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Disiloxane Synthesis Based on Silicon-Hydrogen Bond Activation Using Gold and Platinum on Carbon in Water or Heavy Water

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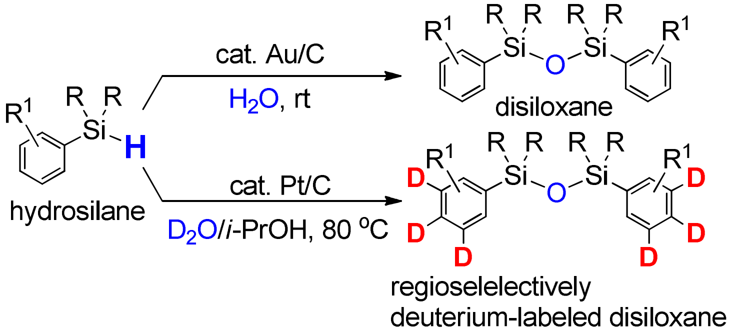
ABSTRACT



Disiloxanes possessing a silicon-oxygen linkage are important as frameworks for the functional materials and coupling partners for Hiyama-type cross coupling. We found that disiloxanes were effectively constructed of hydrosilanes catalyzed by gold on carbon in water as the solvent and oxidant in association with the emission of hydrogen gas at room temperature. The present oxidation could proceed via various reaction pathways, such as the hydration of hydrosilane into silanol, dehydrogenative coupling of hydrosilane into disilane and the subsequent corresponding reactions to disiloxane. Additionally, the platinum on carbon-catalyzed hydrogen-deuterium exchange reaction of arylhydrosilanes as substrates in heavy water proceeded on the aromatic nuclei at 80 °C with high deuterium efficiency and high regioselectivity at the only meta- and para-positions of the aromatic-silicon bond to give the deuterium-labeled disiloxanes.

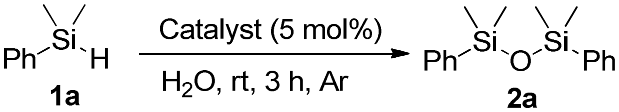
INTRODUCTION

Siloxane possessing a silicon (Si)-oxygen (O) linkage is an important core of functional materials, such as liquid crystals and thermosets,[1] and bioactive compounds[2] (e.g., muscle relaxant[2b]). Furthermore, aryl or vinyl-substituted disiloxanes can be Hiyama-type coupling partners in organic chemistry.[3] The transformation of hydrosilanes to disiloxanes is a straightforward synthetic method, and the direct disiloxane synthesis based on the $InBr_3$-catalyzed air oxidation of hydrosilanes[4] and the homogeneous transition metal-catalyzed reduction of carbonyl compounds by hydrosilanes[5-6] have been reported. Meanwhile, the homogeneous Rh and Re catalytic methods using H_2O as a green solvent and oxidant were also developed.[7] Although reusable heterogeneous catalysts are environmentally-friendly from the viewpoint of green chemistry, the reported heterogeneous transition metal (Au[8], Pt[9], Pd[10], Ni[11] and Ag[12])-catalyzed oxidations of hydrosilanes using H_2O as an additive in organic solvents selectively gave the corresponding silanol as the main product.[13] A recent research finding revealed the carbon nanotube-gold nanohybrid catalysts could selectively oxidize the silanes in H_2O to silanol and the use of homogeneous $AuCl_3$ with the ligands directly provided the disiloxane from silane.[14] In this report, We have newly developed the Au/C-catalyzed direct synthesis of disiloxanes starting from hydrosilanes in water, and the unprecedented and regioselecitive Pt/C-catalyzed deuteration of aromatic nuclei of aryl-substituted disiloxanes generated by the oxidative coupling of hydrosilanes in deuterium oxide (D_2O, heavy water).

RESULTS AND DISCUSSION

We first investigated the catalyst efficiency of the various platinum group metals on carbon (5 mol%) using dimethylphenylsilane (**1a**) as a substrate in H_2O for 3 h at room temperature under atmospheric argon (Table 1). While 10% Pd/C, Pt/C, Rh/C and Ru/C effectively produced the desired diphenyltetramethyldisiloxane (**2a**) in high yields and the corresponding silanol was not obtained (Entries 1-4), the reaction using 10% Au/C most efficiently proceeded to provide **2a** in an excellent yield (97%) (Entry 5). As a result of the comparison with various types of heterogeneous platinum group catalysts,[15] carbon as a support and 10% metal content were found to be adequate (Entries 2 *vs.* 6-9).

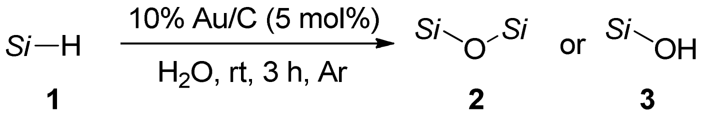
Table 1. Catalyst efficiency of disiloxane synthesis using H_2O.

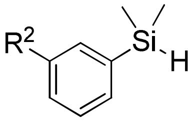
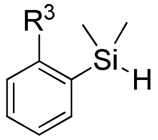
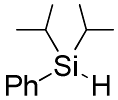


Entry	Catalyst	Conversion (%)	Yield (%)
1	10% Pd/C	100	87
2	10% Pt/C	100	86
3	10% Rh/C	100	81
4	10% Ru/C	100	71
5	10% Au/C	100	97
6	10% Cu/C	100	69
7	10% Ag/C	95	32
8	5% Pt/C	100	49
9	5% Pt/Al_2O_3	100	trace
10	PtO_2	100	24
11	charcoal	53	trace

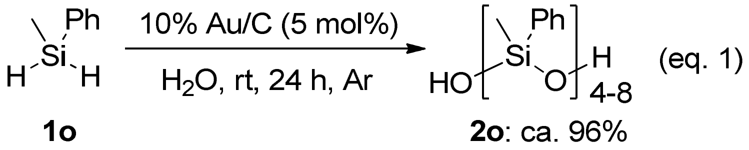
Various aryldimethylsilanes could be used for the Au/C-catalyzed direct synthesis of disiloxanes in H_2O (Table 2). 4-MeO, Me, F, Br and CF_3-phenyl-substituted silanes (**1b-f**) were effectively transformed into the corresponding disiloxanes (**2b-f**) in excellent yields (Entries 1-5). Although hydrogen gas should be generated during the reaction process, TBS ether[16] and alkyne moieties within the molecule could remain without their hydrogenation (Entries 6 and 7). Additionally, 3- or 2-MeO and F-phenyl-substituted silanes (**1i-l**) also underwent the Au/C-catalyzed oxidation in H_2O to give the disiloxanes (**2i-l**) (Entries 8-11). Meanwhile, the sterically-hindered silanes, such as diisopropylphenylsilane (**1m**) and triphenylsilane (**1n**), were transformed into the corresponding silanols (**3m** and **3n**) even by heating at 60 °C (Entries 12 and 13). Furthermore, dihydromethylphenylsilane (**1o**) underwent the continuous oxidative coupling of the hydrosilane moieties to mainly give a mixture of tetramers to octamers (**2o**) (eq. 1). As the result of the reuse test using **1a**, Au/C was found to be reusable at least 5 times without any metal leaching (eq. 2).[17]

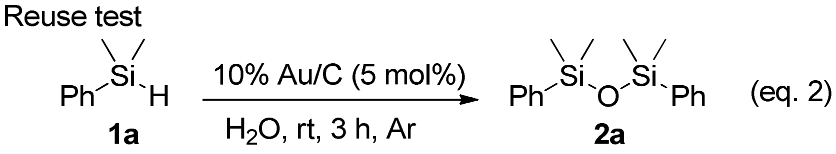
Table 2. Scope of substrates in the disiloxane synthesis.



Entry	Substrate		Product	Yield (%)[e]
1		R^1 = MeO (**1b**)	**2b**	>99
2		R^1 = Me (**1c**)	**2c**	>99
3		R^1 = F (**1d**)	**2d**	97
4		R^1 = Br (**1e**)	**2e**	92
5		R^1 = CF_3 (**1f**)	**2f**	87
6		R^1 = $TBSOCH_2$ (**1g**)	**2g**	91
7		R^1 = PhC≡C (**1h**)	**2h**	82
8		R^2 = MeO (**1i**)	**2i**	97
9[a]		R^2 = F (**1j**)	**2j**	94[a]
10		R^3 = MeO (**1k**)	**2k**	97
11		R^3 = F (**1l**)	**2l**	92
12[b,c]		(**1m**)	**3m**	97[b,c]
13[b,d]	Ph_3SiH	(**1n**)	**3n**	>99[b,d]

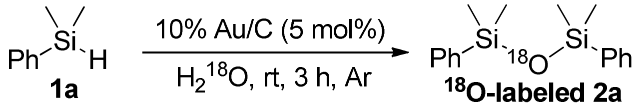
[a] For 6 h. [b] At 60 °C. [c] For 9 h. [d] For 24 h. [e] 100% conversion yields were achieved in all these reactions.



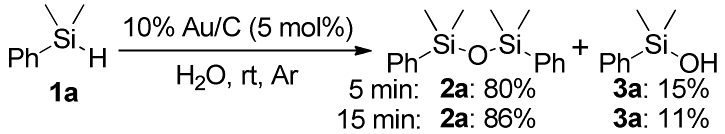


Yield of **2a** ; 1st: 97%, 2nd: 98%, 3rd: 98%, 4th: 99%, 5th: 92%

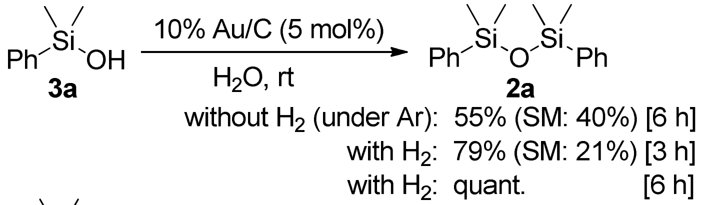
The mechanistic studies were next evaluated. The Au/C-catalyzed oxidation of **1a** in $H_2{}^{18}O$ instead of normal H_2O gave the ^{18}O-labeled **2a**, which clearly indicated that H_2O played the role as an oxidant source (eq. 3). When the reaction was stopped for 5 or 15 min., the desired oxidation of **1a** to **2a** (80 or 86%) proceeded and a small amount of silanol (**3a**; 15 or 11%) was obtained as the reaction intermediate (eq. 4). However, the Au/C-catalyzed dehydration of **3a** was comparatively slow and was not completed within 3 h even under either atmospheric Ar or H_2[18] (eq. 5), while the Au/C-catalyzed oxidation of **1a** into **2a** was completed within 3 h (Table 1, entry 5). Based on these experimental results, two kinds of reaction pathways are considerable. Firstly, the silanol was first generated by the transition metal-catalyzed hydration of hydrosilane,[9-11] and the subsequent dehydration of the silanol could produce the disiloxane.[7a] Alternatively, the first dehydrogenative coupling of the hydrosilane to disilane,[19] and the following hydrolytic oxidation[20] of the disilane give disiloxane. Actually, the disilane (**4a**) was efficiently transformed into the corresponding disiloxane (**2a**) in a quantitative yield in the presence of Au/C in H_2O (eq. 6). Because the transformation of silanol into disiloxane is slow (eq. 4), we propose that the present oxidation of hydrosilane (**1a**) into disiloxane (**2a**) mainly proceeds via the latter dehydrogenative coupling of the hydrosilane to the disilane (**4a**).



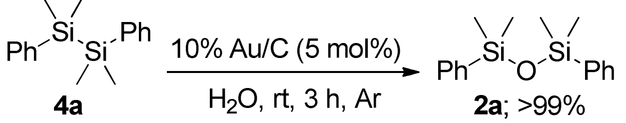
(eq. 3)



(eq. 4)



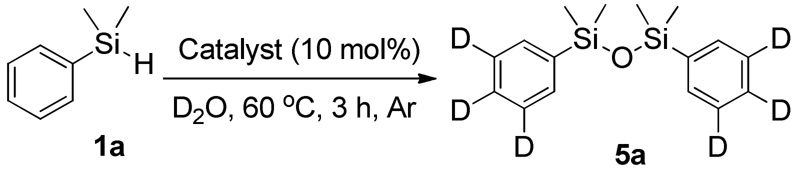
(eq. 5)



(eq. 6)

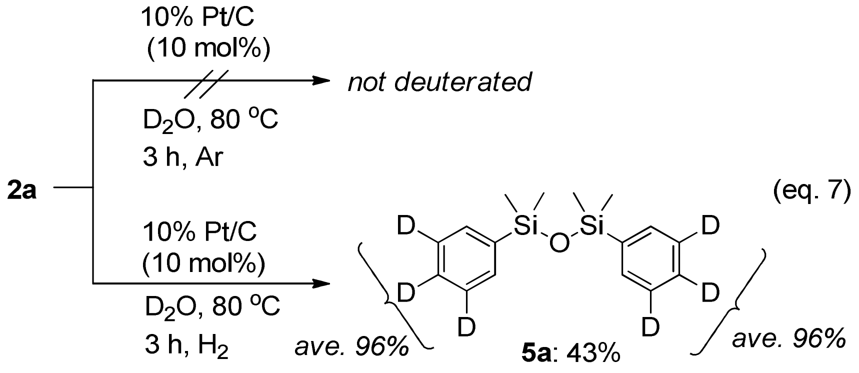
Deuterium-labeled compounds are widely utilized in various fields, such as analytical studies and material chemistry (e.g., fiber optics and heavy drugs).[18f, 21] We have previously developed the mild and platinum group metal on carbon-catalyzed multi-deuteration methods of arenes using D_2O under atmospheric hydrogen as an activating agent of the heterogeneous metal surface.[18] Therefore, we presumed that the deuteration of the arene nuclei of the aryl-substituted disiloxane could proceed in D_2O instead of H_2O by utilizing H_2, HD or D_2 gas generated during the transformation of the hydrosilane to disiloxane. Although 10% Au/C and Rh/C indicated no catalytic activities for the deuteration of the arene (Table 3, Entries 1 and 2), the use of 10% Ru/C, Pd/C and Pt/C in D_2O at 60 °C effectively catalyzed the oxidative coupling of **1a** to disiloxane together with the regioselective deuteration on the arene nuclei at the meta- and para-positions to give the hexadeuterated diphenyldisiloxane (**5a**) (Entries 3-5).[22] The 10% Pt/C was an adequate catalyst (Entry 5) and the reaction at 80 °C provided **5a** with the excellent D contents (Entries 7 vs. 5 and 6). Although the PtO_2-catalyzed regioselective deuteration using diphenyltetramethyldisiloxane (**2a**) as a substrate was reported by Matsubara et al., harsh reaction conditions in a sealed container using microwaves (150 °C) were required.[23,24] Although the direct deuteration of **2a** as the sole substrate under the present reaction conditions (10% Pt/C in D_2O at 80 °C) never proceeded (eq. 7, top), the reaction of **2a** under atmospheric hydrogen conditions smoothly gave the desired deuterated product (**5a**) with a high D efficiency (eq. 7, bottom), which clearly indicated that the hydrogen generated during the first oxidative coupling of the hydrosilane (**1**)[25] was essential to facilitate the one-pot deuteration of the diphenyldisiloxane (**2a**) to **5a**.[26]

Table 3. Regioselective deuteration using phenyldimethyl silane (**1a**) in D_2O.



Entry	Catalyst	D content of phenyl moiety (%)		Yield (%)[c]
		orhto	Average of *meta* and *para*	
1	10% Au/C	0	0	>99
2	10% Rh/C	0	0	64
3	10% Ru/C	0	54	73
4	10% Pd/C	0	80	71
5	10% Pt/C	0	92	65
6[a]	10% Pt/C	0	93	74
7[b]	10% Pt/C	0	97	54

[a] At 40 °C. [b] At 80 °C [c] 100% conversion yields were achieved in all these reactions.

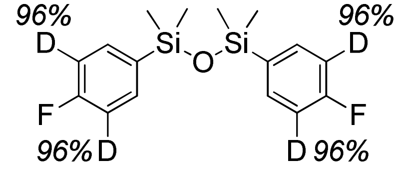
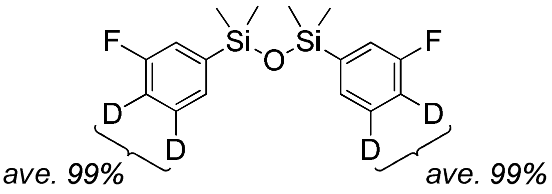
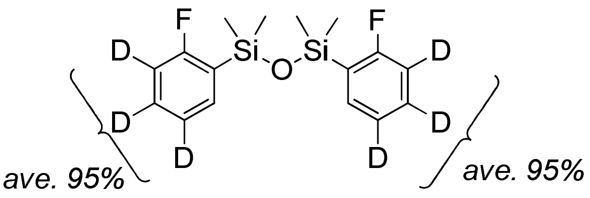


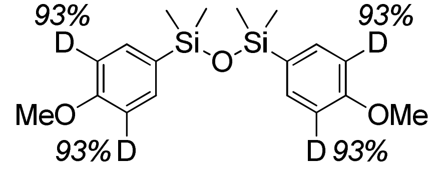
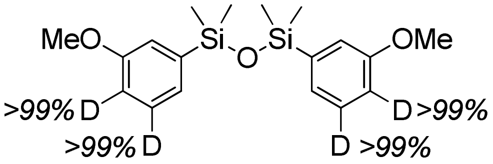
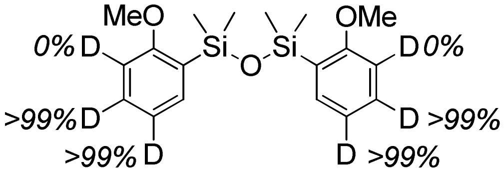
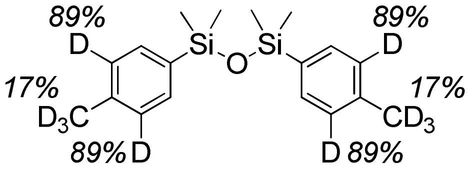
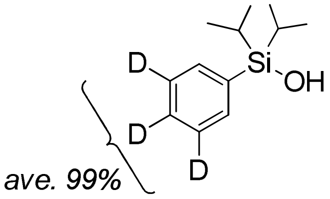
All the reactions (the oxidative coupling of hydrosilanes into disiloxanes and the following deuteration of the arene nuclei) of the various arylsilanes (**1d**, **1j**, **1l**, **1b**, **1i** and **1k**) bearing an electron-withdrawing fluoro- or electron-donating methoxy group at the *ortho*-, *meta*- or *para*- position of the aromatic ring could effectively proceed to give the corresponding deuterium-labeled disiloxanes (**5d**, **5j**,

5l, **5b**, **5i** and **5k**) with high D efficiencies and high regioselectivities at the *meta*- and *para*-positions from the Ar-Si bond due to the sterical hindrance (Table 4, Entries 1-6). The addition of *i*-PrOH as a co-solvent effectively increased the D efficiencies for the reactions in Table 4. We also revealed that the platinum group metal on carbon effectively catalyzed the dehydrogenation of secondary and primary alcohols to generate the corresponding carbonyl products and hydrogen gas,[27] and the *in situ*-generated hydrogen derived from *i*-PrOH was utilized for the hydrogenation[28] and deuteration[29] as a catalyst activator. Namely, hydrogen derived from the hydrosilane and *i*-PrOH synergistically activated the platinum metal[18] to facilitate the desirable deuteration (the comparison of reaction efficiencies with or without *i*-PrOH and the additive effect were depicted in Supporting Information). Additionally, the aromatic nuclei of the silanol (**6m**) derived from 1m were effectively deuterated with the same regioselectivity and high D efficiency, while the oxidative coupling reaction never proceeded due to the steric hindrance effect of the bulky diisopropyl substituents on the Si atom.[30]

Table 4. Scope of substrates in the regioselective deuterated disiloxane synthesis.

$$\text{Substrate }(\mathbf{1}) \xrightarrow[\text{D}_2\text{O, 80 }^{\circ}\text{C, 3 h, Ar}]{\text{10\% Pt/C (10 mol\%)}} \text{Product }(\mathbf{5}, \mathbf{6})$$

Entry	Substrate	Product
1[a]	**1d**	 **5d**: 32%
2[a]	**1j**	 **5j**: 18%
3[a]	**1l**	 **5l**: 23%

4[a]	**1b**	 **5b**: 30%
5[a]	**1i**	 **5i**: 32%
6[a]	**1k**	 **5k**: 20%
7[a]	**1c**	 **5c**: 32%
8[a]	**1m**	 **6m**: 23%

[a] *i*-PrOH (0.8 mL) was added as a co-solvent. [b] 100% conversion yields were achieved in all these reactions.

In conclusion, we have established the heterogeneous Au/C-catalyzed oxidative coupling of hydrosilanes using H_2O as an oxidant to give the corresponding disiloxanes. Furthermore, the Pt/C-catalyzed one-pot deuteration of the arene nuclei accompanied by the transformation of arylhydrosilanes to diaryldisiloxanes with a unique regioselectivity was developed utilizing the *in situ*-generated hydrogen as a catalyst activator. Since the production method of hydrogen as an energy source from organosilanes is important and the diaryltetramethyldisiloxanes are good coupling reagents for the Hiyama-type reaction, the present methods are expected to contribute to various research fields.

EXPERIMENTAL SECTION

General information: 10% Pd/C, Pt/C, Rh/C, Ru/C and Au/C were supplied by N. E. Chemcat Corporation (Tokyo, Japan). All reactions were performed under argon. H_2O and D_2O were purchased from commercial sources and used without further purification. ESI high resolution mass spectra (HRMS) were measured by a hybrid IT-TOF mass spectrometer. Substrates (**1a** and **1m-o**) were purchased from commercial suppliers. Substrates (**1b-l**) were prepared according to the literatures in reference 1-3.

Typical procedure for Tables 1 and 2: A mixture of arylhydrosilane (0.25 mmol), 10% Au/C (5 mol%) and H_2O (3 mL) in 15 mL-test tube was stirred using a personal organic synthesizer at room temperature under argon. After stirring for 3 h, the reaction mixture was passed through a membrane filter (Millipore, Millex, 0.45 μm) to remove Au/C. The filtrate was extracted with AcOEt (3 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo to give the disiloxane or silanol. (**2h** was purified by silica-gel column chromatography)

Typical procedure for Tables 3 and 4: A suspension of arylhydrosilane (0.25 mmol) and 10% Pt/C (10 mol%) in D_2O (3 mL) and *i*PrOH (0.8 mL) was stirred in 15 mL-test tube using a personal organic synthesizer at 80 °C under argon. After stirring for 3 h, the reaction mixture was passed through a membrane filter (Millipore, Millex, 0.45 μm) to remove Pt/C. The filtrate was extracted with AcOEt (3 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo to give the deutrated disiloxane or silanol.

1,3-Diphenyl-1,1,3,3-tetramethyldisiloxane (2a): When using **1a** (34.1 mg, 0.25 mmol) in Table 1, entry 5, **2a** (34.7 mg, 0.12 mmol) was obtained in 97% yield.; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.55-7.54 (4H, m), 7.38-7.34 (6H, m), 0.33 (12H, s); 1H NMR data was identical with that in the reference 31.

1,3-Bis(4'-methoxyphenyl)-1,1,3,3-tetramethyldisiloxane (2b): When using **1b** (41.6 mg, 0.25 mmol), **2b** (43,1 mg, 0.12 mmol) was obtained in >99% yield.; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (4H, d, J = 8.4 Hz), 6.89 (4H, d, J = 8.4 Hz), 3.81 (6H, s), 0.29 (12H, s); ^{1}H NMR data was identical with that in the reference 32.

1,3-Bis(4'-tolyl)-1,1,3,3-tetramethyldisiloxane (2c): When using **1c** (37.6 mg, 0.25 mmol), **2c** (39.1 mg, 0.12 mmol) was obtained in >99% yield.; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.44 (4H, d, J = 7.8 Hz), 7.17 (4H, d, J = 7.8 Hz), 2.35 (6H, s), 0.31 (12H. s) ; ^{1}H NMR data was identical with that in the reference 3d.

1,3-Bis(4'-fuluorophenyl)-1,1,3,3-tetramethyldisiloxane (2d): When using **1d** (38.6 mg, 0.25 mmol), **2d** (39.1 mg, 0.12 mmol) was obtained in 97% yield.; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.50-7.47 (4H, m), 7.06-7.02 (4H, m), 0.31 (12H, s); ^{1}H NMR data was identical with that in the reference 33.

1,3-Bis(4'-bromophenyl)-1,1,3,3-tetramethyldisiloxane (2e): When using **1e** (53.8 mg, 0.25 mmol), **2e** (51.1 mg, 0.12 mmol) was obtained in 92% yield.; Colorless oil; IR (ATR) cm^{-1}: 2956, 2925, 2854, 1574, 1479, 1408, 1376, 1255, 1112, 1065, 1008; ^{1}H NMR (400 MHz, $CDCl_3$): 7.48 (4H, d, J = 8.2 Hz), 7.36 (4H, d, J = 8.2 Hz), 0.31 (12H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 138.3, 134.6, 130.9, 124.2, 0.7; *Anal.* calcd for $C_{16}H_{20}Br_2OSi_2$: C, 43.25; H, 4.54 N, 0. Found: C, 43.21; H, 4.49; N, 0.

1,3-Bis[4'-(trifluoromethyl)phenyl]-1,1,3,3-tetramethyldisiloxane (2f): When using **1f** (51.1 mg, 0.25 mmol), **2f** (46.0 mg, 0.11 mmol) was obtained in 87% yield.; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63—7.57 (8H, m), 0.36 (1H, s); 1H NMR data was identical with that in the reference 31.

1,3-Bis(4'-tert-butyldimethylsiloxymethylphenyl)-1,1,3,3-tetramethyldisiloxane (2g): When using **1g** (70.1 mg, 0.25 mmol), **2g** (65.4 mg, 0.11 mmol) was obtained in 91% yield; Colorless oil; IR (ATR) cm^{-1}: 2956, 2929, 2886, 2857, 1604, 1471, 1462, 1396, 1372, 1255, 1211, 1085, 1019; ^{1}H NMR (400 MHz, $CDCl_3$): 7.51 (4H, d, J = 8.2 Hz), 7.31 (4H, d, J = 8.2 Hz), 4.74 (4H, s) 0.95 (18H, s), 0.31 (12H, s), 0.10 (12H, s); 13C NMR (100 MHz, $CDCl_3$): 142.5, 138.2, 133.0, 125.3, 64.9, 26.0, 18.4, 0.9, -5.2; ESI-HRMS m/z: 597.3051 ($[M+Na]^+$); Calcd for $C_{30}H_{54}O_3Si_4Na$: 597.3042.

1,3-Bis(phenylethynyl)-1,1,3,3-tetramethyldisiloxane (2h): When using **1h** (59.1 mg, 0.25 mmol), **1h** (49.9 mg, 0.10 mmol) was obtained in 82% yield; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.47-7.45 (4H, m), 7.31-7.28 (6H, m), 0.39 (12H, s); 1H NMR data was identical with that in the reference 32.

1,3-Bis(3'-methoxyphenyl)-1,1,3,3-tetramethyldisiloxane (2i): When using **1i** (41.6 mg, 0.25 mmol), **2i** (42.0 mg, 0.12 mmol) was obtained in 97% yield.; Colorless oil; IR (ATR) cm^{-1}: 2953, 2833, 1570, 1480, 1462, 1403, 1315, 1282, 1246, 1228, 1182, 1113, 1040, 992, 903, 860, 815, 774, 731, 695, 650, 559, 443; 1H NMR (500 MHz, $CDCl_3$): 7.31—7.28 (2H, m), 7.12 (2H, d, J = 7.5 Hz), 7.08 (2H, d, J = 2.5 Hz), 6. 91 (2H, dd, J = 8.0, 2.5 Hz), 3.78 (6H, s), 0. 34 (12H, s); 13C NMR (125 MHz, $CDCl_3$):159.0, 141.5, 129.1, 125.3, 118.3, 114.8, 55.1, 1.0; ESI-HRMS m/z: 369.1309 ($[M+Na]^+$); Calcd for $C_{18}H_{26}O_3Si_2Na$: 369.1313.

1,3-Bis(3'-fluorophenyl)-1,1,3,3-tetramethyldisiloxane (2j): When using **1j** (38.6 mg, 0.25 mmol), **2j** (37.9 mg, 0.12 mmol) was obtained in 94% yield.; Colorless oil; IR (ATR) cm^{-1}: 2959, 1574, 1477, 1404, 1258, 1215, 1106, 1046; ^{1}H NMR (400 MHz, $CDCl_3$): 7.35—7.25 (4H, m), 7.20—7.17 (2H, m), 7.06—7.02 (2H, m), 0.33 (12H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 162.6 (d, J = 246.0 Hz), 142.6 (d, J = 3.8 Hz) 129.6 (d, J = 6.6 Hz), 128.4 (d, J = 2.9 Hz), 119.3 (d, J = 18.1 Hz), 116.2 (d, J = 21.0 Hz), 0.7; ESI-HRMS m/z: 321.0927 ([M-H]$^-$); Calcd for $C_{16}H_{20}OSi_2F_2$: 321.0948.

1,3-Bis(2'-methoxyphenyl)-1,1,3,3-tetramethyldisiloxane (2k): When using **1k** (41.6 mg, 0.25 mmol), **2k** (42.0 mg, 0.12 mmol) was obtained in 97% yield.; Colorless oil; IR (ATR) cm^{-1}: 3062, 2955, 2903, 2833, 1588, 1571, 1460, 1428, 1292, 1268, 1233, 1177, 1161, 1130, 1084, 1044, 1023, 908, 831, 784, 756, 718, 701, 646, 577, 485, 452; ^{1}H NMR (500 MHz, $CDCl_3$): 7.54 (2H, dd, J = 7.5, 1.5 Hz), 7.45 (2H, ddd, J = 8.0, 7.5, 1.5 Hz), 6.95 (2H, t, J = 7.5 Hz), 6. 83 (2H, d, J = 8.0 Hz), 3.76 (6H, s), 0. 35 (12H, s); ^{13}C NMR (125 MHz, $CDCl_3$): 163.9, 135.3, 131.0, 127.8, 120.4, 109.4, 59.9, 1.6; ESI-HRMS m/z: 369.1309 ([M+Na]$^+$); Calcd for $C_{18}H_{26}O_3Si_2Na$: 369.1313.

1,3-Bis(2'-fluorophenyl)-1,1,3,3-tetramethyldisiloxane (2l): When using **1l** (38.6 mg, 0.25 mmol)**,** **2l** (37.1 mg, 0.12 mmol) was obtained in 92% yield.; Colorless oil; IR (ATR) cm^{-1}: 3074, 2960, 2926, 2855, 1674, 1603, 1563, 1470, 1439, 1256, 1204, 1155, 1121, 1081, 1060; ^{1}H NMR (400 MHz, $CDCl_3$): 7.50—7.46 (2H, m), 7.39—7.33 (2H, m), 7.12 (2H, t, J = 7.2 Hz), 6.97 (2H, t, J = 8.4 Hz), 0.40 (12 H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 166.9 (d, J = 242.8 Hz), 135.0 (d, J = 11.5 Hz), 131.6 (d, J = 8.2 Hz), 125.6 (d, J = 30.5 Hz), 123.8 (d, J = 2.5 Hz), 114.7 (d, J = 25.4 Hz), 1.3; ESI-HRMS m/z: 345.0896 ([M+Na]$^+$); Calcd for $C_{16}H_{20}OSi_2F_2Na$: 345.0913.

Oligomer (2o): When using **1o** (31.0 mg, 0.25 mmol), **2o** (29.8 mg) was obtained.; brown oil; ESI-HRMS m/z: (tetramer) 585.1382 ([M+Na]$^+$); Calcd for $C_{28}H_{34}O_5Si_4Na$: 585.1376, (pentamer) 721.1704 ([M+Na]$^+$); Calcd for $C_{35}H_{42}O_6Si_5Na$: 721.1720, (hexamer) 857.2062 ([M+Na]$^+$); Calcd for $C_{42}H_{50}O_7Si_6Na$: 857.2064, (heptamer) 993.2347 ([M+Na]$^+$); Calcd for $C_{49}H_{58}O_8Si_7Na$: 993.2409, (octamer) 1129.2744 ([M+Na]$^+$); Calcd for $C_{56}H_{66}O_9Si_8Na$: 1129.2753.

Diisopropylsilanol (3m): When using **1m** (48.1 mg, 0.25 mmol), **3m** (50.5 mg, 0.24 mmol) was obtained in 97% yield.; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56-7.55 (2H, m), 7.40-7.35 (3H, m), 1.75 (1H. brs), 1.26-1.20 (2H, m), 1.06 (6H, d, J = 7.5 Hz), 0.98 (6H, d, J = 7.5 Hz); ^{1}H NMR data was identical with that in the reference 34.

Triphenylsilanol (3n): When using **1n** (65.1 mg, 0.25 mmol), **3n** (68.8 mg, 0.25 mmol) was obtained in >99% yield.; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.64-7.63 (6H, m), 7.45-7.44 (3H, m), 7.41-7.38 (6H, m), 2.48 (1H, s); ^{1}H NMR data was identical with that in the reference 32.

1,3-Diphenyl-1,1,3,3-tetramethylpropanedisiloxane (^{18}O-labeled 2a): When using **1a** (15.9 mg, 0.12 mmol), 91% yield of **^{18}O-labeled 2a** was obtained based on ^{1}H NMR using 1,4-dioxane as an internal standard.; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56-7.54 (4H, m), 7.38-7.34 (6H, m), 0.33 (12H, s); ESI-HRMS m/z: 311.1127 ([M+Na]$^+$); Calcd for $C_{16}H_{22}{}^{18}OSi_2Na$: 311.1144.

Dimethylphenylsilanol (3a): When using **1a** (34.1 mg, 0.25 mmol) for 5 min. in eq. 4, **3a** (5.7 mg, 0.04 mmol) was obtained in 15% yield.; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.61-7.59 (2H, m), 7.40-7.38 (3H, m), 1.82 (1H, s, br), 0.41 (6H, s); ^{1}H NMR data was identical with that in the reference 30.

1,3-Diphenyl-1,1,3,3-tetramethyldisiloxane-*d*$_6$ (5a): When using **1a** (34.1 mg, 0.25 mmol) in Table 3, entry 7, **5a** (19.6 mg, 0.07 mmol) was obtained in 54% yield.; Colorless oil; ^{1}H NMR (500 MHz, CDCl3) δ: 7.56-7.54 (4H, m), 7.38-7.34 (0.18H, m), 0.33 (12H, s); 2H NMR (500 MHz, CDCl3) δ: 7.43 (brs); 2H NMR data was identical with that in the reference 23.

1,3-Bis(4'-fuluoro)-1,1,3,3-tetramethyldisiloxane-*d*$_4$ (5d): When using **1d** (38.6 mg, 0.25 mmol), **5d** (13.1 mg, 0.04 mmol) was obtained in 32% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (4H, d, J = 6.4 Hz), 7.05-7.00 (0.19H, m), 0.31 (12H, s); ^{2}H NMR (500 MHz, $CDCl_3$) δ: 7.08 (brs).

1,3-Bis(3'-fuluoro)-1,1,3,3-tetramethyldisiloxane-*d*$_4$ (5j): When using **1j** (38.6 mg, 0.25 mmol), **5j** (7.3 mg, 0.02 mmol) was obtained in 18% yield; Colorless oil; ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 7.29 (2H, s), 7.18 (2H, dd, J = 0.8 Hz, 9.0 Hz), 0.32 (12H, s); ^{2}H NMR (500 MHz, CH_2Cl_2) δ: 7.39 (s, br), 7.11 (s, br).

1,3-Bis(2'-fuluoro)-1,1,3,3-tetramethyldisiloxane-*d*$_6$ (5l): When using **1l** (38.6 mg, 0.25 mmol), **5l** (9.5 mg, 0.03 mmol) was obtained in 23% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (2H, d, J = 6.5 Hz), 7.36 (0.18H, m), 7.13-7.11 (0.1 H, m), 6.98-6.96 (0.094H, m), 0.40 (12H, s); ^{2}H NMR (500 MHz, $CDCl_3$) δ: 7.41 (brs), 7.18 (brs), 7.02 (brs).

1,3-Bis(4'-methoxyphenyl)-1,1,3,3-tetramethyldisiloxane-*d*$_4$ (5b): When using **1b** (41.6 mg, 0.25 mmol), **5b** (13.1 mg, 0.04 mmol) was obtained in 30% yield.; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (4H, s), 6.90 (0.44H, m), 3.81 (6H, s), 0.29 (12H, s); ^{2}H NMR (500 MHz, $CDCl_3$) δ: 6.95 (brs).

1,3-Bis(3'-methoxyphenyl)-1,1,3,3-tetramethyldisiloxane-*d*$_4$ (5i): When using **1i** (41.6 mg, 0.25 mmol), **5i** (14.0 mg, 0.04 mmol) was obtained in 32% yield.; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) : 7.12 (2H, s), 7.08 (2H, s), 3.77 (6H, s), 0.33 (12H, s); ^{2}H NMR (500 MHz, $CDCl_3$) δ: 7.35 (s, br), 6.97 (brs).

1,3-Bis(2'-methoxyphenyl)-1,1,3,3-tetramethyldisiloxane-*d*$_4$ (5k): When using **1k** (41.6 mg, 0.25 mmol), **5k** (8.8 mg, 0.3 mmol) was obtained in 20% yield.; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) : 7.53 (2H, s), 6.81 (2H, s), 3.76 (6H, s), 0. 35 (12H, s), ^{2}H NMR (500 MHz, $CHCl_3$) : 7.40 (s, br), 6.89 (brs).

1,3-Bis(4'-toryl)-1,1,3,3-tetramethyldisiloxane-*d*$_{10}$ (5c): When using **1c** (37.6 mg, 0.25 mmol), **1c** (12.8 mg, 0.04 mmol) was obtained in 32% yield.; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (4H, s), 7.17 (0.43H, d, J = 7.0 Hz), 2.35 (5.01H, s), 0.30 (12H. s); ^{2}H NMR (500 MHz, CDCl3) δ: 7.22 (brs), 2.32 (m).

Diisopropylphenylsilanol-*d*$_3$ (6m): When using **1m** (48.1 mg, 0.25 mmol), **6m** (12.2 mg, 0.06 mmol) was obtained in 23% yield.; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (2H, s), 7.39-7.36 (0.12H, m), 1.26—1.19 (2H, m), 1.06 (6H, d, J = 7.8 Hz), 0.98 (6H, d, J = 7.8 Hz); ^{2}H NMR (500 MHz, $CDCl_3$) δ: 7.42 (brs).

ASSOCIATED CONTENT

Supporting Information

Synthetic method of substrates and spectroscopic data of substrates and products are described.

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REFERENCES

(1) For recent selected papers; (a) Reihmann, M.; Crudeli, A.; Blanc, C.; Lorman, V.; Panarin, Y. P.; Vij, J. K.; Olsson, N.;Galli, G. *Ferroelectrics* **2004**, *309*, 111-118; (b) (Review) Imrie, C. T.; Henderson, P. A. *Chem. Soc. Rev.* **2007**, *36*, 2096-2124; (c) Shoji, Y.; Ishige, R.; Higashihara, T.; Watanabe, J.; Ueda, M. *Macromolecules* **2010**, *43*, 805-810; (d) Yang, J.; Cheng, Y.; Xiao, F. *Eur. Polym. J.* **2012**, *48*,

751-760; (e) Zelcer, A.; Cecchi, F.; Albores, P.; Guillon, D.; Heinrich, B.; Donnio, B.; Cukiernik, F. D. *Liq. Cryst*. **2013**, *40*, 1121-1134.

(2) (a) (Review) LeVier, R. R.; Chandler, M. L.; S. R. Wendel, S. R. The Pharmacology of Silanes and Siloxanes. In *The Biochemistry of Silicon and Related Problems*; (Eds.; Bendz, G.; Lindqvist, I.) Plenum: Press New York and London, 1978; pp 473-514; (b) Tse, F. L. S.; Chang, T.; Finkelstein, B.; Ballard, F.; Jaffe, J. M. *J. Pharm. Sci.* **1984**, *73*, 1599-1602; (c) Bruns, R. F.; Watson, I. A. *J. Med. Chem.* **2012**, *55*, 9763-9772.

(3) (a) Napier, S.; Marcuccio, S. M.; Tye, H.; Whittaker, M. *Tetrahedron Lett.* **2008**, *49*, 3939-3942; (b) Denmark, S. E.; Butler, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 3690-3704; (c) Sore, H. F.; Boehner, C. M.; MacDonald, S. J. F.; Norton, D.; Fox, D. J.; Spring, D. R. *Org. Biomol. Chem.* **2009**, *7*, 1068-1071; (d) Boehner, C. M.; Frye, E. C.; O'Connell, K. M. G.; Galloway, W. R. J. D.; Sore, H. F.; Dominguez, P. G.; Norton, D.; Hulcoop, D. G.; Owen, M.; Turner, G.; Crawford, C.; Horsley, H.; Spring, D. R. *Chem. Eur. J.* **2011**, *17*, 13230-13239.

(4) Sridhar, M.; Ramanaiah, B. C.; Narsaiah, C.; Swamy, M. K.; Mahesh, B.; Reddy, M. K. K. *Tetrahedron Lett.* **2009**, *50*, 7166-7168.

(5) Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2006**, *128*, 12362-12363.

(6) (a) (Review) Addis, D.; Das, S.; Junge, K.; Beller, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 6004-6011; (b) Arias-Ugarte, R.; Sharma, H. K.; Morris, A. L. C.; Pannell, K. H. *J. Am. Chem. Soc.* **2012**, *134*, 848-851.

(7) (a) Ison, E. A.; R. A. Corbin, R. A.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 11938-11939; (b) Krüger, A.; Albrecht, M. *Chem. Eur. J.* **2012**, *18*, 652-658.

(8) (a) Mitsudome, T.; Noujima, A.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Chem. Commun.* **2009**, 5302-5304; (b) Asao, N.; Ishikawa, Y.; Hatakeyama, N.; Menggenbateer.; Yamamoto, Y.; Chen, M.; Zhang, W.; Inoue, A. *Angew. Chem. Int. Ed.* **2010**, *49*, 10093-10095; (c) John, J.; Gravel, E.; Hagège, A.; Li, H.; Gacoin, T.; Doris, E. *Angew. Chem. Int. Ed.* **2011**, *50*, 7533-7536.

(9) Chauhan, B. P. S.; Sarkar, A.; Chauhan, M.; Roka, A. *Appl. Organometal. Chem.* **2009**, *23*, 385-390.

(10) (a) Shimizu, K.; Kubo, T.; Satsuma, A. *Chem. Eur. J.* **2012**, *18*, 2226-2229; (b) Jeon, M.; Han, J.; Park, J. *ChemCatChem* **2012**, *4*, 521-524.

(11) Shimizu, K.; Shimura, K.; Imaiida, N.; Satsuma, A. *J. Mol. Catal. A: Chem.* **2012**, *365*, 50-54.

(12) (a) Mitsudome, T.; Arita, S.; Mori, H.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Angew. Chem. Int. Ed.* **2008**, *47*, 7938-7940; (b) Kikukawa, Y.; Kuroda, Y.; Yamaguchi, K.; Mizuno, N, *Angew. Chem. Int. Ed.* **2012**, *51*, 2434-2437.

(13) The transformation of hydrosilanes to silanols in water in the absence of organic solvents was accomplished using the hydroxyapatite-supported gold nanoparticles (See reference 8a). The use of a homogeneous Ru or Ir catalyst in an organic solvent including H_2O also gave silanols as the main products, see; (a) Lee, M.; Ko, S.; Chang, S. *J. Am. Chem. Soc.* **2000**, *122*, 12011-12012; (b) Lee, Y.; Seomoon, D.; Kim, S.; Han, H.; Chang, S.; Lee, P. H. *J. Org. Chem.* **2004**, *69*, 1741-1743; (c) Tan, S. T.; Kee, J. W.; Fan, W. Y. *Organometallics* **2011**, *30*, 4008-4013.

(14) Liu, T.; Yang, F.; Li, Y.; Ren, L.; Zhang, L.; Xu, K.; Wang, X.; Xu, C.; Gao, J. *J. Mater. Chem. A* **2014**, *2*, 245-250.

(15) Although Au/C is an optimum catalyst in disiloxane synthesis, various types of Au-supported catalysts are not easily available. Therefore, the effect of support was examined using easily available platinum metal catalysts. The reason for the high catalyst activity of Au/C is unclear.

(16) Ikawa, T.; Hattori, K.; Sajiki, H.; Hirota, K. *Tetrahedron* **2004**, *60*, 6901-6911.

(17) The result of the metal leaching is depicted in the Supporting Information. Compared with XRD, XPS and STEM data between the fresh and used Au/C, the particle size (ca. 33-35 nm), shape and oxidation states (zero valency) indicated no major differences as shown in Supporting Information. The desired disiloxane (**2a**) and the corresponding silanol (**3a**) as an intermediate could be obtained by the use of fresh Au/C in 95% and 5% yields, respectively, for a shortened reaction time (1h). In addition, the reused Au/C after the first run also indicated the similar catalyst activity to give 92% of **2a** and 8% of **3a**.

(18) The hydrogen can activate the transition metal as a weak and bulk-like and/or gaseous reductant for the partially-oxidized metal surface, and we developed various deuteration methods using hydrogen-activated metals, see; (a) Sajiki, H.; Ito, N.; Esaki, H.; Maesawa, T.; Maegawa, T.; Hirota, K. *Tetrahedron Lett.* **2005**, *46*, 6995-6998; (b) Ito, N.; Watahiki, T.; Maesawa, T.; Maegawa, T.; Sajiki, H. *Adv. Synth. Catal.* **2006**, *348*, 1025-1028; (c) Esaki, H.; Aoki, F.; Umemura, M.; Kato, M.; Maegawa, T.; Monguchi, Y.; Sajiki, H. *Chem. Eur. J.* **2007**, *13*, 4052-4063; (d) Ito, N.; Esaki, H.; Maesawa, T.; Imamiya, E.; Maegawa, T.; Sajiki, H. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 278-286; (e) Ito, N.; Watahiki, T.; Maesawa, T.; Maegawa, T.; Sajiki, H. *Synthesis* **2008**, *9*, 1467-1478; (f) (Review) Sawama, Y.; Monguchi, Y.; Sajiki, H. *Synlett* **2012**, *23*, 959-972.

(19)(a) Okazaki, M.; Ohshitanai, S.; Tobita, H.; Ogino, H. *Chem. Lett.* **2001**, *30*, 952-953; (b) Itazaki, M.; Ueda, K.; Nakazawa, H. *Angew. Chem. Int. Ed.* **2009**, *48*, 3313-3316.

(20) (a) Gryparis, C.; Stratakis, M. *Chem. Commun.* **2012**, *48*, 10751-10753; (b) Gualco, P.; Ladeira, S.; Miqueu, K.; Amgoune. A.; Bourissou, D. *Organometallics* **2012**, *31*, 6001-6004.

(21) (Review) (a) Atzrodt, J.; Derdau, V.; Fey, T.; Zimmermann, J. *Angew. Chem. Int. Ed.* **2007**, *46*, 7744–7765; (b) Herbert, J. M.; *J. Labelled Compd. Radiopharm.* **2010**, *53*, 658-661.

(22) Our recent studies reveals that Pd/C and Pt/C are efficient to promote the direct H-D exchange reactions of aromatic rings and the Au/C-catalyzed deuteration never proceeds. The reason of the metal effect is still unclear. Au/C could catalyzed only oxidation of hydrosilanes into disiloxanes in H_2O.

(23) Yamamoto, M.; Oshima, K.; Matsubara, S. *Org. Lett.* **2004**, *6*, 5015-5017.

(24) Although PtO_2 is an effective catalyst for the direct deuteration of disiloxane according to the reference 22, hydrogen generated during Pt/C-catalyzed coupling of hydrosilane into disiloxane is necessary in the present H-D exchange reaction under milder reaction conditions. PtO_2 could not effectively catalyze the coupling reaction of hydrosilane to generate the hydrogen as shown in Table 1.

(25) The generation of hydrogen during the first oxidative coupling of the hydrosilane (**1**) was detected by an indicator tube for hydrogen (Kitagawa Komyo Rikagaku Kogyo, Tube No. 137U).

(26) When the H-D exchange reaction using dimethylphenylhydrosilane (**1a**) at 80 °C was terminated for 30 min, the mixture of the deuterated silanol and disiloxane (**5a**) was obtained in low deuterium contents, which indicated that the regioselective deuteration could proceed on both the silanol and disiloxane.

(27) (a) Sawama, Y.; Morita, K.; Yamada, T.; Nagata, S.; Yabe, Y.; Monguchi, Y.; Sajiki, H. *Green Chem.* **2014**, *16*, 3439–3443; (b) Sawama, Y.; Morita, K.; Asai, S.; Kozawa, M.; Tadokoro, S.; Nakajima, J.; Monguchi, Y.; Sajiki, H. *Adv. Synth. Catal.* **2015**, *357*, 1205-1210.

(28) Sawama, Y.; Yabe, Y.; Shigetsura, M.; Yamada, T.; Nagata S.; Fujiwara, Y.; Maegawa, T.; Monguchi, Y.; Sajiki, H. *Adv. Synth. Catal.* **2012**, *354*, 777-782.

(29) (a) Sawama, Y.; Yamada, T.; Yabe, Y.; Morita, K.; Shibata, K.; Shigetsura, M.; Monguchi, Y.; Sajiki, H. *Adv. Synth. Catal.* **2013**, *355*, 1529-1534; (b) Yamada, T.; Sawama, Y.; Shibata, K.; Morita, K.; Monguchi, Y.; Sajiki, H. *RSC Adv.* **2015**, *5*, 13727-13732.

(30) The reason why the isolated yields decreased in the reaction shown in Table 4 is unclear. Only deuterated products were observed.

(31) Jorapur, Y. R.; Shimada, T. *Synlett* **2012**, *29*, 1633-1638.

(32) Tran, N. T.; Min, T.; Franz, A. K. *Chem. Eur. J.* **2011**, *17*, 9897-9900.

(33) Irie, M.; Kikukawa, K.; Shimizu, N.; Mishima, M. *J. Chem. Soc., Perkin Trans. 2*, **2001**, 923-928.

(34) Huang, C.; Ghavtadze, N.; Godoi, B.; Gevorgyan, V. *Chem. Eur. J.* **2012**, *18*, 9789-9792.

(35) Hamada, T.; Manabe, K.; Kobayashi, S. *Chem. Eur. J.* **2006**, *12*, 1205-1215.