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Coupling agents with 2,4,6,8-tetramethylcyclotetrasiloxane core – synthesis and application in styrene–butadiene rubber production†

Tomasz Sokolnicki, [iD] [a,b] Adrian Franczyk, [iD] [a] Radosław Kozak[c] and Jędrzej Walkowiak [iD] *[a]

A facile one-pot procedure for the functionalization of 2,4,6,8-tetramethylcyclotetrasiloxane **DH₄** to branched organosilicon compounds **DSP₃** or **DS₃P** bearing various, but clearly defined, numbers of silyl groups with an affinity to silica (**S**) and organic groups (alkyl, alkenyl, perfluoroaryl, epoxy, ether and ester) capable of bonding with polymers (**P**) has been demonstrated. Sequential hydrosilylation of allyltrimethoxysilane in the first step and olefin or alkyne in the second (and reverse order of reagents) has been applied in the presence of Karstedt's catalyst, which is commercially available and commonly used in industry. The developed procedure permitted the synthesis of 13 new, branched organosilicon compounds **DSP₃** and **DS₃P** with excellent yields and precise distribution of functional groups. All products were easily isolated by simple filtration followed by drying under reduced pressure and fully characterized by spectroscopic methods (¹H, ¹³C, ²⁹Si NMR, IR) and mass spectrometry (ESI or MALDI). The obtained compounds, because of the presence of two different functional groups with an affinity to inorganic filler and polymer matrix, are regarded as versatile silica modifiers, silane coupling agents for various applications, and starting materials in the preparation of polymer networks and vapor-deposited coatings. The vulcanizates prepared using cyclosiloxane-functionalized rubber showed enhanced rolling resistance and wet skid resistance, proving the compound's potential in producing novel "Green Tire" treads.

Introduction

Over the years, silica and other inorganic fillers have become important reinforcing agents in the synthesis of organic–inorganic hybrid materials.[1,2] The main problem those siliceous fillers generate for industrial applications is related to their hydrophilic nature, which causes difficulties in processing with hydrophobic polymers. Silica particles easily adhere to each other through hydrogen bonding between silanol groups and create agglomerates. Therefore, modification of the silica surface is required to overcome filler–filler interactions and improve filler-polymer compatibility. For this purpose, silane coupling agents (SCAs), which are bifunctional organosilicon compounds, are used. They belong to the most frequently used silica modifiers.[3] These compounds contain two functional end-groups capable of forming covalent bonds with both organic and inorganic substances. One of these groups is a silicon atom with easily hydrolyzable groups (typically alkoxy, acyloxy, or halogen atoms). The other constitutes an organic moiety with an affinity to polymers. Functionalization of the silica surface with SCAs greatly increases the hydrophobicity of the filler and facilitates its dispersion in polymers. Consequently, the introduction of a silica/silane system into polymer matrices improves the mechanical, dynamic, and heat resistance of filled resins and rubbers.[4] On the other hand, SCAs are also commonly applied as adhesion promoters, which are used in the production of adhesives, coatings, dental fillings, films, paints, and inks. Other applications involve cross-linking action (polymer networks, wire insulations), catalyst immobilization, and binding of biomaterials. The global SCAs market is expected to grow from USD 1.2 billion in 2021 to USD 1.6 billion by 2026, indicating the huge applicability of these organosilanes in academia and various branches of industry.[5] Accordingly, a constant demand for new molecules with interesting properties has been observed in recent years.[6,7]

[a]Center for Advanced Technology, Adam Mickiewicz University, Uniwersytetu Poznańskiego 10, 61-614 Poznań, Poland. E-mail: jedrzejw@amu.edu.pl
[b]Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland
[c]Synthos S.A., Chemików 1, 32-600 Oświęcim, Poland

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The catalytic hydrosilylation reaction, which refers to the addition of silicon hydrides across multiple bonds, is a fundamental transformation in the synthesis of organosilicon fine chemicals, silicones, and SCAs.[8] Bifunctional organosilanes able to act as coupling agents can be obtained by the hydrosilylation of two different substrates with silane, which has more than one Si–H bond. Several methodologies for the synthesis of such reagents with various alkenes and alkynes using different Si–H donors, including 1,1,3,3-tetramethyldisiloxane (having two Si–H bonds)[9] and silsesquioxanes (having eight Si–H bonds)[10,11] have recently been described. Herein, we would like to expand the library of new bifunctional silanes obtained by the functionalization of 2,4,6,8-tetramethylcyclotetrasiloxane (DH_4) (bearing four Si–H bonds) with two different unsaturated substrates: allyltrimethoxysilane and another olefin or alkyne. Such molecules have potential applications as silica modifiers, SCAs or substrates in the synthesis of polymer materials.

DH_4 is an example of a cyclic siloxane. This class of compounds is described by the general formula $(SiR_2O)_n$. They might be regarded as silicon analogs of crown ethers, since they form different-sized rings of alternating silicon and oxygen atoms, with various side chains (R = hydrogen atoms, alkyl, or vinyl groups) attached to silicon.[12] These compounds are characterized by flexibility, high strength of Si–O bonds, and high reactivity under specified conditions in miscellaneous organic reactions, *i.e.*, hydrolysis,[13] halogenation,[14] dehydrogenative couplings,[15,16] silylative coupling,[17,18] alkylative cleavage,[19] Piers–Rubinsztajn reaction,[20] ring-opening polymerizations,[21,22] and hydrosilylation.[23–39] 8-Membered compounds such as DH_4, because of the possible modification of peripheral Si–H groups by a hydrosilylation reaction, have opened access to several functional materials. While cyclosiloxanes have been utilized as substrates in the synthesis of dendritic molecules,[40] films[41,42] and coatings,[30,43] sensors,[44,45] liquid crystallines,[46,47] electrolytes,[48] ceramics,[49] and membranes,[50] there are no reports of their use as precursors of silica modifiers or coupling agents. The addition reactions of DH_4 to various olefins have been the subject of numerous reports. The most widely described group of products is DR_4 derivatives, which have four identical groups pendent from the cyclosiloxane core and are obtained by hydrosilylation between DH_4 and unsaturated compounds, including non-functional aliphatic olefins,[38,51] perfluoroalkenes,[23] cycloalkenes,[32] alkenylbenzenes,[24,27,39] allyl alcohol derivatives,[28,34] allylamines,[35,37] alkenyl acid esters,[31,33] vinylsilanes,[25,29,36] and alkynes.[26] Hydrosilylation reactions focused on the modification of DH_4 with two different substrates (olefin or alkyne) leading to products with different content of the groups DSP_3, DS_2P_2 or DS_3P are a more challenging task, definitely less frequently described in the scientific journals, and mainly disclosed in the patent literature.[52–58] Nevertheless, it must be noted that the distribution of both groups coming from two starting materials in the structures of synthesized products is often random. Moreover, detailed characterization of these compounds by NMR methods has not been provided in the

majority of these reports. Therefore, it is impossible to elucidate the precise structure of bifunctional products and the distribution of both groups attached to the cyclosiloxane core. As a result, there has been no reliable method of the synthesis of 2,4,6,8-tetramethylcyclotetrasiloxane derivative with DRR'_3 structure reported in the literature.

Bearing in mind the above-quoted facts about the application and synthesis of modified 2,4,6,8-tetramethylcyclo-tetrasiloxane, as well as the poor selectivity and unclear synthetic protocols for providing bifunctional compounds, here we present a one-pot synthetic protocol for the preparation of a wide gamut of functional organocyclotetrasiloxanes by platinum-catalyzed hydrosilylation of olefins and alkynes. The developed strategy involves the modification of DH_4 in two steps: (i) reaction of DH_4 with olefin possessing alkoxysilyl groups that allow for binding with silica (**S**), leading to a mono-decorated silyl derivative DH_3R with three active Si–H bonds, which then in the second step (ii) react with alkenes or alkynes, which have groups capable of bonding with polymers (**P**). This pathway leads to derivatives with a DSP_3 structure. Another procedure using both reagents in the reverse order produced coupling agents with a DS_3P structure.

This work constitutes the first example of the synthesis of 2,4,6,8-tetramethylcyclotetrasiloxanes DSP_3 or DS_3P with a well-defined number of functional groups supported by comprehensive NMR, IR, and MS characterization of the synthesized compounds. Moreover, application tests of a selected compound in the production of "Green Tires" are presented.

Experimental

General procedure for the one-pot hydrosilylation of 2,4,6,8-tetramethylcyclotetrasiloxane DH₄ with olefin 2a–c and allyltrimethoxysilane 2d – synthesis of silane coupling agents 5a–5c

The syntheses of compounds were conducted in two steps in a one-pot mode.

Step I. Anhydrous toluene (2 mL) was placed in the oven-dried Schlenk vessel equipped with a magnetic stirrer. Then, 2,4,6,8-tetramethylcyclotetrasiloxane DH_4 (6 equiv., 1.5 mmol, 370 μL), olefin **2a–c** (0.25 equiv., 0.25 mmol), and Karstedt's catalyst solution (2.5×10^{-4} mmola Pt, 3 μL) were added sequentially. The reaction was carried out at 50 °C for 24 hours. The total conversion of olefin was confirmed by GC-MS analysis. Volatiles (the solvent and the excess of cyclic siloxane) were evaporated and the residue was dried under reduced pressure and used directly in step II.

Step II. The intermediates **4a/4b/4c** were redissolved in a new portion of toluene (2 mL). Next, allyltrimethoxysilane **2d** (3 equiv., 0.75 mmol, 130 μL), and Karstedt's catalyst solution (7.5×10^{-4} mmola Pt, 9 μL) were injected into the Schlenk vessel and the reaction was conducted at 100 °C for 24 hours. The post-reaction mixture was then passed through a plug of Cellite®. The final products were isolated after concentration on a rotatory evaporator and dried under reduced pressure.

Hydrosilylation of 2,4,6,8-tetramethylcyclotetrasiloxane DH$_4$ with allyltrimethoxysilane 2d and second olefin 2a–c, 2e–h – synthesis of silane coupling agents 5d–5j

The syntheses were carried out using an analogous procedure to that described in the previous section, but allyltrimethoxysilane **2d** was applied in step I (leading to intermediate **4d**), and another olefin **2a–c**, **2e–h** (3 equiv.) in step II.

Hydrosilylation of 2,4,6,8-tetramethylcyclotetrasiloxane DH$_4$ with allyltrimethoxysilane 2d and alkyne 2i–k – synthesis of silane coupling agents 5k–5m

The syntheses were carried out using an analogous procedure to that described in the previous section, but alkyne **2i–k** (3 equiv.) was used instead of olefin in step II, and both steps were conducted at 50 °C.

Results and discussion

The selective functionalization of **DH$_4$** with two different substrates is challenging, due to the presence of four reactive Si–H bonds. Moreover, hydrosilylation of alkenes or alkynes with this reagent can lead to different constitutional isomers. Dehydrogenative silylation, olefin isomerization, or oligomerization are possible side reactions promoted by transition metal catalysts. Another problem constitutes the control of Si–H polyaddition to two different substrates, which may result in the formation of mixtures of products with different (very random) distributions of both functional groups (**DR$_2$R′$_2$**, **DR$_3$R′**, **DRR′$_3$**, and others with Si–H bonds that are not fully reacted). Taking into consideration the process's complexity, the proper selection of the catalytic system seems to be of major importance. Due to its excellent effectivity and high functional group tolerance, Pt-catalyzed hydrosilylation has been recognized as one of the most important reactions of homogeneous catalysis, allowing for the synthesis of a plethora of organosilanes and silicons. Therefore, based on reports in the literature and our previous experience[59–65] in the synthesis of functionalized silanes *via* hydrosilylation reactions, we selected Karstedt's catalyst [Pt$_2$(dvs)$_3$, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane] for our research.

In the first stage of our studies, to prove the effectivity of Karstedt's catalyst, we carried out the reaction of **DH$_4$** with an excess of 1-hexene **2a** (5 equiv.), leading to **DR$_4$** derivative **3**. The reaction was conducted in anhydrous toluene in the presence of [Pt$_2$(dvs)$_3$] (1×10^{-3} mmol Pt/1 mmol of Si–H bond) at 100 °C for 24 hours (Table 1, entry 1). Tetrahexyl derivative (**3**) was isolated by filtration through a short plug of Cellite® and dried under reduced pressure, giving the product in excellent 97% yield. ^{1}H and ^{13}C NMR analyses of the pure product confirmed the exclusive formation of the *anti*-Markovnikov product. On the other hand, the multiplicity of signals around 20 ppm on ^{29}Si NMR may imply that the product exists as a mixture of *cis–trans* isomers with different spatial arrangements of methyl and *n*-hexyl groups on silicon centers. Next, our efforts were focused on the introduction of only one ali-

Table 1 Modification of 2,4,6,8-tetramethylcyclotetrasiloxane DH$_4$ *via* hydrosilylation of alkenes **2a–d** in the presence of Pt$_2$(dvs)$_3$ – synthesis of DR$_4$ model compound **3** and SCAs precursors DH$_3$R **4a–d**

Entry	Product	R	Isolated yield of 3 or 4 [b] [%]
1	**3**		97[a]
2	**4a**		94[c]
3	**4b**		92[c]
4	**4c**		90[c]
5	**4d**	Si(OMe)$_3$	93[c]

Reaction conditions: $[\mathbf{DH_4}] : [\mathbf{2}] : [\mathbf{Pt}] = 6 : 1 : 2.5 \times 10^{-4}$, 50 °C, 24 h. [a] Reaction conditions: $[\mathbf{DH_4}] : [\mathbf{2}] : [\mathbf{Pt}] = 1 : 5 : 1 \times 10^{-3}$, 100 °C, 24 h, anhydrous toluene, total conversions of reagents were confirmed by ^{1}H NMR; the selectivity was determined by GC-MS, and ^{1}H, ^{13}C, ^{29}Si NMR. [b] The products exist as a mixture of stereoisomers. [c] Yields based on the amount of alkenes.

phatic chain into the cyclosiloxane ring. Substrates with more than one Si–H bond suffer from the possible uncontrolled polyaddition of Si–H bonds to the unsaturated substrates, giving mixtures of products with a different number of hydrogens and alkyl groups attached to the silicon atoms. Therefore, the hydrosilylation of 1-hexene (**2a**) with an excess of 2,4,6,8-tetramethylcyclotetrasiloxane (**DH$_4$**) was conducted to verify the feasibility of incorporation of only one *n*-hexyl group into the cyclotetrasiloxane ring and to check the stability of targeted compounds with reactive Si–H functionalities. Indeed, applying 6 equiv. excess of **DH$_4$** to 1-hexene (**2a**) resulted in the formation of the hydrosilylation product DH$_3$(*n*-hexyl) decorated with one *n*-hexyl chain **4a** in 94% yield (Table 1, entry 2). In this case, milder conditions compared to the synthesis of the tetra-*n*-hexyl product **3** (lower temperature of 50 °C and lower catalyst concentration of 2.5×10^{-4} mmol Pt/1 mmol of Si–H bond) were applied. Moreover, we observed that 6-fold excess of **DH$_4$** was required to prevent the formation of adducts with more than one Si–H bond reacted. Decreasing the volume of **DH$_4$** resulted in a higher content of DH$_2$(*n*-hexyl)$_2$ in the post-reaction mixture. The excess of **DH$_4$** was

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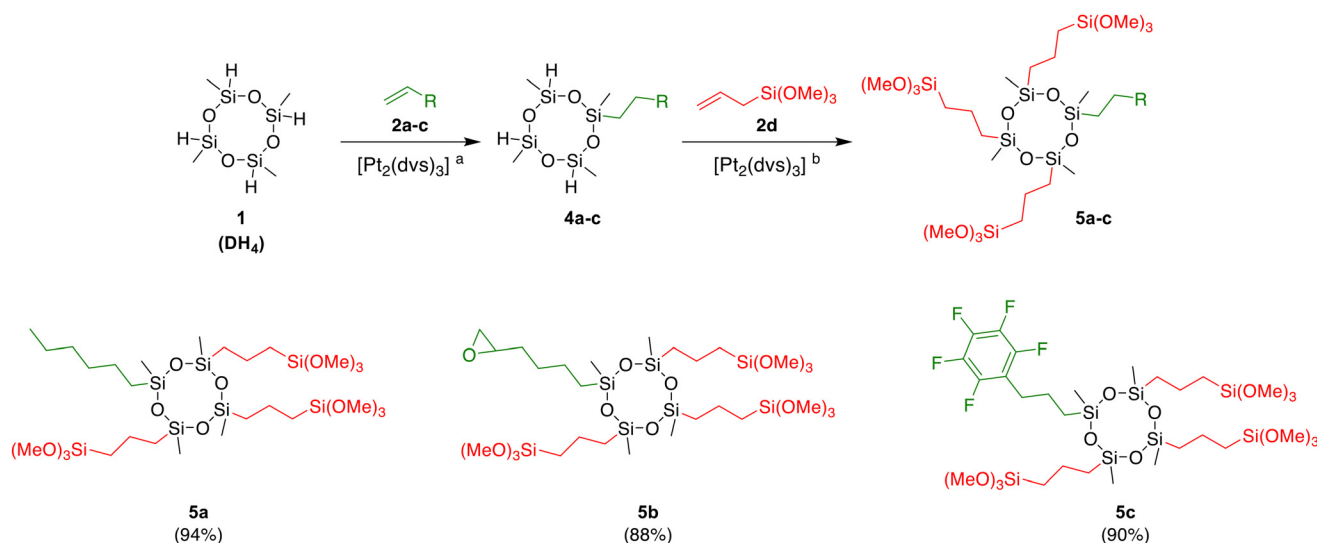*Inorg. Chem. Front.*, 2023, **10**, 5897–5907 | **5899**

removed by fast and simple trap-to-trap distillation which allows its reuse in further tests. GC-MS and NMR techniques confirmed that distillate collected in a cold trap contained only **DH₄**, and other low boiling cyclosiloxane derivatives or products of **DH₄** decomposition were not observed.

On the other hand, analyses of the isolated product **4a** showed that only traces of by-product **DH₂(*n*-hexyl)₂** with two aliphatic arms in its structure had been formed. An analogous procedure was followed for the reactions with 1,2-epoxy-5-hexene **2b**, allylpentafluorobenzene **2c**, and allyltrimethoxysilane **2d**. Targeted products **4b–d** were obtained in 92%, 90%, and 93% yields respectively. The compounds **4a–c** were next subjected to hydrosilylation reactions with allyltrimethoxysilane **2d** (3 equiv.), giving potential silica modifiers (**5**) equipped with one arm with affinity to polymer matrices and three pendent organosilicon moieties (**DS₃P** modifiers) capable of hydrolysis and condensation with OH-rich materials, *e.g.*, silica and other siliceous fillers (Scheme 1).

Products **5a–c** were isolated with excellent yields (94%, 88%, and 90% respectively). Similar results were obtained when the syntheses were repeated in a one-pot procedure, without isolation of the intermediates **4a–c**. Therefore, the next experiments were carried out according to this method (Scheme 2). After completion of the first step, volatiles were removed under reduced pressure, and then a new portion of the solvent, alkene **2a–c**, **2e–h** or alkyne **2i–k** (3 equiv.) and the catalyst solution were added, followed by immediate placement of the reaction vessel in an oil bath heated to 50 °C. Using the described method, three new organocyclosiloxanes with one silylpropyl group and three alkyl **5a**, alkyl epoxide **5b** or perfluoroaryl **5c** chains were synthesized. The desired products with the **DS₃P** structure were obtained with an excellent

yield of 88–94% after filtration through a pad of Cellite and drying under reduced pressure.
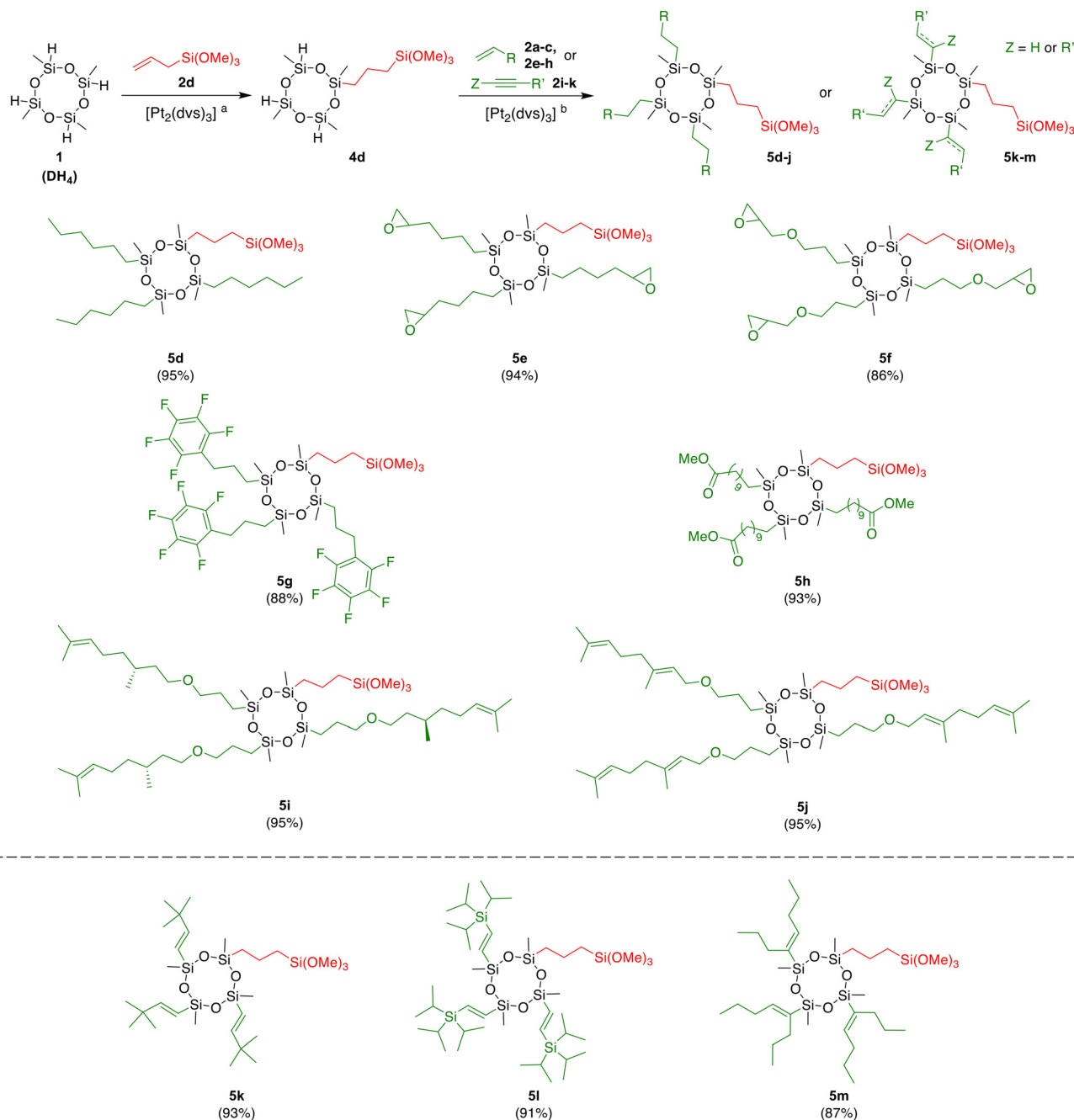
In the next step of our research, we focused on the synthesis of new silanes equipped with one organosilicon moiety, capable of modifying the surface of inorganic fillers, and three moieties reactive towards polymers (**DSP₃** modifiers). For this purpose, we applied the reverse order of reactions. First, the reaction of **DH₄** with allyltrimethoxysilane (**2d**) furnished the intermediate **4d**, which after the evacuation of volatiles was used as the substrate in the second step (Table 1, entry 5). Based on our previous work on the hydrosilylation of various substrates with different silanes, we selected olefins **2a–c**, **2e–h** with groups with an affinity to polymers (alkenyl, epoxy, perfluoroaryl, ester), which might react with compound **4d** in the presence of Karstedt's catalyst, giving access to the new molecules. Such compounds have potential as attractive additives or modifiers in materials chemistry and in various branches of industry. All hydrosilylation experiments between compound **4d** and olefins **2a–c**, **2e–h** (3 equiv.) were carried out in anhydrous toluene at 100 °C for 24 h. The total conversion of reagents was confirmed by ¹H NMR spectroscopy. Moreover, the equimolar ratio of reagents permitted simplification of the separation procedure. Products were isolated using the aforementioned procedure, giving viscous oils with excellent yields (Scheme 2). The hydrosilylation of 1-hexene **2a** furnished compound **5d** in an almost quantitative yield (95%). Although this compound does not possess a chemical group with an affinity to polymers, it may be considered a hydrophobing agent. Further reactions conducted with 1,2-epoxy-5-hexene **2b** and allyl glycidyl ether **2e** led to the cyclotetrasiloxanes **5e** and **5f**, equipped with a reactive epoxy group in 94% and 86% yields, respectively. Silanes functionalized with oxirane rings are

Scheme 1 Synthesis of new organocyclosiloxanes **DS₃P** from 2,4,6,8-tetramethylcyclotetrasiloxane **DH₄** by one-pot hydrosilylation of alkenes **2a–c** (I step) and allyltrimethoxysilane **2d** (II step). ᵃReaction conditions: [**DH₄**] : [**2a–c**] : [**Pt**] = 6 : 1 : 1 × 10⁻³, 50 °C, toluene, 24 h. ᵇReaction conditions: [**4**] : [**2d**] : [**Pt**] = 1 : 3 : 3 × 10⁻³, 100 °C, toluene, 24 h. Conversion and structure of products were confirmed by ¹H, ¹³C, ²⁹Si NMR, and MS (MALDI or ESI). The isolated yields are presented in brackets. The products exist as a mixture of stereoisomers.

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Scheme 2 Synthesis of new organocyclosiloxanes DSP_3 from 2,4,6,8-tetramethylcyclotetrasiloxane DH_4 by one-pot hydrosilylation of allyltri-methoxysilane **2d** (I step) and alkenes **2a–c**, **2e–h** or alkynes **2i–k** (II step). [a]Reaction conditions: $[DH_4] : [2] : [Pt] = 6 : 1 : 1 \times 10^{-3}$, 50 °C, toluene, 24 h. [b]Reaction conditions: $[4] : [2] : [Pt] = 1 : 3 : 3 \times 10^{-3}$, 100 °C (50 °C when alkynes were applied in the second step), toluene, 24 h. Conversion and structure of products were confirmed by ^{1}H, ^{13}C, ^{29}Si NMR, and MS (MALDI or ESI). The isolated yields are presented in brackets. The products exist as a mixture of stereoisomers.

essential components of modern resins, coatings, adhesives, and other epoxy-containing hybrid organic–inorganic materials.[66,67] The hydrosilylation of allylpentafluorobenzene **2c** with **4d** resulted in the formation of derivative **5g** with three perfluoroaryl moieties in 88% yield. Fluorosilanes are commonly known for their wide applicability in the preparation of superhydrophobic materials.[68,69] The developed strategy was

also compatible with compounds that have ester moieties in their structures. The hydrosilylation of methyl 10-undecenoate **2f** furnished long-chain functionalized cyclotetrasiloxane **5h** in 93% yield. We also investigated the hydrosilylation of unsymmetrical allyl ethers derived from citronellol **2g**, and geraniol **2h**, which have one and two trisubstituted C=C bonds in their structures, respectively. The addition of Si–H bonds of inter-

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mediate **4d** to these bio-based substrates proceeded chemoselectively on allyl endings, producing β-isomers exclusively. Competitive hydrosilylation of more substituted terpene multiple bonds was not observed. The products **5i** and **5j**, which have alkenyl functionalities, were obtained with excellent isolated yields (95%). The synthesis of new additives of high implementation potential from naturally occurring compounds rather than petrochemical resources complies with the Sustainable Goals highlighted by the United Nations. Coupling agents with alkenyl moieties have been reported as valuable fiber modifiers in thiol–ene click reactions,[70] and were also used in the synthesis of nanocomposites by copolymerization.[71]

Another approach which also led to cyclosiloxane modifiers fitted with unsaturated moieties was the hydrosilylation of alkynes **2i–k** with compound **4d**. All reactions were performed using analogical reaction conditions, previously optimized for olefins; however, alkynes seemed to be more reactive and 50 °C was sufficient to achieve the total conversion of reagents (100 °C was applied for olefins). Very good yields were observed for the three starting materials tested. Hydrosilylation of 3,3-dimethyl-1-butyne **2i** with **4d** led to regio- and stereoselective addition of Si–H across carbon–carbon multiple bonds with the predominant formation of (E)-isomer **5k** ($^3J_{H-H}$ = 19.1 Hz) in 93% yield. On the other hand, the presence of a silicon atom in the alkyne structure impaired the selectivity of the reaction. Hydrosilylation of (triisopropylsilyl)acetylene **2j** afforded product **5l** bearing three alkenyl arms in 91% yield (mixture of geometric isomers). For internal alkenes, *cis*-hydrosilylation occurred, giving the product **5m** in 87% yield, obtained by the reaction of compound **4d** with 3 equiv. of 4-octyne **2k**.

All organocyclosiloxanes obtained by the selective modification of 2,4,6,8-tetramethylcyclotetrasiloxane **DH₄** with two different substrates were synthesized with very good to excellent yields. They were fully characterized by spectroscopic methods (^{1}H, ^{13}C, ^{29}Si NMR, IR) and mass spectrometry (ESI or MALDI). In particular, ^{29}Si NMR analysis is of crucial importance in the identification of such systems, as it permits fast differentiation between the possible products (Fig. 1). 2,4,6,8-Tetramethylcyclotetrasiloxane **DH₄** displays one signal split into four resonance peaks around −32 ppm, while 2,4,6,8-tetrahexyl-2,4,6,8-tetramethylcyclotetrasiloxane **3** shows a signal shifted to *ca.* −20 ppm, which is also visible in the form of four peaks. On the other hand, cyclotetrasiloxane derivative decorated with one *n*-hexyl arm **4a** is characterized by a signal at −16.6 ppm, representing the silicon atom substituted with two alkyl groups (Me and *n*-hex), and by a group of signals around −32 ppm, which correspond to three Si atoms with hydrogen and methyl groups bonded respectively (mixture of *cis–trans* stereoisomers). The ^{29}Si NMR spectrum of tetramethylcyclotetrasiloxane decorated with one propyltrimethoxysilyl moiety **4d** shows the same chemical shifts as the monohexyl-decorated compound. Additionally, it has a signal around −42 ppm, which comes from the trimethoxysilyl group. Ultimately, the final products with two types of silicon
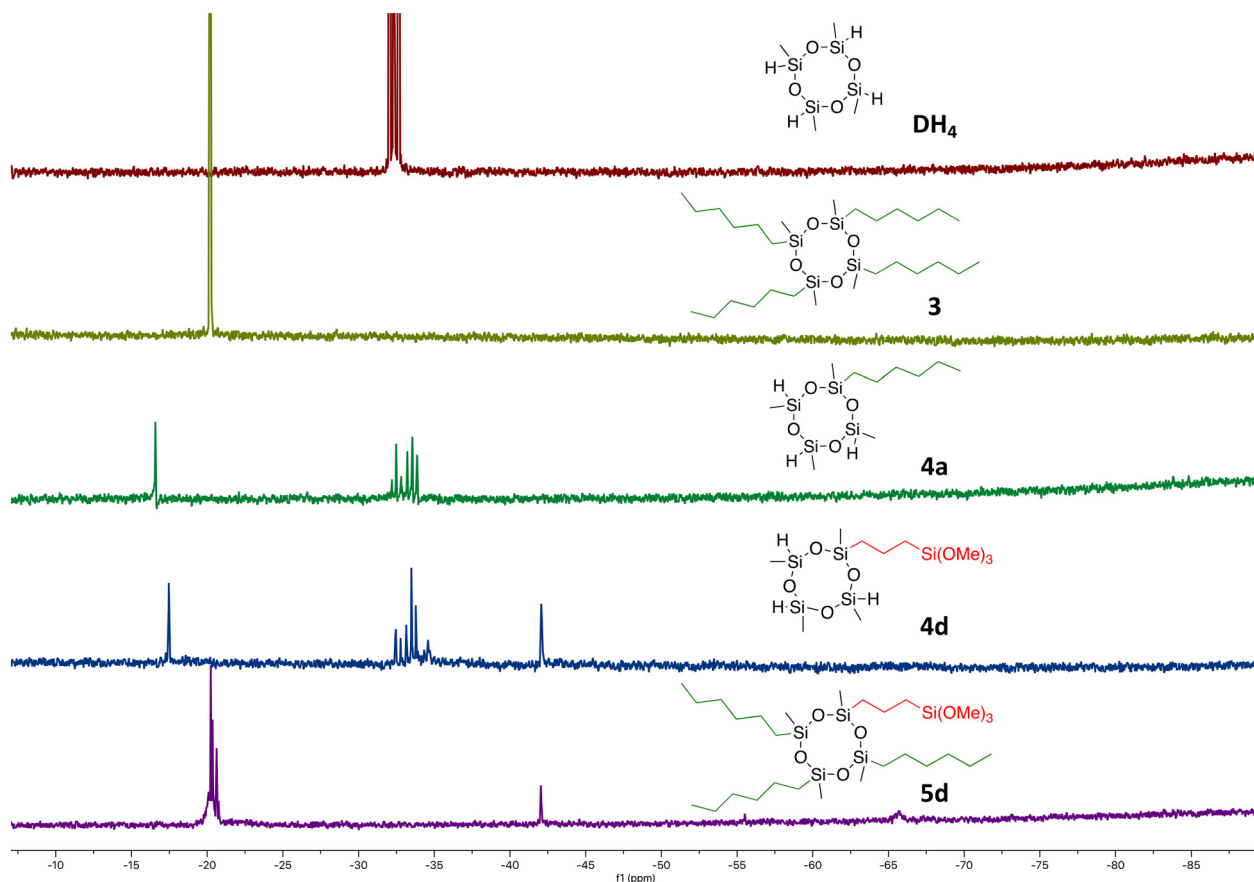
atoms in their structures **5d** can be distinguished by the presence of the two signals at *ca.* −20 and −42 ppm, coming from silicon atoms in the cyclosiloxane ring and the aliphatic external chain respectively.

The application of Karstedt's catalyst, which is simple, commercially available and of high industrial importance, allowed for the introduction of structurally different groups such as alkyl, alkenyl, epoxy, perfluoroaryl, ester and alkoxysilyl into the cyclosiloxane core. A series of new compounds have been synthesized for the first time (three compounds with the structure **DS₃P**, and 10 products with the structure **DSP₃**). The simple isolation procedure, which involves filtration of the post-reaction mixture through a short Cellite® plug and drying under reduced pressure is advantageous and reduces time-consuming purification steps. Moreover, the **DH₄** used in excess in the first step of the protocol can easily be evaporated under vacuum, condensed in a cooling trap and reused in the next syntheses. The proper management of reagents is important for the possible application of the procedure on a larger scale. Due to the presence of two reactive groups, these newly synthesized silanes might be considered potential silica modifiers, SCAs for various applications, or additives in the synthesis of polymers or vapor-deposited coatings.

To check the application potential of the synthesized products, in the final stage of our research, a representative example (chosen with the Synthos S.A. company specialized in the production of rubbers), compound **5e**, equipped with one organosilicon moiety (capable of forming stable bonds with silica) and three epoxy groups with an affinity to polymer was applied as an SCA in the synthesis of silica-filled styrene–butadiene rubber vulcanizates with the potential to produce "Green Tire" treads. Such tires are characterized by lower rolling resistance and enhanced wet grip compared to tires that only contain carbon black as a filler. Tires with low rolling resistance need less energy to keep rolling, which corresponds to decreased fuel consumption by mechanical vehicles and therefore contributes to the reduction of global emissions of CO_2 into the atmosphere. This is actually of a great importance due to the need to reduce the emission of greenhouse gases. On the other hand, the improvement in the dry handling and wet grip properties of car tire treads has a profound influence on driving comfort and safety. Tread parameters are highly dependent on the tire components and the coupling agents used in their production.

In this work, we decided to investigate the influence of the functionalization of Syntion 2150® rubber with cyclosiloxane SCA **5e** on the properties of the final composites and compare them with unmodified commercially available rubber. Modified rubber was prepared *via* anionic polymerization using *n*-butyl-lithium as an initiator (the detailed procedure is described in ESI, section 4.1†). Rubber compounds were prepared based on a model recipe for a passenger car tire tread using Syntion 2150® and Synteca 44® rubbers, silica as the main filler, and various processing additives.[72] Compounding of the rubbers was conducted in a Banbury-type internal mixer, while the final pass was completed on a lab-sized two-

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Fig. 1 ^{29}Si NMR analysis of products obtained by the modification of 2,4,6,8-tetramethylcyclotetrasiloxane **DH$_4$** *via* hydrosilylation reactions of 1-hexene **2a** and allyltrimethoxysilane **2d**.

roll mill. Next, rubber compounds and vulcanizates were subjected to several tests to determine their dynamic and mechanical properties (the detailed rubber characterization, compound composition, mixing procedure, and analytical methods used to characterize the compounds and vulcanizates are presented in the ESI, sections 4.2.–4.4. and Tables S1–S5†).

After preparing the rubber compounds, the Payne effect was measured using a rotorless shear rheometer (please see ESI, section 4.5., Tables S6, S7 and Fig. S58†). The Payne effect is an important parameter which can be considered a measure of filler micro-dispersion, as it is attributed to strain-induced breakage and recovery of weak physical bonding between filler clusters. The results show that the Payne effect for rubber functionalized with **5e** is lower than for unmodified rubber. The lower the value of the Payne effect, the better the micro-dispersion of the filler in the rubber compound, which usually corresponds to lower energy losses (lower values of the rolling resistance predictor). Next, rubber compounds were vulcanized at 170 °C (curing characteristics are presented in ESI, Table S8 and Fig. S59†) and mechanical and dynamic characterization of vulcanizates was carried out. Dynamic mechanical analysis (DMA) was performed with the aid of DMA 450 + Metravib with the attached 450 N load cell in shear. The loss factor (tan δ) and storage modulus (G') for vulcanizates as a function of temperature are
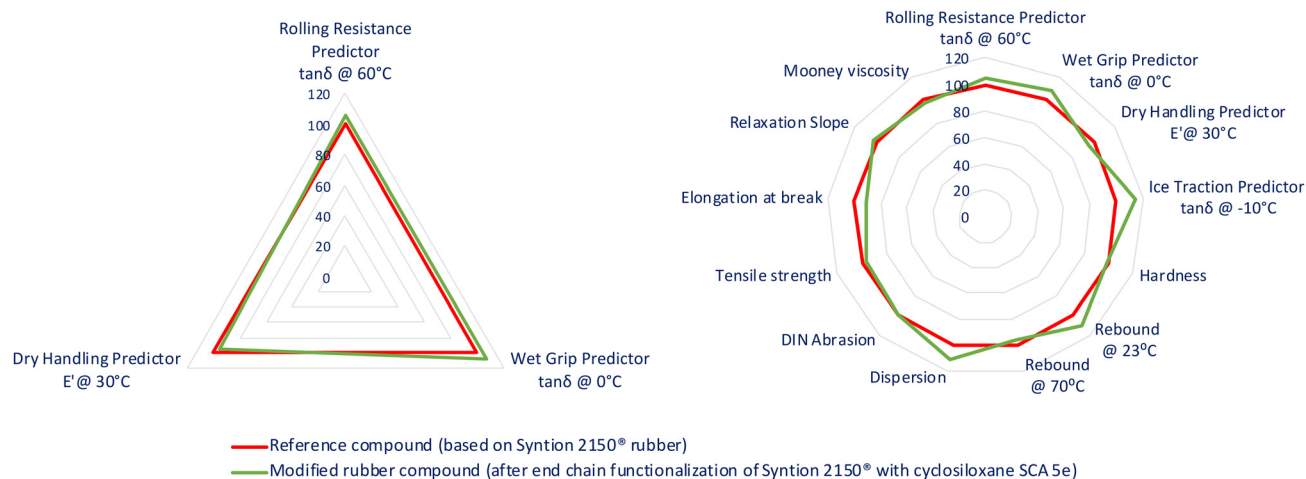
listed in ESI in Table S9† and depicted in Fig. S60.† The tire predictors were determined as follows: rolling resistance measured as tan δ at 60 °C, wet traction measured as tan δ at 0 °C, ice traction measured as tan δ at −10 °C and dry handling as G' at 30 °C. Crucial parameters for the development of new "Green Tire" rubbers prepared with the use of the synthesized cyclosiloxane coupling agent have been depicted in the form of a triangle chart, including rolling resistance, dry handling, and wet grip predictors, while all measured parameters are presented as a radar chart in Fig. 2 (please see also ESI, Table S10†).

It was observed that the rolling resistance of vulcanizates functionalized with **5e** was improved by 6% compared to that of unmodified vulcanizates, showing the compound's potential in the preparation of fuel-saving tire treads. Moreover, the wet grip and ice traction predictors for the modified rubber turned out to be enhanced by 7% and 15% respectively, which would have a positive impact on driving safety. Vulcanizates modified with **5e** were also characterized by improved filler dispersion and rebound at room temperature (by 11% for both parameters). Furthermore, the rubber's mechanical properties, *i.e.*, hardness, tensile strength, and abrasion resistance, were comparable to those of the unmodified rubber.

The improvement of rolling resistance and wet skid properties (wet grip and ice traction predictors) of vulcanizates

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Fig. 2 Results of tests performed for compounds and vulcanizates prepared with the application of rubber functionalized with cyclosiloxane coupling agent **5e** (in comparison with reference unmodified Syntion 2150® rubber.

prepared with the rubbers functionalized with a newly synthesized cyclosiloxane coupling agent confirmed the possibility of its application in the production of "Green Tire" treads. Reduced rolling resistance causes lower fuel consumption since less energy is being used as the tires roll along the road and therefore has a positive impact on the environment by reducing a vehicle's carbon footprint. On the other hand, wet grip properties are crucial parameters which influence road traction, directional control, and deceleration on wet and icy surfaces. Enhanced wet grip predictors indicate a shorter braking distance on slippery roads, which would significantly improve driving safety.

Currently, we are working on the synthesis of new compounds intended to improve the wear resistance of rubbers. The results of this investigation will be the subject of another article in a more specialized journal.

Conclusions

In conclusion, we have developed a one-pot procedure for the synthesis of new organosilanes by selective modification of 2,4,6,8-tetramethylcyclotetrasiloxane *via* the subsequent hydrosilylation reaction of two different substrates: allyltrimethoxysilane and another olefin or alkyne. The application of Karstedt's catalyst, which is highly effective and commercially available, permitted the incorporation of a wide spectrum of functional groups, including alkenyl, perfluoroaryl, ether, ester, and epoxy moieties, into the cyclotetrasiloxane core, leading to 13 new products in very high, almost quantitative yields. All compounds were isolated by simple filtration through a thin pad of Cellite® and drying under reduced pressure, which makes the target products easily accessible. Hydrosilylation of alkenes proceeded in a regioselective manner, giving *anti*-Markovnikov isomers as major products. The addition of **DH₃R** intermediates to sterically hindered

terminal alkyne led to the predominant formation of *trans* isomer, while hydrosilylation of silylacetylene gave a mixture of geometric isomers. All products were characterized by spectroscopic methods (^{1}H, ^{13}C, ^{29}Si NMR, IR) and by mass spectrometry (ESI or MALDI).

Due to the presence of two groups of different chemical reactivity – readily hydrolyzable organosilicon moiety and organic functions with an affinity to polymers – the synthesized compounds might be considered novel, versatile silica modifiers, coupling agents, or substrates in the synthesis of polymer networks or vapor-deposited coatings, potentially leading to materials with improved physicochemical properties.

To prove its application potential, cyclosiloxane coupling agent **5e** was applied in the functionalization of styrene–butadiene rubber (Syntion 2150®) *via* anionic polymerization. The obtained modified rubber was applied in the preparation of silica-reinforced vulcanizates intended for the production of "Green Tires". The final composites exhibited improved rolling resistance and wet grip properties compared to unmodified rubber, showing the potential of this compound in the manufacture of novel tire treads for the car industry that could reduce fuel consumption and CO_2 emissions.

Conflicts of interest

There are no conflicts to declare.

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