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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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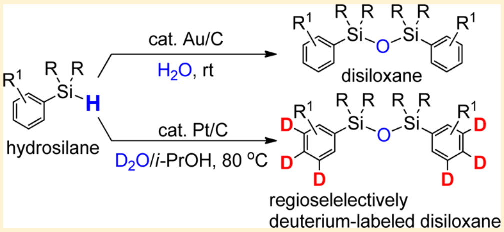
S Supporting Information

ABSTRACT: Disiloxanes possessing a silicon–oxygen linkage are important as frameworks for 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, homogeneous Rh and Re catalytic methods using H_2O as a green solvent and oxidant have also been 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 that 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 the 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 regioselective 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 (entry 2 vs entries 8–11).

Various aryldimethylsilanes could be used for the Au/C-catalyzed direct synthesis of disiloxanes in H_2O (Table 2). 4-MeO-, 4-Me-, 4-F-, 4-Br-, and 4-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, the 3- or 2-MeO-phenyl and 2-F-phenyl-

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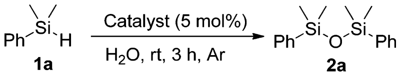
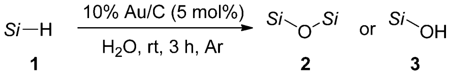
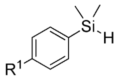
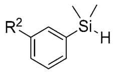
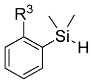
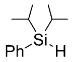
Table 1. Catalyst Efficiency of Disiloxane Synthesis using H_2O



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

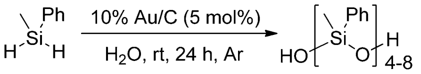
Table 2. Scope of Substrates in the Disiloxane Synthesis



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.

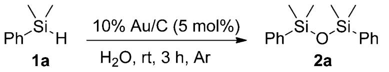
substituted silanes **1i–l** also underwent the Au/C-catalyzed oxidation in H_2O to give the disiloxanes **2i–l** (entries 8–11). Meanwhile, sterically hindered silanes, such as diisopropylphenylsilane (**1m**) and triphenylsilane (**1n**), were transformed into the corresponding silanols **3m,n** even 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 a result of the reuse test using **1a**, Au/C was found to be reusable at least five times without any metal leaching (eq 2).[17]



(eq. 1)

1o **2o**: ca. 96%

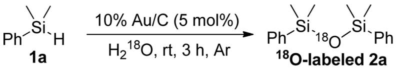
Reuse test



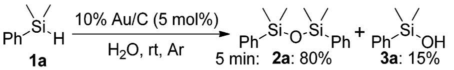
(eq. 2)

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 ^{18}O-labeled **2a**, which clearly indicated that H_2O played the role of 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 complete 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). On the basis of these experimental results, two kinds of reaction pathways can be considered. First, 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 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**.

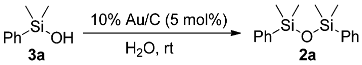


(eq. 3)



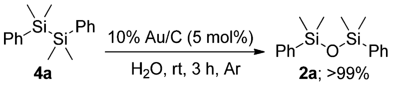
(eq. 4)

5 min: **2a**: 80% **3a**: 15%
15 min: **2a**: 86% **3a**: 11%



(eq. 5)

without H_2 (under Ar): 55% (SM: 40%) [6 h]
with H_2: 79% (SM: 21%) [3 h]
with H_2: quant. [6 h]



(eq. 6)

Deuterium-labeled compounds are widely utilized in various fields, such as analytical studies and materials chemistry (e.g., fiber optics and heavy drugs).[18f,21] We have previously developed the mild, platinum-group-metal on carbon catalyzed multideuteration 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

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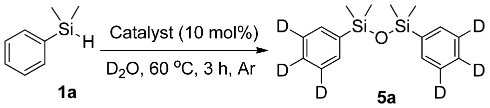
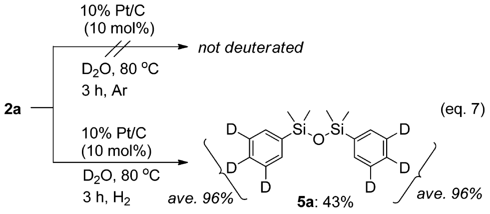
Table 3. Regioselective Deuteration Using Phenyldimethylsilane (1a) in D_2O



		D content of phenyl moiety (%)		
entry	catalyst	ortho	av of meta and para	yield (%)[c]
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 of these reactions.

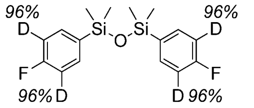
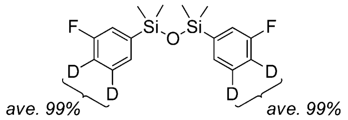
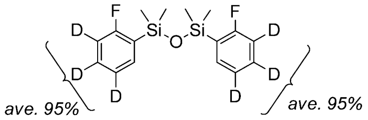
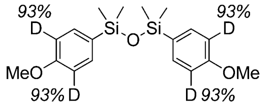
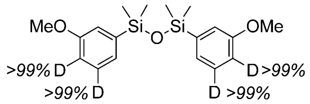
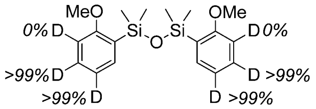
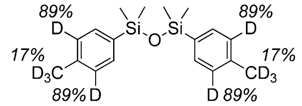
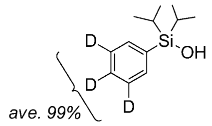
of **1a** to disiloxane together with the regioselective deuteration on the arene nuclei at the meta and para positions to give the hexadeuterated diphenyldisiloxane **5a** (entries 3–5).[22] The 10% Pt/C was an adequate catalyst (entry 5), and the reaction at 80 °C provided **5a** with excellent D contents (entry 7 vs entries 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]



All of the reactions (the oxidative coupling of hydrosilanes into disiloxanes and the following deuteration of the arene nuclei) of the various arylsilanes **1b,d,i–l** 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 **5b,d,i–l** with high D efficiencies and high regioselectivities at the meta and para positions from the Ar–Si bond due to the steric hindrance (Table 4, entries 1–6). The addition of *i*-PrOH as a cosolvent 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 (a comparison of reaction efficiencies with or without *i*-PrOH and the additive effect are depicted in the 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

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

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 cosolvent. 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**,**m**−**o** were purchased from commercial suppliers. Substrates **1b**−**l** were prepared according to refs 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 a 15 mL test tube was stirred using a personal organic synthesizer at room temperature under argon. After it was stirred 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 a 15 mL test tube using a personal organic synthesizer at 80 °C under argon. After it was stirred 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); ^{1}H NMR data were identical with those in ref 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 were identical with those in ref 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 were identical with those in ref 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 were identical with those in ref 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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 were identical with those in ref 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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 were identical with those in ref 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; ^{1}H NMR (500 MHz, $CDCl_3$) δ 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); ^{13}C NMR (125 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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. br s), 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 were identical with those in ref 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 were identical with those in ref 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 on the basis of ^{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 were identical with those in ref 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, $CDCl_3$) 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 (br s); ^{2}H NMR data were identical with those in ref 23.

*1,3-Bis(4′-fluoro)-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 (br s).

*1,3-Bis(3′-fluoro)-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′-fluoro)-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 (br s), 7.18 (br s), 7.02 (br s).

*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 (br s).

*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, $CDCl_3$) δ 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 (br s).

*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, $CDCl_3$) δ 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 (br s).

*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, $CDCl_3$) δ 7.22 (br s), 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 (br s).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00556.

Synthetic method for the substrates and spectroscopic data of substrates and products (PDF)

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Notes

The authors declare no competing financial interest.

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