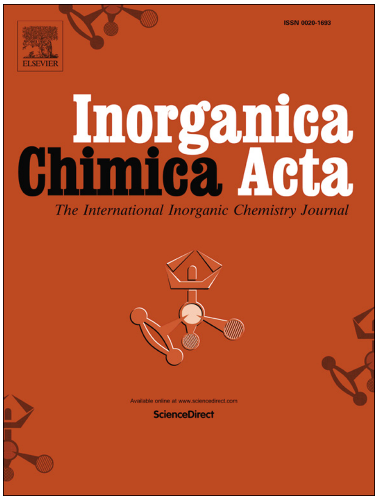

Research paper

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Synthesis of novel bifunctional organosilicon dendrons via platinum-catalyzed hydrosilylation

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Abstract: The synthesis of novel bifunctional organosilicon dendrons has been successfully achieved. The synthetic route is based on sequential platinum-catalyzed hydrosilylation reactions, that efficiently leads to the corresponding carbosilane dendrons containing a wide range of functional groups, such as –$OSiMe_3$, -Cl, -F and -COOCR. Finally, the core of these dendrons comprises reactive alkoxy groups that can be further used for grafting in various materials.

Keywords: hydrosilylation; platinum; dendrons; silanes; alkoxysilanes; synthetic methods

1. Introduction

Dendrons and dendrimers make an interesting class of compounds [1]. Their names come from the Greek word for tree. The molecules of these compounds resemble tree branches and have a unique three-dimensional molecular architecture connected to attractive properties like high degree of arrangement and multifunctionality [2–13]. In this respect, they are eye-catching and marketable for high-end sectors of the biochemical industry [14–19]. What is more, they play a significant role as the supports for the catalysts [20–23] and as the connectors between organic and inorganic species (hybrid materials) [24,25]. Alkoxysilanes are chemicals with several applications. Their use for silanization of various materials still is an active area of research . The formation of strong covalent bonds to different materials surfaces offers lots of advantages for many biochemical applications [26]. On the other hand, hydrosilylation is one of the most important synthetic methods for derivatization of organosilicon compounds [27–33]. It is compatible with atom economy strategy and widely used in industry. It provides simple pathway to a wide range of pharmaceuticals and fine-chemicals .

Herein, we present a detailed synthetic approach to a series of novel bifunctional carbosilane dendrons, including hydroxy, halogen, silyl, ester and perfluorinated ether groups as peripheral functional groups. The core of these dendrons is a mono or trialkoxy group that can be further used to modify surface of various materials. In our previous work we have synthesized a few monoalkoxy cored carbosilanes with amine and epoxy peripheral groups that were used in the silanization of glass surface.

2. Material and methods

2.1 General Information

Olefins, trivinylethoxysilane (95%), triethoxysilane (95%), tetravinylsilane (95%) 1,1,1,3,3,3-hexamethyldisilazane (98.5%), trivinylmethylsilane (95%), Karstedt catalyst and other chemicals used for experiments were purchased from Sigma-Aldrich Co., Gelest Inc. and ABCR GmbH & Co. KG and used without further purification. Reactions were carried out under air atmosphere. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance III HD NanoBay (400 MHz) spectrometer using C_6D_6 as solvent. GC analyses were performed on a Varian 3400 with a Megabore column (30 m) and TCD. Mass spectra of products were determined by GC-MS analysis on a Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and Finnigan Mat 800 ion trap detector. IR spectra were measured on a FT-IR Nicolet iS 50 spectrometer. HRMS were recorded using a hybrid QTOF instrument (AB Sciex, model 5600+). Ions were generated by electrospray ionization in a positive mode (ESI+) under the following conditions: a flow rate of 10 mL/min, a dry gas flow of 8 L/min, a nebulizer pressure of 1.5 bar, a spray voltage of 5200 V, and a drying gas temperature of 200 ^{o}C. Analyst 1.6 TF software (AB Sciex) was used to process the raw spectra.

2.2 Synthesis of dendron 1D

A mixture consisting of 10.28 g (7.8×10^{-2} mol) of 1,2-bis(dimethylsilyl)ethane, 10 ml of anhydrous toluene, 3×10^{-4} eq. of $[Pt_2\{(CH_2{=}CHSiMe_2)_2O\}_3]$ and 3 g (1.9×10^{-2} mol) of trivinylethoxysilane was placed in a 25 ml Schlenk bomb flask, fitted with a plug valve, at room temperature for 12 h. After that time, the solvent was removed under reduced pressure and 9.1 g (85%) of product **1D** was afforded.

2.3 Synthesis of dendron precursor (1)

A mixture consisting of 5 g (4.0×10^{-2} mol) of trivinylmethylsilane, 10 ml of anhydrous toluene, 3×10^{-4} eq. of $[Pt_2\{(CH_2{=}CHSiMe_2)_2O\}_3]$ was placed in a 25 ml Schlenk bomb flask fitted with a plug valve under argon atmosphere. Next, a portion of triethoxysilane (2.2 g, 1.3 x 10^{-2} mol) was added and stirred for 3 hours. After that time, the crude product was separated from the residues of trivinylmethylsilane by bulb-to-bulb distillation. After that, the rest of the substrate as well as toluene were placed again in a 25 ml Schlenk bomb flask to repeat the procedure (it was repeated two more times). After that time, the solvent was removed under reduced pressure. Other residues were separated by bulb-to-bulb distillation and 8.6 g (74%) of product **1** was afforded.

2.4 Synthesis of dendron 2D

A mixture consisting of 10.13 g (6.9 × 10^{-2} mol) of 1,2-bis(dimethylsilyl)ethane, 10 ml of anhydrous toluene, 3 × 10^{-4} eq. of $[Pt_2\{(CH_2=CHSiMe_2)_2O\}_3]$ and 5 g (1.7 × 10^{-2} mol) of triethoxy(2-(methyldivinylsilyl)ethyl)silane (**1**) was placed in a 25 ml Schlenk bomb flask, fitted with a plug valve, at room temperature for 12 h. After that time, the solvent was removed under reduced pressure and 8.6 g (86%) of product **2D** was afforded.

2.5 Synthesis of dendron precursor (2)

A mixture including 5 g (3.7 × 10^{-2} mol) of tetravinylsilane, 10 ml of anhydrous toluene, 3 × 10^{-4} eq. of $[Pt_2\{(CH_2=CHSiMe_2)_2O\}_3]$ was placed in a 25 ml Schlenk bomb flask fitted with a plug valve under argon atmosphere. Next, a portion of triethoxysilane (2.0 g, 1.2 x 10^{-2} mol) was added and stirred for 2.5 hours. After that time, the crude product was separated from the residues of tetravinylsilane by bulb-to-bulb distillation. After that, the rest of substrate as well as toluene were placed again in a 25 ml Schlenk bomb flask to repeat the procedure (it was repeated two more times). After that time, the solvent was removed under reduced pressure. Other residues were separated by bulb-to-bulb distillation and 7.8 g (71%) of product **2** was afforded.

2.6 Synthesis of dendron 3D

A mixture composed of 11.68 g (7.8 × 10^{-2} mol) of 1,2-bis(dimethylsilyl)ethane, 10 ml of anhydrous toluene, 3 × 10^{-4} eq. of $[Pt_2\{(CH_2=CHSiMe_2)_2O\}_3]$ and 6 g (2.0 × 10^{-2} mol) of triethoxy(2-(trivinylsilyl)ethyl)silane (**2**) was placed in a 25 ml Schlenk bomb flask, fitted with a plug valve, at room temperature for 12 h. After that time, the solvent was removed under reduced pressure and 13.3 g (90%) of product **3D** was afforded.

2.7 General procedure for the synthesis of bifunctional dendrons (Table 1, entries 1-4)

A mixture composed of 0.5 g (8.5×10^{-4} mol) of **1D**, 3 ml of anhydrous toluene, 3×10^{-3} eq. of $[Pt_2\{(CH_2{=}CHSiMe_2)_2O\}_3]$ and 3.4×10^{-3} mol of olefin (**Table 1, entries 1-4**) was placed in a 25 ml Schlenk bomb flask, fitted with a plug valve, at room temperature for 12 h. After that time, the solvent was removed under reduced pressure and 0.66-0.80 g (80-94%) of products (**Table 1, entries 1-4**) were afforded.

2.8 General procedure for the synthesis of bifunctional dendrons (Table 1, entries 5-12)

A mixture of 0.5 g (8.6×10^{-4} mol) of **2D**, 3 ml of anhydrous toluene, 2×10^{-3} eq. of $[Pt_2\{(CH_2{=}CHSiMe_2)_2O\}_3]$ and 3.4×10^{-3} mol of olefin (**Table 1, entries 5-12**) was placed in a 25 ml Schlenk bomb flask, fitted with a plug valve, at room temperature for 12 h. After that time, the solvent was removed under reduced pressure and 0.49-0.78 g (75-98%) of products (**Table 1, entries 5-12**) were afforded.

2.9 General procedure for the synthesis of bifunctional dendrons (Table 1, entries 13-18)

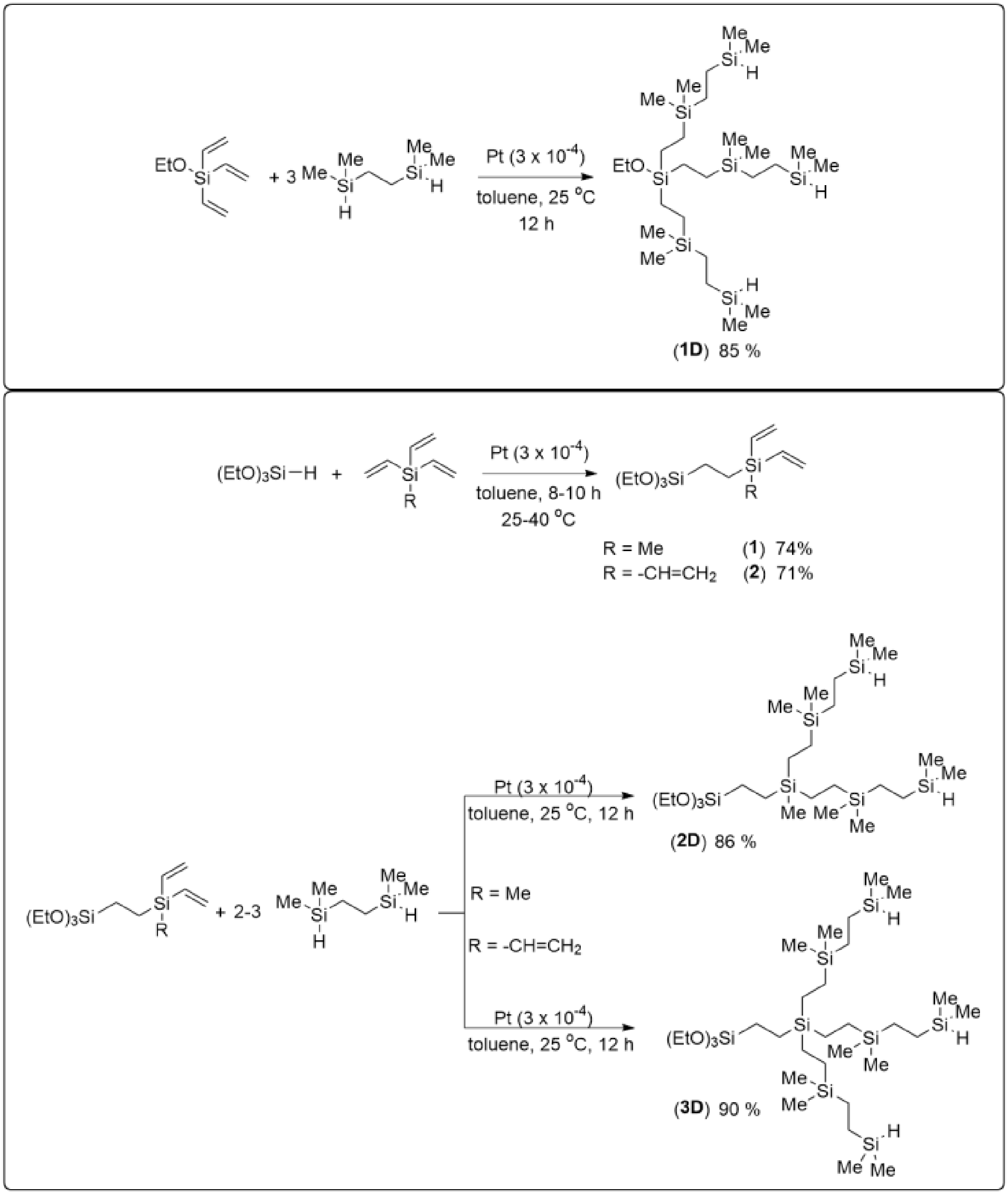
A mixture of 0.5 g (6.8×10^{-4} mol) of **3D**, 3 ml of anhydrous toluene, 3×10^{-3} eq. of $[Pt_2\{(CH_2{=}CHSiMe_2)_2O\}_3]$ and 3.4×10^{-3} mol of olefin (**Table 1, entries 13-18**) was placed in a 25 ml Schlenk bomb flask, fitted with a plug valve, at room temperature for 12 h. After that time, the solvent was removed under reduced pressure and 0.68-0.76 g (75-98%) of products (**Table 1, entries 13-18**) were afforded.

3. Results and discussion

The above described methods were based on the use of commercially available trivinylethoxysilane and 1,2-bis(dimethylsilyl)ethane in the hydrosilylation reaction. Following the procedures applied in preliminary studies, we prepared novel mono- and trialkoxy cored carbosilane terminated with free Si-H groups, that can be readily hydrosilylated with various olefins (**Scheme 1**). To the best of our knowledge, only one example of the synthesis of trialkoxy-cored silicon dendrons has been reported so far [34].

As a starting point, the conditions of the hydrosilylation to get compounds **1D-3D** were optimized. It was established that the best results were observed when the substrates were stirred in small amount of toluene for 12 hours in the presence 3×10^{-4} eq. of Karstedt catalyst at room temperature. The substrates were used at the ratio 1:4 of vinylsilane: 1,2-bis(dimethylsilyl)-ethane. After several attempts the desired products (**1D-3D**) were obtained selectively in good yields (85-90%).

Scheme 1. The synthesis of ethoxy-substituted dendrons



The synthesis of monoethoxy-cored dendron (**1D**) was fairly simple. The synthesis of other precursors (**2D and 3D**) was more complicated. The first step was the preparation of 1-(triethoxysilyl)-2-(methyldivinylsilyl)ethane (**1**) and 1-(triethoxysilyl)-2-(trivinylsilyl)ethane (**2**), respectively (**Scheme 1**). In the presence of two or three vinyl groups in the substrate molecules , the side reactions could take place in the studied system. The equimolar reaction between triethoxysilane and trivinylmethylsilane or tetravinylsilane in the presence of platinum catalyst led to the mixture of products, as well as residues of vinyl substrates. It was a consequence of the addition of triethoxysilane to more than one vinyl group. It is a common problem in the hydrosilylation of multi-unsaturated compounds. Our study of this catalytic system has shown that the above-mentioned side reactions can be minimized by sequential hydrosilylation in excess of vinylsilanes. This method is described in detail in the Experimental Section. As a result, triethoxy(2-(methyldivinylsilyl)-ethyl)silane (**1**) and triethoxy(2-(trivinylsilyl)ethyl)silane (**2**) were obtained in moderate yields (74% and 71%). Alkoxysilane with two vinyl groups (**1**) was dominantly obtained in *anti*-Markovnikov fashion. Alkoxysilane with three vinyl groups (**2**) was obtained at the ratio ~ 70:30 of both regioisomers. With both precursors (**1, 2**) in hand, the hydrosilylation reaction with 1,2-bis(dimethylsilyl)ethane was investigated. It proceeded smoothly to produce **2D** and **3D**, respectively, in high yields (86% and 90%). In the ^{1}H NMR spectra, as well as IR spectra, the presence of Si-H groups was confirmed (δ ~ 4.00 – 4.20 ppm, ν ~ 2110 cm^{-1}). Prompted by the successful synthesis of dendrons **1D-3D**, our next goal was the introduction of various functional groups into the dendron periphery (Table 1). It is noteworthy, that hydrosilylation displays tolerance to a wide range of functional groups [28].

Ethers containing protected hydroxy group, perfluorinated ethers, esters, styrenes and silanes containing halogens, as well as vinyl sulfides were investigated in the presence of platinum catalyst. We found that most of substrates used could be readily incorporated with good yield (68-97%) with excellent regioselectivity. However, ethyl vinyl sulfide (**Table 1, entry 11**), , seemed to have the poorest reactivity as compared to that of the other olefins, which might be due to the sulfur-catalyst interaction (one week – 68%). What is more, IR and NMR spectroscopies revealed that a few of Si-H groups were untouched, which was not observed for other olefins. The substrates containing hydroxy groups (**Table 1, entries 4, 9, 10, 13-15**) were preliminary silylated, because that moiety hindered the hydrosilylation with alkoxysilanes. The silylation was carried out in the presence of 1,1,1,3,3,3-hexamethyldisilazane and bismuth(III) triflate as the catalyst (**Scheme 2**) [35–37].

Scheme 2. The silylation of unsaturated ethers

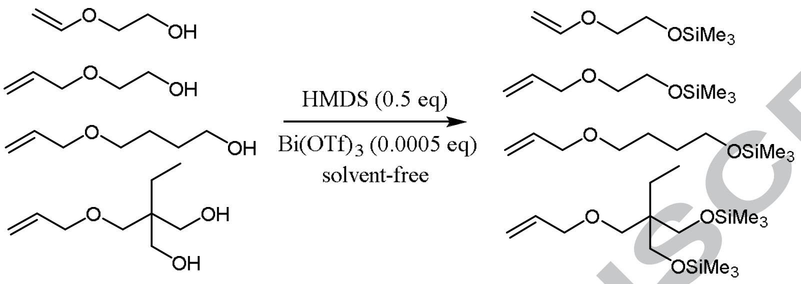
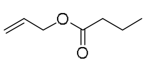
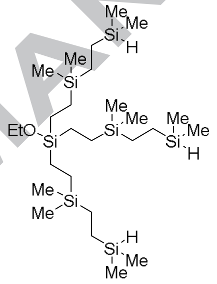
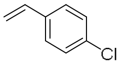
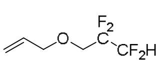
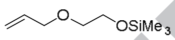
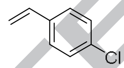
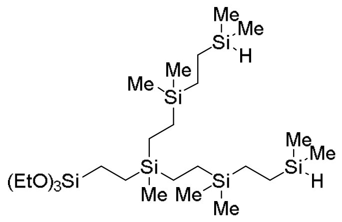
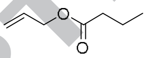
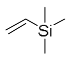
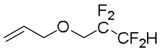
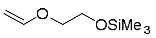
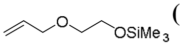
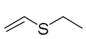
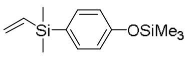
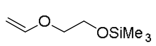
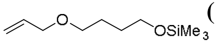
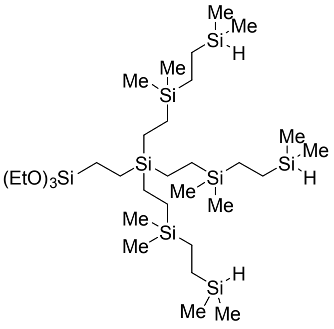
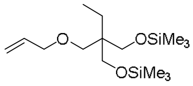
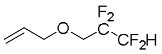
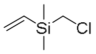
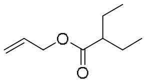


Table 1. The synthesis of bifunctional silicon dendrons[a]

Entry	Olefin	Substrate	Yield (%)
1	 **(3)**		80
2	 **(4)**		94
3	 **(5)**		82
4	 **(6)**		80
5	 **(7)**		97
6	 **(8)**		94
7	 **(9)**		98
8	 **(10)**		93
9	 **(11)**		88
10	 **(12)**		81
11[b]	 **(13)**		68[c]
12	 **(14)**		81

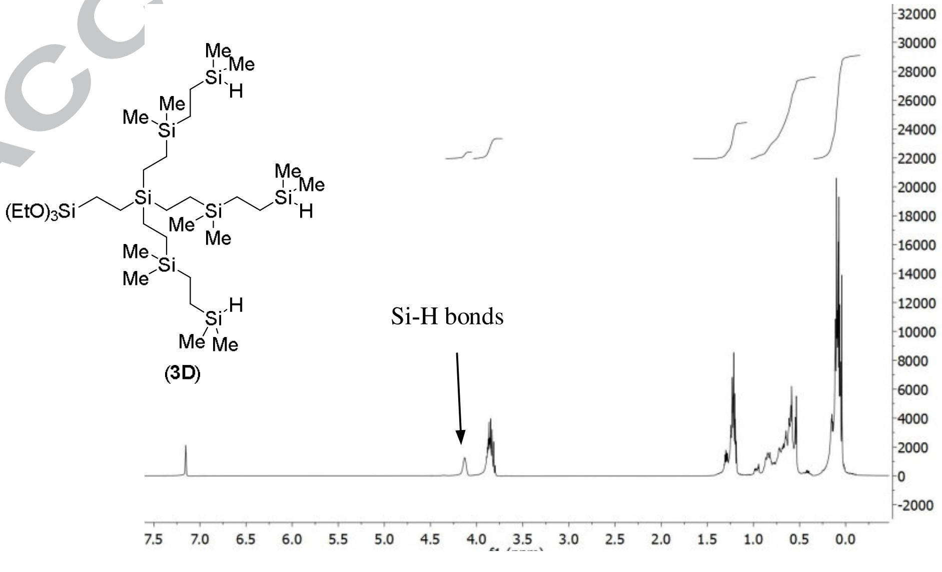
13		**(15)**		83
14		**(16)**		80
15		**(17)**		78
16		**(18)**		90
17		**(19)**		92
18		**(20)**		88

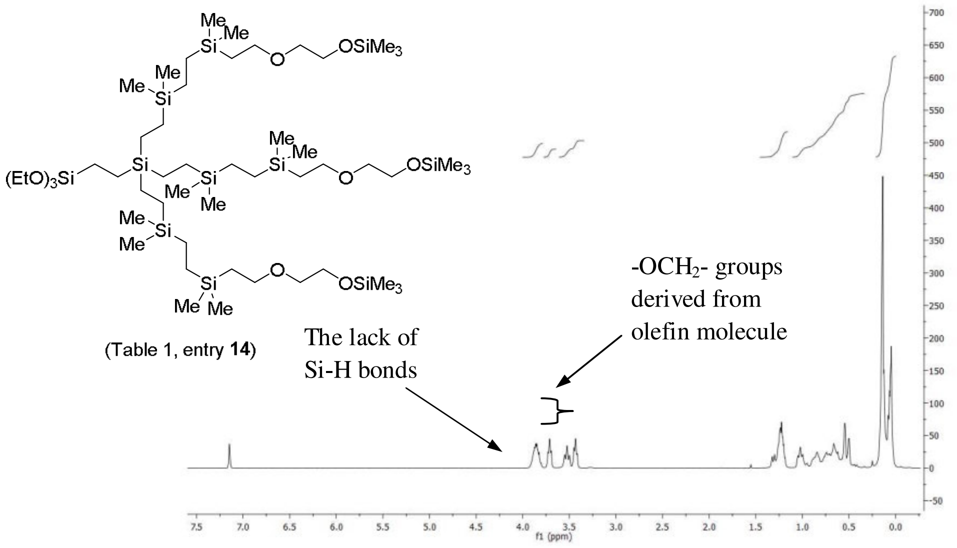
[a]Reaction conditions: dendron (1D-3D): olefin ratio 1:4, toluene (1 M), catalyst (3 x 10^{-3}), 60 °C, 12 h, argon atmosphere. [b]90 °C, dendron 2D: vinyl ethyl sulfide 1:20, catalyst 9 x 10^{-3}, one week. [c]IR spectra revealed the presence of some unreacted Si-H bonds.

Silylated unsaturated ethers were continuously used in the hydrosilylation reaction yielding dendritic wedges. Their possible use for grafting of silica for the preparation of supports to biomolecules' immobilization is being actively pursued in our laboratory.

In general, the NMR spectra of the products were similar to those obtained for the parental dendrons (**1D-3D**). The functional groups gave typical signals in the ^{1}H and ^{13}C NMR spectra, which confirmed the introduced function and was consistent with the disappearance of Si-H signals of the output compounds (**Figure 1**).The same observations were made in the IR spectra of the products obtained (*see Supporting Information File*). The core's alkoxy groups remain unchanged and are ready to be used in the grafting process.

Figure 1. The exemplary ^{1}H NMR spectra of **3D** and hydrosilylation product (**Table 1, entry 13**).





4. Conclusions

In summary, we have developed an efficient and operationally simple method for the platinum-catalyzed hydrosilylation of various olefins affording novel, bifunctional carbosilane dendrons. The proposed method of hydrosilylation was tolerant a wide range of functional groups. As a continuation of the study on these bifunctional dendrons we will focus on harnessing them for grafting to silica, titania, glass and other materials. The obtained carbosilane frameworks offer the possibility to reduce the steric hindrance at material's surface and improve the accessibility to functional groups. These features make carbosilane dendrons much promising in biochemical applications. Additional studies of the use dendrons terminated with protected OH groups in the immobilization of some biomolecules are currently underway.

5. Supporting information

The Supporting Information File is available free of charge on the website at DOI which contains synthetic procedures, NMR, IR and ESI-MS data and spectra of compounds synthesized in the study reported in this paper.

6. Acknowledgement

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Vitae

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Graphical abstract