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A new protocol for synthesis of bifunctional alkynyl[vinyl or (*E*)-alkenyl] substituted organosilicon compounds

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ABSTRACT

A new efficient route for selective synthesis of various, novel alkynyl(vinyl)substituted silicon (**6**) and alkynyl[(*E*)-alkenyl]substituted silicon compounds (**9**) via silylative coupling of alkynes and their products catalyzed by ruthenium(+2) complexes is described. The tandem procedure facilitates the formation of **9** synthesized in a high yield and stereoselectivity by a sequential silylative coupling of terminal alkynes with divinylsubstituted silicon compounds followed by silylative coupling reaction of **6** with styrenes in the presence of ruthenium hydride complexes ([RuHCl(CO)(PR₃)_{3-n}]; R = Cy (*n* = 1), *i*-Pr (*n* = 1), Ph (*n* = 0)).

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1. Introduction

Alkynylsubstituted organosilicon compounds bearing a second unsaturated functional group at silicon atom, e.g. vinyl substituent, make a class of attractive starting materials for organometallic synthesis [1]. Recently, vinyl and alkynyl groups have been shown to be of particular interest in the contest of consecutive intermolecular 1,2-hydroboration and intramolecular 1,1-organoboration of alkynyl(vinyl)silanes leading to effective synthesis of 1-silacyclohex-2-enes [1]. Ethynyl(vinyl)silanes have also been applied as reagents in photoinitiated reaction with ethanethiol and its derivatives indicating the possibility of either vinyl or ethynyl group to be involved in the homolytic addition of alkanethiols [2]. Another transition-metal mediated reaction where alkynyl(vinyl)silanes can be used as reagents is carbonylative, intermolecular alkyne-alkyne coupling in the presence of dicobalt carbonyl(0) complex [3]. This is a modification of the well-known Pauson-Khand reaction (coupling between alkyne and alkene). The alkyne-alkyne carbonylative coupling reaction has rarely been investigated although it gives cyclopentadienones, potentially important intermediates.

Despite numerous possible applications of alkynyl(vinyl) substituted organosilicon compounds, there are still a limited

number of reports on their synthesis. It is probably due to the possible problems in the known methods of their synthesis, especially when there are other functional groups involved in the compound structure. The most frequently used route to obtain the above mentioned compounds is a stoichiometric reaction between chlorosilanes and organolithium compounds [1a]. There have been no papers on catalytic path leading to synthesis of functionalized, unsaturated alkynylsubstituted organosilicon compounds.

The transition-metal (TM)-catalyzed (M = Ru, Rh, Ir, Co) transmetallation of olefins with vinylsubstituted metalloid (E = Si, Ge, B) compounds, which we have worked out in the last two decades, proved a valuable synthetic tool in preparation of vinylsubstituted organometalloid reagents as well as polymers [4]. This process appeared to be a new effective catalytic activation of the C–H bond of olefins and C–E bond of organometalloid compounds (generally occurring in the presence of complexes containing initially or generating in situ M–H and M–E bonds).

In search for new reactions in the chemistry of vinylsubstituted metalloid (E = Si, Ge, B) compounds, we turned to acetylenes and recently reported on new type of transformation, i.e. a ruthenium (complexes containing [Ru]–H and/or [Ru]–E bonds –E = Si, Ge) catalyzed silylative and germylative coupling of terminal alkynes with vinylsubstituted silicon and germanium compounds (Scheme 1) [5,6].

The reactions are widely recognized as efficient catalytic activation of *sp*-C–H and =C–E (E = Si, Ge) bonds of a vinylmetalloid with evolution of ethylene. The mechanism of these reactions

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Scheme 1. Silylative/Germylative Coupling of terminal alkynes with divinylsubstituted silicon and germanium compounds.



Scheme 2. Silylative Coupling of terminal alkynes with divinylsubstituted silicon compounds.

involves the insertion of vinyl–E into the [Ru]–H bond and β metalloid transfer to the metal with elimination of ethylene and generation of the [Ru]–E complex. It is followed by the insertion of alkyne into the [Ru]–E bond and β -hydrogen transfer to the metal to eliminate the substituted alkynylsilane and recovery of the

Table 1a

Silylative coupling of $\mathbf{4}$ with divinyl-disiloxane and -disilazane $(\mathbf{5})^a$.

[Ru]–H complex [5]. Preliminary reports on alkynyl(vinyl)disilicon compounds formation via ruthenium catalyzed silylative coupling of terminal alkynes with divinylsubstituted silicon compounds have been published by our group [5a].

Recently, particularly interesting reports on the possibility of application of one-pot and sequential reactions in the synthesis of organic compounds have appeared. There are numerous papers concerning synthetic methodologies based on sequential hydrosilylation/Hiyama coupling [7], silylative coupling/Hiyama coupling [8], Heck arylation/Hiyama coupling processes [9]. The unsaturated organosilicon compounds act as precursors or/and intermediates and have been used as various double bond equivalents in the consecutive construction of unsaturated, often π -conjugated organic systems. These alternative synthetic paths are essentially attractive in view of the economy of the processes, eliminating the step of isolation and purification of intermediate products.

We here disclose a direct synthesis of various unsaturated bifunctional alkynylsubstituted silicon compounds (**6**, **9**) mediated by ruthenium(+2) hydride complexes ([RuHCl(CO)(PR₃)_{3-n}]; R = Cy (n = 1) (1), *i*-Pr (n = 1) (2), Ph (n = 0) (3)). The 6 are obtained via silylative coupling (**SC**) reaction of terminal alkynes (**4**) with divinylsubstituted silicon compounds (**5**). With regard to the

Entry	4	5	[Ru]:[5]:[4]	Conversion of 4 (%)(Yield of 6 (%)) ^b		Selectivity: (6):(7) (%)
1 2			$10^{-2}:2:1^{e}$ $10^{-2}:2:1^{f}$	41 67		92:8 86:14
3 4 5 6 7 8	HC≡CSiMe₂Ph		$\begin{array}{c} 10^{-2}:2:1^{h}\\ 10^{-2}:1:1\\ 10^{-2}:2:1\\ 10^{-2}:4:1\\ 0.5\times10^{-2}:2:1\\ 10^{-2}:2:1 \end{array}$	59 63 97 99 75 48		67:33 77:23 88:12 77:6 ⁴ 84:16 86:14 ^c
9	= <mark>OSiMe₃</mark>		10 ⁻² :3:1 ^g	98 (83)	6a	85:15
10	=-{		$2\times10^{-2}{:}3{:}1$	78 (70)	6b	91:10 ^c
11	$HC \equiv CC_5H_{11}$		$2\times10^{-2}{:}3{:}1$	99 (91)	6c	92:8 ^c
12	HC≡CSiEt ₃		10 ⁻² :2.5:1	77		64:36 ^c
13	≡ ⊖ OSiMe₃	OEt OEt Si ^{-O} -Si OEt OEt	10 ⁻² :3:1	87		95:5
14	=-{>		2×10^{-2} :2.5:1	54		69:31
15	$HC \equiv CC_5H_{11}$		2×10^{-2} :2.5:1	94		87:13
16	$HC \equiv CSiMe_2Ph$, , ^H ,	10 ⁻² :2:1	58		85:15 ^c
17	⊖SiMe₃ =		10 ⁻² :3:1 ^g	99 (73)	6d	73:27
18	=-{		$2\times10^{-2}{:}3{:}1$	84 (62)	6e	72:28
19	$HC \equiv CC_5H_{11}$		2×10^{-2} :3:1	98 (67)	6f	65:35

^a Reaction conditions: Ar, open glass ampoules, catalyst 1, toluene [0.5 M], 120 °C, 24 h.

^b Yield of isolated product.

^c accompanied by traces of divinylsilicon homocoupling products.

^d accompanied by divinylsilicon homocoupling products.

^e 80 °C.

^f 100 °C.

^g catalyst **2**.

h catalyst 3.

possible functionalization of the vinyl group left in the molecule, those compounds are used as hydrogen acceptors in the well-known silylative coupling with styrenes, representative of alkenes [10]. The reaction leads to a new group of bifunctional organosilicon compounds, i.e. alkynyl[(E)-alkenyl]substituted silicon compounds (**9**), which were also obtained using another synthetic path based on sequential reaction of SC of divinylsubstituted silicon compounds with alkynes followed by silylative coupling of obtained product with styrenes in the presence of ruthenium(+2) catalysts.

2. Results and discussion

Our recent reports on selective synthesis of substituted alkynylsilanes have revealed the possibility of formation of alkynyl (vinyl)substituted organosilicon compounds with a divinylsubstituted silicon compound used as a source of hydrogen acceptor [5a,6b]. There are few examples of asymmetrically substituted divinylorganosilicon compounds, yielded as main products and efficiently isolated from the reaction mixture [11].

Herein, we present the results of our synthetic studies of 6 and their further functionalization. The products desired were obtained via silylative coupling reaction of terminal alkynes (**4**) with various divinylsubstituted organosilicon compounds (**5**) containing one or two silicon atoms in the molecule in the presence of ruthenium (+2) hydride complexes: [RuHCl(CO)(PCy₃)₂] (**1**), {RuHCl(CO)[P(*i*-Pr₃)₂]} (**2**) (Scheme 2).

The reactions were performed in an open system under a gentle flow of argon at 110-120 °C for 24–48 h. The results obtained are

Table 1b

Silylative coupling of ${\bf 4}$ with divinyl substituted disilicon compounds $({\bf 5})^a$.

collected in Table 1a and Table 1b. Conversion of substrates and selectivity were determined using a GC method with an internal standard. The results show that the best catalytic system contains at least 1% of [RuHCl(CO)(PCy₃)₂] relative to the alkynyl compound and the reduction of the catalyst amount to 0.5 mol% lowers the alkyne conversion (entry 7). Temperature is also important and should be maintained in the range 110–120 °C (entry 1, 2). The alkyne conversion depends also on the nature of the substituents (steric and electronic aspects) attached to the silicon atom as well as the alkyne moiety. In order to avoid the high plausible dimerization of terminal alkyne [12], the twofold (or more) excess of divinyl compound is used. However, the overflow of 5 favours (in the condition employed) silvlative homocoupling reaction, known since the 1990s [4b], so the reagents ratio is pivotal and optimization needs to be done. To investigate the generality of this reaction a series of divinyldisilicon compounds bearing various substituents was subjected to similar reaction conditions. The results show high effectiveness of (1) and its regioselectivity to produce alkynyl(vinyl)substituted silicon and disilicon compounds where the two atoms of silicon are separated either by heteroatom (Table 1a) or by alkyl/aryl unit (Table 1b). Although the main product is in all cases inherently accompanied with traces of the dialkynylsubstituted disilicon compounds (7) they can be discarded during isolation.

Given our optimized conditions, we investigated the scope of this reaction with divinylsilicon bearing only one metalloid atom in the particle. To obtain high alkyne conversions, a six fold excess of methyldivinylphenylsilane was used. The results obtained are

Entry	4	5	[Ru]:[5]:[4]	Conversion of 4 (%)(Yield of 6 (%)) ^b		Selectivity: (6):(7) (%)
1	HC≡CSiEt ₃		10 ⁻² :1.8:1	92 (75)	6g	85:15
2	HC≡CSiMe₂Ph		10 ⁻² :2:1	91 (84)	6h	97:3
3	≡ ⊖ OSiMe₃		10 ⁻² :2:1 ^d	99 (82)	6i	85:15
4	⊖SiMe₃ =		10 ⁻² :3:1	85 (75)	6j	83:17
5	\equiv		$\textbf{1.5}\times\textbf{10}^{-2}\textbf{:3}\textbf{:}\textbf{1}^{d}$	62 (53)	6k	98:2
6	$HC \equiv CC_5H_{11}$		1.5×10^{-2} :3:1	72 (66)	61	95:5 ^c
7	HC≡CSiEt ₃	≫ [¦] Si∽_Si∕	10 ⁻² :4:1	48		94:6
8	HC≡CSiMe ₂ Ph		10 ⁻² :3:1	58		85:15 ^c
9	≡ ⊖ OSiMe ₃		10 ⁻² :3:1 ^d	99 (89)	6m	90:10 ^c
10	= − _ \		10 ⁻² :3:1 ^d	95 (82)	6n	92:8
11	≡-{		2×10^{-2} :3.5:1	88 (68)	60	78:21
12	$HC \equiv CC_5H_{11}$		2×10^{-2} :3.5:1	91 (74)	6р	89:11

 $^{\rm a}\,$ Reaction conditions: Ar, open glass ampoules, catalyst 1, toluene [0.5 M], 120 °C, 24 h.

^b Yield of isolated product.

^c accompanied by traces of divinylsilicon homocoupling products.

^d catalyst **2**.

Table 3

Silulative coupling of **6** with styrenes $(\mathbf{8})^a$

Table 2		
Silvlative coupling of 4 with methylphenyldivinylsilane ((5)	^a .

Entry	4	Conversion of 4 (%)(Yield of 6 (%)) ^b		Selectivity: (6):(7) (%)
1	HC≡CSiEt ₃	50 (40)	6q	93:7
2	HC≡CSi(<i>i</i> -Pr) ₃	100 (88)	6r	95:5
3	$HC \equiv CGeEt_3$	46 ^c		100:0
4	⊖SiMe₃ =	57 (48)	6s	94:6
5	≡ OSiMe ₃	98 (90)	6t	93:7
6	≡-∕	67 ^c (60)	6u	97:3
7	$HC \equiv CC_5H_{11}$	80 ^c (73)	6w	94:6

^a Reaction Conditions: Ar, open glass ampoules; catalyst **1**; **[1**]:**[5**]:**[4**] = 10^{-2} :6:1; toluene [0.5 M]; 120 °C; 24 h.

^b Yield of isolated product.

^c [1]:[5]:[4] = 2×10^{-2} :6:1.

collected in Table 2. Also in this case, the high effectiveness of (1) and its regioselectivity to produce alkynyl(vinyl)substituted silicon/ germanium compounds is noted. The divinylsilicon moiety is less susceptible to undergo homocoupling (silylative) reaction so the two or six fold excess of methyldivinylphenylsilane could have been applied to increase the alkyne conversion.

Trans-silylation of vinylsubstituted silanes was proved to be an excellent method for stereoselective synthesis of (E)-(alkenyl) silanes [10]. This fact was employed to modify the tri- and tetra-vinylsubstituted cyclosiloxanes, cyclosilazanes [13] and also mon-oalkynylsubstituted di- and trivinylcyclosiloxanes and silazanes [14]. We also tried to apply this technique to perform further functionalization of the remaining vinyl group at the silicon atom in both groups of isolated alkynyl(vinyl)substituted silicon and disilicon compounds (**6**) (Scheme 3).



Selected compounds containing vinyl and substituted alkynyl moiety in the structure were successfully used as substrates of silylative coupling reaction with styrenes (**8**) in the presence of ruthenium(+2) hydride complex (**1**, **2** or **3**) yielding novel alkynyl [(*E*)-alkenyl]substituted silicon compounds (**9**). Respective results of this reaction are presented in Table 3.

All of these products were isolated and characterized by ¹H, ¹³C NMR spectroscopy. The coupling constants of protons at carbon double bond atoms ($J_{H-H} = 19$ Hz) evidence the (E) geometry of the sp^2 -hybridized carbon–carbon bonds. The ¹H, ¹³C{¹H} NMR and HETCOR ¹H{¹³C} spectra of the selected product i.e. 1-{[(cyclohexyl) ethynyl]dimethylsilyl}-4-{[(E)-styryl]dimethylsilyl}benzene (**9e**) are presented in Supporting Information (Figs. 1, 2 and 3).

The results of the study prompted us to perform experiments aiming at working out the sequential reaction system to achieve **9** without isolation of **6**. The selected divinylsubstituted silicon compounds were used as substrates in silylative coupling reaction with **4** followed, without isolation, by silylative coupling with styrenes (**8**), according to Scheme 4.

Entry	6	R ″	Conversion of 6 (%) (Yield of 9 (%)) ^b	
1	Et ₃ Ge	Н	98 (95)	9a
2		Cl	99 (96)	9b
3	C5H11=-\$i-{_}si-{_}si-{_}	Н	99 (96)	9c
4		Cl	99 (97)	9d
5	Si-√Si-″	Н	99 (96)	9e
6	Et ₃ Ge—Si~Si	Н	99 (93)	9f
7		Cl	99 (94)	9g
8	si~si_	Н	98 (94)	9h
9	OSiMe ₃	Cl	99 (95)	9i
10	OSiMe₃ ↓ =si~_si	Н	99 (95)	9j
11	1 1	Cl	98 (95)	9k
12	$C_5H_{11} = S_1^{i_1} S_1^{i_2}$	Н	98 (90)	91
13		Н	95 (90)	9m
14	-	Cl	97 (90)	9n
15	(i-Pr) ₃ SiSi	Н	97 (95)	90
16		Cl	99 (95)	9p
17		Me	96 (94)	9q
18		OMe	97 (93)	9r

^a Reaction conditions: Ar, open glass ampoules; catalyst 1, 2 or 3; toluene [0.5 M], 90 °C; 24 h; [catalyst]:[6]:[8] = 10^{-2} :1:3.

^b Yield of isolated product.

The first step of this sequential process was the synthesis of **6**. The reaction conditions corresponded to those found for **6**, i.e. ruthenium(+2) hydride complex (**1** or **2**) at 1–2 mol% loading, toluene as solvent, optimized excess of **5** and temperature 120 °C. The course of the reaction was followed by gas chromatography. After 24 h, the solvent (and the possible unreacted substrates) was gently evaporated under vacuum pump and the components for the silylative coupling of **6** with styrenes (**8**) (catalyst (**1**, **2** or **3**) at least 1 mol% loading, toluene and styrene or $4-C_8H_7R''$) were introduced. The second step of the reaction was performed at a lower temperature (80–90 °C) for 24 h. In the specified reaction conditions, the desired alkynyl[(*E*)-alkenyl]substituted silicon compounds (**9**j–**9**p) were obtained with perfect stereoselectivity and very high yield (Table 4). All of the compounds were isolated on the silica gel chromatographic column (hexane) and their



Table 4

Sequence of reactions involving consecutive silylative coupling of **4** with selected divinylsubstituted silicon compounds and silylative coupling of these products with **8**^a.

	5	4	[catalyst]:[5]:[4]	R″	Total Yield (%) ^b	
1	≈ [¦] i∽ ⁱ si∕	s ≡	10 ⁻² :3:1	Н	80	9j
2			10 ⁻² :3:1	Cl	82	9k
3	Si ^{_O} `Si,∕∕∕	$HC \equiv CC_5H_{11}$	$2\times10^{-2}{:}3{:}1^{c}$	Н	85	91
4			10 ⁻² :3:1 ^c	Н	85	9m
5		OSIME3	10 ⁻² :3:1 ^c	Cl	86	9n
6	Me Si	HC≡CSi(<i>i</i> -Pr) ₃	10 ⁻² :6:1	Н	85	90
7			10 ⁻² :6:1	Cl	86	9p

^a Reaction condition: Ar, open glass ampoules, toluene [0.5 M]; 1st step: 120 °C, 24 h, catalyst 1; 2nd step: 90 °C, 24 h, catalyst 1 or 2 or 3, [catalyst]:[6]:[8] = 10^{-2} :1:3.

^b Yield of isolated product.

^c catalyst **2** in the 1st step.

spectroscopic characteristics correspond with the analysis of **9** obtained according to the Scheme 3.

In order to verify the possibility of performing the total synthesis of **9** based on a one-pot procedure we accomplished relevant tests. However, after the 1st step of this process, in the reaction mixture there were always residues of unreacted **5** which was used in excess along with the product (**6**) and the rest of catalyst (which most of decomposes after the reaction). In consequence, the addition of catalyst and styrenes (**8**) to the reaction bulb to complete the 2nd step of the synthesis of **9** resulted a mixture of **9** and a product of silylative coupling of **5** with styrenes (reaction known from the literature [15]). In order to avoid silylative coupling of unreacted **5** with styrenes used in the 2nd step of the process, the remains of **5** needed to be evaporated (along with the solvent), leaving the crude product (**6**) and decomposed catalyst. Hence, to obtain **9** with very good conversion and selectivity the sequential procedure is the most promising.

3. Conclusion

In summary, we have devised a versatile protocol for preparation alkynyl(vinyl)substituted silicon (**6**) and alkynyl[(E)-alkenyl] substituted silicon compounds (**9**) from easily available terminal alkynes, divinylsubstituted silicon compounds and styrenes [16]. The synthetic methodology to obtain **9** involves a sequential silylative coupling of terminal alkynes (**4**) with divinylsubstituted silicon compounds (**5**) followed by silylative coupling reaction of **6** with styrenes (**8**) in the presence of ruthenium(+2) hydride complex [17]. The simplicity of the experimental technique and high yields of resulting products enabled us to synthesize, isolate and characterized 38 novel functionalized alkynylsubstituted organosilicon compounds.

4. Experimental

4.1. General procedures

NMR spectra were recorded in CDCl₃ using Varian Mercury (300 MHz) and Bruker Ultra Shield spectrometers (400 MHz) and referenced to the residual protonated solvent peaks (¹H $\delta_{\rm H}$ = 7.26 ppm,

¹³C $\delta_{\rm C} = 77.0$ ppm for CDCl₃) or external Si(CH₃)₄ (²⁹Si $\delta_{\rm Si} = 0.00$ ppm). Coupling constants are reported in Hz. Gas phase analyses were performed on Varian CP-3800 gas chromatography (GC) apparatus equipped with a TCD detector and capillary column VF-5ms (30 m \times 0.53 mm). Mass spectra of the reagents and products were obtained by GC-MS analysis (Varian Saturn 2100T, equipped with a CP-SIL 6CB column (30 m \times 0.25 mm) and an ion trap detector). Elemental analyses were performed on Vario EL Elemantar (Germany). Column chromatography was conducted with silica gel 60 (70-230 mesh, Fluka), deactivated by hexamethyldisilazane prior to use, when needed. Toluene was dried by distillation from sodium, similarly hexane was distilled from calcium hydride under argon. Tetrahydrofuran (THF) was distilled from sodium/ benzophenone under argon. All liquid substrates were also dried and degassed by bulb-to-bulb distillation under argon prior to use. All the reactions were carried out under argon dry atmosphere.

4.2. Materials

The chemicals were obtained from the following sources: toluene, decane, and hexane (Fluka), 1, 1, 3, 3-tetramethyl-1, 3-divinyldisiloxane (Sigma-Aldrich), 1,1,3,3-tetramethyl-1,3-divinyldisilazane (Sigma-Aldrich), 1,1,3,3-tetraethoxy-1,3-divinyldisiloxane (Gelest), 1,4-bis (dimethylovinylsilyl)ethane (Gelest), 1,4-bis(dimethylovinylsilyl) benzene (Gelest), ethynylcyclohexane (Sigma-Aldrich), 1-heptyn (Sigma–Aldrich), 1-ethynylcyclohexanol (Sigma–Aldrich), 3methyl-1-pentyn-3-ol (Sigma-Aldrich), ethynyltriethylsilane (Gelest), ethynyldimethylphenylsilane (Gelest), 1 M THF solution of vinylmagnesium bromide (Sigma-Aldrich), styrene (Sigma-Aldrich), 4-chlorostyrene (Sigma–Aldrich), 4-methylstyrene (Sigma– Aldrich), 4-methoxystyrene (Sigma-Aldrich). 1-ethynyl-1-(trimethylsilyloxy)cyclohexane, and 3-methyl-3-(trimethylsilyloxy)pent-1yne were prepared according to the modified literature procedures [18]. The ruthenium complex [RuHCl(CO)(PCy₃)₂](1), {RuHCl(CO)[P(i- Pr_{3}_{2} (2), $[RuHCl(CO)(PPh_{3})_{3}]$ (3) were prepared according to the literature procedure [19].

4.3. Catalytic examinations of silylative coupling reaction of terminal alkynes (4) with divinylsubstituted organosilicon compounds (5)

In a typical experiment, the ruthenium catalyst (**1** or **2** mol%) was placed in a glass ampoule under argon and dissolved in toluene. The decane (5% by volume of all components), divinylsubstituted organosilicon compound and the acetylene (usually used in the molar ratio: [Ru]:[**5**]:[**4**] = (0.01-0.02) : (1.8-6) : 1) were added. Subsequently, the ampoule was heated to 120 °C and maintained at that temperature for 24 h. The progress of the reaction was monitored by GC and GC–MS. The final products were separated from the residues of the catalyst and reactants by purification on an SiO₂ column (modified with 15% of Et₃N when needed) with hexane as eluent. All the products (**6**) were colourless or pale yellow oily liquids.

4.4. Catalytic examinations of a sequential silylative coupling reaction

In a typical catalytic test, alkynyl(vinyl)substituted organosilicon compound (**6**) was not isolated after silylative coupling reaction with terminal alkynes (**4**) (5% decane as internal standard, amount calculated from GC analyses). Then, the solvent and possible remains of substrates were gently evaporated under vacuum pump, leaving the crude product (**6**) and decomposed catalyst. The ruthenium catalyst (**1**, **2** or **3**) (1 mol%) was placed in a glass ampoule. After that, appropriate amounts of toluene and styrene were placed in the ampoule under argon afterwards (usually used at the molar ratio: [6]:[8] = 1:3). Next, the mixture was heated at 90 °C and maintained at that temperature for 24 h. The final products were separated using the analogous technique, described above.

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Appendix. Supplementary material

See Supplementary material for full ¹H, ¹³C, and ²⁹Si NMR spectra, the GC–MS traces, and the elemental analysis data of the products (**6** and **9**) as well as ¹H, ¹³C{¹H} NMR and HETCOR ¹H{¹³C} spectra of **9e** (Figs. 1–3). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j. biomaterials.2010.09.006.

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