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Palladium-catalyzed decarboxylative coupling reaction with alkynyl carboxylic acids and arylsiloxanes

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ABSTRACT

A decarboxylative coupling reaction for alkynyl carboxylic acids and arylsiloxanes was developed using a palladium catalyst. This method provided the desired coupled products in moderate to good yields by reacting the alkynyl carboxylic acids and arylsiloxanes with Pd(dba)$_2$ (1.0 mol %), 1,1-bis(diphenylphosphino)methane (1.0 mol %), and AgF$_2$ (2.0 equiv) at 60 °C for 6 h.

Organosilanes have been employed as coupling partners in palladium-catalyzed cross coupling reactions since Hiyama first reported the coupling of aryl halides and arylsiloxanes in 1988.[1] Organosilanes have several advantages, being stable, non-toxic, and easily prepared. As a coupling partner of organosilane, aryl halide is one of the most frequently used substrates.[2] Recently, a C–H activated substrate was reported to give a coupled product by reacting with an organosilane in the presence of a nickel catalyst.[3]

The coupling reaction of a terminal alkyne and an aryl halide, known as the Sonogashira reaction, is one of the most useful tools for the synthesis of aryl alkynes, and is conducted using palladium and copper catalysts.[4] For over four decades, Sonogashira-type coupling reactions have been developed and widely employed in the construction of aryl alkyne moieties.[5] A variety of transition metals, such as copper, silver, gold, iron, and cobalt have been used as catalysts.[6]

We first reported that alkynyl carboxylic acids coupled with aryl halides to provide the Sonogashira-type product with good yields via decarboxylative coupling.[7] Since then, significant progress has been made by us and other groups.[8] A variety of substrates have been successfully employed as coupling partners, such as benzyl halide,[9] C–H activated heteroarenes,[10] organoboranes,[11] amides,[12] and organophosphorus[13] and organosulfur[14] compounds. Very recently, we reported a decarboxylative coupling reaction with organosilane using a nickel catalyst, which provided the diaryl alkyne in moderate to good yields.[15] Organosilanes have been used as coupling partners less than other coupling reagents, such as aryl halide and organoborane, even though they are stable, inexpensive, and easily prepared. A palladium-catalyzed coupling of terminal alkyne and organosilane was reported by Cheng.[16]

Our previous success in decarboxylative coupling with organosilane stimulated us to develop its palladium catalyst version. This catalytic system must meet two requirements: (i) the catalyst amount must be less than the amount of nickel, and (ii) the reaction temperature must be mild.

To achieve these goals, an appropriate palladium source was investigated first. A variety of palladium sources were employed in the reaction of phenylpropiolic acid with trimethoxysilylbenzene as shown in Table 1. When the reaction was conducted with 10 mol % Pd without any ligand, Pd(dba)$_2$ exhibited the best result (entry 1), while others gave the desired product in unsatisfactory yields (entries 2–5). The numerous ligands, such as chelating phosphines **L1**–**L7** and chelating amines **L8** and **L9**, were tested with Pd(dba)$_2$ at 60 °C. 1,1-Bis(diphenyphosphino)methane (**L1**) afforded desired product **3a** with 65% (entry 6). Other chelating phosphine ligands exhibited less activity than **L1** (entries 7–12). In all cases with phosphine ligands, diphenyl acetylene, which was formed from homocoupling of phenylpropiolic acid, obtained as a byproduct with 5–11% yields. 2,2-Bipyridine (**L8**) and 1,10-phenanthroline (**L9**) gave poor product yields (entries 13 and 14). In the absence of palladium catalyst and ligand, no desired product was formed and trace amounts of homocoupled product were detected

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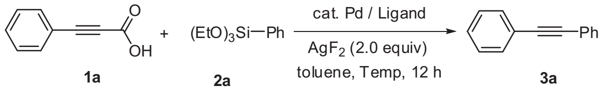
Table 1
Screening of Pd source, ligand, and temperature in the Pd-catalyzed Hiyama-type decarboxylative coupling reaction[a]



Entry	Pd	Ligand[b]	Temp (°C)	**3a** Yield[c] (%)	By-Prod.[d] (%)[c]
1	Pd(dba)$_2$	—	85	20	1
2	Pd(OAc)$_2$	—	85	Trace	2
3	Pd(acac)$_2$	—	85	3	—
4	Pd(CH$_3$CN)$_2$Cl$_2$	—	85	3	—
5	Pd(PPh$_3$)$_2$Cl$_2$	—	85	10	—
6	Pd(dba)$_2$	**L1**	60	65	6
7	Pd(dba)$_2$	**L2**	60	37	8
8	Pd(dba)$_2$	**L3**	60	44	6
9	Pd(dba)$_2$	**L4**	60	39	11
10	Pd(dba)$_2$	**L5**	60	50	6
11	Pd(dba)$_2$	**L6**	60	57	5
12	Pd(dba)$_2$	**L7**	60	50	6
13	Pd(dba)$_2$	**L8**	60	9	—
14	Pd(dba)$_2$	**L9**	60	5	—
15	—	—	60	—	Trace

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), Pd (0.03 mmol), ligand (0.03 mmol), and AgF$_2$ (0.6 mmol) were reacted in toluene for 12 h.
[c] Determined by gas chromatography analysis with an internal standard.
[d] 1,4-Diphenylbutadiyne.
[b] Ligands

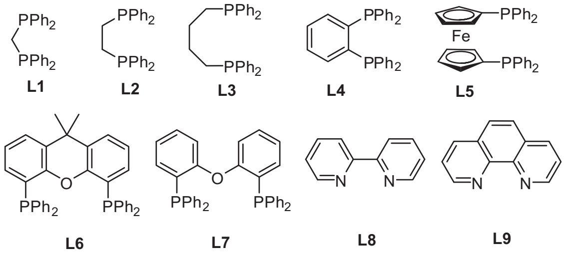
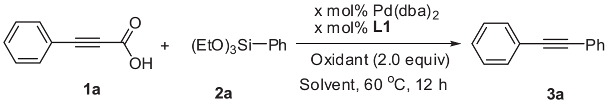


Table 2
Screening of oxidant, additive, and solvent in the Pd-catalyzed Hiyama-type decarboxylative coupling reaction[a]



Entry	Pd/L (mol %)	Oxid./Addit.	Solvent	**3a** Yield (%)[d]	By-Prod.[e] (%)[d]
1	10	AgF	Toluene	4	17
2	10	Ag$_2$CO$_3$	Toluene	–	33
3	10	Ag$_2$O	Toluene	–	31
4	10	CuF$_2$	Toluene	15	31
5	10	AgF$_2$/CsF	Toluene	17	31
6	10	AgF$_2$/KF	Toluene	20	21
7	10	AgF/CsF	Toluene	4	27
8	10	AgF/KF	Toluene	4	31
9	10	AgF$_2$	DMF	46	9
10	10	AgF$_2$	DMSO	40	15
11	10	AgF$_2$	Diglyme	36	9
12	10	AgF$_2$	CH$_3$CN	45	12
13	10	AgF$_2$	Dioxane	29	8
14	10	AgF$_2$	THF	63	7
15	10	AgF$_2$	Xylene	62	9
16	5	AgF$_2$	Toluene	68	9
17	1	AgF$_2$	Toluene	75	5
18[b]	1	AgF$_2$	Toluene	25	1
19	0.5	AgF$_2$	Toluene	29	1
20[c]	1	AgF$_2$	Toluene	69	3

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), Pd(dba)$_2$ (0.03, 0.015, 0.003 mmol), **L1** (0.03, 0.015, 0.003 mmol), and oxidant (0.6 mmol) were reacted at 60 °C for 12 h.
[b] Reaction temperature = 25 °C.
[c] Reaction time = 3 h.
[d] Determined by gas chromatography analysis with an internal standard.
[e] 1,4-Diphenylbutadiyne.