

Palladium-Catalyzed Silylation of Aryl Chlorides with Hexamethyldisilane

Eric McNeill, Timothy E. Barder and Stephen L. Buchwald*

Department of Chemistry, Massachusetts Institute of Technology,

Cambridge, Massachusetts 02139

[*sbuchwal@mit.edu*](mailto:sbuchwal@mit.edu)

Supporting Information

General considerations. All reactions were carried out under an argon atmosphere. Anhydrous 1,4-dioxane and *N,N*-dimethylformamide were purchased from Aldrich and used without further purification. All starting materials are commercially available and were used without further purification. KF was purchased from Aldrich. The bulk of KF was stored in a nitrogen-filled glovebox; however, 1-2 g portions were removed from the glovebox, stored in a benchtop dessicator and weighed in the air. Anhydrous LiOAc was purchased from Aldrich and stored in a desiccator.

Analytical Methods. All new compounds were characterized by ^1H , ^{13}C NMR and IR spectroscopy, elemental analysis, and melting point where appropriate. Known compounds were characterized by ^1H and ^{13}C NMR and melting point where appropriate. Melting points were determined using a Mel-Temp II (Laboratory Devices) and are uncorrected. NMR spectra were recorded using a Varian Mercury 300 instrument. All ^1H NMR chemical shifts were reported in parts per million (ppm) relative to the residual protonated solvent peak (7.26 ppm for CDCl_3). Proton-decoupled ^{13}C NMR chemical shifts were reported relative to the solvent peak (77.23 ppm for CDCl_3). Infrared spectra were recorded on a Perkin-Elmer Model 2000 FT-IR using NaCl plates (thin film). Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. Gas chromatographic analyses were performed on Hewlett-Packard 6890 gas chromatography instrument with a FID detector using 25m x 0.20 mm capillary column with cross-linked methyl siloxane as a stationary phase. The yields in Tables 2, 4 and 5 refer to

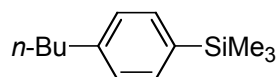
isolated yields of compounds estimated to be $\geq 95\%$ pure as determined by combustion analysis or ^1H NMR and are the average of two runs. The procedures described in this Supporting Information are representative, and hence the yields may differ slightly from those reported in Tables 2 and 4.

Cross-coupling of aryl chlorides with hexamethyldisilane, procedure A (electron-rich aryl chlorides). A screw-cap vial with Teflon septum was charged with a magnetic stir bar, tris(dibenzylideneacetone)dipalladium(0), 2-(dicyclohexylphosphino)biphenyl (**1b**, in a 3:1 ratio of **1b**:Pd), and anhydrous potassium fluoride (5 mmol, 290 mg). The vial was sealed, evacuated and filled with argon (2 cycles). Aryl chloride (1 mmol), dioxane (3 mL), hexamethyldisilane (1.2 – 1.8 mmol), and water (1 - 2 mmol) were added via syringe. Solid aryl chlorides were added prior to sealing the vial. The reaction mixture was stirred at 100 °C for 24 h, then allowed to cool to room temperature. The reaction was diluted with H_2O (3 mL) and extracted with hexanes (4 x 3 mL). The combined organic layers were dried over MgSO_4 , concentrated *in vacuo*, and purified by silica gel chromatography.

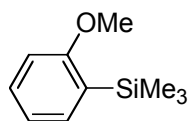
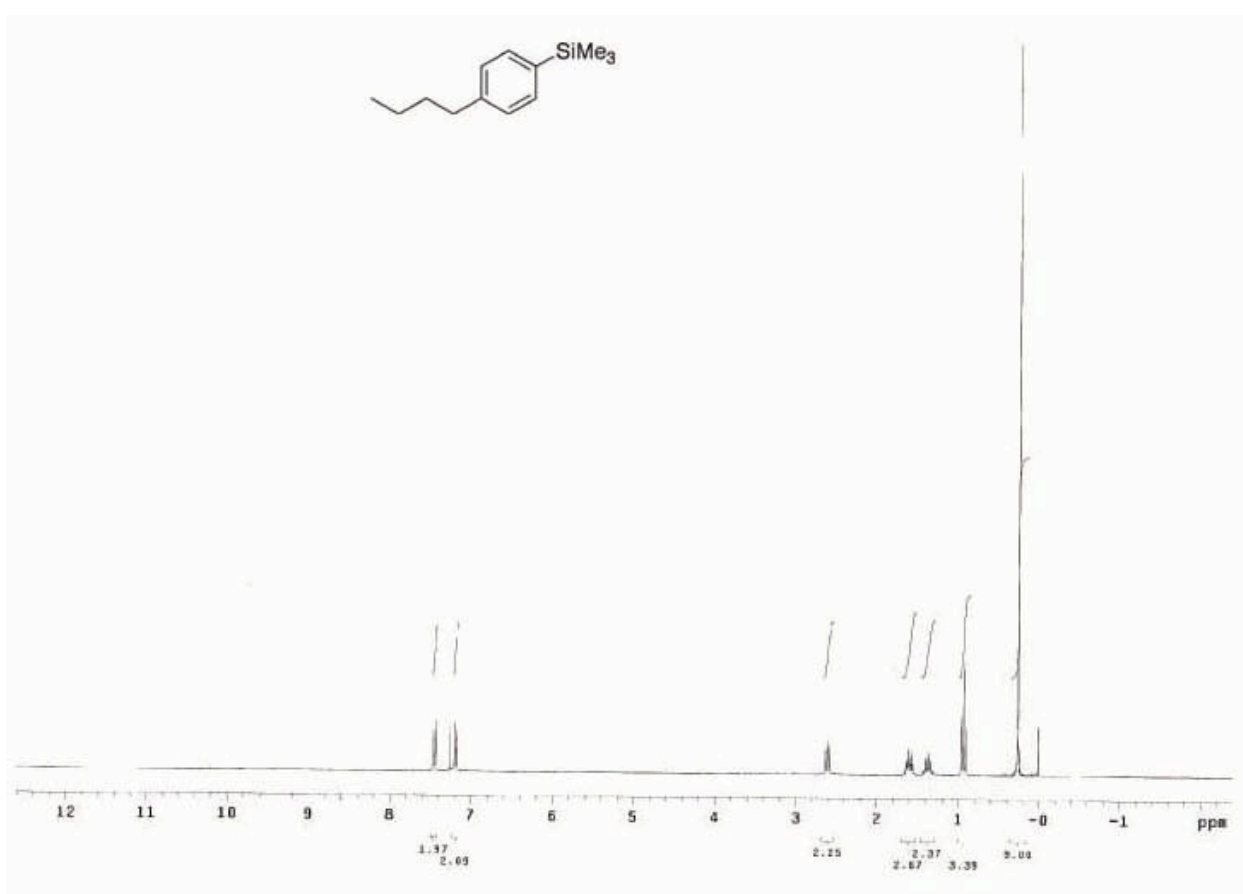
Cross-coupling of aryl chlorides with hexamethyldisilane, procedure B (electron-deficient aryl chlorides). A screw-cap vial with Teflon septum was charged with a magnetic stir bar, tris(dibenzylideneacetone)dipalladium(0) (0.015 mmol, 13.7 mg), 2'-(dimethylamino)-2-(di-*tert*-butylphosphino)biphenyl (**1d**, 0.09 mmol, 31.5 mg), and anhydrous lithium acetate (5 mmol, 330 mg). The vial was sealed, evacuated and filled with argon (2 cycles). Aryl chloride (1 mmol), water (2 mmol, 36 μL), hexamethyldisilane (1.2 mmol, 250 μL), and *N,N*-dimethylformamide (3 mL) were added via syringe. Solid aryl chlorides were added prior to sealing the vial. The reaction mixture was stirred at 100 °C for 24 h, then allowed to cool to room temperature. The reaction was diluted with H_2O (3 mL) and extracted with hexanes (4 x 3 mL). The combined organic layers were dried over MgSO_4 , concentrated *in vacuo*, and purified by silica gel chromatography.

One-pot sequential trimethylsilylation/iodination of electron-rich aryl chlorides. A screw-cap vial with Teflon septum was charged with a magnetic stir bar, tris(dibenzylideneacetone)dipalladium(0) (0.015 mmol, 13.7 mg), 2-(dicyclohexylphosphino)-

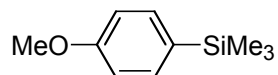
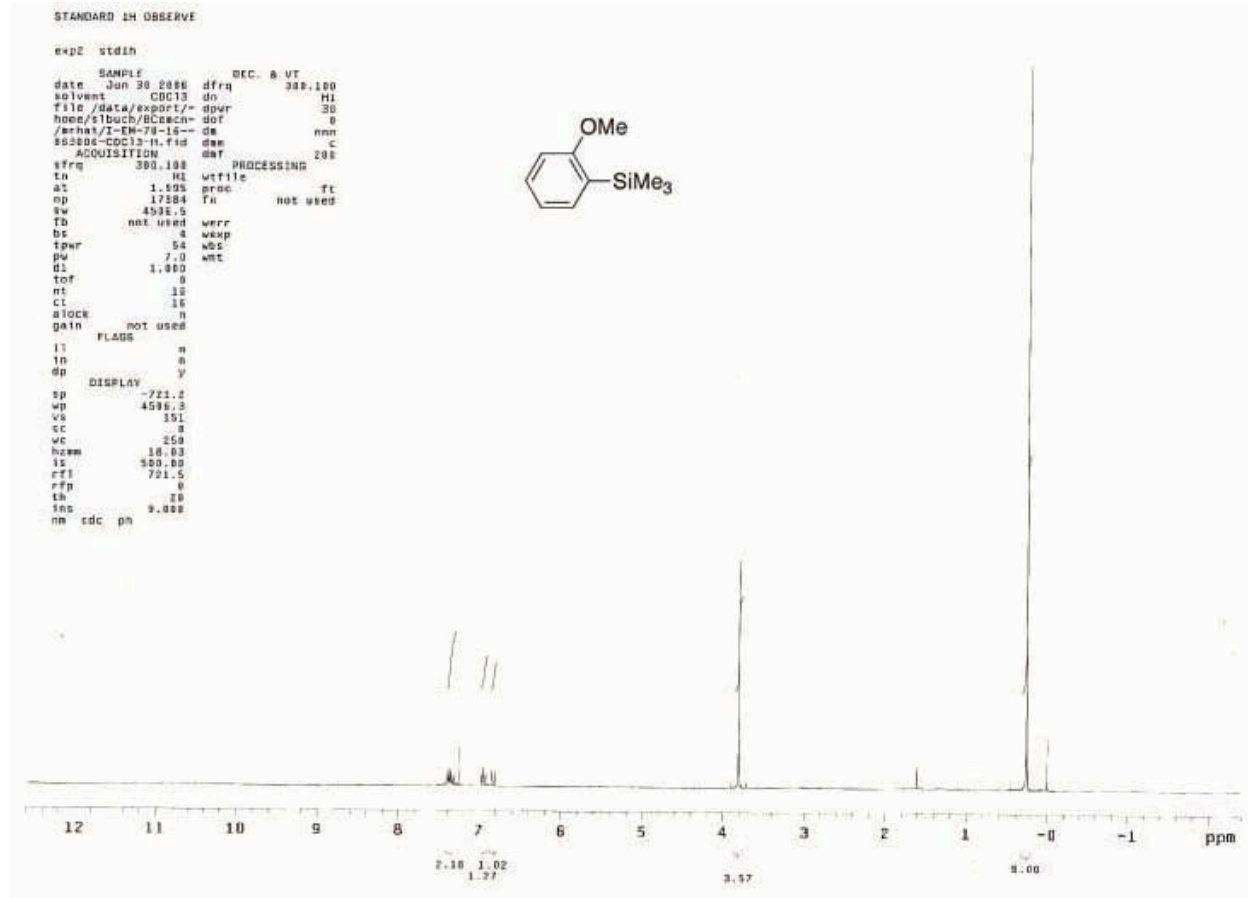
biphenyl (**1b**, 0.09 mmol, 31.5 mg), and anhydrous potassium fluoride (5 mmol, 290 mg). The vial was sealed, evacuated and filled with argon (2 cycles). Aryl chloride (1.0 mmol), hexamethyldisilane (1.2 mmol, 250 μ L), water (2 mmol, 36 μ L), and dioxane (3 mL) were added via syringe. The reaction was stirred at 100 $^{\circ}$ C for 24 h, then allowed to cool to room temperature. Iodine monochloride (1.5 mmol, as a 1.0M solution in CH_2Cl_2) was added via syringe, and the reaction mixture was stirred at room temperature for 4 h. The reaction was diluted with a 1M solution of $\text{Na}_2\text{S}_2\text{O}_3$ (3 mL) and extracted with hexanes (4 x 3 mL). The combined organic layers were dried over MgSO_4 , concentrated *in vacuo*, and purified by column chromatography.



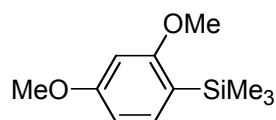
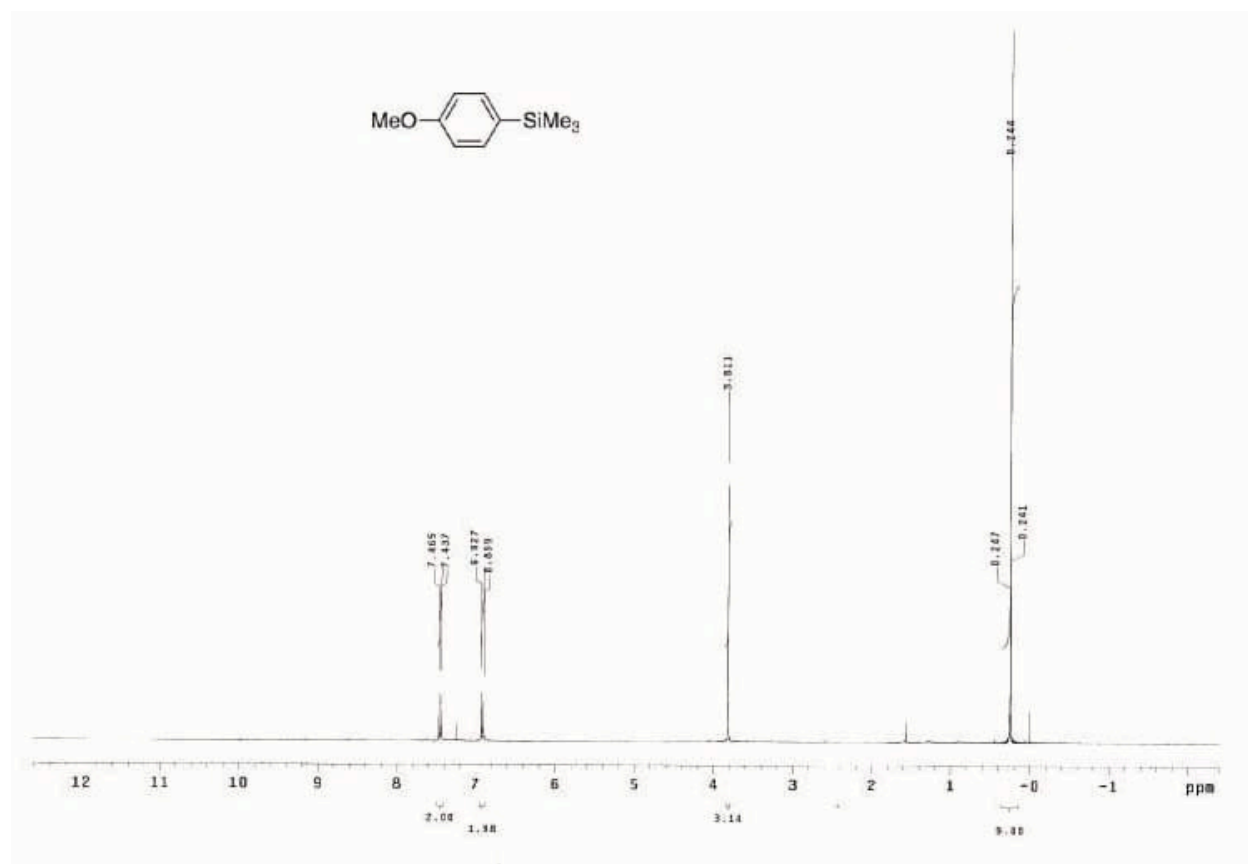
(4-*n*-Butylphenyl)trimethylsilane (Table 2, entry 1).^[1] Following procedure A, a mixture of 4-chloro-*n*-butylbenzene (1.0 mmol, 158 mg), KF (5 mmol, 290 mg), hexamethyldisilane (1.2 mmol, 250 μ L), Pd_2dba_3 (0.0075 mmol, 7 mg), **1b** (0.045 mmol, 16.5 mg) and H_2O (2 mmol, 36 μ L) in dioxane (3 mL) was heated to 100 $^{\circ}$ C with stirring for 24 h. The crude product was purified via column chromatography on silica gel (hexanes) to afford the title compound as a colorless oil (185 mg, 90%). ^1H NMR (300 MHz, CDCl_3): δ 7.45 (d, J = 8 Hz, 2H), 7.19 (d, J = 8 Hz, 2H), 2.60 (t, J = 7 Hz, 2H), 1.61 (m, 2H), 1.37 (dt, J = 7 Hz, 8 Hz, 2H), 0.94 (t, J = 7 Hz), 0.27 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ 143.8, 137.3, 133.6, 128.2, 35.9, 33.8, 22.7, 14.2, -0.8. A copy of the ^1H NMR spectrum is provided below.



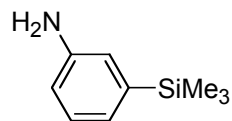
2-Trimethylsilylanisole (Table 2, entry 2).^[2] Following procedure A, a mixture of 2-chloroanisole (1.0 mmol, 143 mg), KF (5 mmol, 290 mg), hexamethyldisilane (1.5 mmol, 313 μ L), Pd₂dba₃ (0.015 mmol, 13.7 mg), **1b** (0.09 mmol, 31.5 mg) in dioxane (3 mL) was heated to 100 °C with stirring for 24 h (H₂O omitted for this reaction). The crude product was purified via column chromatography on silica gel (hexanes) to afford the title compound as a colorless oil (143 mg, 79%). ¹H NMR (300 MHz, CDCl₃): δ 7.42-7.35 (m, 2H), 6.97 (t, J = 7 Hz, 1H), 6.85 (d, J = 8 Hz, 1H), 3.82 (s, 3H), 0.29 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 164.6, 135.2, 131.0, 128.1, 120.6, 109.7, 55.2, -0.7. A copy of the ¹H NMR spectrum is provided below.



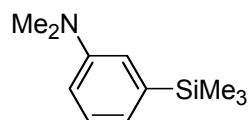
4-Trimethylsilylanisole (Table 2, entry 3).^[2] Following procedure A, a mixture of 4-chloroanisole (1.0 mmol, 143 mg), KF (5 mmol, 290 mg), hexamethyldisilane (1.2 mmol, 250 μ L), Pd₂dba₃ (0.01 mmol, 9.4 mg), **1b** (0.06 mmol, 22 mg) and H₂O (2 mmol, 36 μ L) in dioxane (3 mL) was heated to 100 °C with stirring for 24 h. The crude product was purified via column chromatography on silica gel (hexanes) to afford the title compound as a colorless oil (158 mg, 96%). ¹H NMR (300 MHz, CDCl₃): δ 7.45 (d, *J* = 8 Hz, 2H), 6.91 (d, *J* = 8 Hz, 2H), 3.81 (s, 3H), 0.24 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 160.2, 134.7, 131.3, 113.5, 55.0, -1.0. A copy of the ¹H NMR spectrum is provided below.



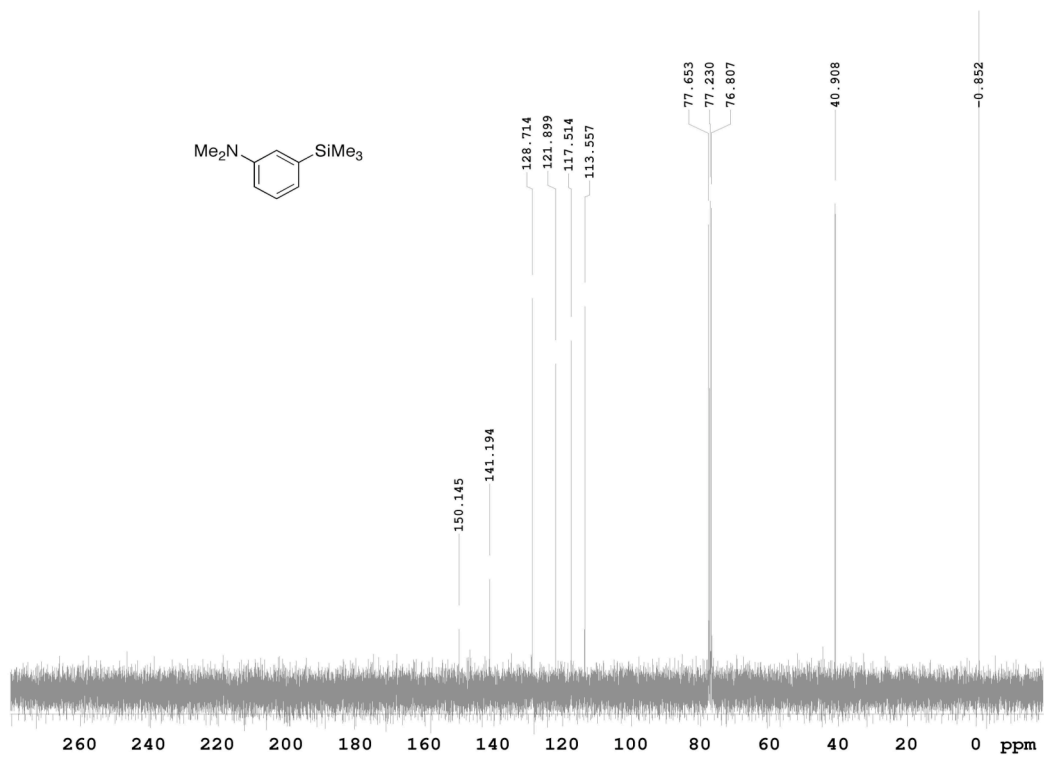
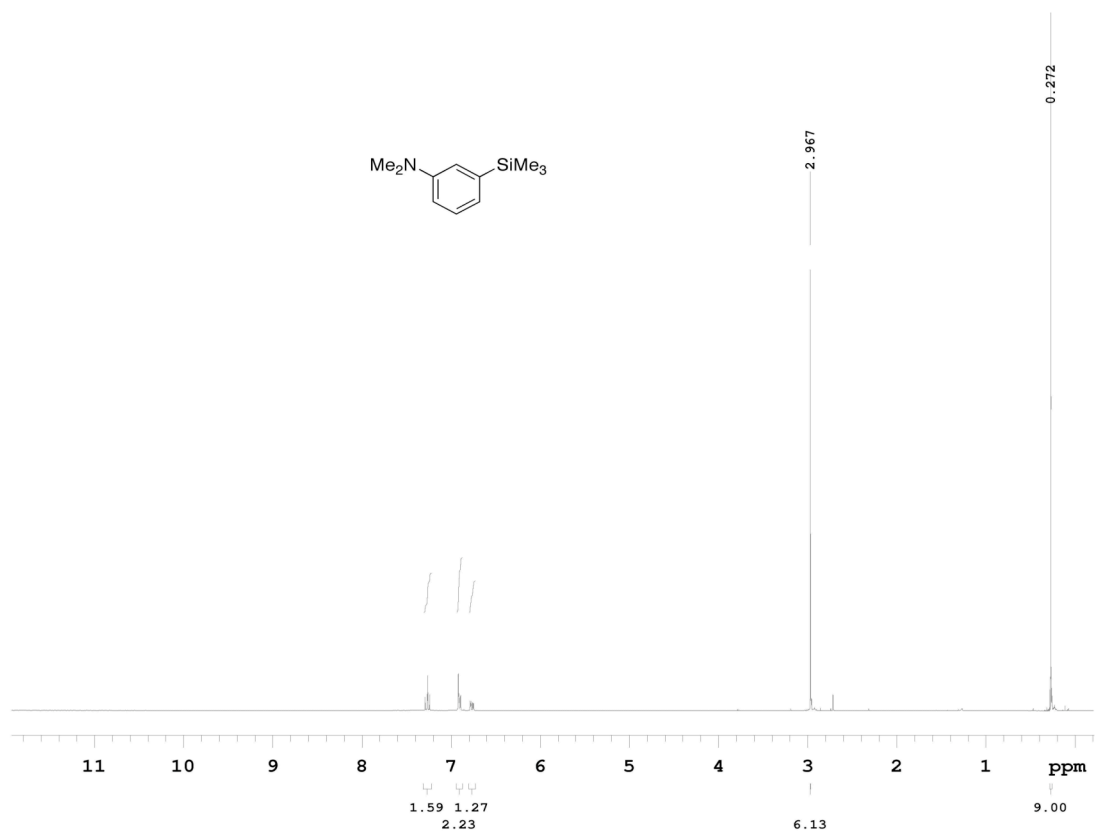
(2,4-Dimethoxyphenyl)trimethylsilane (Table 2, entry 4). Following procedure A, a mixture of 1-chloro-2,4-dimethoxybenzene (1.0 mmol, 173 mg), KF (5 mmol, 290 mg), hexamethyldisilane (1.8 mmol, 375 μ L), Pd₂dba₃ (0.015 mmol, 13.7 mg), **1b** (0.09 mmol, 31.5 mg) in dioxane (3 mL) was heated to 100 °C with stirring for 24 h (H₂O omitted for this reaction). The crude product was purified via column chromatography on silica gel (1:20 ethyl acetate:hexanes) to afford the title compound as a colorless oil (196 mg, 90%). ¹H NMR (300 MHz, CDCl₃): δ 6.95 (d, *J* = 3 Hz, 1H), 6.86 (dd, *J* = 9 Hz, 3 Hz, 2H), 6.77 (d, *J* = 9 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 0.27 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 153.6, 129.7, 121.4, 114.9, 114.6, 110.6, 56.0, 55.9, -0.8. IR (neat): 2996, 2952, 2901, 2832, 1583, 1509, 1480, 1400, 1274, 1220, 1178, 1048, 1026, 885, 839, 726 cm⁻¹. Anal. Calcd. for C₁₁H₁₈O₂Si: C 62.81%, H 8.63%. Found: C 63.02%, H 8.69%.

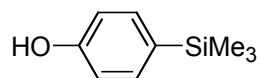


3-Trimethylsilylaniline (Table 2, entry 5). Following procedure A, a mixture of 3-chloroaniline (1.0 mmol, 128 mg), KF (5 mmol, 290 mg), hexamethyldisilane (1.8 mmol, 375 μ L), Pd₂dba₃ (0.01 mmol, 9.4 mg), **1b** (0.06 mmol, 22 mg), and H₂O (1 mmol, 18 μ L) in dioxane (3 mL) was heated to 100 °C with stirring for 24 h. The crude product was purified via column chromatography on silica gel (1:20 ethyl acetate:hexanes) to afford the title compound as a pale yellow oil (132 mg, 80%). ¹H NMR (300 MHz, CDCl₃): δ 7.17 (t, J = 7 Hz, 1H), 6.93 (dt, J = 7 Hz, 1 Hz, 1H), 6.85 (d, J = 1 Hz, 1H), 6.69 (ddd, J = 8 Hz, 3 Hz, 1 Hz, 1H), 3.64 (bs, 2H), 0.25 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 145.8, 141.8, 128.9, 123.7, 120.1, 115.9, -0.9. IR (neat): 3452, 3372, 2955, 1618, 1591, 1485, 1426, 1248, 1128, 1093, 898, 837, 753, 690, 621 cm⁻¹. Anal. Calcd. for C₉H₁₅NSi: C 65.39%, H 9.15%. Found: C 65.32%, H 9.12%.

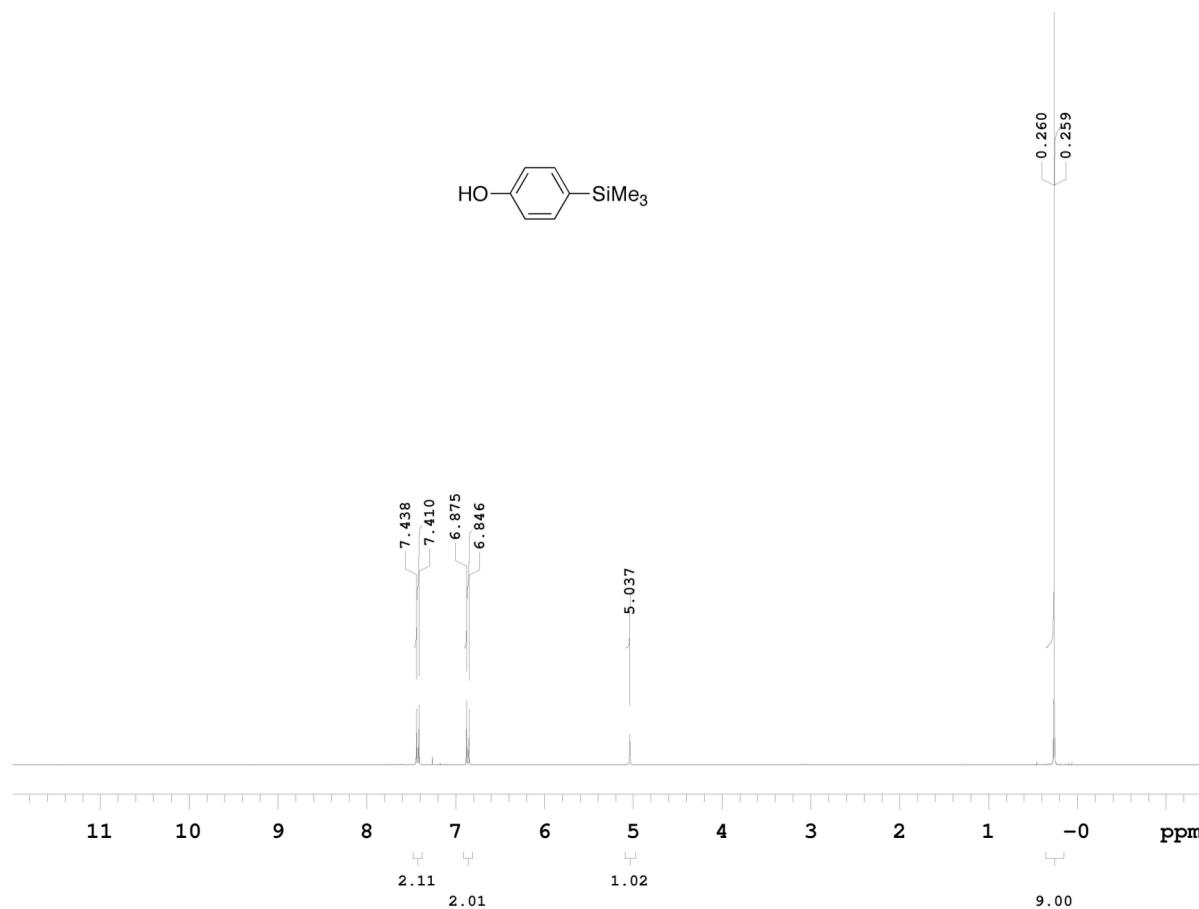


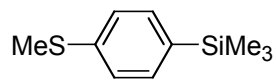
3-Trimethylsilyl-N,N-dimethylaniline (Table 2, entry 6). Following procedure A, a mixture of 3-chloro-N,N-dimethylaniline (1.0 mmol, 156 mg), KF (5 mmol, 290 mg), hexamethyldisilane (1.2 mmol, 250 μ L), Pd₂dba₃ (0.01 mmol, 9.4 mg), **1b** (0.06 mmol, 22 mg), and H₂O (2 mmol, 36 μ L) in dioxane (3 mL) was heated 100 °C with stirring for 24 h. The crude product was purified via column chromatography on silica gel (1:20 ethyl acetate:hexanes) to afford the title compound as a colorless oil (181 mg, 94%). ¹H NMR (300 MHz, CDCl₃): δ 7.26 (dd, J = 8 Hz, 7 Hz, 1H), 6.90 (m, 2H), 6.76 (ddd, J = 8 Hz, 3 Hz, 2 Hz, 1H), 3.00 (s, 6H), 0.27 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 150.1, 141.2, 128.7, 121.9, 117.5, 113.6, 40.9, -0.8. IR (neat): 2955, 2985, 2800, 1588, 1566, 1491, 1417, 1346, 1247, 1183, 1122, 993, 857, 840, 753, 690 cm⁻¹. A satisfactory elemental analysis could not be obtained for this compound. Copies of the ¹H and ¹³C NMR spectra are provided below.



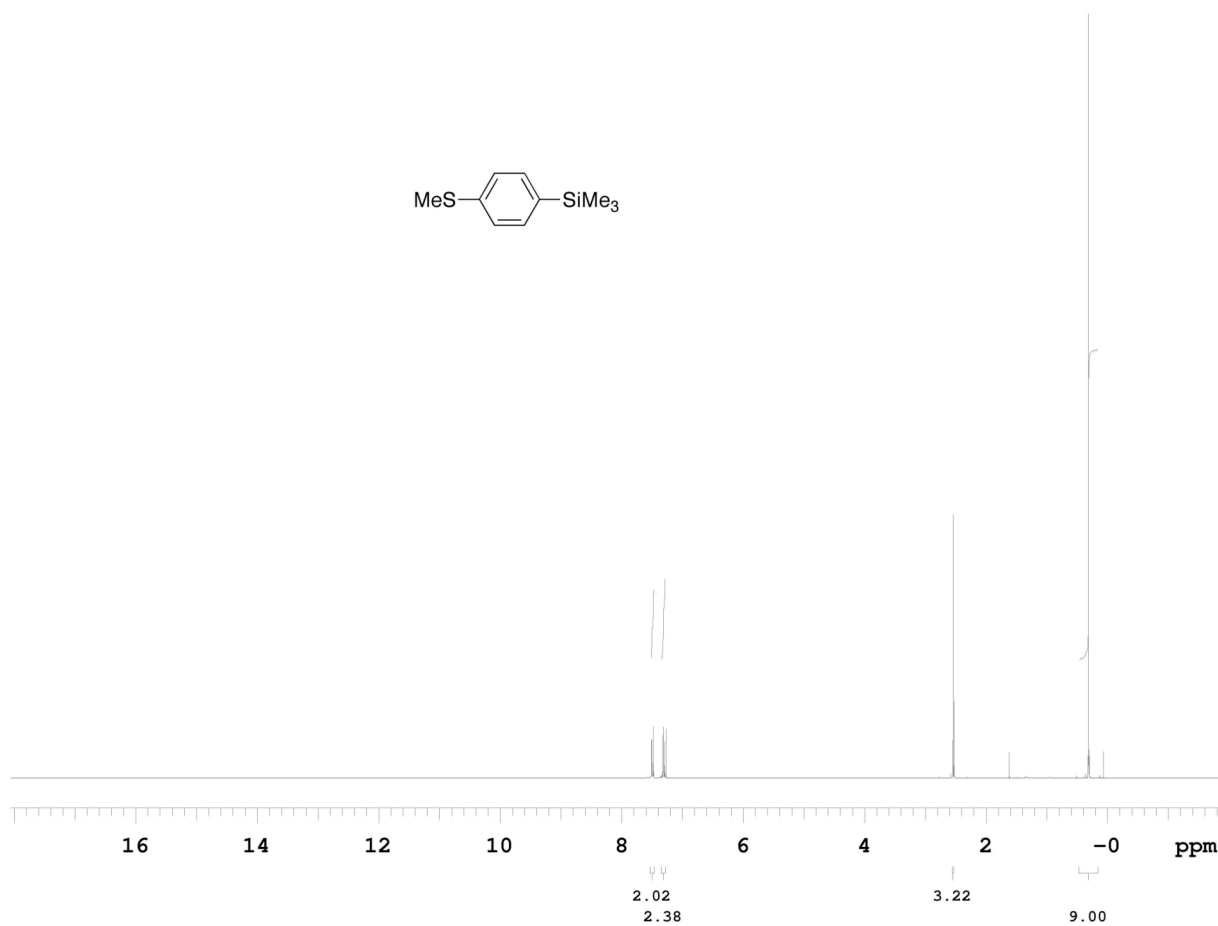


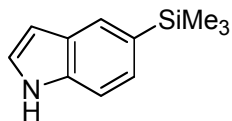
4-Trimethylsilylphenol (Table 2, entry 7).^[21] Following procedure A, a mixture of 4-chlorophenol (1.0 mmol, 129 mg), KF (5 mmol, 290 mg), hexamethyldisilane (1.2 mmol, 250 μ L), Pd₂dba₃ (0.015 mmol, 13.7 mg), **1b** (0.09 mmol, 31.5 mg), and H₂O (2 mmol, 36 μ L) in dioxane (3 mL) was heated 100 °C with stirring for 24 h. The crude product was purified via column chromatography on silica gel (1:25 ethyl acetate:hexanes) to afford the title compound as a colorless solid (120 mg, 72%). MP: 73-75 °C (lit. 74-75 °C). ¹H NMR (300 MHz, CDCl₃): δ 7.42 (dt, J = 8 Hz, 2 Hz, 2H), 6.86 (dt, J = 7 Hz, 1 Hz, 2H), 5.04 (bs, 1H), 0.26 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 156.3, 135.2, 131.9, 115.1, -0.7. A copy of the ¹H NMR spectrum is provided below.



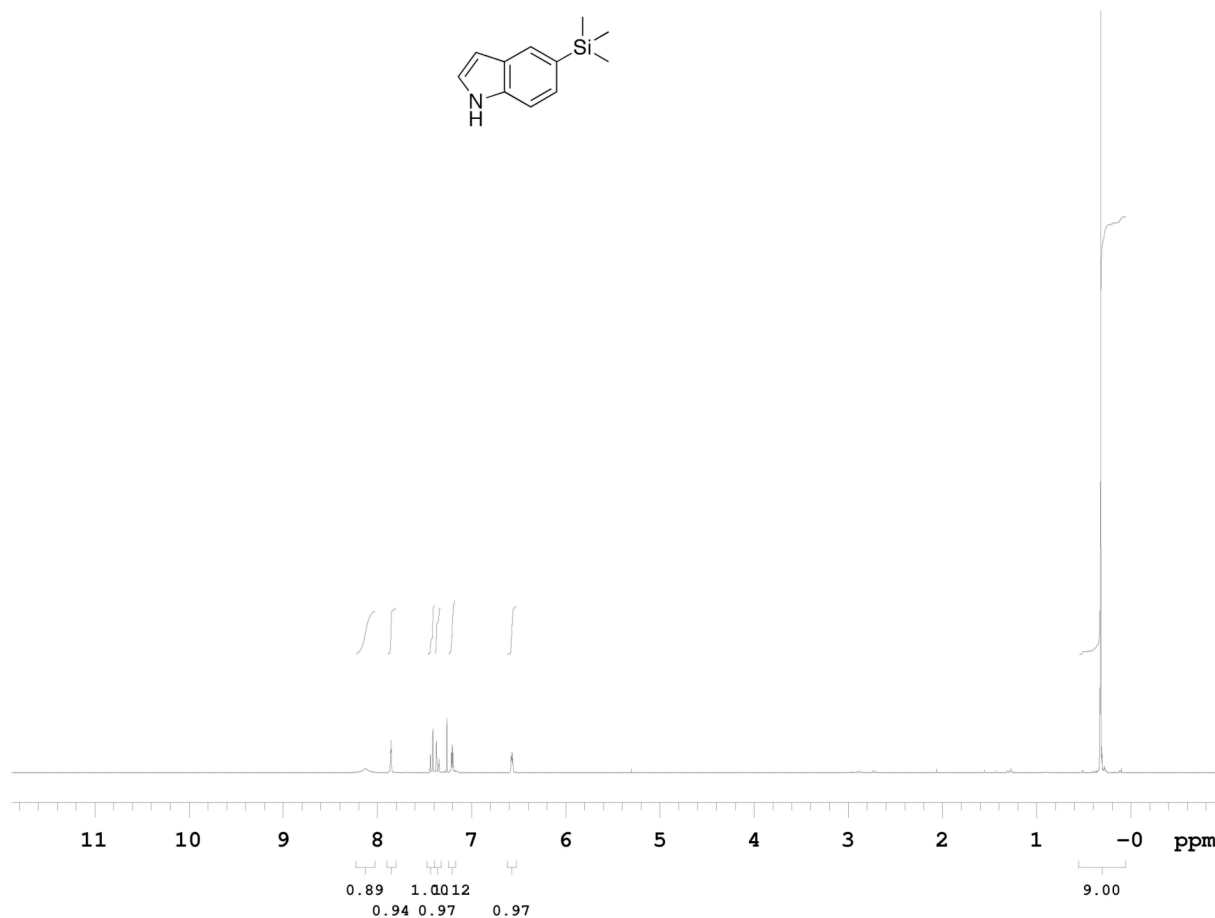


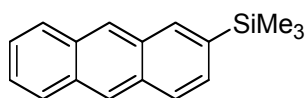
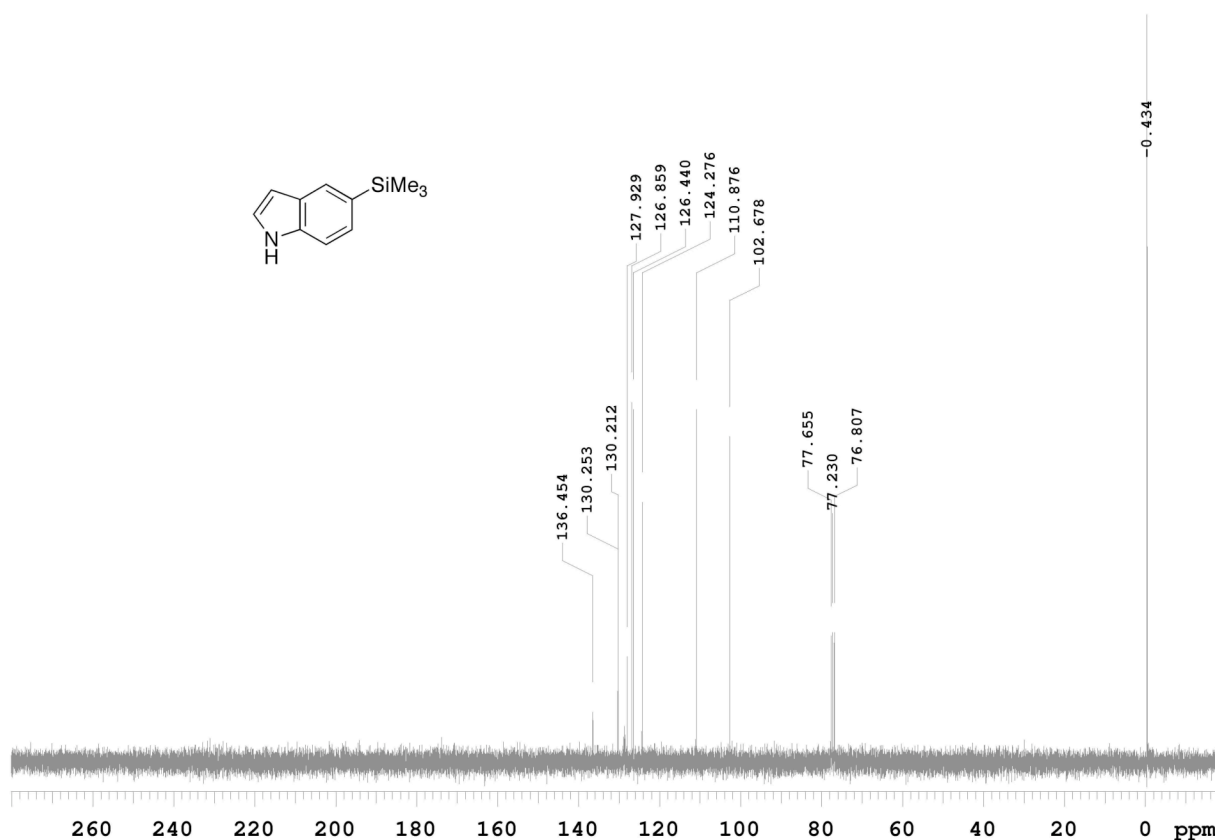
4-Trimethylsilylthioanisole (Table 2, entry 8).^[3] Following procedure A, a mixture of 4-chlorothioanisole (1.0 mmol, 159 mg), KF (5 mmol, 290 mg), hexamethyldisilane (1.8 mmol, 375 μ L), Pd₂dba₃ (0.015 mmol, 13.7 mg), **1b** (0.09 mmol, 31.5 mg), and H₂O (2 mmol, 36 μ L) in dioxane (3 mL) was heated to 100 °C with stirring for 24 h. The crude product was purified via column chromatography on silica gel (1:50 ethyl acetate:hexanes) to afford the title compound as a pale yellow oil (168 mg, 86%). ¹H NMR (300 MHz, CDCl₃): δ 7.48 (d, J = 8 Hz, 2H), 7.30 (d, J = 8 Hz, 2H), 2.48 (s, 3H), 0.25 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 139.6, 136.7, 134.0, 125.9, 15.7, -0.9. A copy of the ¹H NMR spectrum is provided below.



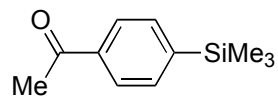


5-Trimethylsilyl-1H-indole (Table 2, entry 9). Following procedure A, a mixture of 5-chloro-1H-indole (1.0 mmol, 152 mg), KF (5 mmol, 290 mg), hexamethyldisilane (1.8 mmol, 375 μ L), Pd₂dba₃ (0.01 mmol, 9.4 mg), **1b** (0.06 mmol, 22 mg), and H₂O (2 mmol, 36 μ L) in dioxane (3 mL) was heated to 100 °C with stirring for 24 h. The crude product was purified via column chromatography on silica gel (1:20 ethyl acetate:hexanes) to afford the title compound as a colorless oil (159 mg, 84%). ¹H NMR (300 MHz, CDCl₃): δ 8.12 (bs, 1H), 7.85 (m, 1H), 7.42 (dt, J = 9 Hz, 1 Hz, 1H), 7.35 (m, 1H), 7.20 (t, J = 3 Hz, 1H), 6.57 (m, 1H), 0.32 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 136.5, 130.2, 127.9, 126.9, 126.4, 124.3, 110.9, 102.7, -0.4. IR (neat): 3412, 2954, 1608, 1459, 1413, 1296, 1247, 1075, 915, 837, 752, 723, 691, 621, 418 cm⁻¹. A satisfactory elemental analysis could not be obtained for this compound. Copies of the ¹H and ¹³C NMR spectra are provided below.

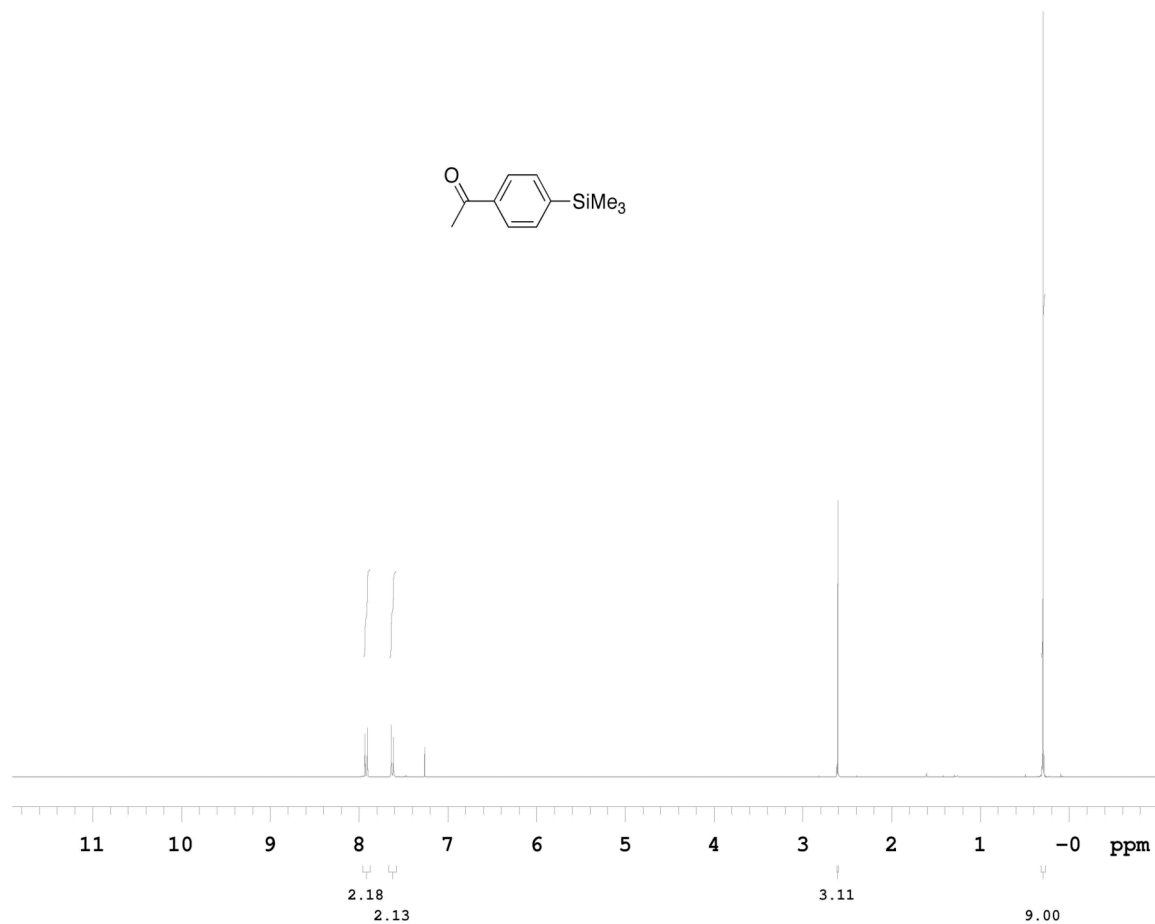


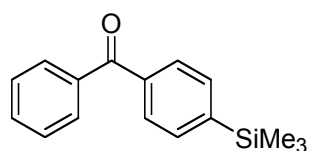
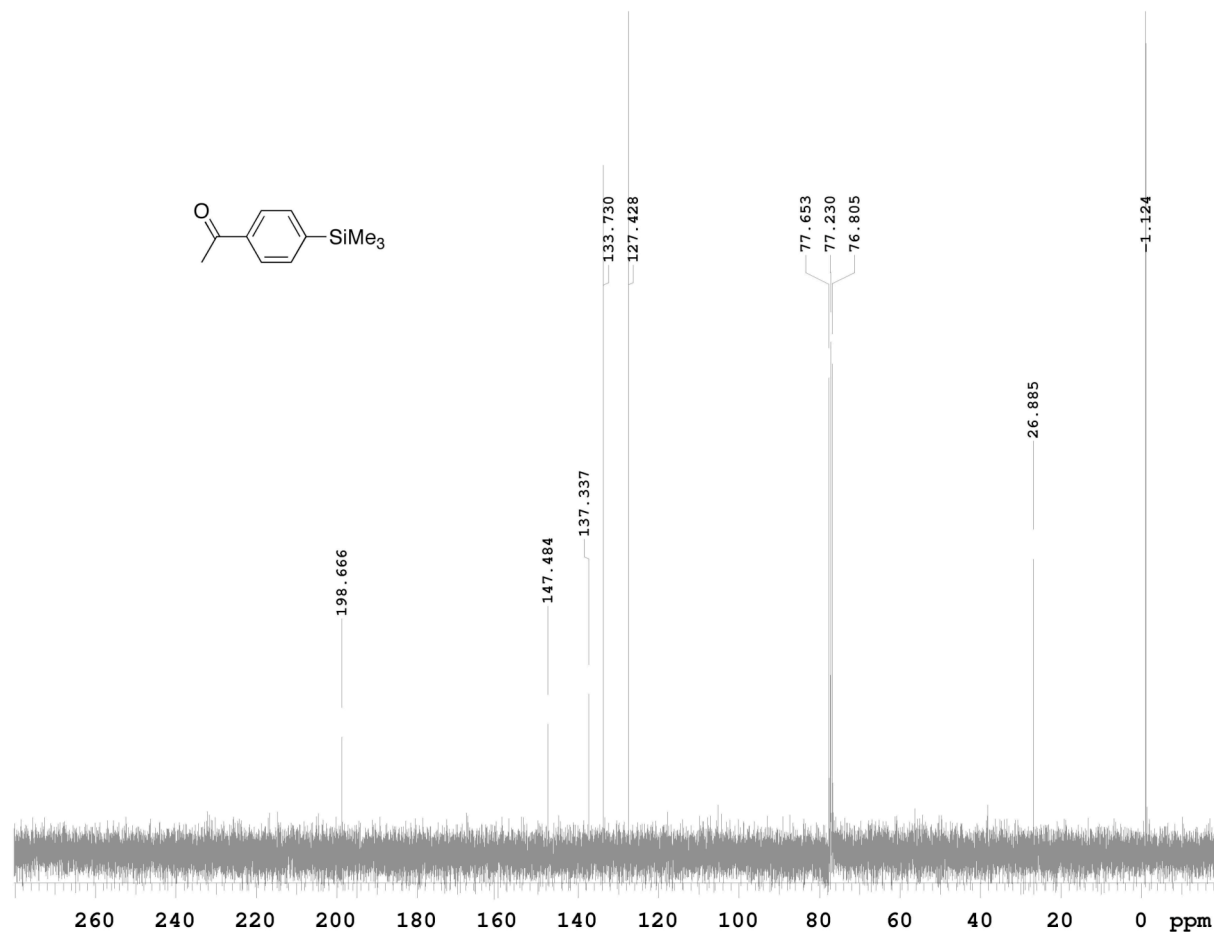


2-Trimethylsilylanthracene (Table 2, entry 10). Following procedure A, a mixture of 2-chloroanthracene (1.0 mmol, 213 mg), KF (5 mmol, 290 mg), hexamethyldisilane (1.2 mmol, 250 μ L), Pd₂dba₃ (0.015 mmol, 13.7 mg), **1b** (0.09 mmol, 31.5 mg), and H₂O (2 mmol, 36 μ L) in dioxane (3 mL) was heated to 100 °C with stirring for 24 h. The crude product was purified via column chromatography on silica gel (hexanes) to afford the title compound as a pale yellow solid (173 mg, 69%). MP: 137-139 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.44 (s, 1H), 8.40 (s, 1H), 8.18 (s, 1H), 8.06-7.96 (m, 3H), 7.57 (d, J = 8.4 Hz, 1H), 7.50-7.43 (m, 2H), 0.39 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 137.6, 134.6, 132.1, 132.0, 131.4, 129.1, 128.5, 128.4, 127.3, 126.6, 126.1, 125.6, 125.5, 125.4, -0.9. IR (neat): 2952, 1615, 1384, 1298, 1245, 1078, 961, 910, 896, 873, 834, 743 cm⁻¹. Anal. Calcd. for C₁₇H₁₈Si: C 81.54%, H 7.25%. Found: C 81.48%, H 7.10%.



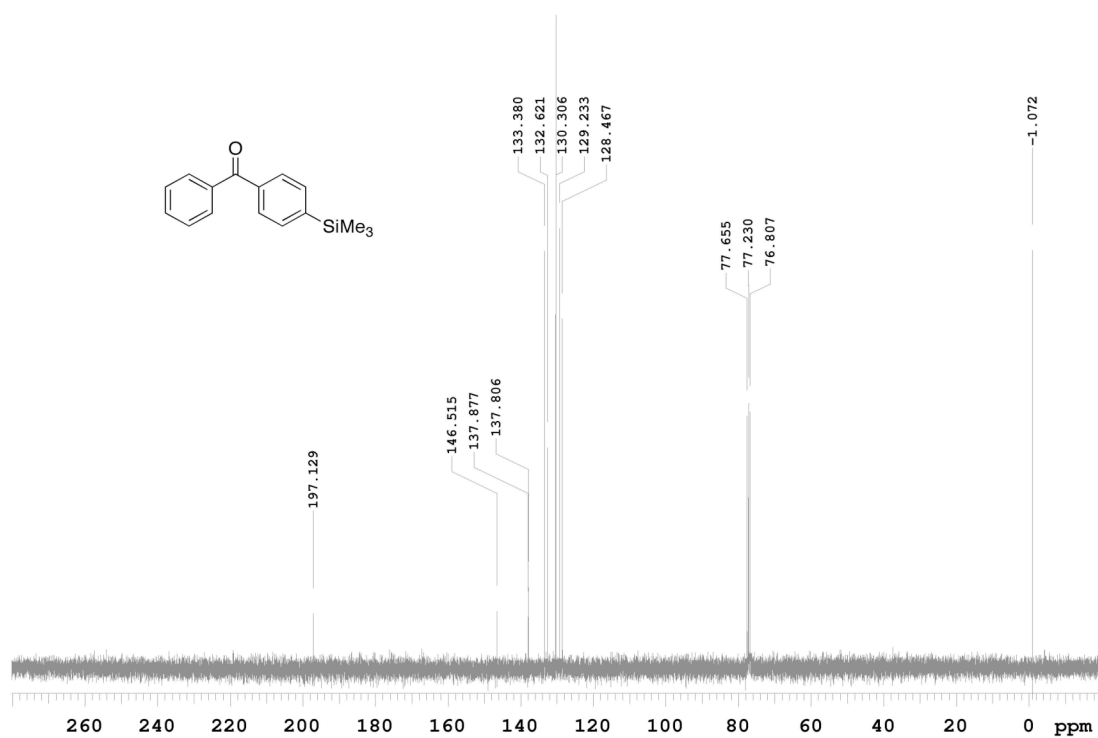
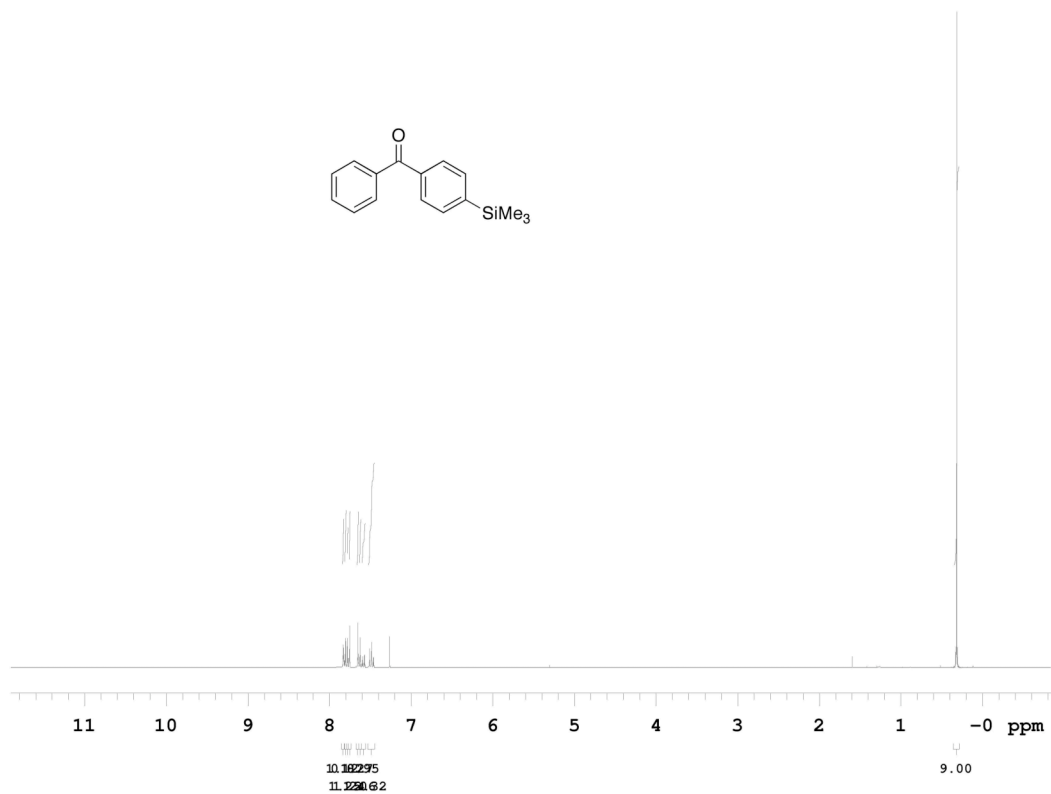
4-Trimethylsilylacetophenone (Table 4, entry 1). Following procedure B, a mixture of 4-chloroacetophenone (1.0 mmol, 155 mg), LiOAc (5 mmol, 330 mg), hexamethyldisilane (1.2 mmol, 250 μ L), Pd₂dba₃ (0.015 mmol, 13.7 mg), **1d** (0.09 mmol, 31.5 mg), and H₂O (2 mmol, 36 μ L) in DMF (3 mL) was heated to 100 °C with stirring for 24 h. The crude product was purified via column chromatography on silica gel (1:50 ethyl acetate:hexanes) to afford the title compound as a colorless oil (183 mg, 95%). ¹H NMR (300 MHz, CDCl₃): δ 7.92 (d, J = 8 Hz, 2H), 7.62 (d, J = 8 Hz, 2H), 2.61 (s, 3H), 0.29 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 198.7, 147.5, 137.3, 133.7, 127.4, 26.9, -1.1. IR (neat): 2957, 1687, 1595, 1388, 1357, 1273, 1250, 1114, 842, 818, 759, 637 cm⁻¹. A satisfactory elemental analysis could not be obtained for this compound. Copies of the ¹H and ¹³C NMR spectra are provided below.

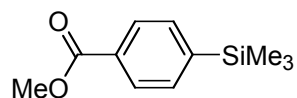




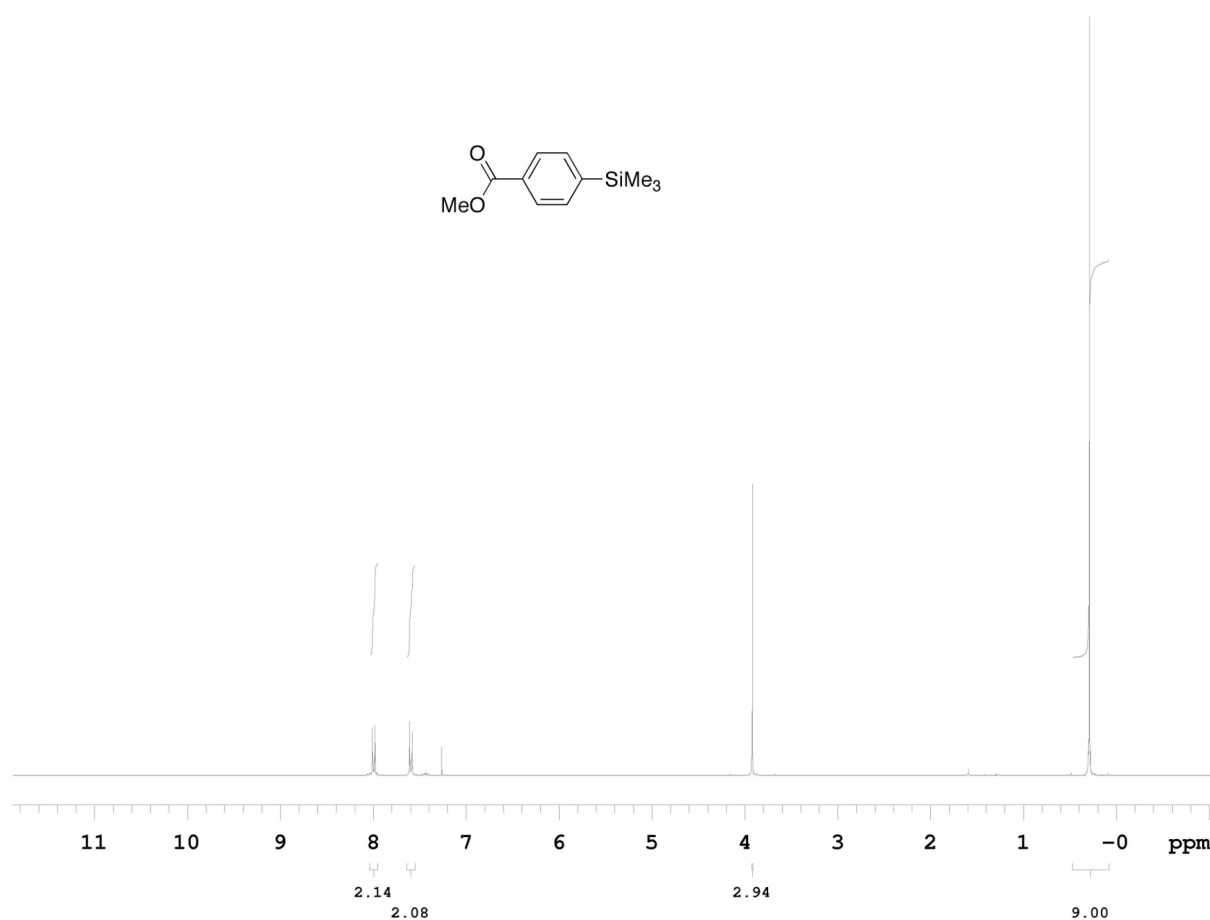
4-Trimethylsilylbenzophenone (Table 4, entry 2). Following procedure B, a mixture 4-chlorobenzophenone (1.0 mmol, 217 mg), LiOAc (5 mmol, 330 mg), hexamethyldisilane (1.2 mmol, 250 μ L), Pd₂dba₃ (0.015 mmol, 13.7 mg), **1d** (0.09 mmol, 31.5 mg), and H₂O (2 mmol, 36 μ L) in DMF (3 mL) was heated to 100 °C with stirring for 24 h. The crude product was purified via column chromatography on silica gel (3:100 ethyl acetate:hexanes) to afford the title compound as a colorless oil (209 mg, 82%). ¹H NMR (300 MHz, CDCl₃): δ 7.83 (m, 1H), 7.80 (m, 1H), 7.78 (m, 1H), 7.76 (m, 1H), 7.65 (m, 1H), 7.63 (m, 1H), 7.58 (m, 1H), 7.52-7.45 (m, 2H), 0.32 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 197.1, 146.5, 137.9, 137.8, 133.4, 132.6, 130.3, 129.2, 128.5, -1.1. IR (neat): 2955, 1660, 1597, 1448, 1388, 1317, 1280, 1249, 1103, 937,

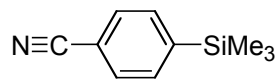
922, 836, 728, 700, 662, 475 cm^{-1} . A satisfactory elemental analysis could not be obtained for this compound. Copies of the ^1H and ^{13}C NMR spectra are provided below.



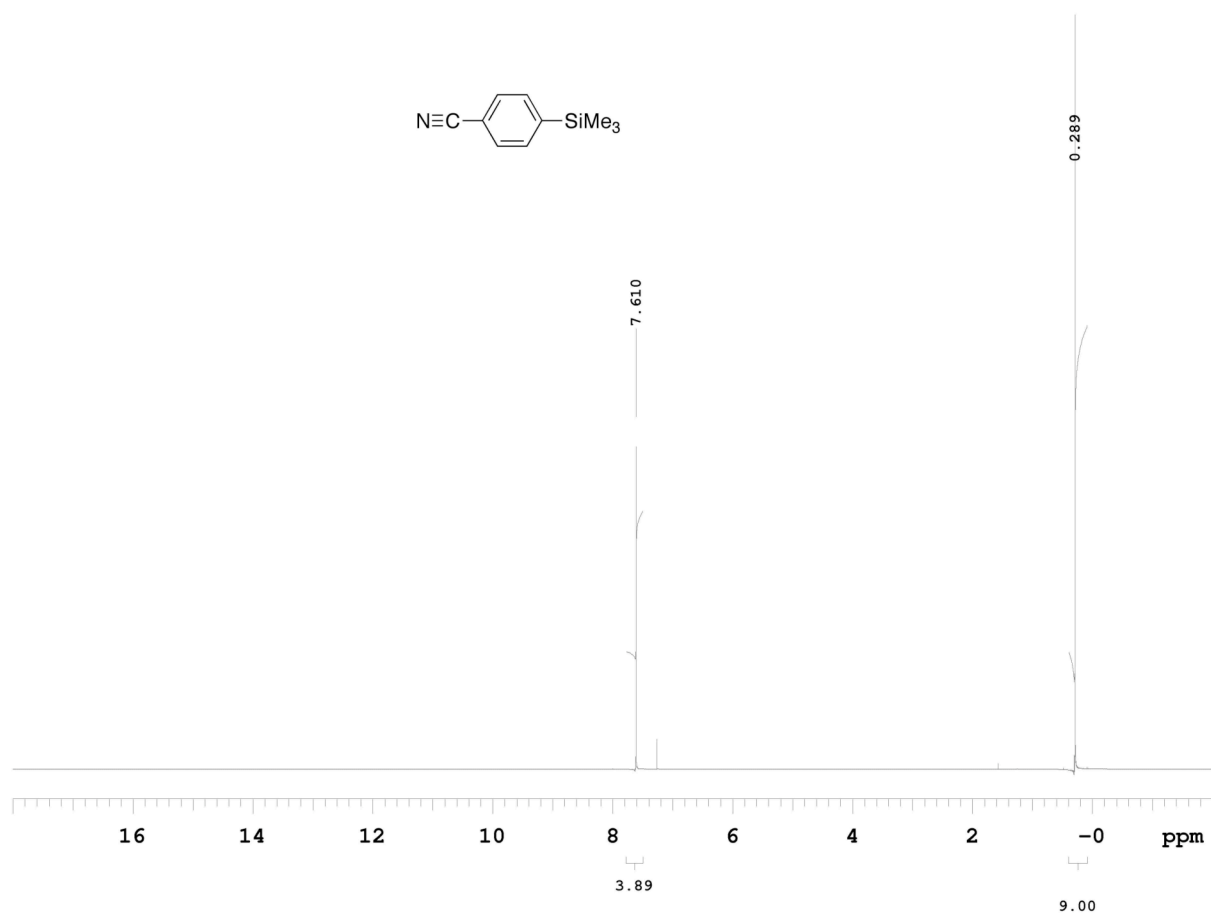


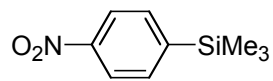
Methyl 4-trimethylsilylbenzoate (Table 4, entry 3).¹⁴ Following procedure B, a mixture of methyl 4-chlorobenzoate (1.0 mmol, 171 mg), LiOAc (5 mmol, 330 mg), hexamethyldisilane (1.2 mmol, 250 μ L), Pd₂dba₃ (0.015 mmol, 13.7 mg), **1d** (0.09 mmol, 31.5 mg), and H₂O (2 mmol, 36 μ L) in DMF (3 mL) was heated to 100 °C with stirring for 24 h. The crude product was purified via column chromatography on silica gel (1:50 ether:hexanes) to afford the title compound as a colorless oil (150 mg, 72%). ¹H NMR (300 MHz, CDCl₃): δ 7.99 (d, J = 8 Hz, 2H), 7.59 (d, J = 8 Hz, 2H), 3.92 (s, 3H), 0.29 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 167.6, 147.1, 133.5, 130.5, 128.7, 52.3, -1.1. A copy of the ¹H NMR spectrum is provided below.



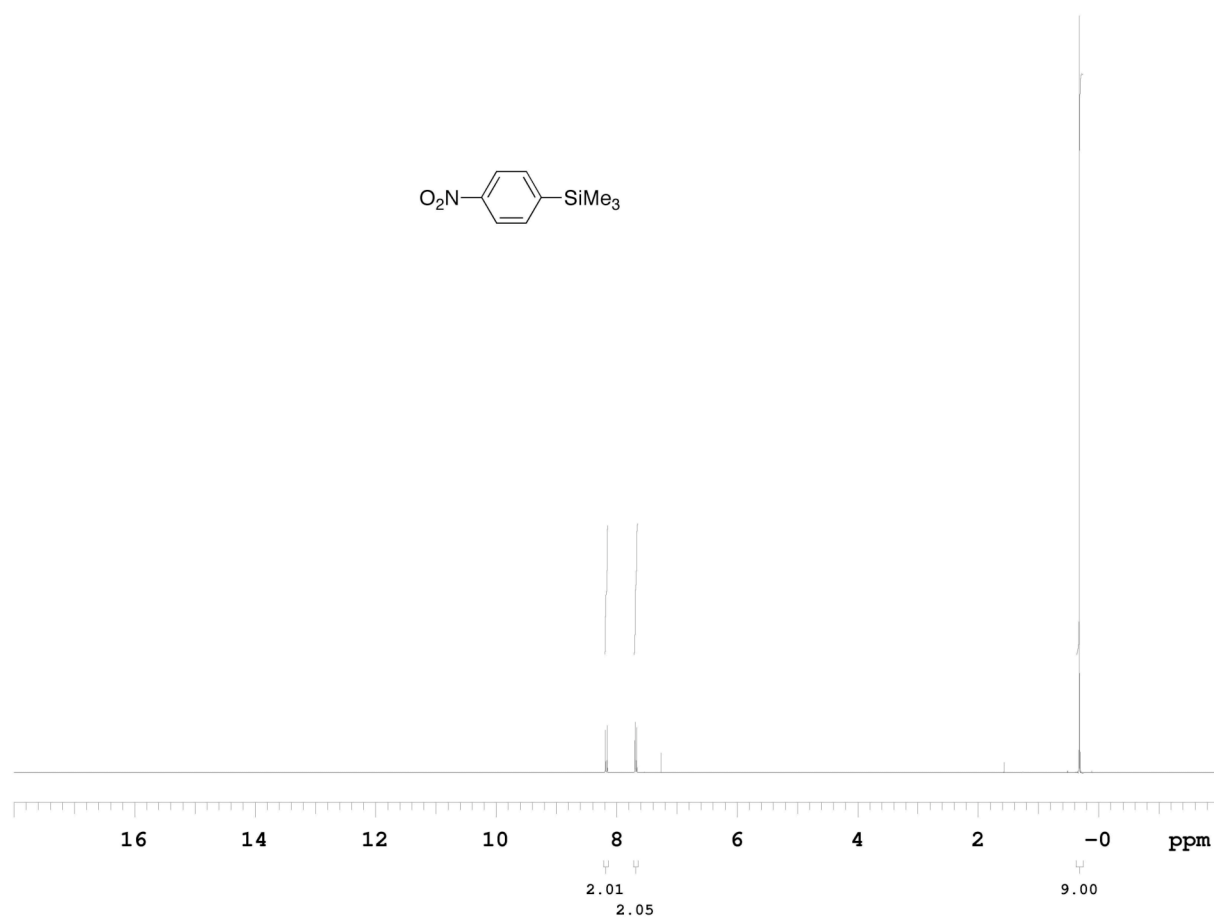


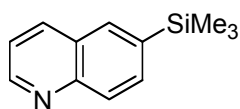
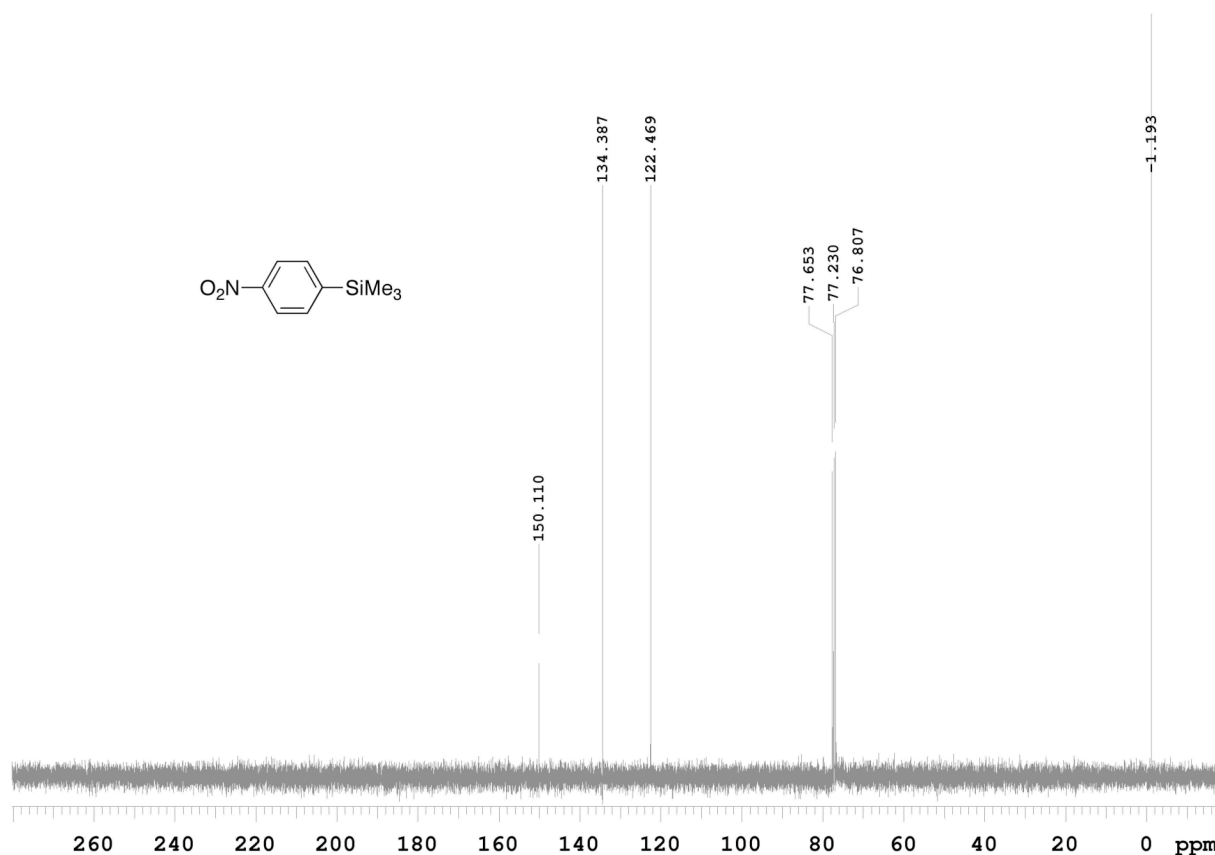
(4-Cyanophenyl)trimethylsilane (Table 4, entry 4).^[31] Following procedure B, a mixture of 4-chlorobenzonitrile (1.0 mmol, 138 mg), LiOAc (5 mmol, 330 mg), hexamethyldisilane (1.2 mmol, 250 μ L), Pd₂dba₃ (0.015 mmol, 13.7 mg), **1d** (0.09 mmol, 31.5 mg), and H₂O (2 mmol, 36 μ L) in DMF (3 mL) was heated to 100 °C with stirring for 24 h. The crude product was purified via column chromatography on silica gel (1:50 ether:hexanes) to afford the title compound as a colorless oil (143 mg, 81%). ¹H NMR (300 MHz, CDCl₃): δ 7.61 (s, 4H), 0.29 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 147.6, 134.0, 131.2, 119.3, 112.5, -1.3. IR (neat): 2958, 2229, 1385, 1251, 1103, 844, 821, 759, 714, 634, 552 cm⁻¹. A copy of the ¹H NMR spectrum is provided below.



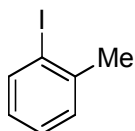


(4-Nitrophenyl)trimethylsilane (Table 4, entry 5). Following procedure B, a mixture of 1-chloro-4-nitrobenzene (1.18 mmol, 186 mg), LiOAc (5 mmol, 330 mg), hexamethyldisilane (1.2 mmol, 250 μL), Pd_2dba_3 (0.015 mmol, 13.7 mg), **1d** (0.09 mmol, 31.5 mg), and H_2O (2 mmol, 36 μL) in DMF (3 mL) was heated to 100 $^\circ\text{C}$ with stirring for 24 h. The crude product was purified via column chromatography on silica gel (hexanes) to afford the title compound as a colorless solid (176 mg, 76%). ^1H NMR (300 MHz, CDCl_3): δ 8.17 (d, $J = 8$ Hz, 2H), 7.68 (d, $J = 8$ Hz, 2H), 0.32 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ 150.1, 134.4, 122.5, -1.2. IR (neat): 3451, 2959, 1595, 1515, 1385, 1354, 1251, 1112, 1097, 911, 835, 731, 628, 470 cm^{-1} . A satisfactory elemental analysis could not be obtained for this compound. Copies of the ^1H and ^{13}C NMR spectra are provided below.

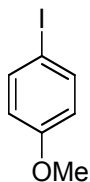




6-Trimethylsilylquinoline (Table 4, entry 6). Following procedure B, a mixture of 6-chloroquinoline (1.0 mmol, 164 mg), LiOAc (5 mmol, 330 mg), hexamethyldisilane (1.2 mmol, 250 μL), Pd_2dba_3 (0.015 mmol, 13.7 mg), **1d** (0.09 mmol, 31.5 mg), and H_2O (2 mmol, 36 μL) in DMF (3 mL) was heated to 100 $^\circ\text{C}$ with stirring for 24 h. The crude product was purified via column chromatography on silica gel (1:10 ethyl acetate:hexanes) to afford the title compound as a pale yellow oil (173 mg, 86%). ^1H NMR (300 MHz, CDCl_3): δ 8.91 (dd, $J = 4$ Hz, 2 Hz, 1H), 8.16 (d, $J = 8$ Hz, 1H), 8.08 (d, $J = 8$ Hz, 1H), 7.97 (s, 1H), 7.85 (dd, $J = 8$ Hz, 1Hz, 1H), 7.40 (dd, $J = 8$ Hz, 4 Hz, 1H), 0.36 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ 150.9, 148.7, 139.5, 136.3, 133.84, 133.75, 128.6, 127.9, 121.3, -0.9. IR (neat): 3060, 3022, 2955, 2897, 1939, 1615, 1585, 1566, 1492, 1449, 1420, 1370, 1249, 1154, 1123, 1083, 948, 876, 840, 771, 751, 694, 647, 618, 504, 478 cm^{-1} . Anal. Calcd. for $\text{C}_{12}\text{H}_{15}\text{NSi}$: C 71.58%, H 7.51%. Found: C 71.81%, H 7.72%.



2-Iodotoluene (Table 5, entry 1).^[5] Following the procedure for the one-pot sequential trimethylsilylation/iodination of electron-rich aryl chlorides, a mixture of 2-chlorotoluene (1.0 mmol, 127 mg), KF (5 mmol, 290 mg), hexamethyldisilane (1.2 mmol, 250 μ L), Pd₂dba₃ (0.015 mmol, 13.7 mg), **1b** (0.09 mmol, 31.5 mg), and H₂O (2 mmol, 36 μ L) in 1,4-dioxane was heated to 100 °C with stirring for 24 h. The reaction was then cooled to rt, iodine monochloride (1.5 mmol, 1.0 M solution in CH₂Cl₂) was added via syringe, and the reaction was stirred for 4 h at rt. After workup, the crude product was purified by column chromatography on silica gel (hexanes) to afford the title compound as a colorless oil (111 mg, 51%). ¹H NMR (300 MHz, CDCl₃): δ 7.81 (d, *J* = 8 Hz, 1H), 7.24 (dd, *J* = 5 Hz, 1 Hz, 2H), 6.90-6.80 (m, 1H), 2.43 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 141.6, 139.1, 130.0, 128.4, 127.6, 101.4, 28.4. Anal. Calcd. for C₇H₇I: C 38.56%, H 3.24%. Found: C 38.56%, H 3.29%.



4-iodoanisole (Table 5, entry 2).^[6] Following the procedure for the one-pot sequential trimethylsilylation/iodination of electron-rich aryl chlorides, a mixture of 4-chloroanisole (1.0 mmol, 143 mg), KF (5 mmol, 290 mg), hexamethyldisilane (1.2 mmol, 250 μ L), Pd₂dba₃ (0.015 mmol, 13.7 mg), **1b** (0.09 mmol, 31.5 mg), and H₂O (2 mmol, 36 μ L) in 1,4-dioxane was heated to 100 °C with stirring for 24 h. The reaction was then cooled to rt, iodine monochloride (1.5 mmol, 1.0 M solution in CH₂Cl₂) was added via syringe, and the reaction was stirred for 4 h at rt. After workup, the crude product was purified by column chromatography on silica gel (hexanes) to afford the title compound as a white solid (188 mg, 80%). MP: 50-52 °C (lit. 50-53 °C). ¹H NMR (300 MHz, CDCl₃): δ 7.56 (d, *J* = 9 Hz, 2H), 6.69 (d, *J* = 9 Hz, 2H), 3.78 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 159.6, 138.4, 116.5, 82.9, 55.5. Anal. Calcd. for C₇H₇IO: C 35.92%, H 3.01%. Found: C 36.12%, H 3.02%.

References

- (1) Itami, K.; Terakawa, K.; Yoshida, J.; Kajimoto, O. *J. Am. Chem. Soc.* **2003**, *125*, 6058-6059.
- (2) Hevesi, L.; Dehon, M.; Crutzen, R.; Lazarescu-Grigore, A. *J. Org. Chem.* **1997**, *62*, 2011-2017.
- (3) van Walree, C. A.; Lauteslager, X. Y.; van Wageningen, A. M. A.; Zwikker, J. W.; Jenneskens, L. W. *J. Organomet. Chem.* **1995**, *496*, 117-125.
- (4) Tobisu, M.; Kita, Y.; Chatani, N. *J. Am. Chem. Soc.* **2006**, *128*, 8152-8153.
- (5) Bailey, W. F.; Cioffi, E. A.; Wiberg, K. B. *J. Org. Chem.* **1981**, *46*, 4219-4225.
- (6) Wan, S.; Wang, S. R.; Lu, W. *J. Org. Chem.* **2006**, *71*, 4349-4352.