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Tetrahedron 62 (2006) 3103–3111

Mg-promoted reductive coupling of aromatic carbonyl compounds with trimethylsilyl chloride and bis(chlorodimethylsilyl) compounds☆

Tetsuro Uchida,[a] Yoshio Kita,[b] Hirofumi Maekawa[a] and Ikuzo Nishiguchi[a,*]

[a]*Department of Chemistry, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan*
[b]*Orient Chemical Industries, 8-1, Sanrahigashi-machi, Neyagawa, Osaka 572-8581, Japan*

Received 23 November 2005; revised 9 January 2006; accepted 10 January 2006

Available online 13 February 2006

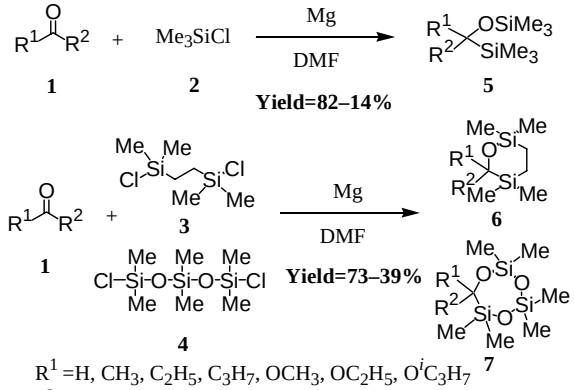
Abstract—Mg-promoted reductive coupling of aromatic carbonyl compounds (**1**) with chlorosilanes, such as trimethylsilyl chloride (TMSCl:**2**), 1,2-bis(chlorodimethylsilyl)ethane (**3**) and 1,5-dichlorohexamethyltrisiloxane (**4**), in *N*,*N*-dimethylformamide (DMF) at room temperature brought about selective and facile reductive formation of both of carbon–silicon and oxygen–silicon bonds to give the corresponding α-trimethylsilylalkyl trimethylsilyl ethers (**5**) and cyclic siloxanes (**6**), (**7**) in moderate to good yields, respectively. The present facile and selective coupling may be initiated through electron transfer from Mg metal to aromatic carbonyl compounds (**1**).

1. Introduction

Effective formation of a carbon–silicon bond is one of the most attractive subjects in organic synthesis[2] because of much usefulness and important functions of organosilicon compounds. It have been reported[3] that carbon–silicon bond formation was accomplished by treatment of carbonyl compounds and activated olefins with an alkali metal such as Li or Na in THF or DME as the solvent in the presence of trimethylsilyl chloride (TMSCl), although selectivity and/or yield of *C*-silylated products were not always satisfactory and special caution was generally needed for treatment of these alkali metals.

On the other hand, a variety of Mg-promoted carbon-silylation of carbonyl compounds and activated olefins were reported by Calas et al.,[4] although carcinogenic hexamethylphosphoric triamide (HMPA)[5,6] was necessary to use as the solvent.

We now wish to report a facile method for selective and effective carbon–silicon bond formation through Mg-promoted reductive coupling of carbonyl compounds (**1**) with TMSCl (**2**) in DMF at room temperature to give the corresponding α-trimethylsilylalkyl trimethylsilyl ethers (**5**) in good yields. Furthermore, Mg-promoted one-pot cyclization of aromatic carbonyl compounds (**1**), including ketones, and esters, with bis(chlorodimethylsilyl) compounds, such as 1,2-bis(chlorodimethylsilyl)ethane (**3**) or 1,5-dichlorohexamethyltrisiloxane (**4**), to give the corresponding cyclic siloxane compounds (**6**, **7**) in good yields, respectively (Scheme 1).



Scheme 1.

☆ See, Ref. 1.

Keywords: Silylation; Electron transfer; Aromatic carbonyl compounds; Magnesium.
* Corresponding author. Tel.: +81 258 47 9307; fax: +81 258 47 9300; e-mail: nishiiku@vos.nagaokaut.ac.jp

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doi:10.1016/j.tet.2006.01.026

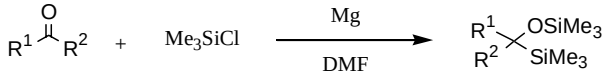
2. Result and discussion

2.1. Mg-promoted reductive coupling of carbonyl compounds with TMSCl

It was found that treatment of benzaldehyde (**1a**) with TMSCl in the presence of commercially available magnesium turnings for Grignard reagents in DMF at room temperature brought about facile and selective reductive formation of carbon–silicon and oxygen–silicon bonds to give α-trimethylsilyloxyl benzyltrimethylsilane (**5a**) in a 82% yield. Among a variety of reactive metals such as Zn, Al, and Mg, Mg showed the best result in present reaction, and no or little formation of **5a** was observed when Zn or Al was employed instead of Mg. It may be noteworthy that any reactions did not occur to recover **1a** quantitatively when TMSCl was absent in the reaction system. This reductive coupling reaction was also considerably influenced by a relative ratio of Mg, **2**, and **1a**. The best result for formation of **3a** was obtained when the relative proportion of Mg/**2**/**1a** was 3:8:1.[7] Employment of DMF as a solvent gave the best result among acetonitrile, tetrahydrofuran, dimethoxyethane and *N*,*N*-dimethyl-acetoamide.

Under the similar optimized reaction conditions, a variety of trimethylsilylated adducts **5a–l** were efficiently obtained in good to excellent yields, as shown in Table 1. It was quite interesting that the present reaction readily proceeded with not only aromatic aldehydes (**1a–g**) but also aromatic ketones (**1h–k**) and ester (**1l**). The α-trimethylsilylalkyl trimethylsilyl ethers (**5**) were readily hydrolyzed with an acidic aqueous solution to the corresponding α-trimethylsilyl alcohols.

Table 1. Mg-promoted silylation of aldehydes, ketones and esters with TMSCl (**2**)[a]

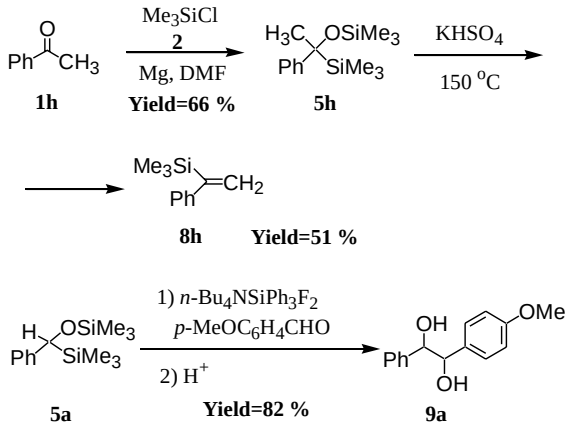


1 **2** **5**

Entry	R^1 in **1**	R^2 in **1**		Yield of **5** (%)[b]
1	H	C_6H_5	(**1a**)	82 (**5a**)
2	H	*o*-ClC_6H_4	(**1b**)	79 (**5b**)
3	H	*m*-ClC_6H_4	(**1c**)	75 (**5c**)
4	H	*p*-ClC_6H_4	(**1d**)	73 (**5d**)
5	H	*p*-$CF_3C_6H_4$	(**1e**)	54 (**5e**)
6	H	*o*-$CH_3OC_6H_4$	(**1f**)	78 (**5f**)
7	H	2-Thienyl	(**1g**)	52 (**5g**)
8	CH_3	C_6H_5	(**1h**)	74 (**5h**)
9	C_2H_5	C_6H_5	(**1i**)	14 (**5i**)[c]
10	C_6H_5	C_6H_5	(**1j**)	68 (**5j**)
11	CH_3	2-Thienyl	(**1k**)	42 (**5k**)
12	OC_2H_5	C_6H_5	(**1l**)	56 (**5l**)

[a] Reaction condition: substrate (5 mmol), trimethysilylchloride (**2**) (8.0 equiv per mol), magnesium (3.0 equiv per mol), DMF (60 mL), 20 h, room temperature, under N_2 atmosphere.
[b] Isolated yield.
[c] 4-Trimethylsilylpropiophenone was obtained in 20% yield.

The product **5a–l** can be easily transformed to many useful compounds such as esters, aldehydes, ketones, alcohols, and ethers.[8] For example, treatment of the product **5h** with $KHSO_4$, and that of the product **5a** with *n*-$Bu_4NSiPh_3F_2$/*p*-methoxybenzaldehyde gave α-silylstyrene (**8h**) and the mixed diarylethanediol (**9a**) in good yields, respectively (Scheme 2).



1h **Yield=66 %** **5h** **8h** **Yield=51 %** **5a** **Yield=82 %** **9a**

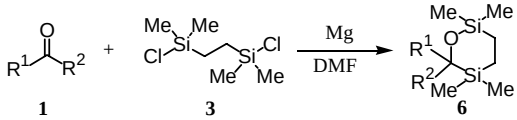
Scheme 2.

2.2. Mg-promoted one-pot cyclization of aromatic carbonyl compounds with bis(chlorodimethylsilyl) compounds (3, 4)

At the next step, use of bis(chlorodimethylsilyl) compounds (**3**, **4**) instead of TMSCl in the present cross coupling brought about efficient and selective one-pot cyclization of aromatic carbonyl compounds (**1**) to give the corresponding cyclic siloxanes (**6h–v**, **7h–t**) successfully.

Generally the reaction was carried out in anhydrous DMF at room temperature with magnetically stirring under nitrogen atmosphere for 20 h. Commercially available magnesium turnings for Grignard reaction was also used without any pre-treatment in the present cyclization. After usual work-up of the reaction mixture, column chromatography of the crude products gave the corresponding cyclic siloxanes (**6h–v**, **7h–t**) in 39–73% yields, as shown in Tables 2 and 3.

Table 2. Cyclization of aromatic carbonyl compounds in the presence of 1,2-bis(chlorodimethylsilyl)ethane (**3**)[a]

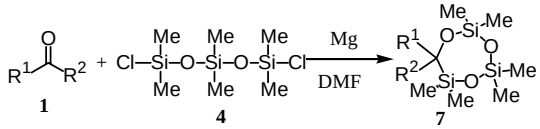


1 **3** **6**

Entry	R^1 in **1**	R^2 in **1**		Yield of **6** (%)[b]
1	CH_3	C_6H_5	(**1h**)	43 (**6h**)
2	CH_3	*m*-$MeOC_6H_4$	(**1m**)	43 (**6m**)
3	CH_3	*p*-$MeOC_6H_4$	(**1n**)	43 (**6n**)
4	CH_3	*m*-ClC_6H_4	(**1o**)	47 (**6o**)
5	CH_3	*p*-ClC_6H_4	(**1p**)	49 (**6p**)
6	C_2H_5	C_6H_5	(**1i**)	53 (**6i**)
7	C_3H_7	C_6H_5	(**1q**)	48 (**6q**)
8	OC_2H_5	C_6H_5	(**1l**)	54 (**6l**)
9	OC_2H_5	*m*-$MeOC_6H_4$	(**1r**)	73 (**6r**)
10	OC_2H_5	*p*-MeC_6H_4	(**1s**)	60 (**6s**)
11	OC_2H_5	*m*-ClC_6H_4	(**1t**)	69 (**6t**)
12	OCH_3	C_6H_5	(**1u**)	66 (**6u**)
13	$O^iC_3H_7$	C_6H_5	(**1v**)	73 (**6v**)

[a] Reaction condition: substrate (5 mmol), 1,2-bis(chlorodimethylsilyl)-ethene (**3**) (4.5 equiv per mol), magnesium (6.0 equiv per mol), DMF (60 mL), 20 h, room temperature, under N_2 atmosphere.
[b] GC yield.

Table 3. Cyclization of aromatic carbonyl compounds in the presence of 1,5-dichlorohexamethyltrisiloxane (**4**)[a]



1 **4** **7**

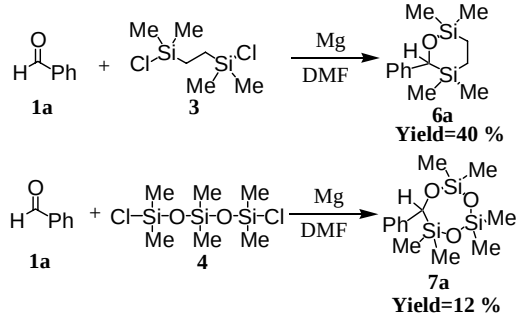
Entry	R^1 in **1**	R^2 in **1**		Yield of **7** (%)[b]
1	CH_3	C_6H_5	(**1h**)	43 (**7h**)
2	CH_3	*m*-$MeOC_6H_4$	(**1m**)	43 (**7m**)
3	CH_3	*p*-MeC_6H_4	(**1n**)	43 (**7n**)
4	CH_3	*p*-MeC_6H_4	(**1w**)	47 (**7w**)
5	CH_3	*p*-ClC_6H_4	(**1p**)	49 (**7p**)
6	OC_2H_5	C_6H_5	(**1l**)	54 (**7l**)
7	OC_2H_5	*m*-$MeOC_6H_4$	(**1r**)	73 (**7r**)
8	OC_2H_5	*p*-MeC_6H_4	(**1s**)	60 (**7s**)
9	OC_2H_5	*m*-ClC_6H_4	(**1t**)	69 (**7t**)

[a] Reaction condition: substrate (5 mmol), 1,5-dichlorohexamethyltrisiloxane) (**4**) (4.5 equiv per mol), magnesium (6.0 equiv per mol), DMF (60 mL), 20 h, room temperature, under N_2 atmosphere.
[b] GC yield.

These cyclic siloxanes (**6l–v**, **7l–t**) as well as non-cyclic product **5l**, the reductive coupling products from aromatic esters, may be useful reagents in organic synthesis as masked acyl silanes.[9]

It may be noteworthy tendency in the present cyclization that the reaction of aromatic esters (**1l**, **1r–t**) with both of 1,2-bis(chlorodimethylsilyl)ethane (**3**) and 1,5-dichlorohexamethyltrisiloxane (**4**) gave the corresponding cyclic siloxanes (**6l**, **6r–t**, **7l**, **7r–t**) in moderate to good yields (entries 8–13 in Table 2 and entries 6–9 in Table 3) while the similar cyclic siloxanes (**6h–p**, **7h–w**) were obtained in relatively low yields from the reaction of aromatic ketones (**1h**, **1i**, **1m–p**, **1w**) with bis(chlorodimethylsilyl) compounds (**3**, **4**) (entries 1–7 in Table 2 and entries 1–5 in Table 3).[10]

Furthermore, similar treatment of benzaldehydes with bis(chlorodimethylsilyl) compounds (**3**, **4**) led to formation the corresponding cyclization products (**6a**, **7a**) in 40 and 12% yields, respectively (Scheme 3).



1a **3** **6a**

1a **4** **7a**

Scheme 3.

This tendency was unusual since the reaction of aromatic aldehydes with TMSCl gave better yields than the similar reductive coupling of aromatic esters with the same reagent, as shown above.

Also, reduction potential of aromatic esters (**1l**, **1r–v**) are generally more positive (less reducible) than that of aromatic aldehydes and ketones.

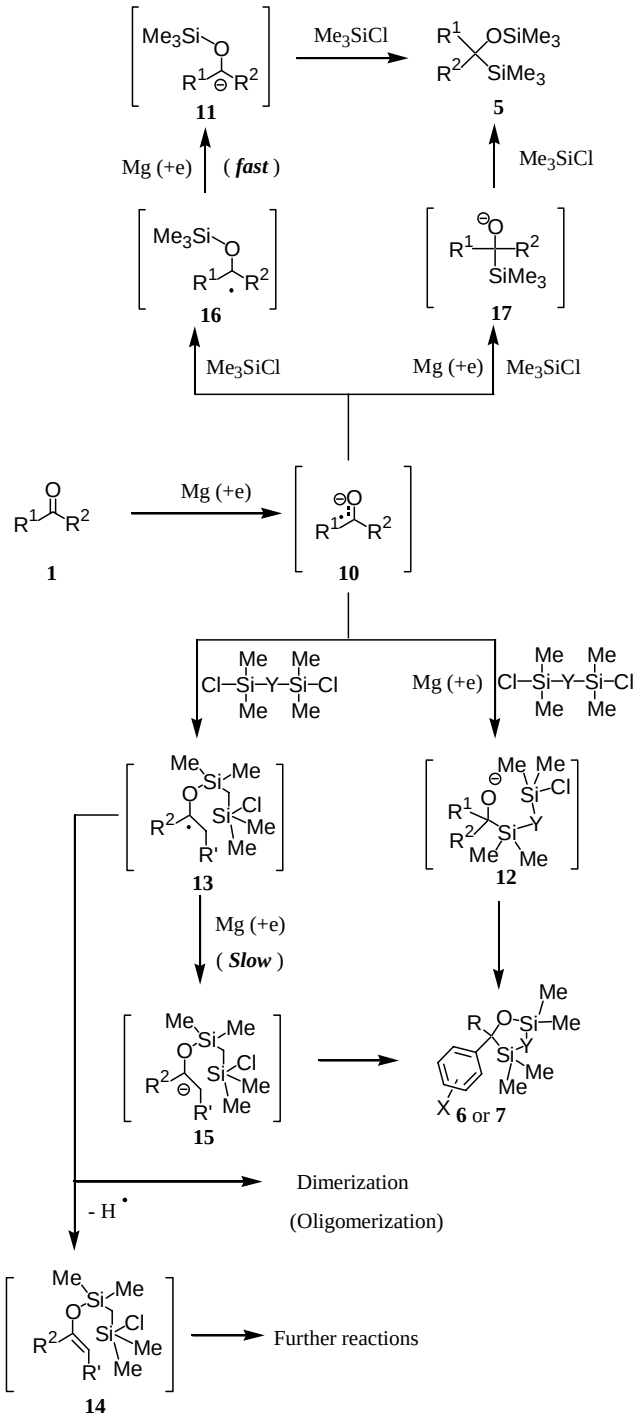
This unexpected phenomenon observed in this study may be probably attributed to some side-reactions[11] of aromatic aldehydes and ketones with bis(chlorodimethylsilyl) compounds (**3**, **4**), because our recent study[12] showed that Mg-promoted facile formation of enol trimethylsilyl ethers was observed in the reaction of aromatic ketones with trimethylsilyl choride under the similar conditions.

The reaction of aromatic aldehydes with bis(chlorodimethylsilyl) compounds (**3**, **4**) may be possibly accompanied with formation of pinacol type of complex dimeric product mixtures, because of lower electrophilicity of **3** and **4** in comparison with that of TMSCl as well as more stability (longer life-time) of the anion radical of aromatic aldehydes in comparison with that of aromatic esters.

It may be also interesting that the presence of an electron-withdrawing group on the phenyl ring of benzoic esters brought about some increase in the yield of the cyclic siloxanes (**6**, **7**) (entries 9 and 11 of Table 1), although similar substituent effect was not clearly observed in the reaction of acetophenone derivatives. The yield is not sensitive to a steric bulkiness of an alkoxy substituent of benzoic esters (entries 11–13 of Table 1).

Although the detailed role of TMSCl (**2**) and bis(chlorodimethylsilyl) compounds (**3** or **4**) in this reaction still remains ambiguous,[13] the following reaction mechanism may be proposed for the present Mg-promoted reductive coupling and cyclization from these experimental results as shown in Scheme 4. Cyclic voltammetry of the chlorosilanes, TMSCl (**2**), 1,2-bis(chlorodimethylsilyl)ethane (**3**) and 1,5-dichlorohexamethyltrisiloxane (**4**) do not give any reduction peak up to 3.0 V versus Ag/Ag^+ in DMF, while aromatic aldehydes, ketones and esters show their reduction peaks at -1.93, 2.10 and -2.36 V versus Ag/Ag^+ in DMF, respectively. Therefore, the first electron transfer from the Mg-metal to aromatic carbonyl compounds (**1**) may generate the corresponding anion radical, which may be subjected to the first electrophilic attack by TMSCl (**2**), 1,2-bis(chlorodimethylsilyl)ethane (**3**) or 1,5-dichlorohexamethyltrisiloxane (**4**) to the carbon atoms of carbonyl compounds followed by the fast second electron transfer giving the corresponding anionic intermediates (**12**). The second electrophilic attack to the oxygen atoms of the anonic intermediates (**12**) by TMSCl (**2**), 1,2-bis(chlorodimethylsilyl)ethane (**3**) or 1,5-dichlorohexamethyltrisiloxane (**4**) gave the α-trimethylsilylalkyl trimethylsilyl ethers (**5**) and final cyclic siloxane products (**6**, **7**), respectively (Scheme 2).

Electrophilic attack of bis(chlorodimethylsilyl) compounds (**3**, **4**) to the oxygen atoms of the carbonyl anion radicals (**10**) may generate α-silyloxy radicals (**13**), which may be subjected to the second slower electron transfer to the radical intermediate (**13**) giving the anion intermediate (**15**) in comparison with the faster electron transfer to the radical intermediate (**16**), giving the anion intermediate (**11**), because of steric effect in the electron transfer process



Scheme 4.

from Mg metal.[14] That may result in long-life time of the radical intermediate (**13**), to give various type of side-reactions such as dimerization, oligomerization, or elimination of hydrogen radicals in the case of aromatic ketones giving reactive silyloxy enol ethers (**14**) under the reaction conditions.

In conclusion, we have successfully developed one-pot selective formation of carbon–silicon and oxygen–silicon bonds and efficient novel cyclization, that are initiated by electron transfer from Mg metal. The present reactions may be characterized by simple procedure, unique reaction pattern, high selectivity, good yield and interesting functions of the products, which may possess high potentiality in organic chemistry.

3. Experimental

3.1. General

N,*N*-Dimethylformamide (DMF) was distilled from CaH_2. Unless otherwise mentioned, all the materials commercially obtained were used without further purification. Organic extracts were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure by a rotary evaporator. Flash chromatography was carried out using Merck 60 (Mesh 230–400) silica gel. Reactants and chromatography fractions were analyzed using precoated silica gel 60 F_{254} plates (Merck). ^{1}H NMR spectra at 270 and 400 MHz were measured in the CCl_4 and $CDCl_3$ solutions. Chemical shifts are expressed in ppm downfield from internal dichloromethane (5.32 ppm). The apparatus of cyclic voltammetry was ASL model 600 (ASL).

3.2. Cyclic voltammetry analysis

Cyclic voltammetry was performed in a beaker-type cell equipped with Pt electrodes as the anode and the cathode, a reference electrode (Ag/AgCl) at room temperature. The solvent was DMF containing 1 wt% Bu_4NClO_4 as a supporting electrolyte. Sweep rate was 200 mV/s.

3.3. General procedure for synthesis of α-trimethylsilyl-alkyl trimethylsilyl ethers (5)

A typical procedure is as follows. A solution containing TMSCl (8 mmol) and Mg turnings (15 mmol) in 60 ml of dry DMF was stirred under nitrogen atmosphere. A DMF solution of benzaldehyde (**1a**) (10 mmol/5 ml) was dropwise added to the solution for 1 h at room temperature, which was then stirred for about 4 h. Then the reaction mixture was poured into 200 ml of a saturated aqueous ammonium chloride solution and was extracted by three 100 ml portions of ether. Usual work-up and subsequent column chromatography or distillation of the residue gave α-trimethylsilyl-α-trimethyl-siloxytoluene (**5a**) in a good yield with formation of a small amount of the homo-coupling by-product, 1,2-diphenyl-1,2-ethanediol.

3.3.1. α-Trimethylsilyl-α-trimethylsiloxytoluene (5a). ^{1}H NMR (CCl_4, 270 MHz) δ (ppm): 0.07 (9H, s), 0.14 (9H, s), 4.56 (1H, d), 7.18–7.50 (5H, m). ^{13}C NMR (CCl_4, 67.5 MHz) δ (ppm): −4.13, 0.00, 70.29, 124.83, 125.09, 127.40, 144.38. IR (neat) ν (cm^{-1}): 1250, 1050. MS *m*/*z* 252 (M). Anal. Calcd for $C_{13}H_{24}OSi_2$: C, 61.84; H, 9.58. Found: C, 62.05; H, 9.41.

3.3.2. α-Trimethylsilyl-α-trimethylsiloxy-*o*-chlorotoluene (5b). ^{1}H NMR (CCl_4, 270 MHz) δ (ppm): 0.03 (9H, s), 0.03 (9H, s), 4.99 (1H, s), 7.01–7.48 (4H, m). ^{13}C NMR (CCl_4, 67.5 MHz) δ (ppm): −3.74, −0.12, 66.04, 126.29, 126.45, 127.98, 128.81, 129.94, 142.32. IR (neat) ν (cm^{-1}): 1250, 1055. MS *m*/*z* 286 (M^+). Anal. Calcd for $C_{13}H_{23}ClOSi_2$: C, 54.41; H, 8.08. Found: C, 54.26; H, 8.25.

3.3.3. α-Trimethylsilyl-α-trimethylsiloxy-*m*-chrolotoluene (5c). ^{1}H NMR (CCl_4, 270 MHz) δ (ppm): −0.04 (9H, s), 0.03 (9H, s), 4.41 (1H, s), 6.98–7.26 (4H, m). ^{13}C NMR (CCl_4, 67.5 MHz) δ (ppm): −4.17, −0.03, 69.83, 122.86, 124.74, 125.27, 128.97, 133.82, 146.77. IR (neat) ν (cm^{-1}): 1250, 1055. MS *m/z* 286 (M). Anal. Calcd for $C_{13}H_{23}ClOSi_2$: C, 54.41; H, 8.08. Found: C, 54.11; H, 8.36.

3.3.4. α-Trimethylsilyl-α-trimethylsiloxy-*p*-chlorotoluene (5d). ^{1}H NMR (CCl_4, 270 MHz) δ (ppm): −0.03 (9H, s), 0.04 (9H, s), 4.43 (1H, s), 7.09 (2H, d, J=8.4 Hz), 7.24 (2H, d, J=8.4 Hz). ^{13}C NMR (CCl_4, 67.5 MHz) δ (ppm): −4.18, 0.02, 69.79, 126.07, 127.92, 130.67, 143.02. IR (neat) ν (cm^{-1}): 1245, 1050. MS *m/z* 286 (M^+). Anal. Calcd for $C_{13}H_{23}ClOSi_2$: C, 54.41; H, 8.08. Found: C, 54.36; H, 8.11.

3.3.5. α-Trimethylsilyl-α-trimethylsiloxy-*p*-trifluoromethyltoluene (5e). ^{1}H NMR (CCl_4, 270 MHz) δ (ppm): −0.04 (9H, s), 0.11 (9H, s), 4.61 (1H, s), 7.34 (2H, d, J=8.1 Hz), 7.59 (2H, d, J=8.1 Hz). IR (neat) ν (cm^{-1}): 1250, 1050. MS *m/z* 320 (M^+). Anal. Calcd for $C_{14}H_{23}F_3OSi_2$: C, 52.47; H, 7.23. Found: C, 54.26; H, 7.11.

3.3.6. α-Trimethylsilyl-α-trimethylsiloxy-*o*-methoxyltoluene (5f). ^{1}H NMR (CCl_4, 270 MHz) δ (ppm): −0.05 (9H, s), 0.02 (9H, s), 3.78 (3H, s), 4.94 (1H, s), 6.78 (1H, dd, J=1.0, 7.6 Hz), 6.93 (1H, ddd, J=7.6, 7.6, 1.0 Hz), 7.11 (1H, ddd, J=1.3, 6.0, 7.6 Hz), 7.34 (1H, dd, J=1.3, 7.6 Hz). ^{13}C NMR (CCl_4, 67.5 MHz) δ (ppm): −3.88, −0.05, 54.72, 63.27, 109.08, 120.29, 125.57, 126.52, 133.10, 154.30. IR (neat) ν (cm^{-1}): 1250, 1050. MS *m/z* 267 ($M-Me)^+$). Anal. Calcd for $C_{14}H_{26}O_2Si_2$: C, 59.52; H, 9.28. Found: C, 59.80; H, 9.03.

3.3.7. α-Trimethylsilyl-α-trimethylsiloxy-2-methylthiophene (5g). ^{1}H NMR (CCl_4, 270 MHz) δ (ppm): 0.03 (9H, s), 0.07 (9H, s), 4.71 (1H, s), 6.71 (1H, dd, J=1.0, 3.5 Hz), 6.93 (1H, dd, J=3.5, 4.6 Hz), 7.10 (1H, dd, J=1.0, 4.6 Hz). ^{13}C NMR (CCl_4, 67.5 MHz) δ (ppm): −4.08, −0.02, 66.90, 120.59, 122.10, 126.36, 148.95. IR (neat) ν (cm^{-1}): 1250, 1050. MS *m/z* 258 (M^+). Anal. Calcd for $C_{11}H_{22}OSSi_2$: C, 51.10; H, 8.58. Found: C, 51.23; H, 8.62.

3.3.8. α-Trimethylsilyl-α-trimethylsiloxyethylbenzene (5h). ^{1}H NMR (CCl_4, 270 MHz) δ (ppm): 0.03 (9H, s), 0.19 (9H, s), 1.82 (3H, s), 7.18–7.39 (5H, m). ^{13}C NMR (CCl_4, 67.5 MHz) δ (ppm): −4.36, 2.84, 24.08, 73.10, 124.87, 124.98, 127.57, 148.07. IR (neat) ν (cm^{-1}): 1250, 1050. MS *m/z* 209 ($(M-57)^+$). Anal. Calcd for $C_{14}H_{26}OSi_2$: C, 63.09; H, 9.83. Found: C, 63.20; H, 10.01.

3.3.9. α-Trimethylsilyl-α-trimethylsiloxypropylbenzene (5i). ^{1}H NMR (CCl_4, 270 MHz) δ (ppm): −0.39 (9H, s), −0.12 (9H, s), 0.55 (3H, d, J=7.3 Hz), 1.73–1.83 (2H, m), 6.78–7.00 (5H, m). ^{13}C NMR (CCl_4, 67.5 MHz) δ (ppm): −3.72, 2.19, 8.52, 18.23, 78.44, 124.60, 125.32, 127.44, 145.44. IR (neat) ν (cm^{-1}): 2940, 1250, 1120, 1050, 1020, 835. MS *m/z* 280 (M^+). Anal. Calcd for $C_{15}H_{28}OSi_2$: C, 64.22; H, 10.06. Found: C, 64.05; H, 11.0.

3.3.10. Diphenyl-trimethylsilyl-trimethyloxymethane (5j). ^{1}H NMR (CCl_4, 270 MHz) δ (ppm): 0.04 (18H, s), 7.38–7.41 (10H, m). ^{13}C NMR (CCl_4, 67.5 MHz) δ (ppm): 1.82, 86.84, 128.24, 128.33, 128.46, 140.79. IR (neat) ν (cm^{-1}): 2950, 1740, 1490, 1445, 1250, 895, 840, 700. MS *m/z* 328 (M^+). Anal. Calcd for $C_{19}H_{28}OSi_2$: C, 69.45; H, 8.59. Found: C, 69.15; H, 8.41.

3.3.11. α-Trimethylsilyl-α-trimethylsiloxy-2-ethylthiophene (5k). ^{1}H NMR (CCl_4, 270 MHz) δ (ppm): 0.01 (9H, s), 0.12 (9H, s), 1.73 (1H, s), 6.67 (1H, dd, J=1.0, 3.6 Hz), 7.00 (1H, dd, J=3.6, 5.0 Hz), 7.12 (1H, dd, J=1.0, 5.0 Hz). ^{13}C NMR (CCl_4, 67.5 MHz) δ (ppm): −4.40, 2.55, 25.18, 71.89, 120.32, 122.03, 126.49, 154.27. IR (neat) ν (cm^{-1}): 1250, 1040. MS *m/z* 272 (M^+). Anal. Calcd for $C_{12}H_{24}OSSi_2$: C, 52.88; H, 8.88. Found: C, 53.01; H, 8.93.

3.3.12. α-Ethoxy-α-trimethylsiloxy-α-trimethylsiloxytoluene (5l). ^{1}H NMR (CCl_4, 270 MHz) δ (ppm): 0.04 (9H, s), 0.21 (9H, s), 1.28–1.32 (3H, m), 3.50–3.55 (2H, m), 7.16–7.54 (5H, m). ^{13}C NMR (CCl_4, 67.5 MHz) δ (ppm): −2.49, 2.21, 15.55, 58.96, 104.30, 124.77, 126.61, 127.33, 143.91. IR (neat) ν (cm^{-1}): 2950, 1250, 1100, 1040, 840 cm^{-1}. MS *m/z* 267 ($(M-OEt)^+$). Anal. Calcd for $C_{15}H_{28}O_2Si_2$: C, 60.75; H, 9.25. Found: C, 60.72; H, 9.20.

3.4. Procedure for synthesis of α-trimethylsilylstylene (8h)

A solution containing **5h** (10 mmol) and 6 N HCl aqueous (2 ml) in 20 ml of dry DMF was stirred for 8 h under a nitrogen atmosphere. Then the reaction mixture was poured into 200 ml of a saturated $NaHCO_3$ solution and was extracted by three 100 ml portions of ether. Usual work-up and subsequent evaporation of ether under reduced pressure gave the α-hydroxy-α-trimethylsilylethylbenzenein a 66% yield. Then anhydrous $KHSO_4$ and α-hydroxy-α-trimethylsilylethylbenzene was stirred at 150 °C in vacuo (10 mmHg). Distillation of reaction mixture gave the **8h** in a 55% yield.

3.4.1. α-Trimethylsilylstylene (8h). ^{1}H NMR (CCl_4, 270 MHz) δ (ppm): 0.20 (9H, s), 5.62 (1H, d, J=3.0 Hz), 5.81 (1H, d, J=3.0 Hz), 7.20–7.35 (5H, m). ^{13}C NMR (CCl_4, 67.5 MHz) δ (ppm): −0.88, 126.22, 126.69, 127.13, 144.76, 128.14, 153.51. IR (neat) ν (cm^{-1}): 2950, 1400, 1250, 840, 680 cm^{-1}. MS *m/z* 176 (M^+). Anal. Calcd for $C_{11}H_{16}Si$: C, 74.93; H, 9.15. Found: C, 74.88; H, 9.27.

3.5. Procedure for synthesis of 1-(4-methoxyphenyl)-2-phenyl-ethane-1,2-diol (9a)

A solution containing **5a** (1 mmol), *p*-methoxybenzaldehyde (3 mmol) and powder MS 4 Å (3 wt equiv) in 20 ml of dry THF was stirred for 2 h under nitrogen atmosphere. Then *n*-$Bu_4NSiPh_3F_2$ (2 mmol) was added to the solution at room temperature, and the mixture was stirred for another 2 h. After removal of THF, MeOH (20 ml) and acetic acid (0.3 ml) were added to the solution at room temperature, the resulting mixture was stirred for about 8 h. Subsequent removal of MS 4 Å by filtration and that of the solvent by distillation from the reaction mixture gave a crude oil. Purification of the crude oil by the column chromatography to gave **9a** in a 82% yield.

3.5.1. 1-(4-Methoxyphenyl)-2-phenyl-ethane-1,2-diol (9a).[15] One isomer was isolated by recrystallization (hexnane–AcOEt).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.10 (1H, d, J= 2.8 Hz), 2.15 (1H, d, J=2.8 Hz), 3.77 (3H, s), 4.78 (1H, dd, J=2.8, 2.8 Hz), 4.81 (1H, dd, J=2.8, 2.8 Hz), 6.84–6.88 (2H, m), 7.18–7.22 (2H, m), 7.26–7.35 (5H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 55.26, 77.81, 78.12, 113.69, 127.07, 128.08, 128.26, 128.32, 131.81, 139.93, 159.46. IR (neat) ν (cm^{-1}): 3350, 1460, 1040. MS *m/z* 244 (M). Mp: 129.2–131.0 °C (lit.: 135 °C).

3.6. General procedure for synthesis of cyclic siloxane (6,7)

To a 100 ml three-necked round flask equipped with a thermometer and a dropping funnel was placed aromatic carbonyl compound (**1**) (5 mmol) and magnesium turnings (30 mmol) in dry DMF (40 ml). After cooling the flask in a ice bath, 1,2-bis(chlorodimethylsilyl)ethane (**3**) or 1,5-dichloro-hexamethyltrisiloxane (**4**) (22.5 mmol) in DMF (20 ml) was added under magnetic stirring over 20 min. The resulting solution was stirred for 20 h at room temperature under nitrogen atmosphere. After stirring, the reaction solution was added in $NaHCO_3$ aqueous (300 ml) over 30 min and was extracted with ether. After evaporation of ether under reduced pressure, column chromatography of the crude products (eluent; hexane/EtOAc=20:1 or 10:1) gave the corresponding cyclic siloxane (**6**,**7**). All new products were identified by spectroscopic methods (^{1}H, ^{13}C NMR, IR, MASS) and elemental analysis.

3.6.1. 2,2,5,5,6-Pentamethyl-1-oxa-2,4-disilacyclohex-6-yl-benzene (6h). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.33 (3H, s), 0.09 (3H, s), 0.25 (3H, s), 0.26 (3H, s), 0.84–1.05 (4H, m), 1.70 (3H, s), 7.11–7.33 (5H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −6.38, −4.22, 0.54, 1.53, 5.75, 9.36, 26.67, 73.09, 123.72, 124.64, 127.67, 148.70. IR (neat) ν (cm^{-1}): 3085, 3057, 3020, 2959, 2903, 1600, 1491, 1444, 1416, 1367, 1249, 1115, 1093, 1066, 1051. MS *m/z* 264 (M^+). Anal. Calcd for $C_{14}H_{24}OSi_2$: C, 63.57; H, 9.15. Found: C, 63.30; H, 9.04.

3.6.2. 3-(2,2,5,5,6-Pentamethyl-1-oxa-2,4-disilacyclohex-6-yl)-methoxybenzene (6m). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.31 (3H, s), 0.10 (3H, s), 0.25 (3H, s), 0.26 (3H, s), 0.79–1.04 (4H, m), 1.68 (3H, s), 3.82 (3H, s), 6.69 (1H, ddd, J=0.8, 2.8, 8.0 Hz), 6.82 (1H, ddd, J=0.8, 2.8, 8.0 Hz), 6.91 (1H, dd, J=1.6, 2.8 Hz), 7.21 (1H, t, J=8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −6.36, −4.11, 0.54, 1.49, 5.78, 9.33, 26.75, 73.13, 109.65, 110.08, 116.28, 128.57, 150.72, 159.27. IR (neat) ν (cm^{-1}): 3078, 2956, 2903, 2832, 1600, 1579, 1482, 1464, 1431, 1367, 1313, 1284, 1250, 1195, 1162, 1050. MS *m/z* 294 (M^+). Anal. Calcd for $C_{15}H_{26}O_2Si_2$: C, 61.17; H, 8.90. Found: C, 60.94; H, 8.80.

3.6.3. 4-(2,2,5,5,6-Pentamethyl-1-oxa-2,4-disilacyclohex-6-yl)-toluene (6n). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.33 (3H, s), 0.08 (3H, s), 0.24 (3H, s), 0.25 (3H, s), 0.75–1.07 (4H, m), 1.67 (3H, s), 2.33 (3H, s), 7.09–7.17 (4H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −6.32, −4.19, 0.57, 1.55, 5.78, 9.41, 20.95, 26.79, 72.96, 123.68, 128.37, 133.93, 145.73. IR (neat) ν (cm^{-1}): 3088, 3021, 2959, 2903, 1508, 1445, 1414, 1366, 1249, 1183, 1117, 1076, 1050. MS *m/z* 278 (M^+). Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41. Found: C, 64.45; H, 9.19.

3.6.4. 3-(2,2,5,5,6-Pentamethyl-1-oxa-2,4-disilacyclohex-6-yl)-chlorobenzene (6o). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.31 (3H, s), 0.10 (3H, s), 0.25 (6H, s), 0.75–1.19 (4H, m), 1.67 (3H, s), 7.10–7.29 (4H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −6.41, −4.19, 0.49, 1.48, 5.68, 9.23, 26.70, 72.92, 121.88, 124.01, 124.78, 128.88, 133.88, 151.19. IR (neat) ν (cm^{-1}): 3068, 2959, 2903, 1592, 1567, 1476, 1453, 1416, 1368, 1250, 1213, 1112, 1065, 1051. MS *m/z* 298 (M^+, ^{35}Cl), 300 (M^+, ^{37}Cl). Anal. Calcd for $C_{14}H_{23}ClOSi_2$: C, 56.25; H, 7.75. Found: C, 56.11; H, 7.67.

3.6.5. 4-(2,2,5,5,6-Pentamethyl-1-oxa-2,4-disilacyclohex-6-yl)-chlorobenzene (6p). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.33 (3H, s), 0.08 (3H, s), 0.24 (3H, s), 0.26 (3H, s), 0.92 (4H, m), 1.67 (3H, s), 7.19–7.28 (4H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −6.43, −4.26, 0.51, 1.48, 5.64, 9.28, 26.62, 72.88, 125.19, 127.74, 130.32, 147.42. IR (neat) ν (cm^{-1}): 3084, 2959, 2903, 2801, 1899, 1486, 1445, 1397, 1367, 1250, 1216, 1172, 1115, 1092, 1074, 1049, 1011, 1074, 1049. MS *m/z* 298 (M^+, ^{35}Cl), 300 (M^+, ^{37}Cl). Anal. Calcd for $C_{14}H_{23}ClOSi_2$: C, 56.25; H, 7.75. Found: C, 56.28; H, 7.61.

3.6.6. 4-(6-Ethyl-2,2,5,5-tetramethyl-1-oxa-2,4-disilacyclohex-6-yl)benzene (6i). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.38 (3H, s), 0.09 (3H, s), 0.26 (6H, s), 0.72 (3H, t, J=7.0 Hz), 0.78–1.07 (4H, m), 2.12 (2H, m), 7.10–7.32 (5H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −6.41, −4.24, 0.60, 0.71, 5.85, 6.37, 9.42, 29.91, 76.23, 124.27, 124.28, 127.63, 146.26. IR (neat) ν (cm^{-1}): 3084, 3057, 3020, 2962, 2934, 2904, 1599, 1492, 1444, 1418, 1372, 1249, 1103, 1089, 1056, 1008. MS *m/z* 278 (M^+). Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41. Found: C, 64.44; H, 9.21.

3.6.7. 6-Propyl-2,2,5,5-tetramethyl-1-oxa-2,4-disilacyclohex-6-ylbenzene (6q). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.39 (3H, s), 0.07 (3H, s), 0.11 (3H, s), 0.25 (3H, s), 0.74–1.09 (8H, m), 1.37–1.49 (1H, m), 1.98–2.06 (2H, m), 7.09–7.14 (1H, m), 7.21–7.31 (4H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −6.55, −4.24, −0.35, 0.57, 5.81, 9.41, 14.36, 15.04, 39.82, 76.15, 124.06, 124.25, 127.62, 146.69. IR (neat) ν (cm^{-1}): 3084, 3058, 3020, 2957, 2905, 2873, 2360, 1598, 1493, 1465, 1444, 1418, 1250, 1132, 1117, 1058, 1030. MS *m/z* 292 (M^+). Anal. Calcd for $C_{16}H_{28}OSi_2$: C, 65.69; H, 9.65. Found: C, 65.43; H, 9.40.

3.6.8. 6-Ethoxy-2,2,5,5-tetramethyl-1-oxa-2,4-disilacyclohex-6-ylbenzene (6l). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.36 (3H, s), 0.12 (3H, s), 0.26 (3H, s), 0.29 (3H, s), 0.77–0.96 (3H, m), 1.15 (3H, t, J=7.0 Hz), 1.19–1.24 (1H, m), 3.18 (1H, dq, J=7.2, 9.2 Hz), 3.46 (1H, J= 7.2, 9.2 Hz), 7.20 (1H, m), 7.32 (3H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −6.04, −4.96, −0.07, −0.02, 5.25, 9.18, 15.21, 55.29, 102.58, 125.99, 126.07, 127.70, 143.11. IR (neat) ν (cm^{-1}): 3089, 3024, 2963, 2923, 2868, 1600,

1509, 1454, 1406, 1369, 1259, 1224, 1210, 1184, 1124, 1054. MS *m/z* 294 (M^+). Anal. Calcd for $C_{15}H_{26}O_2Si_2$: C, 61.17; H, 8.90. Found: C, 60.92; H, 8.99.

3.6.9. 3-(6-Ethoxy-2,2,5,5-tetramethyl-1-oxa-2,4-disilacyclohex-6-yl)methoxybenzene (6r). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.33 (3H, s), 0.14 (3H, s), 0.26 (3H, s), 0.29 (3H, s), 0.77–0.96 (3H, m), 1.16 (3H, t, J=7.0 Hz), 1.19–1.24 (1H, m), 3.20 (1H, dq, J=7.2, 9.2 Hz), 3.46 (1H, dq, J=7.2, 9.2 Hz), 6.75–6.78 (1H, m), 6.90–6.93 (2H, m), 7.23–7.29 (1H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −6.05, −4.86, −0.07, −0.02, 5.22, 9.12, 15.22, 55.09, 55.36, 102.47, 111.19, 111.85, 118.54, 128.65, 145.02, 159.28. IR (neat) ν (cm^{-1}): 3078, 2956, 2897, 2832, 1599, 1581, 1484, 1465, 1433, 1419, 1387, 1284, 1250. MS *m/z* 324 (M^+). Anal. Calcd for $C_{16}H_{28}O_3Si_2$: C, 59.21; H, 8.93. Found: C, 58.97; H, 8.93.

3.6.10. 4-(6-Ethoxy-2,2,5,5-tetramethyl-1-oxa-2,4-disilacyclohex-6-yl)methylbenzene (6s). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.35 (3H, s), 0.11 (3H, s), 0.25 (3H, s), 0.29 (3H, s), 0.77–0.96 (3H, m), 1.14 (3H, t, J=7.0 Hz), 1.19–1.23 (1H, m), 3.17 (1H, dq, J=7.2, 9.2 Hz), 3.43 (1H, dq, J=7.2, 9.2 Hz), 7.09–7.20 (4H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −6.00, −4.93, −0.07, −0.01, 5.26, 9.22, 15.21, 21.12, 55.12, 102.57, 125.94, 128.41, 135.49, 140.12. IR (neat) ν (cm^{-1}): 3022, 2971, 2896, 2801, 1605, 1586, 1482, 1443, 1408, 1386, 1248. MS *m/z* 308 (M^+). Anal. Calcd for $C_{16}H_{28}O_2Si_2$: C, 62.28; H, 9.15. Found: C, 62.39; H, 9.31.

3.6.11. 3-(6-Ethoxy-2,2,5,5-tetramethyl-1-oxa-2,4-disilacyclohex-6-yl)chlorobenzene (6t). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.34 (3H, s), 0.12 (3H, s), 0.26 (3H, s), 0.29 (3H, s), 0.77–0.96 (3H, m), 1.15 (3H, t, J=7.0 Hz), 1.13–1.23 (1H, m), 3.12 (1H, dq, J=7.2, 9.2 Hz), 3.45 (1H, dq, J=7.2, 9.2 Hz), 7.16–7.31 (4H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −6.05, −4.97, −0.11, −0.09, 5.14, 9.04, 15.17, 55.54, 102.07, 124.14, 126.13, 126.25, 128.99, 133.95, 145.56. IR (neat) ν (cm^{-1}): 3067, 2957, 2930, 2897, 1593, 1570, 1471, 1409, 1250. MS *m/z* 328 (M^+, ^{35}Cl), 330 (M^+, ^{37}Cl). Anal. Calcd for $C_{15}H_{25}ClO_2Si_2$: C, 54.76; H, 7.66. Found: C, 54.82; H, 7.43.

3.6.12. 6-Methoxy-2,2,5,5-tetramethyl-1-oxa-2,4-disilacyclohex-6-ylbenzene (6u). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.33 (3H, s), 0.11 (3H, s), 0.27 (3H, s), 0.32 (3H, s), 0.80–0.98 (3H, m), 1.16–1.25 (1H, m), 3.06 (3H, s), 7.21–7.37 (5H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −6.09, −5.03, −0.07, −0.02, 5.23, 9.19, 48.25, 102.81, 126.14, 126.26, 127.76, 142.34. IR (neat) ν (cm^{-1}): 3058, 3063, 3023, 2958, 2905, 2878, 2822, 1599, 1494, 1482, 1446, 1415, 1249. MS *m/z* 280 (M^+). Anal. Calcd for $C_{14}H_{24}O_2Si_2$: C, 59.94; H, 8.62. Found: C, 59.72; H, 8.91.

3.6.13. 6-Isoprpyl-2,2,5,5-tetramethyl-1-oxa-2,4-disilacyclohex-6-ylbenzene (6v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.45 (3H, s), 0.21 (3H, s), 0.28 (3H, s), 0.33 (3H, s), 0.74–0.95 (3H, m), 0.98 (3H, d, J=6.0 Hz), 1.04–1.19 (1H, m), 1.11 (3H, d, J=6.0 Hz), 3.91 (1H, sept, J=6.0 Hz), 7.19–7.38 (5H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −5.32, −4.14, 0.60, 1.46, 5.26, 8.51, 24.44, 25.29, 65.45, 102.86, 126.04, 126.16, 127.50, 144.36. IR (neat) ν (cm^{-1}): 3058, 3064, 3022, 2967, 2907, 2879, 1484, 1466, 1445, 1419, 1378, 1366, 1250. MS *m/z* 308 (M^+). Anal. Calcd for $C_{16}H_{28}O_2Si_2$: C, 62.28; H, 9.15. Found: C, 62.01; H, 9.33.

3.6.14. 2,2,5,5-Pentamethyl-1-oxa-2,4-disilacyclohex-6-yl-benzene (6a). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.16 (3H, s), 0.01 (3H, s), 0.24 (3H, s), 0.25 (3H, s), 0.78–1.68 (4H, m), 4.78 (1H, s), 7.11–7.33 (5H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −8.08, −4.17, −3.20, −0.72, 7.54, 9.33, 71.13, 124.27, 125.09, 127.87, 143.27. IR (neat) ν (cm^{-1}): 3083, 3061, 3023, 2957, 2900, 2822, 1601, 1439, 1449, 1415, 1249, 1204, 1157, 1076, 1048, 1024. MS *m/z* 250 (M^+). Anal. Calcd for $C_{13}H_{22}OSi_2$: C, 62.33; H, 8.85. Found: C, 62.51; H, 8.99.

3.6.15. 2,2,4,4,6,6,7-Heptamethyl-1,3,5-trioxa-2,4,6-trisilacyclohept-7-ylbenzene (7h). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.10 (3H, s), 0.17 (3H, s), 0.18 (3H, s), 0.21 (3H, s), 0.22 (3H, s), 0.25 (3H, s), 1.79 (3H, s), 7.17–7.36 (5H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −3.67, −2.71, 0.69, 0.94, 1.24, 2.59, 24.79, 75.40, 124.56, 125.18, 127.69, 146.83. IR (neat) ν (cm^{-1}): 3086, 3057, 3022, 2963, 2925, 2903, 2868, 1599, 1492, 1444, 1409, 1370, 1261, 1220, 1072. MS *m/z* 326 (M^+). Anal. Calcd for $C_{14}H_{26}O_3Si_3$: C, 51.48; H, 8.02. Found: C, 51.23; H, 7.98.

3.6.16. 3-(2,2,4,4,6,6,7-Heptamethyl-1,3,5-trioxa-2,4,6-trisilacyclohept-7-yl)methoxybenzene (7m). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.07 (3H, s), 0.15 (3H, s), 0.18 (3H, s), 0.22 (3H, s), 0.24 (3H, s), 0.26 (3H, s), 1.79 (3H, s), 3.84 (3H, s), 6.73 (1H, ddd, J=0.8, 2.8, 8.0 Hz), 6.89 (1H, ddd, J=0.8, 2.8, 8.0 Hz), 6.99 (1H, dd, J=1.6, 2.8 Hz), 7.24 (1H, t, J=8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −3.59, −2.57, 0.68, 0.71, 0.93, 2.58, 24.87, 55.07, 75.42, 109.96, 111.07, 117.03, 128.59, 148.80, 159.21. IR (neat) ν (cm^{-1}): 3081, 2963, 2833, 1599, 1580, 1486, 1464, 1432, 1370, 1314, 1286, 1260, 1196, 1165, 1120, 1058, 1012. MS *m/z* 356 (M^+). Anal. Calcd for $C_{15}H_{28}O_4Si_3$: C, 50.52; H, 7.91. Found: C, 50.47; H, 7.69.

3.6.17. 3-(2,2,4,4,6,6,7-Heptamethyl-1,3,5-trioxa-2,4,6-trisilacyclohept-7-yl)toluene (7n). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.09 (3H, s), 0.11 (3H, s), 0.16 (3H, s), 0.21 (3H, s), 0.22 (3H, s), 0.25 (3H, s), 1.78 (3H, s), 2.37 (3H, s), 6.98–7.20 (4H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −3.62, −2.65, 0.69, 0.74, 0.95, 2.61, 21.80, 24.86, 75.37, 121.71, 125.28, 125.95, 127.59, 137.08, 146.81. IR (neat) ν (cm^{-1}): 3023, 2963, 2923, 2867, 1604, 1586, 1487, 1455, 1409, 1370, 1259, 1174, 1058. MS *m/z* 340 (M^+). Anal. Calcd for $C_{15}H_{28}O_3Si_3$: C, 52.89; H, 8.29. Found: C, 52.63; H, 8.19.

3.6.18. 4-(2,2,4,4,6,6,7-Heptamethyl-1,3,5-trioxa-2,4,6-trisilacyclohept-7-yl)toluene (7w). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.09 (3H, s), 0.11 (3H, s), 0.16 (3H, s), 0.20 (3H, s), 0.21 (3H, s), 0.24 (3H, s), 1.77 (3H, s), 2.34 (3H, s), 7.11–7.27 (4H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −3.64, −2.71, 0.69, 0.73, 0.95, 2.58, 20.95, 24.86, 75.24, 124.54, 128.42, 134.62, 143.83. IR (neat) ν (cm^{-1}): 3089, 3024, 2963, 2923, 2868, 1600, 1509, 1454, 1406, 1369, 1259, 1224, 1210, 1184, 1124, 1054. MS *m/z* 340

(M^+). Anal. Calcd for $C_{15}H_{28}O_3Si_3$: C, 52.89; H, 8.29. Found: C, 52.82; H, 8.01.

3.6.19. 4-(2,2,4,4,6,6,7-Heptamethyl-1,3,5-trioxa-2,4,6-trisilacyclohept-7-yl)chlorobenzene (7p). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.09 (3H, s), 0.12 (3H, s), 0.18 (3H, s), 0.23 (3H, s), 0.24 (3H, s), 0.26 (3H, s), 1.78 (3H, s), 7.16–7.32 (4H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −3.74, −2.77, 0.66, 0.71, 0.93, 2.57, 24.73, 75.18, 126.01, 127.78, 130.94, 145.54. IR (neat) ν (cm^{-1}): 3086, 3034, 2963, 2925, 2903, 2868, 1489, 1456, 1398, 1370, 1258. MS *m/z* 361 (M^+, ^{35}Cl), 363 (M^+, ^{37}Cl). Anal. Calcd for $C_{14}H_{25}ClO_3Si_3$: C, 46.57; H, 6.98. Found: C, 46.49; H, 6.72.

3.6.20. 7-Ethoxy-2,2,4,4,6,6,-hexamethyl-1,3,5-trioxa-2,4,6-trisilacyclohept-7-ylbenzene (7l). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.16 (3H, s), 0.16 (3H, s), 0.19 (3H, s), 0.27 (6H, s), 0.31 (3H, s), 1.21 (3H, t, J=7.0 Hz), 3.30–3.37 (1H, m), 3.41–3.48 (1H, m), 7.22–7.38 (5H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −2.71, −2.66, 0.68, 0.79, 0.99, 0.99, 15.34, 56.32, 126.63, 126.81, 127.70, 141.76. IR (neat) ν (cm^{-1}): 3064, 2965, 2899, 1259, 1206, 1126, 1090, 1037, 1014. MS *m/z* 356 (M^+). Anal. Calcd for $C_{14}H_{26}O_3Si_3$: C, 51.48; H, 8.02. Found: C, 51.23; H, 7.98.

3.6.21. 3-(7-Ethoxy-2,2,4,4,6,6,-hexamethyl-1,3,5-trioxa-2,4,6-trisilacyclohept-7-yl)methoxybenzene (7r). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.14 (3H, s), 0.15 (3H, s), 0.20 (3H, s), 0.26 (6H, s), 0.28 (3H, s), 1.20 (3H, t, J=7.0 Hz), 3.34 (1H, dq, J=7.2, 9.2 Hz), 3.45 (1H, dq, J=7.2, 9.2 Hz), 3.83 (3H, s), 6.77–6.79 (1H, m), 6.94–6.96 (2H, m), 7.23–7.28 (1H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −2.63, −2.52, 0.68, 0.79, 0.97, 1.00, 15.36, 55.13, 56.39, 103.74, 111.66, 112.80, 119.33, 128.65, 143.66, 159.24. IR (neat) ν (cm^{-1}):3079, 2963, 2901, 2833, 1599, 1582, 1487, 1465, 1433, 1314, 1285, 1258. MS *m/z* 386 (M^+). Anal. Calcd for $C_{16}H_{30}O_5Si_3$: C, 49.70; H, 7.82. Found: C, 49.89; H, 7.99.

3.6.22. 4-(7-Ethoxy-2,2,4,4,6,6,-hexamethyl-1,3,5-trioxa-2,4,6-trisilacyclohept-7-yl)toluene (7s). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.15 (3H, s), 0.15 (3H, s), 0.18 (3H, Si–CH_3, s), 0.26 (6H, s), 0.31 (3H, s), 1.20 (3H, t, J=7.0 Hz), 2.38 (3H, s), 3.34 (1H, dq, J=7.2, 9.2 Hz), 3.43 (1H, dq, J=7.2, 9.2 Hz), 7.04–7.06 (1H, m), 7.14–7.28 (3H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −2.68, −2.61, 0.69, 0.81, 1.01, 1.03, 15.37, 21.73, 56.26, 103.86, 123.96, 127.35, 127.42, 127.56, 137.17, 141.66. IR (neat) ν (cm^{-1}): 3024, 2964, 2900, 1605, 1587, 1484, 1444, 1410, 1387, 1258. MS *m/z* 370 (M^+). Anal. Calcd for $C_{16}H_{30}O_4Si_3$: C, 51.85; H, 8.16. Found: C, 51.69; H, δ 8.02.

3.6.23. 3-(7-Ethoxy-2,2,4,4,6,6,-hexamethyl-1,3,5-trioxa-2,4,6-trisilacyclohept-7-yl)chlorobenzene (7t). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.15 (3H, s), 0.15 (3H, s), 0.19 (3H, s), 0.25 (3H, s), 0.26 (3H, s), 0.31 (3H, s), 1.20 (3H, t, J=7.0 Hz), 3.28 (1H, m), 3.44 (1H, m), 7.21–7.35 (4H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −2.69, −2.67, 0.64, 0.76, 0.94, 1.02, 15.31, 56.55, 103.34, 124.94, 126.79, 126.90, 128.97, 133.94, 144.27. IR (neat) ν (cm^{-1}): 3069, 2964, 2900, 1593, 1571, 1472, 1444, 1410, 1388, 1259, 1198. MS *m/z* 390 (M^+, ^{35}Cl), 392 (M^+, ^{37}Cl). Anal. Calcd for $C_{15}H_{27}ClO_4Si_3$: C, 46.07; H, 6.96. Found: C, 45.98; H, 6.79.

3.6.24. 2,2,4,4,6,6,-Hexamethyl-1,3,5-trioxa-2,4,6-trisilacyclohept-7-ylbenzene (7a). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.02 (3H, s), 0.14 (3H, s), 0.19 (3H, s), 0.22 (6H, s), 0.27 (3H, s), 4.79 (1H, s), 7.13–7.22 (1H, m), 7.27–7.35 (4H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −4.69, −2.41, −1.96, −0.57, 0.70, 0.92, 71.03, 124.71, 125.49, 127.91, 142.06. IR (KBr) ν (cm^{-1}): 3082, 3063, 3024, 3002, 2962, 2900, 2843, 1600, 1494, 1452, 1411, 1259. MS *m/z* 312 (M^+). Anal. Calcd for $C_{13}H_{24}O_3Si_3$: C, 49.95; H, 7.74. Found: C, 49.99; H, 7.85.

Acknowledgements

This work was partially supported by the 21st Century Center of Excellent (COE) Program of Nagaoka University of Technology provided by The Ministry of Education, Culture, Sports, Science and Technology, Japan.

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10. The present coupling of aromatic alkyl ketones (**1h**, **1i**, **1q**) with bis(chlorodimethylsilyl)ethane (**3**) gave the corresponding cyclic coupling products (**6h**, **6i**, **6q**) in similar yields, although that of **1i** with TMSCl gave the corresponding product (**5i**) in only 14% yield, accompanying unusual formation of 4-trimethylsilylpropiophenone (20%). This surprising phenomenon may be partially elucidated by much higher reactivity of TMSCl in comparison with bis(chlorodimethylsilyl)ethane (**3**), as shown in unusual attack of TMSCl to the *p*-position of reactive anion radical intermediate of **1i**.
11. Formation of a variety of by-products and tarric materials resulted in relatively low yield of the desired products (**6** and **7**) in Mg-promoted cyclization of aromatic ketones with dichlorosilanes (**3** and **4**).
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14. Ring strain of the cyclic products from the reaction of aromatic alkyl ketones (**1**) with bis(chlorodimethylsilyl) compounds (**3**, **4**) may be an additional effect for their lower yield.
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