Electronic Supplementary Information

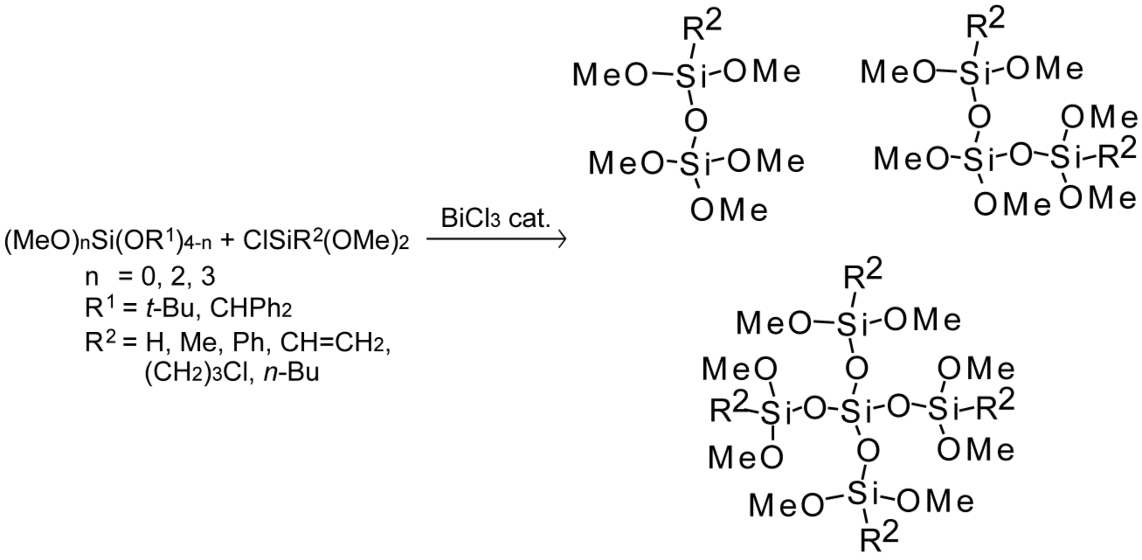
Synthesis of a multifunctional alkoxysiloxane oligomer

Masashi Yoshikawa,[a] Ryutaro Wakabayashi,[a,b] Misa Tamai,[a] and Kazuyuki Kuroda*[a.b]

[a] M.Yoshikawa, R. Wakabayashi, M. Tamai, and K. Kuroda
Department of Applied Chemistry
Faculty of Science and Engineering, Waseda University,
Ohkubo3-4-1, Shinjuku-ku, Tokyo, 169-8555, Japan.
Fax: +81 3 5286 3199; Tel: +81 3 5286 3199
E-mail: kuroda@waseda.jp
[b] R. Wakabayashi and K. Kuroda
Kagami Memorial Research Institute for Materials Science and Technology
Waseda University,
Nishiwaseda2-8-26, Shinjuku-ku, Tokyo, 169-0051, Japan.

Contents

page
Scheme S1. Synthesis of alkoxysiloxane oligomers. ·· 2
Experimental details.
Synthesis of (t-BuO)$_2$MeSiCl and (t-BuO)$_2$MeSiOH and their ^{1}H, ^{13}C and ^{29}Si NMR spectra. ···-9······ 3
Synthesis of (MeO)$_2$(CH$_2$=CH)SiCl and its ^{1}H, ^{13}C and ^{29}Si NMR spectra.······· 10-13
Synthesis of (t-BuO)$_2$MeSiOSi(CH=CH$_2$)(OMe)$_2$ and its ^{1}H, ^{13}C and ^{29}Si NMR spectra. ···-17···· 14
Synthesis of Cl(CH$_2$)$_3$SiCl(OMe)$_2$, and its ^{1}H, ^{13}C and ^{29}Si NMR spectra.········ 18-21
^{13}C NMR spectra of compound **1** hydrolyzed for different reaction times. ·········· 22
Interpretation of the ^{13}C NMR spectra of compound **1** hydrolyzed for different reaction times (Fig. S16) and the assignment of signals. ·· 23
References···5······ 2



Scheme S1 Synthesis of alkoxysiloxane oligomers.[1]

Experimental details

Synthesis of (t-BuO)$_2$MeSiOH.

Potassium *tert*-butoxide (*t*-BuOK, 25 g, 0.22 mol) was dried *in vacuo* in a three neck flask (500 mL). After hexane (150 mL) was added into the flask under N_2 atmosphere, trichloromethylsilane ($MeSiCl_3$, 11.8 mL, 0.10 mol) was dropped into the same flask and the mixture was stirred for 1 h at 0 °C and then stirred for 4 h at room temperature. The molar ratio of *t*-BuOK / $MeSiCl_3$ was 1/2.2. KCl and excess *t*-BuOK were removed by filtration under N_2 atmosphere. Then, yellow clear liquid, (t-BuO)$_2$MeSiCl, was obtained after evaporation of the solvent. The possibility of the formation of (t-BuO)MeSiCl$_2$ and its hydrolysed/polymerized byproducts was excluded on the basis of the ^{29}Si NMR spectrum of the product, because no signals due to those species were observed. Excess of pyridine and water were added to (t-BuO)$_2$MeSiCl and stirred for 0.5 h at room temperature. After separating the water layer from the organic layer, residual organic species probably containing silanol groups in the water layer were extracted with hexane. The extracted organic species in hexane were added into the separated organic layer, and the mixture was dehydrated with anhydrous Na_2SO_4. The possibility of the formation of disiloxane species during the treatment with water was excluded because no signals due to the species were observed. Colorless clear liquid ((t-BuO)$_2$MeSiOH, 11.0 g, yield 52.7 %) was obtained by evaporation of the solvent after the solid residue was removed by filtration.

(t-BuO)$_2$MeSiCl. ^{1}H NMR (500 MHz; $CDCl_3$; 25 °C; TMS) δ = 0.41 (s, 3H), 1.36 ppm (s, 18H); ^{13}C NMR (126 MHz; $CDCl_3$; 25 °C; TMS) δ = 3.9, 31.5, 75.0 ppm; ^{29}Si (99 MHz; $CDCl_3$; 25 °C; TMS) δ = -43.3 ppm (1Si, D^0).
A small amount of hexane remained.

(t-BuO)$_2$MeSiOH. ^{1}H NMR (500 MHz; $CDCl_3$; 25 °C; TMS) δ = 0.16 (s, 3H), 1.33 ppm (s, 18H); ^{13}C NMR (126 MHz; $CDCl_3$; 25 °C; TMS) δ = -0.6, 31.7, 72.5 ppm; ^{29}Si (99 MHz; $CDCl_3$; 25 °C; TMS) δ = -50.8 ppm (1Si, T^0) ; HRMS (ESI, 1500V) calcd. for $C_9H_{22}O_3SiNa^+$ $[M+Na]^+$: 229.1230; found: 229.1232.
A small amount of pyridine remained.

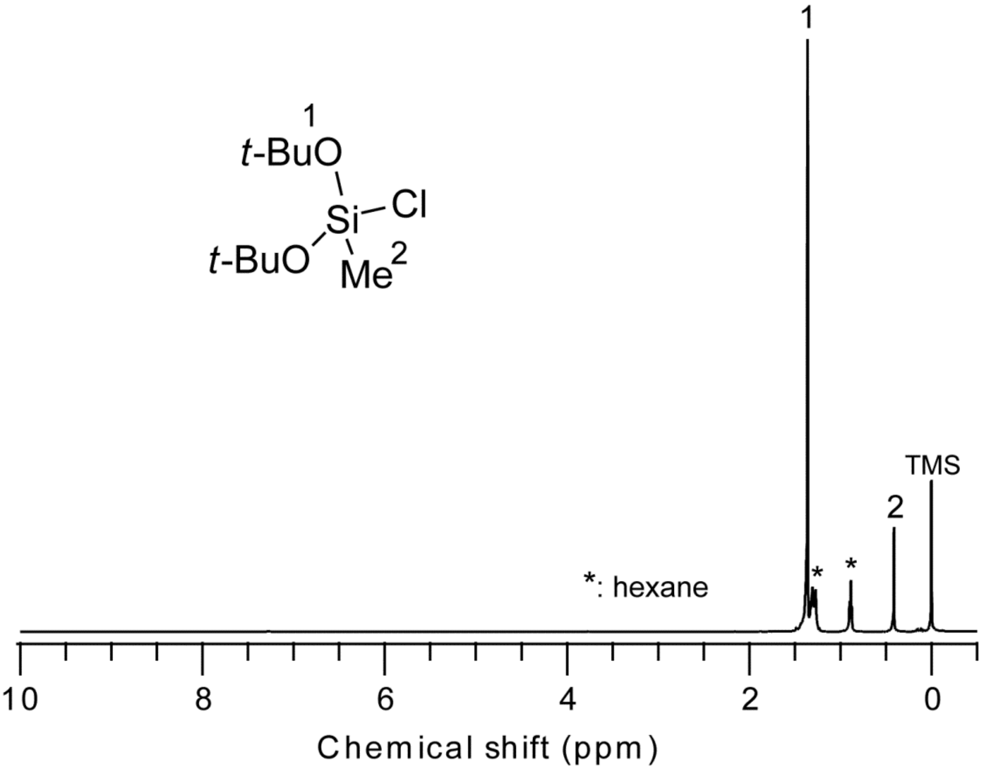


Fig. S1 ^{1}H NMR spectrum of (t-BuO)$_2$MeSiCl.

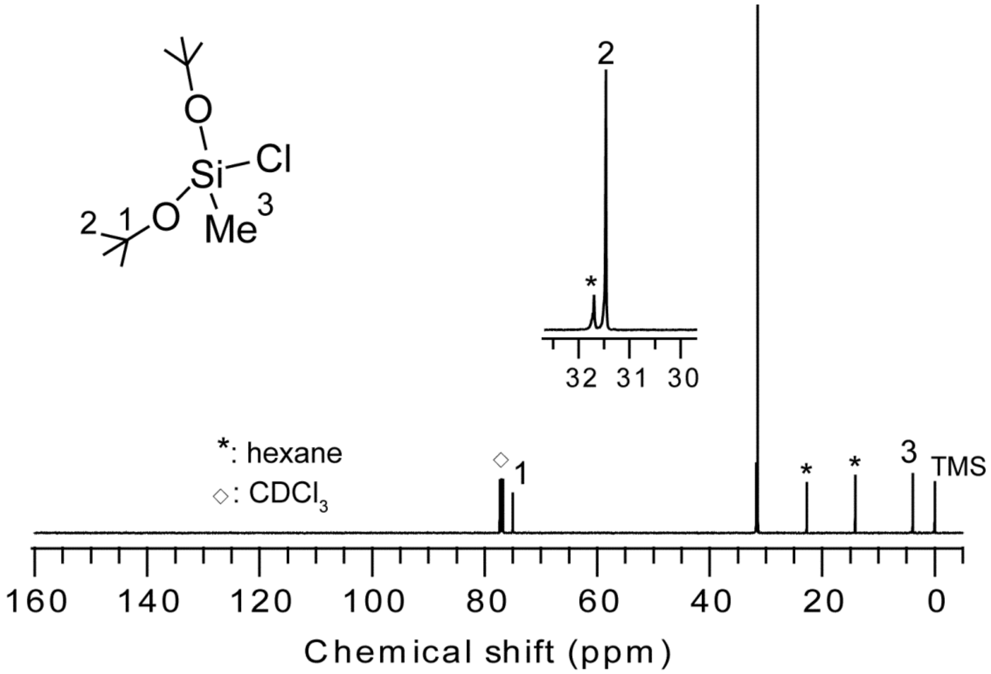


Fig. S2 ^{13}C NMR spectrum of (*t*-BuO)$_2$MeSiCl.

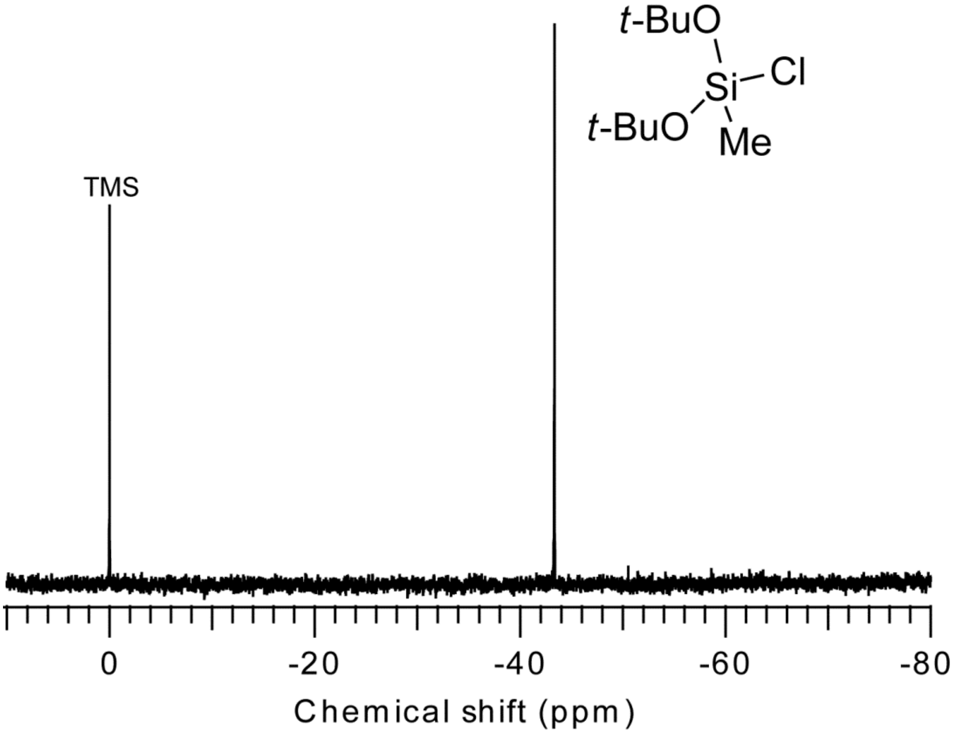


Fig. S3 ^{29}Si NMR spectrum of (*t*-BuO)$_2$MeSiCl.

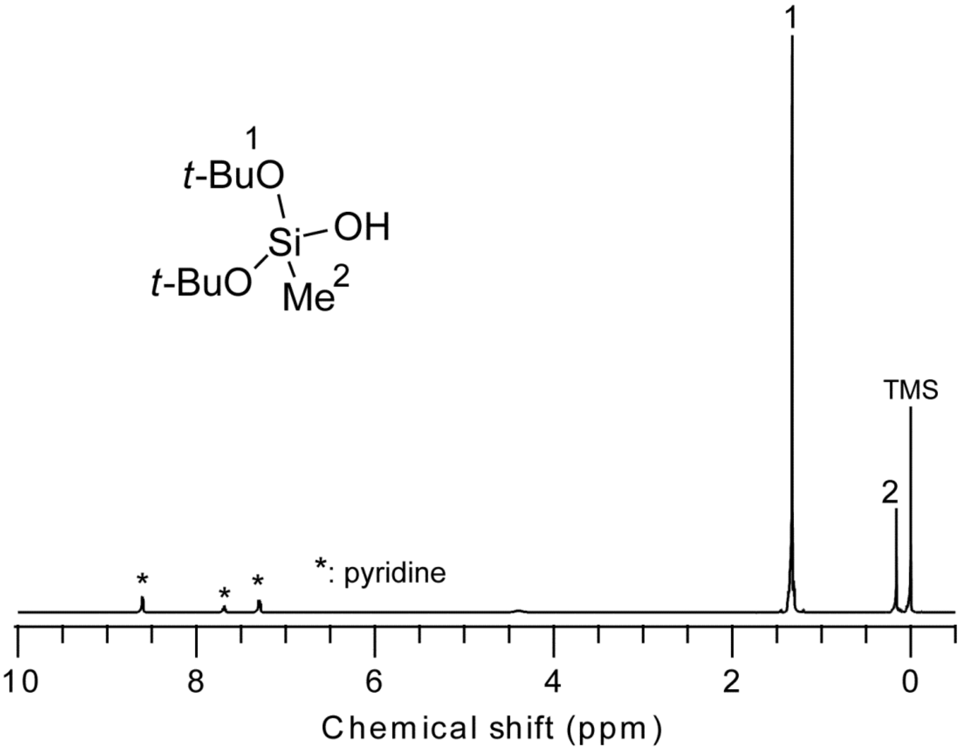


Fig. S4 ^{1}H NMR spectrum of (t-BuO)$_2$MeSiOH.

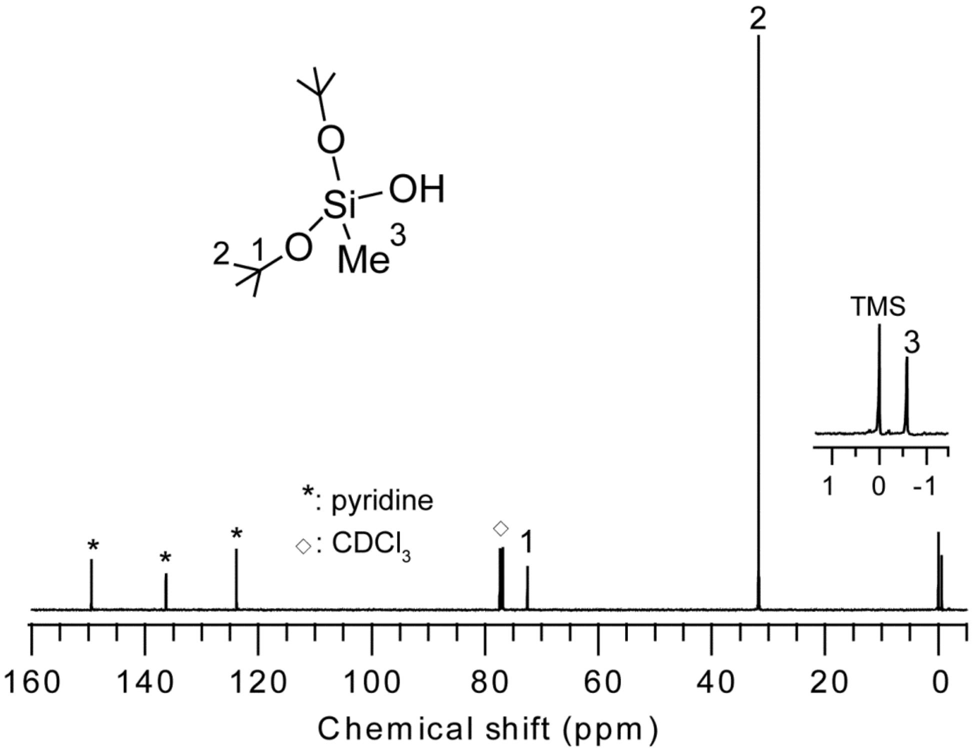


Fig. S5 ^{13}C NMR spectrum of (t-BuO)$_2$MeSiOH.

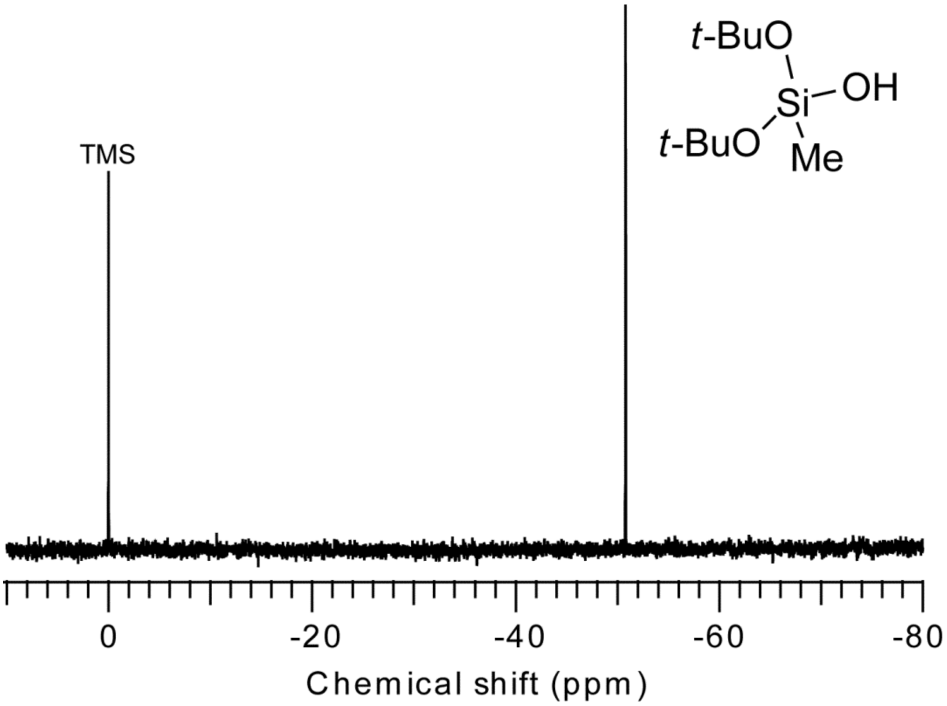


Fig. S6 ^{29}Si NMR spectrum of (t-BuO)$_2$MeSiOH.

Synthesis of $(MeO)_2(CH_2{=}CH)SiCl$.[2]

$BiCl_3$ (0.2697 g, 0.86 mmol) was dried *in vacuo* in a Schlenk flask (200 mL). MeCN (10 mL) was added into the flask under N_2 atmosphere and the mixture was stirred until $BiCl_3$ was dissolved. Trichlorovinylsilane ($(CH_2{=}CH)SiCl_3$, 10.7 mL, 0.084 mol) was added into the mixture at 0 °C, and then *t*-butyl methyl ether (22.9 mL, 0.193 mol) was dropped into the mixture. The mixture was stirred for 6 h at room temperature to form yellow clear liquid. The molar ratio of $(CH_2{=}CH)SiCl_3$ / *t*-butyl methyl ether / $BiCl_3$ was 1/2.3/0.01. Although $(CH_2{=}CH)Si(OMe)_3$ was also present in the solution, proved by NMR data (please see Figures S7-9), the solution was used for alkoxysilylation of $(t\text{-}BuO)_2MeSiOH$ without further purification because $(CH_2{=}CH)Si(OMe)_3$ does not possess SiCl groups, therefore it does not affect the reaction. The formation of *tert*-butyl chloride was confirmed, which also indicates the proceeding of methoxylation. Because the presence of this compound does not affect the following reaction, the solution obtained in this stage was directly used for the next step of silylation of $(t\text{-}BuO)_2MeSiOH$.

$(MeO)_2(CH_2{=}CH)SiCl$. ^1H NMR (500 MHz; $CDCl_3$; 25 °C; TMS) $\delta = 3.61$ (s, 9H), 5.91-5.97 (dd, 1H), 6.08-6.12 (dd, 1H(*cis*)), 6.19-6.22 ppm (dd, 1H(*trans*)); ^{13}C NMR (126 MHz; $CDCl_3$; 25 °C; TMS) $\delta = 51.2$, 128.8, 138.6 ppm; ^{29}Si (99 MHz; $CDCl_3$; 25 °C; TMS) $\delta = -40.1$ ppm (1Si, D^0).

$(CH_2{=}CH)Si(OMe)_3$ as a byproduct. ^1H NMR (500 MHz; $CDCl_3$; 25 °C; TMS) 3.56 (s, 6H), 5.82-5.88 (dd, 1H), 5.99-6.03 (dd, 1H(*cis*)), 6.14-6.17 ppm (dd, 1H(*trans*)); ^{13}C NMR (126 MHz; $CDCl_3$; 25 °C; TMS) $\delta = 50.5$, 128.0, 137.7 ppm; ^{29}Si (99 MHz; $CDCl_3$; 25 °C; TMS) $\delta = -55.3$ ppm (1Si, T^0).

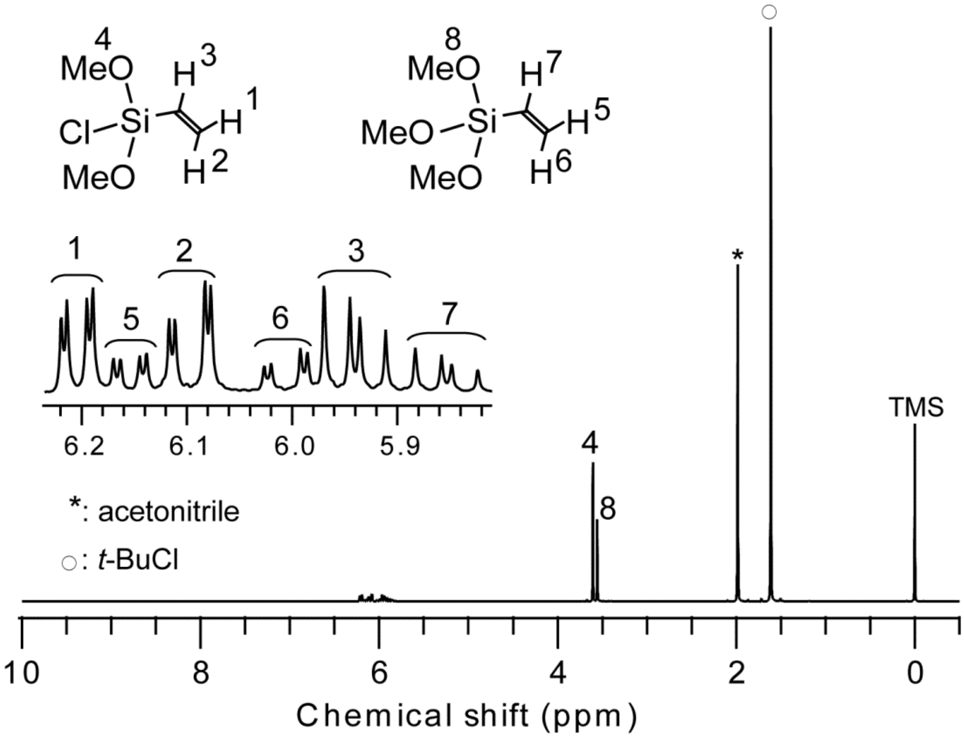


Fig. S7 ^{1}H NMR spectrum of $(MeO)_2(CH_2{=}CH)SiCl$.

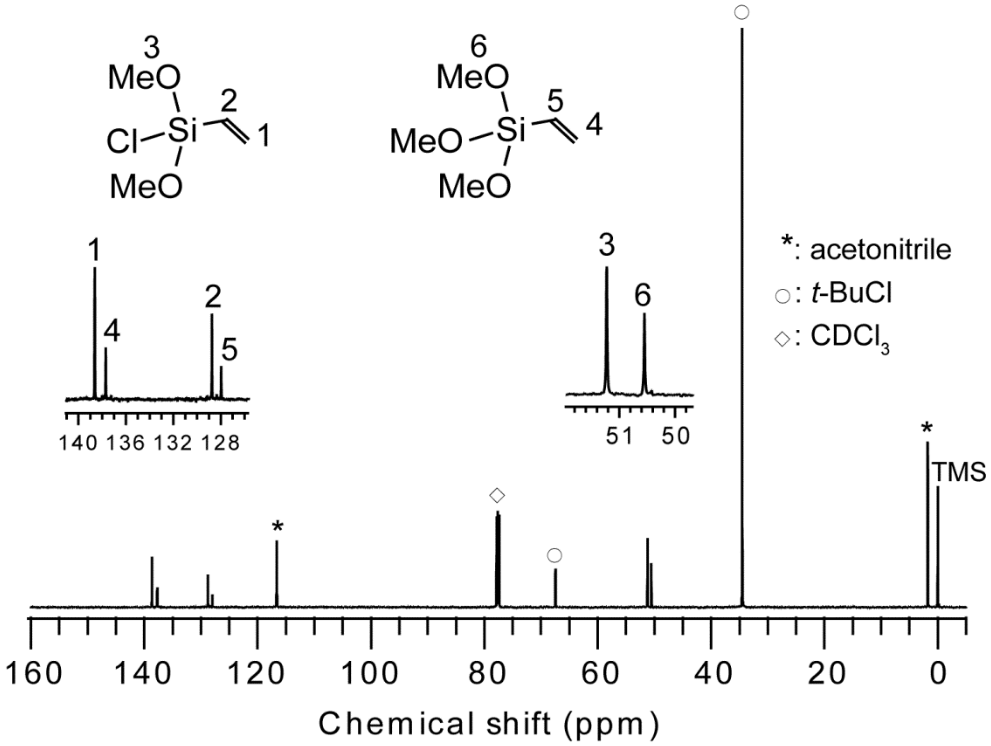


Fig. S8 ^{13}C NMR spectrum of $(MeO)_2(CH_2{=}CH)SiCl$.

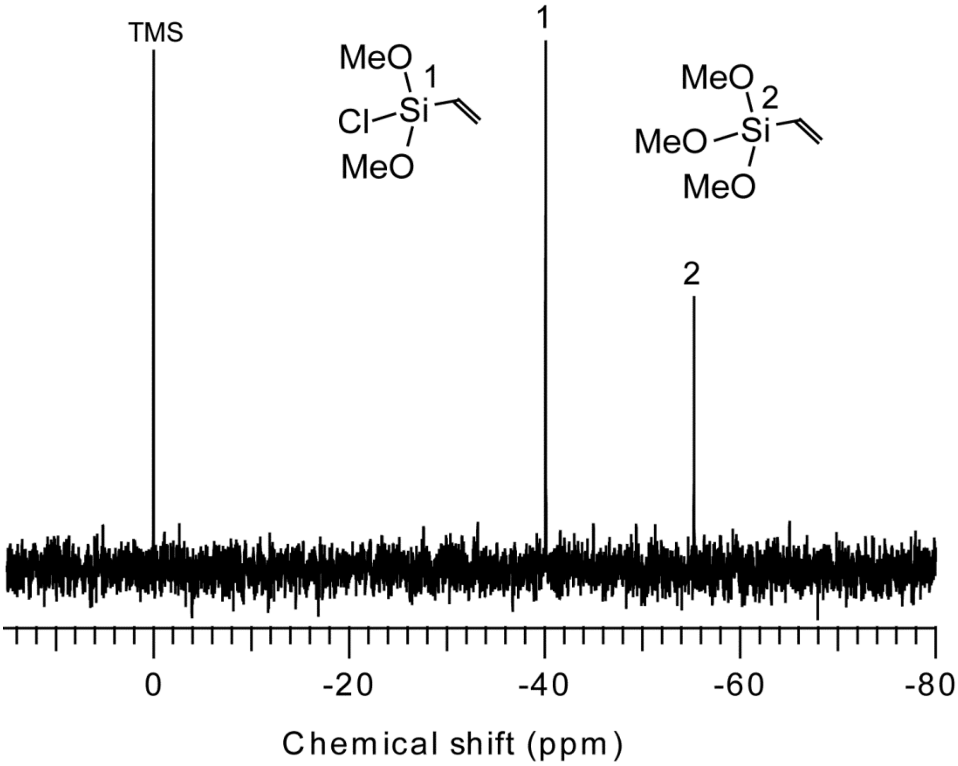


Fig. S9 ^{29}Si NMR spectrum of $(MeO)_2(CH_2{=}CH)SiCl$.

Synthesis of $(t\text{-BuO})_2$MeSiOSi(CH=CH$_2$)(OMe)$_2$.

Pyridine was added to the solution containing $(MeO)_2(CH_2=CH)SiCl$ described above. The mixture was cooled at 0 °C and a hexane solution of $(t\text{-BuO})_2MeSiOH$ (11.0 g, 0.053 mol) was dropped to the mixture. The molar ratio of $(t\text{-BuO})_2MeSiOH$ / $(MeO)_2(CH_2=CH)SiCl$ was 1/1.1. The mixture was stirred for 30 min at room temperature and excess pyridine and methanol were added for methoxylation of remaining SiCl groups. After stirring for 30 min at room temperature, the solvents (hexane and MeCN), *tert*-butyl chloride, remaining pyridine, and methanol were evaporated *in vacuo* and the solid residue was removed by filtration. Yellow clear liquid (11.1 g, yield 64.6 %) was obtained after vacuum distillation.

$(t\text{-BuO})_2MeSiOSi(CH=CH_2)(OMe)_2$. ^{1}H NMR (500 MHz; $CDCl_3$; 25 °C; TMS) δ = 0.15 (s, 3H), 1.30 ppm (s, 18H), 3.56 (s, 6H), 5.89-5.93 (dd, 1H), 6.00-6.05 (dd, 1H(*cis*)), 6.08-6.12 ppm (dd, 1H(*trans*)); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS) δ = -0.3, 31.7, 72.7, 129.7, 136.5 ppm; ^{29}Si (99 MHz; $CDCl_3$; 25 °C; TMS) δ = -61.7 (1Si, T^1), -64.2 ppm (1Si, T^1); HRMS (ESI, 1500V) calcd. for $C_{13}H_{30}O_5Si_2Na^+$ $[M+Na]^+$: 345.1524; found: 345.1524.

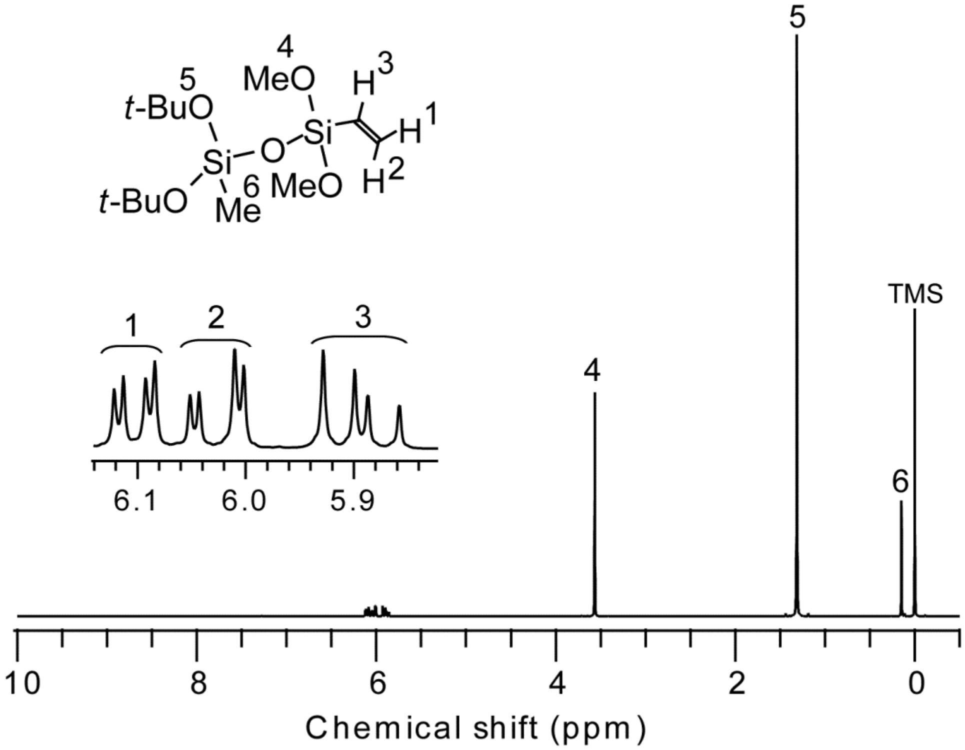


Fig. S10 ^{1}H NMR spectrum of (t-BuO)$_2$MeSiOSi(CH=CH$_2$)(OMe)$_2$.

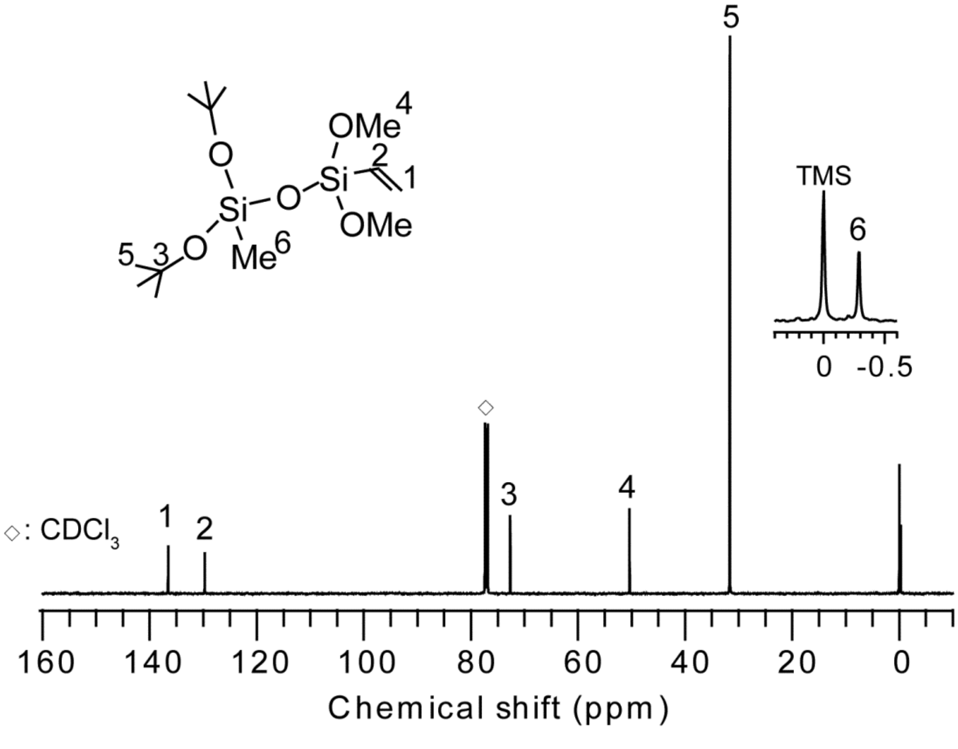


Fig. S11 ^{13}C NMR spectrum of (*t*-BuO)$_2$MeSiOSi(CH=CH$_2$)(OMe)$_2$.

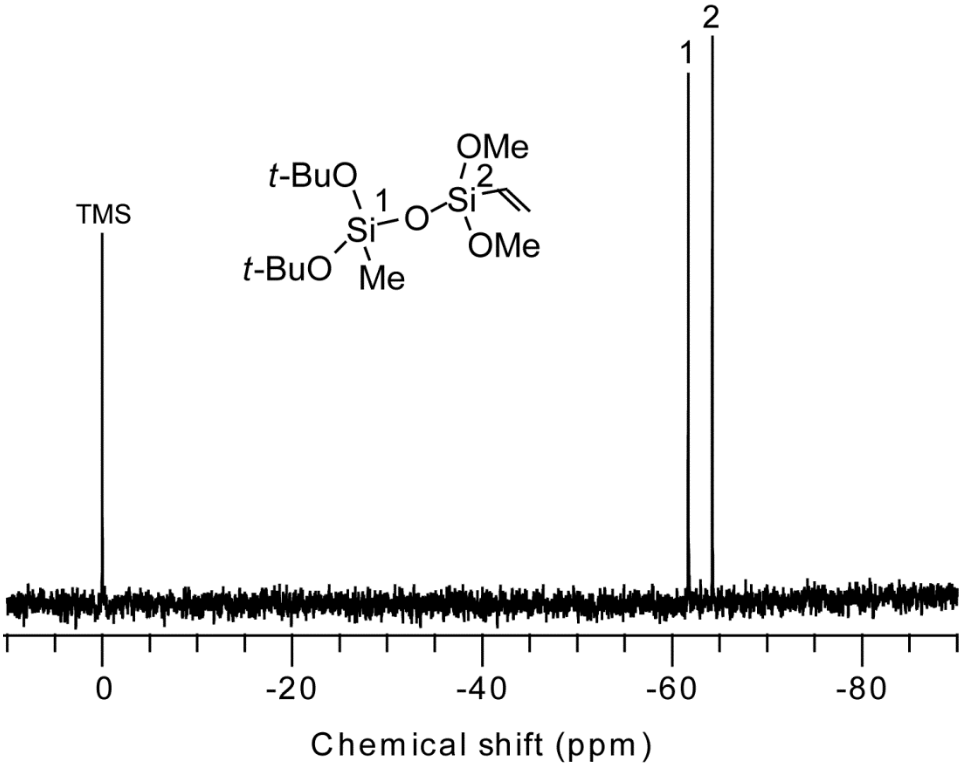


Fig. S12 ^{29}Si NMR spectrum of $(t\text{-BuO})_2$MeSiOSi(CH=CH$_2$)(OMe)$_2$.

Synthesis of $Cl(CH_2)_3SiCl(OMe)_2$.[2]

$Cl(CH_2)_3SiCl(OMe)_2$ was synthesized according to a manner similar to the synthesis of $(MeO)_2(CH_2{=}CH)SiCl$. $Cl(CH_2)_3SiCl_3$ was used instead of $(CH_2{=}CH)SiCl_3$ in the synthesis of $(MeO)_2(CH_2{=}CH)SiCl$. $Cl(CH_2)_3Si(OMe)_3$ was also formed. (please see Figures S13-S15) As mentioned above for the synthesis of $(MeO)_2(CH_2{=}CH)SiCl$, $Cl(CH_2)_3Si(OMe)_3$ was not removed because $Cl(CH_2)_3Si(OMe)_3$ does not affect the synthesis of compound **1**.

$Cl(CH_2)_3SiCl(OMe)_2$. ^1H NMR (500 MHz; $CDCl_3$; 25 °C; TMS) $\delta = 0.98\sim1.02$ (m, 2H), 1.89~1.95 (m, 2H), 3.53~3.55 (t, 2H), 3.61 ppm (s, 6H); ^{13}C NMR (126 MHz; $CDCl_3$; 25 °C; TMS) $\delta = 12.0, 25.9, 46.8, 51.3$ ppm; ^{29}Si (99 MHz; $CDCl_3$; 25 °C; TMS) $\delta = -27.0$ ppm (1Si, D^0).

$Cl(CH_2)_3Si(OMe)_3$. ^1H NMR (500 MHz; $CDCl_3$; 25 °C; TMS) $\delta = 0.75\sim0.79$ (m, 2H), 1.86~1.89 (m, 2H), 3.52~3.53 (t, 2H), 3.57 ppm (s, 9H); ^{13}C NMR (126 MHz; $CDCl_3$; 25 °C; TMS) $\delta = 6.8, 26.3, 47.4, 50.6$ ppm; ^{29}Si (99 MHz; $CDCl_3$; 25 °C; TMS) $\delta = -42.8$ ppm (1Si, T^0).

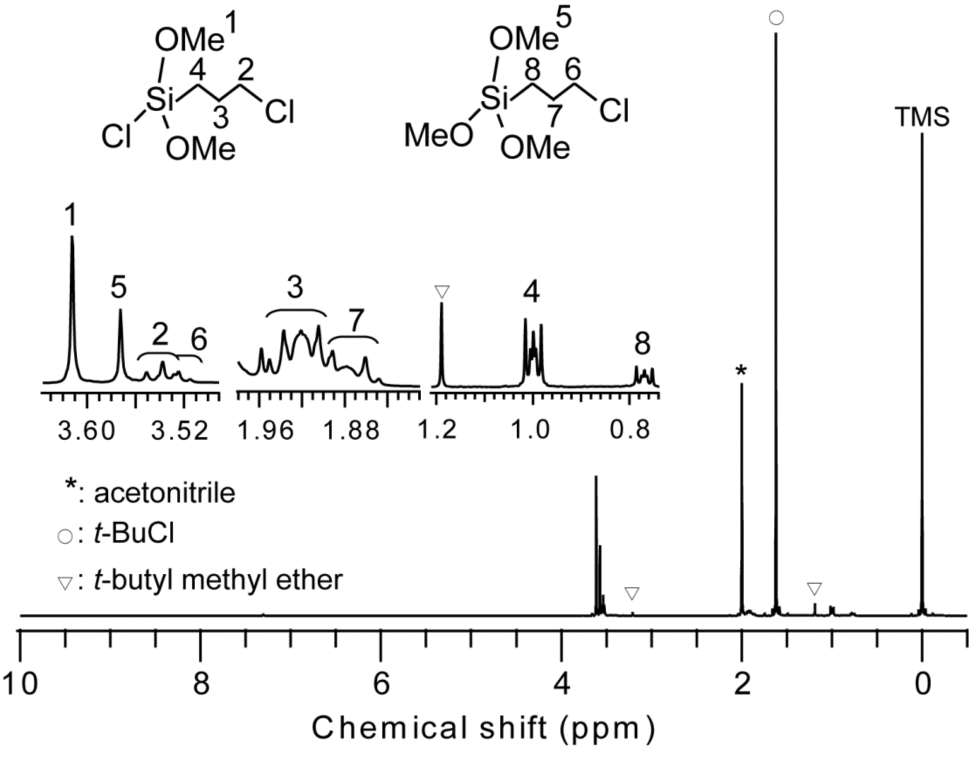


Fig. S13 ^{1}H NMR spectrum of $Cl(CH_2)_3SiCl(OMe)_2$.

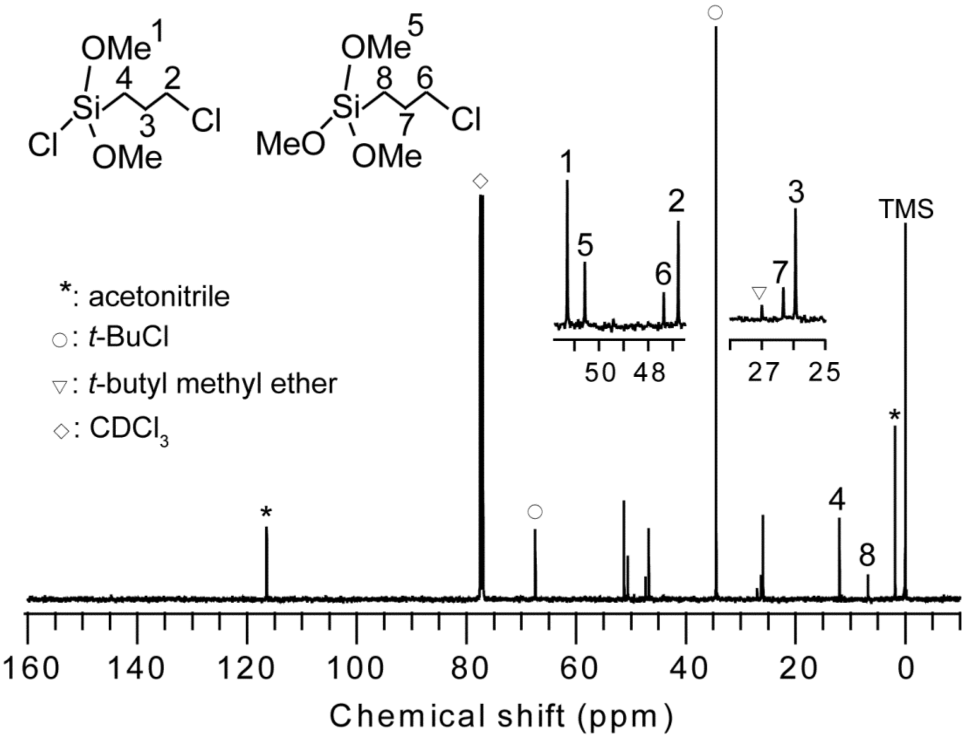


Fig. S14 ^{13}C NMR spectrum of $Cl(CH_2)_3SiCl(OMe)_2$.

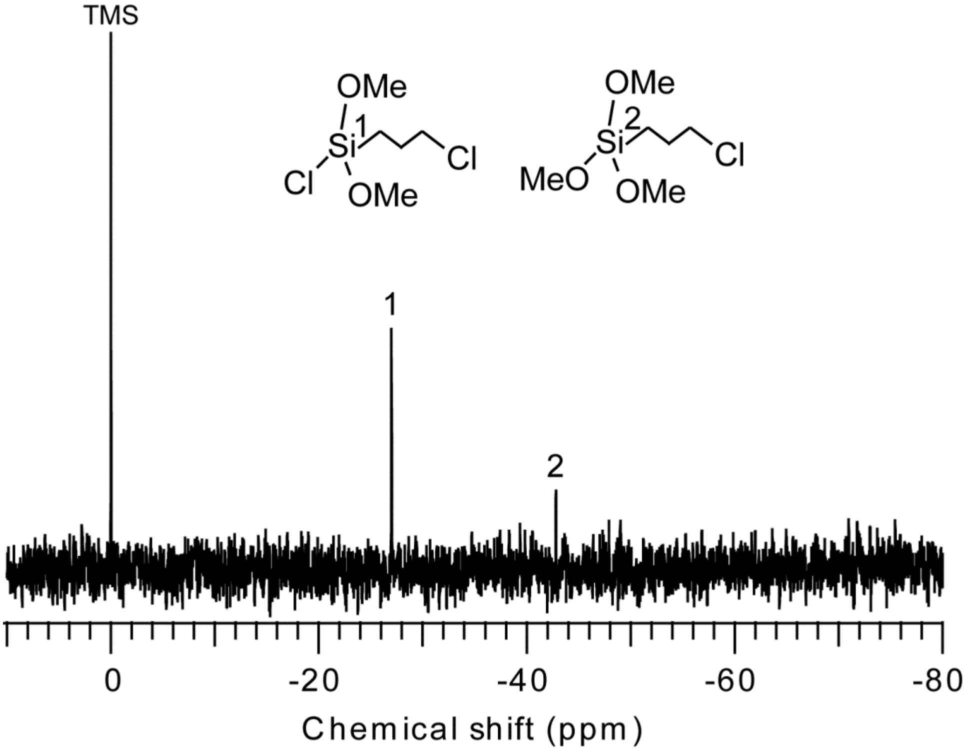


Fig. S15 ^{29}Si NMR spectrum of $Cl(CH_2)_3SiCl(OMe)_2$.

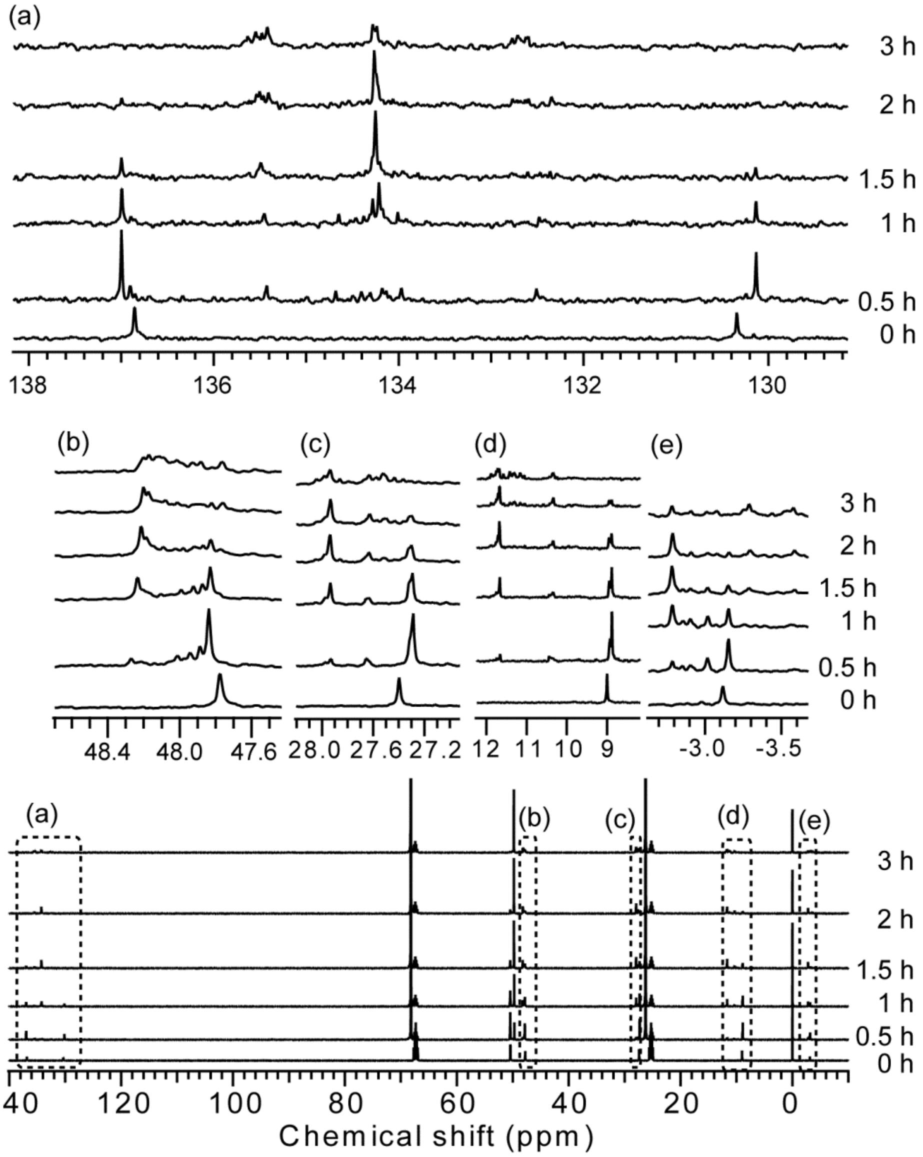


Fig. S16 ^{13}C NMR spectra of compound **1** hydrolyzed for different reaction times.

Interpretation of the ^{13}C NMR spectra of compound 1 hydrolyzed for different reaction times (Fig. S16) and the assignment of signals.

Interpretation of the ^{13}C NMR spectra of compound **1** hydrolyzed for different reaction times (Fig. S16) and the assignment of signals are discussed here by focusing the signals due to vinyl group of compound **1**. The reason why vinyl group is chosen for the discussion is as follows. Chemical shifts of two carbon atoms of vinyl group are affected by the variation in the environment of Si atom linked to vinyl group, and the degree of variation is different between $\text{-Si}\underline{\mathbf{C}}\text{H=CH}_2$ and $\text{-SiCH=}\underline{\mathbf{C}}\text{H}_2$. Therefore, vinyl group is suitable for discussing the structural transformations of compound **1** than methyl and chloropropyl groups.

Many signals due to vinyl groups around 130 ppm ~ 140 ppm and their variations in the chemical shifts during the hydrolysis and condensation are discussed as follows.

1) A. Gordillo *et al*. reported that the ^{13}C NMR signals due to $\text{-Si}\underline{\mathbf{C}}\text{H=CH}_2$ and $\text{-SiCH=}\underline{\mathbf{C}}\text{H}_2$ of triethoxyvinylsilane appeared at 129.2 ppm and 137.4 ppm, respectively.[3] When triethoxyvinylsilane is hydrolyzed to form monosodiumoxyvinylsilanediol the signals due to $\text{-Si}\underline{\mathbf{C}}\text{H=CH}_2$ and $\text{-SiCH=}\underline{\mathbf{C}}\text{H}_2$ shift to downfield and upfield by about 3 ppm and 1.5 ppm, respectively. It should be noted that in the case of ref. 3, the substance is monomeric. On the other hand, the substance studied here is oligomeric and the effect of neighboring Si on the chemical shift should be large, if we consider the electron withdrawing effect of siloxane bond,[4] though this is rather qualitative.

2) According to Cai and Weber,[5] the ^{13}C NMR signals due to $\text{-Si}\underline{\mathbf{C}}\text{H=CH}_2$ and $\text{-SiCH=}\underline{\mathbf{C}}\text{H}_2$ in 2,4,6-trivinyl-2,4,6-trimethylcyclotrisiloxane appeared at 134.2~134.4 ppm (the variation comes from *cis-trans* conformation) and 135.5~135.8 ppm (the same *cis-trans* conformation), respectively. And the two signals appeared at 133.3~133.5 ppm and 136.1~136.4 ppm for 2,4,6,8-tetravinyl-2,4,6,8-tetramethylcyclotetrasiloxane, respectively. Consequently, by the increase in the ring size, the upfield shift is observed for $\text{-Si}\underline{\mathbf{C}}\text{H=CH}_2$ and the downfield shift is observed for $\text{-SiCH=}\underline{\mathbf{C}}\text{H}_2$.

On the basis of these interpretations, we consider the assignments of ^{13}C NMR signals around 130 ppm ~ 140 ppm.

i) The assignments for the signals

Many ^{13}C NMR signals observed around 132.6 ppm, around 134.2 ppm, and around 135.5 ppm can be assigned to $\text{-Si}\underline{\mathbf{C}}\text{H=CH}_2$ (Si atoms do not participate in the trisiloxane ring formation), $\text{-Si}\underline{\mathbf{C}}\text{H=CH}_2$ (Si atoms participate in the trisiloxane ring formation), and

$\mathrm{-SiCH{=}\underline{\mathbf{C}}H_2}$, respectively. The reasons for these assigments are shown below.

a) Gordillo *et al*. reported that the ^{13}C NMR signals due to $\mathrm{-Si\underline{\mathbf{C}}H{=}CH_2}$ and $\mathrm{-SiCH{=}\underline{\mathbf{C}}H_2}$ of trialkoxyvinylsilane shift to downfield and upfield by hydrolysis, respectively.[3]

b) The shift of $\mathrm{-Si\underline{\mathbf{C}}H{=}CH_2}$ is larger than that of $\mathrm{-SiCH{=}\underline{\mathbf{C}}H_2}$ because the distance from the hydrolysis reaction sites (-SiOMe) to $\mathrm{-Si\underline{\mathbf{C}}H{=}CH_2}$ is shorter than that of $\mathrm{-SiCH{=}\underline{\mathbf{C}}H_2}$.

c) On the basis of ^{29}Si NMR measurements (Fig. 3), compound **1** is converted to cyclic siloxanes by hydrolysis and intramolecular condensation.

d) By comparison the ^{13}C NMR signals reported by Cai and Weber[5] with our data, we can conclude cyclotrisiloxanes are formed by hydrolysis of compound **1**.

e) As shown in Scheme 2, two kinds of cyclotrisiloxanes are formed, one contains Si atom having a vinyl group within the cyclic structure and the other does not.

f) According to the two papers[3,5], the signals due to $\mathrm{-SiCH{=}\underline{\mathbf{C}}H_2}$ appear in almost same chemical shifts, irrespective the molecular structures (monomeric and cyclic compounds). On the other hand, the signals due to $\mathrm{-Si\underline{\mathbf{C}}H{=}CH_2}$ of monomeric compounds appear upfield than those of cyclic compounds. Therefore, the signals around 132.6 ppm are assigned to $\mathrm{-Si\underline{\mathbf{C}}H{=}CH_2}$ whose Si atoms are not involved in the trisiloxane ring formation, and the signals around 134.2 ppm are assigned to $\mathrm{-Si\underline{\mathbf{C}}H{=}CH_2}$ whose Si atoms participate in the trisiloxane ring formation.

ii) The decrease in the number of signals can be explained as follows.

Because compound **1** contains six -SiOMe groups, very many kinds of molecules will be generated by hydrolysis and intra/intermolecular condensation of compound **1**. In fact, the initial step of hydrolysis (0.5 h), a lot of signals are observed in the range of 130 ppm ~ 140 ppm. These signals can be assigned to molecules in which a few -SiOMe groups are hydrolyzed. The decrease in the number of these signals in 1 h - 3 h is explained by the reduction of the kind of molecules after full hydrolysis of -SiOMe groups. After 2 h -3 h from the beginning of the hydrolysis, the formation of cyclic siloxanes is suggested by ^{29}Si NMR measurements. Therefore, the strongest peak (134.2 ppm) can be assigned to the cyclic siloxanes. The enlarged spectrum after 2 h from the beginning of hydrolysis showed that the signal at 134.2 ppm has a shoulder, and the enlarged spectrum after 3 h indicated the two signals at 134.2 ppm. These signals can be caused by the formation of stereoisomers of cyclic siloxanes.

References

1 (a) R. Wakabayashi, K. Kawahara, K. Kuroda, *Angew. Chem. Int. Ed.*, 2010, **49**, 5273; (b) R. Wakabayashi, M. Tamai, K. Kawahara, H. Tachibana, Y. Imamura, H. Nakai, K. Kuroda, *J. Organomet. Chem.*, 2012, **716**, 26.

2 R. Wakabayashi, Y. Sugiura, T. Shibue, K. Kuroda, *Angew. Chem. Int. Ed.*, 2011, **50**, 10708.

3 Á. Gordillo, E. Jesús, C. López-Mardomingo, *J. Am. Chem. Soc.*, 2009, **131**, 4584.

4 C. J. Brinker and G. W. Scherer, Sol-Gel Science, Academic Press, Inc.,1990.

5 G. Cai and W. P. Weber, *Polymer*, 2002, **43**, 1753.