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Highly stereoselective synthesis and application of functionalized tetravinylcyclotetrasiloxanes *via* catalytic reactions

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Abstract

An effective selective silylative coupling functionalization of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane with olefins catalyzed by ruthenium-hydride complex [RuHCl(CO)(PCy_3)$_2$] has been described. We have obtained numerous unsaturated derivatives of cyclosiloxane possessing a SiCH=CHX fragments (where X = alkyl, aryl, silyl, alkoxy, amine and amide groups). One of the products synthesized (1,3,5,7-tetramethyl-1,3,5,7-tetra-(*E*)-4-bromostyrylcyclotetrasiloxane) has been efficiently coupled with aryl iodides in the presence of palladium(0) catalyst to yield substituted 4-bromostilbenes.

Keywords: Vinylcyclosiloxanes; Silylative coupling; Hiyama coupling; Ruthenium(II) complex

1. Introduction

Functionalized cyclosiloxanes have been widely used as fundamental starting materials for anionic and cationic ring-opening polymerization and copolymerization to yield respective organofunctional silicon polymers [1]. Moreover, much attention has been currently devoted to alkenyl-substituted cyclosiloxanes because of their importance in many other fields, such as synthesis of carbosiloxane dendrimers [2], applications in organic synthesis (*via* Pd-catalyzed Hiyama coupling) [3] as well as ligands for transition metal complexes [4].

In the last two decades we have developed a new type of transition metal catalyzed reaction of vinyl-substituted organosilicon compounds with a wide range of olefins, known as the silylative coupling or *trans*-silylation. This reaction occurs by cleavage of the =C–H bond of the olefin and the C–Si bond of vinylsilane. Various transition-metal complexes (i.e. Ru [5], Rh [6], Ir [7], Co [8]), having M–H or M–Si bonds initially or generated in situ, catalyze this process (Scheme 1).

The mechanism of catalysis proceeds by insertion of vinylsilane into M–H bond and β-silyl transfer to the metal center with elimination of ethylene to generate M–Si species, followed by insertion of olefin into M–Si bond and β-H transfer to the metal with elimination of substituted vinylsilane (Scheme 2) [5].

Our investigation of the ruthenium(II) or rhodium(I) complexes catalyzed silylative coupling of vinylsilanes with terminal alkenes, substituted styrenes [9a–c] and heteroatom-containing olefins, such as vinyl ethers [9d], amides [9c,e] and amines [9f], has led to chemo- and regioselective syntheses of corresponding β-substituted vinylsilanes. Contrary to the above mentioned substrates, in the reaction with vinylboranes exclusively 1-(silyl)-1-(boryl)ethenes have been obtained [9g]. Such β-substituted organosilicon derivatives are difficult to synthesize *via* other transition metal-catalyzed reactions, e.g. hydrosilylation and cross-metathesis. Although we have recently reported an efficient cross-metathesis of vinylsilanes with electron-withdrawing (e.g. alkoxy, siloxy, chloro) substituents [10], this reaction cannot be applied to methyl-vinyl-substituted silicon compounds [10b,11].

Silylative coupling reaction versus cross-metathesis has been also successfully applied to the synthesis of functionalized multivinyl-substituted derivatives such as 1,3,5-tris(dimethylvinylsilyl)benzene [12a], octavinylsilsesquioxane [12b], tetramethyltetravinylcyclotetrasilazane, and trimethyltrivinylcyclotrisiloxane (D_3^{Vi}) [12c]. We have also reported on the high efficiency of [RuH(Cl)(CO)(PCy_3)$_2$] catalyst in the stereoselective silylative coupling of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D_4^{Vi}) with styrene.

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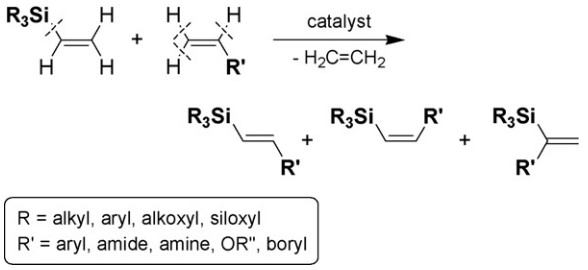
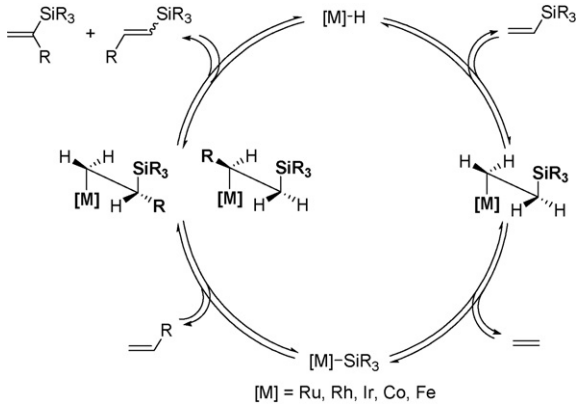


Scheme 1. Silylative coupling reaction.



Scheme 2. Silylative coupling mechanism.

The aim of this paper is to report on the use of the silylative coupling reaction for functionalization of D_4^{Vi} with *p*-substituted styrenes and heteroatom (N, O, Si) containing olefins. We employ D_4^{Vi} as a starting material for functionalized cyclosiloxanes because of the potential application of its unsaturated derivatives in ring-opening polymerization. Moreover, common availability and low cost of D_4^{Vi} allow us to use it as an ancillary reagent to synthesize 1,2-diaryl-substituted ethenes *via* Pd-catalyzed Hiyama coupling reaction.

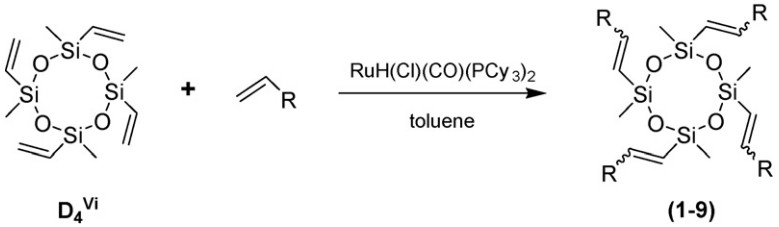
2. Results and discussion

At first, we have investigated a functionalization of tetravinylcyclotetrasiloxane D_4^{Vi} with *p*-substituted styrenes (Scheme 3).

The ruthenium-hydride complex: $[RuHCl(CO)(PCy_3)_2]$ has been recently reported as an effective catalyst for the selective coupling reaction of mono and multivinyl substituted organosilicon compounds [12]. In view of our previous experience we have chosen to start with styrenes because of their highest activity in silylation coupling reaction. The conditions for an effective transformation of D_4^{Vi} into (*E*)-*p*-styryl-substituted cyclosiloxanes (**1**–**3**) in the presence of ruthenium catalyst have been optimized *via* catalytic screening, using ^1H NMR spectroscopy to control the substrate conversion. We have found that reaction of D_4^{Vi} with *p*-substituted styrenes (4-methylstyrene, 4-methoxystyrene and 4-bromostyrene) occurs efficiently at the catalyst loading 0.5 mol% per one vinylsilyl group and at 80 °C for 24 h. Since styrenes are inactive in the silylative coupling, they can be used in excess in order to avoid the homo-coupling of tetravinylcyclotetrasiloxane. A six-fold excess of styrene (molar ratio of D_4^{Vi} to styrene 1:6) appears to be sufficient for exclusive synthesis of (*E*)-styryl-products. Moreover, the reactions have been carried out in the 0.5 M solution in toluene to minimize polymeryzation of styrene. It is noteworthy that this process offers quantitative conversion of the D_4^{Vi} and the styryl-substituted cyclosiloxanes are isolated in excellent yields (92–95%) after short column chromatography. The results are presented in Table 1.

Analogously to D_4^{Vi} which consists of four geometrical isomers, each of the synthesized products (**1**–**9**) have also formed impossible to isolate mixtures of isomers. Although separation of these compounds has been generally not successful, for tetra(*p*-bromostyryl)cyclotetrasiloxane (**3**) and tetrakis(9-carbazyl-vinyl)cyclotetrasiloxane (**9**) we obtained the respective isomers using fractional recrystallization (Et_2O/MeOH 1:1 (**3**); toluene (**9**)) of an isomeric mixture and their X-ray crystal structures were successfully determined.

Thermal-ellipsoid representations of molecules **3** and **9** are shown in Figs. 1 and 2, respectively. The bond lengths and angles are typical for this class of compounds, as compared with the data from the Cambridge Structural Database [16]; some mean values are listed in Table 2. The conformation of the eight-membered rings can be described as distorted twisted-chair (very approximate C_2 symmetry); the values of the torsion angles along the ring are given in Table 2. In **3**, three of the phenyl-vinyl groups are on one side of the plane defined by four oxygen atoms while the fourth one lies on the other side (the deviations from mean square plane made by four oxygens are: 2.11 Å for C_{11}, 2.08 Å for C_{21}, 2.43 Å for C_{31} and −2.57 Å for C_{41}, see Fig. 1a). In **9**, perhaps due to a larger size of the substituents, two vinyl-carbazole groups lie above and two below the four-oxygen atoms plane (the deviations are −2.47, 2.00, −1.85 and 2.51 Å (Fig. 2a)).



R = *p*-C_6H_4Me, *p*-C_6H_4OMe, *p*-C_6H_4Br, ^nBu, $SiMe_3$, O^nBu, O^tBu, N-pyrrolidinone, 9-carbazole

Scheme 3. Functionalization of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D_4^{Vi}).

Table 1
Reactions of D_4^{Vi} with olefins

Product	R[a]	mol% of catalyst[b]	Temperature (°C)[c]	Selectivity (*E*/*Z*)[d]	Yield (%)
1	*p*-C_6H_4Me	0.5	80	100/0	92
2	*p*-C_6H_4OMe	0.5	80	100/0	93
3	*p*-C_6H_4Br	0.5	80	100/0	95
4	^{n}Bu	1.0	60	Complex mixture	85
5	O^{n}Bu	1.0	80	95/5	90
6	O^{t}Bu	1.0	80	92/8	93
7	$SiMe_3$[e]	1.0	60	(E/gem) 90/10	94
8	*N*-Pyrrolidinone	2.0	110[f]	99/1	87
9	9-Carbazole	2.0	110[f]	98/2	86

[a] Molar ratio of olefin to D_4^{Vi} 6:1.
[b] mol% of $[RuHCl(CO)(PCy_3)_2]$ per vinyl silyl group.
[c] Reaction time 24 h.
[d] Calculated by ^{1}H NMR spectroscopy.
[e] Molar ratio of olefin to D_4^{Vi} 24:1.
[f] Reaction time 48 h.

Tetravinylcyclotetrasiloxane D_4^{Vi} was also successfully functionalized with 1-hexene and various heteroatom-substituted olefins in the presence of $[RuHCl(CO)(PCy_3)_2]$, affording cyclosiloxanes possessing SiCH=CHX fragments (X = butyl, trimethylsilyl, alkoxy, amine or amide group), which are difficult to obtain by other transition metal-catalyzed reactions (Scheme 3). Selectivities obtained with the heteroatom-substituted olefins were slightly lower than those observed with the *p*-substituted styrenes. Nevertheless, most of the reactions proceeded with strong preference for the formation of the (*E*)-isomers, accompanied only by small amounts of the (*Z*)-isomers (1–8%). However, as determined from ^{1}H NMR and ^{13}C NMR experiments, product **7** was found as a mixture of isomeric components, which contain (*E*)-2-(trimethylsilyl)vinyl groups and 1-(trimethylsilyl)vinyl fragments. When aliphatic 1-alkene (1-hexene) was applied as a substrate, the course of the reaction was different, due to the competitive ruthenium-hydride complex-catalyzed isomerization of the olefin. As a result, we obtained a mixture of geometrical isomers (*E* + *Z*) of the 1-hexenyl-substituted cyclotetrasiloxanes as well as a small amount (about 6%) of the compound containing 2-hexenylsilyl groups in the molecule.

To demonstrate the potential applications of functionalized cyclosiloxanes, we pursued transformation of the obtained styryl-substituted product into derivatives of (*E*)-stilbene. Unsymmetrical stilbenes are receiving increasing attention because of their ability to act as "plant antibiotics" [13]. This important family of organic compounds, showing a wide range of biological activities can be synthesized *via* tandem silylative coupling and Hiyama coupling reactions. Combination of the two Ru/Pd-catalyzed processes, using tetravinylcyclotetrasiloxane as a supporting

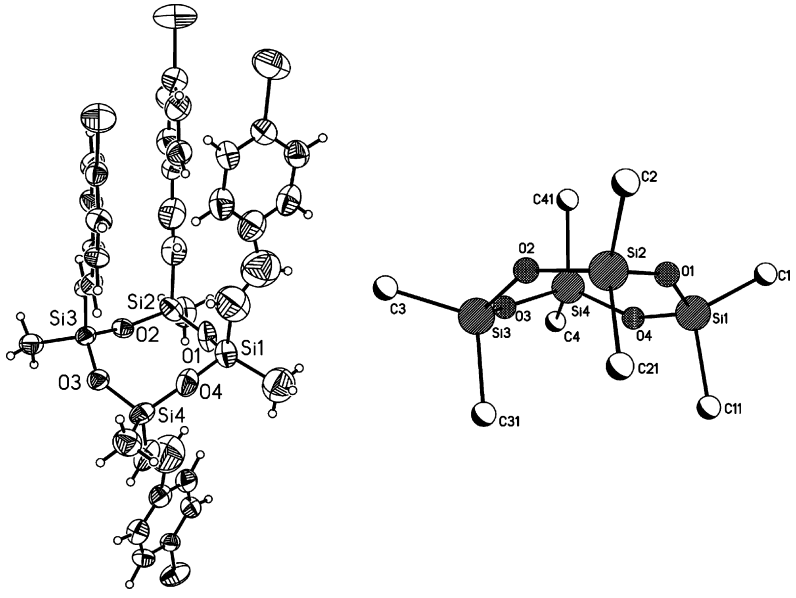


Fig. 1. (Left) perspective view of the molecule 3 [22]. The anisotropic displacement ellipsoids were drawn at 33% probability level, hydrogen atoms are depicted as spheres with arbitrary radii. (Right) the conformation of the eight-membered ring and the positions of substituents [22]. The double-digit numbered carbon atoms are from vinyl fragments.

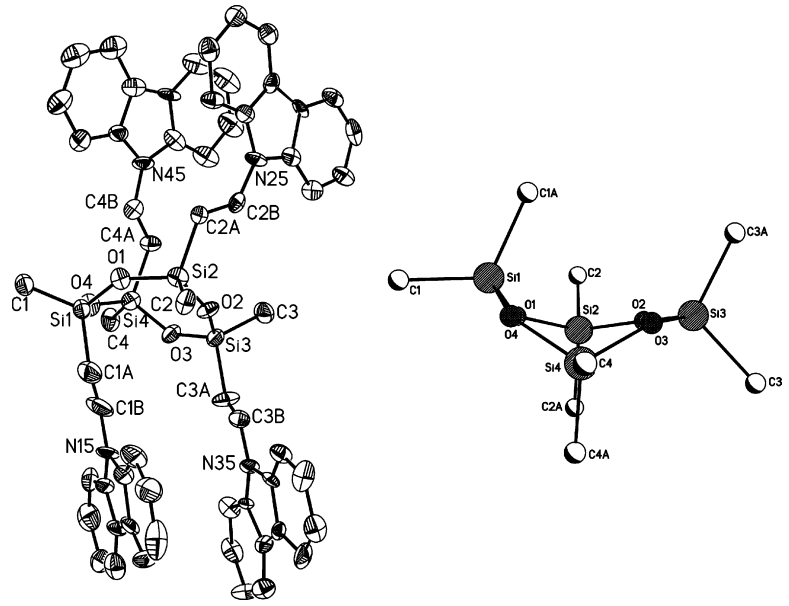
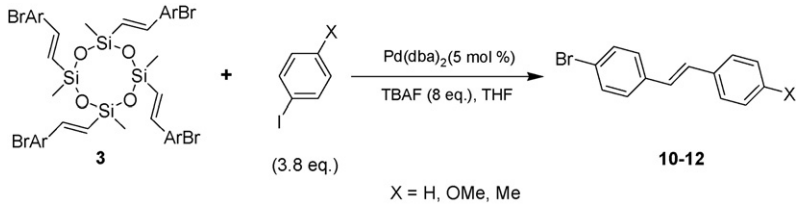


Fig. 2. (left) Perspective view of the molecule 9 [22]. The anisotropic displacement ellipsoids were drawn at 33% probability level, hydrogen atoms are depicted as spheres with arbitrary radii (right). The conformation of the eight-membered ring and the positions of substituents [22]. The double-digit numbered carbon atoms are from vinyl fragments.



Scheme 4. Synthesis of unsymmetrical stilbenes.

reagent leads to stereoselective exclusive synthesis of (*E*)-stilbene with very high yield. 1,3,5,7-Tetramethyl-1,3,5,7-tetra-(*E*)-4-bromostyrylcyclotetrasiloxane (**3**) have been selected for testing the activity of unsaturated cyclosiloxanes in the Hiyama coupling process (Scheme 4). The cross-coupling reactions of compound **3** with iodobenzene and *p*-substituted aryl iodide have been performed in the presence of a [Pd(dba)$_2$]/TBAF (tetrabutylammonioum fluoride) system in THF solution. Three unsymmetrical (*E*)-4-bromostilbenes (where X: H (**10**), OMe (**11**), Me (**12**)) have been selectively synthesized with high yield (85%, 88% and 92%, respectively).

Table 2
Selected geometrical parameters (Å, °)

	3	**9**
⟨O–Si⟩	1.617	1.623
⟨O–Si–O⟩	109.9	110.3
⟨Si–O–Si⟩	143.8	144.7
O_4–Si_1–O_1–Si_2	56.4	−74.9
Si_1–O_1–Si_2–O_2	−56.7	22.8
O_1–Si_2–O_2–Si_3	61.0	20.2
Si_2–O_2–Si_3–O_3	−78.3	−1.7
O_2–Si_3–O_3–Si_4	22.2	33.2
Si_3–O_3–Si_4–O_4	40.7	−81.4
O_3–Si_4–O_4–Si_1	−76.7	40.6
Si_4–O_4–Si_1–O_1	27.1	35.0

3. Conclusions

In conclusion, we have described a general and highly stereoselective method for the synthesis of β-functionalized tetravinylcyclotetrasiloxanes *via* ruthenium-hydride complex-catalyzed silylative coupling of tetravinylcyclotetrasiloxane with *p*-substituted styrenes and heteroatom (O, N, Si) substituted ethenes, which are difficult to synthesize using other transition-metal catalyzed reactions. The products obtained can serve as important intermediates in organic synthesis. The preliminary results on the palladium-catalyzed stereoselective transformation of the resulting 1,3,5,7-tetramethyl-1,3,5,7-tetra-(*E*)-4-bromostyrylcyclotetrasiloxane into *p*-substituted 4-bromostilbenes with high yield are reported.

4. Experimental

4.1. General information

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a Varian XL 300 spectrometer using $CDCl_3$ and CD_2Cl_2

as solvents. GC analyses and mass spectra of the products were determined by GC–MS analysis on a Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and a Finigan Mat 800 ion trap detector. Elemental analyses were carried out by Vario EL III instrument (Elementar GmbH). The chemicals were obtained from the following sources: 4-methoxystyrene, 4-bromostyrene, 4-methylstyrene, 1-vinyl-2-pyrrolidinone, 1-hexene, butyl vinyl ether, *tert*-butyl vinyl ether, tetrabutylammonioum fluoride (1 M solution in THF), iodobenzene, 4-iodotoluene and 4-iodoanisole from Aldrich, tetravinylcyclotetrasiloxane and vinyltrimethylsilane from ABCR, 9-vinylcarbazole from Fluka [$Pd(dba)_2$] from Strem, toluene, *n*-hexane and ethyl acetate from POCh (Poland). Toluene and THF were dried according to standard procedures and freshly distilled prior to use. [$RuHCl(CO)(PCy_3)_2$] was prepared according to a literature method [14]. All the silylative and Hiyama coupling reactions were carried out under argon using standard Schlenk techniques.

4.2. Procedure for synthesis of functionalized cyclosiloxanes

In a typical silylative coupling reaction, tetravinylcyclotetrasiloxane D_4^{Vi} (1 g, 2.4 mmol) and olefin (14.4 mmol) were added to a solution of the catalyst [$RuHCl(CO)(PCy_3)_2$] in dry toluene (5 mL), and the reaction mixture was heated under the conditions shown in Table 1 under the flow of argon. After the substrate disappearance was confirmed by ^{1}H NMR, the volatiles were removed under vacuum and the residue was subjected to column chromatography (silica gel, eluent-hexane/ethyl acetate 20:1 (**1**, **2**, **3**, **9**); hexane/Et_2O 20:1 (**4**, **7**); hexane/Et_2O 10:1 (**5**, **6**); ethyl acetate (**8**)) to afford products as a white solid or pale-yellow oil.

4.3. Analytical data of the new products

4.3.1. 1,3,5,7-Tetramethyl-1,3,5,7-tetra-(E)-4-methylstyrylcyclotetrasiloxane (*1*)

White solid, 92% yield; mp 135–137 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.308, 0.318, 0.322, 0.334 (s, 12 H, $SiCH_3$), 2.35 (s, 12H $>CCH_3$), 6.25, 6.30, 6.32, 6.34 (d, J = 19.2 Hz, 4H, =CH–Si), 7.02–7.12 (m, 4H, =CH–Ar), 7.21–7.40 (m, 16H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 0.306, 0.316, 0.322 ($SiCH_3$), 25.48 (CH_3), 118.55 (=CH–Si), 126.30, 128.32, 132.87 (Ar), 148.43 (=*C*H–, Ar). Anal. calcd. for $C_{40}H_{48}O_4Si_4$: C, 68.13; H, 6.86; Found: C, 68.21; H, 6.96.

4.3.2. 1,3,5,7-Tetramethyl-1,3,5,7-tetra-(E)-4-methoxystyrylcyclotetrasiloxane (*2*)

White solid, 93% yield; mp 117–119 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.302, 0.311, 0.315, 0.322, 0.332, 0.338 (s, 12 H, $SiCH_3$), 3.80 (s, 12H, OCH_3), 6.15, 6.17, 6.20, 6.23 (d, J = 19.2 Hz, 4H, =CH–Si), 6.85, 6.87, 6.94, 7.00 (d, J = 19.2 Hz, 4H, =CH–Ar), 7.25–7.45 (m, 16H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$,) δ (ppm): −0.30 ($SiCH_3$), 55.28 (OCH_3), 111.55, 113.78, 113.86 (Ar), 122.59 (=CH–Si), 127.36, 128.00 (Ar), 145.35 (=*C*H–Ar). Anal. calcd. for $C_{40}H_{48}O_8Si_4$: C, 62.46; H, 6.29; Found: C, 62.83; H, 6.63.

4.3.3. 1,3,5,7-Tetramethyl-1,3,5,7-tetra-(E)-4-bromostyrylcyclotetrasiloxane (*3*)

White solid, 95% yield; mp 161–164 °C. ^{1}H NMR (300 MHz, $CDCl_3$,) δ (ppm): 0.308, 0.314, 0.321, 0.332, 0.347 (s, 12 H, $SiCH_3$), 6.26, 6.28, 6.31, 6.36 (d, J = 19.4 Hz, 4H, =CH–Si), 6.92–7.05 (m, 4H, =CH–Ar), 7.11–7.50 (m, 16H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$,) δ (ppm): −0.37, −0.27 ($SiCH_3$), 122.49 (=CH–Si), 125.75, 125.89, 128.07, 128. 12, 131.66, 136.61 (Ar), 144.79 (=*C*H–Ar). Anal. calcd. for $C_{36}H_{36}Br_4O_4Si_4$: C, 44.82; H, 3.76; found: C, 44.64; H, 3.94.

4.3.4. 1,3,5,7-Tetramethyl-1,3,5,7-tetrakis(hexenyl)cyclotetrasiloxane (*4*)

Colorless oil, 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.067, 0.079, 0.084, 0,131, 0.141, 0.146, 0.150, 0.163, 0.175 (s, 12 H, $SiCH_3$), 0.85–0.92 (m, 12 H, CH_3), 1.25–1.48 (m, 16H, $CH_3CH_2CH_2CH_2$), 1.94–1.96, 2.10–2.17 (m, CH_2CH=, (*E*)), 2.20–2.25 (m, CH_2CH=, (*Z*)), 5.32–5.39 (m, =CHSi, (*Z*)), 5.48–5.53 (d, J = 18.2 =CHSi, (*E*)), 5.95–6.00 (m, =$CHCH_2$, (Z)), 6.18–6.46 (m, 4H, =$CHCH_2$, (*E*)). ^{13}C NMR (75 MHz, $CDCl_3$,) δ (ppm): −2.26, −0.64, −0.25 ($SiCH_3$), 13.76, 14.05, 14.22 (CH_3), 22.34, 22.54 ($CH_3CH_2CH_2CH_2CH$=, (*E*)), 22.74, 22.99 ($CH_3CH_2CH_2CH_2CH$=, (*Z*)), 30.68 ($CH_3CH_2CH_2CH$=, (*E*)), 31.00 ($CH_3CH_2CH_2CH$=, (*Z*)), 35.05 (CH_2CH=, (*Z*)), 36.12 (CH_2CH=, (*E*)), 124.45 (SiCH=, (*E*)), 126.45 (SiCH=, (*Z*)), 129.89 (*C*H=CH), 133.07 (CH=*C*H), 149.72 (CH_2CH=CHSi, (*E*)). Anal. calcd. for $C_{28}H_{56}O_4Si_4$: C, 59.09; H, 9.92; found: C, 59.26; H, 10.05.

4.3.5. 1,3,5,7-Tetramethyl-1,3,5,7-tetrakis(2-n-butoxyvinyl)cyclotetrasiloxane (*5*)

Pale yellow oil, 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$,) δ (ppm): 0.147, 0.161, 0.167, 0.179, 0.183, 0.188, 0.196, 0.207 (s, 12 H, $SiCH_3$), 0.87–0.95 (m, 12H, CH_3CH_2), 1.25–1.30 (m, 8H, $CH_3CH_2CH_2$), 1.55–1.65 (m, 8H, $CH_3CH_2CH_2$), 3.35–3.38 (m, $CH_3(CH_2)_2CH_2O$, (*Z*)), 3.65–3.72 (m, $CH_3(CH_2)_2CH_2O$, (*E*)), 3.83 (d, J = 8.4 Hz, =CH–Si, (*Z*)), 4.40 (d, J = 15.1 Hz, =CH–Si, (*E*)), 6.48–6.56 (m, =CH–O, (*Z*)), 6.60 (d, J = 15.1 Hz, =CH–O, (*E*)). ^{13}C NMR (75 MHz, $CDCl_3$,) δ (ppm): 0.54, 0.62, 0.68, 1.02 ($SiCH_3$), 13.75, 13.80, 13.93 (CH_3), 18.96 (CH_3CH_2, (*Z*)), 19.19 (CH_3CH_2, (*E*)), 31.05 (CH_2CH_2O, (*E*)), 31.87 (CH_2CH_2O, (*Z*)), 67.58, 67.60, 67.63 (CH_2CH_2O, (*E*)), 72.51 (CH_2CH_2O, (*Z*)), 76.57, 77.00, 77.42 (=CH–Si, (*E*)), 93.17, 93.22 (=CH–Si, (*Z*)), 158.43, 158.50 (=CH–O, (*E*)), 158.57 (=CH–O, (*Z*)). Anal. calcd. for $C_{28}H_{56}O_8Si_4$: 53.12; H, 8.92; found: 53.31; H, 9.07.

4.3.6. 1,3,5,7-Tetramethyl-1,3,5,7-tetrakis(2-tert-butoxyvinyl)cyclotetrasiloxane (*6*)

Pale yellow oil, 93% yield. ^{1}H NMR (300 MHz, $CDCl_3$,) δ (ppm): 0.142, 0.164, 0.168, 0.184, 0.188, 0.196, 0.208 (s, 12 H, $SiCH_3$), 1.22 (s, $(CH_3)_3COCH$=, (*Z*)), 1.28 (s, $(CH_3)_3COCH$=, (*E*)), 4.10–4.16 (m, =CH–Si, (*Z*)), 4.50 (d, J = 14.4 Hz, =CH–Si,

(*E*)), 6.68–6.74 (m, =CH–O, (*Z*)), 6.83 (d, $J = 14.4$ Hz, =CH–O, (*E*)). ^{13}C NMR (75 MHz, $CDCl_3$,) δ (ppm): 0.52, 0.60, 0.66, 0.82, 0.92 ($SiCH_3$), 28.42, 28.66, 28.90 (($CH_3)_3CO$, (*E*)), 29.84 (($CH_3)_3CO$, (*Z*)), 77.78, 77.86 (($CH_3)_3C$), 88.47, 88.60, 88.91 (=CH–Si (*E*)), 92.27, 92.44 (=CH–Si, (*Z*)), 156.03, 156.12 (=CH–O, (*E*)), 157.09 (=CH–O, (*Z*)). Anal. calcd. for $C_{28}H_{56}O_8Si_4$: C, 53.12; H, 8.92; found: C, 53.29; H, 8.80.

*4.3.7. 1,3,5,7-Tetramethyl-1,3,5,7-tetrakis(2-(trimethylsilyl)vinyl)cyclotetrasiloxane (**7**)*

White solid, 94% yield; mp 267–270 °C. ^{1}H NMR (300 MHz, $CDCl_3$,) δ (ppm): 0.02, 0.04, 0.05, 0.08, 0.11, 0.14, 0.15, 0.18 (s, 48 H, $SiCH_3$), 6.22–6.36 (m, =CH–Si), 6.58–6.63 (m, $=CH_2$), 6.98–7.08 (m, $=CH–SiO_2Me$). ^{13}C NMR (75 MHz, $CDCl_3$,) δ (ppm): −2.02, −1.96, −1.64, −1.08 ($SiCH_3$), 137.22, 137.38, 137.49 (=*C*H$SiMe_3$), 139.69 ($=CH_2$), 154.22 (=C<). Anal. calcd. for $C_{24}H_{56}O_4Si_8$: C, 45.51; H, 8.91; found: C, 45.83; H, 9.11.

*4.3.8. 1,3,5,7-Tetramethyl-1,3,5,7-tetrakis(2-(pyrrolidin-2-onyl)vinyl)cyclotetrasiloxane (**8**)*

Pale yellow oil, 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$,) δ (ppm): 0.182, 0.184, 0.198, 0.204, 0.207, 0.219, 0.227 (s, 12 H, $SiCH_3$), 2.04 (q, $J = 7.7$ Hz, 8H, NCH_2CH_2), 2.32–2.51 (m, 8H, $COCH_2$), 3.48–3.55 (m, 8H, NCH_2), 4.58–4.68 (m, 4H, =CH–Si), 7.15–7.30 (m, =CH–N). ^{13}C NMR (75 MHz, $CDCl_3$,) δ (ppm): 1.14, 1.22, 1.28 ($SiCH_3$), 17.45 (NCH_2CH_2), 31.38, 31.99 ($COCH_2$), 44.56 (NCH_2), 94.27 (>C=O), 135.02 (=CH–Si), 143.32 (=CHN). Anal. calcd. for $C_{28}H_{44}N_4O_8Si_4$: C, 49.67; H, 6.55; N, 8.28; found: C, 49.52; H, 6.66; N, 8.22.

*4.3.9. 1,3,5,7-Tetramethyl-1,3,5,7-tetrakis(9-carbazyl-vinyl)cyclotetrasiloxane (**9**)*

White solid (melting point was unclear because it gradually decomposed above 225 °C). ^{1}H NMR (300 MHz, CD_2Cl_2,) δ (ppm): 0.177, 0.181, 0.190, 0.202, 0.206, 0.216 (s, 12 H, $SiCH_3$), 5.52–5.58 (m, 4H, =CH–Si), 7.25–7.70 (m, 24H, Ar), 7.82 (d, 4H $J = 17.2$ Hz, =CH–N), 7.98–8.02 (m, 8H, Ar). ^{13}C NMR (75 MHz, CD_2Cl_2,) δ (ppm): 1.44, 1.48, 1.58 ($SiCH_3$), 110.5, 110.9, 119.6, 120.1, 120.4, 120.6, 126.0, 126.5 (Ar), 133.2 (=CH–Si), 139.8 (=CHN). Anal. calcd. for $C_{60}H_{52}N_4O_4Si_4$: C, 71.68; H, 5.21; N, 5.57; found: C, 72.03; H, 5.35; N, 5.42.

4.4. A representative procedure for the Hiyama coupling reaction

The Schlenk flask was charged with 1,3,5,7-tetramethyl-1,3,5,7-tetra-(*E*)-4-bromostyrylcyclotetrasiloxane **3** (1 equiv.) and a solution of TBAF (8 equiv.). The resulting mixture was stirred for 10 min and then added sequentially aryl iodide (3.8 equiv.) and [$Pd(dba)_2$] (5 mol%). The reaction was carried out at 65 °C and its progress was controlled by GC–MS. After 20 h, the reaction mixture was filtered though a short column (silica gel, eluent-Et_2O). The eluate was concentrated by rotary evaporation and the crude product was purified by column chromatography (silica gel, hexane/ethyl acetate 50:1) to afford respective bromostilbene derivative as a white solid. The structure of synthesized compounds was confirmed by GC–MS and NMR spectroscopy maching data reported in the literature [15].

Table 3
Crystal data, data collection and structure refinement for **3** and **9**

	3	**9**
Formula	$C_{36}H_{36}Br_4O_4Si_4$	$C_{60}H_{52}N_4O_4Si_4$
Formula weight	964.65	1005.44
Crystal system	Triclinic	Triclinic
Space group	P-1 (no. 2)	P-1 (no. 2)
a (Å)	9.588(3)	8.626(2)
b (Å)	12.575(3)	12.574(4)
c (Å)	18.307(6)	24.400(7)
α (°)	84.71(3)	94.21(3)
β (°)	78.78(3)	98.65(2)
γ (°)	71.00(3)	98.04(2)
V (Å^3)	2046.1(10)	2578.5(13)
Z	2	2
D_x (g cm^{-3})	1.566	1.295
F (0 0 0)	960	1056
μ (mm^{-1})	4.086	0.167
Crystal size (mm)	0.2 × 0.1 × 0.1	0.4 × 0.2 × 0.1
Θ range (°)	2.28–25.00	2.47–25.00
$h\,k\,l$ range	$-11 \le h \le 9$, $-11 \le h \le 9$, $-21 \le l \le 18$	$-9 \le h \le 10$, $-12 \le h \le 14$, $-28 \le l \le 28$
Reflections		
Collected	13745	20678
Unique (R_{int})	7064 (0.10)	9016(0.18)
$R(F)$ [$I > 2\sigma(I)$]	0.086	0.092
$wR(F^2)$ [$I > 2\sigma(I)$]	0.173	0.169
Goodness of fit	0.94	0.81
Max/min, $\Delta\rho$ (Einstein Å^{-3})	0.82/−0.61	0.36/−0.24

4.5. X-ray crystal structure analysis

The poorly diffracting crystals of **3** and **9** were grown from hexane solution. The X-ray diffraction data were collected on Oxford Diffraction four-circle diffractometer equipped with CCD detector [17] at 295 K. The data were corrected for Lp [18] and for **3** additionally for absorption with SORTAV [19]. The crystal data together with some experimental and refinement details are given in Table 3. The structures were solved by direct methods with SHELXS97 [20] and refined by full-matrix least squares with SHELXL97 [21]. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were located from the ideal geometry [22] and refined as 'riding model'. The isotropic displacement parameters of hydrogen atoms were set at 1.2 (1.5 for methyl groups) times the equivalent displacement parameters of appropriate carrier atoms. Due to the relatively poor data some weak restraints (SAME and ISOR [20]) were applied for the geometry and thermal parameters of C=C groups in **3**.

4.6. Supplementary materials

Crystallographic data (excluding structure factors) for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, No. CCDC-289520 (**3**) and CCDC-294367 (**9**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk, or www.ccdc.cam.ac.uk.

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