Supporting Information

Non-Sonogashira Type Palladium-Catalyzed Coupling Reactions of Terminal Alkynes Assisted by Silver(I) Oxide or Tetrabutylammonium Fluoride

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Experimental procedure for the coupling of a terminal alkyne and aryl iodide in the presence of silver(I) oxide.

To a 20 mL of Schlenk tube was added $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol), Ag_2O (46.3 mg, 0.2 mmol) and THF (2 mL). Then 4-methoxy-iodobenzene (46.8 mg, 0.2 mmol) and 1-octyne (0.048 mL, 0.24 mmol) was succesively added to the mixutre. The resulting mixture was heated at 60 °C and stirring was continued for 6 h. After cooling to an ambient temperature, the mixure was diluted with 10 mL of diethyl ether and then passed through a Celite pad to remove the silver residue, which was washed with 20 mL of diethyl ether. The combined filtrate was concentrated under reduced pressure to leave a crude oil, which was subjected to column chromatography on silica gel (hexane-ethyl acetate as an eluent) to afford 38.9 mg of 1-(4-methoxyphenyl)-1-octyne (90%). The product was identical with the authentic sample.

Experimental procedure for the coupling of a terminal alkyne and aryl iodide in the presence of TBAF.

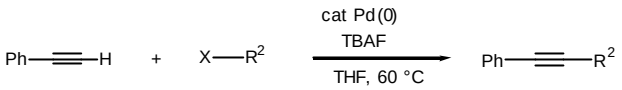
To a 20 mL of Schlenk tube was added $Pd_2(dba)_3CHCl_3$ (0.0025 mmol, 2.6 mg), PPh_3 (2.6 mg, 0.01 mmol) and 4-methoxy-iodobenzene (117 mg, 0.5 mol). The mixture was dissolved in 2 mL of THF under an argon atmosphere. To the solution were succesively added 1-phenylethyne (0.066 mL, 0.6 mmol) and TBAF (0.6 mL, 0.6 mmol; 1M THF solution, water content 5 wt%: available from Aldrich). The resulting mixture was then heated at 60 °C. The progress of the reaction was monitored by TLC and heating was continued until the consumption of starting materials was confirmed (6 h). After the

reaction was complete, the mixture was cooled to room temperature and the solvent was removed under reduced pressure to leave a crude oil, which was subjected to column chromatography on silica gel (hexane-ethny acetate as an eluent) to yield 86 mg of 2-(4-methoxyphenyl)-1-phenylethyne (83%).

Results on optimization of reaction conditions in the palladium-catalyzed coupling of terminal alkyne and aryl halide in the presence of TBAF:

Palladium-catalyzed coupling of 1-phenylethyne with aryl halides in the presence of TBAF was shown in Table 1. (1) A variety of palladium catalyst was found similarly effective. (2) Although several diphosphines were examined, little rate enhancement was observed. (3) The reactions with aryl bromides were found to proceed in lower yields than those of iodides. Their yields were slightly improved when the increased amount of catalyst was employed. (4) The reaction using a catalytic amount of TBAF afforded the coupling product in the yield approximately corresponding amount of TBAF employed (20mol%: 28%, 50 mol%: 67%).

Table 1. The Pd(0)-catalyzed cross coupling of a terminal alkyne and aryl halide with TBAF.[a]



X-R^2	Pd catalyst (mol amt.)	TBAF, mol amt.	time, h	yield, %[b]
4-I-C_6H_4-OMe	$Pd(PPh_3)_4$ (0.05)	1.2	5	94[c]
	$Pd(PPh_3)_4$ (0.01)		6	87[c]
	$Pd_2(dba)_3$ (0.005)-PPh_3 (0.02)[d]	1.1	6	83[c]
	$Pd_2(dba)_3$ (0.005)-PPh_3 (0.04)		6	86[c]
	$[\eta^3$-$C_3H_5)PdCl]_2$ (0.005)-PPh_3 (0.02)		6	82[c]
	$PdCl_2(PPh_3)_2$ (0.01)		6	80[c]
	$Pd_2(dba)_3$ (0.005)-dppe[e] (0.01)		6	74[c]
	$Pd_2(dba)_3$ (0.005)-dppp[f] (0.01)		6	68[c]
I-C_6H_5	$Pd_2(dba)_3$ (0.025)-PPh_3 (0.1)	1.2	1	93
4-I-C_6H_4-COMe	$Pd_2(dba)_3$ (0.025)-PPh_3 (0.1)	1.1	5	77
4-I-C_6H_4-CN	$Pd_2(dba)_3$ (0.005)-PPh_3 (0.02)	1.1	5	86
4-I-C_6H_4-OMe	$Pd_2(dba)_3$ (0.005)-PPh_3 (0.02)	1.2	6	76
		0.5	6	67
		0.2	6	28
4-Br-C_6H_4-OMe	$Pd_2(dba)_3$ (0.005)-PPh_3 (0.02)	1.1	48	54
	$Pd_2(dba)_3$ (0.025)-PPh_3 (0.1)		24	71

[a]The reaction was carried out at 60 °C in THF using 1.2 mol amount of alkyne and 1.0 mol amount of X-R^2. [b]The yield was given as isolated unless noted. [c]Yield estimated by ^{1}H NMR. [d]dba:1,3-dibenzylideneacetone, palladium(0) was used as $Pd_2(dba)_3CHCl_3$. [e]dppe: 1,2-bis(diphenylphosphino)ethane. [f]dppp: 1,3-bis(diphenylphosphino)propane