (ATRP) process*". As a result of this cooperation, three scientific articles were published:

1. "Synthesis of high molecular weight polymethacrylates with polyhedral oligomeric silsesquioxane moieties by atom transfer radical polymerization", **Adrian Franczyk**, Hongkun He, Joanna Burdyńska, Chin Ming Hui, Krzysztof Matyjaszewski*, Bogdan Marciniak*, *ACS Macro Letters* **2014**, *3*, 799-802. (DOI: 10.1021/mz5003799 2).
2. "Polymethacrylates with polyhedral oligomeric silsesquioxane (POSS) moieties: influence of spacer length on packing, thermodynamics, and dynamics", Stelios Alexandris,

Adrian Franczyk, George Papamokos, Bogdan Marciniak, Krzysztof Matyjaszewski, Kaloian Koynov, Markus Mezger, George Floudas*, *Macromolecules*, **2015**, *48* (10), 3376–3385 (DOI: 10.1021/acs.macromol.5b00663).

3. “*Dynamic heterogeneity in random copolymers of polymethacrylates bearing different polyhedral oligomeric silsesquioxane moieties (POSS)*”, Stelios Alexandris, **Adrian Franczyk**, George Papamokos, Bogdan Marciniak, Robert Graf, Krzysztof Matyjaszewski, Kaloian Koynov, George Floudas*, *Macromolecules* **2017**, *50*(10), 4043-4053 (DOI: 10.1021/acs.macromol.7b00660).

Articles marked with numbers 2 and 3 have been enriched with research conducted in cooperation with the research groups of Prof. Kaloian Koynov from Physics of Interfaces, Max Planck Institute for Polymer Research (Mainz, Germany) and Prof. George Floudas from Soft Matter Physics Lab, Department of Physics, University of Ioannina (Ioannina, Greece).

Additionally, I completed two internships in chemical companies (one foreign, one domestic). The first one in the period 04.2007–09.2007 (6 months), at the Chemical Laboratory, Mitsubishi Chemical Group Science and Technology Research Center (Yokohama, Japan). As part of this internship, I completed a research project titled: “*Post-metallocene catalysts for ethylene polymerization*”. The scientific internship was carried out in the laboratory of the Mitsubishi Research and Development Center under the supervision of Dr. Fumihiko Shimizu.

I completed my second internship at the Cracking, Alkylation, and Lubricating Oils Laboratory at Orlen Laboratorium (Orlen, Plock). The internship aimed to become familiar with the methods and standards for determining the quality of oils produced by the Orlen concern (11.09 2006–29.09.2006, two weeks).

Throughout my academic career, I have published collaborative research articles with domestic and foreign research groups, including:

- Prof. Rebecca Mellen (Cardiff University, Cardiff, Great Britain),
“*Hydroelementation of diyne*”, Jędrzej Walkowiak*, Jakub Szyling, **Adrian Franczyk**, Rebecca L. Mellen*, *Chemical Society Reviews* **2022**, *51*(3), 869-994 (DOI: 10.1039/D1CS00485A).
- Prof. Krystyna Czaja and Prof. Marzena Białek (University of Opole)
“*Synthesis of bimetallic silsesquioxane complex of titanium(IV) and its polymeric counterpart and their catalytic properties in the polymerization of olefins*”,

Monika Pochwała, Marzena Białek*, **Adrian Franczyk**, Krystyna Czaja, Bogdan Marciniak, *Polimery*, **2016**, 61(9), 591–599.

- Prof. Krzysztof Pielichowski (Cracow University of Technology),

"*Polyurethanes modified with functionalized silsesquioxane – synthesis and properties*", Krzysztof Pielichowski*, Małgorzata Jancia, Edyta Hebda, Joanna Pagacz, Jan Pielichowski, Bogdan Marciniak, **Adrian Franczyk**, *Polimery* **2013**, 58(10), 783–793.

6. Information about teaching, organizational, and science achievements

6.1. Supervision of scientific works

So far, I have promoted one doctor of chemical sciences as an auxiliary supervisor. I am currently an assistant supervisor of two Ph.D. students. Under my supervision, four students completed their bachelor's theses, and other 5 theses I reviewed. During my scientific work, I supervised over 10 students conducting research at the Center for Advanced Technology of Adam Mickiewicz University, and previously at the Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University. It should be emphasized that as an employee of the Center for Advanced Technology of the Adam Mickiewicz University, I do not conduct teaching classes, and the above substantive care for students is carried out in cooperation with the Faculty of Chemistry of the Adam Mickiewicz University.

6.2. Conducting teaching classes

During my doctoral studies, I conducted classes for 4 years with students of the Faculty of Chemistry of Adam Mickiewicz University in the following subjects: Basics of inorganic chemistry - laboratories, Inorganic chemistry - calculation exercises.

I also conducted classes/seminars as part of bachelor's and doctoral theses. I am currently employed in a research position with no teaching hours assigned. However, I actively train students and Ph.D. students in the fields of organometallic chemistry, catalysis, and polymer chemistry.

6.3. Organization of events popularizing science

1. I participated in the work of organizing committees of national and international scientific conferences:

- a) The mission of chemo-, bio-, and nanotechnology at the Wielkopolska Center for Advanced Technology: materials and biomaterials, 28-29.11.2011, Poznan.
- b) 17th International Symposium on Homogeneous Catalysis - ISHC 17, 4-9.07.2010, Poznan;
- c) 5th International School on Molecular Catalysis – Organic and Polymer Synthesis and Catalysis, 12-16.08.2005, Poznan;
- d) The 16th International Symposium on Olefin Metathesis and Related Chemistry - ISOM XVI, 7-12.08.2005, Poznan.

2. As part of the ID-UB AMU project, I initiated the invitation of Prof. Chao-Jun Li from McGill University in Montreal, Canada, and Prof. Timothy Noel from the University of Amsterdam in the Netherlands. Their visit aimed to give lectures to the Adam Mickiewicz University community.

3. I helped organize a chemistry competition for secondary schools - conducting a competition for a group of students, 2006.

4. I took part in organizing the autumn and spring editions of laboratory workshops for secondary school students - academic year 2005-2006.

7. Apart from the information set out in 1-6 above, the applicant may include other information about his/her professional career, which he/she deems important

During my scientific career, my work was awarded the following distinctions:

2020-2023-financial support from the Excellence Initiative - Research University:

- Support for the most scientifically productive young scientists (“bonus for young”);
- Support for talent management - stopping brain drain;
- Support for the participation of scientists and Ph.D. students in prestigious scientific conferences;
- Support for publishing in prestigious scientific journals;

- Support for the internationalization of Adam Mickiewicz University - arrivals of outstanding foreign scientists as a part of the UAM Excellence Visiting Post-doctoral Researchers and UAM Excellence Visiting Professors programs - Short-term stay (up to 2 weeks).

2021 - Scholarship of the Minister of Education and Science for outstanding young scientists;

2019 - Team Award of the Rector of Adam Mickiewicz University for scientific achievements (1st degree).

2018 - Team Award of the Rector of Adam Mickiewicz University for scientific achievements (2nd degree).

2015 - Laureate of the START Program financed by the Foundation for Polish Science.

2015 - distinction in the competition: Awards of the City of Poznan for outstanding master's or doctoral thesis, competition organized by the City of Poznan, 2015 edition.

2014 - distinction for a scientific report entitled "Polymerization of POSS-MA by ATRP" awarded at the POLYMAT60 International Conference, Zabrze, Poland.

2013 - Scholarship support for Ph.D. students in fields considered strategic from the point of view of the development of Wielkopolska, awarded by the Provincial Labor Office in Poznan.

2012 - Scholarship from the Foundation Kulczyk family for doctoral students of the Adam Mickiewicz University.

2012 - distinction for a scientific communication entitled "*Synthesis of mono- and difunctionalized silsesquioxanes*" awarded at the Sixteenth International Symposium on Silicon Chemistry (ISOS XVI), McMaster University, Hamilton, Ontario, Canada.

2012 - A pro-quality scholarship awarded by the Rector of Adam Mickiewicz University for doctoral students for their outstanding research and teaching work.

2010-2012 - Ventures program awarded by the Foundation for Polish Science.

2009-2012 - AMU Rector's scholarship for the best Ph.D. students.

2010 - Scholarship support for Ph.D. students in fields considered strategic from the point of view of the development of Wielkopolska, awarded by the Provincial Labor Office in Poznan.

2007 - Scholarship of the Minister of Education and Higher Education for achievements in science and research.

Adrian Franczyk
(the applicant's signature)