Palladium-Catalyzed Silylation of Aryl Bromides Leading to Functionalized Aryldimethylsilanols

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SUPPORTING INFORMATION

General Experimental

All reactions were performed in oven (140 °C) and/or flame dried glassware under an atmosphere of dry nitrogen or argon, unless noted. Reaction solvents tetrahydrofuran (Fisher, HPLC grade), diethyl ether (Fisher, BHT stabilized ACS grade) and methylene chloride (Fisher, unstabilized HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvents hexane (Fisher, OPTIMA grade) and toluene (Fisher, ACS grade) were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon. Reaction solvents 1-methyl-2-pyrrolidinone (Aldrich anhydrous) and acetonitrile (Fisher, HPLC grade) were used without further purification. Solvents for filtration and chromatography were certified ACS grade. “Brine” refers to a saturated solution of sodium chloride. All reaction temperatures correspond to internal temperatures measured with Teflon coated thermocouples.

¹H and ¹³C NMR were recorded on a Varian Unity 500 (500 MHz, ¹H; 126 MHz, ¹³C) spectrometer. Spectra were referenced to residual chloroform (7.26 ppm, ¹H; 77.0 ppm, ¹³C). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory. Mass Spectrometry was performed by the University of Illinois Mass Spectrometer Center. Electron Impact (EI) spectra were performed on a Finnagin-MAT C5 spectrometer. Electrospray ionization (ESI) was performed on a Micromass Quattro spectrometer. Data are reported in the form of *m/z* (intensity relative to the base peak = 100). Infrared spectra (IR) were recorded on a Perkin Elmer Spectrum BX spectrophotometer in NaCl

cells. Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%), w (weak, 0-33%). Kugelrohr distillations were performed on a Büchi GKR-50 Kugelrohr and boiling points correspond to uncorrected air bath temperatures (ABT). Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV(254) or potassium permanganate (KMnO_4). Column chromatography was performed using 230-400 mesh silica gel purchased from EM Science.

Analytical gas chromatography (GC) was performed using a Hewlett-Packard 5890 Series II Gas Chromatograph fitted with a flame ionization detector. GC Method 1: Injections were made onto a Hewlett-Packard HP-1 (50 meter) capillary column. Injector temperature was 250°C ; the detector temperature was 300°C with a H_2 carrier gas flow of 16.7 mL/min. The column oven temperature program is as follows: 75°C for 0 minutes, 75°C to 250°C ramp at $30^\circ\text{C}/\text{minute}$, 250°C for 6.2 minutes. Total run time is 12 minutes. Retention times (t_R) were obtained using Agilent Chemstation software. Measurement of pH was performed using a Metrohm model 691 pH meter equipped with a Metrohm combined LL micro pH glass electrode (6.0234.110) calibrated prior to use with pH = 2 and 9 buffers.

4-Iodoanisole (Aldrich), 4'-iodoacetophenone (Aldrich), 4-iodonitrobenzene (Aldrich), 4'-bromoacetophenone (Acros), 4-bromonitrobenzene (TCI), 2-bromobenzonitrile (Acros) were purified by recrystallization from EtOH prior to use. 4-bromoanisole (Acros), ethyl 4-bromobenzoate (Acros), 4-bromobenzonitrile (Acros), 4-bromotoluene (Aldrich), ethyl 2-bromobenzoate (Acros), 2-bromoanisole (Acros), and acetyl chloride (Acros) were purified by distillation prior to use. Diisopropylethylamine, triethylamine, pyridine and diisopropylamine were distilled from CaH_2 prior to use. Hexamethyldisilane (Gelest), ethoxydimethylsilane (Gelest), aluminum chloride (EM Science), palladium chloride (Fluka), 2-(di-*t*-butylphosphino)biphenyl (Strem), bis(diphenylphosphino)propane (Aldrich), $\text{Pd}(\text{PPh}_3)\text{Cl}_2$ (Strem), allyl palladium chloride dimer (Acros), 2,6-lutidine (Aldrich), KH_2PO_4 (Fisher) and 2-(dimethylamino)ethanethiol hydrochloride (Aldrich) were used as received.

Literature Preparations

4-[(2-Tetrahydropyranyloxy)methyl]bromobenzene was prepared by the literature procedure.¹

Response Factors

Response factors (Rf) for quantitative GC analysis for GC Method 1 were obtained by the equation below:

$$\text{Eq 1: Response factor for A} = \frac{(\text{mmol A} * \text{area naphthalene})}{(\text{mmol naphthalene} * \text{area A})}$$

naphthalene (mmol)	naphthalene (area)	ethyl 4-bromobenzoate (mmol)	ethyl 4-bromobenzoate (area)	Response factor (Rf)
0.1092	6.31e6	0.0716	2.47e6	1.27
0.1092	5.50e6	0.0716	2.28e6	1.25
0.1092	7.27e6	0.0716	3.02e6	1.30
0.1248	5.85e6	0.0803	2.41e6	1.27
0.1248	8.27e6	0.0803	3.54e6	1.25
0.1248	6.04e6	0.0803	2.37e6	1.28

naphthalene (mmol)	naphthalene (area)	silylation product 3d (mmol)	silylation product 3d (area)	Response factor (Rf)
0.1006	1.69e7	0.0416	5.33e6	1.28
0.1006	9.41e6	0.0416	3.39e6	1.12
0.1006	1.40e7	0.0416	4.70e6	1.20
0.1069	1.95e7	0.0475	6.96e6	1.22
0.1069	1.72e7	0.0475	6.48e6	1.15
0.1069	1.28e7	0.0475	4.63e6	1.20

naphthalene (mmol)	naphthalene (area)	silanol product 8d (mmol)	silanol product 8d (area)	Response factor (Rf)
0.0944	1.05e7	0.0490	5.21e6	1.05
0.0944	1.57e7	0.0490	7.54e6	1.08
0.0944	1.05e7	0.0490	5.26e6	1.04
0.0694	9.76e6	0.0503	6.58e6	1.08
0.0694	1.26e7	0.0503	8.55e6	1.07
0.0694	8.16e6	0.0503	5.63e6	1.05

naphthalene (mmol)	naphthalene (area)	disiloxane product 9d (mmol)	disiloxane product 9d (area)	Response factor (Rf)
0.0749	2.56e6	0.0272	1.05e6	0.89
0.0749	3.62e6	0.0272	1.54e6	0.85
0.0749	2.41e6	0.0272	1.03e6	0.85
0.1045	3.89e6	0.0353	1.61e6	0.82
0.1045	4.22e6	0.0353	1.80e6	0.79
0.1045	3.42e6	0.0353	1.34e6	0.87

Preparation of 1,2-Dichloro-1,1,2,2-tetramethyldisilane

A 500-mL, 3-neck, flame-dried, round-bottom flask purged with nitrogen containing aluminum chloride (109 g, 820 mmol, 2.05 equiv) in CH_2Cl_2 (250 mL) was cooled to 0 °C in an ice bath. To this slurry, acetyl chloride (56.5 mL, 820 mmol, 2.05 equiv) was added over 20 min. The resulting solution was added to a solution of hexamethyldisilane (58.6 g, 400 mmol) in CH_2Cl_2 (150 mL) at 0 °C in a 1-L 3-neck, round-bottom flask over 30 min while maintaining a temperature below 20 °C. The reaction flask was equipped with a reflux condenser and the reaction mixture was heated under nitrogen at 40 °C for 12 h after which time ~300 mL of the CH_2Cl_2 was removed by distillation. The remaining orange solution was cooled to rt and pentane (300 mL) was added. The resulting bottom layer was removed via cannulation under nitrogen and was extracted with pentane (2 x 150 mL).² Removal of the pentane by distillation left the crude product which was further purified by fractional distillation affording 56.53 g (76%) of 1,2-dichloro-1,1,2,2-tetramethyldisilane. The spectroscopic data matched those from the literature.³

Data for 1, 2-Dichloro-1,1,2,2-tetramethyldisilane:

bp: 143-148 °C
¹H NMR: (500 MHz, CDCl_3)
0.58 (s, 12 H).
¹³C NMR: (126 MHz, CDCl_3)
1.2

Preparation of 1,2-Diethoxy-1,1,2,2-tetramethyldisilane (5)

To 1-L, round-bottom flask containing a solution of 1,2-dichloro-1,1,2,2-tetramethyldisilane (37.2 g, 199 mmol) in CH_2Cl_2 (250 mL) at 0 °C was added ethanol (24.4 mL, 418 mmol, 2.1 equiv) followed by addition of triethylamine (58.3 mL, 418 mmol, 2.1 equiv) over 30 min. After being stirred at 0 °C for 30 min the white slurry was filtered through Celite and the filter cake was washed with pentane (150 mL). The filtrate was then condensed *in vacuo* to afford a cloudy mixture. Pentane (200 mL) was added to the resulting mixture which was once again filtered and washed with pentane (2 x 25 mL). Condensation of this second filtrate gave a clear solution which was purified further by short path distillation to afford 33.67 g (82%) of **5** as a clear, colorless liquid.

Data for 5:

bp: 90-93 °C (50 mmHg)

¹H NMR: (400 MHz, CDCl_3)

3.66 (q, $J = 7.2$, 4 H, HC(2)), 1.18 (t, $J = 7.0$, 6 H, HC(3)), 0.23 (s, 6 H, HC(1)).

¹³C NMR: (100 MHz, CDCl_3)

59.9 C(2), 18.6 C(3), -0.2 C(1).

General Procedure I: Palladium-Catalyzed Silylation of Aryl Iodides using Ethoxydimethylsilane

To a 5-mL, 2-neck, oven-dried, round-bottom flask purged with argon containing palladium chloride (4.4 mg, 0.025 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (15 mg, 0.05 mmol, 0.1 equiv) and the aryl iodide (0.5 mmol), was added 1-methyl-2-pyrrolidinone (1.0 mL) and diisopropylethylamine (0.26 mL, 1.5 mmol, 3.0 equiv). The reaction mixture was stirred for 30 min at rt under an argon atmosphere before addition of ethoxydimethylsilane (57 mg, 0.55 mmol, 1.1 equiv) and continued to be stirred at rt under an argon atmosphere. The progress of the reaction was monitored by GC as follows: an aliquot of the reaction mixture was filtered through a small amount of silica gel and analyzed by GC Method 1.

Table 1, entry 1:

Following General Procedure I, palladium chloride (4.4 mg, 0.025 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (15 mg, 0.05 mmol, 0.1 equiv), 4-iodoanisole (117 mg, 0.5 mmol), 1-methyl-2-pyrrolidinone (1.0 mL), diisopropylethylamine (0.26 mL, 1.5 mmol, 3.0 equiv) and ethoxydimethylsilane (57 mg, 0.55 mmol, 1.1 equiv) were stirred at rt for 30 min. An aliquot of the reaction mixture was analyzed by GC Method 1. **4a**, t_R 0.94 min (7%); **3a**, t_R 3.1 min (93%).

Table 1, entry 2:

Following General Procedure I, palladium chloride (4.4 mg, 0.025 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (15 mg, 0.05 mmol, 0.1 equiv), 4'-iodoacetophenone (123 mg, 0.5 mmol), 1-methyl-2-pyrrolidinone (1.0 mL), diisopropylethylamine (0.26 mL, 1.5 mmol, 3.0 equiv) and ethoxydimethylsilane (57 mg, 0.55 mmol, 1.1 equiv) were stirred at rt for 30 min. An aliquot of the reaction mixture was analyzed by GC Method 1. **4b**, t_R 1.5 min (64%); **3b**, t_R 3.8 min (35%).

Table 1, entry 3:

Following General Procedure I, palladium chloride (4.4 mg, 0.025 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (15 mg, 0.05 mmol, 0.1 equiv), 4-iodonitrobenzene (125 mg, 0.5 mmol), 1-methyl-2-pyrrolidinone (1.0 mL), diisopropylethylamine (0.26 mL, 1.5 mmol, 3.0 equiv) and ethoxydimethylsilane (57 mg, 0.55 mmol, 1.1 equiv) were stirred at rt for 30 min. An aliquot of the reaction mixture was analyzed by GC Method 1. **4c**, t_R 1.6 min (90%); **3c**, t_R 3.9 min (5%).

General Procedure II: Palladium-Catalyzed Silylation of Aryl Halides using 1,2-Diethoxy-1,1,2,2-tetramethyldisilane

To a 5-mL 2-neck, oven-dried, round-bottom flask purged with argon containing palladium chloride (4.4 mg, 0.025 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (15 mg, 0.05 mmol, 0.1 equiv) and the aryl halide (0.5 mmol), was added 1-methyl-2-pyrrolidinone (1.0 mL) and diisopropylethylamine (0.26 mL, 1.5 mmol, 3.0 equiv). The reaction mixture was stirred for the specified time and temperature under an argon atmosphere before addition of 1,2-diethoxy-1,1,2,2-tetramethyldisilane (113 mg, 0.55 mmol, 1.1 equiv) and continued to be stirred

at the specified temperature under an argon atmosphere. The progress of the reaction was monitored by GC as follows: an aliquot of the reaction mixture was filtered through a small amount of silica gel and analyzed by GC Method 1.

Table 2, entry 1:

Following General Procedure II, palladium chloride (4.4 mg, 0.025 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (15 mg, 0.05 mmol, 0.1 equiv), 4-iodoanisole (117 mg, 0.5 mmol), 1-methyl-2-pyrrolidinone (1.0 mL) and diisopropylethylamine (0.26 mL, 1.5 mmol, 3.0 equiv) were stirred at rt for 30 min before addition of 1,2-diethoxy-1,1,2,2-tetramethyldisilane (113 mg, 0.55 mmol, 1.1 equiv). The reaction mixture was stirred at rt for 48 h. An aliquot of the mixture was analyzed by GC Method 1. **4a**, t_R 0.94 min (17%); **2a**, t_R 2.7 min (1%); **3a**, t_R 3.1 min (66%); **6a**, t_R 5.3 min (16%).

Table 2, entry 2:

Following General Procedure II, palladium chloride (4.4 mg, 0.025 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (15 mg, 0.05 mmol, 0.1 equiv), 4-iodoanisole (117 mg, 0.5 mmol), 1-methyl-2-pyrrolidinone (1.0 mL) and diisopropylethylamine (0.26 mL, 1.5 mmol, 3.0 equiv) were stirred at rt for 10 min before addition of 1,2-diethoxy-1,1,2,2-tetramethyldisilane (113 mg, 0.55 mmol, 1.1 equiv). The reaction mixture was heated at 60 °C for 2 h. An aliquot of the mixture was analyzed by GC Method 1. **4a**, t_R 0.94 min (4%); **2a**, t_R 2.7 min (0%); **3a**, t_R 3.1 min (54%); **6a**, t_R 5.3 min (41%).

Table 2, entry 3:

Following General Procedure II, palladium chloride (4.4 mg, 0.025 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (15 mg, 0.05 mmol, 0.1 equiv), 4-bromoanisole (94 mg, 0.5 mmol), 1-methyl-2-pyrrolidinone (1.0 mL) and diisopropylethylamine (0.26 mL, 1.5 mmol, 3.0 equiv) were stirred at rt for 10 min before addition of 1,2-diethoxy-1,1,2,2-tetramethyldisilane (113 mg, 0.55 mmol, 1.1 equiv). The reaction mixture was heated at 60 °C for 10 h. An aliquot of the mixture was analyzed by GC Method 1. **4a**, t_R 0.94 min (3%); **7a**, t_R 2.2 min (2%); **3a**, t_R 3.1 min (94%); **6a**, t_R 5.3 min (1%).

Table 2, entry 4:

Following General Procedure II, palladium chloride (2.2 mg, 0.0125 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (7.5 mg, 0.025 mmol, 0.1 equiv), ethyl 4-bromobenzoate (58 mg, 0.25 mmol), 1-methyl-2-pyrrolidinone (0.5 mL) and diisopropylethylamine (0.2136 mL, 0.75 mmol, 3.0 equiv) were stirred at 60 °C for 10 min before addition of 1,2-diethoxy-1,1,2,2-tetramethyldisilane (57 mg, 0.275 mmol, 1.1 equiv). The reaction mixture was stirred at 60 °C for 10 h. An aliquot of the mixture was analyzed by GC Method 1. **4d**, t_R 2.1 min (2%); **7d**, t_R 3.3 min (0%); **3d**, t_R 4.3 min (93%); **6d**, t_R 7.7 min (5%).

General Procedure III: Palladium-Catalyzed Silylation of Ethyl 4-Bromobenzoate using 1,2-Diethoxy-1,1,2,2-tetramethyldisilane

To a 5-mL 2-neck, oven-dried, round-bottom flask purged with argon containing the palladium (0.05 equiv), ligand (0.1 equiv) and ethyl 4-bromobenzoate (58 mg, 0.25 mmol, 1.0 equiv), was added 1-methyl-2-pyrrolidinone (0.5 mL) and base (1.1 to 3.0 equiv). The reaction mixture was stirred for 10 min at 60 °C under an argon atmosphere before addition of 1,2-diethoxy-1,1,2,2-tetramethyldisilane (57 mg, 0.275 mmol, 1.1 equiv) and continued to be stirred at 60 °C under an argon atmosphere. The progress of the reaction was monitored by GC as follows: an aliquot of the reaction mixture was filtered through a small amount of silica gel and analyzed by GC Method 1.

Table 3, entry 1

Following General Procedure III, palladium chloride (2.2 mg, 0.0125 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (7.5 mg, 0.025 mmol, 0.1 equiv), ethyl 4-bromobenzoate (58 mg, 0.25 mmol), 1-methyl-2-pyrrolidinone (0.5 mL), diisopropylethylamine (0.13 mL, 0.75 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (57 mg, 0.275 mmol, 1.1 equiv) were stirred at 60 °C for 2 h. An aliquot of the reaction mixture was analyzed by GC method 1. **3d** t_R 4.25 min (5.078e5, 90%).

Table 3, entry 2

Following General Procedure III, palladium chloride (2.2 mg, 0.0125 mmol, 0.05 equiv), dppb (5.3 mg, 0.0125 mmol, 0.05 equiv), ethyl 4-bromobenzoate (58 mg, 0.25 mmol), 1-methyl-2-pyrrolidinone (0.5 mL), diisopropylethylamine (0.13 mL, 0.75 mmol, 3.0 equiv) and 1,2-

diethoxy-1,1,2,2-tetramethyldisilane (57 mg, 0.275 mmol, 1.1 equiv) were stirred at 60 °C for 2 h. An aliquot of the reaction mixture was analyzed by GC method 1. **3d** t_R 4.25 min (2.474e4, 4%).

Table 3, entry 3

Following General Procedure III, Pd(PPh₃)₂Cl₂ (8.8 mg, 0.0125 mmol, 0.05 equiv), ethyl 4-bromobenzoate (58 mg, 0.25 mmol), 1-methyl-2-pyrrolidinone (0.5 mL), diisopropylethylamine (0.13 mL, 0.75 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (57 mg, 0.275 mmol, 1.1 equiv) were stirred at 60 °C for 2 h. An aliquot of the reaction mixture was analyzed by GC method 1. **3d** t_R 4.25 min (2.84e3, 0.3%).

Table 3, entry 4

Following General Procedure III, Pd(dba)₂ (7.0 mg, 0.0125 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (7.5 mg, 0.025 mmol, 0.1 equiv), ethyl 4-bromobenzoate (58 mg, 0.25 mmol), 1-methyl-2-pyrrolidinone (0.5 mL), diisopropylethylamine (0.13 mL, 0.75 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (57 mg, 0.275 mmol, 1.1 equiv) were stirred at 60 °C for 2 h. An aliquot of the reaction mixture was analyzed by GC method 1. **3d** t_R 4.25 min (3.794e5, 65%).

Table 3, entry 5

Following General Procedure III, allylpalladium chloride dimer (2.3 mg, 0.0063 mmol, 0.025 equiv), 2-(di-*t*-butylphosphino)biphenyl (7.5 mg, 0.025 mmol, 0.1 equiv), ethyl 4-bromobenzoate (58 mg, 0.25 mmol), 1-methyl-2-pyrrolidinone (0.5 mL), diisopropylethylamine (0.13 mL, 0.75 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (57 mg, 0.275 mmol, 1.1 equiv) were stirred at 60 °C for 2 h. An aliquot of the reaction mixture was analyzed by GC method 1. **3d** t_R 4.25 min (4.136e5, 87%).

Table 4, entry 1

Following General Procedure III, palladium chloride (2.2 mg, 0.0125 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (7.5 mg, 0.025 mmol, 0.1 equiv), ethyl 4-bromobenzoate (58 mg, 0.25 mmol), 1-methyl-2-pyrrolidinone (0.5 mL), diisopropylethylamine (0.13 mL, 0.75 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (57 mg, 0.275 mmol, 1.1 equiv)

were stirred at 60 °C for 2 h. An aliquot of the reaction mixture was analyzed by GC method 1. **3d** t_R 4.25 min (5.07794e5, 90%).

Table 4, entry 2

Following General Procedure III, palladium chloride (2.2 mg, 0.0125 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (7.5 mg, 0.025 mmol, 0.1 equiv), ethyl 4-bromobenzoate (58 mg, 0.25 mmol), 1-methyl-2-pyrrolidinone (0.5 mL), diisopropylethylamine (0.05 mL, 0.275 mmol, 1.1 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (57 mg, 0.275 mmol, 1.1 equiv) were stirred at 60 °C for 2 h. An aliquot of the reaction mixture was analyzed by GC method 1. **3d** t_R 4.25 min (1.042e6, 55%).

Table 4, entry 3

Following General Procedure III, palladium chloride (2.2 mg, 0.0125 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (7.5 mg, 0.025 mmol, 0.1 equiv), ethyl 4-bromobenzoate (58 mg, 0.25 mmol), 1-methyl-2-pyrrolidinone (0.5 mL), triethylamine (0.10 mL, 0.75 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (57 mg, 0.275 mmol, 1.1 equiv) were stirred at 60 °C for 2 h. An aliquot of the reaction mixture was analyzed by GC method 1. **3d** t_R 4.25 min (3.006e5, 45%).

Table 4, entry 4

Following General Procedure III, palladium chloride (2.2 mg, 0.0125 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (7.5 mg, 0.025 mmol, 0.1 equiv), ethyl 4-bromobenzoate (58 mg, 0.25 mmol), 1-methyl-2-pyrrolidinone (0.5 mL), pyridine (0.06 mL, 0.75 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (57 mg, 0.275 mmol, 1.1 equiv) were stirred at 60 °C for 2 h. An aliquot of the reaction mixture was analyzed by GC method 1. **3d** t_R 4.25 min (0, 0%).

Table 4, entry 5

Following General Procedure III, palladium chloride (2.2 mg, 0.0125 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (7.5 mg, 0.025 mmol, 0.1 equiv), ethyl 4-bromobenzoate (58 mg, 0.25 mmol), 1-methyl-2-pyrrolidinone (0.5 mL), 2,6-lutidine (0.09 mL, 0.75 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (57 mg, 0.275 mmol, 1.1 equiv) were stirred

at 60 °C for 2 h. An aliquot of the reaction mixture was analyzed by GC method 1. **3d** t_R 4.25 min (0, 0%).

Table 4, entry 6

Following General Procedure III, palladium chloride (2.2 mg, 0.0125 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (7.5 mg, 0.025 mmol, 0.1 equiv), ethyl 4-bromobenzoate (58 mg, 0.25 mmol), 1-methyl-2-pyrrolidinone (0.5 mL), diisopropylamine (0.11 mL, 0.75 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (57 mg, 0.275 mmol, 1.1 equiv) were stirred at 60 °C for 2 h. An aliquot of the reaction mixture was analyzed by GC method 1. **3d** t_R 4.25 min (3.545e3, 0.3%).

Table 4, entry 7

Following General Procedure III, palladium chloride (2.2 mg, 0.0125 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (7.5 mg, 0.025 mmol, 0.1 equiv), ethyl 4-bromobenzoate (58 mg, 0.25 mmol), 1-methyl-2-pyrrolidinone (0.5 mL), potassium dihydrogen phosphate (104 mg, 0.75 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (57 mg, 0.275 mmol, 1.1 equiv) were stirred at 60 °C for 2 h. An aliquot of the reaction mixture was analyzed by GC method 1. **8d**, t_R 4.1 min (2.480e5, 31%); **3d** t_R 4.25 min (9.987e3, 1%).

General Procedure IV: Hydrolysis of 3d using an Acidic or Basic Buffer.

To a 5-mL, 2-neck, oven-dried, round-bottom flask purged with argon containing palladium chloride (8.8 mg, 0.05 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (30 mg, 0.1 mmol, 0.1 equiv) and ethyl 4-bromobenzoate (229 mg, 1.0 mmol), was added 1-methyl-2-pyrrolidinone (2.0 mL) and diisopropylethylamine (0.52 mL, 3.0 mmol, 3.0 equiv). The reaction mixture was stirred for 10 min at 60 °C under an argon atmosphere whereupon 1,2-diethoxy-1,1,2,2-tetramethyldisilane (232 mg, 1.1 mmol, 1.1 equiv) was added. The reaction mixture was stirred at 60 °C for 3 h then was cooled to rt. Without purification, a portion of the homogeneous reaction mixture (0.20 mL) was added to a 1.0 mL conical vial equipped with a magnetic stir bar. Acetonitrile (0.20 mL) and the acidic or basic buffer (0.30 mL) were added. The reaction mixture was stirred at rt for the set time. The reaction mixture was extracted with a small amount of EtOAc. The pH of the aqueous layer was measured. The organic layer was washed with a

10% aqueous solution of 2-(dimethylamino)ethanethiol hydrochloride and then was passed through a small amount of silica gel and then was analyzed by GC Method 1.

Table 5, entry 1

Following General Procedure IV, the silylation reaction mixture (0.20 mL), CH₃CN (0.20 mL) and 10.0 M HOAc (0.3 mL) were stirred at rt for 2 h. Extraction with EtOAc left an aqueous layer with pH = 4.20. The organic layer was washed with a 10% aqueous solution of 2-(dimethylamino)ethanethiol hydrochloride and was passed through a small amount of silica gel followed by analysis with GC Method 1. **8d**, t_R 4.36 min (1.710e6, 74.5%); **3d**, t_R 4.47 min (3.071e3, 1.5%); **9d**, t_R 10.7 min (2.241e4, 2.2%).

Table 5, entry 2

Following General Procedure IV, the silylation reaction mixture (0.20 mL), CH₃CN (0.20 mL) and 2.0 M HOAc (0.3 mL) were stirred at rt for 2 h. Extraction with EtOAc left an aqueous layer with pH = 5.16. The organic layer was washed with a 10% aqueous solution of 2-(dimethylamino)ethanethiol hydrochloride and was passed through a small amount of silica gel followed by analysis with GC Method 1. **8d**, t_R 4.36 min (2.855e6, 83%); **3d**, t_R 4.47 min (5.29e3, 1.7%); **9d**, t_R 10.7 min (1.044e4, 0.7%).

Table 5, entry 3

Following General Procedure IV, the silylation reaction mixture (0.20 mL), CH₃CN (0.20 mL) and 1.0 M HOAc (0.3 mL) were stirred at rt for 2 h. Extraction with EtOAc left an aqueous layer with pH = 5.63. The organic layer was washed with a 10% aqueous solution of 2-(dimethylamino)ethanethiol hydrochloride and was passed through a small amount of silica gel followed by analysis with GC Method 1. **8d**, t_R 4.36 min (8.168e6, 77%); **3d**, t_R 4.47 min (3.059e4, 0.3%); **9d**, t_R 10.7 min (4.139e4, 0.8%).

Table 5, entry 4

Following General Procedure IV, the silylation reaction mixture (0.20 mL), CH₃CN (0.20 mL) and 1.0 M HOAc/NaOAc buffer (pH = 2.89) (0.3 mL) were stirred at rt for 2 h. Extraction with EtOAc left an aqueous layer with pH = 6.17. The organic layer was washed with a 10% aqueous solution of 2-(dimethylamino)ethanethiol hydrochloride and was passed through a small

amount of silica gel followed by analysis with GC Method 1. **8d**, t_R 4.36 min (3.310e6, 80%); **3d**, t_R 4.47 min (8.990e3, 0.3%); **9d**, t_R 10.7 min (9.403e3, 0.5%).

Table 5, entry 5

Following General Procedure IV, the silylation reaction mixture (0.20 mL), CH₃CN (0.20 mL) and 1.0 M HOAc/NaOAc buffer (pH = 3.79) (0.3 mL) were stirred at rt for 2 h. Extraction with EtOAc left an aqueous layer with pH = 6.31. The organic layer was washed with a 10% aqueous solution of 2-(dimethylamino)ethanethiol hydrochloride and was passed through a small amount of silica gel followed by analysis with GC Method 1. **8d**, t_R 4.36 min (9.701e6, 82%); **3d**, t_R 4.47 min (1.329e4, 0.1%); **9d**, t_R 10.7 min (5.110e4, 1.0%).

Table 5, entry 6

Following General Procedure IV, the silylation reaction mixture (0.20 mL), CH₃CN (0.20 mL) and 1.0 M HOAc/NaOAc buffer (pH = 4.92) (0.3 mL) were stirred at rt for 2 h. Extraction with EtOAc left an aqueous layer with pH = 6.97. The organic layer was washed with a 10% aqueous solution of 2-(dimethylamino)ethanethiol hydrochloride and was passed through a small amount of silica gel followed by analysis with GC Method 1. **8d**, t_R 4.36 min (3.871e6, 80%); **3d**, t_R 4.47 min (0, 0%); **9d**, t_R 10.7 min (1.467e4, 0.6%).

Table 5, entry 7

Following General Procedure IV, the silylation reaction mixture (0.20 mL), CH₃CN (0.20 mL) and 1.0 M HOAc/NaOAc buffer (pH = 5.98) (0.3 mL) were stirred at rt for 2 h. Extraction with EtOAc left an aqueous layer with pH = 8.98. The organic layer was washed with a 10% aqueous solution of 2-(dimethylamino)ethanethiol hydrochloride and was passed through a small amount of silica gel followed by analysis with GC Method 1. **8d**, t_R 4.36 min (3.87147e6, 62%); **3d**, t_R 4.47 min (4.520e5, 8%); **9d**, t_R 10.7 min (2.670e5, 10%).

Table 5, entry 8

Following General Procedure IV, the silylation reaction mixture (0.20 mL), CH₃CN (0.20 mL) and 1.0 M KH₂PO₄/K₂HPO₄ buffer (pH = 4.46) (0.3 mL) were stirred at rt for 2 h. Extraction with EtOAc left an aqueous layer with pH = 6.98. The organic layer was washed with a 10% aqueous solution of 2-(dimethylamino)ethanethiol hydrochloride and was passed through

a small amount of silica gel followed by analysis with GC Method 1. **8d**, t_R 4.36 min (1.052e6, 25%); **3d**, t_R 4.47 min (2.630e6, 71%); **9d**, t_R 10.7 min (6.207e3, 0.3%).

Table 5, entry 9

Following General Procedure IV, the silylation reaction mixture (0.20 mL), CH₃CN (0.20 mL) and 1.0 M KH₂PO₄/K₂HPO₄ buffer (pH = 5.44) (0.3 mL) were stirred at rt for 2 h. Extraction with EtOAc left an aqueous layer with pH = 7.25. The organic layer was washed with a 10% aqueous solution of 2-(dimethylamino)ethanethiol hydrochloride and was passed through a small amount of silica gel followed by analysis with GC Method 1. **8d**, t_R 4.36 min (9.496e5, 17%); **3d**, t_R 4.47 min (4.516e6, 88%); **9d**, t_R 10.7 min (8.482e3, 0.3%).

Table 5, entry 10

Following General Procedure IV, the silylation reaction mixture (0.20 mL), CH₃CN (0.20 mL) and 1.0 M KH₂PO₄/K₂HPO₄ buffer (pH = 6.70) (0.3 mL) were stirred at rt for 2 h. Extraction with EtOAc left an aqueous layer with pH = 8.62. The organic layer was washed with a 10% aqueous solution of 2-(dimethylamino)ethanethiol hydrochloride and was passed through a small amount of silica gel followed by analysis with GC Method 1. **8d**, t_R 4.36 min (1.120e6, 18%); **3d**, t_R 4.47 min (4.538e6, 80%); **9d**, t_R 10.7 min (2.371e4, 0.8%).

Table 5, entry 11

Following General Procedure IV, the silylation reaction mixture (0.20 mL), CH₃CN (0.20 mL) and 1.0 M KH₂PO₄/K₂HPO₄ buffer (pH = 7.96) (0.3 mL) were stirred at rt for 2 h. Extraction with EtOAc left an aqueous layer with pH = 9.06. The organic layer was washed with a 10% aqueous solution of 2-(dimethylamino)ethanethiol hydrochloride and was passed through a small amount of silica gel followed by analysis with GC Method 1. **8d**, t_R 4.36 min (2.523e6, 63%); **3d**, t_R 4.47 min (3.133e5, 9%); **9d**, t_R 10.7 min (1.910e5, 11%).

Table 5, entry 12

Following General Procedure IV, the silylation reaction mixture (0.20 mL), CH₃CN (0.20 mL) and 1.0 M KH₂PO₄/K₂HPO₄ buffer (pH = 8.72) (0.3 mL) were stirred at rt for 2 h. Extraction with EtOAc left an aqueous layer with pH = 9.00. The organic layer was washed with a 10% aqueous solution of 2-(dimethylamino)ethanethiol hydrochloride and was passed through

a small amount of silica gel followed by analysis with GC Method 1. **8d**, t_R 4.36 min (1.949e6, 63%); **3d**, t_R 4.47 min (1.594e4, 0.6%); **9d**, t_R 10.7 min (1.669e5, 12%).

General Procedure V: Palladium-Catalyzed Silylation of 4-Substituted Aryl Bromides using 1,2-Diethoxy-1,1,2,2-tetramethyldisilane Followed by Hydrolysis

To a 100-mL, oven-dried, round-bottom flask purged with argon containing palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv) and the aryl bromide (5.0 mmol), was added 1-methyl-2-pyrrolidinone (10.0 mL) and diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv). The reaction mixture was stirred for 10 min at 60 °C under an argon atmosphere whereupon 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.13 g, 5.5 mmol, 1.1 equiv or 1.55 g, 7.5 mmol, 1.5 equiv) was added. The reaction mixture was heated at 60 °C under an argon atmosphere and was monitored by GC analysis (4-24 h). After completion, the reaction mixture as cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added. The resulting mixture was stirred rapidly at rt for 2 h then was extracted with benzene (50 mL, 2 x 25 mL). The combined benzene extracts were washed with water (3 x 50 mL) and brine (25 mL). Concentration of the filtrate *in vacuo* yielded the crude aryl dimethylsilanol. Purification by column chromatography (SiO₂, 150 g) gave the aryl dimethylsilanol which was free of major impurities⁴ by ¹H NMR analysis.

Dimethyl(4-methoxyphenyl)silanol (8a) (Table 6, entry 1)

1.1 Equiv 1,2-Diethoxy-1,1,2,2-tetramethyldisilane:

Following General Procedure V, palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv), 4-bromoanisole (0.935g, 5.0 mmol), 1-methyl-2-pyrrolidinone (10.0 mL), diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.13 g, 5.5 mmol, 1.1 equiv) were stirred

for 24 h at 60 °C. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added and the mixture was stirred at rt for 2 h. Purification by column chromatography (SiO₂, 150 g, pentane/Et₂O, 4/1) afforded 0.497 g (55%) of **8a** which was free of major impurities by ¹H NMR analysis. The spectroscopic data matched those from the literature.⁵

1.5 Equiv 1,2-Diethoxy-1,1,2,2-tetramethyldisilane:

Following General Procedure V, palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv), 4-bromoanisole (0.935 g, 5.0 mmol), 1-methyl-2-pyrrolidinone (10.0 mL), diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.55 g, 7.5 mmol, 1.5 equiv) were stirred for 18 h at 60 °C. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added and the mixture was stirred at rt for 2 h. Purification by column chromatography (SiO₂, 150 g, pentane/Et₂O, 4/1) afforded 0.692 g (76%) of **8a** which was free of major impurities by ¹H NMR analysis. The spectroscopic data matched those from the literature.⁵

Data for 8a:

¹H NMR: (500 MHz, CDCl₃)

7.52 (d, *J* = 8.4, 2 H, HC(2)), 6.93 (d, *J* = 8.2, 2 H, HC(3)), 3.82 (s, 3 H, HC(5)), 2.6-2.2 (br s, 1 H, HO), 0.38 (s, 6 H, HC(6)).

¹³C NMR: (126 MHz, CDCl₃)

160.8 (C(4)), 134.6 (C(2)), 130.2 (C(1)), 113.5 (C(3)), 55.0 (C(5)), -0.01 (C(6)).

IR: (neat)

3307 (br, m), 2957 (m), 1596 (s), 1504 (s), 1280 (s), 1249 (s), 1183 (s), 1117 (s).

MS: (EI, 70 eV)

182 (M⁺, 20), 167 (100).

TLC: *R_f* 0.26 (pentane/Et₂O, 4/1) [silica gel, UV]

GC: *t_R* 3.08 min (GC Method 1)

Dimethyl(4-(1-oxoethyl)phenyl)silanol (8b) (Table 6, entry 2) **1.1 Equiv 1,2-Diethoxy-1,1,2,2-tetramethyldisilane:**

Following General Procedure V, palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv), 4'-bromoacetophenone (0.995 g, 5.0 mmol), 1-methyl-2-pyrrolidinone (10.0 mL), diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.13 g, 5.5 mmol, 1.1 equiv) were stirred for 4 h at 60 °C. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)-ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added and stirred at rt for 2 h. Purification by column chromatography (SiO₂, 150 g, CH₂Cl₂/acetone, 9/1) afforded 0.619 g (64%) of **8b** which was free of major impurities by ¹H NMR analysis. An analytical sample was obtained by sacrificial Kugelrohr distillation.

1.5 Equiv 1,2-Diethoxy-1,1,2,2-tetramethyldisilane:

Following General Procedure V, palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv), 4'-bromoacetophenone (0.995 g, 5.0 mmol), 1-methyl-2-pyrrolidinone (10.0 mL), diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.55 g, 7.5 mmol, 1.5 equiv) were stirred for 4 h at 60 °C. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)-ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added and stirred at rt for 2 h. Purification by column chromatography (SiO₂, 150 g, CH₂Cl₂/acetone, 9/1) afforded 0.676 g (70%) of **8b** which was free of major impurities by ¹H NMR analysis.

Data for 8b:

bp: 150 °C (0.05 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.91 (d, *J* = 7.5, 2 H, HC(3)), 7.68 (dd, *J* = 7.4, 0.8, 2 H, HC(2)), 2.7-2.5 (br s, 1 H, HO), 2.59 (s, 3 H, HC(6)), 0.41 (d, *J* = 0.6, 6 H, HC(7))

¹³C NMR: (126 MHz, CDCl₃)

198.7 (C(5)), 145.7 (C(1)), 137.6 (C(4)), 133.3 (C(2)), 127.4 (C(3)), 26.6 (C(6)), -0.1 (C(7))

IR: (neat)

3412 (br, s), 2960 (w), 1672 (s), 1596 (m), 1389 (m), 1358 (w), 1275 (m), 1254 (m), 1118 (m)

MS: (EI, 70 eV)

194 (M⁺, 13.3), 180 (16.0), 179 (100), 75 (10.2)

TLC: *R_f* 0.45 (CH₂Cl₂/acetone, 9/1) [silica gel, UV]

GC: *t_R* 3.81 min (GC Method 1)

Analysis: C₁₀H₁₄O₂Si (194.30)

Calcd: C, 61.81; H, 7.26%

Found: C, 61.63; H, 7.07%

Dimethyl(4-nitrophenyl)silanol (8c) (Table 6 entry 3)

1.1 Equiv 1,2-Diethoxy-1,1,2,2-tetramethyldisilane:

Following General Procedure V, palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv), 4-bromonitrobenzene (1.010 g, 5.0 mmol), 1-methyl-2-pyrrolidinone (10.0 mL), diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.13 g, 5.5 mmol, 1.1 equiv) were stirred for 4 h at 60 °C. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)-ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added and stirred at rt for 2 h. Purification by column chromatography (SiO₂, 150 g,

CH₂Cl₂/acetone, 97/3) afforded 0.530 g (54%) of **8c** which was free of major impurities by ¹H NMR analysis. An analytical sample was obtained by sacrificial Kugelrohr distillation.

1.5 Equiv 1,2-Diethoxy-1,1,2,2-tetramethyldisilane:

Following General Procedure V, palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv), 4-bromonitrobenzene (1.010 g, 5.0 mmol), 1-methyl-2-pyrrolidinone (10.0 mL), diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.55 g, 7.5 mmol, 1.5 equiv) were stirred for 4 h at 60 °C. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)-ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added and stirred at rt for 2 h. Purification by column chromatography (SiO₂, 150 g, pentane/Et₂O, 4/1) afforded 0.712 g (72%) of **8c** which was free of major impurities by ¹H NMR analysis.

Data for **8c**:

bp: 160 °C (0.2 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

8.16 (d, *J* = 8.6, 2 H, HC(3)), 7.75 (d, *J* = 8.6, 2 H, HC(2)), 2.6-2.5 (br s, 1 H, HO), 0.43 (s, 6 H, HC(5))

¹³C NMR: (126 MHz, CDCl₃)

148.8 (C(4)), 148.1 (C(1)), 134.0 (C(3)), 122.4 (C(2)), -0.1 (C(5))

IR: (neat)

3392 (br, s), 3044 (m), 2961 (m), 1596 (m), 1517 (s), 1386 (m), 1355 (s), 1256 (s), 1114 (s)

MS: (EI, 70 eV)

197 (M⁺, 7), 3 (14), 182 (100), 136 (22), 75 (15)

TLC: *R_f* 0.39 (CH₂Cl₂/acetone, 97/3) [silica gel, UV]

GC: *t_R* 3.89 min (GC Method 1)

Analysis: C₈H₁₁NO₃Si (197.26)

Calcd: C, 48.71; H, 5.62; N, 7.10%

Found: C, 48.53; H, 5.66; N, 7.02%

Ethyl 4-(Dimethylhydroxysilyl)benzoate (8d) (Table 6, entry 4) **1.1 Equiv 1,2-Diethoxy-1,1,2,2-tetramethyldisilane:**

Following General Procedure V, palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv), ethyl 4-bromobenzoate (1.145 g, 5.0 mmol), 1-methyl-2-pyrrolidinone (10.0 mL), diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.13 g, 5.5 mmol, 1.1 equiv) were stirred for 4 h at 60 °C. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)-ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added and stirred at rt for 2 h. Purification by column chromatography (SiO₂, 150 g, pentane/Et₂O, 4/1) afforded 0.884 g (79%) of **8d** which was free of major impurities by ¹H NMR analysis. An analytical sample was obtained by sacrificial Kugelrohr distillation.

1.5 Equiv 1,2-Diethoxy-1,1,2,2-tetramethyldisilane:

Following General Procedure V, palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv), ethyl 4-bromobenzoate (1.145 g, 5.0 mmol), 1-methyl-2-pyrrolidinone (10.0 mL), diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.55 g, 7.5 mmol, 1.5 equiv) were stirred for 4 h at 60 °C. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)-ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added and stirred at rt for 2 h. Purification by column chromatography (SiO₂, 150 g, pentane/Et₂O, 4/1) afforded 0.908 g (81%) of **8d** which was free of major impurities by ¹H NMR analysis.

Data for **8d:**

bp: 160 °C (0.15 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)
 8.02 (d, *J* = 8.4, 2 H, HC(3)), 7.66 (d, *J* = 8.4, 2 H, HC(2)), 4.38 (q, *J* = 7.1, 2 H, HC(6)), 2.1-2.0 (br s, 1 H, HO), 1.4 (t, 3 H, HC(7)), 0.42 (s, 6 H, HC(8))

¹³C NMR: (126 MHz, CDCl₃)
 166.7 (C(5)), 145.0 (C(1)), 133.0 (C(2)), 131.3 (C(4)), 128.6 (C(3)), 61.0 (C(6)), 14.3 (C(7)), -0.1 (C(8))

IR: (neat)
 3422 (br, m), 2961 (m), 1719 (s), 1698 (s), 1390 (m), 1362 (m), 1280 (s), 1097 (s)

MS: (EI, 70 eV)
 224 (M⁺, 11.2), 210 (16.8), 209 (100), 181 (18.4), 179 (10.8), 75 (10.8)

TLC: *R_f* 0.17 (pentane/Et₂O, 4/1) [silica gel, UV]

GC: *t_R* 4.23 min (GC Method 1)

Analysis: C₁₁H₁₆O₃Si (224.33)
 Calcd: C, 58.99; H, 7.19%
 Found: C, 58.67; H, 7.06%

Dimethyl(4-cyanophenyl)silanol (**8e**) (Table 6, entry 5)

1.1 Equiv 1,2-Diethoxy-1,1,2,2-tetramethyldisilane:

Following General Procedure V, palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv), 4-bromobenzonitrile (0.910 g, 5.0 mmol), 1-methyl-2-pyrrolidinone (10.0 mL), diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.13 g, 5.5 mmol, 1.1 equiv) were stirred for 4 h at 60 °C. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)-ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added and stirred at rt for 2 h. Purification by column chromatography (SiO₂, 150 g, CH₂Cl₂/acetone, 93/7) afforded 0.701 g (79%) of **8e** which was free of major impurities by ¹H NMR analysis. An analytical sample was obtained by sacrificial Kugelrohr distillation.

1.5 Equiv 1,2-Diethoxy-1,1,2,2-tetramethyldisilane:

Following General Procedure V, palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv), 4-bromobenzonitrile (0.910 g, 5.0 mmol), 1-methyl-2-pyrrolidinone (10.0 mL), diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.55 g, 7.5 mmol, 1.5 equiv) were stirred for 4 h at 60 °C. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)-ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added and stirred at rt for 2 h. Purification by column chromatography (SiO₂, 150 g, CH₂Cl₂/acetone, 95/5) afforded 0.706 g (80%) of **8e** which was free of major impurities by ¹H NMR analysis.

Data for 8e:

bp: 140 °C (0.2 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)
7.68 (d, *J* = 8.2, 2 H, HC(2)), 7.61 (d, *J* = 9.0, 2 H, HC(3)), 2.67 (s, 1 H, HO),
0.42 (s, 6 H, HC(6))

¹³C NMR: (126 MHz, CDCl₃)
145.8 (C(1)), 133.5 (C(2)), 131.1 (C(3)), 118.9 (C(5)), 112.8 (C(4)), -0.2 (C(6))

IR: (neat)
3412 (br, s), 2961 (w), 2230 (m), 1644, (br, m), 1386 (w), 1254 (w), 1106 (w)

MS: (EI, 70 eV)
177 (M⁺, 9), 163 (15), 162 (100).

TLC: *R_f* 0.48 (CH₂Cl₂/acetone, 93/7) [silica gel, UV]

GC: *t_R* 3.35 min (GC Method 1)

Analysis: C₉H₁₁NOSi (177.28)

Calcd:	C, 60.98;	H, 6.25;	N, 7.90%
Found:	C, 61.04;	H, 6.31;	N, 7.56%

Dimethyl[[4-(2-tetrahydropyranyloxy)methyl]phenyl]silanol (8f) (Table 6, entry 6) **1.5 Equiv 1,2-Diethoxy-1,1,2,2-tetramethyldisilane:**

Following General Procedure V, palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv), 4-[(2-tetrahydropyranyloxy)]-methylbromobenzene (1.36 g, 5.0 mmol), 1-methyl-2-pyrrolidinone (10.0 mL), diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.55 g, 7.5 mmol, 1.5 equiv) were stirred for 4 h at 60 °C. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)-ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added and stirred at rt for 2 h. Purification by column chromatography (SiO₂, 150 g, pentane/Et₂O, 3/1) afforded 0.920 g (69%) of **8f** which was free of major impurities by ¹H NMR analysis. An analytical sample was obtained by sacrificial Kugelrohr distillation.

Data for 8f:

bp: 180 °C (0.25 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.57 (d, *J* = 7.9, 2 H, HC(2)), 7.36 (d, *J* = 7.7, 2 H, HC(3)), 4.77 (d, *J* = 12.2, 1 H, HC(6)), 4.70 (t, *J* = 3.5, 1 H, HC(7)), 4.48 (d, *J* = 12.2, 1 H, HC(6)), 3.93-3.87 (m, 1 H, HC(11)), 3.57-3.52 (m, 1 H, HC(11)), 2.80 (s, 1 H, HO), 1.90-1.80 (m, 1 H, HC(9)), 1.75-1.50 (m, 5 H, HC(8, 9, 10)), 0.38 (s, 6 H, HC(5))

¹³C NMR: (126 MHz, CDCl₃)

139.6 (C(4)), 138.4 (C(1)), 133.1 (C(2)), 127.2 (C(3)), 97.6 (C(7)), 68.6 (C(6)), 61.9 (C(11)), 30.4 (C(9)), 25.3 (C(8)), 19.1 (C(10)), -0.06 (C(5))

IR: (neat)

3400 (br, s), 2952 (w), 2871 (m), 1389 (m), 1352 (w), 1252 (s), 1201 (m), 1114(s), 1030 (s)

MS: (EI, 70 eV)

251 (6), 165 (100), 151 (12), 147 (13), 105 (33), 85 (38), 75 (20)

TLC: R_f 0.22 (pentane/Et₂O, 3/1) [silica gel, UV]

GC: t_R 5.572 min (GC Method 1)

Analysis: C₉H₁₁NOSi (266.41)

Calcd: C, 63.12; H, 8.32%

Found: C, 62.84; H, 8.28%

Dimethyl(4-methylphenyl)silanol (**8g**) (Table 6, entry 7)

1.1 Equiv 1,2-Diethoxy-1,1,2,2-tetramethyldisilane:

Following General Procedure V, palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv), 4-bromotoluene (0.855 g, 5.0 mmol), 1-methyl-2-pyrrolidinone (10.0 mL), diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.13 g, 5.5 mmol, 1.1 equiv) were stirred for 18 h at 60 °C. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added and stirred at rt for 2 h. Purification by column chromatography (SiO₂, 150 g, pentane/Et₂O, 4/1) afforded 0.502 g (60%) of **8g** which was free of major impurities by ¹H NMR analysis. The spectroscopic data matched those from the literature.⁵

1.5 Equiv 1,2-Diethoxy-1,1,2,2-tetramethyldisilane:

Following General Procedure V, palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv), 4-bromotoluene (0.855 g, 5.0 mmol), 1-methyl-2-pyrrolidinone (10.0 mL), diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.55 g, 7.5 mmol, 1.5 equiv) were stirred for 12 h at 60 °C. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic

acid (20 mL) were added and stirred at rt for 2 h. Purification by column chromatography (SiO₂, 150 g, pentane/Et₂O, 4/1) afforded 0.586 g (71%) of **8g** which was free of major impurities by ¹H NMR analysis. The spectroscopic data matched those from the literature.⁵

Data for **8g:**

¹H NMR: (500 MHz, CDCl₃)

7.52 (d, *J* = 7.9, 2 H, HC(2)), 7.23 (d, *J* = 7.5, 2 H, HC(3)), 2.8-2.6 (br s, 1 H, HO), 2.40 (s, 3 H, HC(5)), 0.40 (s, 6 H, HC(6))

¹³C NMR: (126 MHz, CDCl₃)

139.5 (C(1)), 135.6 (C(4)), 133.1 (C(2)), 128.6 (C(3)), 21.4 (C(5)), -0.1 (C(6))

IR: (neat)

3293 (br, m), 2959 (m), 1605 (m), 1392 (w), 1252 (s), 1112 (s)

MS: (EI, 70 eV)

166 (M⁺, 20), 151 (100)

TLC: *R_f* 0.47 (pentane/Et₂O, 4/1) [silica gel, UV]

GC: *t_R* 2.41 min (GC Method 1)

Dimethyl(2-cyanophenyl)silanol (8h**) (Table 7, entries 1,2)**

1.1 Equiv 1,2-Diethoxy-1,1,2,2-tetramethyldisilane:

Following General Procedure V, palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv), 2-bromobenzonitrile (0.910 g, 5.0 mmol), 1-methyl-2-pyrrolidinone (10.0 mL), diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.13 g, 5.5 mmol, 1.1 equiv) were stirred for 24 h at 60 °C. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)-ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added and stirred at rt for 2 h. Purification by column chromatography (SiO₂,

150 g, pentane/Et₂O, 3/1) afforded 0.508 g (57%) of **8h** which was free of major impurities by ¹H NMR analysis. An analytical sample was obtained by sacrificial Kugelrohr distillation.

1.5 Equiv 1,2-Diethoxy-1,1,2,2-tetramethyldisilane:

Following General Procedure V, palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv), 2-bromobenzonitrile (0.910 g, 5.0 mmol), 1-methyl-2-pyrrolidinone (10.0 mL), diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv) and 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.55 g, 7.5 mmol, 1.5 equiv) were stirred for 12 h at 60 °C. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)-ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added and stirred at rt for 2 h. Purification by column chromatography (SiO₂, 150 g, pentane/Et₂O, 3/1) afforded 0.724 g (82%) of **8h** which was free of major impurities by ¹H NMR analysis.

Data for **8h**:

bp: 110 °C (0.2 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.72 (d, *J* = 7.1, 1 H, HC(6)), 7.68 (d, *J* = 7.6, 1 H, HC(3)), 7.57 (dt, *J* = 1.2, 7.5, 1 H, HC(5)), 7.46 (dt, *J* = 1.2, 7.7, 1 H, HC(4)), 2.86 (br s, 1 H, HO), 0.53 (s, 6 H, HC(7))

¹³C NMR: (126 MHz, CDCl₃)

144.2 (C(1)), 134.3 (C(6)), 133.2 (C(3)), 131.8 (C(5)), 129.7 (C(4)), 120.0 (C(8)), 116.2 (C(2)), -0.05 (C(7))

IR: (neat)

3401 (br, s), 2962 (m), 2225 (m), 1432 (w), 1258 (s), 1131 (s), 1073 (m)

MS: (EI, 70 eV)

177 (M⁺, 5), 163 (15), 162 (100), 91 (15)

TLC: *R_f* 0.21 (pentane/Et₂O, 3/1) [silica gel, UV]

GC: *t_R* 2.99 min (GC Method 1)

Analysis: C₉H₁₁NOSi (177.28)

Calcd: C, 60.98; H, 6.25; N, 7.90%

Found: C, 60.65; H, 6.28; N, 7.96%

Ethyl 2-(Dimethylhydroxysilyl)benzoate (8i) (Table 7, entry 3)

To a 100-mL, oven-dried, round-bottom flask purged with argon containing palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv) and ethyl 2-bromobenzoate (1.15 g, 5.0 mmol), was added 1-methyl-2-pyrrolidinone (10.0 mL) and diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv). The reaction mixture was stirred for 10 min at 80 °C under an argon atmosphere whereupon 1,2-diethoxy-1,1,2,2-tetramethyldisilane (1.55 g, 7.5 mmol, 1.5 equiv) was added. The reaction mixture was heated at 80 °C under an argon atmosphere for 24 h. The reaction mixture was cooled to rt and CH₃CN (13 mL), 2-(dimethylamino)ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added. The resulting mixture was stirred rapidly at rt for 2 h then was extracted with benzene (50 mL, 2 x 25 mL). The combined benzene extracts were washed with water (3 x 50 mL) and brine (25 mL). Concentration of the filtrate *in vacuo* yielded crude aryldimethylsilanol. Purification by column chromatography (SiO₂, 100 g, CH₂Cl₂/acetone, 97/3) afforded 0.630 g (56%) of **8i** which was free of major impurities by NMR analysis. The product was further purified by sacrificial Kugelrohr distillation.

Data for 8i:

bp: 115 °C (0.15 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

8.09 (dt, *J* = 7.8, 0.6, 1 H, HC(3)), 7.76 (dt, *J* = 6.5, 0.6, 1 H, HC(6)), 7.57 (td, *J* = 7.4, 1.3, 1 H, HC(5)), 7.46 (dt, *J* = 7.6, 1.4, 1 H, HC(4)), 4.40 (q, *J* = 7.2, 2 H, HC(9)), 3.20 (br s, 1 H, HO), 1.42 (t, *J* = 7.2, 3 H, HC(10)), 0.43 (s, 6 H, HC(7))

¹³C NMR: (126 MHz, CDCl₃)

169.2 (C(8)), 142.3 (C(1)), 135.0 (C(6)), 134.7 (C(2)), 132.1 (C(5)), 130.1 (C(3)), 129.3 (C(4)), 61.5 (C(9)), 14.2 (C(10)), 0.32 (C(7))

IR: (neat)

3398 (br, m), 3059 (w), 2982 (m), 1712 (s), 1368 (m), 1274 (s), 1141 (m), 1116 (s), 1068 (m)

MS: (ESI)

224 (M^+ , 5), 207 (100).

HRMS: calcd for $C_{10}H_{13}O_3Si$ ($M^+ - CH_3$): 209.06340; found: 209.06167

TLC: R_f 0.53 (CH_2Cl_2 /acetone, 97/3) [silica gel, UV]

GC: t_R 4.05 min (GC Method 1)

Dimethyl(2-methoxyphenyl)silanol (8j) (Table 7, entry 4)

To a 100-mL, oven-dried, round-bottom flask purged with argon containing palladium chloride (44.0 mg, 0.25 mmol, 0.05 equiv), 2-(di-*t*-butylphosphino)biphenyl (149 mg, 0.5 mmol, 0.1 equiv) and 2-bromoanisole (0.935 g, 5.0 mmol), was added 1-methyl-2-pyrrolidinone (10.0 mL) and diisopropylethylamine (2.6 mL, 15.0 mmol, 3.0 equiv). The reaction mixture was stirred for 10 min at 80 °C under an argon atmosphere whereupon 1,2-diethoxy-1,1,2,2-tetramethyldisilane (2.06 g, 10.0 mmol, 2.0 equiv) was added. The reaction mixture was heated at 80 °C under an argon atmosphere for 24 h. The reaction mixture was cooled to rt and CH_3CN (13 mL), 2-(dimethylamino)ethanethiol hydrochloride (177 mg, 1.25 mmol, 0.25 equiv) and 1.0 M acetic acid (20 mL) were added. The resulting mixture was stirred rapidly at rt for 2 h then was extracted with benzene (50 mL, 2 x 25 mL). The combined benzene extracts were washed with water (3 x 50 mL) and brine (25 mL). Concentration of the filtrate *in vacuo* yielded crude aryldimethylsilanol. Purification by column chromatography (SiO_2 , 100 g, CH_2Cl_2 /acetone, 97/3) afforded 0.430 g (47%) of **8j** which was free of major impurities by NMR. Chromatography also afforded 0.093g (10%) of **7j**. The product **8j** was further purified by sacrificial Kugelrohr distillation.

Data for 8j:

bp: 140 °C (0.2 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.43 (dd, *J* = 7.1, 1.9, 1 H, HC(6)), 7.38 (td, *J* = 7.0, 1.9, 1 H, HC(4)), 7.00 (td, *J* = 7.3, 0.9, 1 H, HC(5)), 6.87 (d, *J* = 8.2, 1 H, HC(3)), 3.84 (s, 3 H, HC(8)), 2.44 (br s, 1 H, HO), 0.40 (s, 6 H, HC(7))

¹³C NMR: (126 MHz, CDCl₃)

163.9 (C(2)), 134.6 (C(6)), 131.3 (C(4)), 126.9 (C(1)), 120.8 (C(5)), 109.7 (C(3)), 55.2 (C(8)), 0.27 (C(7))

IR: (neat)

3392 (br, m), 3066 (w), 2958 (m), 1589 (s), 1572 (m), 1474 (m), 1462 (m), 1430 (s), 1237 (s), 1178 (w), 1131 (m)

MS: (EI, 70 eV)

182 (M⁺, 26), 167 (38), 137 (100), 121 (89), 91 (80), 78 (16), 77 (14), 75 (16)

HRMS: calcd for C₉H₁₄O₂Si (M⁺): 182.07631; found: 182.07694

TLC: *R_f* 0.26 (pentane/Et₂O, 4/1) [silica gel, UV]

GC: *t_R* 2.85 min (GC Method 1)

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