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## Testing the 1,1,3,3-tetramethyldisiloxane linker in olefin metathesis

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## ARTICLE INFO

## Article history:

Received 30 October 2012

Accepted after revision 24 January 2013

Available online 1 March 2013

## Keywords:

Catalysis

Olefin metathesis

Ruthenium

Stilbenes

## ABSTRACT

Compounds **12–15**, possessing two styrenes connected by a silicon linker [1,1,3,3-tetramethyl-di-siloxane], were synthesized, characterized and used as model compounds for the ring-closing metathesis (RCM) catalyzed by commercially available ruthenium catalysts **1**, **2** and **3**. The RCM reactions of **12** and **15** in the presence of catalysts **1** or **2** resulted exclusively in the formation of (*E*)-stilbenes. The RCM reactions of **13** and **14**, compounds possessing alkoxide substituents in the *ortho* position to styrene functionality, were not observed in the presence of **2**, presumably due to the formation of inactive Hoveyda type ruthenium complexes. The RCM of mixture of **12** and **15**, with **2**, was used for the detailed examination of the mechanism of metathesis reactions investigated in this work. They revealed that both inter- and intramolecular metathesis is possible, in this case, despite the use of siloxane linker.

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### 1. Introduction

Stilbenoids are well-known compounds applied in the pharmaceutical industry. Some stilbenoids occur in nature, but their synthetic analogs are also known [1,2]. Naturally occurring stilbenoids are prominent building blocks in organic synthesis. Both (*E*)- and (*Z*)-stilbenoids have important biological activities [3,4]. They possess anti-oxidative, anti-microbial and anti-tumor properties [5], induce apoptosis (programmed cell death) [6], cause vascular disruption in tumors [7] or inhibit tubulin polymerization [8]. Among (*E*)-stilbenoids, resveratrol and its derivatives play a crucial role in cancer therapy due to their physiological and therapeutic properties [9]. Among (*Z*)-stilbenoids combretastatins possess the most interesting properties for pharmaceutical industry, due to their ability to inhibit tubulin polymerization [8].

For economic reasons, stable stilbenoids that can be isolated in large quantities from natural sources are most

often examined for their utility as drugs components. For example, they can be isolated from grapes and combretastatins from the willow bush. Stilbenoids can also be modified to enhance their medicinal properties [10]. However, currently known synthetic methods for obtaining stilbenoids are frequently complex and not efficient enough. Therefore, it is important to find novel and simple methods to synthesize stilbenoid derivatives [11,12].

Stilbenes were initially obtained in Wittig [13] and Horner–Wadsworth–Emmons reactions [14]. Unfortunately, these reactions have led to the formation of carbon–carbon double bonds, providing unsatisfactory (*E*)/(*Z*) selectivity. To enhance the (*E*)/(*Z*) selectivity a number of transition metal-based catalysts were later used, such as palladium complexes in Heck [15], Negishi–Stille [16], Suzuki [17] and tandem [18] processes. Alternatively, low-valent titanium complexes were in a stoichiometric manner used for coupling two aldehydes or ketones in a McMurry reaction [19]. Moreover, in the presence of molybdenum [20] or ruthenium [21] complexes, a new carbon–carbon double bond can be directly formed in the olefin metathesis reaction between two styrenes. This method is very promising as it allows the use

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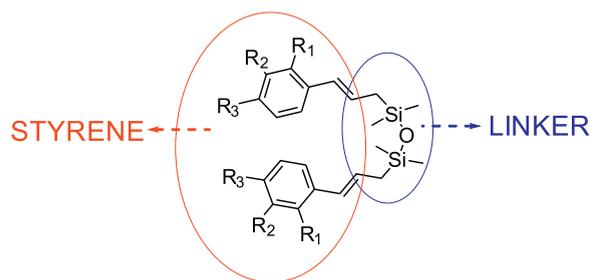


Fig. 1. Substrates used in the present study.

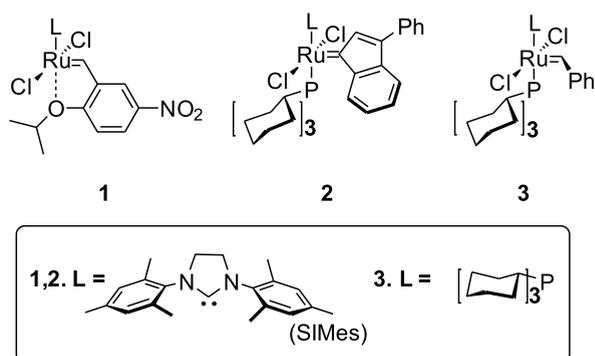
of a broad range of substrates and requires only a small amount of catalyst under relatively mild experimental conditions. However, problems with (*E*)/(*Z*) stereoselectivity and the tendency for the formation of the mixture of products due to cross-metathesis (CM) or homo-dimerization (HD) are the main drawbacks of this approach. Therefore, according to our knowledge, only a few examples of stilbene formation using alkene metathesis are reported in the literature [20–22].

In order to eliminate the drawbacks of the stilbenoid synthesis via metathesis, which are indicated above, we have investigated the system where two styrenes are connected by silicon linker [1,1,3,3-tetramethyldisiloxane], as shown in Fig. 1. Here, we describe the effect of the use of such linker in the stilbenoid synthesis on the selectivity of metathesis reaction using standard metathesis condition (dichloromethane [DCM] at 40 °C and toluene at 80 °C) and commercially available catalysts **1–3** (Fig. 2).

## 2. Results and discussion

### 2.1. Preparation of 1,3-dicinnamyl-1,1,3,3-tetramethyldisiloxane derivatives

For our studies, we have chosen 1,3-dicinnamyl-1,1,3,3-tetramethyldisiloxane derivatives (Fig. 3) as model compounds as in this case two styrenes are connected by silicon linker. Following the synthetic route presented in Fig. 3, desired lithium reagents were obtained by metalation of allyl-substituted arenes **4–7** by *n*-butyllithium-tetramethylethylenediamine (*n*-BuLi–TMEDA) in tetrahydrofuran (THF) at 0 °C, resulting in the formation of lithium

Fig. 2. Structures of the ruthenium catalysts **1**, **2** and **3** used in this study.

reagents **8–11**, respectively. The completeness of the metalation step was guaranteed by rising the temperature from 0 to 25 °C. The reaction of cinammyllithium derivatives **8–11** with 0.6 equiv. of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane afforded exclusively compounds **12–15**. We obtained the products with (*E*)-isomer excess of 88–92%.

Initially, we have examined the reactivity of compound **12** in olefin metathesis using complexes **1–3** (Fig. 1) at 40 °C in DCM and 80 °C in toluene (Table 1). The reaction did not proceed in the presence of the first-generation Grubbs catalyst **3** (5 mol%) in DCM at 40 °C (Table 1, entry 3), and **12** was still present in the reaction mixture, indicating no degradation of the substrate under the reaction conditions. Even an increase of temperature had no effect on the reaction performed with catalyst **3** (5 mol%) in toluene at 80 °C (Table 1, entry 5). The use of catalysts **1** and **2** at 40 °C (Table 1, entry 1 and 2) led to the formation of stilbene in 44% and 91% yields, respectively. At high temperature (80 °C), catalyst **2** promoted the reaction very effectively, resulting in 90% of yield (Table 1, entry 4). In all cases the formation of stilbene has been proven by GC–MS analysis (Tab. I). In the case of reactions catalyzed by **1** and **2**, we compared the retention times of the reaction product and the (*Z*)- and (*E*)-stilbene standards, and found that only (*E*)-isomer was formed.

On the basis of initial results presented above, catalyst **2** (Umicore™ M2) was chosen for further examination of the metathesis reactions of compounds **13–15** (Figs. 4 and 5).

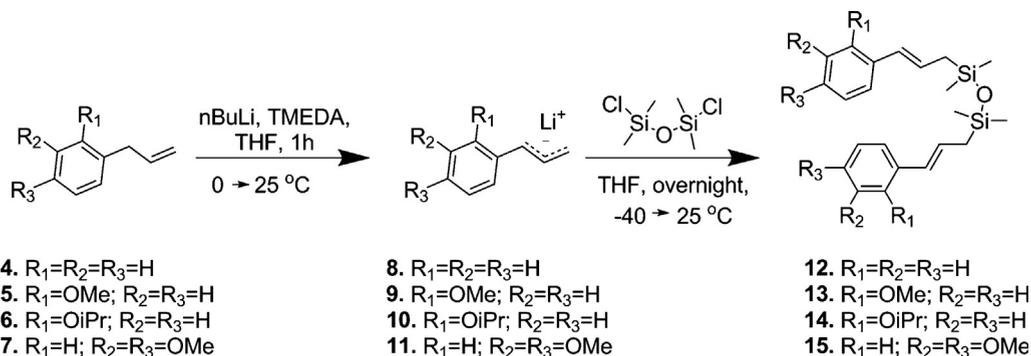


Fig. 3. Synthetic route of 1,3-dicinnamyl-1,1,3,3-tetramethyldisiloxane derivatives.

**Table 1**  
Metathesis of substrate **12** with catalysts **1–3**.

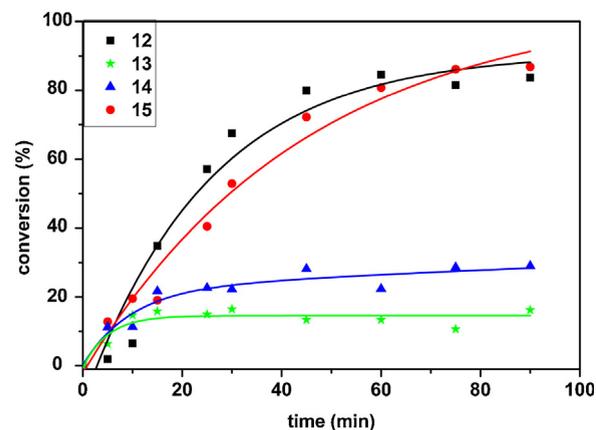
	Catalyst	Solvent	Temperature (°C)	Yield (%) <sup>a</sup>
1	<b>1</b>	DCM	40	44
2	<b>2</b>	DCM	40	91
3	<b>3</b>	DCM	40	0
4	<b>2</b>	Toluene	80	90
5	<b>3</b>	Toluene	80	0

Conditions: catalyst (5 mol%),  $t = 12$  h,  $c = 0.1$  mol/L.

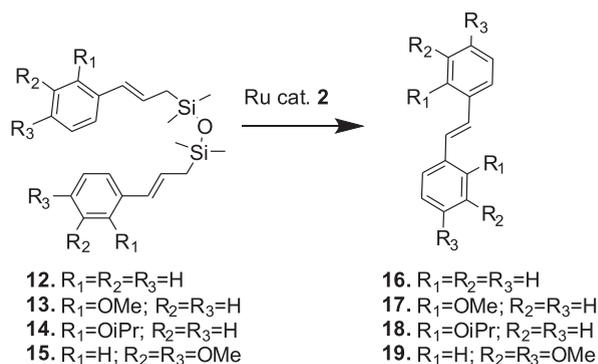
<sup>a</sup> Yields determined by GC–MS analysis of the reaction mixture.

The reactivity of substrate **15** was found to be similar to the reactivity of **12**. Despite noticeable (*E*)/(*Z*) isomerisation of substrate **15** resulting in (*E*)/(*Z*) of 88/12, we observed that metathesis of **15** led exclusively to the (*E*)-stilbene and was also fast and efficient, and no other products were formed. However, both **13** and **14** were inactive towards metathesis and the formation of stilbene **17** and **18**, respectively, was not observed (Table 1).

In order to explain the lack of metathesis activity of **13** and **14** catalyzed by **2**, we performed the equimolar reaction between **13** and catalyst **2**, obtaining compound **20** (Fig. 6). Compound **20** was isolated as green crystals in 49% yield. Noteworthy, the formation of the new catalyst inactive in the metathesis of **13**, explains the lack of formation of **17**. It should be noted that complex **20** [23] is a methyl analog of Hoveyda–Grubbs catalyst (**21**), which apparently exhibits low activity in olefin metathesis with this specific substrate. As **21** is expected to be formed in the case of an equimolar reaction between **14** and **2**, the lack of formation of **18** should be explained by low catalytic activity of **21** in the metathesis of **14**. In order to check the stability of substrates under the reaction conditions, we performed the stability tests in the absence of Ru catalysts by heating compounds **12–15** at 80 °C for 3 h. It was confirmed that the substrates are stable under these conditions. To support our findings discussed above, the formation of the catalyst **20** in the RCM of **13** prevents further metathesis reaction, we performed RCM of **13** with



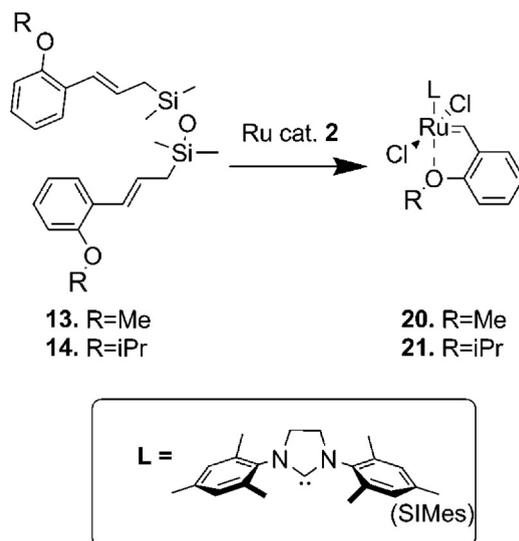
**Fig. 4.** Reaction profiles of the compounds **12–15** with catalyst **2** (5 mol%).



**Fig. 5.** Metathesis reaction promoted by catalyst **2**.

**1.** For the latter the lack of RCM of **13** is in line with our earlier observations.

In the next step, we performed the metathesis reaction using the mixture of compounds **12** and **15** in order to show whether inter- or intramolecular process operate in that case (Fig. 7). The metathesis of **12:15** (1:1) was catalyzed by **2** (5 mol%,  $c = 0.02$  mol/L). We monitored the reaction progress by the GC–MS and observed that initially (after 15 min), only compound **23** was formed. After prolonged reaction time, the formation of compounds **16**, **19** and **22** was observed. After 5 h, the products **16**, **19** and **22** were present in 26:17:49 molar ratios, respectively. Noteworthy, the metathesis reaction of **12 + 15** (mixed in molar ratio 1:1) proceeded more slowly in comparison with the metathesis reaction performed separately for compound **12** or **15**. This experiment indicates that both CM and RCM may operate in the investigated system. The control CM reaction with styrene and 3,4 dimethoxystyrene promoted with catalyst **2** (the experiment was performed analogously to the one with **12** and **15**) shows



**Fig. 6.** Formation of Hoveyda–Grubbs catalysts in reaction of **13** and **14**.

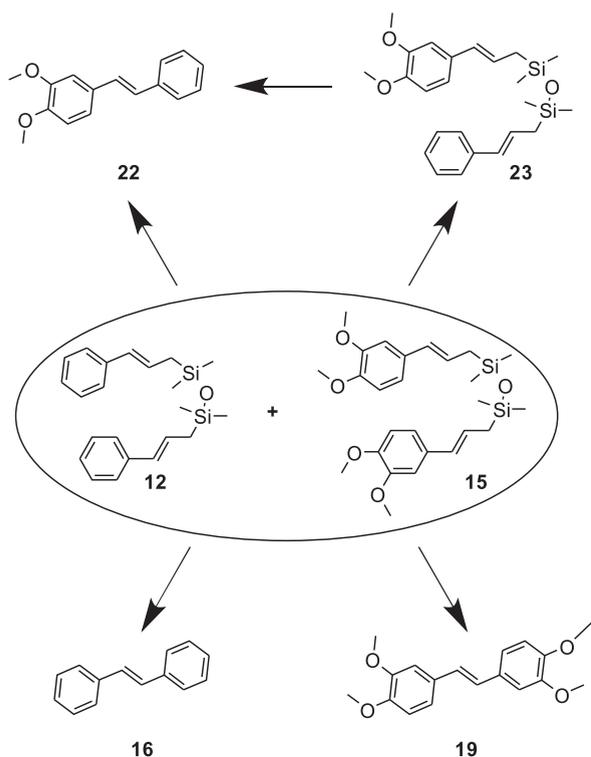


Fig. 7. Structures of the possible products formed in the metathesis of **12+15** mixture.

that simple CM of these substrates leads to the formation of **16**, **19** and **22** in 32:26:48 molar ratios, respectively. It shows that the presence of siloxane linker influences the distribution of products.

In order to investigate the concentration effect on the product distribution, we also performed the experiment described above using two different concentrations, 0.1 mol/L or 0.02 mol/L, of both **12** and **15**. After 2 h for the reaction in concentration 0.1 mol/L, we obtained stilbene derivatives **16**, **19** and **22** in 12:17:30 molar ratio, respectively. In the reaction mixture, a small amount of **23**

Table 2  
Products formed in the metathesis of **12+15** mixture.

Time (min)	Concentration (mol/L)	Yield (%) <sup>a</sup>		
		<b>16</b>	<b>19</b>	<b>22</b>
<b>5</b>	0.1	0	0	0
	0.02	0	0	0
<b>15</b>	0.1	0	0	0
	0.02	0	3	0
<b>30</b>	0.1	0	5	7
	0.02	1	4	4
<b>60</b>	0.1	6	12	23
	0.02	6	11	17
<b>120</b>	0.1	11	16	30
	0.02	14	16	35
<b>300</b>	0.02	26	17	49

Conditions: catalyst **2** (5 mol%).

<sup>a</sup> Yields determined by GC–MS analysis of the reaction mixture.

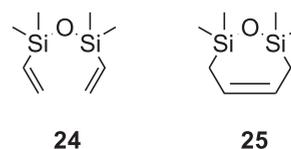


Fig. 8. Possible structures for the silane by-product.

was detected by GC–MS. For the concentration of 0.02 mol/L, we observed the same stilbene derivatives, in 14:16:35 molar ratio, respectively. The above study showed that concentration of **12** and **15** influences the composition of the products formed only slightly (Table 2).

After characterization of the styrene derivatives formed in metathesis of **12–15**, we have focused on the fate of the disiloxane part. The GC–MS analysis of the reaction mixtures revealed the presence of only one silane-containing product for both **12** and **15**. The GC–MS peak, representing this product had a retention time of 7.67 min. This retention time and the mass spectrum shown on (Fig. 9) indicate the presence of divinylsiloxane **24**, according to the mass spectra library. However, unambiguous identification was not possible due to some differences between the spectrum shown in Fig. 9 and the mass spectrum of compound **24** in the NIST library. Fragmentation process of both compounds (showed in Supplementary data, Figs. S3 and S4), most likely begins with the elimination of methyl radical leading to the formation of the ion  $m/z = 171$ .

The most significant difference between the spectrum of the compounds is the absence of the ion  $m/z = 159$  for the silane obtained in this work. For the divinylsiloxane **24**, this ion is most likely produced by the silicon–carbon bond cleavage and the elimination of the ethene radical from the ion  $m/z = 186$ .

However, on account of the cyclic nature of the compound **25** showed on Fig. 8, such a bond cleavage will not lead to the formation of the ion  $m/z = 159$ . Cyclic structure of the silane present in the reaction mixture is supported by the higher intensity of the molecular ion  $m/z = 186$  compared with the mass spectrum of the divinylsiloxane **24**. As it is showed on Fig. 9, the remaining peaks in the mass spectrum can be formed from both silanes. Therefore, the cyclic silane **25** showed on Fig. 8 is most likely present in the reaction mixture. Due to the short retention time of the investigated compound, it was reasonable to assume that the silane had relatively small molecular weight, and thus, we did not consider aggregates. The formation of both **24** and **25** in the presence of ruthenium catalysts can be explained. A vinylsilane derivative **24** can be formed if the double bond isomerisation and subsequent metathesis reaction occurred. Both reactions could be catalyzed by ruthenium species. Compound **25** is expected to be formed in the metathesis reaction of **12–15** in two subsequent metathesis processes. The first is the formation of ruthenium complex with silane chain and styrene derivative abstraction. The second includes intramolecular cyclization, which leads to the oxadisilopine derivatives and benzylidene ruthenium catalyst. Noteworthy the

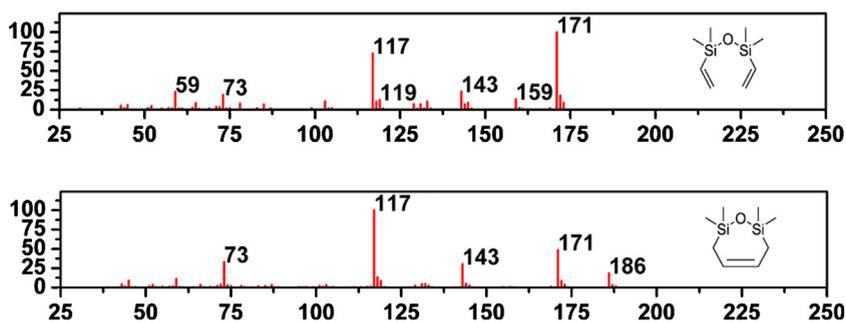


Fig. 9. Comparison of mass spectra of the vinylsilane derivative **24** and the obtained compound **25**.

presence of **25** supports the intramolecular process operating in the investigated system.

### 3. Conclusions

A series of compounds including two styrenes connected by a siloxane linker (**12–15**) were synthesized and investigated in metathesis reactions catalyzed by selected ruthenium catalysts **1–3**. Indenylidene ruthenium catalyst **2** (Umicore™ M2) was the most efficient in the metathesis of **12** and **15** and as a result (*E*)-stilbene derivatives were formed. In the case of **13** and **14**, the presence of the *ortho*-alkoxide substituents in the aromatic ring led to the formation of Hoveyda–Grubbs type catalysts, which were essentially inactive in the studied process. Therefore no metathesis product could be obtained in this case. Finally, despite the presence of the linker both inter- or intramolecular metathesis processes operate for the studied substrates.

### 4. Experimental

#### 4.1. General information

All reactions were performed under argon using standard Schlenk techniques. Solvents were distilled from standard drying agents and kept under argon. NMR spectra were recorded with a Varian 500.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are listed in ppm using  $\text{CDCl}_3$  as a standard. Column chromatography: Merck silica gel (230–400 mesh).

Gas chromatography (GC) was performed using GC–MS–QP2010 Ultra gas chromatograph coupled to QP–5000 (Shimadzu) quadrupole mass spectrometer (MS); GC–MS was equipped with an AOC–5000 auto-sampler (Shimadzu). Separation of the studied compounds was carried out with HP–5ms (Agilent) chemically bonded fused silica capillary column (30 m  $\times$  0.25 mm, 0.25  $\mu\text{m}$ ). Carrier gas (He) was delivered at a flow rate of 36.8 mL/min, split ratio was 50:1 and the pressure was maintained constantly. Chromatographic conditions were as follows: injector temperature 300  $^\circ\text{C}$ ; temperatures of the MS transfer line and ion source were set to 300  $^\circ\text{C}$  and 320  $^\circ\text{C}$ , respectively. The following temperature program of the column oven was used: initially 40  $^\circ\text{C}$  maintained for 2 min, then 12  $^\circ\text{C}$ /

min to 300  $^\circ\text{C}$ , maintained for 10 min; analysis was completed in 33.7 min. MS was equipped with electron impact (EI) ion source (70 eV) and the spectrum was acquired in the total ion current (TIC) mode in the mass range of 35–500  $m/z$ , solvent cut was 5 min. GC–MS solution 2.53 (Shimadzu) software was used to process the data.

To check the linearity of the MS detector response, a linear regression analysis of the peaks areas versus concentration of the studied compounds was carried out. The linearity was determined by the square correlation coefficients of the calibration curves that were generated by injections of the standard solutions at concentration levels between 0.1 and 0.5 mg/mL. The straight lines with the regression coefficients  $\geq 0.99$  were obtained.

#### 4.1.1. Starting materials

Catalyst [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(3-phenyl-1H-inden-1-ylidene) (tricyclohexylphosphine)ruthenium **2** was purchased from UMICORE and used without purification. Catalyst bis(tricyclohexylphosphine)benzylidene ruthenium dichloride **3** was purchased from Aldrich and used without purification. Catalyst **1** was synthesized according literature [24].

#### 4.2. Typical procedure for synthesis of 12–15 derivatives

A Schlenk tube was charged with an allylbenzene (1 mmol), TMEDA (1.2 mmol) and THF (10 mL) under an argon atmosphere. The solution was cooled to 0  $^\circ\text{C}$ . *n*-Butyllithium (1.2 mmol; 2.5 mol/L solution in *n*-Hexane) was slowly added. Next, a cooling bath was removed and the reaction mixture was stirred at 25  $^\circ\text{C}$  for 1 h. Then, after cooling the reaction mixture to –40  $^\circ\text{C}$ , 1,3-dichloro-1,1,3,3-tetramethyldisiloxane (0.6 mmol) was added. Reaction proceeded at –40  $^\circ\text{C}$  for 30 min and then the reaction mixture was allowed to reach room temperature. The mixture was stirred at room temperature for 15 h, while the reaction progress was checked by TLC analysis. After that time, the solvent was removed from the reaction mixture by evaporation. Oily residue was purified by column chromatography (*n*-Hexane/ $\text{Et}_2\text{O}$  97:3). The (*E*)/(*Z*) ratio was determined by  $^1\text{H}$  NMR.

#### 4.2.1. Compound 12: 1,3-dicinnamyl-1,1,3,3-tetramethyldisiloxane

Colorless oil, mixture of (*E*)- and (*Z*)-isomers, 92% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 0.12 (s, 6H), 1.71 (bd, 2H,  $J$  = 6.79 Hz); 6.16–6.28 (m, 2H); 7.12–7.18 (m, 2H), 7.22–7.32 (m, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 0.2; 25.6; 125.5; 126.3; 126.7; 128.4; 129.0; 138.4 ppm; HRMS (ESI) calcd for  $[\text{M}+\text{Na}^+]$  ( $\text{C}_{22}\text{H}_{30}\text{OSi}_2\text{Na}$ ): 389.1750; found: 389.1733; IR (film):  $\nu$  3024, 2956, 1253 (stretching Si–O–Si), 1064, 961, 851, 831, 799, 748, 692  $\text{cm}^{-1}$

#### 4.2.2. Compound 13: 1,3-di[3-(2-methoxyphenyl)allyl]-1,1,3,3-tetramethyldisiloxane

Colorless oil, mixture of (*E*) and (*Z*) isomer 91:9; 86% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 0.21 (s, 6H); 1.83 (dd, 2H,  $J$  = 1.29 Hz,  $J$  = 8.25 Hz); 3.87 (s, 3H); 6.30 (dt, 1H,  $J$  = 15.84,  $J$  = 8.25 Hz); 6.66 (d, 1H,  $J$  = 15.84 Hz); 6.89 (dd, 1H,  $J$  = 0.8,  $J$  = 8.25 Hz); 6.95 (ddd, 1H,  $J$  = 0.65,  $J$  = 7.43,  $J$  = 7.6 Hz); 7.21 (ddd, 1H,  $J$  = 1.78,  $J$  = 7.43,  $J$  = 8.25 Hz); 7.43 (dd, 1H,  $J$  = 1.78,  $J$  = 7.6 Hz) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 0.2; 26.1; 55.4; 110.8; 120.6; 123.6; 126.0; 127.2; 127.4; 127.6; 156.0 ppm; HRMS (ESI) calcd for  $[\text{M}+\text{Na}^+]$  ( $\text{C}_{24}\text{H}_{34}\text{O}_3\text{Si}_2\text{Na}$ ): 449.1944; found: 449.1935; IR (film):  $\nu$  2956, 1488, 1242 (stretching Si–O–Si), 1052, 1031, 806, 748  $\text{cm}^{-1}$

#### 4.2.3. Compound 14: 1,3-di[3-(2-isopropoxyphenyl)allyl]-1,1,3,3-tetramethyldisiloxane

Colorless oil, mixture of (*E*) and (*Z*) isomers 92: 8; 92% yield,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 0.13 (s, 6H); 1.34 (d, 6H  $J$  = 6.15 Hz); 1.75 (dd, 2H  $J$  = 1.29,  $J$  = 8.24 Hz); 4.51 (sept, 1H,  $J$  = 6.15); 6.22 (dt, 1H,  $J$  = 15.85,  $J$  = 8.24 Hz); 6.57 (d, 1H,  $J$  = 15.85 Hz); 6.83–6.91 (m, 2H); 7.11 (m, 1H); 7.37 (dd, 1H,  $J$  = 7.60,  $J$  = 1.61 Hz) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 0.2; 22.3; 26.1; 70.7; 114.4; 120.7; 124.1; 126.2; 126.9; 127.0; 128.9; 154.4 ppm; HRMS (ESI) calcd for  $[\text{M}+\text{Na}^+]$  ( $\text{C}_{28}\text{H}_{42}\text{O}_3\text{Si}_2\text{Na}$ ): 505.2570; found: 505.2575; IR (film):  $\nu$  2976, 1484, 1238 (stretching Si–O–Si), 1119, 1062, 844, 803, 747  $\text{cm}^{-1}$

#### 4.2.4. Compound 15: 1,3-di[3-(3,4-dimethoxyphenyl)allyl]-1,1,3,3-tetramethyldisiloxane

Pale yellow oil, mixture of (*E*) and (*Z*) isomers 88:12; 90% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 0.13 (s, 6H); 1.69 (dd, 2H  $J$  = 0.97,  $J$  = 8.08); 3.86 (s, 3H); 3.87 (s, 3H); 6.08 (dt, 1H,  $J$  = 7.92,  $J$  = 8.09,  $J$  = 15.68), 6.19 (d, 1H,  $J$  = 15.67); 6.78 (d, 1H,  $J$  = 8.25); 6.82 (dd, 1H,  $J$  = 1.78,  $J$  = 8.91); 6.85 (d, 1H,  $J$  = 1.78) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 0.2; 25.4; 55.8; 55.9; 108.4; 111.3; 118.2; 124.7; 128.6; 131.7; 147.9; 149.0 ppm; HRMS (ESI) calcd for  $[\text{M}+\text{Na}^+]$  ( $\text{C}_{26}\text{H}_{38}\text{O}_5\text{Si}_2\text{Na}$ ): 509.2155; found: 509.2138; IR (film):  $\nu$  2955, 1514, 1256 (stretching Si–O–Si), 1234, 1158, 1139, 1059, 1028, 836, 802  $\text{cm}^{-1}$

#### 4.3. Typical procedure for metathesis reaction

A Schlenk tube was charged with disiloxane derivatives (0.25 mmol) and the catalyst (0.0125 mmol) in dry toluene (2.5 mL; or DCM) under an argon atmosphere. The mixture was stirred in an oil bath at 80 °C (or 40 °C,

respectively). Reaction progress was checked by GC–MS analysis. Next, the solvent was removed on a rotary evaporator. Oily residue was purified by column chromatography (*n*-Hexane/ $\text{Et}_2\text{O}$  97:3), and the product was obtained as white crystals. The crude product was crystallized from toluene at –20 °C.

Metathesis of compound **12** yields product **16** as white crystals (67% yield).  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra were according to the literature [25].

Metathesis of compound **13** gives the product as white crystals of compound **19**. 60% yield.  $^1\text{H}$ ,  $^{13}\text{C}$  spectra were according to the literature [26].

#### 4.4. Typical procedure for a stability test

A Schlenk tube was charged with disiloxane derivatives **12**–**15** (0.25 mmol) and dry toluene (2.5 mL) was added under an argon atmosphere. Next, a 10  $\mu\text{L}$  sample of this solution was taken and diluted to 1 mL with the same solvent and analysed by GC–MS. The mixture was then stirred in an oil bath at 80 °C for 3 h. Next, the second GC–MS analysis was made in the same manner. No change was observed.

#### 4.5. Catalyst 20 formation

Disiloxane derivative **12** (0.156 mmol), catalyst **2** (0.13 mmol) and copper(I) chloride (0.13 mmol) were added to the Schlenk flask in dry toluene (1.5 mL) under argon atmosphere. The mixture was stirred in an oil bath at 80 °C; progress of the reaction was controlled by TLC. Full conversion was observed after 15 min. The reaction mixture was cooled to room temperature, the solvent was removed in vacuo, and the product was purified by column chromatography (*c*-Hexane/Ethyl Acetate 4:1). Removal of the solvent, washing with a small amount of *n*-pentane and drying under vacuum afforded the product as a green solid in 49% yield.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were according to the literature [24].

#### Acknowledgements

Financial support was provided by the University of Warsaw (Grant No. 501/86-DSM-100100 and No. 501/86-DSM-102400). We wish to thank Dr. Hanna Majewska-Elżanowska for proof reading the manuscript.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.crci.2013.01.017>.

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