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Synthesis of 2-methylidene-1-silacyclohexanes by intramolecular hydrosilylation

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ABSTRACT

The preparation of various (hex-5-ynyl)silanes was achieved following two different synthetic approaches from readily available materials such as 4-bromobutene, 6-iodohexyne and chlorosilanes. Different reaction conditions for intramolecular hydrosilylation were tested to prepare the corresponding 2-methylidene-1-silacyclohexanes. Notably, the use of Speier's catalyst allowed the regioselective formation of the desired products in moderate yields.

1. Introduction

The unique properties of silicon [1] have led to its wide utilization in organic chemistry as protective group [2], temporary tether [3] or in the Peterson reaction [4], Sakurai reaction [5] and Tamao oxidation [6]. The hydrosilylation of alkenes and alkynes is one of the most powerful methods for the formation of Si–C bonds [7]. The intramolecular version of this reaction is an elegant approach to the synthesis of silacycles. Even though few examples of intramolecular hydrosilylation of alkynes have been reported, it is commonly acknowledged that it can lead to the formation of three different types of silacycles according to the cyclization mode (*endo* or *exo*) and the regioselectivity of the addition of the Si–H bond (*trans* or *cis*): *endo-trans*, *exo-trans* or *exo-cis*. To date, no example of *endo-cis* intramolecular hydrosilylation is known. The selectivity of this reaction depends on the nature of the alkynyl chain and on the catalytic system.

In the case of platinum-catalyzed intramolecular hydrosilylation, the *cis* addition of hydrosilanes on the triple bond is usually observed. For instance, the reaction of a (pent-4-ynyl)silane in the presence of hexachloroplatinic acid (Speier's catalyst) leads to the formation of a methylidenesilacyclopentane resulting of an *exo-cis* cyclization as the only cyclic product [8]. Despite the complete selectivity of this reaction, the formation of dimers and oligomers considerably lowers the yield of the desired product. The same cyclization mode has been observed from silyl ether derivatives of homopropargylic alcohols to yield methylideneoxasilacyclopentanes [9]. In these examples, the platinum-catalyzed reaction of disubstituted alkynes generates vinylsilanes of defined *E* configuration, which is in accordance with the commonly accepted Chalk–Harrod mechanism [10]. The formation of *Z*-vinylsilanes by ruthenium-catalyzed intramolecular hydrosilylation has been recently reported [11]. However, cationic ruthenium-based systems yielded *endo-trans* products which can be rationalized with a new mechanistic pathway involving the formation of a ruthenacyclopropene intermediate [12]. The same *trans* addition of a hydrosilane onto a substituted carbon–carbon triple bond has been reported in Lewis acid-catalyzed intramolecular hydrosilylation [13], but in this case the alkynyl chain length was shown to govern the cyclization mode.

We were interested in the preparation of 2-methylidene-1-silacyclohexanes because the synthesis of such vinylsilanes is still challenging despite numerous publications concerning the formation of silacycles [14]. To the best of our knowledge, prior to our recent report about the preparation of this type of silacyclohexanes from di- or trihalosilanes and a dibromohexene [15], the only reported unsubstituted 2-methylidene-1-silacyclohexane had been prepared by a Wittig reaction with a 2-silacyclohexan-1-one [16]. Herein, we report the preparation of (hex-5-ynyl)silanes by two related synthetic approaches and their subsequent intramolecular hydrosilylation to yield a number of 2-methylidene-1-silacyclohexanes (Scheme 1).

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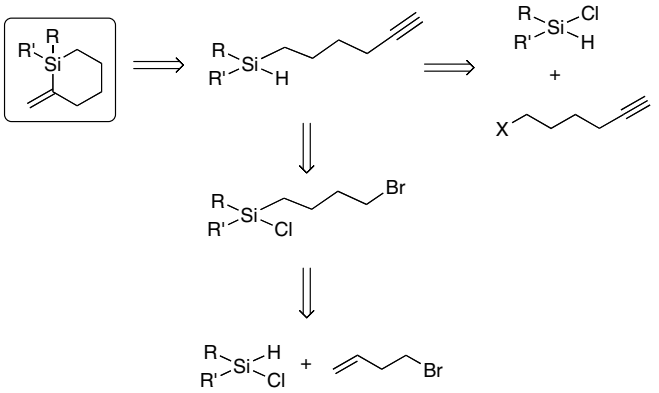


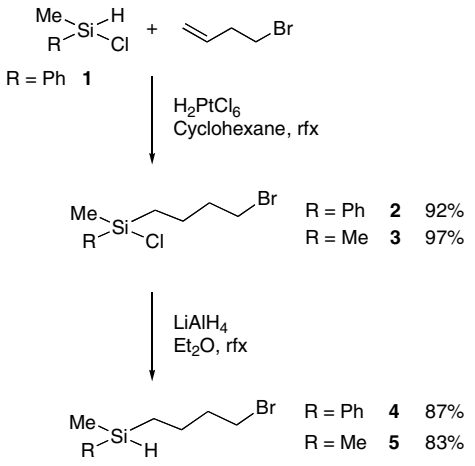
Scheme 1. Retrosynthetic approaches for the preparation of 2-methylidene-1-silacyclohexanes.

2. Results and discussion

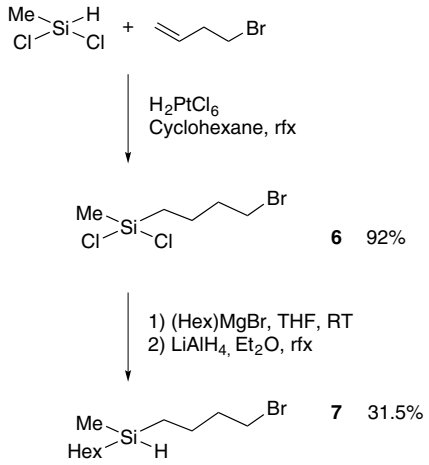
2.1. Preparation of (hex-5-ynyl)hydrosilanes

In order to test the intramolecular hydrosilylation of alkynes, a number of (hex-5-ynyl)hydrosilanes were synthesized. Our initial efforts were focused on a similar approach to the one reported for the preparation of (pent-4-ynyl)hydrosilanes [8]. The platinum-catalyzed hydrosilylation of 4-bromobutene by chloromethylphenylsilane **1** [17] or chlorodimethylsilane in refluxing cyclohexane led to the formation of the corresponding (4-bromobutyl)chlorosilanes **2** and **3** in excellent yields after distillation (Scheme 2). The subsequent substitution of the chlorine on the silicon atom by a hydride was achieved after treatment with $LiAlH_4$ (Scheme 2). No significant reduction of the alkyl chain was observed under these reaction conditions. Noteworthy, even though the formation of the chlorosilanes **2** and **3** is extremely clean, they must be distilled before being engaged in the next step; otherwise total decomposition, with liberation of a gas (probably dihydrogen) is observed during the concentration of **4** and **5**. We believe that despite the work-up of the reduction reaction, remaining traces of platinum species might catalyze this decomposition reaction.

A similar approach was employed for the preparation of (4-bromobutyl)hexylsilane **7**. The hydrosilylation of 4-bromobutene by dichloromethylsilane, under the conditions described above, led to the formation of (4-bromobutyl)silane **6** in high yield (Scheme 3). The hexylsilane **7** was obtained after reaction of **6** with hexylmagnesium bromide in THF followed by an in situ reduction with $LiAlH_4$ (Scheme 3).



Scheme 2. Preparation of (4-bromobutyl)silanes **4** and **5**.



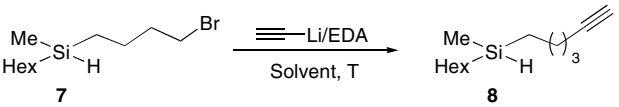
Scheme 3. Preparation of (4-bromobutyl)silane (**7**).

Next, we carried out the substitution reaction of the bromine atom by an ethynyl group. The conditions previously reported for the substitution of an iodine atom (1.3 equiv. of ethynyllithium/ethylenediamine in DMSO at room temperature for 2 h) [8] led to the formation of the expected alkyne in low yield due to a low conversion (Table 1, entry 1). Optimization studies on this reaction for our system showed that yields could be improved with longer reaction times or by using larger excess of the lithium complex (Table 1, entries 2 and 3). On the contrary, some degradation products were detected when the reaction temperature was raised to 50 °C (Table 1, entry 4). Finally, the best results were obtained in THF using hexamethylphosphorous triamide (HMPA) as additive (Table 1, entries 5 and 7). The reaction time was optimized to 2 h at room temperature in order to avoid any undesirable decomposition (Table 1, entries 5 and 6).

Surprisingly, these optimized conditions for the synthesis of **8** did not allow us to obtain the hexynylsilanes **9** and **10** (Scheme 4). From methylphenylsilane **4**, a complex mixture was obtained and only the disubstituted product **11** could be partially identified [18]. In this particular case, the hydrogen atom on the silicon center is in a *pseudo*-benzylic position, which may explain its higher reactivity. On the other hand, reaction of the dimethylsilane **5** under the same conditions led to the formation of degradation products. These experiments clearly show how such a simple modification in the nature of the substituents on the silicon atom can dramatically change the reactivity of the molecule.

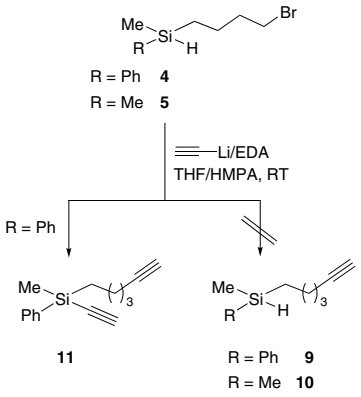
These results led us to exchange the bromine by an iodine on silanes **4** and **5** prior to the reaction with the ethynyllithium

Table 1
Optimization studies for the preparation of (hex-5-ynyl)silane **8**



7 **8**

Entry	Solvent	Equivalent [Li]	T (°C)	Time (h)	Yield (%)
1	DMSO	1.3	20	2	36
2	DMSO	2.2	20	3	46
3	DMSO	2.2	20	5	60
4	DMSO	2.2	50	5	53
5	THF/HMPA	2.2	20	2	78
6	THF/HMPA	2.2	20	4	37
7	THF/HMPA	2.2	−10	7	74

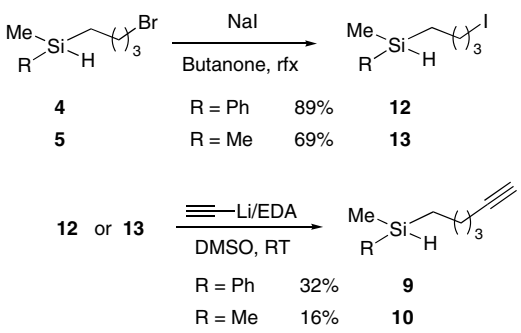


Scheme 4. Attempts of preparation of (hex-5-ynyl)silanes **9** and **10**.

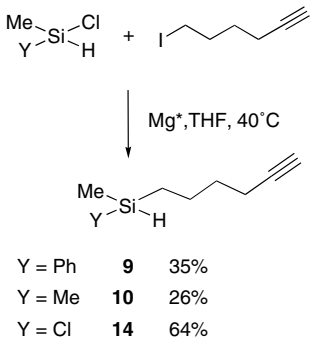
(Scheme 5). In this case, the expected hexynylsilanes could be isolated with similar yields to the ones reported in the synthesis of (pent-4-ynyl)silanes [8].

Our alternative approach for the synthesis of (hex-5-ynyl)silanes relies on the one-pot reaction of an halohexyne with a chlorosilane in the presence of activated magnesium (Barbier-type conditions) [19]. For this transformation, the protection of the terminal triple bond was not necessary, but the reaction temperature must be carefully controlled at 40 °C in order to avoid undesired carbometallation reactions. Under these conditions, hexynylsilanes **9** and **10** could be successfully synthesized in moderate yields. Moreover, chloro(hexynyl)silane **14**, which would be difficult to prepare by the first approach, was also prepared in good yield (Scheme 6).

Besides the possibility of carbometallated by-products formation, the main difficulty of this reaction is that it takes place in the presence of two different types of acidic protons, acetylenic and propargylic. Alternatively, organozinc and organocuprate reagents are commonly known for their weakly ionic carbon–metal bonds, therefore acidic protons are well tolerated in their presence [20]. The preparation of organozinc iodides, followed by a transmetallation with CuCN·2LiCl leads to the formation of RCu(CN)ZnI-type reagents which can react with diverse organic electrophiles [21]. We attempted the synthesis of this type of reagent from 6-iodohexyne and used dichloromethylsilane as electrophile. After the addition of the copper salt, the reaction mixture turned red, implying the formation of the desired organocuprate intermediate. However, the ^{1}H NMR spectrum of the reaction mixture did not show any signal attributable to the desired product **14**. After distillation of the crude, the ^{1}H NMR of the isolated fraction was in accordance with the major formation of carbometallated products [22].



Scheme 5. Preparation of (hex-5-ynyl)silanes **9** and **10**.



Scheme 6. Preparation of (hex-5-ynyl)silanes under Barbier-type conditions.

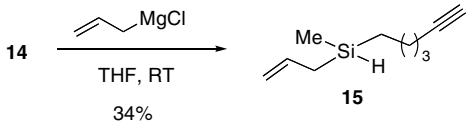
A last precursor for the intramolecular hydrosilylation was prepared from the chlorosilane **14** by reaction with allylmagnesium chloride at room temperature (Scheme 7). The isolated yield in allylsilane **15** after purification, even if moderate, seems acceptable for this kind of substrate.

2.2. Preparation of 2-methylidene-1-silacyclohexanes

To access the 2-methylidene-1-silacyclohexanes, we tested the intramolecular hydrosilylation of the corresponding (hex-5-ynyl)-silanes in the presence of hexachloroplatinic acid in refluxing cyclohexane. Of note, these reactions were carried out in air after we observed that an inert atmosphere inhibited the cyclization process. In fact, in some platinum-catalyzed hydrosilylation reactions, it has been postulated that the oxygen acts as a co-catalyst [23]. It is believed that the presence of oxygen prevents the irreversible agglomeration of colloidal-platinum particles formed from the catalyst and its coordination to the intermediate species, making them more reactive towards the unsaturation.

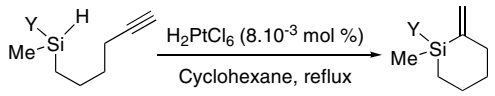
After slow addition of a solution of the starting material over a refluxing suspension of the catalyst (final concentration = 0.025 M), the reaction mixture was quickly filtered over silica gel in order to separate the platinum species and avoid the total oligomerization of the formed methylidenesilacyclohexanes during the concentration step. Results obtained under these conditions are presented in Table 2. A good yield was obtained for the silane **16** bearing an hexyl chain on the silicon atom. For silanes **17** and **20**, the spectroscopic data were identical to the products obtained from a dibromohexene and dihalosilanes [15]. Even though an important formation of oligomers was detected by GC, it is worth noting that the formation of silacycloheptenes, resulting of an *endo* cyclization, was never detected.

Dimethylsilacyclohexane **18** (Table 2, entry 3) proved to be unstable on silica gel and when its purification was attempted by vacuum distillation only decomposition products were obtained. The crude silane **18** could be characterized however by ^{1}H NMR and LRMS [24]. Remarkably, the allylsilane **15** yielded some cyclic product albeit in low yield (Table 2, entry 5). In this case, a lower reaction temperature (70 °C) and a higher dilution (0.007 M) were required to avoid the complete oligomerization of the species in the reaction mixture.



Scheme 7. Preparation of allyl(hex-5-ynyl)silane **15**.

Table 2
Platinum-catalyzed intramolecular hydrosilylation of (hex-5-ynyl)silanes



Entry	Y	SM	Product	Yield (%)
1	Hexyl	**8**	**16**	66
2	Ph	**9**	**17**	42
3	Me	**10**	**18**	Not isolated[a]
4	Cl	**14**	**19**	0
5	Allyl	**15**	**20**	18[b]

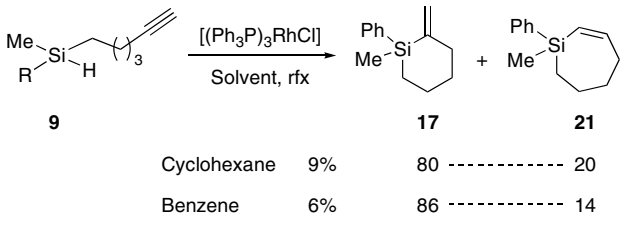
[a] Reaction in refluxing pentane.
[b] Reaction at 70 °C with a final concentration of 0.007 M.

On the other hand, the ^{1}H NMR of the crude product obtained from chlorosilane **14** showed the complete consumption of this starting material as well as the appearance of two doublets at 5.23 and 5.48 ppm which suggest formation of a cyclic product. However, no singlet assignable to a methyl group bound to a chlorosilane was observed. We were aware of the instability of 2-methylidenesilacyclohexanes under the reaction conditions [25], but in this case a filtration over silica gel was not possible. Attempts of separation by vacuum evaporation, even extremely fast, only led to the recovery of complex mixture of oligomerization products. It is probable that the higher reactivity of **14** and/or **19** eases their oligomerization while in the reaction mixture.

We tried to overcome this difficulty by testing the initiation of the hydrosilylation of **14** with benzoyl peroxide [26]. However, the reaction, after 15 h in refluxing cyclohexane, resulted principally in the recovery of the starting material.

Along with Speier's catalyst, Wilkinson's catalyst, [$(Ph_3P)_3RhCl$], is one of the most commonly used catalyst for the hydrosilylation reaction. The intermolecular hydrosilylation of 1-alkynes catalyzed by this rhodium complex has been reported to lead to the formation of *cis*-1-silylalkenes in good yields [27]. In this case, the *trans* addition observed is surprising as it is generally accepted that transition metal complexes promote *cis* addition of hydrosilanes on triple bonds. In the present case, the rhodium-catalyzed cyclization of the silane **9** led to the formation of a mixture 80/20 of methylidenesilacyclohexane **17** and 3-silacyclohept-1-ene (**21**) (Scheme 8) [28]. Similar results were observed when cyclohexane was replaced by benzene. However, as it had already been reported in the presence of this catalyst [29], the main products of this reaction are oligomers which explains the extremely low yield in cyclic products.

Finally, we studied the Lewis acid-catalyzed hydrosilylation of one of our substrates. While no reaction was observed with (hex-5-ynyl)silane **9** in the presence of $AlCl_3$, the major formation of oligomers was observed when a solution of $EtAlCl_2$ was used. After purification by flash chromatography, 26% of the starting material was recovered along with 3% of a silanol resulting from the hydrolysis of the Si–H bond in **9** [30]. This result indicates that the use of a disubstituted silaalkyne might be necessary in order to form a cyclic product [19].



Scheme 8. Rhodium-catalyzed intramolecular hydrosilylation of silane **9**.

3. Conclusions

We have prepared a series of (hex-5-ynyl)silanes using two different approaches. The reaction of chlorohydrosilanes and 6-iodohexyne with activated magnesium represents a direct and convenient strategy for the preparation of this family of products. On the other hand, the synthetic approach from chlorohydrosilanes and a bromobutene remains interesting since it highlights the great influence of the substitution on the silicon atom on the reactivity of the molecule.

Different catalytic systems have been studied for the intramolecular hydrosilylation of these (hex-5-ynyl)silanes. The best results were achieved in the presence of Speier's catalyst, with which the cyclization takes place in a complete selective *exo-cis* manner. The reported moderate yields can be rationalized by the fact that the starting material and the expected product can lead to the significant formation of oligomers under the reaction conditions. Taking into account the few rare reports in the literature concerning the synthesis of *exo*-cyclic vinylsilanes, the simplicity of this strategy is remarkable.

It is important to note that this methodology is complementary to our previous work in which 2-methylidene-1-silacyclohexanes were prepared from a dibromohexene and halosilanes under Grignard or Barbier-type conditions. We hope that the present hydrosilylation-based approach will find an extention to the diastereoselective synthesis of more complex cyclic products. The study of the potential reactivity of these 2-methylidene-1-silacyclohexanes is currently ongoing in our laboratories.

4. Experimental

4.1. General considerations

All reactions were carried out in dry glassware under an argon atmosphere unless otherwise indicated. All commercially available chemicals were used as received. 4-Bromobut-1-ene [31] and 6-iodohex-1-yne [32] were synthesized according to the literature procedures. Hexachloroplatinic acid and sodium iodide were kept in presence of P_2O_5 at atmospheric pressure. Solvents were distilled from appropriate drying agents. Column chromatography was performed on silica gel SDS (70–200 μm). ^{1}H NMR and ^{13}C NMR were recorded on Bruker spectrometers at room temperature. Chemical shifts (δ) are reported with respect to tetramethylsilane as internal standard in ppm. Assignments of some ^{1}H and ^{13}C NMR signals rely on COSY, HSQC (or HMBC), DEPT and/or TOCSY experiments on a DRX 400 spectrometer. The infrared spectra were performed on a FT-IR Spectrum One spectrometer. All of them were made on a film of pure product placed in between two sodium chloride pellets. The low-resolution mass spectra in electronic impact were registered on a Nermag R10-10-type spectrometer coupled to an OKI DP125 chromatographer. The high-resolution mass spectra were made on a Finnigan MAT 95 S spectrometer (precision: 5/1000^e). The elemental analyses were performed by the elemental analysis service of the Institut de Chimie des Substance Naturelles de Gif-sur-Yvette (France).

4.2. Chloromethylphenylsilane (*1*)

In a round-bottom-flask, 4 mL (29.1 mmol) of methylphenylsilane were added over 8.04 g (59.8 mmol) of anhydrous $CuCl_2$ and 0.17 g (0.9 mmol) of CuI. After 5 h of stirring under a regular lamp, the reaction mixture was washed with dry pentane and filtered under argon. Concentration of the filtrate, followed by vacuum distillation, afforded 4.20 g of chloromethylphenylsilane **1** as a colorless oil (92%). B.p. 56 °C/5 mm Hg. Spectroscopic data were in accordance with a commercial sample of the title compound.

4.3. (4-Bromobutyl)chloromethylphenylsilane (**2**)

Over 20 mL of refluxing cyclohexane containing a little grain of H_2PtCl_6 (≈1 mg), 4 g (25.6 mmol) of chloromethylphenylsilane **1** and 1.71 mL (16.7 mmol) of 4-bromobutene were added. After 12 h at reflux, the solvent was evaporated and the crude product was purified by vacuum distillation to yield 6.31 g of the title compound as a colorless oil (92%). B.p. 101 °C/0.08 torr; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.72 (s, 3 H, Si–CH_3), 1.02–1.21 (m, 2H, Si–CH_2), 1.54–1.76 (m, 2H, Si–CH_2–CH_2), 1.95 (quintet, J = 6.3 Hz, 2H, CH_2–CH_2Br), 3.43 (t, J = 6.3 Hz, 2H, CH_2Br), 7.37–7.56 (m, 3H, CH^{Ar}), 7.56–7.73 (m, 2H, CH^{Ar}); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 0.2 (Si–CH_3), 17.0 (Si–CH_2), 21.6 (Si–CH_2–CH_2), 33.1 (CH_2–CH_2Br), 35.5 (CH_2Br), 128.1 (*m*-CH^{Ar}), 130.4 (*p*-CH^{Ar}), 133.2 (*o*-CH^{Ar}), 134.9 (C); LRMS (70 eV) *m*/*z* (relative intensity) 279 (3, M^+–15), 277 (10, M^+–15), 275 (8, M^+–15), 236 (12), 221 (24), 219 (20), 157 (46), 157 (17), 155 (100), 133 (12), 105 (14), 91 (72), 79 (14), 78 (15), 77 (18), 65 (35), 63 (74), 56 (16), 55 (22), 53 (11); IR 3073 (m, $\nu_{=CH}$), 3056 (m, $\nu_{=CH}$), 3028 (m, $\nu_{=CH}$), 2964 (S), 2937 (S), 2168 (S, ν_{Si-H}), 1591 (w, $\nu_{C=C}$), 1429 (S, ν_{Si-Ar}), 1258 (SS, δ_{Si-CH3}), 1116 (SS, δ_{Si-Ar}), 900 (S), 789 (S) cm^{-1}; HRMS Calc. for $C_{11}H_{16}BrClSi$: 289.9893. Found: 289.9890.

4.4. (4-Bromobutyl)chlorodimethylsilane (**3**)

Following the procedure described for the preparation of **2** with 6 mL (54 mmol) of chlorodimethylsilane and 3.7 mL (36 mmol) of 4-bromobutene, 7.53 g of the title compound were isolated after vacuum distillation (97%). B.p. 80 °C/5 mm Hg. Spectroscopic data were consistent with previously reported data for this compound [33].

4.5. (4-Bromobutyl)methylphenylsilane (**4**)

Over 32 mL (7.01 mmol) of a 0.22 M solution of $LiAlH_4$ in diethyl ether, 6.16 g (21.1 mmol) of chlorosilane **2** were added. After 12 h at reflux, the reaction mixture was cooled down to ambient temperature and treated with 50 mL of cold water. After extraction of the aqueous phase with diethyl ether, the combined organic phases were dried over sodium sulfate. The crude product was purified by vacuum distillation to yield 4.74 g of the title compound as a colorless oil (87%). B.p. 95 °C/4 mbar; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.34 (d, J = 3.6 Hz, 3H, Si–CH_3), 0.78–0.94 (m, 2H, Si–CH_2), 1.44–1.65 (m, 2H, Si–CH_2–CH_2), 1.91 (quintet, J = 6.9 Hz, 2H, CH_2–CH_2Br), 3.40 (t, J = 6.9 Hz, 2H, CH_2Br), 4.36 (sextet, J = 3.6 Hz, 1H, Si–H), 7.30–7.47 (m, 3H, *m*-CH^{Ar} +*p*-CH^{Ar}), 7.47–7.60 (m, 2H, *o*-CH^{Ar}); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ −5.8 (Si–CH_3), 12.4 (Si–CH_2), 22.9 (Si–CH_2–CH_2), 33.4 (CH_2–CH_2Br), 35.8 (CH_2Br), 127.8 (*m*-CH^{Ar}), 129.3 (*p*-CH^{Ar}), 134.2 (*o*-CH^{Ar}), 136.0 (C); LRMS (70 eV) *m*/*z* (relative intensity) 258 (0.1, M^+), 256 (0.1, M^+), 243 (13), 241 (11), 202 (11), 201 (20), 200 (12), 199 (17), 187 (36), 185 (36), 152 (70), 150 (68), 124 (19), 122 (16), 121 (100), 105 (33), 69 (12), 43 (13); IR 2930 (m), 2115 (S, ν_{Si-H}), 1427 (S, ν_{Si-Ar}), 1251 (m, δ_{Si-CH3}), 1115 (S, δ_{Si-Ar}), 879 (SS), 701 (S) cm^{-1}; HRMS Calc. for $C_{11}H_{17}BrSi$: 256.0291. Found: 256.0293.

4.6. (4-Bromobutyl)dimethylsilane (**5**)

Following the procedure described for the preparation of chlorosilane **4** with 7.53 g (32.8 mmol) of chlorosilane **3**, 5.31 g of the title compound were isolated after vacuum distillation (83%). B.p. 58 °C/5 mm Hg; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.10 (d, J = 3.8 Hz, 6 H, Si–CH_3), 0.54–0.70 (m, 2H, Si–CH_2), 1.41–1.60 (m, 2H, Si–CH_2–CH_2), 1.91 (quintet, J = 6.4 Hz, 2H, CH_2–CH_2Br), 3.43 (t, J = 6.4 Hz, 2H, CH_2Br), 3.77–3.84 (m, 1H, Si–H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ −4.6 (Si–CH_3), 13.2 (Si–CH_2), 22.9 (Si–CH_2–CH_2), 33.4 (CH_2–CH_2Br), 35.9 (CH_2Br); LRMS (70 eV) *m*/*z* (relative intensity) 181 (10, M^+–15), 179 (9, M^+–15), 153 (6), 151 (6), 140 (7), 139 (100), 138 (8), 125 (51), 123 (50), 59 (69), 56 (32), 43 (13); IR 2959 (m), 2931 (m), 2112 (S, ν_{Si-H}), 1591 (m), 1271 (m), 1250 (S, δ_{Si-CH3}), 887 (SS), 836 (S) cm^{-1}; HRMS Calc. for $C_6H_{15}BrSi$: 194.0126. Found: 194.0121.

4.7. (4-Bromobutyl)dichloromethylsilane (**6**)

Following the procedure described for the preparation of **2** with 3 mL (28.8 mmol) of dichloromethylsilane and 2.25 mL (22.2 mmol) of 4-bromobutene, 4.90 g of the title compound were isolated after vacuum distillation (88%). B.p. 40 °C/0.12 torr; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.80 (s, 3H, Si–CH_3), 1.08–1.22 (m, 2H, Si–CH_2), 1.60–1.79 (m, 2H, Si–CH_2–CH_2), 1.99 (quintet, J = 7.0 Hz, 2H, CH_2–CH_2Br), 3.44 (t, J = 7.0 Hz, 2H, CH_2Br); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 5.1 (Si–CH_3), 20.5 (Si–CH_2), 21.0 (Si–CH_2–CH_2), 32.7 (CH_2–CH_2Br), 34.8 (CH_2Br); LRMS (70 eV) *m*/*z* (relative intensity) 250 (1, M^+), 248 (1, M^+), 237 (14), 235 (32), 233 (18), 179 (11), 135 (11), 118 (3), 117 (15), 116 (5), 114 (100), 113 (89), 63 (11), 56 (42), 55 (16); IR 2938 (S), 1262 (S, δ_{Si-CH3}), 1224 (m), 810 (S), 788 (SS), 748 (S), 702 (S) cm^{-1}; HRMS Calc. for $C_5H_{11}BrCl_2Si$: 247.9190. Found: 247.9176.

4.8. (4-Bromobutyl)hexylmethylsilane (**7**)

A THF solution of hexylmagnesium bromide was prepared from 0.38 g (16 mmol) of magnesium turnings activated with 85 μL (1 mmol) of 1,2-dibromoethane and 2.1 mL (15 mmol) of 1-bromohexane in 12 mL of dry THF. 7.2 mL of this Grignard solution were added over 2.26 g (9.02 mmol) of dichlorosilane **6** in 10 mL of THF cooled at 0°C. After 12 h of stirring at room temperature, THF was evaporated and the remaining mixture was treated with dry pentane. The resulting suspension was filtered under argon through a canula to separate the magnesium salts. The filtrate was concentrated, then added over 14.5 mL (5.78 mmol) of a diethyl ether solution 0.4 M in $LiAlH_4$. After 12 h of reflux, the reaction mixture was allowed to cool down to ambient temperature and treated with cold water. After extraction of the aqueous phase with diethyl ether, the combined organic phases were dried over sodium sulfate, then concentrated. The crude product was purified by vacuum distillation to obtain 0.75 g of the title compound as a colorless oil (31.5% over three steps). B.p. 84 °C/0.9 torr; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.06 (d, J = 3.5 Hz, 3H, Si–CH_3), 0.50–0.71 (m, 4H, CH_2–Si–CH_2), 0.90 (t, J = 5.5 Hz, 3H, CH_2–CH_3), 1.18–1.40 (m, 8H, CH_2–CH_2–CH_2–CH_2–CH_3), 1.43–1.60 (m, 2H, CH_2–CH_2–CH_2Br), 1.87 (quintet, J = 6.9 Hz, 2H, CH_2–CH_2Br), 3.43 (t, J = 6.9 Hz, 2H, CH_2Br), 3.78 (sextet, J = 3.5 Hz, 1H, Si–H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: −6.2 (Si–CH_3), 11.9 (Si–CH_2), 12.7 (Si–CH_2), 14.2 (CH_2–CH_3), 22.7 (CH_2^{Hex}), 23.2 (Si–CH_2–CH_2), 24.5 (CH_2^{Hex}), 31.7 (CH_2^{Hex}), 33.0 (CH_2^{Hex}), 33.5 (CH_2–CH_2Br), 36.1 (CH_2Br); LRMS (70 eV) *m*/*z* (relative intensity) 266 (1, M^+), 264 (1, M^+), 181 (47), 179 (44), 153 (27), 151 (28), 140 (6), 139 (98), 138 (7), 137 (100), 131 (7), 129 (6), 124 (8), 123 (97), 99 (18), 73 (23), 72 (7), 71 (7), 69 (11), 59 (22); IR 2957 (S), 2923 (SS), 2855 (S), 2106 (S, ν_{Si-H}), 1456 (S), 1270 (m), 1251 (S, δ_{Si-CH3}), 958 (m), 881 (S) cm^{-1}; HRMS calcd for $C_{11}H_{25}BrSi$: 264.0909. Found: 264.0911.

4.9. Hexyl(hex-5-ynyl)methylsilane (**8**)

In a round-bottom-flask, 38 mg (0.42 mmol) of ethynyllithium/ethylenediamine complex were stirred in 0.3 mL (8.8 mmol) of hexamethylphosphorous triamide and 1 mL of THF for 20 min before addition of 49 μL (0.19 mmol) of (4-bromobutyl)silane **7**. After 2 h of stirring at ambient temperature, the reaction mixture was diluted with pentane and washed with cold water. After extraction

of the aqueous phase with pentane, the combined organic phases were washed with water and brine, then dried over sodium sulfate and concentrated. Purification of the crude product by column chromatography (pentane) afforded 31 mg of the title compound as a colorless oil (78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.07 (d, J = 3.5 Hz, 3H, Si–CH_3), 0.48–0.69 (m, 4H, CH_2–Si–CH_2), 0.91 (t, J = 6.8 Hz, 3H, CH_2–CH_3), 1.16–1.40 (m, 8H, CH_2–CH_2–CH_2–CH_2–CH_3), 1.48 (quintet, J = 8.0 Hz, 2H, Si–CH_2–CH_2), 1.58 (quintet, J = 7.3 Hz 2H, CH_2–CH_2–C≡CH), 1.95 (t, J = 2.5 Hz, 1H, C≡CH), 2.20 (dt, J = 2.5, 7.3 Hz, 2H, CH_2–C≡CH), 4.79 (octet, J = 3.5 Hz, 1H, Si–H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: −6.3 (Si–CH_3), 12.2 (Si–CH_2), 12.6 (Si–CH_2), 14.1 (CH_2–CH_3), 18.0 (CH_2–C≡CH), 22.6 (CH_2^{Hex}), 23.6 (Si–CH_2–CH_2), 24.4 (CH_2^{Hex}), 31.6 (CH_2^{Hex}), 31.8 (CH_2–CH_2–C≡CH), 32.9 (CH_2^{Hex}), 68.1 (C≡CH), 84.6 (C≡CH); IR 3313 (S, $\nu_{\equiv CH}$), 2957 (S), 2923 (SS), 2856 (S), 2106 (S, ν_{Si-H} or $\nu_{C\equiv C}$), 1459 (m), 1251 (S, δ_{Si-CH3}), 881 (F), 630 (S) cm^{-1}; Elemental analysis Calc. for $C_{13}H_{26}Si$: C, 74.20; H, 12.45. Found: C, 74.35; H, 12.38%.

4.10. (Hex-5-ynyl)methylphenylsilane (**9**)

(A) Following the procedure described for the preparation of **8** with 1.69 g (5.56 mmol) of (4-iodobutyl)phenylsilane **12** and 0.62 g (6.76 mmol) of ethynyllithium/ethylenediamine complex in 4 mL of DMSO, 0.36 g of the title compound were isolated as a colorless oil after vacuum distillation (32%). (B) In a three-neck round-bottom-flask, 0.47 g (20 mmol) of magnesium turnings, 0.17 mL (2 mmol) of 1,2-dibromethane and 5 mL of THF were introduced. This mixture was gently heated until gas evolution and then a solution containing 1.5 mL (10 mmol) of chlorosilane **1** and 1.5 mL (10 mmol) of 6-iodohexyne in 5 mL of THF were added in a rate that allowed to maintain the reaction mixture temperature below 40 °C (Caution: this reaction is very exothermic, specially in the beginning of the addition). Once the addition finished, the reaction mixture was stirred at 40 °C for two hours before being cooled at ambient temperature and filtered in order to separate the unreacted magnesium. The filtrate was diluted with diethyl ether and treated with a saturated solution of ammonium chloride. After extraction of the aqueous phase with diethyl ether, the combined organic phases were washed with water until neutrality, then dried over sodium sulfate and concentrated. Purification of the crude material by vacuum distillation afforded 0.14 g of the title compound as a colorless oil (35%). B.p. 64 °C/0.08 torr. Spectroscopic data were consistent with previously reported data for this compound [19].

4.11. (Hex-5-ynyl)dimethylsilane (**10**)

(A) Following the procedure described for the preparation of the **8** with 1.58 g (6.5 mmol) of (4-iodobutyl)silane **13** and 0.72 g (7.9 mmol) of ethynyllithium/ethylenediamine complex in 5 mL of DMSO, 0.15 g of the title compound were isolated as a colorless oil after vacuum distillation (16%). (B) Following the procedure B described for the preparation of **9** with 1.1 mL (10 mmol) of chlorodimethylsilane and 1.5 mL (10 mmol) of 6-iodohexyne, 0.36 g of the title compound were isolated after vacuum distillation (26%). B.p. 62 °C/40 mm Hg; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.08 (d, J = 3.4 Hz, 6H, Si–CH_3), 0.53–0.68 (m, 2H, Si–CH_2), 1.36–1.65 (m, 4H, Si–CH_2–CH_2–CH_2), 1.95 (t, J = 2.8 Hz, 1H, C≡CH), 2.20 (dt, J = 2.8, 7.6 Hz, 2H, CH_2–C≡CH), 3.86–3.94 (m, 1H, Si–H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: −4.6 (Si–CH_3), 13.6 (Si–CH_2), 18.0 (CH_2–C≡CH), 23.5 (Si–CH_2–CH_2), 31.7 (CH_2–CH_2–C≡CH), 68.1 (C≡CH), 84.4 (C≡CH); LRMS (70 eV) m/z (relative intensity) 140 (2, M$^+$), 139 (11), 125 (66), 99 (16), 98 (100), 97 (34), 83 (57), 80 (13), 69 (23), 67 (13), 59 (42), 43 (18); IR 3312 (S, $\nu_{\equiv CH}$), 2935 (S), 2112 (S, ν_{Si-H}), 1250 (S, δ_{Si-CH3}), 889 (SS), 836 (m), 630 (m) cm^{-1}; HRMS Calc. for $C_8H_{16}Si$: 140.1021. Found: 140.1016. Elemental analysis Calc. for $C_8H_{16}Si$: C, 68.49; H, 11.49. Found: C, 68.12; H, 11.67%.

4.12. (4-Iodobutyl)methylphenylsilane (**12**)

Over 1.22 g (8.14 mmol) of sodium iodide in 8 mL of refluxing butanone, 1.61 g (6.27 mmol) of (4-bromobutyl)silane **4** were added. After 14 h of reaction, the reaction mixture was cooled at ambient temperature, then filtered. The filtrate was diluted with pentane and washed successively with water, an aqueous solution 0.1 M of sodium bicarbonate, water, a saturated aqueous solution of sodium thiosulfate and brine, then dried over sodium sulfate and concentrated. The crude product was purified by vacuum distillation to obtain 1.69 g of the title compound as a colorless oil (89%). B.p. 88 °C/0.1 mbar; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.37 (d, J = 3.4 Hz, 3H, Si–CH_3), 0.78–0.93 (m, 2H, Si–CH_2), 1.42–1.59 (m, 2H, Si–CH_2–CH_2), 1.87 (quintet, J = 6.6 Hz, 2H, CH_2–CH_2I), 3.18 (t, J = 6.6 Hz, 2H, CH_2I), 4.36 (sextet, J = 3.4 Hz, 1H, Si–H), 7.33–7.44 (m, 3H, m-CH^{Ar} + p-CH^{Ar}), 7.48–7.60 (m, 2H, o-CH^{Ar}); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 5.7 (Si–CH_3), 6.5 (Si–CH_2), 12.3 (Si–CH_2–CH_2), 25.2 (CH_2–CH_2I), 36.5 (CH_2I), 127.9 (m-CH^{Ar}), 129.3 (p-CH^{Ar}), 134.2 (o-CH^{Ar}), 136.1 (C); LRMS (70 eV) m/z (relative intensity) 304 (1, M$^+$), 290 (8), 289 (57), 245 (24), 233 (52), 226 (19), 122 (22), 121 (100), 105 (28), 100 (9), 99 (87), 43 (7); IR 3067 (m, $\nu_{=CH}$), 3044 (m, $\nu_{=CH}$), 3056 (m, $\nu_{=CH}$), 2926 (F), 2144 (SS, ν_{Si-H}), 1427 (S, ν_{Si-Ar}), 1251 (S, δ_{Si-CH3}), 1200 (m), 1115 (SS, δ_{Si-Ar}), 878 (SS), 850 (SS), 723 (S); HRMS Calc. for $C_{11}H_{17}ISi$: 304.0139. Found: 304.0121.

4.13. (4-Iodobutyl)dimethylsilane (**13**)

Following the procedure described for the preparation of **12** with 3.66 g (18.8 mmol) of (4-bromobutyl)silane **5**, 3.15 g of the title compound were isolated as a colorless oil after vacuum distillation (69%). B.p. 82 °C/5 mm Hg; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.09 (d, J = 3.6 Hz, 6H, Si–CH_3), 0.54–0.68 (m, 2H, Si–CH_2), 1.37–1.53 (m, 2H, Si–CH_2–CH_2), 1.86 (quintet, J = 6.8 Hz, 2H, CH_2–CH_2I), 3.20 (t, J = 6.8 Hz, 2H, CH_2I), 3.38–3.93 (m, 1H, Si–H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ −4.5 (Si–CH_3), 6.8 (Si–CH_2), 13.0 (Si–CH_2–CH_2), 25.3 (CH_2–CH_2I), 36.5 (CH_2I); LRMS (70 eV) m/z (relative intensity) 242 (2, M$^+$), 227 (42), 186 (14), 185 (31), 171 (38), 127 (2), 87 (12), 73 (17), 60 (18), 59 (100), 57 (7), 44 (7), 43 (33); IR 2957 (m), 2926 (m), 2111 (S, ν_{Si-H}), 1249 (S, δ_{Si-CH3}), 1201 (m), 888 (SS), 836 (m) cm^{-1}; HRMS Calc. for $C_6H_{15}ISi$: 241.9988. Found: 241.9986.

4.14. Chloro(hex-5-ynyl)methylsilane (**14**)

Following the procedure B described for the preparation of **9** with 2.1 mL (20 mmol) of dichloromethylsilane and 1.5 mL (10 mmol) of 6-iodohexyne, 1.03 g of the title compound were isolated after filtration under argon through a cannula, followed by vacuum distillation (64%). B.p. 85 °C/10 mm Hg; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.52 (d, J = 3.3 Hz, 3H, Si–CH_3), 0.87–1.12 (m, 2H, Si–CH_2), 1.40–1.74 (m, 4H, Si–CH_2–CH_2–CH_2), 1.96 (t, J = 2.6 Hz, 1H, C≡CH), 2.22 (dt, J = 2.6, 6.4 Hz, 2H, CH_2–C≡CH), 4.82 (sextet, J = 3.3 Hz, 1H, Si–H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 1.2 (Si–CH_3), 16.2 (Si–CH_2), 18.0 (CH_2–C≡CH), 22.0 (Si–CH_2–CH_2), 31.5 (CH_2–CH_2–C≡CH), 68.1 (C≡CH), 84.4 (C≡CH); LRMS (70 eV) m/z (relative intensity) 125 (36, M$^+$–Cl), 109 (6), 99 (13), 98 (11), 97 (100), 95 (26), 85 (24), 83 (17), 79 (21), 71 (29), 69 (17), 59 (67), 55 (12), 45 (51), 43 (77); IR 3306 (m, $\nu_{\equiv CH}$), 2937 (S), 2863 (m), 2162 (S, ν_{Si-H}), 2119 (w, $\nu_{C\equiv C}$), 1258 (S, δ_{Si-CH3}), 1095 (S), 891 (SS), 635 (m) cm^{-1}; Elemental analysis Calc. for $C_7H_{13}ClSi$: C, 52.31; H, 8.15. Found: C, 52.55; H, 8.01%.

4.15. Allyl(hex-5-ynyl)methylsilane (**15**)

Over 0.46 g (2.8 mmol) of chlorosilane **14** in 3 mL of THF, 1.55 mL (2.8 mmol) of a THF solution 1.8 M in allylmagnesium chloride were added. After 14 h of stirring at room temperature, the reaction mixture was treated with a saturated solution of ammonium chloride. After extraction of the aqueous phase with diethyl ether, the combined organic phases were washed with water until neutrality, then dried over sodium sulfate and concentrated. Purification of the crude product by column chromatography (pentane) afforded 0.16 g of the title compound as a colorless oil (34%). ^{1}H NMR (250 MHz, $CDCl_3$) δ: 0.09 (d, J = 3.5 Hz, 3H, Si–CH_3), 0.55–0.73 (m, 2H, Si–CH_2–CH_2), 1.36–1.70 (m, Si–CH_2–CH_2–CH_2) and 1.52 (d, J = 6.5 Hz, Si–CH_2–CH═) (6H), 1.95 (t, J = 2.6 Hz, 1H, C≡CH), 2.21 (dt, J = 2.6, 6.6 Hz, 2H, CH_2–C≡CH), 3.78–3.87 (m, 1H, Si–H), 4.87 (d, J = 9.8 Hz, 1H, CH═CH_2 *cis*), 4.90 (d, J = 18.7 Hz, 1H, CH═CH_2 *trans*), 5.82 (ddt, J = 6.5, 9.8, 18.7 Hz, 1H, Si–CH_2–CH═); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: −6.7 (Si–CH_3), 11.7 (Si–CH_2), 18.0 (CH_2–C≡CH), 20.3 (Si–CH_2–CH═), 23.4 (Si–CH_2–CH_2), 31.7 (CH_2–CH_2–C≡CH), 68.1 (C≡CH), 84.5 (C≡CH), 113.3 (CH═CH_2), 134.7 (CH═CH_2); LRMS (70 eV) m/z (relative intensity) 151 (3, M^+−15), 126 (8), 99 (16), 98 (15), 97 (100), 95 (30), 85 (21), 83 (21), 83 (15), 79 (19), 71 (26), 69 (17), 67 (10), 59 (74), 57 (10), 55 (17), 53 (13), 45 (65), 43 (91); IR 3310 (S, $\nu_{\equiv CH}$), 3078 (m, $\nu_{=CH}$), 2934 (SS), 2115 (SS, ν_{Si-H}), 1631 (S, $\nu_{C=C}$), 1419 (m, $\delta_{=CH}$), 2153 (S, δ_{Si-CH3}), 1159 (m), 992 (S, $\delta_{=CH}$), 882 (S), 812 (S), 632 (S) cm^{-1}; Elemental analysis Calc. for $C_{10}H_{18}Si$: C, 72.21; H, 10.91. Found: C, 72.39; H, 11.15%.

4.16. General procedure for the intramolecular hydrosilylation of (hex-5-ynyl)silanes

In a two-neck round-bottom-flask with a condenser fitted with a calcium chloride guard, a little grain of hexachloroplatinic acid (≈1 mg) and 6.5 mL of cyclohexane were heated to reflux. A solution of 0.25 mmol of a (hex-5-ynyl)silane in 3.5 mL of cyclohexane was then added over 40 min. At the end of the addition, the reaction mixture was cooled down to ambient temperature, then filtered over a plug of silica gel (diethyl ether). After evaporation of the solvent, the crude product was purified by column chromatography.

4.17. 1-Hexyl-1-methyl-2-methylidene-1-silacyclohexane (**16**)

Following the general procedure for the intramolecular hydrosilylation, from 53 mg (0.25 mmol) of silane **8** and after purification by column chromatography (pentane), 35 mg of the title compound were isolated as a colorless oil (66%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.08 (s, 3H, Si–CH_3), 0.60 (ddd, J = 4.6, 9.7, 14.0 Hz, Si–CH_2^{Cy}) and 0.60–0.73 (m, Si–CH_2^{Hex}) (3H), 0.74 (ddd, J = 4.6, 7.1, 14.0 Hz, 1H, Si–CH_2^{Cy}), 0.92 (t, 3H, J = 6.8 Hz, CH_3–CH_2), 1.13–1.39 (m, 8H, CH_2–CH_2–CH_2–CH_2–CH_3), 1.39–1.52 (m, 1H, Si–CH_2–CH_2–CH_2^{Cy}), 1.52–1.64 (m, 1H, Si–CH_2–CH_2–CH_2^{Cy}), 1.64–1.86 (m, 2H, Si–CH_2–CH_2^{Cy}), 2.25–2.41 (m, 2H, Si–C–CH_2), 5.10 (d, J = 3.5 Hz, 1H, C═CH_2), 5.45 (d, J = 3.5 Hz, 1H, C═CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: −5.5 (Si–CH_3), 12.8 (Si–CH_2^{Hex}), 13.6 (Si–CH_2^{Cy}), 14.1 (CH_3–CH_2), 22.6 (CH_2^{Hex}), 23.7 (CH_2^{Hex}), 24.5 (Si–CH_2–CH_2^{Cy}), 31.0 (Si–CH_2–CH_2–CH_2^{Cy}), 31.6 (CH_2^{Hex}), 33.3 (CH_2^{Hex}), 39.9 (Si–C–CH_2), 121.2 (C═CH_2), 152.3 (C═CH_2); LRMS (70 eV) m/z (relative intensity) 210 (6, M^+), 195 (2), 127 (16), 126 (52), 125 (86), 111 (27), 109 (11), 99 (27), 98 (21), 97 (100), 95 (19), 85 (21), 83 (26), 81 (11), 73 (17), 71 (40), 69 (16), 59 (61), 58 (10), 57 (11), 55 (17), 45 (29), 43 (49); HRMS Calc. for $C_{13}H_{26}Si$: 210.1804. Found: 210.1804. Elemental analysis Calc. for $C_{13}H_{26}Si$: C, 74.20; H, 12.45. Found: C, 74.04; H, 12.61%.

4.18. 1-Methyl-2-methylidene-1-phenyl-1-silacyclohexane (**17**)

Following the general procedure for the intramolecular hydrosilylation, from 51 mg (0.25 mmol) of silane **9** and after purification by column chromatography (pentane), 21 mg of the title compound were isolated as a colorless oil (42%). Spectroscopic data were consistent with previously reported data for this compound [15].

4.19. 1-Allyl-1-methyl-2-methylidene-1-silacyclohexane (**20**)

Following the general procedure for the intramolecular hydrosilylation but at 70 °C and with a final calculated concentration of 0.007 M, from 139 mg (0.83 mmol) of silane **15** and after purification by column chromatography (pentane), 25 mg of the title compound were isolated as a colorless oil (18%). Spectroscopic data were consistent with previously reported data for this compound [15].

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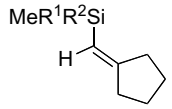

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