Palladium-Catalyzed Cross-Coupling of Substituted Aryl(dimethyl)silanols

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SUPPORTING INFORMATION

General Experimental

All reactions were performed in oven (140 °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: CaH₂; methanol: Mg(OMe)₂; ethyl acetate: K₂CO₃. "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 (CaCl₂); ethyl acetate (K₂CO₃). 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 KMnO₄ solution.

Analytical gas chromatography (GC) was performed using a Hewlett Packard 5890 Series II Gas Chromatograph fitted with a flame ionization detector (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.

¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Varian Unity-500 (500 MHz ¹H, 126 MHz ¹³C, 470 MHz ¹⁹F) spectrometer in deuterochloroform unless otherwise stated using chloroform as an internal reference for ¹H and ¹³C (7.26 ppm, ¹H; 77.2 ppm, ¹³C) or hexafluorobenzene as an internal reference for ¹⁹F NMR (-160,0 ppm, ¹⁹F). Chemical shifts are reported in ppm (d); 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 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 and cesium hydroxide monohydrate were 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 dimer¹, (4-methoxyphenyl)dimethylsilanol² (4-trifluoromethylphenyl)dimethylsilanol², and (2-methylphenyl)dimethylsilanol² were prepared by literature methods.

General Procedure I: Optimization Experiments for the Palladium-Catalyzed Cross-Coupling of (4-Methoxyphenyl)dimethylsilanol with Ethyl 4-Iodobenzoate.

The selected base (1.0 mmol, 2.0 equiv.) was suspended in dry solvent (0.5 mL) at room temperature in a 5-mL one-neck 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]₂ (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. Reaction progress was monitored by GC analysis at certain intervals until completion. Sampling of the reaction was performed by removing a 10 μ L aliquot of the mixture by syringe. The aliquot was filtered through a small plug of silica gel and was eluted with 5 mL of ethyl acetate. The aliquot was then analyzed by GC. Response factors were obtained by equation 1 and are shown below:

Eq 1: Response factor for $A =$		(mmol A * area internal standard)			
		(mmol internal standard * area A)			
		ethyl 4-	ethyl 4-		
		iodobenzoate	iodobenzoate		
biphenyl (mmol)	biphenyl (area)	(mmol)	(area)	response factor	
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	
		cross-coupling			
		product 2a	cross-coupling		
biphenyl (mmol)	biphenyl (area)	(mmol)	product 2a (area)	response factor	
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	
		homo-coupling			
		product 3a	homo-coupling		
biphenyl (mmol)	biphenyl (area)	(mmol)	product 3a (area)	response factor	
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	
napthalene		4-bromoanisole	4-bromoanisole		
(mmol)	napthalene (area)	(mmol)	(area)	response factor	
0.0975	4.11360e6	0.0999	4.30301e6	0.980	
0.0967	3.78922e6	0.0994	4.01888e6	0.969	
0.0975	3.99367e6	0.0994	4.24302e6	0.960	

		cross-coupling		
napthalene		product 4a	cross-coupling	
(mmol)	napthalene (area)	(mmol)	product 4a (area)	response factor
0.0.998	4.51758e6	0.0974	4.18431e6	1.054
0.1001	5.00090e6	0.0999	4.69867e6	1.062
0.0983	4.70181e6	0.1010	4.51839e6	1.069
		homo-coupling		
napthalene		product 2h	homo-coupling	
(mmol)	napthalene (area)	(mmol)	product 2h (area)	response factor
0.1001	4.07850e6	0.0998	4.08494e6	0.995
0.0975	3.85694e6	0.1008	4.18439e6	0.953
0.1001	3.90184e6	0.1003	4.0385e6	0.968

Eq 2: Conversion of Iodide =

(area iodide * Rf) / ((area iodide* Rf) + (area 2a * Rf) + (2 * area 3a *Rf)) X 100

Eq 3: Ratio of **2a** : **3b** =

(area 2a * Rf) / (area 3a * Rf)

Table 1, entry 1:

Following General Procedure I, a mixture of TBAF (1.0 mL, 1.0 mmol, 2.0 equiv.) in THF (1.0 M), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.) was stirred at 60 °C for 12 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, t_R 0.92 min (0%); **2a**, t_R 3.65 min (75%); **3a**, t_R 5.05 min (25%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 1, entry 2:

Following General Procedure I, a mixture of potassium trimethylsilanolate (257 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol, 1.0), **1** (109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.) was stirred at 60 °C for 6 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, t_R 0.92 min (0%); **2a**, t_R 3.65 min (0%); **3a**, t_R 5.05 min (0%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 1, entry 3:

Following General Procedure I, a mixture of potassium trimethylsilanolate (128 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), 4-iodotoluene (109 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.) was stirred at 60 °C for 12 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, t_R 0.92 min (64%); **2a**, t_R 3.65 min (28%); **3a**, t_R 5.05 min (8%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 1, entry 4:

Following General Procedure I, a mixture of sodium carbonate (105 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.) was stirred at 60 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, t_R 0.92 min (100%); **2a**, t_R 3.65 min (0%); **3a**, t_R 5.05 min (0%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 1, entry 5:

Following General Procedure I, a mixture of potassium carbonate (139 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.) was stirred at 60 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, t_R 0.92 min (100%); **2a**, t_R 3.65 min (0%); **3a**, t_R 5.05 min (0%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 1, entry 6:

Following General Procedure I, a mixture of rubidium carbonate (231 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.) was stirred at 60 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, t_R 0.92 min (92%); **2a**, t_R 3.65 min (5%); **3a**, t_R 5.05 min (3%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 1, entry 7:

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.) was stirred at 60 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, t_R 0.92 min (55%); **2a**, t_R 3.65 min (41%); **3a**, t_R 5.05 min (4%) (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.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (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 (22%); **2a**, t_R 3.65 min (71%); **3a**, t_R 5.05 min (7%) (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.) in dioxane (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (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 (12%); **2a**, t_R 3.65 min (71%); **3a**, t_R 5.05 min (17%) (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.) in dimethoxyethane (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (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 (2%); **2a**, t_R 3.65 min (60%); **3a**, t_R 5.05 min (40%) (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.) in dimethylformamide (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (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 (0%); **2a**, t_R 3.65 min (17%); **3a**, t_R 5.05 min (83%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 3, entry 1:

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and triphenylphosphine (26.2 mg, 0.1 mmol, 2.0 equiv./Pd) 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 (0%); **2a**, t_R 3.65 min (68%); **3a**, t_R 5.05 min (32%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 3, entry 2:

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and tri-*o*-tolylphosphine (30.4 mg, 0.1 mmol, 2.0 equiv./Pd) 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 (33%); **2a**, t_R 3.65 min (56%); **3a**, t_R 5.05 min (11%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 3, entry 3:

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and tris(pentafluorophenyl)phosphine (53.2 mg, 0.1 mmol, 2.0 equiv./Pd) 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 (32%); **2a**, t_R 3.65 min (37%); **3a**, t_R 5.05 min (31%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 3, entry 4:

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and tri-*t*-butylphosphine (20.3 mg, 0.1 mmol, 2.0 equiv./Pd) 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 (5.84479e4, 1%); **2a**, t_R 3.65 min (62%); **3a**, t_R 5.05 min (37%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 3, entry 5:

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and tri-2-furylphosphine (23.2 mg, 0.1 mmol, 2.0 equiv./Pd) 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 (1%); **2a**, t_R 3.65 min (78%); **3a**, t_R 5.05 min (21%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 3, entry 6:

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and triphenylarsine (30.6 mg, 0.1 mmol, 2.0 equiv./Pd) 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 (0%); **2a**, t_R 3.65 min (92%); **3a**, t_R 5.05 min (8%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 3, entry 7:

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and triphenylarsine (15.3 mg, 0.1 mmol, 1.0 equiv./Pd) 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 (0%); **2a**, t_R 3.65 min (92%); **3a**, t_R 5.05 min (8%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 3, entry 8:

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and 2-(di-t-butylphosphino)biphenyl (29.8 mg, 0.1 mmol, 2.0 equiv./Pd) 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 (1%); **2a**, t_R 3.65 min (12%); **3a**, t_R 5.05 min (87%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 3, entry 9:

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and 1,3-bis(diphenylphosphino)-propane (18.3 mg, 0.05 mmol, 2.0 equiv./Pd) 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 (1%); **2a**, t_R 3.65 min (72%); **3a**, t_R 5.05 min (27%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 3, entry 10:

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and 1,4-bis(diphenylphosphino)-butane (21.3 mg, 0.05 mmol, 1.0 equiv./Pd) 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 (1%); **2a**, t_R 3.65 min (85%); **3a**, t_R 5.05 min (14%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 5, entry 11:

Following General Procedure I, a mixture of cesium carbonate (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and 1,1'-bis(diphenylphosphino)-ferrocene (27.7 mg, 0.05 mmol, 1.0 equiv./Pd) 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 (1%); **2a**, t_R 3.65 min (72%); **3a**, t_R 5.05 min (27%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 4, entry 1:

Following General Procedure I, a mixture of cesium carbonate^{3a} (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 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 (15%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 4, entry 2:

Following General Procedure I, a mixture of cesium carbonate^{3b} (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 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 (27%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 4, entry 3:

Following General Procedure I, a mixture of cesium carbonate^{3c} (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 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 (32%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 4, entry 4:

Following General Procedure I, a mixture of cesium carbonate^{3d} (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 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 (59%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 4, entry 5:

Following General Procedure I, a mixture of commercially available cesium carbonate^{3e} (325 mg, 1.0 mmol, 2.0 equiv.) in toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1**

(109 mg, 0.6 mmol, 1.2 equiv.), and [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.) was stirred at 90 °C for 3 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, $t_{\rm R}$ 0.92 min (66%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Figure 1, 0.0 equivalents:

Following General Procedure I, a mixture of commercially available cesium carbonate^{3e} (325 mg, 1.0 mmol, 2.0 equiv.), toluene (0.5 mL), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), 1 (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and triphenylarsine (15.3 mg, 0.05 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 3 h. An aliquot of the mixture was then taken for GC analysis. Ethyl 4-iodobenzoate, $t_{\rm R}$ 4.81 min (75%) (HP-5, 270 °C, 16 psi)

Figure 1, 1.0 equivalents:

Following General Procedure I, a mixture of commercially available cesium carbonate^{3e} (325 mg, 1.0 mmol, 2.0 equiv.), toluene (0.5 mL), H₂O (18 μ L, 1.0 mmol, 1.0 equiv./Cs₂CO₃), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and triphenylarsine (15.3 mg, 0.05 mmol, 1.0 equiv./Pd) 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 (50%) (HP-5, 270 °C, 16 psi)

Figure 1, 2.0 equivalents:

Following General Procedure I, a mixture of commercially available cesium carbonate^{3e} (325 mg, 1.0 mmol, 2.0 equiv.), toluene (0.5 mL), H₂O (36 μ L, 2.0 mmol, 2.0 equiv./Cs₂CO₃), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and triphenylarsine (15.3 mg, 0.05 mmol, 1.0 equiv./Pd) 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 (37%) (HP-5, 270 °C, 16 psi)

Figure 1, 3.0 equivalents:

Following General Procedure I, a mixture of commercially available cesium carbonate^{3e} (325 mg, 1.0 mmol, 2.0 equiv.), toluene (0.5 mL), H₂O (54 μL, 3.0 mmol, 3.0 equiv./Cs₂CO₃),

ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), $[allylPdCl]_2$ (9.1 mg, 0.025 mmol, 0.05 equiv.), and triphenylarsine (15.3 mg, 0.05 mmol, 1.0 equiv./Pd) 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 (29%) (HP-5, 270 °C, 16 psi)

Figure 1, 4.0 equivalents:

Following General Procedure I, a mixture of commercially available cesium carbonate^{3e} (325 mg, 1.0 mmol, 2.0 equiv.), toluene (0.5 mL), H₂O (72 μ L, 4.0 mmol, 4.0 equiv./Cs₂CO₃), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and triphenylarsine (15.3 mg, 0.05 mmol, 1.0 equiv./Pd) 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 (34%) (HP-5, 270 °C, 16 psi)

Figure 1, 5.0 equivalents:

Following General Procedure I, a mixture of commercially available cesium carbonate^{3e} (325 mg, 1.0 mmol, 2.0 equiv.), toluene (0.5 mL), H₂O (90 μ L, 5.0 mmol, 5.0 equiv./Cs₂CO₃), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and triphenylarsine (15.3 mg, 0.05 mmol, 1.0 equiv./Pd) 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 (38%) (HP-5, 270 °C, 16 psi)

Figure 1, 6.0 equivalents:

Following General Procedure I, a mixture of commercially available cesium carbonate^{3e} (325 mg, 1.0 mmol, 2.0 equiv.), toluene (0.5 mL), H₂O (90 μ L, 5.0 mmol, 5.0 equiv./Cs₂CO₃), ethyl 4-iodobenzoate (138 mg, 0.5 mmol), **1** (109 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and triphenylarsine (15.3 mg, 0.05 mmol, 1.0 equiv./Pd) 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 (75%) (HP-5, 270 °C, 16 psi)

Figure 2, 1.0 equivalents:

Following General Procedure I, a mixture of cesium hydroxide monohydrate (168 mg, 1.0 mmol, 2.0 equiv.), dioxane (0.5 mL), H₂O (18 μ L, 1.0 mmol, 1.0 equiv./CsOH•H₂O), 4bromoanisole (94 mg, 0.5 mmol), **5** (100 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and dppb (21.3 mg, 0.2 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. 4-iodoanisole, t_R 1.03 min (26%); **4a**, t_R 2.63 min (56%); **2h**, t_R 3.77 min (19%) (HP-1, 150 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Figure 2, 2.0 equivalents:

Following General Procedure I, a mixture of cesium hydroxide monohydrate (168 mg, 1.0 mmol, 2.0 equiv.), dioxane (0.5 mL), H₂O (36 μ L, 2.0 mmol, 2.0 equiv./CsOH•H₂O), 4bromoanisole (94 mg, 0.5 mmol), **5** (100 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and dppb (21.3 mg, 0.2 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. 4-iodoanisole, t_R 1.03 min (0%); **4a**, t_R 2.63 min (91%); **2h**, t_R 3.77 min (9%) (HP-1, 150 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Figure 2, 3.0 equivalents:

Following General Procedure I, a mixture of cesium hydroxide monohydrate (168 mg, 1.0 mmol, 2.0 equiv.), dioxane (0.5 mL), H₂O (54 μ L, 3.0 mmol, 3.0 equiv./CsOH•H₂O), 4bromoanisole (94 mg, 0.5 mmol), **5** (100 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and dppb (21.3 mg, 0.2 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. 4-iodoanisole, t_R 1.03 min (26%); **4a**, t_R 2.63 min (68%); **2h**, t_R 3.77 min (6%) (HP-1, 150 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Figure 2, 4.0 equivalents:

Following General Procedure I, a mixture of cesium hydroxide monohydrate (168 mg, 1.0 mmol, 2.0 equiv.), dioxane (0.5 mL), H₂O (72 μ L, 4.0 mmol, 4.0 equiv./CsOH•H₂O), 4bromoanisole (94 mg, 0.5 mmol), **5** (100 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and dppb (21.3 mg, 0.2 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. 4-iodoanisole, t_R 1.03 min (75%); **4a**, t_R 2.63 min (25%); **2h**, t_R 3.77 min (0%) (HP-1, 150 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 8, entry 1:

Following General Procedure I, a mixture of cesium hydroxide monohydrate (168 mg, 1.0 mmol, 2.0 equiv.), dioxane (0.5 mL), H₂O (36 μ L, 2 mmol, 2.0 equiv./CsOH•H₂O), 4bromoanisole (94 mg, 0.5 mmol), **5** (100 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and dppb (21.3 mg, 0.2 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. 4-iodoanisole, t_R 1.03 min (0%); **4a**, t_R 2.63 min (91%); **2h**, t_R 3.77 min (9%) (HP-1, 150 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 8, entry 2:

Following General Procedure I, a mixture of cesium hydroxide monohydrate (168 mg, 1.0 mmol, 2.0 equiv.), dioxane (0.4 mL), toluene (0.1 mL), H₂O (36 μ L, 2.0 mmol, 2.0 equiv./CsOH•H₂O), 4-bromoanisole (94 mg, 0.5 mmol), **5** (100 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and dppb (21.3 mg, 0.2 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. 4-iodoanisole, t_R 1.03 min (4%); **4a**, t_R 2.63 min (90%); **2h**, t_R 3.77 min (5%) (HP-1, 150 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 8, entry 3:

Following General Procedure I, a mixture of cesium hydroxide monohydrate (168 mg, 1.0 mmol, 2.0 equiv.), dioxane (0.3 mL), toluene (0.2 mL), H₂O (36 μ L, 2.0 mmol, 2.0 equiv./ CsOH•H₂O), 4-bromoanisole (94 mg, 0.5 mmol), **5** (100 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and dppb (21.3 mg, 0.2 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. 4-iodoanisole, t_R 1.03 min (8%); **4a**, t_R 2.63 min (86%); **2h**, t_R 3.77 min (6%) (HP-1, 150 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 8, entry 4:

Following General Procedure I, a mixture of cesium hydroxide monohydrate (168 mg, 1.0 mmol, 2.0 equiv.), dioxane (0.2 mL), toluene (0.3 mL), H₂O (36 μ L, 2.0 mmol, 2.0 equiv./ CsOH•H₂O), 4-bromoanisole (94 mg, 0.5 mmol), **5** (100 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and dppb (21.3 mg, 0.2 mmol, 1.0 equiv./Pd) was stirred at

90 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. 4-iodoanisole, t_R 1.03 min (13%); **4a**, t_R 2.63 min (83%); **2h**, t_R 3.77 min (4%) (HP-1, 150 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 8, entry 5:

Following General Procedure I, a mixture of cesium hydroxide monohydrate (168 mg, 1.0 mmol, 2.0 equiv.), dioxane (0.1 mL), toluene (0.4 mL), H₂O (36 μ L, 2.0 mmol, 2.0 equiv./CsOH•H₂O), 4-bromoanisole (94 mg, 0.5 mmol), **5** (100 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and dppb (21.3 mg, 0.2 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. 4-iodoanisole, t_R 1.03 min (25%); **4a**, t_R 2.63 min (73%); **2h**, t_R 3.77 min (1%) (HP-1, 150 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 8, entry 6:

Following General Procedure I, a mixture of cesium hydroxide monohydrate (168 mg, 1.0 mmol, 2.0 equiv.), toluene (0.5 mL), H₂O (36 μ L, 2.0 mmol, 2.0 equiv./CsOH•H₂O), 4iodoanisole (117 mg, 0.5 mmol), **5** (100 mg, 0.6 mmol, 1.2 equiv.), [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and dppb (21.3 mg, 0.2 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. An aliquot of the mixture was then taken for GC analysis. 4-iodoanisole, t_R 1.03 min (62%); **4a**, t_R 2.63 min (38%); **2h**, t_R 3.77 min (0%) (HP-1, 150 °C (2 min), 50 °C/min, 250 °C, 16 psi)

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

Commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.) was suspended in dry toluene (1.0 mL) at room temperature in a one-neck, 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 H₂O (108 μ L, 6.0 mmol, 3.0 equiv./Cs₂CO₃) and the resulting slurry was allowed to stir for 10 min. The aryl iodide (1.0 mmol), and **1** (218 mg, 1.2 mmol, 1.2 equiv.) were then added, followed by [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and triphenylarsine (30.6 mg, 0.1 mmol, 1.0 equiv./Pd). The flask was then purged with argon and was placed in a 90 °C oil bath. Reaction progress was monitored by GC analysis at certain intervals until completion. Sampling of the reaction was performed by removing a 10 μ L aliquot of the mixture by syringe. The aliquot was filtered through a small plug of silica gel and was eluted with 5 mL of ethyl acetate. The aliquot was then analyzed by GC. Upon completion, the reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo. The crude product was purified by column chromatography (SiO₂) to afford the corresponding product which was further purified by recrystallization.

Preparation of 4-Carbethoxy-4'-methoxybiphenyl (2a) (Table 5, entry 1)



Following General Procedure II, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (108 μ L, 6.0 mmol, 3 equiv./Cs₂CO₃), ethyl 4-iodobenzoate (276 mg, 1.0 mmol), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and triphenylarsine (30.6 mg, 0.1 mmol, 1 equiv./Pd) was stirred at 90 °C for 8 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid that was purified by column chromatography (SiO₂ (20 mm), hexane (20 mL) to hexane/EtOAc, 20/1) and recrystallized (10 mL, boiling

EtOH) to afford 160 mg (87%) of 2a as a colorless solid. The physical and spectroscopic data from 2a matched those from the literature.⁴

Data for 4'-Carbethoxy	y-4-methox	ybi	phen	yl ((2a)):

103-104 °C (EtOH)
(500 MHz, CHCl ₃)
8.09 (d, <i>J</i> = 8.6, 2 H, HC(3)), 7.62 (d, <i>J</i> = 8.8, 2 H, HC(2)), 7.57 (d, <i>J</i> = 8.8, 2 H,
HC(2')), 7.00 (d, <i>J</i> = 8.8, 2 H, HC(3')), 4.40 (q, <i>J</i> = 7.1, 2 H, HC(1")), 3.86 (s, 3
H, H ₃ C(3")), 1.42 (t, <i>J</i> = 7.2, 3 H, HC(2"))
(126 MHz, CHCl ₃)
166.6 (C(1")), 159.8 (C(4")), 145.1(C(4")), 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(1"))
R_f 0.29 (hexane/EtOAc, 20/1) [silica gel, UV]
2a, t _R 3.66 min (96%); 3a, t _R 5.05 min (4%) (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 II, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (108 μ L, 6.0 mmol, 3.0 equiv./Cs₂CO₃), 4-iodotoluene (218 mg, 1.0 mmol), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and triphenylarsine (30.6 mg, 0.1 mmol, 1 equiv./Pd) was stirred at 90 °C for 6 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid which was purified by column chromatography (SiO₂ (20 mm), toluene) and recrystallized (10 mL, boiling EtOH) to afford 231 mg (90%) of **2b** as a colorless solid. The physical and spectroscopic data from **2b** matched those from the literature.⁵

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

<u>mp</u> :	109-110 °C (EtOH)
¹ <u>H NMR</u> :	(500 MHz, CHCl ₃)
	7.54 (d, <i>J</i> = 8.6, 2 H, HC(2)), 7.48 (d, <i>J</i> = 8.2, 2 H, HC(2')), 7.25 (d, <i>J</i> = 8.4, 2 H,
	HC(3)), 6.99 (d, $J = 8.8$, 2 H, HC(3')), 3.86 (s, 3 H, H ₃ C(2")), 2.41 (s, 3 H,
	H ₃ C(1"))
¹³ <u>C NMR</u> :	(126 MHz, 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"))
<u>TLC</u> :	$R_f 0.78$ (toluene) [silica gel, UV]
<u>GC</u> :	2b , <i>t</i> _R 1.80 min (94%); 3b , <i>t</i> _R 1.14 min (6%) (HP-1, 200 °C (2 min), 50 °C/min,

250 °C, 16 psi)

Preparation of 4-Acetyl-4'-methoxybiphenyl (2c) (Table 5, entry 3)



Following General Procedure II, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H_2O (108 µL, 6.0 mmol, 3.0 equiv./Cs₂CO₃), 4iodoacetophenone (246 mg, 1.0 mmol), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and triphenylarsine (30.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 3 h. The reaction mixture was cooled to rt, treated with H_2O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid which was purified by column chromatography (SiO₂ (20 mm), hexane (20 mL) to hexane/EtOAc, 20/1) and recrystallized (10 mL, boiling EtOH) to afford 206 mg (91%) of **2c** as a colorless solid. The physical and spectroscopic data from 2c matched those from the literature.⁵

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

<u>mp</u>: 152-153 °C (EtOH)

- ¹<u>H NMR</u>: (500 MHz, CHCl₃) 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, H₃C(3'')), 2.63 (s, 3 H, H₃C(2''))
- ¹³<u>C NMR</u>: (126 MHz, CHCl₃) 198.0 (C(1")), 160.2 (C(4')), 145.6 (C(1)), 135.5 (C(4)), 132.5.1 (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")) <u>TLC</u>: R_f 0.33 (hexane/EtOAc, 20/1) [silica gel, UV]
 - <u>GC</u>: **2c**, *t*_R 3.27 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Preparation of 4-Methoxy-biphenyl (2d) (Table 5, entry 4)



Following General Procedure II, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (108 μ L, 6.0 mmol, 3.0 equiv./Cs₂CO₃), iodobenzene (204 mg, 1.0 mmol), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and triphenylarsine (30.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 8 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid which was purified by column chromatography (SiO₂ (20 mm), toluene) and recrystallized (10 mL, boiling EtOH) to afford 168 mg (91%) of **2d** as a colorless solid. The physical and spectroscopic data from **2d** matched those from the literature.⁶

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

<u>mp</u>: 90-91 °C (EtOH)

¹<u>H NMR</u>: (500 MHz, CHCl₃) 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, H₃C(1'')) ¹³<u>C NMR</u>: (126 MHz, CHCl₃)
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''))

- <u>TLC</u>: $R_f 0.81$ (toluene) [silica gel, UV]
 - <u>GC</u>: **2d**, $t_{\rm R}$ 1.29 min (94%); **3d**, $t_{\rm R}$ 0.82 min (6%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

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



Following General Procedure II, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (108 μ L, 6.0 mmol, 3.0 equiv.), 4-iodobenzonitrile (229 mg, 1.0 mmol), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and triphenylarsine (30.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 6 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid which was purified by column chromatography (SiO₂ (20 mm), hexane (20 mL) to hexane/EtOAc, 20/1) and recrystallized (10 mL, boiling EtOH) to afford 178 mg (85%) of **2e** as a off-white solid. The physical and spectroscopic data from **2e** matched those from the literature.⁷

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

<u>mp</u> :	103-104 °C	C (EtOH)
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¹<u>H NMR</u>: (500 MHz, CHCl₃)

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, H₃C(2''))

- ¹³<u>C NMR</u>: (126 MHz, CHCl₃) 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''))
 - <u>TLC</u>: $R_f 0.35$ (hexane/EtOAc, 20/1) [silica gel, UV]

<u>GC</u>: **2e**, $t_{\rm R}$ 2.88 min (93.3%); **3e**, $t_{\rm R}$ 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 5, entry 6)



Following General Procedure II, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H_2O (108 µL, 6.0 mmol, 3.0 equiv./Cs₂CO₃), 4iodobenzotrifluoride (272 mg, 1.0 mmol), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and triphenylarsine (30.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 3 h. The reaction mixture was cooled to rt, treated with H_2O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid which was purified by column chromatography (SiO₂ (20 mm), toluene) and recrystallized (10 mL, boiling EtOH) to afford 218 mg (87%) of **2f** as a colorless solid. The physical and spectroscopic data from **2f** matched those from the literature.⁸

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

<u>mp</u>: 124-125 °C (EtOH)

¹<u>H NMR</u>: (500 MHz, CHCl₃) 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, H₃C(2''))

¹³<u>C NMR</u>: (126 MHz, CHCl₃) 160.1 (C(4')), 144.5 (C(1)), 132.4 (C(1')), 128.7 (q, ${}^{2}J_{CF} = 32.2$, C(4)), 128.6 (C(2')), 127.1 (C(2)), 125.9 (q, ${}^{3}J_{CF} = 3.7$, C(3)), 124.6 (q, ${}^{1}J_{CF} = 271.6$. C(1")), 114.6 (C(3')), 55.4 (C(2"))

¹⁹<u>F NMR</u>: (470 MHz, C₆F₆) -62.5 (FC(1"))

<u>TLC</u>: $R_f 0.79$ (toluene) [silica gel, UV]

<u>GC</u>: **2f**, $t_{\rm R}$ 1.64 min (95%); **3f**, $t_{\rm R}$ 2.37 min (5%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Preparation of 4-Methoxy-4'-nitrobiphenyl (2g) (Table 5, entry 7)



Following General Procedure II, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H_2O (108 µL, 6.0 mmol, 3.0 equiv./Cs₂CO₃), 4iodonitrobenzene (249 mg, 1.0 mmol), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and triphenylarsine (30.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 6 h. The reaction mixture was cooled to rt, treated with H_2O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid which was purified by column chromatography (SiO₂ (20 mm), hexane (20 mL) to hexane/EtOAc, 20/1) and recrystallized (10 mL, boiling EtOH) to afford 201 mg (88%) of **2g** as a colorless solid. The physical and spectroscopic data matched those from the literature.⁵

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

- <u>mp</u>: 107-108 °C (EtOH)
- ¹<u>H NMR</u>: (500 MHz, CHCl₃) 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, H₃C(1"))
- ¹³<u>C NMR</u>: (126 MHz, CHCl₃) 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''))
 - <u>TLC</u>: $R_f 0.21$ (hexane/EtOAc, 20/1) [silica gel, UV]
 - <u>GC</u>: **2g**, t_R 3.39 min (94%); **3g**, t_R 2.92 min (6%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

General Procedure III: Cesium Carbonate Activated Palladium-Catalyzed Cross-Coupling of (4-Methoxyphenyl)dimethylsilanol with 2-Substituted Aryl Iodides.

Commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.) was suspended in dry dioxane (1.0 mL) at room temperature in a one-neck, 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 H₂O (72 µL, 4.0 mmol, 2.0 equiv./Cs₂CO₃) and the resulting slurry was allowed to stir for 10 min. The arvl iodide (1.0 mmol), and 1 (218 mg, 1.2 mmol, 1.2 equiv.) were then added, followed by [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and triphenylarsine (30.6 mg, 0.1 mmol, 1.0 equiv./Pd). The flask was then purged with argon and was placed in a 90 °C oil bath. Reaction progress was monitored by GC analysis at certain intervals until completion. Sampling of the reaction was performed by removing a 10 uL aliguot of the mixture via syringe. The aliquot was filtered through a small plug of silica gel and was eluted with 5 mL of ethyl acetate. The aliquot was then analyzed by GC. Upon completion, the reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo. The crude product was further purified by column chromatography (SiO₂) to afford the corresponding product which was purified by bulb-to-bulb distillation or recrystallization.

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



Following General Procedure III, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (72 μ L, 4.0 mmol, 2.0 equiv./Cs₂CO₃), 2-iodotoluene (218 mg, 1 mmol), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and triphenylarsine (30.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown liquid which was purified by column

chromatography (SiO₂ (20 mm), toluene) and bulb-to-bulb distillation to afford 168 mg (85%) of **4a** as a colorless oil. The physical and spectroscopic data from **4a** matched those from the literature.⁶

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

- <u>bp</u>: 120 °C (1 mm Hg, ABT) ¹<u>H NMR</u>: (500 MHz, CHCl₃) 7.27-7.23 (m, 6 H), 6.96 (d, J = 8.5, 2 H, HC(3)), 3.86 (s, 3 H, H₃C(2")), 2.30 (s, 3 H, H₃C(1")) ¹³<u>C NMR</u>: (126 MHz, CHCl₃) 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_f 0.77 (toluene) [silica gel, UV]
 - <u>GC</u>: **4a**, *t*_R 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 III, a mixture of commercially available cesium carbonate^{3e} (1.310 mg, 4.0 mmol, 2.0 equiv.), H₂O (144 μ L, 8.0 mmol, 2.0 equiv./Cs₂CO₃), 2iodobenzotrifluoride (544 mg, 2.0 mmol), **1** (436 mg, 2.2 mmol, 1.2 equiv.), [allylPdCl]₂ (36.6 mg, 0.1 mmol, 0.05 equiv.), and triphenylarsine (61.2 mg, 0.2 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown liquid which was purified by column chromatography (SiO₂ (30 mm), toluene) and recrystallized (20 mL, boiling 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):

<u>mp</u> :	54-55 °C (sublm. 50 °C, 0.1 mm Hg)
1 <u>H NMR</u> :	(500 MHz, CHCl ₃)
	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, <i>J</i> = 7.7, 1 H, HC(6)), 7.25 (d, <i>J</i> = 8.4, 2 H, HC(2')), 6.94 (d, <i>J</i> =
	8.8 2 H, HC(3')), 3.86 (s, 3 H, H ₃ C(2"))
¹³ <u>C NMR</u> :	(126 MHz, 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, ${}^{2}J_{CF} = 29.5$, C(2)), 127.0 (C(5)), 126.0 (C(3)) 124.2 (q, ${}^{2}J_{CF} =$
	274.34, C(1")), 113.4 (C(3')), 55.2 (C(2"))
¹⁹ <u>F NMR</u> :	(126 MHz, CHCl ₃)
	-56.9 (FC(1"))
<u>IR</u> :	(CHCl ₃)
	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)
<u>MS</u> :	(EI, 70 eV)
	252 (M, 100), 237 (25), 222 (2), 209 (37), 183 (8), 159 (4), 129 (6), 100 (2), 63
	(3)
<u>TLC</u> :	$R_f 0.82$ (toluene) [silica gel, UV]
<u>GC</u> :	4b , <i>t</i> _R 0.95 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)
Analysis:	$C_{14}H_{11}F_{3}O_{1}$ (252.23)

Calcd:	C, 66.66;	Н, 4.40
Found:	C, 66.83;	Н, 4.35

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



Following General Procedure III, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (72 μ L, 4.0 mmol, 2.0 equiv./Cs₂CO₃), 2-iodoanisole (234 mg, 1 mmol), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and triphenylarsine (30.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to rt and was extracted to afford a brown liquid which was purified by column chromatography (SiO₂ (20 mm), hexane (20 mL) to hexane/EtOAc, 20/1) and recrystallized (10 mL, boiling EtOH) to afford 182 mg (84%) of **4c** as a colorless solid. The physical and spectroscopic data from **4c** matched those from the literature.⁶

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

<u>mp</u>: 69-70 °C (EtOH)

¹<u>H NMR</u>: (500 MHz, CHCl₃)

7.48 (d, J = 8.8, 2 H, HC(2')), 7.31 (m, 2 H, HC(4), HC(5)), 7.02 (m, 4 H, HC(3'), HC(3), HC(6)), 3.85 (s, 3 H, H₃C(1'')), 3.82 (s, 3 H, H₃C(2''))

¹³<u>C NMR</u>: (126 MHz, CHCl₃)
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''))

- <u>IR</u>: (CHCl₃) 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)
- <u>TLC</u>: $R_f 0.40$ (toluene) [silica gel, UV]
- <u>GC</u>: **4c**, *t*_R 1.99 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

 $\begin{array}{ccc} \underline{Analysis:} & C_{14}H_{14}O_2\ (214.26) \\ & Calcd: & C,\ 78.48; & H,\ 6.59 \\ & Found: & C,\ 78.44; & H,\ 6.55 \end{array}$

Preparation of 4-Methoxy-2'-nitrobiphenyl (4e) (Table 6, entry 4)



Following General Procedure III, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (72 μ L, 4.0 mmol, 2.0 equiv./Cs₂CO₃), 2-iodonitrobenzene (249 mg, 1.0 mmol), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and triphenylarsine (30.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown liquid which was purified by column chromatography (SiO₂ (20 mm), hexane (20 mL) to hexane/EtOAc, 20/1) and recrystallized (10 mL, boiling EtOH) to afford 191 mg (83%) of **4d** as a colorless solid. The physical and spectroscopic data from **4d** matched those from the literature.⁹

Data for 4-Methoxy-2'-nitrobiphenyl (4d):

<u>mp</u>: 62-64 °C (EtOH)

¹<u>H NMR</u>: (500 MHz, CHCl₃)

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, HC(5'), HC(6')), 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, HC(1''))

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<sup>13</sup><u>C NMR</u>: (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''))
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<u>TLC</u>: $R_f 0.21$ (toluene) [silica gel, UV]

<u>GC</u>: 4d, *t*_R 2.69 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Preparation of 2-Carbmethoxy-4'-methoxybiphenyl (4f) (Table 6, entry 5)



Following General Procedure III, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (72 μ L, 4.0 mmol, 2.0 equiv./Cs₂CO₃), methyl 2iodobenzoate (262 mg, 1.0 mmol), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and triphenylarsine (30.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown liquid which was purified by column chromatography (SiO₂ (20 mm), hexane (20 mL) to hexane/EtOAc, 20/1) and bulb-to-bulb distillation to afford 213 mg (88%) of **4e** as a colorless solid. The physical and spectroscopic data from **4e** matched those from the literature.⁹

Data for 2-Carbmethoxy-4'-methoxybiphenyl (4e):

<u>bp</u>: 185 °C (1 mm Hg, ABT)

¹<u>H NMR</u>: (500 MHz, CHCl₃)

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, H₃C(2'')), 2.45 (s, 3 H, H₃C(1''))

- ¹³<u>C NMR</u>: (126 MHz, CHCl₃)
 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"))
 - <u>TLC</u>: $R_f 0.35$ (toluene) [silica gel, UV]
 - <u>GC</u>: **4e**, *t*_R 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 III, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (72 μ L, 4.0 mmol, 2.0 equiv./Cs₂CO₃), 1-iodonaphthalene (254 mg, 1.0 mmol), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and triphenylarsine (30.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown liquid which was purified by column chromatography (SiO₂ (20 mm), toluene) and recrystallized (10 mL, boiling EtOH) to afford 202 mg (86%) of **4f** as a colorless solid. The physical and spectroscopic data from **4f** matched those from the literature.¹⁰

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

<u>mp</u>: 115-116 °C (EtOH)

¹<u>H NMR</u>: (500 MHz, CHCl₃)

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, H₃C(1")

¹³<u>C NMR</u>: (126 MHz, CHCl₃)
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(9')), 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''))

- <u>TLC</u>: $R_f 0.75$ (toluene) [silica gel, UV]
 - <u>GC</u>: **4f**, *t*_R 3.38 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

General Procedure IV: The Cesium Carbonate Activated Palladium-Catalyzed Cross-Coupling of (4-Methoxyphenyl)dimethylsilanol with 4-Substituted Aryl Bromides.

Commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.) was suspended in dry toluene (1.0 mL) at room temperature in a one-neck, 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 H₂O (108 µL, 6.0 mmol, 3.0 equiv./Cs₂CO₃) and the resulting slurry was allowed to stir for 10 min. The arvl bromide (1.0 mmol), and 1 (218 mg, 1.2 mmol, 1.2 equiv.) were then added, followed by [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and 1,4-bis(diphenylphosphino)-butane (dppb) (42.6 mg, 0.1 mmol, 1.0 equiv./Pd). The flask was then purged with argon and was placed in a 90 °C oil bath. Reaction progress was monitored by GC analysis at certain intervals until completion. Sampling of the reaction was performed by removing a 10 µL aliquot of the mixture by 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 mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo. The crude product was purified by column chromatography (SiO₂) to afford the corresponding product which was further purified by bulbto-bulb distillation or recrystallization.

Preparation 4-Carbethoxy-4'-methoxybiphenyl (2a) (Table 7, entry 1)



Following General Procedure IV, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (108 μ L, 6.0 mmol, 3.0 equiv./Cs₂CO₃), ethyl 4bromobenzoate (229 mg, 1 mmol, 1.0), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and dppb (42.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a redish-brown solid which was purified by column chromatography (SiO₂ (20 mm), hexane (20 mL) to hexane/EtOAc, 20/1) and recrystallized (10 mL, boiling EtOH) to afford 215 mg (90%) of 2a as a colorless solid. The physical and spectroscopic data from 2a matched those from the literature.⁴

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

<u>mp</u>: 103-104 °C (EtOH)

 1 <u>H NMR</u>: (500 MHz, CHCl₃)

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, H₂C(2'')), 3.86 (s, 3 H, H₃C(3'')), 1.42 (t, *J* = 7.2, 3 H, H₃C(3''))

¹³<u>C NMR</u>: (126 MHz, CHCl₃) 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"))

- <u>TLC</u>: $R_f 0.29$ (hexane/EtOAc, 20/1) [silica gel, UV]
- <u>GC</u>: **2a**, *t*_R 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 7, entry 2)



Following General Procedure IV, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (108 μ L, 6.0 mmol, 3.0 equiv./Cs₂CO₃), 4-bromotoluene (171 mg, 1.0 mmol), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and dppb (42.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 18 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid which was purified by column chromatography (SiO₂ (20 mm), toluene) and recrystallized (10 mL, boiling EtOH) to afford 231 mg (90%) of **2b** as a colorless solid. The physical and spectroscopic data from **2b** matched those from the literature.⁵

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

<u>mp</u> :	109-110 °C (EtOH)
¹ <u>H NMR</u> :	(500 MHz, CHCl ₃)
	7.54 (d, <i>J</i> = 8.6, 2 H, HC(2)), 7.48 (d, <i>J</i> = 8.2, 2 H, HC(2')), 7.25 (d, <i>J</i> = 8.4, 2 H,
	HC(3)), 6.99 (d, $J = 8.8$, 2 H, HC(3')), 3.86 (s, 3 H, H ₃ C(2'')), 2.41 (s, 3 H,
	H ₃ C(1"))
¹³ <u>C NMR</u> :	(126 MHz, 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"))
<u>TLC</u> :	$R_f 0.78$ (toluene) [silica gel, UV]
<u>GC</u> :	2b , <i>t</i> _R 1.77 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Preparation of 4-Methoxybiphenyl (2d) (Table 7, entry 3)



Following General Procedure IV, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (108 μ L, 6.0 mmol, 3.0 equiv./Cs₂CO₃), bromobenzene (157 mg, 1.0 mmol), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and dppb (42.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 12 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid which was purified by column chromatography (SiO₂ (20 mm), toluene) and recrystallized (10 mL, boiling EtOH) to afford 168 mg (85%) of **2d** as a colorless solid. The physical and spectroscopic data from **2d** matched those from the literature.¹¹

Data for 4-Methoxybiphenyl (2d):

<u>mp</u>: 90-91 °C (EtOH)

¹<u>H NMR</u>: (500 MHz, CHCl₃)

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, H₃C(1''))

- ¹³<u>C NMR</u>: (126 MHz, CHCl₃) 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''))
 - <u>TLC</u>: $R_f 0.81$ (toluene) [silica gel, UV]
 - <u>GC</u>: **3d**, *t*_R 1.27 min (94%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Preparation of 4,4'-Dimethoxybiphenyl (2h) (Table 7, entry 4)



Following General Procedure IV, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (108 μ L, 6.0 mmol, 3.0 equiv./Cs₂CO₃), 4-bromoanisole (187 mg, 1.0 mmol, 1.0 equiv.), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and dppb (42.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 18 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid which was purified by column chromatography (SiO₂ (20 mm), hexane (20 mL) to hexane/EtOAc, 20/1) and recrystallized (10 mL, boiling EtOH) to afford 200 mg (92%) of **2h** as a colorless solid. The physical and spectroscopic data matched those from the literature.¹¹

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

<u>mp</u>: 178-179 °C (EtOH)

¹<u>H NMR</u>: (500 MHz, CHCl₃)
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, H₃C(1"), H₃C(2"))
¹³<u>C NMR</u>: (126 MHz, CHCl₃)
158.6 (C(4)), 133.4 (C(1)), 127.5 (C(2)), 114.1 (C(3)), 55.3 (C(1"))

<u>TLC</u>: $R_f 0.44$ (toluene) [silica gel, UV]

<u>GC</u>: **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 7, entry 5)



Following General Procedure III, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (108 μ L, 6.0 mmol, 3.0 equiv./Cs₂CO₃), 4bromocyclohexylbenzene (239 mg, 1.0 mmol), **1** (218 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and dppb (42.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 18 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid which was purified by column chromatography (SiO₂ (20 mm), toluene) and recrystallized (10 mL, boiling EtOH) to afford 228 mg (86 %) of **2i** as a colorless solid.

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

<u>mp</u>: 115-117 °C (EtOH)

¹<u>H NMR</u>: (500 MHz, CHCl₃)

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, 2 H, HC(3')), 3.85, (s, 3 H, H₃C(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<u>C NMR</u>: (126 MHz, CHCl₃)
 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"))
 - <u>IR</u>: $(CHCl_3)$

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)

<u>MS</u> :	(EI, 70 eV)				
	266 (M100)), 251 (1), 223	(22), 210 (7), 197 (23), 184 (3), 167 (6), 152 (4), 115		
	(3), 91 (4)				
<u>TLC</u> :	$R_{f} 0.74$ (to	luene) [silica ge	l, UV]		
<u>GC</u> :	3i , <i>t</i> _R min	(100%) (HP-1, 2	200 °C (2 min), 50 °C/min, 250 °C, 16 psi)		
<u>Analysis</u> :	$C_{19}H_{22}O_1$ ((266.38)			
	Calcd:	C, 85.67;	Н, 8.32		
	Found	C 85.96 [.]	Н 8 62		

Preparation of 4'-Carbethoxy-1-methylbiphenyl (2j) (Equation 1)



Following General Procedure IV, a mixture of commercially available cesium carbonate^{3e} (651 g, 2.0 mmol, 2.0 equiv.), H₂O (108 μ L, 6.0 mmol, 3.0 equiv./Cs₂CO₃), ethyl 4bromobenzoate (229 mg, 1.0 mmol), **5** (200 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and dppb (42.1 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 18 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid which was purified by column chromatography (SiO₂ (20 mm), hexane/EtOAc, 20/1) and bulb-to-bulb distillation to afford 261.4 mg (58%) of **2j** as a colorless oil. The physical and spectroscopic data from **2j** matched those from the literature.¹²

Data for 4'-Carbethoxy-1-methylbiphenyl (2j):

<u>mp</u>: 154 °C (1 mm Hg, ABT)

¹<u>H NMR</u>: $(500 \text{ MHz}, \text{CHCl}_3)$

8.07 (d, J = 8.8, 2 H, HC(3')), 7.40 (d, J = 8.8, 2 H, HC(2')), 7.29-7.19 (m, 2 H, HC(5), HC(2), HC(4)), 7.10 (t, J = 7.1, 1 H, HC(3)), 4.39 (q, J = 7.1, 2 H, H₂C(3")), 2.26 (s, 3 H, H₃C(1")), 1.42 (t, J = 7.1, 3 H, H₃C(4"))

¹³<u>C NMR</u>: (126 MHz, CHCl₃)
166.4 (C(2")), 146.6 (C(1')), 140.9 (C(6)), 135.0 (C(1)), 130.1 (C(3')), 130.0 (C(4')), 129.1 (C(2)), 129.0 (C(3)), 128.9 (C(2')), 127.8 (C(5)), 125.8 (C(4)), 61.0 (C(3")), 21.4 (C(1")), 14.4 (C(4"))

- <u>TLC</u>: $R_f 0.31$ (hexane/EtOAc 20/1) [silica gel, UV]
 - <u>GC</u>: **2j**, *t*_R 5.322 min (74%); 9.818 min (26%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Preparation of 1-(4"-Carbethoxyphenyl)-naphthalene (2k) (Equation 2)



Following General Procedure IV, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (108 μ L, 6.0 mmol, 3.0 equiv./Cs₂CO₃), ethyl 4bromobenzoate (229 mg, 1.0 mmol), **6** (243 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and dppb (42.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 90 °C for 24 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid which was purified by column chromatography (SiO₂ (20 mm), hexane/EtOAc, 20/1) and recrystallized (10 mL, boiling EtOH) to afford 380 mg (69%) of **2k** as a colorless solid. The physical and spectroscopic data from **2k** matched those from the literature.^{4,13}

Data for 1-(4"-Carbethoxyphenyl)-naphthalene (2k):

- <u>mp</u>: 113-114 °C (EtOH)
- ¹<u>H NMR</u>: (500 MHz, CHCl₃)

8.17 (d, *J* = 7.9, 2 H, HC(3')), 7.92 (d, *J* = 8.4 1 H, HC(8)), 7.89 (d, *J* = 7.9, 1 H, HC(5)), 7.84 (d, *J* = 7.9, 1 H, HC(4)), 7.58 (d, *J* = 8.1, 2 H, HC(2')), 7.57-7.50 (m, 2 H, HC(2), HC(3)), 7.44 (q, *J* = 3.2, 2 H, HC(6), HC(7)), 4.44 (q, *J* = 7.1, 2 H, H₂C(2'')), 1.44 (t, *J* = 7.1, 3 H, H₃C(3''))

¹³<u>C NMR</u>: (126 MHz, CHCl₃)
166.6 (C(1")), 145.5 (C(1')), 139.2 (C(1), 133.7 (C(9)), 131.2 (C(10)), 130.1 (C(3')), 129.5 (C(4')), 129.4 (C(5)), 128.4 (C(8), 128.3 (C(2')), 126.9 (C(4)), 126.3 (C(3)), 125.9 (C(6)), 125.6 (C(7)), 125.3 (C(2)), 61.0 (C(2")), 14.4 (C(1")

- <u>TLC</u>: $R_f 0.81$ (hexane/EtOAc, 20/1) [silica gel, UV]
 - <u>GC</u>: **2k**, *t*_R 9.27 min (81%); 9.82 (19%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Preparation of 4'-Carbethoxy-(1-trifluoromethyl)biphenyl (2i) (Equation 3)



Following General Procedure IV, a mixture of commercially available cesium carbonate^{3e} (651 mg, 2.0 mmol, 2.0 equiv.), H₂O (108 μ L, 6.0 mmol, 3.0 equiv./Cs₂CO₃), ethyl 4bromobenzoate (229 mg, 1.0 mmol), 7 (264 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and dppb (42.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 110 °C for 24 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid which was purified by column chromatography (SiO₂ (20 mm), hexane/EtOAc, 20/1) and recrystallized (10 mL, boiling EtOH) to afford 231 mg (39%) of **2i** as a colorless solid which was further purified by sublimation (50 °C, 0.5 mmHg).

Data for 4'-Carbethoxy-(1-trifluoromethyl)biphenyl (2i):

<u>mp</u>: 60 °C (sublm. 50 °C, 0.5 mmHg)

¹<u>H NMR</u>: (500 MHz, CHCl₃)

8.15 (d, *J* = 8.6, 2 H, HC(3)), 7.69 (m, 4 H, HC(3), HC(2)), 7.66 (d, *J* = 8.6, 2 H, HC(2)), 4.41 (d, *J* = 7.1, 2 H, H₂C(3")), 1.42 (t, *J* = 7.1, 3 H, H₃C(4"))

¹³ <u>C NMR</u> :	(126 MHz, CHCl ₃)
	166.3 (C(2")), 144.0 (C(1"), 143.6 (C(1)), 130.2 (C(2")), 130.1 (C(4)), 130.0
	(C(2)), 127.6 (C(2')), 127.2 (C(3)), 125.8 (q, ${}^{2}J_{CF} = 3.7$, C(1")) 125.2 (C(3')),
	61.1 (C(3")), 14.3 (C(4"))

¹⁹<u>F NMR</u>: (126 MHz, CHCl₃)
 -62.9 (FC(1"))
 <u>IR</u>: (CHCl₃)
 2985 (w), 2358 (m), 22341 (m), 1713 (s), 1610 (w), 1396 (w), 1369 (2), 1326 (s),

1282 (s), 1171 (m), 1130 (m), 1112 (m), 1071 (m), 1026 (w), 1007 (w), 890 (m), 837 (w), 667 (w), 647 (s), 654 (m), 602 (w), 539 (w)

<u>MS</u>: (EI, 70 eV) 294 (M, 100), 221 (14), 220 (7), 219 (7), 202 (9), 201 (49), 170 (6), 153 (9), 152 (57), 151 (11), 100 (6), 76 (5), 75 (6)

<u>TLC</u>: $R_f 0.25$ (hexane/EtOAc, 20/1) [silica gel, UV]

<u>GC</u>: **4b**, *t*_R 0.95 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

<u>Analysis</u>: $C_{16}H_{13}F_{3}O_{2}$ (294.27)

Calcd:	C, 65.30;	Н, 4.45
Found:	C, 65.33;	Н, 4.40

General Procedure V: Cesium Hydroxide Monohydrate Activated Palladium-Catalyzed Cross-Coupling of Substituted Aryl(dimethyl)silanols with Substituted Aryl Bromides.

Cesium hydroxide monohydrate (336 mg, 2.0 mmol, 2.0 equiv.) was suspended in a mixture of dry toluene (0.8 mL) and dry dioxane (0.2 mL) at room temperature in a one-neck, 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 H₂O (72 μ L, 4.0 mmol, 2.0 equiv./ CsOH•H₂O) and the resulting slurry was allowed' to stir for 10 min. The aryl bromide (1.0 mmol), and 1 (218 mg, 1.2 mmol, 1.2 equiv.) were then added, followed by [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and 1,4-bis(diphenylphosphino)butane (dppb) (42.6 mg, 0.1 mmol, 1.0 equiv./Pd). The flask was then purged with argon and was placed in a heated oil bath. Reaction progress was monitored by GC analysis at certain intervals until completion. Sampling of the reaction was performed by removing a 10 μ L aliquot of the mixture by syringe. The

aliquot was filtered through a small plug of silica gel and was eluted with 5 mL of ethyl acetate. The aliquot was then analyzed by GC. Upon completion, the reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo. The crude product was purified by column chromatography (SiO₂) to afford the corresponding product which was further purified by bulb-to-bulb distillation or recrystallization.

Preparation of 4'-Methoxy-2-methylbiphenyl (4a) (Table 9, entry 1)



Following General Procedure V, a mixture of cesium hydroxide monohydrate (336 mg, 2.0 mmol, 2.0 equiv.), H₂O (72 μ L, 4.0 mmol, 2.0 equiv./CsOH•H₂O), 4-bromoanisole (187 mg, 1.0 mmol), **5** (200 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and dppb (42.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 110 °C for 24 h. reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown liquid which was purified by column chromatography (SiO₂ (20 mm), toluene) and bulb-to-bulb distillation to afford 164 mg (83%) of **4a** as a colorless oil. The physical and spectroscopic data matched from **4a** those from the literature.⁶

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

 $\underline{bp}: 120 \ ^{\circ}C (1 \ \text{mm Hg, ABT})$ $^{1}\underline{H \ NMR}: (500 \ \text{MHz, CHCl}_3)$ $7.27-7.23 \ (\text{m, 6 H}), \ 6.96 \ (\text{d}, J = 8.5, 2 \ \text{H}, \text{HC}(3)), \ 3.86 \ (\text{s}, 3 \ \text{H}, \text{H}_3\text{C}(2^{\prime\prime})), \ 2.30 \ (\text{s}, 3 \ \text{H}, \text{H}_3\text{C}(1^{\prime\prime}))$ $^{13}\underline{C \ NMR}: (126 \ \text{MHz, CHCl}_3)$ $158.8 \ (C(4^{\prime})), \ 141.8 \ (C(2)), \ 135.7 \ (C(1)), \ 134.6 \ (C(3)), \ 130.6 \ (C(1^{\prime})), \ 130.5 \ (C(2^{\prime\prime})), \ 130.1 \ (C(4)), \ 127.2 \ (C(6)), \ 126.0 \ (C(5)), \ 113.7 \ (C(3^{\prime})), \ 55.5 \ (C(2^{\prime\prime})), \ 20.7 \ (C(1^{\prime\prime})))$

- <u>TLC</u>: $R_f 0.77$ (toluene) [silica gel, UV]
- <u>GC</u>: **4a**, $t_{\rm R}$ 1.29 min (91%); **4b** $t_{\rm R}$ 3.77 min (9%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Preparation of 1-(4-Methoxyphenyl)-naphthalene (4f) (Table 9, entry 2)



Following General Procedure V, a mixture of cesium hydroxide monohydrate (336 mg, 2.0 mmol, 2.0 equiv.), H₂O (72 μ L, 4.0 mmol, 2.0 equiv./CsOH•H₂O), 4-bromoanisole (187 mg, 1.0 mmol), **6** (405 mg, 2.0 mmol, 2.0 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 1.0 equiv./Pd), and dppb (42.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 110 °C for 24 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown liquid which was purified by column chromatography (SiO₂ (20 mm), toluene) and recrystallized (10 mL, boiling EtOH) to afford 192 mg (82%) of **4f** as a colorless solid. The physical and spectroscopic data from **4f** matched those from the literature.¹⁰

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

<u>mp</u>: 115-116 °C (EtOH)

¹<u>H NMR</u>: (500 MHz, CHCl₃) 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, H₃C(1")

¹³<u>C NMR</u>: (126 MHz, CHCl₃)
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(9')), 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''))

<u>TLC</u>: $R_f 0.75$ (toluene) [silica gel, UV]

<u>GC</u>: **4f**, t_R 3.38 min (93%); **3f**, t_R 9.81 min (7%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Preparation of 4'-Methoxy-4-(trifluoromethyl)biphenyl (2f) (Table 9, entry 3)



Following General Procedure V, a mixture of cesium hydroxide monohydrate (336 mg, 2.0 mmol, 2.0 equiv.), H₂O (72 μ L, 4.0 mmol, 2.0 equiv./CsOH•H₂O), 4-bromoanisole (187 mg, 1.0 mmol), 7 (264 mg, 1.2 mmol, 1.2 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and dppb (42.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 110 °C for 24 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid which was purified by column chromatography (SiO₂ (20 mm), toluene) and recrystallized (10 mL, boiling EtOH) to afford 137 mg (54%) of **2f** as a colorless solid. The physical and spectroscopic data from **2f** matched those from the literature.⁸

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

<u>mp</u> : 124-125 °C	(EtOH)
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- ¹<u>H NMR</u>: (500 MHz, CHCl₃) 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, H₃C(2''))
- ¹³<u>C NMR</u>: (126 MHz, CHCl₃) 160.1 (C(4')), 144.5 (C(1)), 132.4 (C(1')), 128.7 (q, ${}^{2}J_{CF} = 32.2$, C(4)), 128.6 (C(2')), 127.1 (C(2)), 125.9 (q, ${}^{3}J_{CF} = 3.7$, C(3)), 124.6 (q, ${}^{1}J_{CF} = 271.6$. C(1")), 114.6 (C(3')), 55.4 (C(2"))
- ¹⁹<u>F NMR</u>: (470 MHz, C_6F_6) -62.5 (FC(1"))
 - <u>TLC</u>: $R_f 0.79$ (toluene) [silica gel, UV]

<u>GC</u>: **2f**, *t*_R 1.64 min (83%); **3f**, *t*_R 2.37 min (17%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Preparation of 1'-(2-Methylphenyl)-naphthalene (4g) (Table 8, entry 5)



Following General Procedure V, a mixture of cesium hydroxide monohydrate (336 mg, 2.0 mmol, 2.0 equiv.), H₂O (72 μ L, 4.0 mmol, 2.0 equiv./CsOH•H₂O), 2-bromotoluene (171 mg, 1.0 mmol), **6** (405 mg, 2 mmol, 2.0 equiv.), [allylPdCl]₂ (18.3 mg, 0.05 mmol, 0.05 equiv.), and dppb (42.6 mg, 0.1 mmol, 1.0 equiv./Pd) was stirred at 110 °C for 24 h. The reaction mixture was cooled to rt, treated with H₂O (10 mL) and was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and concentrated in vacuo to afford a brown solid which was purified by column chromatography (SiO₂ (20 mm), toluene) and recrystallized (10 mL, boiling EtOH) to afford 186 mg (85%) of **4g** as a colorless solid. The physical and spectroscopic data from **4g** matched those from the literature.¹³

Data for 1'-(2-Methylphenyl)-naphthalene (4g):

<u>mp</u>: 65-67 °C (EtOH)

¹<u>H NMR</u>: (500 MHz, CHCl₃)

7.89 (d, J = 1.7, 1 H, HC(5'), HC(8')), 7.85 (d, J = 7.8, 2 H, HC(4'), HC(2')), 7.77-7.75 (m, 1 H, HC(3')), 7.45 (d, J = 8.8, 2 H, HC(6'), HC(7')), 7.37 (d, J = 2.0, 1 H, HC(6)), 7.31 (sept, J = 2.0, 2 H, HC(3), HC(5)), 7.25 (hept, J = 2.0, 1 H, HC(4)), 2.02 (s, 3 H, H₃C(1")

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<sup>13</sup><u>C NMR</u>: (126 MHz, CHCl<sub>3</sub>)
140.3 (C(1')), 140.0 (C(1), 136.7 (C(2)), 133.6 (C(2')), 132.0 (C(9)), 130.4 (C(10)), 130.3 (C(3)), 129.8 (C(6)), 128.1 (C(4)), 127.5 (C(5')), 127.4 (C(4')), 126.6 (C(3')), 126.0 (C(7')), 125.9 (C(5)), 125.6 (C(6')), 125.4, (C(2)), 20.1 (C(1"))
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<u>TLC</u>: $R_f 0.75$ (toluene) [silica gel, UV]

<u>GC</u>: **4g**, *t*_R 5.10 min (100%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Preparation of 1-Naphthalene(dimethyl)silanol (6)



A flame dried, three-neck round-bottom flask fitted with a nitrogen adapter, thermocouple, magnetic stir bar and rubber septum was charged with 1-iodonaphthlene (6.35 g, 25.0 mmol) and Et₂O (100 mL) under dry N₂. The mixture was cooled to -78 °C (CO₂ / *i*-PrOH), and *n*-butyllithium (1.60 M in hexane, 15.6 mL, 25.0 mmol) was added over 15 min. The reaction mixture was stirred at -78 °C for 1 h. Hexamethylcyclotrisiloxane (1.85 g, 8.3 mmol) in Et₂O (10 mL) was then added at -78 °C. The mixture was slowly warmed to room temperature over a 12 h period followed by the addition of H₂O (10 mL). The reaction mixture was then extracted with Et₂O (3 X 25 mL). The combined organic layers were washed with H₂O (10 mL), brine (10 mL), dried (MgSO₄), and concentrated in vacuo providing the crude product as a brown oil which was purified by column chromatography (SiO₂ (30 mm), hexane/EtOAc, 10/1) and recrystallized (20 mL Et₂O / 30 mL pentane, -20 °C) to afford 3.39 g (67%) of **6** as a colorless cubes.

Data for 1-naphthalene(dimethyl)silanol (6):

<u>mp</u>: 82-84 °C (Et₂O/pentane)

 1 <u>H NMR</u>: (500 MHz, CHCl₃)

8.28 (d, *J* = 8.4, 1 H, HC(8)), 7.89 (t, *J* = 8.4, 2 H, HC(3), HC(7)), 7.78 (d, *J* = 7.9, 1 H, HC(2)), 7.55-7.46 (m, 3 H, HC(4), HC(5), HC(6)), 2.07 (bs, OH), 0.59 (s, 6 H, H₃C(1'))

¹³<u>C NMR</u>: (126 MHz, CHCl₃)
 136.6 (C(10)), 136.3 (C(2)), 133.1 (C(9)), 133.0 (C(1)), 130.2 (C(4)), 128.7 (C(3)), 127.8 (C(8)), 125.7 (C(5)), 125.3 (C(6)), 124.8 (C(7)), 1.05 (C(1'))
 <u>IR</u>: (CHCl₃)

	3666 (bs),	3058 (w), 2961 ((w), 2359 (w), 2249 (m), 1589 (2), 1505 (m), 1404 (w)	
	1319 (w),	1256 (s), 1219 (v	w), 1146 (m), 1024 (w), 986 (m), 893 (s), 850 (s), 800	
	(m), 782 (s), 750 (s), 724 (s	s), 676 (m), 654 (m), 640 (w) 524 (w)	
<u>MS</u> :	(EI, 70 eV)			
	202 (M, 39), 187 (100), 169	9 (15), 141 (6), 128 (9), 115 (6), 94 (5), 75 (6)	
HRMS:	(EI, 70 eV)			
	202.08086	7		
<u>TLC</u> :	$R_f 0.14$ (he	exane/EtOAc, 10	/1) [silica gel, UV]	
<u>Analysis</u> :	$C_{12}H_{14}O_1S$	i ₁ (202.32)		
	Calcd:	C, 71.24;	Н, 6.97	
	Found:	C, 71.25;	Н, 7.01	

Preparation of Sodium (4-Methoxyphenyl)dimethylsilanolate (9a)



To a suspension of sodium hydride (478 mg, 20.0 mmol, 2.0 equiv.) in THF (15 mL) was added silanol **1** (1.82 mg, 10.0 mmol) dropwise over 5 min. The resultant mixture was stirred for 25 min further, and then added by syringe into 2 vials previously purged with argon. The vials were then centrifuged for 10 minutes, and the supernatant was removed by syringe, with care taken not to disturb the excess NaH and NaOH precipitate at the bottom of the vials. The supernatant was then placed in a pre-weighed argon-purged one-neck round-bottom flask containing a magnetic stir bar. The solution was then stirred under vacuum to slowly remove all the solvent. After 6 h, all the solvent was removed leaving **9a** (1.51 g, 74%) as a solid residue.

Data for sodium (4-methoxyphenyl)dimethylsilanolate (9a)

1 <u>H NMR</u> : (50	0 MHz, THF)
	7.49 (d, <i>J</i> = 8.4, 2 H, HC(2)), 6.80 (d, <i>J</i> = 8.4, 2 H, HC(3)), 3.72 (s, 3 H, H ₃ C(2')),
	0.13 (s, 6 H, H ₃ C(1'))
¹³ <u>C NMR</u> :	(126 MHz, THF)
	160.7 (C(4)), 139.8 (C(2)), 135.1 (C(1)), 113.6 (C(3)), 55.0 (C(2')), 4.2 (C(1'))

HRMS:	: (ESI, 70 eV)			
	205.0662			
<u>Analysis</u> :	$C_9H_{13}O_2Si_1$			
	Calcd:	C, 52.92;	Н, 6.41	
	Found:	C, 52.81;	Н, 6.56	

Preparation of Potassium (4-Methoxyphenyl)dimethylsilanolate (9b)



To a suspension of potassium hydride (802 mg, 20.0 mmol, 2.0 equiv.) in THF (15 mL) was added silanol **1** (1.82 g, 10.0 mmol) dropwise over 5 min. The resultant mixture was stirred for 25 min further, and then added by syringe into 2 vials previously purged with argon. The vials were then centrifuged for 10 minutes, and the supernatant was removed by syringe, with care taken not to disturb the excess KH and KOH precipitate at the bottom of the vials. The supernatant was then placed in a pre-weighed argon-purged one-neck round-bottom flask containing a magnetic stir bar. The solution was then stirred under vacuum to slowly remove all the solvent. After 6 h, all the solvent was removed leaving **9b** (1.55 g, 70%) as a solid residue (containing ~0.8% disiloxane **8**).¹⁴

Data for potassium (4-methoxyphenyl)dimethylsilanolate (9b)

1 <u>H NMR</u> :	(500 MHz, THF)			
	7.45 (d, <i>J</i> = 8.6, 2 H, HC(2)), 6.79 (d, <i>J</i> = 8.6, 2 H, HC(3)), 3.72 (s, 3 H, H ₃ C(2')),			
	0.05 (s, 6 H	I, H ₃ C(1'))		
¹³ <u>C NMR</u> :	(126 MHz, THF)			
	160.3 (C(4))), 141.2 (C(2)),	134.8 (C(1)), 113.7 (C(3)), 55.0 (C(2')), 4.1 (C(1'))	
<u>Analysis</u> :	$C_9H_{13}O_2Si_1$	K ₁ (220.38)		
	Calcd:	C, 49.05;	Н, 5.95	
	Found:	C, 48.36;	Н, 5.97	

Preparation of Rubidium (4-Methoxyphenyl)dimethylsilanolate (9c)



In a dry box, a one-neck flask was charged with benzene (15 mL) followed by rubidium (427 mg, 5.0 mmol, 1.0 equiv.). To this suspension was added silanol 1 (911 mg, 5.0 mmol) dropwise over 5 min. The resultant mixture was stirred for 25 min further, and then filtered through a medium porosity glass frit into a pre-weighed one-neck flask fitted with a stop-cock gas adaptor. The flask was removed from the dry box and the solvent removed under vacuum (0.5 mm Hg) leaving **9c** (1.00 g, 75%) as a solid residue (containing ~1.0% disiloxane **8**).¹⁴ Data for rubidium (4-methoxyphenyl)dimethylsilanolate (**9c**)

¹<u>H NMR</u>: (500 MHz, THF)

 $\begin{array}{rl} 7.45 \ (d, J = 8.6, 2 \ H, \ HC(2)), \ 6.79 \ (d, J = 8.4, 2 \ H, \ HC(3)), \ 3.72 \ (s, 3 \ H, \ H_3C(2')), \\ 0.06 \ (s, 6 \ H, \ H_3C(1')) \\ \end{array}$

Preparation of Cesium (4-Methoxyphenyl)dimethylsilanolate (9d)



In a dry box, a one-neck flask was charged with benzene (15 mL) followed by cesium (532 mg, 4.0 mmol, 1.0 equiv.). To this suspension was added silanol 1 (729 mg, 5.0 mmol) dropwise over 5 min. The resultant mixture was stirred for 25 min further, and then filtered

through a medium porosity glass frit into a pre-weighed one-neck flask fitted with a stop-cock gas adaptor. The flask was removed from the dry box and the solvent removed under vacuum (0.5 mm Hg) leaving **9d** (1.00 g, 80%) as a solid residue.

Data for cesium (4-methoxyphenyl)dimethylsilanolate (9d)

¹<u>H NMR</u>: (500 MHz, THF)

	7.46 (d, <i>J</i> =	= 8.4, 2 H, HC(2)), 6.79 (d, $J = 8.6$, 2 H, HC(3)), 3.72 (s, 3 H, H ₃ C(2')),	
	0.06 (s, 6 H	H, H ₃ C(1'))		
¹³ <u>C NMR</u> :	(126 MHz, THF)			
	160.2 (C(4)), 141.4 (C(2)),	135.2 (C(1)), 113.6 (C(3)), 54.9 (C(2')), 4.1 (C(1'))	
Analysis:	$C_9H_{13}O_2Si_1Cs_1$ (314.19)			
	Calcd:	C, 34.40;	Н, 4.17	
	Found:	C, 34.10;	Н, 4.38	

Table 10, entry 1:

Sodium silanolate **9a** (204 mg, 1.0 mmol, 2.0 equiv.) was suspended in dry toluene (0.5 mL) at room temperature in a one-neck, 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 bromobenzene (78.5 mg, 1.0 mmol), followed by [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and dppb (21.3 mg, 0.05 mmol, 1.0 equiv./Pd). The flask was then purged with argon and was placed in a 90 °C oil bath for 1 h. Reaction progress was monitored by GC analysis. Sampling of the reaction was performed by removing a 10 μ L aliquot of the mixture by syringe. The aliquot was filtered through a small plug of silica gel and was eluted with 5 mL of ethyl acetate. The aliquot was then analyzed by GC. Bromobenzene, *t*_R 0.92 min (45%); **2d**, *t*_R 3.49 min (50%); **3d**, *t*_R 3.05 min (5%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 10, entry 2:

Potassium silanolate **9b** (220 mg, 1.0 mmol, 2.0 equiv.) was suspended in dry toluene (0.5 mL) at room temperature in a one-neck, 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 bromobenzene (78.5 mg, 1.0 mmol), followed by [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and dppb (21.3 mg, 0.05 mmol, 1.0 equiv./Pd). The flask was then purged with argon and was

placed in a 90 °C oil bath for 1 h. Reaction progress was monitored by GC. Sampling of the reaction was performed by removing a 10 μ L aliquot of the mixture by syringe. The aliquot was filtered through a small plug of silica gel and was eluted with 5 mL of ethyl acetate. The aliquot was then analyzed by GC. Bromobenzene, t_R 0.92 min (20%); **2d**, t_R 3.49 min (71%); **3d**, t_R 3.05 min (9%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 10, entry 3:

Rubidium silanolate **9c** (267 mg, 1.0 mmol, 2.0 equiv.) was suspended in dry toluene (0.5 mL) at room temperature in a one-neck, 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 bromobenzene (78.5 mg, 1.0 mmol), followed by [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and dppb (21.3 mg, 0.05 mmol, 1.0 equiv./Pd). The flask was then purged with argon and was placed in a 90 °C oil bath for 1 h. Reaction progress was monitored by GC analysis. Sampling of the reaction was performed by removing a 10 μ L aliquot of the mixture by syringe. The aliquot was filtered through a small plug of silica gel and was eluted with 5 mL of ethyl acetate. The aliquot was then analyzed by GC. Bromobenzene, *t*_R 0.92 min (19%); **2d**, *t*_R 3.49 min (72%); **3d**, *t*_R 3.05 min (8%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

Table 10, entry 4:

Cesium silanolate **9d** (314 mg, 1.0 mmol, 2.0 equiv.) was suspended in dry toluene (0.5 mL) at room temperature in a one-neck, 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 bromobenzene (78.5 mg, 1.0 mmol), followed by [allylPdCl]₂ (9.1 mg, 0.025 mmol, 0.05 equiv.), and dppb (21.3 mg, 0.05 mmol, 1.0 equiv./Pd). The flask was then purged with argon and was placed in a 90 °C oil bath for 1 h. Reaction progress was monitored by GC analysis. Sampling of the reaction was performed by removing a 10 μ L aliquot of the mixture by syringe. The aliquot was filtered through a small plug of silica gel and was eluted with 5 mL of ethyl acetate. The aliquot was then analyzed by GC. Bromobenzene, *t*_R 0.92 min (9%); **2d**, *t*_R 3.49 min (79%); **3d**, *t*_R 3.05 min (11%) (HP-1, 200 °C (2 min), 50 °C/min, 250 °C, 16 psi)

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3.76 (s, 3 H), 0.24 (s, 6 H, H₃C(1'))