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Direct alkoxysilylation of alkoxysilanes for the synthesis of explicit alkoxysiloxane oligomers

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ABSTRACT

Direct alkoxysilylation, which is a powerful tool to provide explicit alkoxysiloxanes, is developed and its versatility is investigated. Siloxane pentamers $Si[OSiR^1(OMe)_2]_4$ having various functional groups (R^1 = methyl, vinyl, phenyl, chloropropyl and *n*-butyl groups) were successfully obtained by direct alkoxysilylation of $Si(OR)_4$ (R = t-Bu, CHPh₂). Thus, the versatility of the reaction is confirmed on organic functional groups R^1 . Functional group tolerance of the reaction is discussed on the basis of electronegativity of the R^1 groups. Alkoxysilylation of $Si(Ot-Bu)_2(OMe)_2$ and $Si(Ot-Bu)(OMe)_3$ selectively gives trimer (MeO)₂Si[OSiMe(OMe)₂]₂ and dimer (MeO)₃SiOSiMe(OMe)₂, respectively. Thus, the feasibility on siloxane structure is also confirmed. Various siloxane compounds are synthesized by this newly developed reaction for the first time.

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1. Introduction

Construction of siloxane framework under a controlled manner is a common issue in materials chemistry. Siloxane bond accounts for main component of silicone, silsesquioxane, silica, silicate and zeolite. Properties of these materials strongly depend on the siloxane structures. Therefore, synthetic methodologies for siloxanes are explored and developed by many researchers until now. Explicit siloxane compounds are useful as "molecular building blocks" for the precise assembly of siloxane framework in above synthetic methodologies [1–13].

Alkoxysilyl group is quite valuable functional group for their utility to siloxane formation, such as sol—gel process, nonhydrolytic sol—gel process and Piers—Rubinsztajn reaction. Preparation of nano- and meso-structured silica-based hybrid materials is demonstrated by the use of discrete alkoxysiloxane oligomers (explicit siloxane compounds having alkoxy groups).

In spite of their advantages, the number of actual discrete alkoxysiloxane oligomers and synthetic routes to them is quite limited, because silanols or silicates are required as their precursors

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[9–16]. Otherwise, their molecular weight, siloxane structure and compositions cannot be regulated. Silanols have a strong tendency to self-condense, thus they usually require stabilization by introducing bulky functional groups [15–17]. It is difficult to develop synthetic approaches to silicates for the purposes explored here because the reactions are quite complicated, involving the competitive formation and dissociation of siloxane bonds in water. To solve this problem, we have developed a nonhydrolytic reaction to synthesize discrete alkoxysiloxane oligomers [18]. It is accomplished by optimizing nonhydrolytic sol-gel process generally for preparing amorphous silica and other inorganic oxides [19–24]. Specific alkoxysilanes [Si(Ot-Bu)₄ or Si(OCHPh₂)₄] are used instead of silanols or silicates. These unusual alkoxysilanes can release stable carbocations and enable formation of discrete alkoxysiloxane oligomer in the presence of BiCl₃ as Lewis acid catalyst. In addition, their large steric hindrance makes them more stable than conventional alkoxysilanes (ethoxysilanes and methoxysilanes) toward hydrolysis.

However, the alkoxysilylation reaction is examined only with chlorosilanes having Si–H group in previous communication. Application of the reaction with other functional groups is highly desirable because silica-organic hybrid materials introduce various functional groups to materials that can be used as catalysts and adsorbents for example. Previously, we demonstrated the synthesis

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Scheme 1. Synthesis of discrete alkoxysiloxane oligomers by direct alkoxysilylation reaction.

of Si[OSiH(OMe)₂]₄ and Si[OSiH(OEt)₂]₄ [18]. Therefore, our interests are focused whether functional groups can be successfully introduced to oligomers by the reaction. Moreover, the ratio of organic groups to Si is also required to control functional group content in the resulting silica-organic hybrid materials, thus we also synthesized oligomers having other T/Q ratios (amount of organic group in hybrid materials). (Silicone nomenclature: $T^n = R^1Si(OSi)_n(OH)_{3-n}$; $Q^n = Si(OSi)_n(OH)_{4-n}$.)

Herein we report the functional group tolerance on the synthesis of discrete alkoxysiloxane oligomers (Scheme 1). In contrast to previous syntheses using silanols or silicates, the reaction proposed here can realize the synthesis of discrete alkoxysiloxane oligomers having various functional groups together with siloxane structures.

2. Results and discussion

2.1. Synthesis of alkoxysiloxane oligomers $Si[OSiR^1(OMe)_2]_4$ to investigate functional group (R^1) tolerance

To investigate functional group tolerance in alkoxysilylation, Si $[OSiR^1(OMe)_2]_4$ compounds containing various functional groups R^1 were synthesized (Scheme 2 top).

Fig. 1 shows the ²⁹Si NMR spectra of the crude products of compounds $Si[OSiR^1(OMe)_2]_4$ (1–5). Please note that these NMR



Fig. 1. ²⁹Si NMR spectra of crude Si[OSiR¹(OMe)₂]₄ before distillation (solvent: CDCl₃) (the product was filtered through celite pad and removed solvents and excess chlorosilanes up to 40 °C under vacuum): (a) $R^1 = Me(1)$; (b) $R^1 = -CH=CH_2$ (2); (c) $R^1 = Ph(3)$; (d) $R^1 = -(CH_2)_3Cl(4)$; (e) $R^1 = n$ -Bu (5).

spectra were recorded after solvent evaporation and filtration through a celite pad but that no further purification was conducted.

Each ²⁹Si NMR spectrum in Fig. 1 shows signals due to Q⁴ {*Si* [OSiR¹(OMe)₂]₄} and T¹ {Si[OSiR¹(OMe)₂]₄}. The chemical shift of T⁰ and T¹ is known to be affected by R¹ groups [26,27]. Compounds R¹Si(OMe)₃ (shown as T⁰ signals in Fig. 1) are impurities formed by the synthesis of ClSiR¹(OMe)₂. They are also formed by quenching the reaction by adding pyridine and methanol. Although a Q³ signal (ca. –100 ppm, OSi(OSi)₃) and small T¹ signal besides main T¹



Scheme 2. Synthesis of Si[OSiR¹(OMe)₂]₄ with various R¹ groups.

appears at Fig. 1(b), Si[OSiR¹(OMe)₂]₄ is undoubtedly the main product by complete alkoxysilylation of Si(Ot-Bu)₄ or Si(OCHPh₂)₄. A Q³ signal (Fig. 1(b)) implies the formation of (MeO)Si [OSiR¹(OMe)₂]₃ through partial transesterification between diphenylmethoxy and methoxy groups competitive to siloxane formation. The ¹³C NMR spectra (see Supplementary data for details) only show the signals due to R¹ group and methoxy groups (around ca. 50 ppm), which show the selective silylation of *tert*butoxy or diphenylmethoxy groups and retention of methoxy groups with all R¹ groups. The ¹H NMR spectra also support the results of ¹³C NMR spectra (see Supplementary data for details). The formation of these compounds was demonstrated via highresolution MS measurements (see Experimental section). On the basis of these results, the oligomers Si[OSiR¹(OMe)₂]₄ were successfully obtained with R¹ = methyl (1), vinyl (2), phenyl (3), chloropropyl (4) and *n*-butyl (5) groups.

All oligomers, except **3**, were isolated by vacuum distillation (see Experimental section; isolated yields: 35% (**1**), 10% (**2**), 69% (**4**), 32% (**5**)). Although the formation of Si[OSiR¹(OMe)₂]₄ with R¹ = Ph (**3**) is suggested by the same analyses above, its isolation was unsuccessful because of its high boiling point for vacuum distillation and its potential reactivity toward silica in flash chromatography. On the other hand, branched oligomer Si[OSiR¹(OMe)₂]₄ was not obtained at all when R¹ = OMe (Scheme 2 bottom), and a mixture of linear alkoxysiloxane oligomers was formed as mentioned in our previous report [18].

2.2. Discussion of functional group tolerance

We investigated the effect of R^1 group on the reaction using *ab initio* calculations with Spartan'08 software [28]. As mentioned above, functional group $R^1 = OMe$ is the only functional group that is unsuccessful for direct alkoxysilylation targeting Si $[OSiR^1(OMe)_2]_4$. The steric and electronic effects are considered to explain the differences arising from the R^1 group in the synthesis. Fig. 2 shows the molecular structures of $ClSiR^1(OMe)_2$ optimized at the B3LYP/6-31G^{**} level in order to compare the size of functional groups. The size of methoxy group seems similar to that of vinyl group and larger functional groups are successful for the reaction. Therefore, the size of R^1 group should not be a primary factor.

On the other hand, the group electronegativity study with ¹H NMR shows that the methoxy group is the most electron withdrawing of all the R¹ groups used in this study [29]. These data are also consistent with electron density analyses at the B3LYP/6-31G^{**} level (Table S1: see Supplementary data for details). These results suggest that R¹ group should be less electron withdrawing than methoxy group.

This feasibility is similar to that of Piers–Rubinsztajn reaction which forms siloxane bond from hydrosilane and alkoxysilane with $B(C_6F_5)_3$ catalyst. It is said that hydrosilanes containing two or more electron withdrawing functional groups are inert to siloxane formation [30], which shows the similarity between nonhydrolytic sol–gel process and Piers–Rubinsztajn reaction.

2.3. Utility for forming siloxane structure

We examined the synthesis of other siloxane structures to extend the utility of the reaction. Compounds having other T/Q ratios can also be useful for sol-gel processing to control the properties of silica-based hybrids. Scheme 3 shows the synthetic procedure used for $(MeO)_2Si[OSiMe(OMe)_2]_2$ (6) and $(MeO)_3SiO-SiMe(OMe)_2$ (7) from a reactant composed of Si(Ot-Bu)₂(OMe)₂ and Si(Ot-Bu)(OMe)₃.

The reactant was synthesized by adding a controlled amount of *t*-BuOH and MeOH to SiCl₄ in the presence of triethylamine as an acid scavenger. The ²⁹Si NMR spectrum of the reactant (Fig. 3a) shows the signals at $\delta = -83.0$ and -88.0 ppm. These signals can be assigned to Si(Ot-Bu)(OMe)₃ and Si(Ot-Bu)₂(OMe)₂ respectively. These assignments are based on the fact that the signal of Si(OMe)₄ and Si(Ot-Bu)₄ appears at around $\delta = -78.0$ and -98.0 ppm [14,18]. Thus the exchange of one methoxy group with one *tert*-butoxy group should cause a shift upfield by 5 ppm in ²⁹Si NMR measurements were also observed for transesterification between Si(OMe)₄ and other silicon alkoxides [18,31].

The ²⁹Si NMR spectrum of the product (Fig. 3b) shows signals assigned to $(MeO)_2Si[OSiMe(OMe)_2]_2$ (Q²) and $(MeO)_3SiOSi$ - $Me(OMe)_2$ (Q¹) at -93.7 and -85.9 ppm, respectively. There are three signals around -48 ppm, showing T¹ species of methylalkxoysilanes (MeSi(OSi)(OR")₂): R'' = H or Me [26]. These T^1 signals can be assigned to targeted compounds ((MeO)₂Si[OSi- $Me(OMe)_{2}_{2}(-47.7 \text{ ppm}), (MeO)_{3}SiOSiMe(OMe)_{2}(-47.5 \text{ ppm}))$ and a small amount of by-product $\{[(MeO)_2MeSi]_2O\}$ (-47.9 ppm). The ¹³C and ¹H NMR measurements show the signals arising from methoxy and methyl groups (see Supplementary data for details). EI-MS measurements also confirm the formation of (MeO)₂Si[OSi-Me(OMe)₂]₂ and (MeO)₃SiOSiMe(OMe)₂. These data indicate that alkoxysilylation of tert-butoxy groups in the precursors proceeds in a manner similar to the synthesis of $Si[OSiR^1(OMe)_2]_4$ (Scheme 3). These results show the utility of the reaction in the synthesis of targeted siloxane structures. In these experiments, the electron densities of Si and O in Si(Ot-Bu)(OMe)₃ and Si(Ot-Bu)₂(OMe)₂ should be similar to those of Si(Ot-Bu)₄. Thus, the reaction proceeds similarly to alkoxysilylation of Si(Ot-Bu)₄.

3. Conclusion

We have demonstrated direct alkoxysilylation reaction which is a powerful tool for the synthesis of molecular building block in sol-gel process. Our method does not require preparing unstable intermediates like silanols, thus it is applicable for the synthesis of discrete alkoxysiloxane oligomers that have not been synthesized before. Seven new branched alkoxysiloxane oligomers were obtained in good yields by utilizing this reaction. The reaction offers utility for a wide variety of alkoxysilylations of alkoxysilanes except for trialkoxysilylation ($R^1 = OMe$). The experiments and molecular simulation indicate that silicon atom in the trialkoxysilyl group has



Fig. 2. Molecular structures of ClSiR¹(OMe)₂ for comparing the size of functional group R¹ (white: H; gray: C; red: O; yellow: Si; green: Cl). Structure optimization was performed at the B3LYP/6-31G^{**} level with Spartan'08 software (Wavefunction Inc.) [11]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Scheme 3. Alkoxysilylation of Si(Ot-Bu)₂(OMe)₂ and Si(Ot-Bu)(OMe)₃ for the synthesis of a mixture composed of $(MeO)_2Si[OSiMe(OMe)_2]_2$ (**6**) and $(MeO)_3SiOSiMe(OMe)_2$ (**7**).

low electron density due to strong electron withdrawing effects of the alkoxy groups. The synthesis of discrete alkoxysiloxane oligomers is achieved with the other functional groups. In combination with functional group tolerance, the synthesis of oligomers having other T/Q ratios has also been accomplished. We believe that the reaction is quite useful to prepare siloxane compounds of use in the preparation of functional siloxane-based materials.

4. Experimental section

4.1. General

All reactions were carried out under N₂ atmosphere. Chlorosilanes, such as methyltrichlorosilane (MeSiCl₃, >95.0%), vinyltrichlorosilane (CH₂=CHSiCl₃, >98.0%), phenyltrichlorosilane (PhSiCl₃, >98.0%), 3-chloropropyltrichlorosilane (Cl(CH₂)₃SiCl₃, >97.0%), *n*-butyltrichlorosilane (*n*-BuSiCl₃, >98.0%) and tetrachlorosilane (SiCl₄, >98.0%) were purchased from Tokyo Chemical Industry. Tetrakis(diphenylmethoxy)silane (Si(OCHPh₂)₄) and tetra(*tert*-butoxy)silane (Si(O*t*-Bu)₄) were synthesized according to our previous report [18]. Other chemicals, including *tert*-butyl methyl ether (MTBE, *t*-BuOMe, anhydrous, 99.8%, Sigma–Aldrich),



Fig. 3. ²⁹Si NMR spectra of: (a) the reactant, a mixture of $Si(Ot-Bu)_2(OMe)_2$ and $Si(Ot-Bu)(OMe)_3$; (b) the product, a mixture of $(MeO)_2Si[OSiMe(OMe)_2]_2$ (**6**) and $(MeO)_3$ -SiOSiMe $(OMe)_2$ (**7**).

acetonitrile (MeCN, anhydrous, >99.5%, Kanto Chemical), bismuth trichloride (BiCl₃, >98.0%, Kanto Chemical), *tert*-butyl alcohol (*t*-BuOH, >99.0%, Kanto Chemical), methanol (>99.8%, dehydrated, Wako Pure Chemical), triethylamine (>99.0%, Wako Pure Chemical) and pyridine (>99.5%, dehydrated, Wako Pure Chemical) were used as received without further purification.

4.2. Instruments

Liquid-state ¹H, ¹³C and ²⁹Si NMR spectra were obtained on JEOL ECX-500 and JEOL Lambda-500 spectrometers with the resonance frequencies of 500 MHz, 126 MHz and 99 MHz, respectively. Chemical shifts for ¹H, ¹³C and ²⁹Si NMR were referenced to tetramethylsilane at 0 ppm. The repetition time between each pulse for ²⁹Si NMR was 10 s. In order to obtain quantitative spectra, a trace amount of Cr(acac)₃ was added to a sample solution to reduce the ²⁹Si spin-lattice relaxation time (T¹). EI mass analysis was carried out with a JEOL JMS-GCmatell instrument. FAB mass analysis was carried out with a JEOL JMS-SX102A instrument.

4.3. Synthesis of alkoxysiloxane oligomer $Si[OSiR^1(OMe)_2]_4$ ($R^1 = Me$) (1)

In all the oligomer syntheses described here, the syntheses become much easier than those reported previously [18]. Bismuth chloride is used as a catalyst for both chloroalkoxysilane synthesis and direct alkoxysilylation. The by-products in both reactions are the same alkyl chloride (RCl) and easily removed. Methyltrichlorosilane (MeSiCl₃, 11.7 mL, 100 mmol) was slowly added to an acetonitrile (20 mL) solution of BiCl₃ (0.3 mg, 1 mmol) and MTBE (24 mL, 200 mmol) in a 200 mL Schlenk flask at 0 °C [25]. The molar ratio was $MeSiCl_3/MTBE/BiCl_3 = 1:2:0.01$. The mixture was stirred overnight at r.t. and a crude chlorodimethoxymethylsilane (ClSi-Me(OMe)₂) solution was obtained. Although a certain amount of MeSi(OMe)₃ was present in the solution, the solution was used without further purification because the compound does not contain SiCl groups and does not affect the next alkoxysilylation. An acetonitrile solution (40 °C) of Si(OCHPh₂)₄ (7.6 g, 10 mmol) was added to the crude chloroalkoxysilane solution. The mixture was stirred for 3 h at r.t. Then, excess amounts of pyridine and methanol were added to deactivate the Lewis acid and to convert remained SiCl groups to SiOMe groups. The solvents, excess MeSi(OMe)₃ were removed under reduced pressure. Compound 1 was also obtained from Si(Ot-Bu)₄ instead of Si(OCHPh₂)₄. Hexane was used as a solvent instead of acetonitrile at that time. Compound 1 was isolated by vacuum distillation (1.8 g (3.5 mmol), yield 35%). 1: Colorless liquid. ¹H NMR (500 MHz, CDCl₃) $\delta = 0.16$ (s, 12H), 3.56 ppm (s, 24H); ¹³C NMR (128 MHz, CDCl₃): δ = 50.1, -7.0 ppm; ²⁹Si NMR (99 MHz, CDCl₃) $\delta = -48.1$ (4Si, T¹), -110.7 ppm (1Si, Q⁴); HRMS (EI, 70 eV) calcd. for $C_{11}H_{33}O_{12}Si_5^+$ [M–Me]⁺:497.0818; found: 497.0811.

4.4. Synthesis of alkoxysiloxane oligomer Si[OSiR¹(OMe)₂]₄ ($R^1 = -CH=CH_2$) (**2**)

Compound **2** was synthesized according to the manner similar to **1**. Vinyltrichlorosilane (CH₂=CHSiCl₃) was used instead of methyltrichlorosilane in the synthesis of **1**. The compound was isolated by vacuum distillation (0.55 g (1.0 mmol), yield 10%). **2**: Colorless liquid. ¹H NMR (500 MHz, THF-*d*₈) δ = 3.52 (s, 24H), 5.84–6.08 ppm (m, 12H); ¹³C NMR (128 MHz, THF-*d*₈) δ = 50.5, 130.3, 137.1 ppm; ²⁹Si NMR (99 MHz, THF-*d*₈) δ = -64.6 (4Si, T¹), -111.1 ppm (1Si, Q⁴); HRMS (EI, 70 eV) calcd. for C₁₄H₃₃O₁₂Si[±] [M–CH=CH₂]⁺: 533.0818; found: 533.0814.

4.5. Synthesis of alkoxysiloxane oligomer Si[OSiR¹(OMe)₂]₄ $(R^1 = Ph)$ (**3**)

Compound **3** was synthesized according to the manner similar to **1**. Phenyltrichlorosilane (PhSiCl₃) was used instead of methyltrichlorosilane in the synthesis of **1**. A hexane (10 mL) solution of Si(Ot-Bu)₄ (3.2 g, 10 mmol) was used instead of an acetonitrile solution of Si(OtPh₂)₄. The reaction time was 1 day after the addition of Si(Ot-Bu)₄. See Supplementary data for NMR spectra of crude product. Formation of **3** was also estimated with high-resolution MS measurement: HRMS (FAB) calcd. for C₃₁H₄₁O₁₁Si⁺₅ [M-MeO]⁺: 729.1495; found: 729.1484.

4.6. Synthesis of alkoxysiloxane oligomer $Si[OSiR^{1}(OMe)_{2}]_{4}$ ($R^{1} = -(CH_{2})_{3}Cl$) (**4**)

Compound **4** was synthesized according to the manner similar to **1**. 3-Chloropropyltrichlorosilane (Cl(CH₂)₃SiCl₃) was used instead of methyltrichlorosilane in the synthesis of **1**. A hexane (10 mL) solution of Si(Ot-Bu)₄ (3.2 g, 10 mmol) was used instead of a warm acetonitrile solution of Si(OCHPh₂)₄. The reaction time was 3 h after the addition of Si(Ot-Bu)₄. The compound was isolated by Kugelrohr distillation (5.4 g (6.9 mmol), yield 69%). **2**: Yellowish liquid. ¹H NMR (500 MHz, CDCl₃) $\delta = 0.78-0.81$ (m, 8H), 1.87-1.93 (m, 8H), 3.51-3.54 (t, 8H), 3.57 ppm (s, 24H); ¹³C NMR (128 MHz, CDCl₃) $\delta = 8.2$, 26.3, 47.3, 50.3 ppm; ²⁹Si NMR (99 MHz, CDCl₃) $\delta = -51.3$ (4Si, T¹), -111.2 (1Si, Q⁴): HRMS (FAB) calcd. for C₁₉H₄₅O₁₁Cl₄Si⁺₅ [M-MeO]⁺: 729.0562; found: 729.0591.

4.7. Synthesis of alkoxysiloxane oligomer $Si[OSiR^{1}(OMe)_{2}]_{4}$ ($R^{1} = n-Bu$) (**5**)

Compound **5** was synthesized according to the manner similar to **1**. *n*-Butyltrichlorosilane (*n*-BuSiCl₃) was used instead of methyltrichlorosilane in the synthesis of **1**. A hexane (10 mL) solution of Si(Ot-Bu)₄ (3.2 g, 10 mmol) was used instead of a warm acetonitrile solution of Si(OCHPh₂)₄. The reaction time was 3 h after the addition of Si(Ot-Bu)₄. The compound was isolated by Kugelrohr distillation 2.1 g (3.2 mmol, yield 32%). Colorless liquid. ¹H NMR (500 MHz, CDCl₃) δ = 0.65–0.68 (m, 8H), 0.88–0.91 (t, 12H), 1.32–1.45 (m, 16H), 3.56 ppm (s, 24H); ¹³C NMR (128 MHz, CDCl₃) δ = 10.4, 13.7, 24.9, 26.3, 50.2. ²⁹Si NMR (99 MHz, CDCl₃) δ = -50.2 (4Si, T¹), -111.4 ppm (1Si, Q⁴): HRMS (FAB) calcd. for C₂₃H₅₇O₁₁Si[±]₅ [M–MeO]⁺: 649.2747; found: 649.2729.

4.8. Synthesis of alkoxysiloxane trimer (MeO)₂Si[OSiMe(OMe)₂]₂ (6) and dimer (MeO)₃SiOSiMe(OMe)₂ (7)

In addition to the pentamers (1–5) described above, these trimers and dimers were synthesized by the same reaction scheme. Into a dried 3-necked flask equipped with a dropping funnel and stopcock, tert-butanol (30.5 mL, 320 mmol), triethylamine (103 mL, 743 mmol), and hexane (100 mL) were added. The flask was cooled to 0 °C and tetrachlorosilane (SiCl₄, 25 g, 218 mmol) was slowly added. The mixture was stirred for 3 h at r.t., then methanol (13 mL, 320 mmol) was slowly added at 0 °C. Hexane (300 mL) was added for stirring besides the formation of a large amount of triethylamine hydrochloride. The mixture was stirred for 1.5 h at r.t. The solvent and excess reagents were evaporated. Then the mixture was filtered over a celite pad with hexane to remove triethylamine hydrochloride to obtain a crude product (18.4 g) composed of Si(Ot-Bu)₂(OMe)₂ and Si(Ot-Bu)(OMe)₃. The composition of Si(Ot-Bu)₂(OMe)₂ and Si(Ot-Bu)(OMe)₃ is about 1:1 on the basis of the intensity ratio in ²⁹Si NMR measurement. See the ²⁹Si NMR spectrum shown above. See Supplementary data for the ¹³C and ¹H NMR spectra. Si $(Ot-Bu)_2(OMe)_2$ and Si $(Ot-Bu)(OMe)_3$ were subsequently alkoxysilylated with the following procedure. Into a dried 200 mL Schlenck flask, BiCl₃ (0.3 g), acetonitrile (20 mL), methyltrichlorosilane (11.7 mL) were added. The flask was cooled to 0 °C and MTBE (24 mL) was slowly added. The mixture was stirred for overnight and the mixture composed of $Si(Ot-Bu)_2(OMe)_2$ and Si(Ot-Bu)(OMe)₃ (2.15 g) was added. The mixture was stirred for 3 h. then pyridine (4.5 mL) and methanol (8.9 mL), were added at 0 °C. The solvent and excess alkoxysilanes were removed under reduced pressure. The mixture was filtered over a celite pad with hexane. The crude product (1.9 g) was obtained after evaporation of hexane. See the ²⁹Si NMR spectrum shown as Fig. 3. See Supplementary data for ¹³C and ¹H NMR spectra. Formations of titled compounds were also estimated with MS measurements: HRMS for **6** (EI, 70 eV) calcd. for C₇H₂₁O₈Si₃⁺ [M–MeO]⁺ 317.0544; found: 317.0538. HRMS for 7 (EI, 70 eV) calcd. for C5H15O5Si2 [M-MeO]⁺ 211.0458; found: 211.0456.

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Appendix A. Supplementary material

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.jorganchem.2012.05.033.

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