

Access to full text denied by publisher.

Please contact your local library to acquire the following paper:

Citation:

Scope and Limitations of the Palladium-Catalyzed Cross-Coupling Reaction of in situ Generated Organoboranes with Aryl and Vinyl Halides
Shawn P. Maddaford and Brian A. Keay
pp 6501 – 6503.

Abstract:

Summary: The *in situ* palladium(0)-catalyzed Suzuki reaction is shown to be an efficient method for the cross-coupling of aryl-, furyl-, primary, and benzylic boranes with aryl or vinyl bromides and iodides without the isolation of the organoboronic acid or the addition of any external base.

Tables:

Table 1. Various Attempts To Optimize the Yield of Biphenyl via the *in Situ* Suzuki Cross-Coupling Reaction

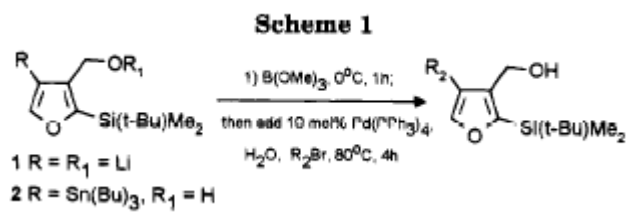
entry	solvent	PhX	water or base	catalyst	time (h)	yield ^a of biphenyl (%)
1	DME	I	Na ₂ CO ₃	Pd(PPh ₃) ₄	20	68
2	DME	I	Na ₂ CO ₃	Pd(PPh ₃) ₄	2	53
3 ^b	benzene	I	Na ₂ CO ₃	Pd(PPh ₃) ₄	16	61 ^c
4 ^b	benzene	I	H ₂ O	Pd(PPh ₃) ₄	16	51 ^d
5 ^b	benzene	I	Na ₂ CO ₃	Pd(OAc) ₂ (PPh ₃) ₂	20	85
6	NMP	Br	H ₂ O	Pd(PPh ₃) ₄	17	63
7	DME	Br	H ₂ O	Pd(PPh ₃) ₄	1.5	62
8	DME	Br	H ₂ O/TMEDA ^e	Pd(PPh ₃) ₄	1.5	59
9	DME	Br	Na ₂ CO ₃	Pd(OAc) ₂ (PPh ₃) ₂	2	76
10	DME	Br	Na ₂ CO ₃	Pd(PPh ₃) ₄	2	49
11	DME	Br	Na ₂ CO ₃	Pd(Pfuryl) ₄	5	53
12	DME	Br	H ₂ O	Pd(PPh ₃) ₄	1.5	59
13	DME	Br	none	Pd(PPh ₃) ₄	2	9
14 ^f	DME	Br	H ₂ O	Pd(PPh ₃) ₄	1.75	21

^a Yield obtained by distillation and NMR analysis of the distillate. ^b Aryllithium generated by halogen-metal change of iodobenzene in ether at -95 °C for 10 min. ^c 16% yield of butylbenzene. ^d 12% yield of butylbenzene. ^e 1.0 equiv of TMEDA was added. ^f Boronic acid prepared from phenylmagnesium chloride.

Table 2. Cross Coupling of *in Situ* Generated Organoboranes with Organo Halides

entry	halide	boronic acid source	catalyst	solvent	water source	time (h)	product (% yield)
1	bromobenzene	5	Pd(PPh ₃) ₄	benzene	H ₂ O	15	10 (55)
2	iodobenzene	iodobenzene	Pd(PPh ₃) ₄	benzene	2 M Na ₂ CO ₃	20	biphenyl (85)
3	bromobenzene	<i>n</i> -BuLi	Pd(OAc) ₂ (PPh ₃) ₂	THF	H ₂ O	20	<i>n</i> -butylbenzene (52)
4	2-bromobenzaldehyde	benzylolithium	Pd(PPh ₃) ₄	toluene	2 M Na ₂ CO ₃	20	2-benzylbenzaldehyde (83)
5	bromobenzene	6	Pd(PPh ₃) ₄	benzene	2 M Na ₂ CO ₃	16	11 (95)
6	bromobenzene	7	Pd(PPh ₃) ₄	THF	H ₂ O	48	12 (39)
7	bromobenzene	<i>s</i> -BuLi	Pd(OAc) ₂ (PPh ₃) ₂	benzene	H ₂ O	16	mixture (<30)
8	3	8	Pd(PPh ₃) ₄	THF	H ₂ O	19	13 (43)
9	4	9	Pd(PPh ₃) ₄	DME	H ₂ O	2	14 (72)

Schemes:



DOI: [10.1021/jo00101a001](https://doi.org/10.1021/jo00101a001)