



Functionalization of vinyl-substituted linear oligo- and polysiloxanes via ruthenium catalyzed silylative coupling with styrene

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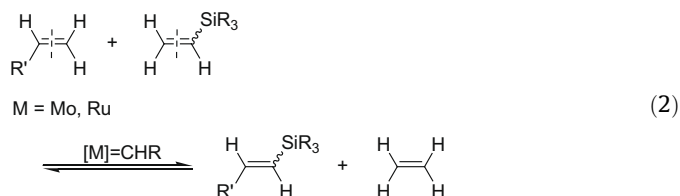
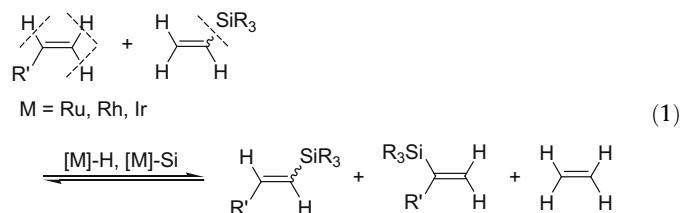
ABSTRACT

Efficient silylative coupling of linear vinyl-substituted oligo- and polysiloxanes with styrene in the presence of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (**1**) and particularly $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ (**2**) combined with copper(I) chloride is described. Treatment of styrene, with terminal or side vinyl group at siloxane skeleton catalyzed by $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]/\text{CuCl}$ results in the quantitative and selective formation of respective silylative coupling products.

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1. Introduction

Substituted vinylsilanes constitute a class of unsaturated organosilicon compounds of prospective wide applicability in organic synthesis [1], especially in the fast developing palladium-catalyzed coupling of vinylsilanes with organic derivatives [2]. Many efficient methodologies for synthesis of vinylsilanes involving classical stoichiometric routes from organometallic reagents as well as transition metal catalyzed transformations of alkynes, silylalkynes and alkenes have been reported [3]. Among them, catalytic hydrosilylation of alkynes plays a crucial role [3c]. In the last two decades two universal, effective and synthetically attractive methods for synthesis of well-defined molecular compounds with vinylsilicon functionality were developed in our group. Both methods i.e. silylative coupling (Eq. (1)) and cross-metathesis, are based on catalytic transformations of vinyl-silicon compounds with olefins (Eq. (2)) and lead to synthesis of respective functionalized vinyl-silicon derivatives [4]



The silylative coupling is catalyzed by complexes containing or generating hydride or silyl ligands ($[\text{M}]\text{-H}$ or $[\text{M}]\text{-Si}$, where $\text{M} = \text{Ru, Rh, Ir}$) and proceeds by a mechanism involving the activation of $=\text{C}\text{-H}$ and $\text{Si}\text{-C}=\text{C}$ bonds (Eq. (1)) [5,6]. On the other hand, cross-metathesis proceeds via the carbene mechanism and is catalyzed by well-defined alkylidene complexes of W, Mo or Ru [7]. The development of a family of ruthenium-based catalysts tolerant of the majority of functional groups and typical organic and polymer processing conditions has allowed a great number of new applications [7]. In the chemistry of unsaturated organosilicon compounds effective metathesis transformations have been described by our group for vinyltris(trimethylsiloxy)silane [8,9], chlorosubstituted vinyldisiloxanes [9] and vinylsubstituted silsesquioxanes [10]. $\text{ViSi}(\text{OEt})_2\text{OSi}(\text{OEt})_2\text{Vi}$ ($\text{Vi} = \text{H}_2\text{C}=\text{CH}-$) can be metathetically copolymerized with 1,9-decadiene [11,12] or divinylbenzene [13] and undergoes ROM/ADMET copolymerization with cyclooctadiene [11]. Divinyldisiloxanes were effectively converted in cross-metathesis with styrenes and 1-decene [14]. Recently, efficient cross-metathesis of linear and cyclic vinyl-substituted oligosiloxanes with selected olefins in the presence of Grubbs type ruthenium alkylidene complexes was described [15]. On the other hand, vinyltris(trimethylsiloxy)silane [16], methylvinylsubstituted cyclosiloxane trimers [17] and tetramers [18], vinylsubstituted

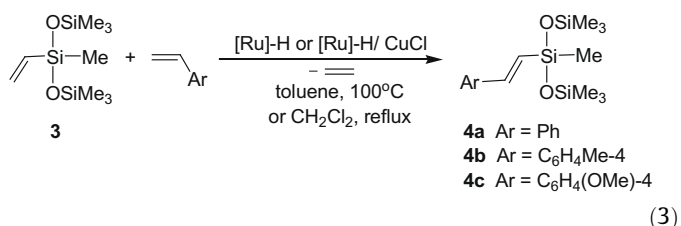
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silsesquioxanes [10] and spherosilicates [19] have been effectively functionalized via silylative coupling with styrene and some other olefins. Both silylative coupling and cross-metathesis provide universal and complementary routes for the synthesis of well-defined vinylsilicon derivatives [4]. Despite the progress in the study of silylative coupling of vinylsilanes, the area of substituted polysiloxanes is relatively unexplored. Non-optimized protocol for silylative coupling of linear poly(dimethylsiloxane-co-methylvinylsiloxane) ($M_n = 3200$) with styrene was proposed, permitting to achieve high conversion after long times of the reaction (up to 144 h) at a relatively high temperature (100 °C) [20].

Now, we report the very efficient silylative coupling of linear vinyl-substituted oligo- and polysiloxanes with styrene, which leads to quantitative and stereoselective functionalization. The procedure uses highly active catalytic system and requires mild conditions. We discuss advantages and drawbacks of the reaction as a general synthetic route for the synthesis of functionalized vinylsiloxanes.

2. Results and discussion

Silylative coupling of 3-vinylheptamethyltrisiloxane (**3**) with styrene was chosen as a model reaction for the study of functionalization of oligo and polysiloxanes containing side vinyl groups. Styrene was used as a reaction partner because it is highly reactive and does not isomerize in the reaction conditions [4]. Treatment of a mixture of vinylheptamethyltrisiloxane and styrene in the presence of 1 mol% of ruthenium hydride complex $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (**1**) in toluene at 100 °C gives rise to evolution of ethene and formation of 3-styrylheptamethyltrisiloxane (Eq. (3)) [16]. The same experiment performed in boiling CH_2Cl_2 shows no detectable conversion after 24 h. Application of 1 mol% of $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ (**2**) permits efficient conversion already at 45 °C. An addition of CuCl as a co-catalyst (5 equiv. relative to catalyst) leads to a significant increase in the catalytic activity, irrespective of the hydride complex used [21].



When an excess (1.5 equiv.) of styrene was used relative to the molar content of vinylsilane, the complete conversion of vinylsilane and nearly quantitative yield of silylstyrene were observed after 3 hours. The excess of styrene was applied in order to retard formation of bis(silyl)ethenes [4]. In the conditions used, the reaction is highly regio- and stereoselective. Only *E*-isomer of silylstyrene was observed by the ^1H NMR spectroscopy. The reaction was found to proceed efficiently also in the presence of substituted styrenes. The results of the catalytic study are summarized in Table 1.

The results obtained have proved a considerably higher catalytic activity of $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ (**2**) than $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (**1**). The system $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]/\text{CuCl}$ was proved the most catalytically active and permits nearly quantitative transformation for all styrenes tested. The fact that the reaction is conducted at the boiling point of the reaction mixture on intense stirring facilitates the migration of ethene from the reaction system, so influences the course of the reaction.

Encouraged by the successful results obtained for 3-vinyltrisiloxane (**3**), we have decided to test the reactivity of styrene towards vinylsubstituted polysiloxanes. Therefore, commercially available poly(methylvinyl)siloxane (**5**) ($M_n = 1280$) containing an

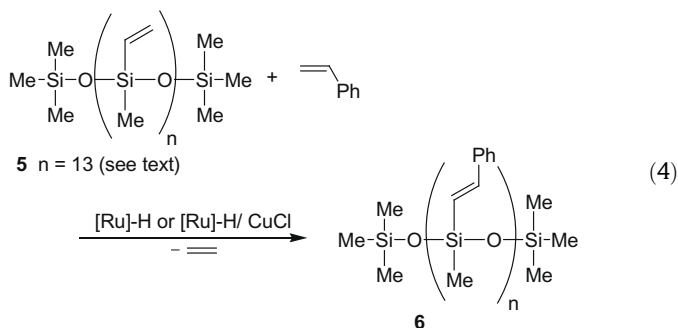
Table 1
Silylative coupling of 3-vinylheptamethyltrisiloxane (**3**) with styrenes.

Catalyst	CuCl	H ₂ C=CHAr Ar =	Time [h]	Yield of 4 [%]
1	–	Ph	24	88 ^a
1	–	Ph	24	0
1	+	Ph	3	22
			18	61
2	–	Ph	3	14
			18	69
2	+	Ph	3	99
2	+	C ₆ H ₄ Me-4	3	99
2	+	C ₆ H ₄ (OMe)-4	2	99

Reaction conditions: CH_2Cl_2 , reflux, $[\text{Ru}]:[\text{ViSi}]:[\text{styrene}] = 1 \times 10^{-2}:1:1.5$, $[\text{Ru}]:[\text{CuCl}] = 1:5$ (if relevant).

^a Toluene, 100 °C.

average number of 13 vinyl side groups in the siloxane chain (as calculated on the basis of ^1H NMR spectroscopic analysis) was treated with styrene. In the presence of complex **2** combined with copper(I) chloride, the reaction proceeds efficiently according to Eq. (4).



The results obtained are compiled in Table 2 and indicate the tendencies similar to those observed for the model reaction (Eq. (1)). The highest activity was observed for the complex $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ (**2**) combined with CuCl, as in the model reaction. In order to shorten the reaction time and to increase the yield the reaction was performed with the use of threefold excess of molar content of styrene relative to the calculated content of vinyl groups.

In another experiment polymer (**5**) was heated in a CH_2Cl_2 solution of $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ (1 mol%) and CuCl (5 mol%) (relative to the number of vinyl groups) in the absence of styrene. Analysis of the reaction mixture by ^1H NMR spectroscopy did not indicate any transformation of vinyl groups in the polymer, which demonstrates that in the reaction conditions applied, no homo-coupling of vinylsilyl groups takes place.

Moreover, an attempt to check the possibility of using this reaction for modification of polymers of higher molecular weights was made. For this purpose the reaction of the commercially available trimethylsiloxy-terminated poly(dimethylsiloxane-co-methylvinyl-

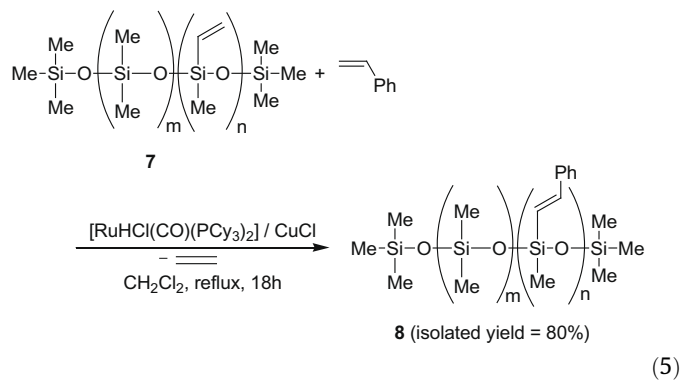
Table 2
Silylative coupling of trimethylsiloxy-terminated poly(vinylmethyl)siloxane (**5**) with styrene.

Catalyst	CuCl	Time [h]	Yield of 6 [%]
1 (1 mol%)	–	24	60 ^a
1 (1 mol%)	+	24	0
2 (1 mol%)	+	8	100
2 (1 mol%)	–	8	60
2 (3 mol%)	+	3	100

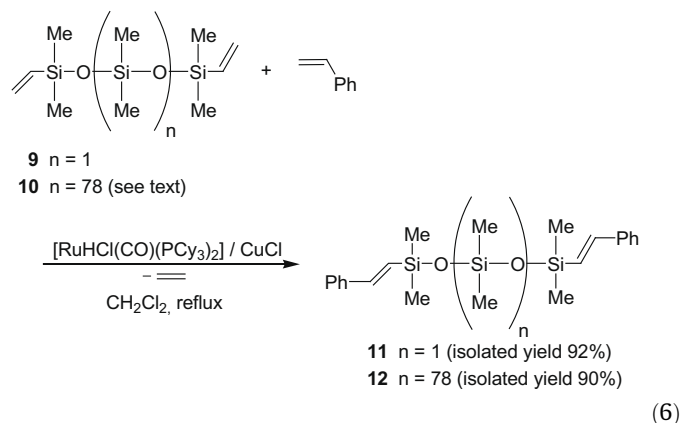
Reaction conditions: CH_2Cl_2 , reflux, $[\text{ViSi}]:[\text{styrene}] = 1:3$, $[\text{Ru}]:[\text{CuCl}] = 1:5$ (if relevant).

^a Benzene, 80 °C.

siloxane) (**7**) ($M_n = 26000$) containing 4.5 mol% of vinylmethylsiloxane unit (as calculated on the basis of ^1H NMR spectrum) was performed with styrene in the presence of $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]/\text{CuCl}$. The high molecular weight poly(methylvinyl)siloxanes have been found to exhibit lower reactivity in the reaction and their satisfactory conversion requires prolonged reaction time and increased catalyst concentration. A complete conversion of **7** was observed after 18 h of the reaction performed in the presence threefold excess of styrene and 3 mol% of $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ (**2**) (in relation to the number of vinyl groups in the co-polymer). Analysis of the reaction mixture by ^1H NMR spectroscopy indicates exclusive formation of silylative coupling product (Eq. (5)).



Finally, we evaluated the applicability of silylative coupling for functionalization of (poly)siloxanes bearing terminal vinyl groups. For this purpose the commercially available 1,5-divinylhexamethyltrisiloxane (**9**) and vinyl dimethylsilyl-terminated poly(dimethylsiloxane) (**10**) ($M_n = 6000$) containing an average number of 78 dimethylsiloxy units in the siloxane chain (as calculated on the basis of ^1H NMR spectrum) were treated with styrene in the presence of $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ (**2**) combined with copper(I) chloride in boiling CH_2Cl_2 . A complete conversion of vinyl groups in compound **9** and quantitative formation of silylative coupling product (**11**) (Eq. (6)) was observed already after 3 h. Standard work-up and purification on column chromatography gave **11** with 92% of isolated yield. Efficient functionalization of vinyl groups in polymer **10** required the reaction to be performed for 18 h. Then full conversion and selective formation of **12** was observed (Eq. (6)). In both cases reactions result in exclusive formation of the *E,E*-isomers.



In all tests performed, particular attention was paid to detect the possible formation of the product of the undesirable styrene polymerization. The procedures presented here ensure the efficient progress of silylative coupling and permit avoidance of the unwanted styrene polymerization without the need of addition of

inhibitors. This effect was achieved thanks to the use of styrene in the possibly lowest excess and application of the mild reaction conditions (45 °C). The mechanism explaining the effect of addition of copper(I) chloride on the reaction course was not examined. The reasonable explanation reported in literature for similar systems indicates that copper salt acts as a phosphine scavenger and thus facilitates formation of catalytically active species [22].

3. Conclusions

Linear oligo- and polysiloxanes with terminal or side vinyl groups at siloxane skeleton undergo efficient silylative coupling with styrene in the presence of $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]/\text{CuCl}$. The reactions proceed quantitatively and lead exclusively to formation of *E* isomers. The procedures proposed ensure elimination of the competitive formation of polystyrene. Making use of substituted styrenes, the silylative coupling permits introduction of a wide range of functional groups into the polymer chain.

4. Experimental

4.1. General methods and chemicals

All syntheses and catalytic tests were carried out under dry argon. ^1H NMR and ^{13}C NMR spectra were recorded in C_6D_6 on a Varian Gemini 300 at 300 and 75 MHz, respectively. Mass spectra of the products were obtained by the GC-MS analysis (Varian Saturn 2100T, equipped with a DB-1 capillary column – 30 m and ion trap detector). GC analyses were performed on a Varian CP 3800 with a 30 m column and TCD. The chemicals were obtained from the following sources: styrene, dichloromethane, benzene- d_6 and copper(I) chloride from Aldrich, vinylmethylbis(trimethylsiloxy)silane, polymethylvinylsiloxane (VMS-T11), trimethylsiloxy-terminated poly(dimethylsiloxane-co-methylvinylsiloxane (VDT-431) and vinyl dimethylsiloxy terminated poly(dimethylsiloxane) (DMS-V21) from Gelest/ABCRC, toluene, benzene and hexane from Chempur. $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (**1**) [23] and $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ (**2**) [24] were prepared according to the literature procedures. All solvents were dried prior to use over CaH_2 and stored under argon. CH_2Cl_2 was additionally passed through a column with alumina and after that it was degassed by repeated freeze-pump-thaw cycles.

4.2. Silylative coupling of vinylheptamethyltrisiloxane (**3**) with styrene

The oven dried 10 mL glass reactor equipped with a condenser and a magnetic stirring bar was charged under argon with CH_2Cl_2 2 mL, vinylheptamethyltrisiloxane 0.035 mL (1.18×10^{-4} mol), decane or dodecane 20 μL (internal standard) and styrene 0.02 mL (1.77×10^{-4} mol). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux (ca. 45 °C). Then a ruthenium complex $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ or $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ (1.18×10^{-6} mol) and after 5 min CuCl 0.0006 g (6.0×10^{-6} mol) were added under argon. The reaction progress was monitored by gas chromatography. The product was isolated and purified by liquid chromatography (silica gel, hexane). Spectral data for (**4a**) ^1H NMR (C_6D_6 , δ , ppm): 6.46 (d, $J = 19.2$ Hz, 1H) =CHSi, 7.19 (d, $J = 19.2$ Hz, 1H) =CHPh, 0.30 (s, 6H) SiMe, 0.22 (s, 18H) OSiMe $_3$; ^{13}C NMR (C_6D_6 , δ , ppm): 1.4 (SiMe), 2.1 (OSiMe $_3$), 126.6 (=CHSi), 145.9 (=CHPh), 127.0, 128.6, 128.9, 138.5 (Ph); MS: m/z (rel. intensity): 45 (7), 73 (14), 133 (5), 145 (8), 159 (5), 161 (8), 205 (6), 207 (6), 219 (6), 221 (6), 265 (5), 267 (12), 293 (18), 294 (6), 308 (6), 309 (100), 310 (30), 311 (15), 324 (6, M^+).

4.3. Silylative coupling of trimethylsiloxy-terminated poly(vinylmethyl)siloxane (**5**) with styrene

The oven dried 10 mL glass reactor equipped with a condenser and a magnetic stirring bar was charged under argon with 2 mL CH_2Cl_2 , trimethylsiloxy-terminated poly(vinylmethyl)siloxane 0.32 mL (3.195×10^{-3} mol of vinyl groups) and styrene 1.1 mL (9.60×10^{-3} mol). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux (ca. 45 °C). Then a ruthenium hydride complex ($[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ or $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_3]$) (3.195×10^{-5} mol) and after 5 min CuCl 0.0159 g (1.598×10^{-4} mol) were added under argon. The mixture was stirred and heated at 45 °C under an argon flow for a certain time. Then the solvent was evaporated and conversion was calculated on the basis of ^1H NMR spectrum. The resulting polymeric product was isolated and purified by liquid chromatography (silica gel, hexane: CH_2Cl_2 = 10:1). Spectral data for (**6**). ^1H NMR (C_6D_6 , δ , ppm): 0.2–0.5 (m, SiMe_3), 6.8–7.4 (m, H, $\text{CH}=\text{CH}$).

4.4. Silylative coupling of trimethylsiloxy-terminated poly(dimethylsiloxane-co-methylvinylsiloxane (**7**) with styrene

The oven dried 10 mL glass reactor equipped with a condenser and a magnetic stirring bar was charged under argon with 2 mL CH_2Cl_2 , trimethylsiloxy-terminated poly(dimethylsiloxane-co-methylvinylsiloxane) 0.46 mL (2.40×10^{-4} mol vinyl group) and styrene 0.14 mL (1.22×10^{-3} mol). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux (ca. 45 °C). Then ruthenium complex $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ 0.0052 g (7.16×10^{-6} mol) and after 5 min. CuCl 0.0036 g (3.58×10^{-5} mol) were added under argon. The mixture was stirred and heated at 45 °C under argon flow for 18 h. After that time, the solvent was evaporated and complete conversion was confirmed by ^1H NMR spectroscopy. The resulting polymeric product was isolated and purified by liquid chromatography (silica gel, hexane: CH_2Cl_2 = 10:1). Isolated yield 80%. Spectral data for (**8**). ^1H NMR (C_6D_6 , δ , ppm): 0.10–0.53 (SiMe), 6.53 (broad d, J = 19.3 Hz, $=\text{CHSi}$), 7.29 (broad d, J = 19.3 Hz, $=\text{CHPh}$), 7.43–7.45 (m, Ph), 7.06–7.14 (m, Ph); ^{13}C NMR (C_6D_6 , δ , ppm): 0.3–2.0 (SiMe), 126.0 ($=\text{CHSi}$), 127.0, 128.7, 128.9, 138.4 (Ph), 146.3 ($=\text{CHPh}$).

4.5. Silylative coupling of vinyl dimethylsiloxy-terminated polydimethylsiloxane (**10**) with styrene

The oven dried 10 mL glass reactor equipped with a condenser and a magnetic stirring bar was charged under argon with 2 mL CH_2Cl_2 , vinyl dimethylsiloxy-terminated polydimethylsiloxane (**10**) 0.97 g (1.6×10^{-4} mol) and styrene 0.0056 g (4.85×10^{-4} mol). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux (ca. 45 °C). Then ruthenium complex $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ 0.0023 g (3.23×10^{-6} mol) was added under argon. After 5 min CuCl 0.0016 g (1.6×10^{-6} mol) was added under argon. The mixture was stirred and heated at 45 °C under argon flow for 18 h. Then the solvent was evaporated. The resulting polymeric product was isolated and purified by use of chromatography column (silica gel, hexane: CH_2Cl_2 = 10:1). Spectral data for (**12**). ^1H NMR (C_6D_6 , δ , ppm): 7.36–7.43 (m, 4H, Ph), 7.06–7.17 (m, 6H, Ph), 7.11 (d, J = 19.2 Hz, 2H, $=\text{CHPh}$), 6.53 (d, J = 19.2 Hz, 2H, $=\text{CHSi}$), 0.12–0.55 (SiMe); ^{13}C NMR (C_6D_6 , δ , ppm): 145.2 ($=\text{CHPh}$), 127.0 ($=\text{CSi}$), 128.2, 128.5, 128.8 (Ph), 0.9, 1.4, 1.5, 1.9 (SiMe). An analogous procedure was used for silylative coupling of 1,5-divinyltetramethyltrisiloxane (**9**) with styrene. Spectral data for (**11**). ^1H NMR (C_6D_6 , δ , ppm): 0.26 (s, 6H, SiMe_2), 0.35 (s, 12H, SiMe_2), 6.55 (d, J = 18.9, 2H, $\text{SiHC}=\text{CHPh}$), 7.15 (d, J = 18.9, 2H,

$\text{SiHC}=\text{CHPh}$), 7.0–7.4 (m, 4H, Ph); ^{13}C NMR (C_6D_6 , δ , ppm): 1.0 (SiMe , terminal), 1.7 (SiMe , internal), 128.3 ($=\text{CHSi}$), 127.0, 128.5, 128.8, 138.5 (Ph), 145.2 ($=\text{CHPh}$); MS: m/z (rel. intensity): 59 (16), 73 (33), 75 (11), 91 (10), 103 (10), 115 (11), 133 (20), 135 (11), 145 (52), 146 (12), 173 (10), 191 (32), 193 (17), 205 (20), 206 (13), 207 (49), 208 (13), 223 (10), 251 (18), 265 (13), 280 (11), 281 (12), 284 (11), 291 (19), 293 (99), 294 (35), 295 (16), 296 (15), 305 (14), 309 (14), 319 (21), 321 (100), 322 (36), 323 (16), 397 (13), 412 (10, M^+).

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