

Supporting Informations for

Pd/C-Catalyzed Cross-Coupling Reaction of Benzyloxysilanes with Halosilanes for Selective Synthesis
of Unsymmetrical Siloxanes

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Experimental

Caution! Dried Pd/Cs are potentially flammable in air. Keep the reaction mixture under an inert atmosphere and moisten Pd/Cs with water for safety after the reaction. Ignoring safety precautions can lead to fire!

Instrumentation and chemicals

^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra of benzyloxysilanes were recorded on a JEOL ECX-400P spectrometer using CDCl_3 as a solvent. ^{29}Si NMR (79.5 MHz) spectra of benzyloxysilanes were recorded on a JEOL LA500 spectrometer using CDCl_3 as a solvent. ^1H (600 MHz), ^{13}C NMR (151 MHz) and ^{29}Si NMR (119 MHz) spectra of siloxanes were recorded on a Bruker AVANCEIII spectrometer equipped with a cryoprobe using CDCl_3 as a solvent. Chemical shifts (δ) are reported in parts per million relative to external standard (tetramethylsilane, 0.00 ppm) for ^1H , ^{13}C and ^{29}Si . Time-of-flight mass spectra of the products were analyzed on a Bruker micrOTOF II equipped with an ESI probe.

Pd/Cs (ASCA-2, NX and OH types) were obtained from N. E. CHEMCAT Co. Ltd. $\text{Ph}_2\text{tBuSiCl}$, anhydrous CDCl_3 and 1,4-bis(trimethylsilyl)benzene were obtained from Aldrich Chemical Co. Et_3N , super dehydrated EtOAc , Na_2SO_4 , Me_2SiCl_2 and CH_2Cl_2 were obtained from Wako Pure Chemicals Ind., Ltd. Ph_3SiCl , Ph_2SiCl_2 , PhSiCl_3 , MeSiCl_3 , SiCl_4 , Me_3SiCl , Me_3SiBr , Me_3SiI , benzyl alcohol, hexamethylbenzene and 4-(dimethylamino)pyridine (DMAP) were obtained from Tokyo Chemical Industry Co., Ltd. Ph_2MeSiCl and PhMe_2SiCl were obtained from Gelest, Inc. H_2 (G1 grade, 99.99999%) was obtained from Taiyo Nippon Sanso Corporation. Benzyloxysilanes except for $\text{Me}_2\text{Si}(\text{OBn})_2$, $\text{MeSi}(\text{OBn})_3$ and $\text{Si}(\text{OBn})_4$ were prepared as reported previously.^{S1}

All Pd/Cs were dried at 120 °C for 48 h under vacuum. Super dehydrated EtOAc and anhydrous CDCl_3 used in the reaction were degassed by three freeze-pump-thaw cycles.

Product characterization and determination of the yields except for $\text{Me}_2\text{Si}(\text{OSiMe}_3)_2$ and $\text{MeSi}(\text{OSiMe}_3)_3$

Characterization of products is based on the comparison of their NMR data with reported data or those of commercial products. Yields of the products except for $\text{Me}_2\text{Si}(\text{OSiMe}_3)_2$ and $\text{MeSi}(\text{OSiMe}_3)_3$ were determined by integral values of ^1H NMR analysis by using hexamethylbenzene as an internal standard.

Determination of the yields for $\text{Me}_2\text{Si}(\text{OSiMe}_3)_2$ and $\text{MeSi}(\text{OSiMe}_3)_3$

Because of volatility of $\text{Me}_2\text{Si}(\text{OSiMe}_3)_2$ and $\text{MeSi}(\text{OSiMe}_3)_3$ and overlapping of their Me proton signals with those of by-products in ^1H NMR spectra, yields of $\text{Me}_2\text{Si}(\text{OSiMe}_3)_2$ and $\text{MeSi}(\text{OSiMe}_3)_3$

were determined by integral values of ^{29}Si NMR signals using inverse-gated decoupling pulse sequence with 1,4-bis(trimethylsilyl)benzene as an internal standard. To ensure quantitative analysis by ^{29}Si NMR, samples were dissolved in CDCl_3 with a trace amount of $\text{Cr}(\text{acac})_3$ as a relaxation agent. At the beginning of the study, we confirmed that the pulse delay time 10 sec is sufficient to quantify the product yields by measuring the ^{29}Si NMR spectra with various pulse delay time 2, 10, 20, 40 and 80 sec for the commercial product of $\text{Me}_2\text{Si}(\text{OSiMe}_3)_2$ (Figure S1). From this result, 10 sec was adopted as pulse delay time for quantitative analysis.

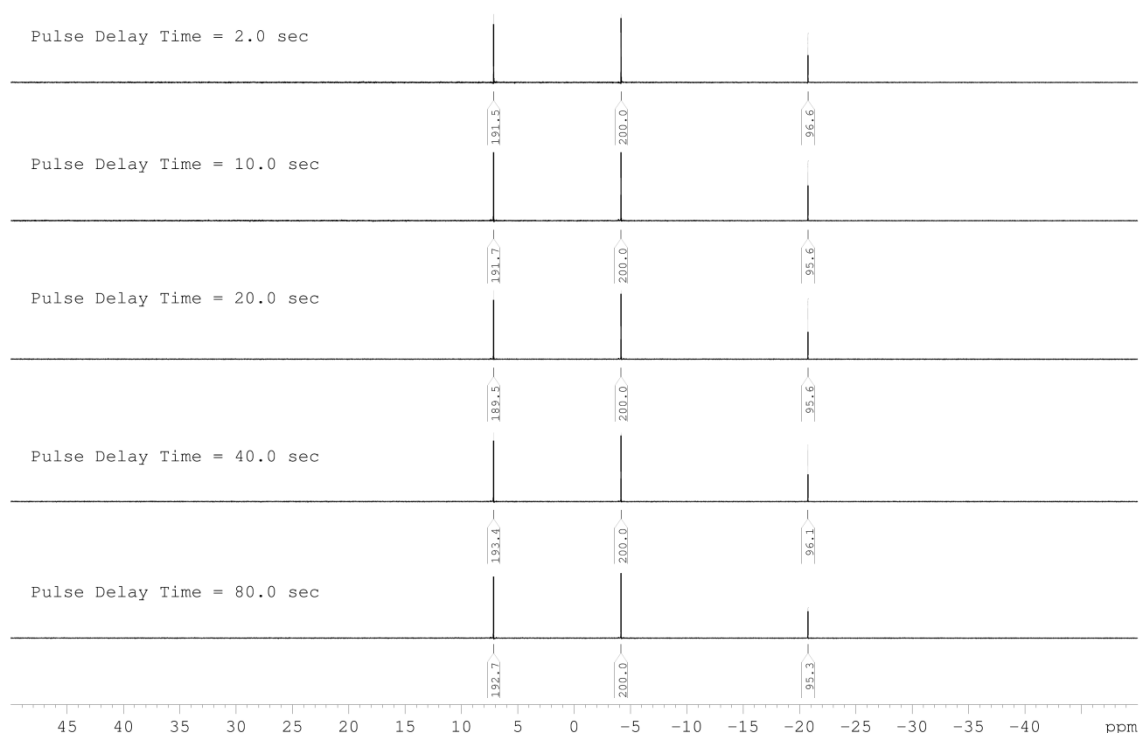


Figure S1. ^{29}Si NMR spectra of a mixture of $\text{Me}_2\text{Si}(\text{OSiMe}_3)_2$ and 1,4-bis(trimethylsilyl)benzene with various relaxation delay times (small amount of $\text{Cr}(\text{acac})_3$ was added as a relaxation agent).

Typical procedure for the synthesis of benzyloxsilanes.^{S1}

As an example, synthesis of $\text{Me}_2\text{Si}(\text{OBn})_2$ ^{S2} are shown below.

To a solution of benzyl alcohol (66.5 g, 615 mmol), Et_3N (62.2 g, 615 mmol) and DMAP (183 mg, 1.50 mmol) in CH_2Cl_2 (500 mL) was added Me_2SiCl_2 (38.7 g, 300 mmol) dropwise under N_2 atmosphere. After the mixture was stirred at room temperature for 24 h, it was diluted with hexane (700 mL), washed with water to remove triethylamine hydrochloride, DMAP, residual benzyl alcohol and Et_3N and dried over Na_2SO_4 . The solvent was removed under reduced pressure, and the residue was purified by Kugelrohr distillation (6 Pa, oven temp. 120 °C) to give $\text{Me}_2\text{Si}(\text{OBn})_2$ 65.6 g (80% yield) as a colorless oil.

^1H NMR (CDCl_3 , δ) 0.22 (s, 6H, Me), 4.77 (s, 4H, $-\text{OCH}_2$), 7.2–7.4 (m, 10H, Ph); ^{13}C NMR (CDCl_3 , δ) – 3.0, 64.5, 126.6, 127.2, 128.3, 140.5; ^{29}Si NMR (CDCl_3 , δ) –1.2; HRMS m/z calcd for $\text{C}_{16}\text{H}_{20}\text{O}_2\text{SiNa}$ 295.1125 [$M + \text{Na}$] $^+$, found 295.1127.

MeSi(OBn) $_3$ ^{S3}

The typical procedure was followed by using MeSiCl $_3$ (29.9 g, 200 mmol), benzyl alcohol (66.0 g, 610 mmol), Et $_3$ N (61.7 g, 610 mmol) and DMAP (244 mg, 2.00 mmol). The crude mixture was purified by Kugelrohr distillation (6 Pa, oven temp. 173 °C) to afford MeSi(OBn) $_3$ (66.3 g, 91% yield) as a colorless oil.

^1H NMR (CDCl_3 , δ) 0.22 (s, 3H, Me), 4.84 (s, 6H, $-\text{OCH}_2$), 7.3–7.4 (m, 15H, Ph); ^{13}C NMR (CDCl_3 , δ) – 6.8, 64.7, 126.7, 127.3, 128.3, 140.2; ^{29}Si NMR (CDCl_3 , δ) –41.3; HRMS m/z calcd for $\text{C}_{22}\text{H}_{24}\text{O}_3\text{SiNa}$ 387.1387 [$M + \text{Na}$] $^+$, found 387.1381.

Si(OBn) $_4$ ^{S4}

The typical procedure was followed by using SiCl $_4$ (3.50 g, 20.6 mmol), benzyl alcohol (9.27 g, 86.5 mmol), Et $_3$ N (8.76 g, 86.5 mmol) and DMAP (403 mg, 3.30 mmol). The crude mixture was purified by Kugelrohr distillation (10 Pa, oven temp. 200 °C) to afford Si(OBn) $_4$ (4.21 g, 45% yield) as a colorless solid.

^1H NMR (CDCl_3 , δ) 4.79 (s, 8H, $-\text{OCH}_2$), 7.1–7.4 (m, 20H, Ph); ^{13}C NMR (CDCl_3 , δ) 65.5 ($-\text{CH}_2\text{Ph}$), 126.7, 127.3, 128.2, 139.7; ^{29}Si NMR (CDCl_3 , δ) –80.7; HRMS m/z calcd for $\text{C}_{28}\text{H}_{28}\text{O}_4\text{SiNa}$ 479.1649 [$M + \text{Na}$] $^+$, found 479.1633.

General procedure for cross-coupling reaction of benzyloxysilanes with Me $_3$ SiCl.

To a stirred mixture of a benzyloxysilane (200 mg), Pd/C (10 mol% of Pd for the total amounts of benzyl group) in EtOAc (6.0 mL) was added 2 equivalents of Me $_3$ SiCl under Ar atmosphere at room temperature. The resulting mixture was stirred for an appropriate time and then filtered through a membrane filter (GE Healthcare Puradisc 13, 0.45 μm). After the removal of the solvent, CDCl_3 , hexamethylbenzene (internal standard) and a trace amount of Cr(acac) $_3$ (relaxation agent) were added to the filtrate. The conversion and the yield were determined by ^1H NMR analysis of the crude mixture. For Me $_2$ Si(OSiMe $_3$) $_2$ and MeSi(OSiMe $_3$) $_3$, the yields were determined by ^{29}Si NMR analysis as mentioned above.

Ph $_3$ SiOSiMe $_3$ ^{S5}

The general procedure was followed by using Ph $_3$ SiOBn (201 mg, 0.548 mmol), Pd/C (58.0 mg, 0.05 mmol) and Me $_3$ SiCl (119 mg, 1.09 mmol). After stirring for 9 h, the mixture was analyzed by ^1H NMR showing the formation of Ph $_3$ SiOSiMe $_3$ in 96% yield.

^1H NMR (CDCl_3 , δ) 0.11 (s, 9H, Me), 7.36–7.60 (m, 15H, Ph); ^{13}C NMR (CDCl_3 , δ) 2.04 (Me), 127.7, 129.7, 135.0, 136.2; ^{29}Si NMR (CDCl_3 , δ) –21.6, 10.8; HRMS m/z calcd for 371.1258 [$M + \text{Na}$] $^+$, found 371.1265.

$\text{Ph}_2^t\text{BuSiOSiMe}_3$ ^{S6}

The general procedure was followed by using $\text{Ph}_2^t\text{BuSiOBn}$ (0.201 g, 0.580 mmol), Pd/C (62.0 mg, 0.058 mmol) and Me_3SiCl (129 mg, 1.19 mmol). After stirring for 72 h, the mixture was analyzed by ^1H NMR showing the formation of $\text{Ph}_2^t\text{BuSiOSiMe}_3$ in 65% yield.

^1H NMR (CDCl_3 , δ) 0.18 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 1.07 (s, 9H, $\text{C}(\text{CH}_3)_3$) 7.36–7.80 (m, 10H, Ph); ^{13}C NMR (CDCl_3 , δ) 2.3 ($\text{Si}(\text{CH}_3)_3$), 19.4, 26.9, 127.6, 129.4, 135.1, 136.2; ^{29}Si NMR (CDCl_3 , δ) –12.6, 8.9; HRMS m/z calcd for 329.1751 [$M + \text{Na}$] $^+$, found 329.1743.

$\text{Ph}_2\text{MeSiOSiMe}_3$ ^{S5}

The general procedure was followed by using $\text{Ph}_2\text{MeSiOBn}$ (0.201 g, 0.66 mmol), Pd/C (70.0 mg, 0.066 mmol) and Me_3SiCl (146 mg, 1.35 mmol). After stirring for 9 h, the mixture was analyzed by ^1H NMR showing the formation of $\text{Ph}_2\text{MeSiOSiMe}_3$ in 74% yield.

^1H NMR (CDCl_3 , δ) 0.21 (s, 9H, SiMe_3), 0.71 (s, 3H, SiPh_2Me) 7.40–7.66 (m, 10H, Ph); ^{13}C NMR (CDCl_3 , δ) –0.3 (SiMe_3), 2.2 (SiPh_2Me), 127.8, 129.6, 134.0, 138.3; ^{29}Si NMR (CDCl_3 , δ) –12.2 (SiPh_2Me), 10.0 (SiMe_3); HRMS m/z calcd for 309.1101 [$M + \text{Na}$] $^+$, found 309.1113.

$\text{PhMe}_2\text{SiOSiMe}_3$ ^{S5}

The general procedure was followed by using $\text{PhMe}_2\text{SiOBn}$ (0.200 g, 0.825 mmol), Pd/C (0.089 g, 0.084 mmol) and Me_3SiCl (181 mg, 1.66 mmol). After stirring for 9 h, the mixture was analyzed by ^1H NMR showing the formation of $\text{PhMe}_2\text{SiOSiMe}_3$ in 54% yield.

^1H NMR (CDCl_3 , δ) 0.13 (s, 9H, SiMe_3), 0.38 (s, 6H, SiPhMe_2), 7.33–7.58 (m, 5H, Ph); ^{13}C NMR (CDCl_3 , δ) 1.5 (SiMe_3), 2.5 (SiPhMe_2), 128.7, 129.6, 133.9, 139.0; ^{29}Si NMR (CDCl_3 , δ) –1.9, 9.0; HRMS m/z calcd for 247.0945 [$M + \text{Na}$] $^+$, found 247.0946.

$\text{Ph}_2\text{Si}(\text{OSiMe}_3)_2$ ^{S7}

The general procedure was followed by using $\text{Ph}_2\text{Si}(\text{OBn})_2$ (0.200 g, 0.504 mmol), Pd/C (107 mg, 0.101 mmol) and Me_3SiCl (219 mg, 2.02 mmol). After stirring for 5 h, the mixture was analyzed by ^1H NMR showing the formation of $\text{Ph}_2\text{Si}(\text{OSiMe}_3)_2$ in 92% yield.

^1H NMR (CDCl_3 , δ) 0.22 (s, 18H, Me), 7.4–7.7 (m, 10H, Ph); ^{13}C NMR (CDCl_3 , δ) 2.1 (Me), 127.7, 129.8, 134.3, 136.8; ^{29}Si NMR (CDCl_3 , δ) –47.3 ($\text{Ph}_2\text{Si}(\text{OSiMe}_3)_2$), 9.8 (OSiMe_3); HRMS m/z calcd for 361.1470 [$M + \text{Na}$] $^+$, found 361.1477.

Me₂Si(OSiMe₃)₂^{S8}

The general procedure was followed by using Me₂Si(OBn)₂ (0.203 g, 0.745 mmol), Pd/C (0.157 g, 0.148 mmol) and Me₃SiCl (318 mg, 2.93 mmol). After stirring for 9 h, the mixture was analyzed by ²⁹Si NMR showing the formation of Me₂Si(OSiMe₃)₂ in 54% yield.

¹H NMR (CDCl₃, δ) 0.09 (s, 6H, SiMe₂), 0.16 (s, 18H, OSiMe₃); ¹³C NMR (CDCl₃, δ) 0.2 (SiMe₂), 0.8 (OSiMe₃); ²⁹Si NMR (CDCl₃, δ) -21.5 (SiMe₂), 6.5 (OSiMe₃).

PhSi(OSiMe₃)₃^{S9}

The general procedure was followed by using PhSi(OBn)₃ (0.200 g, 0.469 mmol), Pd/C (0.141 g, 0.133 mmol) and Me₃SiCl (306 mg, 2.81 mmol). After stirring for 9 h, the mixture was analyzed by ¹H NMR showing the formation of PhSi(OSiMe₃)₃ in 89% yield.

¹H NMR (CDCl₃, δ) 0.23 (s, 27H, Me), 7.2–7.4 (m, 5H, Ph); ¹³C NMR (CDCl₃, δ) 1.9 (Me), 127.6, 129.6, 133.9, 135.6; ²⁹Si NMR (CDCl₃, δ) -77.7 ((Me₃SiO)₃Si), 8.9 (OSiMe₃); HRMS *m/z* calcd for 373.1501 [*M* + Na]⁺, found 373.1499.

MeSi(OSiMe₃)₃^{S10}

The general procedure was followed by using MeSi(OBn)₃ (0.201 g, 0.551 mmol), Pd/C (0.176 g, 0.165 mmol) and Me₃SiCl (357 mg, 3.29 mmol). After stirring for 3 h, the mixture was analyzed by ²⁹Si NMR showing the formation of MeSi(OSiMe₃)₃ in 88% yield.

¹H NMR (CDCl₃, δ) 0.00 (s, 3H, SiMe), 0.07 (s, 27H, OSiMe₃); ¹³C NMR (CDCl₃, δ) -3.2 (SiMe), 0.7 (OSiMe₃); ²⁹Si NMR (CDCl₃, δ) -64.9 (SiMe), 6.9 (OSiMe₃); HRMS *m/z* calcd for 318.0929 [*M* - Me + Na]⁺, found 318.0933.

Si(OSiMe₃)₄^{S10}

The general procedure was followed by using Si(OBn)₄ (0.202 g, 0.442 mmol), Pd/C (0.187 g, 0.176 mmol) and Me₃SiCl (384 mg, 3.54 mmol). After stirring for 6 h, the mixture was analyzed by ¹H NMR showing the formation of Si(OSiMe₃)₄ in 93% yield.

¹H NMR (CDCl₃, δ) 0.18 (s, 54H, Me); ¹³C NMR (CDCl₃, δ) 1.5 (Me); ²⁹Si NMR (CDCl₃, δ) -104.6 ((Me₃SiO)₃Si), 8.4 (OSiMe₃); HRMS *m/z* calcd for 407.1359 [*M* + Na]⁺, found 407.1352.

Large scale synthesis of Ph₃SiOSiMe₃

A mixture of Ph₃SiOBn (10.0 g, 27.3 mmol), Pd/C (2.91 g, 2.73 mmol) and Me₃SiCl (5.93 g, 54.6 mmol) in EtOAc (500 mL) was stirred at room temperature for 1 week. The reaction mixture was then concentrated under reduced pressure to remove residual Me₃SiCl, and then Pd/C was filtered through Hyflo Super Cel using ethyl acetate as a solvent. Then the solution was concentrated under reduced pressure and the residue was purified by Kugelrohr distillation (8 Pa, oven temp. 140 °C) to give **2** (8.93 g,

94%) as a colorless solid.

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