Supporting Information

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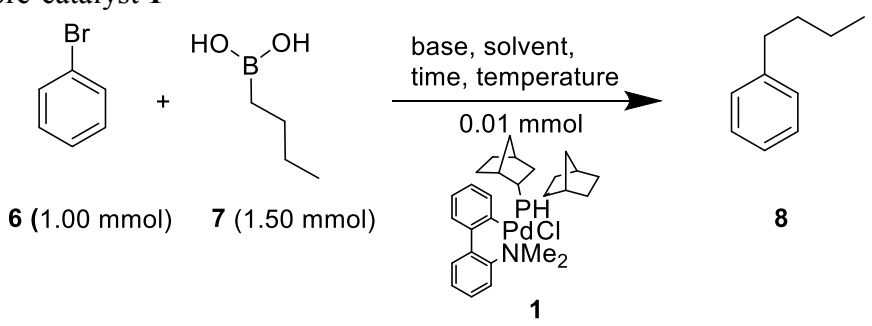
Table 1. Optimization of the Suzuki-Miyaura reaction of bromobenzene **6** and *n*-butylboronic acid **7** using pre-catalyst **1**



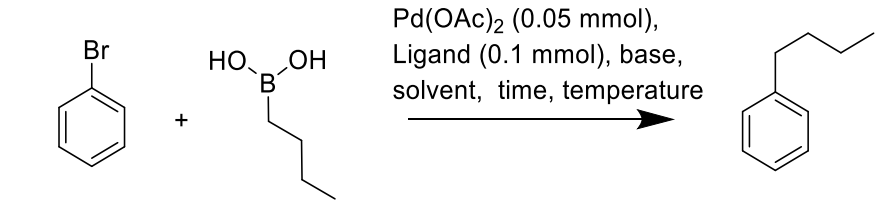
Entry	base, equiv	solvent	conversion, [a/a %] 60°C, 19h [a]	conversion, [a/a %] 105°C, 24h [a]
1	Na_2CO_3, 3	THF	-	16
2	3N NaOH, 3	THF	17	51
3	Na_2CO_3, 3 + Cs_2CO_3, 0.3	THF	12	56
4	K_3PO_4, 3	THF / 5% H_2O	12	49
5	K_2CO_3, 3 + Cs_2CO_3, 0.3	THF / 5% H_2O	8	41
6	3N NaOH, 3	THF / 5% H_2O	15	10
7	Na_2CO_3, 3 + Cs_2CO_3, 0.3	THF / 5% H_2O	< 5	7
8	Na_2CO_3, 3 + Cs_2CO_3, 0.3	dioxane	16	57
9	Na_2CO_3, 3	dioxane	-	6
10	K_2CO_3, 3 + Cs_2CO_3, 0.3	DMAc	-	8
11	Na_2CO_3, 3 + Cs_2CO_3, 0.3	toluene	30	54

[a] Conversion based on GC-MS analysis without isolation and purification, [a/a %: ratio of product peak area / total area].

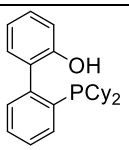
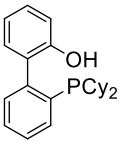
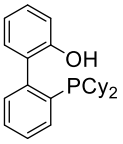
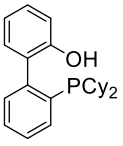
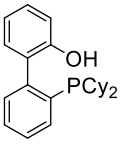
General procedure using ligand 1:

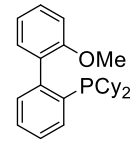
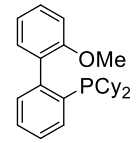
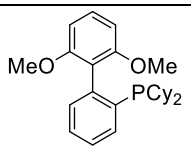
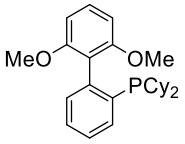
A mixture of bromobenzene (1.0 mmol), n-butylboronic acid (1.5 mmol), base(s), solvent(s) (5 mL) and [Bis(bicyclo[2.2.1]hept-2-yl)phosphine]chloro[2'-(dimethylamino-κN)[1,1'-biphenyl]-2-yl-κC]palladium (**1**) (0.01 mmol) was heated to 60 °C for 19 h and the progress of the reaction was analyzed by GC-MS. The reaction temperature was increased to 105 °C and maintained for 24 h and progress of the reaction was analyzed by GC-MS.

Table 2. Optimization of the cross coupling reaction of bromobenzene **6** with *n*-butylboronic acid **7** using ligands **2** - **5**. Variation of Conditions.



6 (1.00 mmol) **7** (1.50 mmol) **8**

Entry	Ligand	base, equiv	solvent	conversion, [a/a %] 60°C, 19 h [a]	conversion, [a/a %] 105°C, 24 h [a]
1	$P(O^iPr)_3$ **2**	3N NaOH, 3	toluene	---	60
2	$P(O^iPr)_3$ **2**	K_2CO_3, 3 + Cs_2CO_3, 0.3	toluene	---	47
3	$P(O^iPr)_3$ **2**	K_2CO_3, 3 + Cs_2CO_3, 0.3	THF	---	40
4	$P(O^iPr)_3$ **2**	3N NaOH, 3	THF	---	27
5	$P(O^iPr)_3$ **2**	3N NaOH, 3	dioxane	---	18
6	 **3**	Na_2CO_3, 3	toluene	21	58
7	 **3**	K_2CO_3, 3 + Cs_2CO_3, 0.3	dioxane	---	53
8	 **3**	K_2CO_3, 3 + Cs_2CO_3, 0.3	THF	---	62
9	 **3**	K_2CO_3, 3 + Cs_2CO_3, 0.3	DMAc	---	13
10	 **3**	3N NaOH, 3	dioxane	13	37

11	 **4**	3N NaOH, 3	dioxane	39	49
12	 **4**	3N NaOH, 3	THF	28	36
13	 **5**	3N NaOH, 3	dioxane	18	58
14	 **5**	3N NaOH, 3	THF	11	43

[a] Conversion based on GC-MS analysis without isolation and purification, [a/a %: ratio of product peak area / total area].

General procedure using ligands 2-5:

A mixture of bromobenzene (1.0 mmol), *n*-butylboronic acid (1.5 mmol), base(s), solvent(s) (5 mL), palladium acetate (0.05 mmol) and ligand (**2**-**5**) (0.1 mmol) was heated to 60 °C for 19 h, unless otherwise indicated, and the progress of the reaction was analyzed by GC-MS. The reaction temperature was increased to 105 °C and maintained for 24 h and progress of the reaction was analyzed by GC-MS.