

# Cross-Coupling Reactions of Arylsilanols with Substituted Aryl Halides

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## SUPPORTING INFORMATION

### General Experimental

All reactions were performed in oven (150 °C) and/or flame-dried glassware under an inert atmosphere of dry argon. All the solvents used were reagent grade and distilled from the indicated drying agents: dichloromethane:  $P_2O_5$ ; diethyl ether, dioxane and tetrahydrofuran: Na, benzophenone; toluene, hexane, dimethylformamide, and dimethoxyethane:  $CaH_2$ ; methanol:  $Mg(OMe)_2$ ; ethyl acetate:  $K_2CO_3$ . “Brine” refers to a saturated solution of NaCl. Bulb-to-bulb distillations were performed on a Büchi GKR-50 Kugelrohr and boiling points (bp) correspond to the uncorrected recorded air bath temperatures (ABT). Melting points (mp) were recorded in sealed vacuum glass capillaries on a Thomas-Hoover melting point apparatus are corrected. All reaction temperatures correspond to internal temperatures measured by Teflon-coated thermocouples unless otherwise noted.

Column chromatography was performed using 230-400 mesh silica gel purchased from EM Science or 230-400 mesh C18 Reverse Phase (RP) silica gel purchased from Fluka. Methanol and toluene were reagent grade and used as received; other solvents for chromatography and filtration were technical grade and distilled from the indicated drying agents: hexane ( $CaCl_2$ ); ethyl acetate ( $K_2CO_3$ ). Analytical thin layer chromatography was performed on Merck Reverse-Phase C18 silica gel plates (RP C18) with F-254 indicator or Merck silica gel plates with F-254 indicator. Visualization was accomplished with UV light or an aqueous  $KMnO_4$  solution.

Analytical gas chromatography (GC) was performed using a Hewlett Packard 5890 Series II Gas Chromatograph fitted with a flame ionization detector ( $\text{H}_2$  carrier gas, 1 mL/min). Injections were made on a Hewlett-Packard HP-1 (30 meter) capillary column. The injector temperature was 250 °C, the detector temperature was 300 °C, with a split ratio of 100:1. Retention times ( $t_R$ ) and integrated ratios were obtained using Agilent Chemstation Software.

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Varian Unity-500 (500 MHz  $^1\text{H}$ , 126 MHz  $^{13}\text{C}$ , 470 MHz  $^{19}\text{F}$ ) spectrometer in deuteriochloroform unless otherwise stated using chloroform as an internal reference for  $^1\text{H}$  and  $^{13}\text{C}$  NMR (7.26 ppm,  $^1\text{H}$ ; 77.2 ppm,  $^{13}\text{C}$ ) or hexafluorobenzene as an internal reference for  $^{19}\text{F}$  NMR (-160.0 ppm,  $^{19}\text{F}$ ). Chemical shifts are reported in ppm ( ); multiplicities are indicated by s (singlet), d (doublet), q (quartet), qn (quintet), sext (sextet), m (multiplet), and br (broad). Coupling constants,  $J$ , are reported in Hertz (Hz); integration is provided and assignments are indicated. Infrared spectra (IR) were recorded on a Mattson Galaxy 5020 spectrophotometer. Peaks are reported in  $\text{cm}^{-1}$  with indicated relative intensities: s (strong 67-100%); m (medium, 34-66%); w (weak, 0-33%). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

Commercial reagents were purified by distillation or recrystallization prior to use. Anhydrous cesium carbonate was purchased from Aldrich and stored under a dry nitrogen atmosphere. Triphenylarsine was purchased from Aldrich and recrystallized (EtOH) prior to use. 1,4-Bis(diphenylphosphino)butane was purchased from Aldrich and recrystallized (EtOH) prior to use.

### Literature Preparations

Allylpalladium chloride dimer<sup>1</sup> and (4-Methoxyphenyl)dimethylsilanol<sup>2</sup> were prepared by literature methods.

### General Procedure I: Palladium-Catalyzed Cross-Coupling of (4-Methoxyphenyl)-dimethylsilanol with Ethyl 4-Iodobenzoate.

Cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv) was suspended in dry solvent (0.5 mL) at room temperature in a 5-mL, round-bottom flask with a magnetic stir bar and fitted with a reflux condenser and an argon inlet adapter. To this suspension was added ethyl 4-iodobenzoate

(138 mg, 0.5 mmol, 1.0 equiv), and **1** (109 mg, 0.6 mmol, 1.2 equiv), followed by [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and the appropriate ligand (0.1 mmol, 0.2 equiv). The flask was then purged with argon and placed in a 90 °C oil bath. The reaction was monitored by GC analysis at certain intervals until completion. Sampling of the reaction was performed by removing 10 µL aliquot of the mixture via syringe. The aliquot was filtered through a small plug of silica gel and eluted with 5 mL of ethyl acetate. The aliquot was then analyzed by GC. Response factors (Rf) were obtained by equation 1 and are shown below:

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

biphenyl (mmol)	biphenyl (area)	ethyl 4-iodobenzoate (mmol)	ethyl 4-iodobenzoate (area)	response factor (Rf)
0.1991	5.11479e6	0.2000	4.55264e6	1.127
0.2004	4.91489e6	0.2007	4.38663e6	1.121
0.2010	3.52058e6	0.1992	3.05842e6	1.140

biphenyl (mmol)	biphenyl (area)	cross-coupling product <b>2a</b> (mmol)	cross-coupling product <b>2a</b> (area)	response factor (Rf)
0.1997	4.61935e6	0.1990	3.13200e6	1.468
0.1991	5.32007e6	0.1994	3.58784e6	1.490
0.1978	4.01114e6	0.1990	2.75194e6	1.465

biphenyl (mmol)	biphenyl (area)	homo-coupling product <b>3a</b> (mmol)	homocoupling product <b>3a</b> (area)	response factor (Rf)
0.1991	1.39759e6	0.1994	1.26041e6	1.111
0.1997	2.77948e6	0.1998	2.50408e6	1.110
0.1997	1.97075e6	0.2008	1.77943e6	1.113

$$\text{Eq 2: Conversion of Iodide} =$$

$$(\text{area iodide} * \text{Rf}) / [(\text{area iodide} * \text{Rf}) + (\text{area } \mathbf{2a} * \text{Rf}) + (2 * \text{area } \mathbf{3a} * \text{Rf})]$$

$$\text{Eq 3: Ratio of } \mathbf{2a} : \mathbf{3b} =$$

$$(\text{area } \mathbf{2a} * \text{Rf}) / (\text{area } \mathbf{3a} * \text{Rf})$$

**Table 1, entry 1:**

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv) containing 1.9 equivalents of H<sub>2</sub>O, toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), and [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv) was stirred at 90 °C for 12 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, *t*<sub>R</sub> 0.92 min (3.85697e6, 23%); **2a**, *t*<sub>R</sub> 3.65 min (8.77847e6, 70%); **3a**, *t*<sub>R</sub> 5.05 min (1.11323e6, 7%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Table 1, entry 2:**

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv) containing 1.9 equivalents of H<sub>2</sub>O, dioxane (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), and [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv) was stirred at 90 °C for 12 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, *t*<sub>R</sub> 0.92 min (1.66393e6, 14%); **2a**, *t*<sub>R</sub> 3.65 min (6.27598e6, 70%); **3a**, *t*<sub>R</sub> 5.05 min (1.96649e6, 16%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Table 1, entry 3:**

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv) containing 1.9 equivalents of H<sub>2</sub>O, dimethoxyethane (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), and [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv) was stirred at 90 °C for 12 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, *t*<sub>R</sub> 0.92 min (4.32593e4, 2%); **2a**, *t*<sub>R</sub> 3.65 min (8.40654e5, 59%); **3a**, *t*<sub>R</sub> 5.05 min (7.43005e5, 39%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Table 1, entry 4:**

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv) containing 1.9 equivalents of H<sub>2</sub>O, dimethylformamide (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), and [allylPdCl]<sub>2</sub> (9.1 mg, 0.025

mmol, 0.05 equiv) was stirred at 90 °C for 12 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate,  $t_R$  0.92 min (4.32593e4, 1%); **2a**,  $t_R$  3.65 min (8.40654e5, 17%); **3a**,  $t_R$  5.05 min (5.49186e6, 83%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Table 2, entry 1:**

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv) containing 1.9 equivalents of H<sub>2</sub>O, toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and triphenylphosphine (26.2 mg, 0.1 mmol, 0.2 equiv) was stirred at 90 °C for 12 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate,  $t_R$  0.92 min (0e0, 0%); **2a**,  $t_R$  3.65 min (3.16563e6, 68%); **3a**,  $t_R$  5.05 min (1.94635e6, 32%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Table 2, entry 2:**

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv) containing 1.9 equivalents of H<sub>2</sub>O, toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and tri-*o*-tolylphosphine (30.4 mg, 0.1 mmol, 0.2 equiv) was stirred at 90 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate,  $t_R$  0.92 min (1.04832e6, 36%); **2a**,  $t_R$  3.65 min (1.19938e6, 54%); **3a**,  $t_R$  5.05 min (2.95234e5, 10%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Table 2, entry 3:**

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv) containing 1.9 equivalents of H<sub>2</sub>O, toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and tris(pentafluorophenyl)phosphine (53.2 mg, 0.1 mmol, 0.2 equiv) was stirred at 90 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate,  $t_R$  0.92 min (5.00631e5, 41%); **2a**,  $t_R$  3.65 min (3.05832e5, 32%); **3a**,  $t_R$  5.05 min (3.40683e5, 27%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Table 2, entry 4:**

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv) containing 1.9 equivalents of H<sub>2</sub>O, toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and tri-*t*-butylphosphine (20.3 mg, 0.1 mmol, 0.2 equiv) was stirred at 90 °C for 12 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, *t*<sub>R</sub> 0.92 min (5.84479e4, 1%); **2a**, *t*<sub>R</sub> 3.65 min (2.54670e6, 62 %); **3a**, *t*<sub>R</sub> 5.05 min (1.98475e6, 37%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Table 2, entry 5:**

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv) containing 1.9 equivalents of H<sub>2</sub>O, toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and tri-2-furylphosphine (23.2 mg, 0.1 mmol, 0.2 equiv) was stirred at 90 °C for 3 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, *t*<sub>R</sub> 0.92 min (8.49328e4, 1%); **2a**, *t*<sub>R</sub> 3.65 min (5.07380e6, 78%); **3a**, *t*<sub>R</sub> 5.05 min (1.76117e6, 21%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Table 2, entry 6:**

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv) containing 1.9 equivalents of H<sub>2</sub>O, toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and triphenylarsine (30.6 mg, 0.1 mmol, 0.2 equiv) was stirred at 90 °C for 12 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, *t*<sub>R</sub> 0.92 min (0e0, 0%); **2a**, *t*<sub>R</sub> 3.65 min (4.66599e6, 92%); **3a**, *t*<sub>R</sub> 5.05 min (5.70420e5, 8%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Table 2, entry 7:**

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv) containing 1.9 equivalents of H<sub>2</sub>O, toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and 2-(di-*t*-butylphosphino)biphenyl (29.8 mg, 0.1 mmol, 0.2 equiv) was stirred at 90 °C

for 3 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate,  $t_R$  0.92 min (4.51422e4, 2%); **2a**,  $t_R$  3.65 min (1.63511e5, 12%); **3a**,  $t_R$  5.05 min (1.60576e6, 86%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Table 2, entry 8:**

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv) containing 1.9 equivalents of H<sub>2</sub>O, toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and 1,3-bis(diphenylphosphino)-propane (18.3 mg, 0.05 mmol, 0.1 equiv) was stirred at 90 °C for 3 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate,  $t_R$  0.92 min (6.96579e4, 1%); **2a**,  $t_R$  3.65 min (4.35997e6, 72%); **3a**,  $t_R$  5.05 min (2.13248e6, 27%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Table 2, entry 9:**

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv) containing 1.9 equivalents of H<sub>2</sub>O, toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and 1,4-bis(diphenylphosphino)-butane (21.3 mg, 0.05 mmol, 0.1 equiv) was stirred at 90 °C for 3 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate,  $t_R$  0.92 min (5.75893e4, 1%); **2a**,  $t_R$  3.65 min (4.84797e6, 85%); **3a**,  $t_R$  5.05 min (1.05949e6, 14%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Table 2, entry 10:**

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv) containing 1.9 equivalents of H<sub>2</sub>O, toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and 1,1'-bis(diphenylphosphino)-ferrocene (27.7 mg, 0.05 mmol, 0.1 equiv) was stirred at 90 °C for 12 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate,  $t_R$  0.92 min (5.89119e4, 1%); **2a**,  $t_R$  3.65 min (2.49263e6, 72%); **3a**,  $t_R$  5.05 min (1.22098e6, 27%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Table 3, entry 1:**

Following General Procedure I, a mixture of anhydrous cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv), toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and triphenylarsine (15.3 mg, 0.05 mmol, 0.1 equiv) was stirred at 90 °C for 3 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, *t*<sub>R</sub> 4.81 min (3.200e3, 50%); **2a**, *t*<sub>R</sub> 10.53 min (2.475e3, 50%); **3a**, *t*<sub>R</sub> 14.89 min (, 0%) (HP-5, 270 °C, 16 psi)

**Table 3, entry 2:**

Following General Procedure I, a mixture of anhydrous cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv), toluene (0.5 mL), H<sub>2</sub>O (18 µL, 1 mmol, 2 equiv), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and triphenylarsine (15.3 mg, 0.05 mmol, 0.1 equiv) was stirred at 90 °C for 3 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, *t*<sub>R</sub> 4.81 min (2.413e3, 28%); **2a**, *t*<sub>R</sub> 10.53 min (4.391e3, 67%); **3a**, *t*<sub>R</sub> 14.89 min (3.74e2, 4%) (HP-5, 270 °C, 16 psi)

**Table 3, entry 3:**

Following General Procedure I, a mixture of anhydrous cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv), toluene (0.5 mL), H<sub>2</sub>O (36 µL, 2 mmol, 4 equiv), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and triphenylarsine (15.3 mg, 0.05 mmol, 0.1 equiv) was stirred at 90 °C for 3 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, *t*<sub>R</sub> 4.81 min (9.00e2, 14%); **2a**, *t*<sub>R</sub> 10.53 min (4.125e3, 81%); **3a**, *t*<sub>R</sub> 14.89 min (3.50e2, 5%) (HP-5, 270 °C, 16 psi)

**Table 3, entry 4:**

Following General Procedure I, a mixture of anhydrous cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv), toluene (0.5 mL), H<sub>2</sub>O (54 µL, 3 mmol, 6 equiv), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and triphenylarsine (15.3 mg, 0.05 mmol, 0.1 equiv) was stirred at 90 °C for 3 h.



An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate,  $t_R$  4.81 min (1.569e3, 12%); **2a**,  $t_R$  10.53 min (7.942e3, 83%); **3a**,  $t_R$  14.89 min (6.30e2, 5%) (HP-5, 270 °C, 16 psi)

**Table 3, entry 5:**

Following General Procedure I, a mixture of anhydrous cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv), toluene (0.5 mL), H<sub>2</sub>O (72 µL, 4 mmol, 8 equiv), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and triphenylarsine (15.3 mg, 0.05 mmol, 0.1 equiv) was stirred at 90 °C for 3 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate,  $t_R$  4.81 min (2.185e3, 13%); **2a**,  $t_R$  10.53 min (1.0094e4, 81%); **3a**,  $t_R$  14.89 min (9.11e2, 6%) (HP-5, 270 °C, 16 psi)

**Table 3, entry 6:**

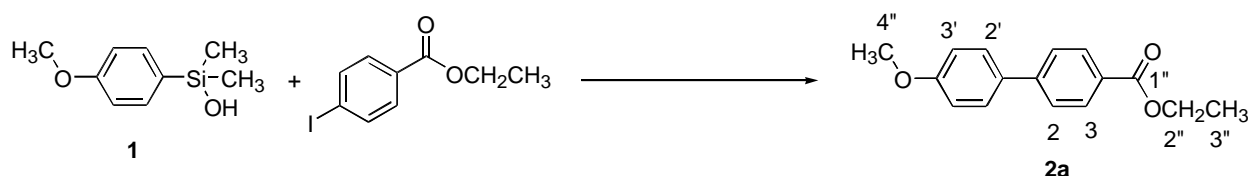
Following General Procedure I, a mixture of anhydrous cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv), toluene (0.5 mL), H<sub>2</sub>O (90 µL, 5 mmol, 10 equiv), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0 equiv), **1** (109 mg, 0.6 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (9.1 mg, 0.025 mmol, 0.05 equiv), and triphenylarsine (15.3 mg, 0.05 mmol, 0.1 equiv) was stirred at 90 °C for 3 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate,  $t_R$  4.81 min (1.903e3, 22%); **2a**,  $t_R$  10.53 min (4.807e3, 72%); **3a**,  $t_R$  14.89 min (5.67e2, 6%) (HP-5, 270 °C, 16 psi)

**General Procedure II: Palladium-Catalyzed Cross-Coupling of (4-Methoxyphenyl)-dimethylsilanol (**1**) with 4-Substituted Aryl Iodides.**

Anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv) was suspended in dry toluene (1.0 mL) at room temperature in a 5-mL, round-bottom flask with a magnetic stir bar and fitted with a reflux condenser and an argon inlet adapter. To this suspension was added drop-wise H<sub>2</sub>O (108 µL, 6.0 mmol, 6.0 equiv) and the resulting slurry was allowed to stir for 10 min. Aryl iodide (1.0 mmol, 1.0 equiv), and **1** (218 mg, 1.2 mmol, 1.2 equiv) were then added, followed by [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and triphenylarsine (30.6 mg, 0.1 mmol, 0.1 equiv). The flask was then purged with argon and placed in a 90 °C oil bath. The

reaction was monitored by GC analysis at certain intervals until completion. Sampling of the reaction was performed by removing 10  $\mu$ L aliquot of the mixture via syringe. The aliquot was filtered through a small plug of silica gel and eluted with 5 mL of ethyl acetate. The aliquot was then analyzed by GC. Upon completion, the reaction was cooled to rt, treated with H<sub>2</sub>O (10 mL) and extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO<sub>4</sub>), and concentrated in vacuo. The crude product was further purified by column chromatography (SiO<sub>2</sub>) to afford the corresponding product which was further purified by recrystallization.

#### Preparation of 4-Carbethoxy-4'-methoxybiphenyl (**2a**) (Table 4, entry 1)



Following General Procedure II, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (108  $\mu$ L, 6.0 mmol, 6.0 equiv), ethyl 4-iodobenzoate (276 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and triphenylarsine (30.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 8 h. The reaction mixture was cooled to rt and extracted to afford a brown solid which was purified by column chromatography (SiO<sub>2</sub> (20 mm), hexane to hexane/EtOAc, 20/1) and recrystallized (EtOH) to afford 160 mg (87%) of **2a** as a colorless solid. The physical and spectroscopic data matched those from the literature.<sup>3</sup>

#### Data for 4'-Carbethoxy-4-methoxybiphenyl (**2a**):

mp: 103-104 °C (EtOH)

<sup>1</sup>H NMR: (500 MHz, CHCl<sub>3</sub>)

8.09 (d, *J* = 8.6, 2 H, HC(3)), 7.62 (d, *J* = 8.8, 2 H, HC(2)), 7.57 (d, *J* = 8.8, 2 H, HC(2')), 7.00 (d, *J* = 8.8, 2 H, HC(3')), 4.40 (q, *J* = 7.1, 2 H, H<sub>2</sub>C(2'')), 3.86 (s, 3 H, H<sub>3</sub>C(1'')), 1.42 (t, *J* = 7.2, 3 H, H<sub>3</sub>C(2''))

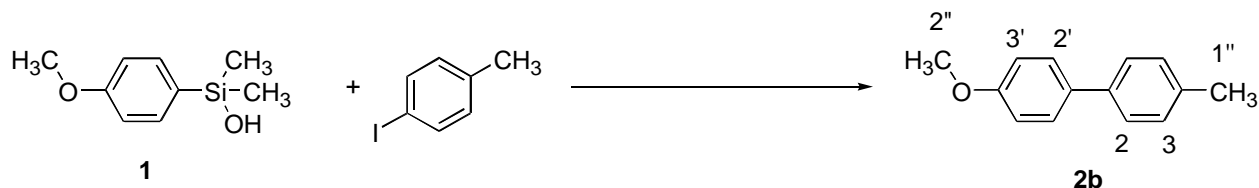
<sup>13</sup>C NMR: (126 MHz, CHCl<sub>3</sub>)

166.6 (C(1'')), 159.8 (C(4')), 145.1(C(1')), 132.4 (C(3)), 130.0 (C(4)), 128.6 (C(1')), 128.3 (C(2'')), 126.4 (C(2)), 114.3 (C(3')), 60.8 (C(2'')), 55.3 (C(4'')), 14.3 (C(3''))

**TLC:**  $R_f$  0.29 (hexane/EtOAc, 20/1) [silica gel, UV]

GC: **2a**,  $t_R$  3.66 min (95.7%); **3a**,  $t_R$  5.05 min (4.3%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

### Preparation of 4'-Methoxy-4-methylbiphenyl (2b) (Table 4, entry 2)



Following General Procedure II, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (108  $\mu$ L, 6.0 mmol, 6.0 equiv), 4-iodotoluene (218 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and triphenylarsine (30.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 6 h. The reaction mixture was cooled to rt and extracted to afford a brown solid which was purified by column chromatography (SiO<sub>2</sub> (20 mm), toluene) and recrystallized (EtOH) to afford 231 mg (90%) of **2b** as a colorless solid. The physical and spectroscopic data matched those from the literature.<sup>4</sup>

Data for 4'-Methoxy-4-methylbiphenyl (**2b**):

mp: 109-110 °C (EtOH)

 $^1\text{H}$  NMR: (500 MHz,  $\text{CHCl}_3$ )

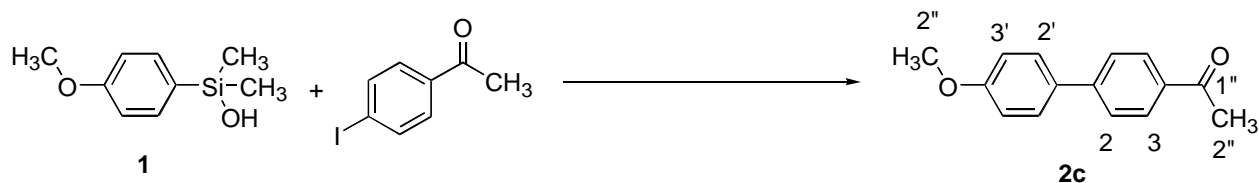
7.54 (d,  $J = 8.6$ , 2 H, HC(2)), 7.48 (d,  $J = 8.2$ , 2 H, HC(2')), 7.25 (d,  $J = 8.4$ , 2 H, HC(3)), 6.99 (d,  $J = 8.8$ , 2 H, HC(3')), 3.86 (s, 3 H, H<sub>3</sub>C(2')), 2.41 (s, 3 H, H<sub>3</sub>C(1'))

 $^{13}\text{C}$  NMR: (126 MHz,  $\text{CHCl}_3$ )

158.9 (C(4')), 138.0 (C(4)), 133.7 (C(1)), 129.4 (C(3)), 127.9 (C(1')), 127.7 (C(2')), 126.5 (C(2)), 114.1 (C(3')), 55.3 (C(2'')), 21.0 (C(1''))

TLC:  $R_f$  0.78 (toluene) [silica gel, UV]

GC: **2b**,  $t_R$  1.80 min (94.2%); **3b**,  $t_R$  1.14 min (5.8%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Preparation of 4-Acetyl-4'-methoxybiphenyl (2c) (Table 4, entry 3)**

Following General Procedure II, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (108  $\mu$ L, 6.0 mmol, 6.0 equiv), 4-iodoacetophenone (246 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and triphenylarsine (30.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 3 h. The reaction mixture was cooled to rt and extracted to afford a brown solid which was purified by column chromatography (SiO<sub>2</sub> (20 mm), hexane to hexane/EtOAc, 20/1) and recrystallized (EtOH) to afford 206 mg (91%) of **2c** as a colorless solid. The physical and spectroscopic data matched those from the literature.<sup>4</sup>

Data for 4-Acetyl-4'-methoxybiphenyl (**2c**):

mp: 152-153 °C (EtOH)

<sup>1</sup>H NMR: (500 MHz, CHCl<sub>3</sub>)

8.01 (d, *J* = 8.3, 2 H, HC(3)), 7.65 (d, *J* = 8.5, 2 H, HC(2)), 7.58 (d, *J* = 8.8, 2 H, HC(2')), 7.00 (d, *J* = 8.8, 2 H, HC(3')), 3.87 (s, 3 H, H<sub>3</sub>C(3')), 2.63 (s, 3 H, H<sub>3</sub>C(2'))

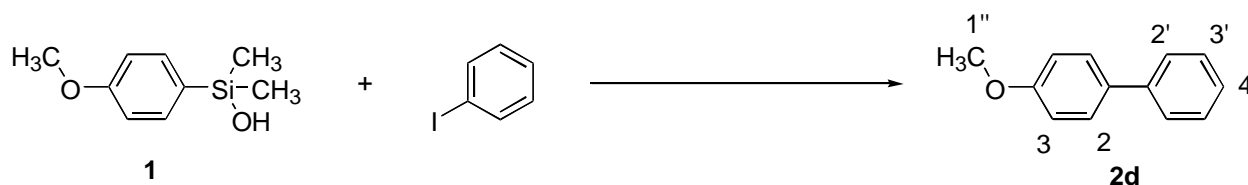
<sup>13</sup>C NMR: (126 MHz, CHCl<sub>3</sub>)

198.0 (C(1')), 160.2 (C(4')), 145.6 (C(1)), 135.5 (C(4)), 132.5 (C(3)), 129.1 (C(1')), 128.6 (C(2')), 126.8 (C(2)), 114.6 (C(3')), 45.6 (C(3')), 26.8 (C(2'))

TLC: *R<sub>f</sub>* 0.33 (hexane/EtOAc, 20/1) [silica gel, UV]

GC: **2c**, *t<sub>R</sub>* 3.27 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

### Preparation of 4-Methoxy-biphenyl (2d) (Table 4, entry 4)



Following General Procedure II, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (108  $\mu$ L, 6 mmol, 6 equiv), iodobenzene (204 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and triphenylarsine (30.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 8 h. The reaction mixture was cooled to rt and extracted to afford a brown solid which was purified by column chromatography (SiO<sub>2</sub> (20 mm), toluene) and recrystallized (EtOH) to afford 168 mg (91%) of **2d** as a colorless solid. The physical and spectroscopic data matched those from the literature.<sup>5</sup>

Data for 4-Methoxy-biphenyl (2d):

mp: 90-91 °C (EtOH)

 $^1\text{H NMR}$ : (500 MHz,  $\text{CHCl}_3$ )

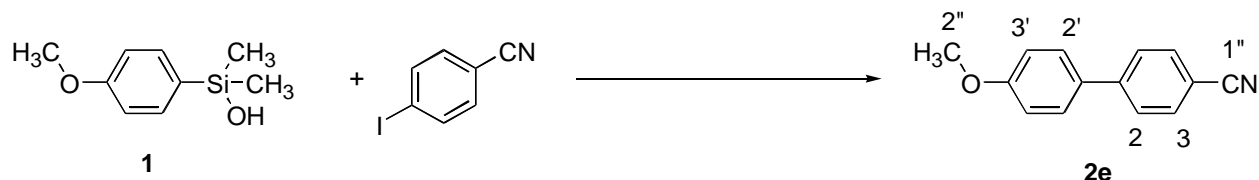
7.57-7.52 (m, 4 H, HC(2), HC(2')), 7.42 (t,  $J = 7.7$ , 2 H, HC(3')), 7.31 (t,  $J = 7.5$ , 1 H, HC(4')), 6.99 (d,  $J = 8.8$ , 2 H, HC(3)), 3.86 (s, 3 H, H<sub>3</sub>C(1'))

 $^{13}\text{C}$  NMR: (126 MHz,  $\text{CHCl}_3$ )

159.2 (C(4)), 140.8 (C(1')), 133.8 (C(3')), 128.7 (C(1)), 128.1 (C(2)), 126.8 (C(2')), 126.7 (C(4')), 114.2 (C(3)), 55.4 (C(1'))

TLC:  $R_f$  0.81 (toluene) [silica gel, UV]

**GC:** **2d**,  $t_R$  1.29 min (93.7%); **3d**,  $t_R$  0.82 min (6.3%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Preparation of 4-Cyano-4'-methoxybiphenyl (2e) (Table 4, entry 5)**

Following General Procedure II, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (108  $\mu$ L, 6.0 mmol, 6.0 equiv), 4-iodobenzonitrile (229 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and triphenylarsine (30.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 6 h. The reaction mixture was cooled to rt and extracted to afford a brown solid which was purified by column chromatography (SiO<sub>2</sub> (20 mm), hexane to hexane/EtOAc, 20/1) and recrystallized (EtOH) to afford 178 mg (85%) of **2e** as a off-white solid. The physical and spectroscopic data matched those from the literature.<sup>6</sup>

Data for 4-Cyano-4'-methoxybiphenyl (**2e**):

mp: 103-104 °C (EtOH)

<sup>1</sup>H NMR: (500 MHz, CHCl<sub>3</sub>)

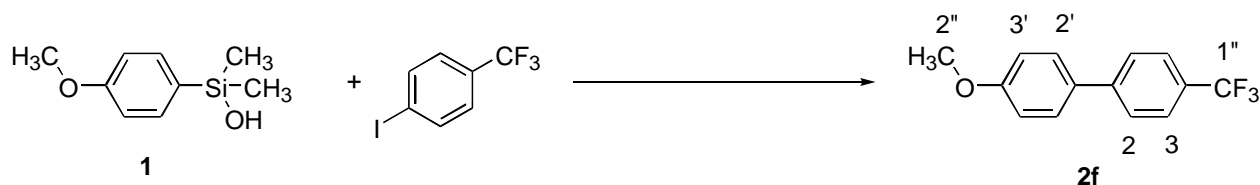
7.70 (d, *J* = 8.1, 2 H, HC(3)), 7.64 (d, *J* = 8.1, 2 H, HC(2)), 7.54 (d, *J* = 8.4, 2 H, HC(2')), 7.01 (d, *J* = 8.6, 2 H, HC(3')), 3.87 (s, 3 H, H<sub>3</sub>C(2''))

<sup>13</sup>C NMR: (126 MHz, CHCl<sub>3</sub>)

160.2 (C(4')), 145.2 (C(1)), 132.6 (C(3)), 131.5 (C(1')), 128.4 (C(2')), 127.1 (C(2)), 119.1 (C(1'')), 114.5 (C(3')), 110.1 (C(4)), 55.4 (C(2''))

TLC: *R<sub>f</sub>* 0.35 (hexane/EtOAc, 20/1) [silica gel, UV]

GC: **2e**, *t<sub>R</sub>* 2.88 min (93.3%); **3e**, *t<sub>R</sub>* 5.33 min (6.7%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Preparation of 4'-Methoxy-4-(trifluoromethyl)biphenyl (2f) (Table 4, entry 6)**

Following General Procedure II, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (108  $\mu$ L, 6.0 mmol, 6.0 equiv), 4-iodobenzotrifluoride (272 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and triphenylarsine (30.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 3 h. The reaction mixture was cooled to rt and extracted to afford a brown solid which was purified by column chromatography (SiO<sub>2</sub> (20 mm), toluene) and recrystallized (EtOH) to afford 218 mg (87%) of **2f** as a colorless solid. The physical and spectroscopic data matched those from the literature.<sup>7</sup>

Data for 4'-Methoxy-4-(trifluoromethyl)biphenyl (**2f**):

mp: 124-125 °C (EtOH)

<sup>1</sup>H NMR: (500 MHz, CHCl<sub>3</sub>)

7.68-7.64 (m, 4 H, HC(3), HC(2)), 7.56 (d, *J* = 8.8, 2 H, HC(2')), 7.01 (d, *J* = 9.0, 2 H, HC(2')), 3.87 (s, 3 H, H<sub>3</sub>C(2''))

<sup>13</sup>C NMR: (126 MHz, CHCl<sub>3</sub>)

160.1 (C(4')), 144.5 (C(1)), 132.4 (C(1')), 128.7 (q, <sup>2</sup>*J*<sub>CF</sub> = 32.2, C(4)), 128.6 (C(2')), 127.1 (C(2)), 125.9 (q, <sup>3</sup>*J*<sub>CF</sub> = 3.7, C(3)), 124.6 (q, <sup>1</sup>*J*<sub>CF</sub> = 271.6, C(1'')), 114.6 (C(3')), 55.4 (C(2''))

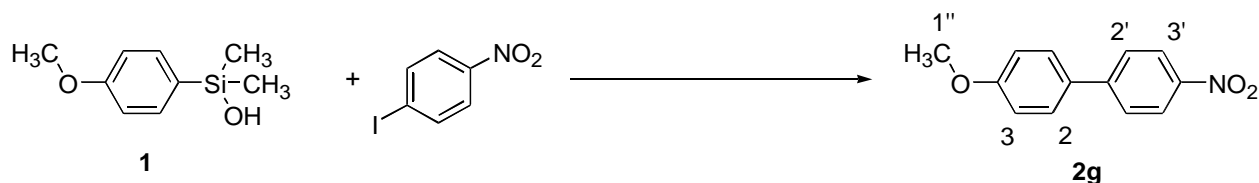
<sup>19</sup>F NMR: (470 MHz, CHCl<sub>3</sub>)

-62.5 (FC(1''))

TLC: *R*<sub>f</sub> 0.79 (toluene) [silica gel, UV]

GC: **2f**, *t*<sub>R</sub> 1.64 min (95.4%); **3f**, *t*<sub>R</sub> 2.37 min (4.6%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)



**Preparation of 4-Methoxy-4'-nitrobiphenyl (2g) (Table 4, entry 7)**

Following General Procedure II, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (108  $\mu$ L, 6.0 mmol, 6.0 equiv), 4-iodonitrobenzene (249 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and triphenylarsine (30.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 6 h. The reaction mixture was cooled to rt and extracted to afford a brown solid which was purified by column chromatography (SiO<sub>2</sub> (20 mm), hexane to hexane/EtOAc, 20/1) and recrystallized (EtOH) to afford 201 mg (88%) of **2g** as a colorless solid. The physical and spectroscopic data matched those from the literature.<sup>4</sup>

Data for 4-Methoxy-4'-nitrobiphenyl (**2g**):

mp: 107-108 °C (EtOH)

<sup>1</sup>H NMR: (500 MHz, CHCl<sub>3</sub>)

8.27 (d, *J* = 9.0, 2 H, HC(3')), 7.70 (d, *J* = 8.8, 2 H, HC(2')), 7.58 (d, *J* = 8.8, 2 H, HC(2)), 7.02 (d, *J* = 8.8, 2 H, HC(3)), 3.88 (s, 3 H, H<sub>3</sub>C(1''))

<sup>13</sup>C NMR: (126 MHz, CHCl<sub>3</sub>)

160.0 (C(4)), 147.3 (C(4')), 145.3 (C(1')), 128.8 (C(1)), 128.4 (C(2)), 127.3 (C(2')), 124.4 (C(3')), 114.6 (C(3)), 55.6 (C(1''))

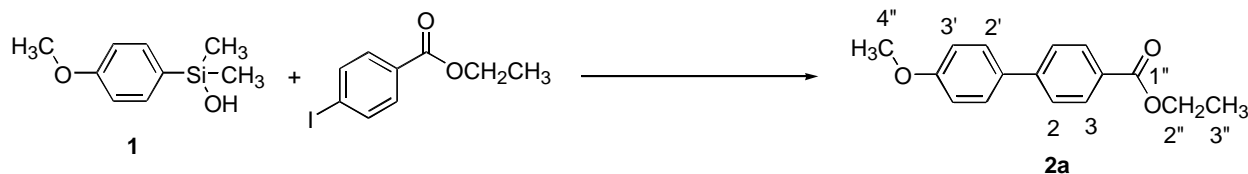
TLC: *R<sub>f</sub>* 0.21 (hexane/EtOAc, 20/1) [silica gel, UV]

GC: **2g**, *t<sub>R</sub>* 3.39 min (94.0%); **3g**, *t<sub>R</sub>* 2.92 min (6.0%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

### General Procedure III: Palladium-Catalyzed Cross-Coupling of (4-Methoxyphenyl)-dimethylsilanol with 4-Substituted Aryl Bromides.

Anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv) was suspended in dry toluene (1.0 mL) at room temperature in a 5-mL, round-bottom flask with a magnetic stir bar and fitted with a reflux condenser and an argon inlet adapter. To this suspension was added dropwise H<sub>2</sub>O (108  $\mu$ L, 6.0 mmol, 6.0 equiv) and the resulting slurry was allowed to stir for 10 min. Aryl bromide (1.0 mmol, 1.0 equiv), and **1** (218 mg, 1.2 mmol, 1.2 equiv) were then added, followed by [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and 1,4-bis(diphenylphosphino)-butane (DPPB) (42.6 mg, 0.1 mmol, 0.1 equiv). The flask was then purged with argon and placed in a 90 °C oil bath. The reaction was monitored by GC analysis at certain intervals until completion. Sampling of the reaction was performed by removing 10  $\mu$ L aliquot of the mixture via syringe. The aliquot was filtered through a small plug of silica gel and eluted with 5 mL of ethyl acetate. The aliquot was then analyzed by GC. Upon completion, the reaction was cooled to rt, treated with H<sub>2</sub>O (10 mL) and extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO<sub>4</sub>), and concentrated in vacuo. The crude product was further purified by column chromatography (SiO<sub>2</sub>) to afford the corresponding product which was further purified by bulb-to-bulb distillation or recrystallization.

### Preparation 4-Carboxy-4'-methoxybiphenyl (**2a**) (Table 5, entry 1)



Following General Procedure III, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (108  $\mu$ L, 6.0 mmol, 6.0 equiv), ethyl 4-bromobenzoate (229 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and DPPB (42.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 24 h. The reaction mixture was cooled to rt and extracted to afford a reddish-brown solid which was purified by column chromatography (SiO<sub>2</sub> (20mm), hexane to hexane/EtOAc, 20/1) and recrystallized

(EtOH) to afford 215 mg (90%) of **2a** as a colorless solid. The physical and spectroscopic data matched those from the literature.<sup>3</sup>

Data for 4'-Carbethoxy-4-methoxybiphenyl (**2a**):

mp: 103-104 °C (EtOH)

<sup>1</sup>H NMR: (500 MHz, CHCl<sub>3</sub>)

8.09 (d, *J* = 8.6, 2 H, HC(3)), 7.62 (d, *J* = 8.8, 2 H, HC(2)), 7.57 (d, *J* = 8.8, 2 H, HC(2')), 7.00 (d, *J* = 8.8, 2 H, HC(3')), 4.40 (q, *J* = 7.1, 2 H, H<sub>2</sub>C(2'')), 3.86 (s, 3 H, H<sub>3</sub>C(1'')), 1.42 (t, *J* = 7.2, 3 H, H<sub>3</sub>C(2''))

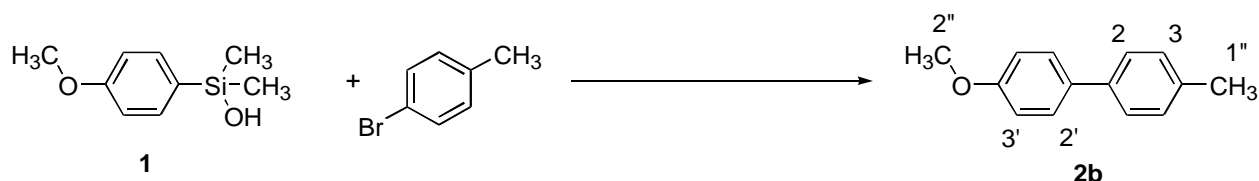
<sup>13</sup>C NMR: (126 MHz, CHCl<sub>3</sub>)

166.6 (C(1'')), 159.8 (C(4')), 145.1 (C(1)), 132.4 (C(3)), 130.0 (C(4)), 128.6 (C(1')), 128.3 (C(2')), 126.4 (C(2)), 114.3 (C(3')), 60.8 (C(2'')), 55.3 (C(4'')), 14.3 (C(3''))

TLC: *R<sub>f</sub>* 0.29 (hexane/EtOAc, 20/1) [silica gel, UV]

GC: **2a**, *t<sub>R</sub>* 3.68 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

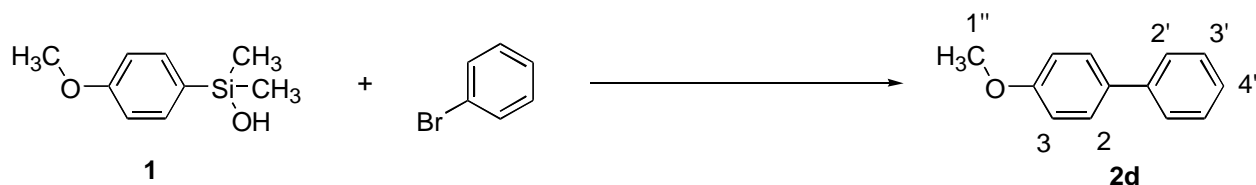
**Preparation of 4'-Methoxy-4-methylbiphenyl (**2b**) (Table 5, entry 2)**



Following General Procedure III, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (108 μL, 6.0 mmol, 6.0 equiv), 4-bromotoluene (171 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and DPPB (42.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 18 h. The reaction mixture was cooled to rt and extracted to afford a brown solid which was purified by column chromatography (SiO<sub>2</sub> (20 mm), toluene) and recrystallized (EtOH) to afford 231 mg (90%) of **2b** as a colorless solid. The physical and spectroscopic data matched those from the literature.<sup>4</sup>

Data for 4'-Methoxy-4-methylbiphenyl (**2b**):mp: 109-110 °C (EtOH)<sup>1</sup>H NMR: (500 MHz, CHCl<sub>3</sub>)7.54 (d, *J* = 8.6, 2 H, HC(2)), 7.48 (d, *J* = 8.2, 2 H, HC(2')), 7.25 (d, *J* = 8.4, 2 H, HC(3)), 6.99 (d, *J* = 8.8, 2 H, HC(3')), 3.86 (s, 3 H, H<sub>3</sub>C(2'')), 2.41 (s, 3 H, H<sub>3</sub>C(1''))<sup>13</sup>C NMR: (126 MHz, CHCl<sub>3</sub>)

158.9 (C(4')), 138.0 (C(4)), 133.7 (C(1)), 129.4 (C(3)), 127.9 (C(1')), 127.7 (C(2')), 126.5 (C(2)), 114.1 (C(3')), 55.3 (C(2'')), 21.0 (C(1''))

TLC: *R<sub>f</sub>* 0.78 (toluene) [silica gel, UV]GC: **2b**, *t<sub>R</sub>* 1.77 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)**Preparation of 4-Methoxybiphenyl (**2d**) (Table 5, entry 3)**

Following General Procedure III, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (108 μL, 6.0 mmol, 6.0 equiv), bromobenzene (157 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and DPPB (42.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 12 h. The reaction mixture was cooled to rt and extracted to afford a brown solid which was purified by column chromatography (SiO<sub>2</sub> (20 mm), toluene) and recrystallized (EtOH) to afford 168 mg (85%) of **2d** as a colorless solid. The physical and spectroscopic data matched those from the literature.<sup>5</sup>

Data for 4-Methoxybiphenyl (**2d**):mp: 90-91 °C (EtOH)<sup>1</sup>H NMR: (500 MHz, CHCl<sub>3</sub>)

7.57-7.52 (m, 4 H, HC(2), HC(2')), 7.42 (t,  $J = 7.7$ , 2 H, HC(3')), 7.31 (t,  $J = 7.5$ , 1 H, HC(4')), 6.99 (d,  $J = 8.8$ , 2 H, HC(3)), 3.86 (s, 3 H, H<sub>3</sub>C(1''))

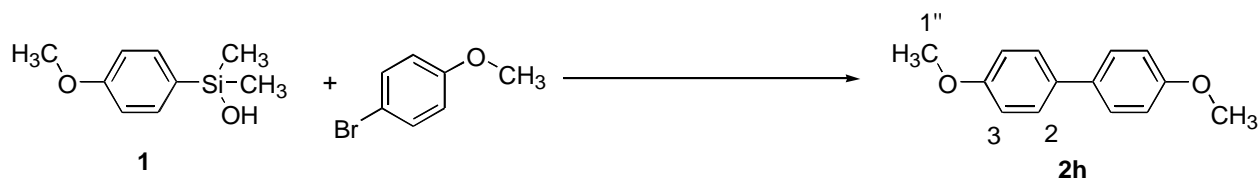
<sup>13</sup>C NMR: (126 MHz, CHCl<sub>3</sub>)

159.2 (C(4)), 140.8 (C(1')), 133.8 (C(3')), 128.7 (C(1)), 128.1 (C(2)), 126.8 (C(2')), 126.7 (C(4')), 114.2 (C(3)), 55.4 (C(1''))

TLC:  $R_f$  0.81 (toluene) [silica gel, UV]

GC: **3d**,  $t_R$  1.27 min (93.7%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

#### Preparation of 4,4'-Dimethoxybiphenyl (**2h**) (Table 5, entry 4)



Following General Procedure III, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (108  $\mu$ L, 6.0 mmol, 6.0 equiv), 4-bromoanisole (187 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and DPPB (42.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 18 h. The reaction mixture was cooled to rt and extracted to afford a brown solid which was purified by column chromatography (SiO<sub>2</sub> (20 mm), hexane to hexane/EtOAc, 20/1) and recrystallized (EtOH) to afford 200 mg (92%) of **2h** as a colorless solid. The physical and spectroscopic data matched those from the literature.<sup>9</sup>

#### Data for 4,4'-Dimethoxybiphenyl (**2h**):

mp: 178-179 °C (EtOH)

<sup>1</sup>H NMR: (500 MHz, CHCl<sub>3</sub>)

7.49 (d,  $J = 8.6$ , 4 H, HC(2), HC(2')), 6.97 (d,  $J = 8.6$ , 4 H, HC(3), HC(3')), 3.86 (s, 6 H, H<sub>3</sub>C(1''), H<sub>3</sub>C(2''))

<sup>13</sup>C NMR: (126 MHz, CHCl<sub>3</sub>)

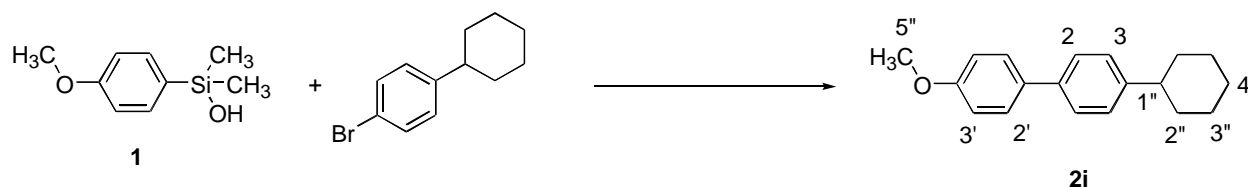
158.6 (C(4)), 133.4 (C(1)), 127.5 (C(2)), 114.1 (C(3)), 55.3 (C(1''))

TLC:  $R_f$  0.44 (toluene) [silica gel, UV]

GC: **2h**,  $t_R$  3.49 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)



### Preparation of 4-cyclohexyl-4'-methoxybiphenyl (2i) (Table 5, entry 5)



Following General Procedure III, a mixture of anhydrous cesium carbonate (1.32 g, 4.0 mmol, 2.0 equiv), H<sub>2</sub>O (216  $\mu$ L, 12.0 mmol, 6.0 equiv), 4-bromocyclohexylbenzene (478 mg, 2.0 mmol, 1.0 equiv), **1** (436 mg, 2.4 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (36.6 mg, 0.10 mmol, 0.05 equiv), and DPPB (85.2 mg, 0.2 mmol, 0.1 equiv) was stirred at 90 °C for 18 h. The reaction mixture was cooled to rt and extracted to afford a brown solid which was purified by column chromatography (SiO<sub>2</sub> (30 mm), toluene) and recrystallized (EtOH) to afford 456 mg (79%) of **2i** as a colorless solid which was further purified by sublimation (90 °C, 0.1 mm Hg).

Data for 4-cyclohexyl-4'-methoxybiphenyl (**2i**):

mp: 115-117 °C (EtOH)

 $^1\text{H}$  NMR: (500 MHz,  $\text{CHCl}_3$ )

7.51 (d,  $J = 8.8$ , 2 H, HC(2)), 7.48 (d,  $J = 8.4$ , 2 H, HC(2')), 7.25 (d,  $J = 7.9$ , 2 H, HC(3)), 6.96 (d,  $J = 8.8$ , HC(3')), 3.85, (s, 3 H, H<sub>3</sub>C(5')), 2.53 (t,  $J = 11.4$ , 1 H, HC(1'')), 1.89 (dd,  $J = 14.4$ , 11.6, 4 H, 2 X HC(2''), 2 X HC(3'')), 1.76 (d,  $J = 13.3$ , 1 H, HC(4'')), 1.43 (sext,  $J = 11.6$ , 4 H, 2 X HC(2''), 2 X HC(3'')), 1.28 (q,  $J = 12.9$ , 1 H, HC(4''))

 $^{13}\text{C}$  NMR: (126 MHz,  $\text{CHCl}_3$ )

159.1 (C(4')), 146.9 (C(4)), 138.6 (C(1)), 134.0 (C(1')), 128.2 (C(2')), 127.4 (C(3)), 126.8 (C(2)), 114.3 (C(3')), 55.5 (C(5')), 44.4 (C(1'')), 34.7 (C(2'')), 27.1 (C(4'')), 26.3 (C(3''))

IR: (CHCl<sub>3</sub>)

3025 (w), 2929 (s), 2854 (m), 2246 (w), 1608 (m), 1498 (s), 1448 (w), 1286 (w),  
1245 (s), 1178 (m), 1041 (m), 821 (s), 709 (w)

MS: (EI, 70 eV)

266 (M,100), 251 (1), 223 (22), 210 (7), 197 (23), 184 (3), 167 (6), 152 (4), 115 (3), 91 (4)

TLC:  $R_f$  0.74 (toluene) [silica gel, UV]

GC: **3i**,  $t_R$  min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Analysis: C<sub>19</sub>H<sub>22</sub>O<sub>1</sub> (266.38)

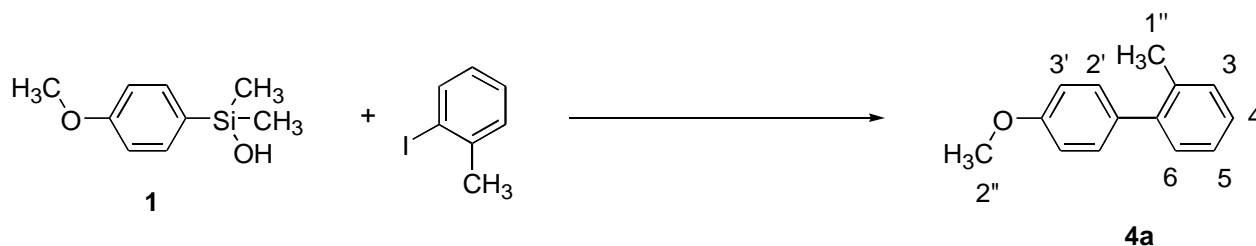
Calcd: C, 85.67%; H, 8.32%

Found: C, 85.96%; H, 8.62%

**General Procedure IV: Palladium-Catalyzed Cross-Coupling of (4-Methoxyphenyl)-dimethylsilanol with 2-Substituted Aryl Iodides.**

Anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv) was suspended in dry dioxane (1.0 mL) at room temperature in a 5-mL, round-bottom flask with a magnetic stir bar and fitted with a reflux condenser and an argon inlet adapter. To this suspension was added drop-wise H<sub>2</sub>O (72 µL, 4.0 mmol, 4.0 equiv) and the resulting slurry was allowed to stir for 10 min. Aryl iodide (1.0 mmol, 1.0 equiv), and **1** (218 mg, 1.2 mmol, 1.2 equiv) were then added, followed by [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and triphenylarsine (30.6 mg, 0.1 mmol, 0.1 equiv). The flask was then purged with argon and placed in a 90 °C oil bath. The reaction was monitored by GC analysis at certain intervals until completion. Sampling of the reaction was performed by removing 10 µL aliquot of the mixture via syringe. The aliquot was filtered through a small plug of silica gel and eluted with 5 mL of ethyl acetate. The aliquot was then analyzed by GC. Upon completion, the reaction was cooled to rt, treated with H<sub>2</sub>O (10 mL) and extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO<sub>4</sub>), and concentrated in vacuo. The crude product was further purified by column chromatography (SiO<sub>2</sub>) to afford the corresponding product which was further purified by bulb-to-bulb distillation or recrystallization.



**Preparation of 4'-Methoxy-2-methylbiphenyl (4a) (Table 6, entry 1)**

Following General Procedure IV, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (72  $\mu$ L, 4.0 mmol, 4.0 equiv), 2-iodotoluene (218 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and triphenylarsine (30.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 24 h. The reaction mixture was cooled to rt and extracted to afford a brown liquid which was purified by column chromatography (SiO<sub>2</sub> (20 mm), toluene) and distilled bulb-to-bulb to afford 168 mg (85%) of **4a** as a colorless oil. The physical and spectroscopic data matched those from the literature.<sup>5</sup>

Data for 4'-Methoxy-2-methylbiphenyl (**4a**):

bp: 120 °C (1 mm Hg, ABT)

<sup>1</sup>H NMR: (500 MHz, CHCl<sub>3</sub>)

7.27-7.23 (m, 6 H), 6.96 (d, *J* = 8.5, 2 H, HC(3)), 3.86 (s, 3 H, HC(2'')), 2.30 (s, 3 H, H<sub>3</sub>C(1''))

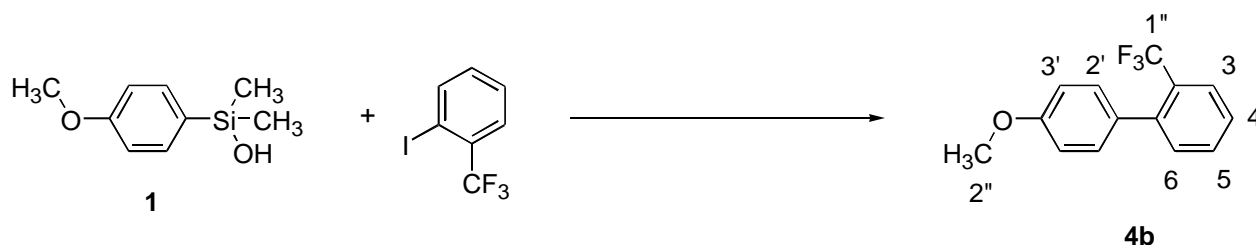
<sup>13</sup>C NMR: (126 MHz, CHCl<sub>3</sub>)

158.8 (C(4')), 141.8 (C(2)), 135.7 (C(1)), 134.6 (C(3)), 130.6 (C(1')), 130.5 (C(2')), 130.1 (C(4)), 127.2 (C(6)), 126.0 (C(5)), 113.7 (C(3')), 55.5 (C(2'')), 20.7 (C(1''))

TLC: *R<sub>f</sub>* 0.77 (toluene) [silica gel, UV]

GC: **4a**, *t<sub>R</sub>* 1.29 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

### Preparation of 4'-Methoxy-2-trifluoromethyl-biphenyl (4b) (Table 6, entry 2)



Following General Procedure IV, a mixture of anhydrous cesium carbonate (1.310 g, 4.0 mmol, 2.0 equiv), H<sub>2</sub>O (144  $\mu$ L, 8.0 mmol, 4.0 equiv), 2-iodobenzotrifluoride (544 mg, 2.0 mmol, 1.0 equiv), **1** (436 mg, 2.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (36.6 mg, 0.1 mmol, 0.05 equiv), and triphenylarsine (36.6 mg, 0.2 mmol, 0.1 equiv) was stirred at 90 °C for 24 h. The reaction mixture was cooled to rt and extracted to afford a brown liquid which was purified by column chromatography (SiO<sub>2</sub> (30 mm), toluene) and recrystallized (EtOH) to afford 405 mg (82%) of **4b** as a colorless solid which was further purified by sublimation (50 °C, 0.1 mm Hg).

Data for 4-Methoxy-2-trifluoromethyl-biphenyl (4b):

mp: 54-55 °C (EtOH)

 $^1\text{H NMR: (500 MHz, CHCl}_3\text{)}$ 

7.73 (d,  $J = 8.3$ , 1 H, HC(3)), 7.54 (t,  $J = 8.2$ , 1 H, HC(4)), 7.44 (t,  $J = 7.9$ , 1 H, HC(5)), 7.32 (d,  $J = 7.7$ , 1 H, HC(6)), 7.25 (d,  $J = 8.4$ , 2 H, HC(2')), 6.94 (d,  $J = 8.8$  2 H, HC(3')), 3.86 (s, 3 H, H<sub>3</sub>C(2''))

 $^{13}\text{C}$  NMR: (126 MHz,  $\text{CHCl}_3$ )

159.2 (C(4')), 141.2 (C(1)), 132.3 (C(4)), 132.2 (C(1)), 131.2 (C(1')), 130.1 (C(2')), 128.6 (q,  $^2J_{\text{CF}} = 29.5$ , C(2)), 127.0 (C(5)), 126.0 (C(3)) 124.2 (q,  $^1J_{\text{CF}} = 274.34$ , C(1')), 113.4 (C(3')), 55.2 (C(2'))

 $^{19}\text{F}$  NMR: (470 MHz,  $\text{CHCl}_3$ )

-56.9 (FC(1''))

IR: (CHCl<sub>3</sub>)

3154 (w), 3006 (m), 2962 (s), 2910 (m), 2838 (m), 2254 (m), 1612 (s), 1519 (m),  
1486 (m), 1448 (m), 1315 (s), 1245 (m), 1172 (s), 1132 (m), 1072 (w), 1037 (m),  
917 (s), 898 (s), 835 (w), 754 (s), 752 (s), 651(s)

**MS:** (EI, 70 eV)

252 (M, 100), 237 (25), 222 (2), 209 (37), 183(8), 159(4), 139 (6), 100 (2), 63 (3)

**TLC:**  $R_f$  0.82 (toluene) [silica gel, UV]

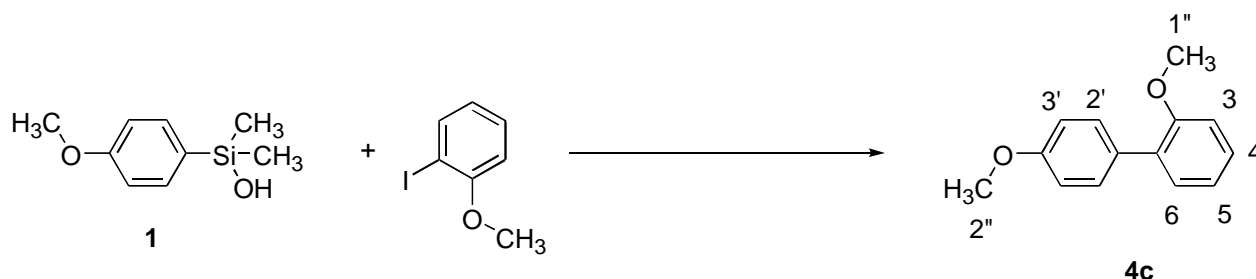
**GC:** **4b**,  $t_R$  0.95 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Analysis:** C<sub>14</sub>H<sub>11</sub>F<sub>3</sub>O<sub>1</sub> (252.23)

Calcd: C, 66.66%; H, 4.40%

Found: C, 66.83%; H, 4.35%

### Preparation of 2,4'-Dimethoxybiphenyl (**4c**) (Table 6, entry 3)



Following General Procedure IV, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (72  $\mu$ L, 4.0 mmol, 4.0 equiv), 2-iodoanisole (234 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and triphenylarsine (30.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 24 h. The reaction mixture was cooled to rt and extracted to afford a brown liquid which was purified by column chromatography (SiO<sub>2</sub> (20 mm), hexane to hexane/EtOAc, 20/1) and recrystallized (EtOH) to afford 182 mg (84%) of **4c** as a colorless solid and further purified by sublimation (90 °C, 0.1 mm Hg). The physical and spectroscopic data matched those from the literature.<sup>5</sup>

#### Data for 2,4'-Dimethoxybiphenyl (**4c**):

**mp:** 69-70 °C (EtOH)

**<sup>1</sup>H NMR:** (500 MHz, CHCl<sub>3</sub>)

7.48 (d,  $J$  = 8.8, 2 H, HC(2')), 7.31 (ABX, 2 H, HC(4), HC(5)), 7.02 (m, 4 H, HC(3'), HC(3), HC(6)), 3.85 (s, 3 H, H<sub>3</sub>C(1'')), 3.82 (s, 3 H, H<sub>3</sub>C(2''))

**<sup>13</sup>C NMR:** (126 MHz, CHCl<sub>3</sub>)

158.6 (C(4')), 156.5 (C(2)), 130.9 (C(1')), 130.7 (C(2')), 130.6 (C(4)), 130.3 (C(6)), 128.2 (C(1)), 120.8 (C(5)), 113.5 (C(3')), 111.2 (C(3)), 55.5 (C(1'')), 55.2 (C(2''))

**IR:** (CHCl<sub>3</sub>)

3066 (w), 3000 (m), 2956 (s), 2908 (m), 2834 (s), 2526 (w), 2049 (w), 1895 (w), 1596 (s), 1617 (s), 1486 (s), 1463 (s), 1409 (w), 1297 (m), 1247 (s), 1180 (s), 1118 (m), 1035 (s) 831 (m), 786 (m), 754 (s)

**TLC:** *R<sub>f</sub>* 0.40 (toluene) [silica gel, UV]

**GC:** **4c**, *t<sub>R</sub>* 1.99 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**Analysis:** C<sub>14</sub>H<sub>14</sub>O<sub>2</sub> (214.26)

Calcd: C, 78.48%; H, 6.59%

Found: C, 78.44%; H, 6.55%

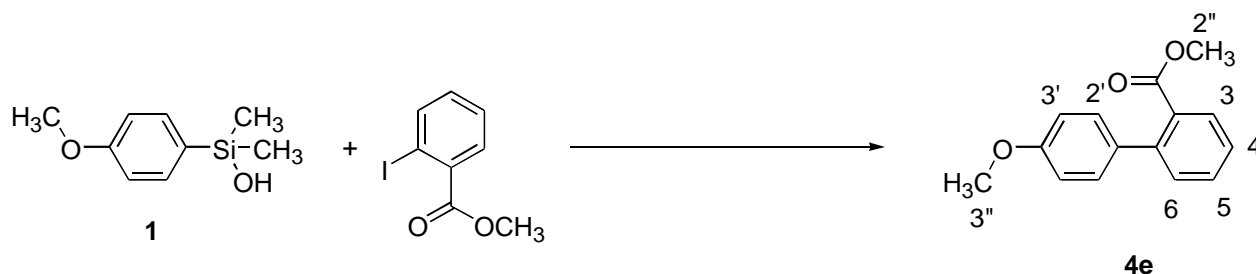
#### Preparation of 4-Methoxy-2'-nitrobiphenyl (**4d**) (Table 6, entry 4)



Following General Procedure IV, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (72  $\mu$ L, 4.0 mmol, 4.0 equiv), 2-iodonitrobenzene (249 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and triphenylarsine (30.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 24 h. The reaction mixture was cooled to rt and extracted to afford a brown liquid which was purified by column chromatography (SiO<sub>2</sub> (20 mm), hexane to hexane/EtOAc, 20/1) and recrystallized (EtOH) to afford 191 mg (83%) of **4d** as a colorless solid. The physical and spectroscopic data matched those from the literature.<sup>11</sup>

Data for 4-Methoxy-2'-nitrobiphenyl (**4d**):mp: 62-64 °C (EtOH)<sup>1</sup>H NMR: (500 MHz, CHCl<sub>3</sub>)7.80 (d, *J* = 8.3, 1 H, HC(3')), 7.59 (t, *J* = 8.6, 1 H, HC(4')), 7.44 (m, 2 H), 7.25 (d, *J* = 8.8, 2 H, HC(2)), 6.95 (d, *J* = 8.8 2 H, HC(3)), 3.85 (s, 3 H, H<sub>3</sub>C(1''))<sup>13</sup>C NMR: (126 MHz, CHCl<sub>3</sub>)

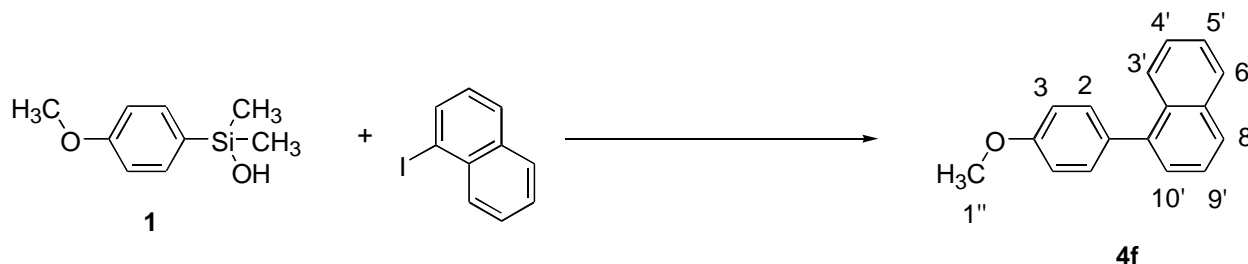
159.9 (C(4)), 149.6 (C(2')), 136.1 (C(5')), 132.4 (C(1')), 132.2 (C(1)), 129.7 (C(2)), 129.4 (C(6')), 127.9 (C(4')), 124.2 (C(3')), 114.4 (C(3)), 55.5 (C(1''))

TLC: *R<sub>f</sub>* 0.21 (toluene) [silica gel, UV]GC: **4d**, *t<sub>R</sub>* 2.69 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)**Preparation of 2-Carbmethoxy-4'-methoxybiphenyl (**4e**) (Table 6, entry 5)**

Following General Procedure IV, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (72 μL, 4.0 mmol, 4.0 equiv), methyl 2-iodobenzoate (262 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and triphenylarsine (30.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 24 h. The reaction mixture was cooled to rt and extracted to afford a brown liquid which was purified by column chromatography (SiO<sub>2</sub> (20 mm), hexane to hexane/EtOAc, 20/1) and distilled bulb-to-bulb to afford 213 mg (88%) of **4e** as a colorless solid. The physical and spectroscopic data matched those from the literature.<sup>12</sup>

Data for 2-Carbmethoxy-4'-methoxybiphenyl (**4e**):bp: 185 °C (1 mm Hg, ABT)<sup>1</sup>H NMR: (500 MHz, CHCl<sub>3</sub>)7.82 (d, *J* = 7.5, 1 H, HC(3)), 7.58 (m, 2 H, HC(4), HC(6)), 7.25 (d, *J* = 4.0, 2 H, HC(3')), 6.89 (m, 1 H, HC(5)), 6.71 (d, *J* = 2.6, 2 H, HC(2')), 3.79 (s, 3 H, H<sub>3</sub>C(2'')), 2.45 (s, 3 H, H<sub>3</sub>C(1''))<sup>13</sup>C NMR: (126 MHz, CHCl<sub>3</sub>)

169.6 (C(1'')), 159.2 (C(4')), 142.2 (C(1)), 133.9 (C(5)), 131.4 (C(3)), 131.1 (C(2)), 130.9 (C(1')), 129.9 (C(2')) , 129.7 (C(4)), 127.0 (C(6)), 113.8 (C(3')), 55.4 (C(3'')), 52.2 (C(2''))

TLC: *R<sub>f</sub>* 0.35 (toluene) [silica gel, UV]GC: **4e**, *t<sub>R</sub>* 2.49 min (100%) ((HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)**Preparation of 1-(4-Methoxyphenyl)naphthalene (**4f**) (Table 6, entry 6)**

Following General Procedure IV, a mixture of anhydrous cesium carbonate (651 mg, 2.0 mmol, 2.0 equiv), H<sub>2</sub>O (72 μL, 4.0 mmol, 4.0 equiv), 1-iodonaphthalene (254 mg, 1.0 mmol, 1.0 equiv), **1** (218 mg, 1.2 mmol, 1.2 equiv), [allylPdCl]<sub>2</sub> (18.3 mg, 0.05 mmol, 0.05 equiv), and triphenylarsine (30.6 mg, 0.1 mmol, 0.1 equiv) was stirred at 90 °C for 24 h. The reaction mixture was cooled to rt and extracted to afford a brown liquid which was purified by column chromatography (SiO<sub>2</sub> (20 mm), toluene) and recrystallized (EtOH) to afford 202 mg (86%) of **4f** as a colorless solid. The physical and spectroscopic data matched those from the literature.<sup>11</sup>

Data for 1-(4-Methoxyphenyl)-naphthalene (4f):

mp: 115-116 °C (EtOH)

<sup>1</sup>H NMR: (500 MHz, CHCl<sub>3</sub>)

7.94-7.84 (m, 3 H), 7.53-7.41 (m, 6 H), 7.04 (d, *J* = 8.8, 2 H, HC(3)), 3.90 (s, 3 H, H<sub>3</sub>C(1''))

<sup>13</sup>C NMR: (126 MHz, CHCl<sub>3</sub>)

158.9 (C(4)), 139.9 (C(1')), 133.8 (C(6')), 133.1 (C(2')), 131.8 (C(1)), 131.1 (C(2)), 128.3 (C(3')), 127.3 (C(6')), 126.9 (C(7')), 126.1 (C(8')), 125.9 (C(4')), 125.7 (C(5')), 125.4 (C(10')), 113.7 (C(3)), 55.3 (C(1''))

TLC: *R<sub>f</sub>* 0.75 (toluene) [silica gel, UV]

GC: **4f**, *t<sub>R</sub>* 3.38 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

**References**

- (1) Dent, W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585.
- (2) Hirabayashi, K.; Takahisa, R.; Nishihara, Y.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1998**, 71, 2409.
- (3) Darses, S.; Jeffery, T.; Brayer, J.-L.; Demoute, J.-P.; Genet, J.-P. *Bull. Soc. Chem. Fr.* **1996**, 133, 1095.
- (4) Hirabayashi, K.; Mori, A.; Kawashima, J.; Suguro, M.; Nishihara, Y.; Hiyama, T. *J. Org. Chem.* **2000**, 65, 5342.
- (5) Lipshutz, B.H.; Siegmann, K.; Garcia, E.; Kayser, F. *J. Am. Chem. Soc.* **1993**, 115, 9276.
- (6) Jutand, A.; Mosleh, A. *J. Org. Chem.* **1997**, 62, 261.
- (7) Gray, G. W.; Mosley, A. *J. Chem. Soc., Perkin Trans. 2.* **1976**, 97.
- (8) Brune, H. A.; Stapp, B.; Schmidtberg, G. *J. Organomet. Chem.* **1986**, 129.
- (9) Wallow, T. I.; Novak, B. M. *J. Org. Chem.* **1994**, 59, 5034.
- (10) (a) Bjorklunk, C. *Acta Chem. Scand.* **1971**, 25, 2825. (b) Holzapfel, C. W.; Dwyer, C. *Heterocycles* **1998**, 48, 1513.

- (11) Roth, P. G.; Carl, E. F. *J. Org. Chem.* **1991**, 56, 3493.
- (12) Genevieve, E.; Dodey, P.; Renaut, P.; Leclerc, G. *Org. Prep. Proced. Int.* **1995**, 4, 500.