Supporting Information

for

Pd-catalyzed Synthesis of Symmetrical and Unsymmetrical Siloxanes

Yu Kurihara, Yoshinori Yamanoi,* and Hiroshi Nishihara*

Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

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1. Chemicals

(A) Hydrosiloxanes

1,1,3,3-Tetramethyldisiloxane and 3-((dimethylsilyl)oxy)-1,1,3,5,5-pentamethyltrisiloxane were commercially sourced and used without further purification. 1,1,3,3-Tetraphenyldisiloxane was prepared according to the literature.¹

(B) Aryl iodides

4-Iodoanisole, 4-iodotoluene, 4-iodocummene, 3-iodobenzonitrile, 4-iodophenol, 2-iodothiophen, 1-(*tert*-butyl)-4-iodobenzene, 3-iodoanisole, and 2-iodoanisole were commercially sourced and used without further purification. 4-Iodo-*N*,*N*-dimethylaniline was prepared according to the literature.²

(C) Other reagents

Water was purified using an Autopure WD500 device (Yamato Scientific Co., Ltd.). Dehydrated tetrahydrofuran (THF), toluene, dichloromethane, and acetonitrile (Kanto Chemical Co., Inc.) were purified through an organic solvent purifier (Nikko Hansen Co., Ltd.) and stored over 4A molecular sieves. *N*,*N*-Diisopropylethylamine was commercially sourced and stored over potassium hydroxide. *N*-Methylpyrrolidone, bis(tri-*tert*-butylphosphine)palladium(0) (Pd(P(*t*-Bu)₃)₂), and dodecane were commercially sourced and used without further purification.

(D) Double arylation of 1,1,3,3-tetramethyldisiloxane

A typical experimental procedure for the palladium-catalyzed double arylation of 1,1,3,3-tetramethyldisiloxane

Aryl iodide (1.25 mmol), *N*,*N*-diisopropylethylamine (2.0 mmol), and 1,1,3,3-tetramethyldisiloxane (0.50 mmol) were added to a solution of $Pd(P(t-Bu)_3)_2$ (0.025 mmol) in THF or toluene (1.25 mL). After stirring for 4 h–1 d at room temperature, the reaction mixture was quenched with water. The aqueous layer was extracted with dichloromethane three times, and dried over sodium sulfate. The solvent was evaporated under reduced pressure, and purified with a TLC plate (silica gel) to afford the desired double arylated product.

1,3-bis(4-methoxyphenyl)-1,1,3,3-tetramethyldisiloxane (3)³: Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, 4H, J = 8.5 Hz), 6.90 (d, 4H, J = 8.8 Hz), 3.82 (s, 6H), 0.29 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 160.5 (C_q), 134.5 (CH), 131.0 (C_q), 113.4 (CH), 55.0 (CH₃), 1.0 (CH₃). EI-MS m/z 346 (M⁺).

1,1,3,3-tetramethyl-1,3-di-p-tolyldisiloxane (4)³: Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.44 (d, 4H, J = 7.6 Hz), 7.17 (d, 4H, J = 7.8 Hz), 2.35 (s, 6H), 0.30 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 139.1 (C_q), 136.3 (C_q), 133.1 (CH), 128.5 (CH), 21.5 (CH₃), 1.0 (CH₃). EI-MS *m/z* 314 (M⁺).

1,3-bis(4-isopropylphenyl)-1,1,3,3-tetramethyldisiloxane (5): Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, 4H, J = 7.8 Hz), 7.22 (d, 4H, J = 7.8 Hz), 2.90 (septet, 2H, J = 6.9 Hz), 1.26 (d, 12H, J = 6.8 Hz), 0.31 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 149.9 (C_q), 136.9 (C_q), 133.1 (CH), 125.8 (CH), 34.1 (CH), 23.9 (CH₃), 1.0 (CH₃). EI-MS *m*/*z* 370 (M⁺). HRMS (FAB) *m*/*z*: [M – H]⁺ Calcd for C₂₂H₃₃OSi₂ 369.2070; found 369.2058.

3,3'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)dibenzonitrile (6): Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (s, 2H), 7.71 (d, 2H, J = 7.8 Hz), 7.66 (dt, 2H, J = 7.8, 1.3 Hz), 7.46 (t, 2H, J = 7.6 Hz), 0.37 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 141.1 (C_q), 136.9 (C_q), 136.5 (C_q), 132.8 (CH), 128.4 (CH), 119.0 (C_q), 112.1 (C_q), 0.5 (CH₃). EI-MS *m*/*z* 336 (M⁺). HRMS (FAB) *m*/*z*: [M + H]⁺ Calcd for C₁₈H₂₁N₂OSi₂ 337.1192; found 337.1165.

4,4'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)diphenol (7)⁴: Colorless solid. ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, 4H, J = 8.6 Hz), 6.82 (d, 4H, J = 8.5 Hz), 4.76 (s, 2H), 0.29 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 156.4 (C_q), 134.8 (CH), 131.3 (C_q), 114.8 (CH), 0.9 (CH₃). EI-MS *m*/z 318 (M⁺).

(E) Double arylation of 1,1,3,3-tetraphenyldisiloxane

A typical experimental procedure for the palladium-catalyzed double arylation of 1,1,3,3-tetraphenyldisiloxane

Aryl iodide (1.25 mmol), *N*,*N*-diisopropylethylamine (2.0 mmol), and 1,1,3,3-tetraphenyldisiloxane (0.50 mmol) were added to a solution of $Pd(P(t-Bu)_3)_2$ (0.025 mmol) in toluene (1.25 mL). After stirring for 3 d at room temperature, the reaction mixture was quenched with water. The aqueous layer was extracted with dichloromethane three times, and dried over sodium sulfate. The solvent was evaporated under reduced pressure, and purified with a TLC plate (silica gel) to afford the desired double arylated product.

1,3-bis(4-methoxyphenyl)-1,1,3,3-tetraphenyldisiloxane (8): Colorless solid. Mp: 155–157 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.49–7.45 (m, 8H), 7.39–7.34 (m, 8H), 7.28–7.23 (m, 8H), 3.79 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.9 (C_q), 136.8 (CH), 135.9 (C_q), 135.1 (CH), 129.6 (CH), 127.6 (CH), 126.5 (C_q), 113.4 (CH), 54.9 (CH₃). HRMS (FAB) *m/z*: M⁺ Calcd for C₃₈H₃₄O₃Si₂ 594.2047; found 594.2073.

(F) Stepwise arylation of 1,1,3,3-tetramethyldisiloxane

A typical experimental procedure for the palladium-catalyzed stepwise arylation of 1,1,3,3-tetramethyldisiloxane

First aryl iodide (1.0 mmol), *N*,*N*-diisopropylethylamine (2.0 mmol), 1,1,3,3-tetramethyldisiloxane (1.5 mmol) were added to a solution of $Pd(P(t-Bu)_3)_2$ (0.050 mmol) in toluene (2.0 mL). After stirring for 2 h at 0 °C, *N*,*N*-diisopropylethylamine (4.0 mmol) and second aryl iodide (2.0 mmol)

were added. After stirring for an additional 1-2 d at 0 °C, the reaction mixture was quenched with water. The aqueous layer was extracted with dichloromethane three times, and dried over sodium sulfate. The solvent was evaporated under reduced pressure, and purified with a TLC plate (silica gel) to afford the desired unsymmetrically arylated product.

1-(4-isopropylphenyl)-3-(4-methoxyphenyl)-1,1,3,3-tetramethyldisiloxane (10, 17): Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.48–7.45 (m, 4H), 7.22 (d, 2H, J = 7.8 Hz), 6.90 (d, 2H, J = 8.6 Hz), 3.82 (s, 3H), 2.90 (septet, 1H, J = 6.9 Hz), 1.26 (d, 6H, J = 7.1 Hz), 0.31 (s, 6H), 0.30 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 160.5 (C_q), 149.9 (C_q), 136.8 (C_q), 134.5 (CH), 133.1 (CH), 131.0 (C_q), 125.8 (CH), 113.4 (CH), 55.0 (CH₃), 34.1 (CH), 23.9 (CH₃), 0.99 (CH₃). HRMS (FAB) *m/z*: M⁺ Calcd for C₂₀H₃₀O₂Si₂: 358.1785; found 358.1761.

1-(4-isopropylphenyl)-3-(3-methoxyphenyl)-1,1,3,3-tetramethyldisiloxane (11): Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, 2H, J = 7.8 Hz), 7.29 (t, 2H, J = 7.8 Hz), 7.21 (d, 2H, J = 7.6 Hz), 7.11 (d, 1H, J = 7.3 Hz), 7.06 (d, 1H, J = 2.2 Hz), 6.90 (dd, 1H, J = 8.2, 2.3 Hz), 3.76 (s, 3H), 2.89 (septet, 1H, J = 6.9 Hz), 1.25 (d, 6H, J = 7.1 Hz), 0.32 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 158.9 (C_q), 150.0 (C_q), 141.6 (C_q), 136.7 (C_q), 133.1 (CH), 128.9 (CH), 125.9 (CH), 125.2 (CH), 118.1 (CH), 114.8 (CH), 55.0 (CH₃), 34.1 (CH), 23.9 (CH₃), 1.0 (CH₃), 0.9 (CH₃). HRMS (FAB) *m/z*: M⁺ Calcd for C₂₀H₃₀O₂Si₂ 358.1785; found 358.1801.

1-(4-isopropylphenyl)-3-(2-methoxyphenyl)-1,1,3,3-tetramethyldisiloxane (12): Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.51–7.48 (m, 3H), 7.35 (t, 1H, *J* = 7.8 Hz), 7.22 (d, 2H, *J* = 7.8 Hz), 6.94 (t, 1H, *J* = 7.2 Hz), 6.81 (d, 1H, *J* = 8.3 Hz), 3.75 (s, 3H), 2.89 (septet, 1H, *J* = 6.9 Hz), 1.28 (d, 6H, *J* = 6.8 Hz), 0.331 (s, 6H), 0.328 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 163.8 (C_q), 149.8 (C_q), 137.2 (C_q), 135.1 (CH), 133.2 (CH), 131.0 (CH), 127.4 (C_q), 125.8 (CH), 120.4 (CH), 54.8 (CH₃), 34.1 (CH), 23.9 (CH₃), 1.4 (CH₃), 1.1 (CH₃). EI-MS *m*/*z* 358 (M⁺); HRMS (FAB) *m*/*z*: [M – CH₃]⁺ Calcd for C₁₉H₂₇O₂Si₂ 343.1550; found 343.1523.

4-(3-(4-isopropylphenyl)-1,1,3,3-tetramethyldisiloxanyl)-*N*,*N*-dimethylaniline (13): Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, 2H, J = 8.1 Hz), 7.42 (d, 2H, J = 8.8 Hz), 7.22 (d, 2H, J = 8.0 Hz), 6.72 (d, 2H, J = 8.5 Hz), 2.96 (s, 6H), 2.90 (septet, 1H, J = 7.1 Hz), 1.26 (d, 6H, J = 7.1 Hz), 0.30 (s, 6H), 0.29 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 151.2 (C_q), 149.8 (C_q), 137.1 (C_q), 134.2 (CH), 133.1 (CH), 125.8 (CH), 125.3 (C_q), 111.7 (CH), 40.2 (CH₃), 34.1 (CH), 23.9 (CH₃), 1.1 (CH₃). HRMS (FAB) *m/z*: M⁺ Calcd for C₂₁H₃₃NOSi₂ 371.2101; found 371.2076.

1-(4-isopropylphenyl)-1,1,3,3-tetramethyl-3-(thiophen-2-yl)disiloxane (14): Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.59 (dd, 1H, J = 4.5, 0.5 Hz), 7.46 (d, 2H, J = 8.1 Hz), 7.28 (d, 1H, J = 3.4 Hz), 7.22 (d, 2H, J = 7.8 Hz), 7.17 (dd, 1H, J = 4.6, 3.4 Hz), 2.89 (septet, 1H, J = 7.0 Hz), 1.25 (d, 6H, J = 6.8 Hz), 0.39 (s, 6H), 0.30 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 150.0 (C_q), 139.5 (C_q), 136.6 (C_q), 134.2 (CH), 133.1 (CH), 130.5 (CH), 127.9 (CH), 125.9 (CH), 34.1 (CH), 23.9 (CH₃), 1.9 (CH₃), 0.9 (CH₃). HRMS (FAB) *m/z*: M⁺ Calcd for C₁₇H₂₆OSSi₂ 334.1243; found

334.1236.

4-(3-(4-methoxyphenyl)-1,1,3,3-tetramethyldisiloxanyl)-*N*,*N*-dimethylaniline (15): Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, 2H, *J* = 8.6 Hz), 7.41 (d, 2H, *J* = 8.8 Hz), 6.90 (d, 2H, *J* = 8.8 Hz), 6.72 (d, 2H, *J* = 8.5 Hz), 3.81 (s, 3H), 2.96 (s, 6H), 0.29 (s, 6H), 0.28 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 160.4 (C_q), 151.1 (C_q), 134.5 (CH), 134.2 (CH), 131.2 (C_q), 125.3 (C_q), 113.3 (CH), 111.7 (CH), 55.0 (CH₃), 40.2 (CH₃), 1.05 (CH₃), 1.04 (CH₃). HRMS (FAB) *m/z*: M⁺ Calcd for C₁₉H₂₉NO₂Si₂ 359.1737; found 359.1713.

3-(3-(4-methoxyphenyl)-1,1,3,3-tetramethyldisiloxanyl)benzonitrile (16): Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.74–7.73 (m, 1H), 7.71 (dt, 1H, *J* = 7.6, 1.2 Hz), 7.45–7.41 (m, 3H), 6.91 (d, 2H, *J* = 8.6 Hz), 3.83 (s, 3H), 0.33 (s, 6H), 0.32 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 160.7 (C_q), 141.8 (C_q), 137.0 (CH), 136.6 (CH), 134.5 (CH), 132.5 (CH), 130.2 (C_q), 128.2 (CH), 119.2 (C_q), 113.5 (CH), 111.9 (C_q), 55.0 (CH₃), 0.74 (CH₃), 0.67 (CH₃). HRMS (FAB) *m/z*: M⁺ Calcd for C₁₈H₂₃NO₂Si₂ 341.1267; found 341.1238.

(G) Triple arylation of hydrosiloxane

A typical experimental procedure for the palladium-catalyzed triple arylation of hydrosiloxane

Aryl iodide (1.75 mmol), *N*,*N*-diisopropylethylamine (3.0 mmol), and 3-((dimethylsilyl)oxy)-1,1,3,5,5-pentamethyltrisiloxane (0.50 mmol) were added to a solution of Pd(P(*t*-Bu)₃)₂ (0.025 mmol) in toluene (1.75 mL). After stirring for 1 d at 0 °C, the reaction mixture was quenched with water. The aqueous layer was extracted with dichloromethane three times, and dried over sodium sulfate. The solvent was evaporated under reduced pressure, and purified with a TLC plate (silica gel) to afford the desired triple arylated product.

1,5-bis(4-methoxyphenyl)-3-(((4-methoxyphenyl)dimethylsilyl)oxy)-1,1,3,5,5-pentamethyltrisilo xane (19): Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, 6H, J = 8.6 Hz), 6.85 (d, 6H, J = 8.6 Hz), 3.81 (s, 6H), 0.27 (s, 18H), -0.01 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.5 (C_q), 134.6 (CH), 130.7 (C_q), 113.3 (CH), 55.0 (CH₃), 0.7 (CH₃), -2.0 (CH₃). HRMS (FAB) m/z: M⁺ Calcd for C₂₈H₄₂O₆Si₄ 586.2059; found 586.2035.

(H) Stepwise triple arylation of hydrosiloxane

A typical experimental procedure for the palladium-catalyzed stepwise triple arylation of hydrosiloxane

First aryl iodide (0.50 mmol), *N*,*N*-diisopropylethylamine (1.0 mmol), and 3-((dimethylsilyl)oxy)-1,1,3,5,5-pentamethyltrisiloxane (0.75 mmol) were added to a solution of Pd(P(*t*-Bu)₃)₂ (0.025 mmol) in toluene (2.25 mL). After stirring for 2 h at 0 °C, *N*,*N*-diisopropylethylamine (1.75 mmol) and second aryl iodide (0.875 mmol) were added. After

stirring for an additional 6 h at 0 °C, *N*,*N*-diisopropylethylamine (1.75 mmol) and third aryl iodide (0.875 mmol) were added. After stirring for an additional 14 h at 0 °C, the reaction mixture was quenched with water. The aqueous layer was extracted with dichloromethane three times, and dried over sodium sulfate. The solvent was evaporated under reduced pressure, and purified by a TLC plate (silica gel) and preparative HPLC (ODS) to afford the desired unsymmetrically triple arylated product.

1-(4-(*tert***-butyl)phenyl)-3-((***dimethyl***(***thiophen-2-yl***)***silyl***)***oxy***)-5-(***4-methoxyphenyl***)-1,1,3,5,5-pe ntamethyltrisiloxane (20):** Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, 1H, J = 4.6 Hz), 7.49–7.45 (m, 4H), 7.36 (d, 2H, J = 8.0 Hz), 7.29 (d, 1H, J = 3.2 Hz), 7.17 (dd, 1H, J = 3.4, 4.6 Hz), 6.88 (d, 2H, J = 8.5 Hz), 3.82 (s, 3H), 1.34 (s, 9H), 0.36 (s, 6H), 0.31 (s, 6H), 0.29 (s, 6H), 0.03 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.5 (C_q), 152.1 (C_q), 139.1 (C_q), 136.0 (C_q), 134.6 (CH), 134.3 (CH), 133.0 (CH), 130.7 (C_q), 130.5 (CH), 127.9 (CH), 124.5 (CH), 113.3 (CH), 55.0 (CH₃), 34.6 (C_q), 31.2 (CH₃), 1.5 (CH₃), 0.64 (CH₃), 0.61 (CH₃), -2.1 (CH₃). HRMS (FAB) *m/z*: M⁺ Calcd for C₂₈H₄₄O₄SSi₄ 588.2037; found 588.2025.

2. Measuring equipment

NMR spectra were measured with a JEOL AL-400 spectrometer or a Bruker DRX-500 spectrometer, and were referenced to tetramethylsilane (0.00 ppm) as an internal standard. GC-MS spectra were recorded with a Shimadzu GC-MS-QP2010 spectrometer. Purification by preparative HPLC was carried out using Japan Analytical Industry Co., Ltd. LC-908 apparatus with GPC or ODS columns. High-resolution FAB mass spectra were measured with a JEOL JMS 700P FAB MS.

3. References

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4. Copies of ¹H NMR and ¹³C NMR spectra































