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Pd-Catalyzed Vinylation of Aryl Halides with Inexpensive Organosilicon Reagents Under Mild Conditions

Chu-Ting Yang,*[a] Jun Han,[a] Jun Liu,[a] Yi Li,[a] Fan Zhang,[a] Hai-Zhu Yu,*[b] Sheng Hu[a], and Xiaolin Wang*[a]

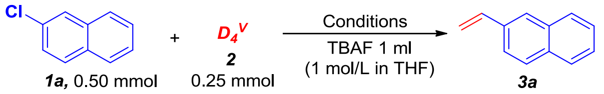
Abstract: Pd-catalyzed Hiyama vinylation reaction of non-activated aryl chlorides and bromides under mild conditions was developed. The use of efficient vinyl donors and electron-rich sterically hindered phosphine ligands was critical for the success of the reaction. The products of this transformation can be used for Am/Cm separation, an important challenge in nuclear fuel reprocessing. The substituent effect on Am/Cm separating selectivity was also achieved, which contributes to the development of new chromatographic materials for the separation of Am and Cm.

Substituted styrenes are one of the most important building blocks for the synthesis of fine chemicals and polymers.[1] In addition, styrenes are used ubiquitously in modern organic reactions, such as cross-metathesis,[2] asymmetric dihydroxylation,[3] aminohydroxylation,[4] and epoxidation.[5] Classical methods for the synthesis of functionalized styrene derivatives involve dehydration of alcohols, dehydrohalogenation of alkyl halides, carbonyl olefination, and the reduction of terminal alkynes.[6] However, these methods suffer from harsh reaction conditions and limited scope of substrates. Thus, recent attention has been given to developing transition-metal-catalyzed methods for the preparation of styrene derivatives. One of the most important examples is Pd-catalyzed vinylation of aryl halides with organometallic vinyl donors,[7] including tin-,[8] boron-,[9] magnesium-,[10] and silicon-based reagents.[11] Among these vinyl donors, organosilicon reagents offer numerous advantages, such as low toxicity, ease of synthesis, low cost, and high chemical stability.[12] Since the pioneering study of Hiyama and co-workers,[11a] a variety of palladium catalytic systems, organosilicon-based vinyl donors, and activating reagents are now used to promote the vinylation reaction under milder conditions.[11,12] Nevertheless, to date, the substrate scope has been predominantly limited to aryl iodides and bromides.[13,14] Moreover, the reaction at room temperature was limited to aryl iodides and activated bromides.[11e,11g] It remains challenging to develop vinylation reactions of aryl bromides and chlorides under milder conditions, especially at room temperature. Such transformations are desirable because they would be amenable to large-scale reactions.

Herein, Pd-catalyzed vinylation of aryl chlorides and bromides, using inexpensive organosilicon reagents and milder reaction conditions, was achieved. The vinylation reactions of non- activated aryl bromides were carried out at room temperature. Moreover, gram-scale reactions were conducted to synthesize vinyl pyridines, which can be used for Am/Cm separation as polyvinyl pyridine (PVP) through polymerization. More importantly, the substituent effect on separating selectivity for pyridine resins was achieved. Hence, this work not only provides a convenient method for the synthesis of substituted styrenes but also contributes to the development of new chromatographic materials for the separation of Am and Cm.

Our study began with an examination of the reaction of 2-chloronaphthalene (**1a**) with an inexpensive, readily available and efficient vinyl donors (1,3,5,7-tetravinyl-1,3,5,7-tetramethyl-cyclotetrasiloxane, D_4^V, **2**).[11e] We initially used $Pd(OAc)_2$ as the catalyst and tetrabutylammonium fluoride trihydrate (TBAF) as the activating agent. The electron-rich sterically hindered phosphine ligands were used to activate aryl chlorides (Table 1, entries 1–7).[15] We were delighted to find that X-phos provided excellent yield (86%, entry 7). The observation is expected, because according to the recent studies, $Pd(OAc)_2$/X-phos is capable to activate aryl chlorides under mild conditions. The coordination of the aromatic ring in X-phos could increase the electron density of metal center (Pd) and promote the oxidative-addition step, which is rate-determining step in this vinylation reaction.[11k,16] Reducing the amount of catalyst (1 mol%) generated a lower yield (68%, entry 8). Other Pd catalysts, including $PdBr_2$ and $Pd(dba)_2$, also promoted the reaction but gave lower yields (entries 9 and 10). By contrast, the reaction did not occur in the absence of a Pd catalyst (entry 11). In a test of various organosilicon-based vinyl donors (entries 12–17), D_4^V generated the best yield. The decrease of reaction temperature to 40°C lowered the yield to 38% (entry 18). The product was not obtained at room temperature (entry 19). Finally, aryl bromide and iodide were also good substrates (entries 21 and 22), but the present conditions were not effective for the coupling of an aryl tosylate (entriy 20).

Table 1. Pd-catalyzed vinylation of 1-chloronaphthalene under various conditions.



Entry	Catalyst (0.01 mmol)	Ligand (0.02 mmol)	Vinyl donor	Temp. (°C)	Time (h)	Yield (%)[a]
1	$Pd(OAc)_2$	PCy_3	D_4^V	67	24	6
2	$Pd(OAc)_2$	DPPF	D_4^V	67	24	Trace
3	$Pd(OAc)_2$	P^tBu_3	D_4^V	67	24	Trace
4	$Pd(OAc)_2$	JohnPhos	D_4^V	67	24	10
5	$Pd(OAc)_2$	RuPhos	D_4^V	67	24	33
6	$Pd(OAc)_2$	S-phos	D_4^V	67	24	17
7	**$Pd(OAc)_2$**	**X-phos**	**D_4^V**	**67**	**24**	**90(86)[b]**
8[c]	$Pd(OAc)_2$	X-phos	D_4^V	67	24	68
9	$PdBr_2$	X-phos	D_4^V	67	24	76
10	$Pd(dba)_2$	X-phos	D_4^V	67	24	59
11	-	X-phos	D_4^V	67	24	Trace
12	$Pd(OAc)_2$	X-phos	D_3^V	67	24	73
13	$Pd(OAc)_2$	X-phos	HVDS	67	24	45
14	$Pd(OAc)_2$	X-phos	DVDS	67	24	64
15	$Pd(OAc)_2$	X-phos	$VS(OMe)_3$	67	24	32

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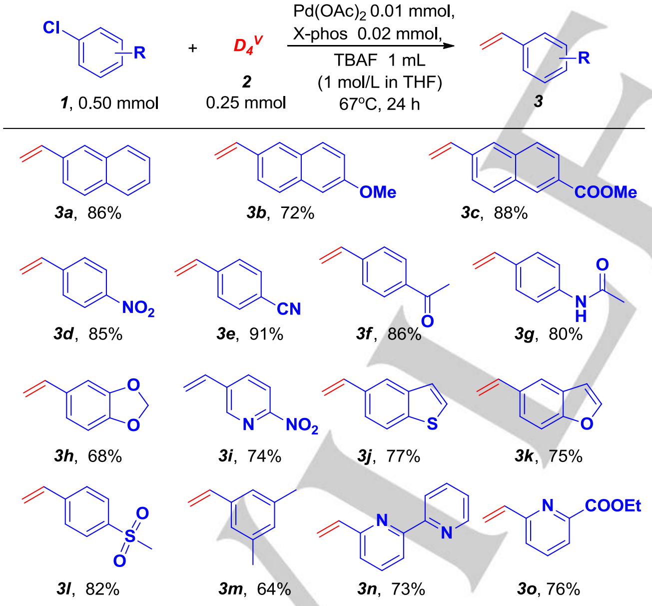
16	$Pd(OAc)_2$	X-phos	$VS(OEt)_3$	67	24	36
17	$Pd(OAc)_2$	X-phos	$VS(O^iPr)_3$	67	24	81
18	$Pd(OAc)_2$	X-phos	D_4^V	40	24	38
19	$Pd(OAc)_2$	X-phos	D_4^V	25	24	Trace
20[d]	$Pd(OAc)_2$	X-phos	D_4^V	67	24	Trace
21[e]	$Pd(OAc)_2$	X-phos	D_4^V	67	24	93
22[f]	$Pd(OAc)_2$	X-phos	D_4^V	67	24	91

[a] Reaction conditions: 2-chloronaphthalene (0.5 mmol), D_4^V (0.25 mmol), TBAF (1 mol/L in THF, 1 mL), catalyst (0.01 mmol), ligand (0.02 mmol), GC yields after 24 h (average of two runs). [b] Isolated yields, TON (turn over number) =45. [c] 0.005 mmol of Pd catalyst was added, TON=68. [d] R-OTs (0.5 mmol) was used. [e] R-Br (0.5 mmol) was used. [f] R-I (0.5 mmol) was used. D_3^V=2,4,6-trimethyl-2,4,6-trivinyl-1,3,5,2,4,6-trioxatrisilinane, HVDS= hexavinyldisiloxane, DVDS=divinyltetramethyldisiloxane, $VS(OMe)_3$=tri-methoxy(vinyl)silane, $VS(OEt)_3$=triethoxy(vinyl)silane, $VS(O^iPr)_3$=tri-isopropoxy(vinyl)silane.

The results of the current study indicate that $Pd(OAc)_2$/X-phos is a suitable catalyst for the vinylation reaction of aryl chlorides. In regard to the scope of this method (Table 2), aryl chlorides with different substituent groups can participate in the reaction. Both electron-donating (**3b, 3h, 3m**) and electron-withdrawing (**3c−g, 3l**) aryl chlorides are good substrates. However, the latter showed better reactive activity and were obtained in good to excellent yields. More importantly, a variety of synthetically useful functional groups, including ether (**3b, 3h**), ester (**3c, 3o**), nitryl (**3d, 3i**), cyano (**3e**), carbonyl (**3f**), amide (**3g**), and sulfoxide (**3l**) can be tolerated in this reaction. Furthermore, the heteroaryl chlorides such as pyridine (**3i, 3o**), thiophene (**3j**), furan (**3k**), and bipyridyl (**3n**) worked well, affording the corresponding styrenes in 73-77% yields.

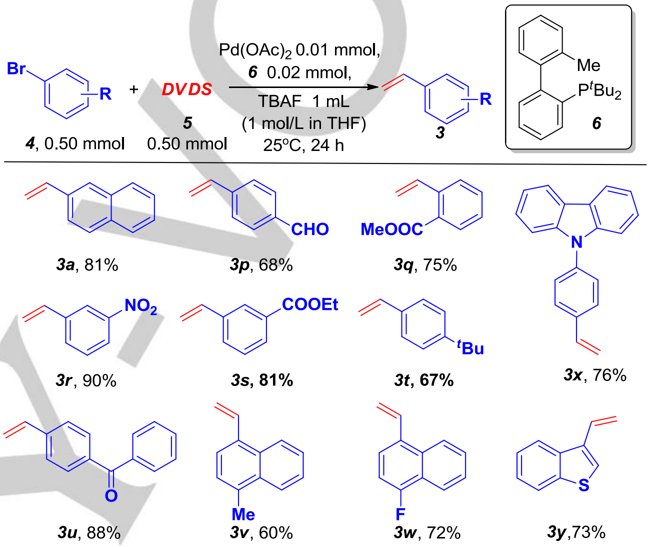
Table 2. Pd-catalyzed vinylation of aryl chlorides.[a]



[a] Reactions were carried out at 67°C for 24 h on a 0.5 mmol scale using 0.01 mmol $Pd(OAc)_2$ and 0.02 mmol X-phos. For details about each substrate please see the Supporting Information. Yields were determined through the isolation of the desired products.

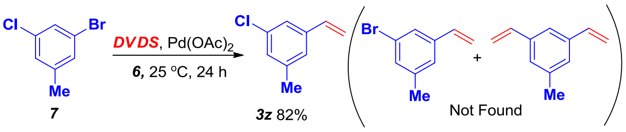
The vinylation of 2-bromonaphthalene provided 93% yield with the present condition but gave only 21% yield at room temperature. Thus, we continued to improve the reaction at room temperature. Through optimizing multiple reaction parameters(see the Supporting Information), we found room temperature Pd-catalyzed vinylation of aryl bromides can be realized with phosphine ligand (**6**, Table 3) and vinyl donor (DVDS). This catalyst was not only effective for the activated aryl bromides (electron withdrawing groups, **3p-3s, 3u**) but also provided good yields for the non-activated substrates (**3a, 3t, 3v-3y**). Interestingly, an aldehyde moiety (**3p**) can survive under these mild reaction conditions, indicating good functional group compatibility of the transformation. It is important to note that in most previous Pd-catalyzed Hiyama vinylation reactions, only aryl iodides and activated bromides could react at room temperature.[11e,11g] This new method, therefore, provides the first example of a Pd-catalyzed Hiyama vinylation reaction of non-activated aryl bromides at room temperature.

Table 3. Pd-catalyzed vinylation of aryl bromides at room temperature.[a]



[a] Reactions were carried out at 25°C for 24 h on a 0.5 mmol scale using 0.01 mmol $Pd(OAc)_2$ and 0.02 mmol **6**. For details about each substrate please see the Supporting Information. Yields were determined through the isolation of the desired products.

Further tests showed the present catalyst ($Pd(OAc)_2$/**6**) cannot promote vinylation of aryl chlorides at room temperature, suggesting good chemoselectivity of the reaction. As shown in Scheme 1, we found that for substrates with both aryl-Br and aryl-Cl sites, the former was much more reactive under the present catalytic conditions. In the reaction of compound **7** and DVDS, mono-vinyl compound (**3z**) was the only product, while aryl-Cl remained intact and was capable of undergoing further functionalization.

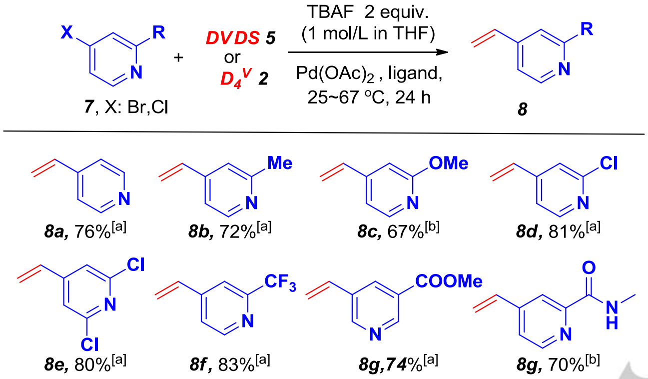


Scheme 1. Selectivity between aryl bromides and chlorides.

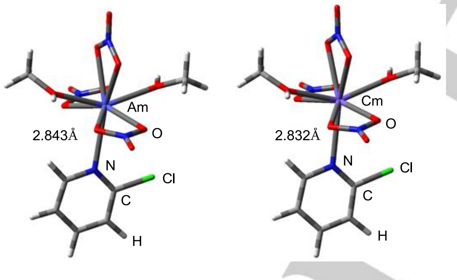
Additionally, gram-scale reactions (Table 4) were conducted to evaluate the efficiency of the new catalyst system in preparative organic synthesis. In the experiments, the Pd-catalyzed vinylation reaction proceeded equally well, in comparison to the smaller scale experiments, and the reaction afforded vinyl pyridines with good isolated yields and high functional-group tolerance. The products were important monomers for polyvinyl pyridine (PVP), which can be can be used as a paper reinforcing agent, surface modifier, support for metal catalyst, template for nanostructure, and pyridine resin.[17] Specifically, pyridine resins have become promising materials for Am/Cm separation,[18] addressing an important challenge in actinides separation chemistry and nuclear fuel reprocessing.[19]

However, the reported resins frequently suffer from the poor Am/Cm selectivity. In order to improve the selectivity, a series of pyridine resins with different substituents embedded in silica beads were synthesized (see the Supporting Information). We found that: 1) The Am/Cm separation factors ($SF_{Am/cm}$) decreased with electron-donating groups (Me, OMe), and this was probably due to the enhanced basic and complexing ability of the nitrogen atom. 2) By contrast, the resin with the CF_3 group revealed the best Am/Cm selectivity ($SF_{Am/cm}$=4.2), due to the softer nitrogen atom. 3) Interestingly, the resins with Cl groups exhibited high Cm selectivity. The separation factors were calculated as $SF_{Cm/Am}$ = 2 and 5 with mono-Cl and di-Cl substituents, respectively.

Table 4. Gram-scale vinylation of halogenated pyridines.



[a] Reactions were carried out at 25°C for 24 h on a 20 mmol scale using 0.4 mmol $Pd(OAc)_2$, 0.8 mmol **6**, 20 mmol bromides and 20 mmol DVDS. [b] Reactions were carried out at 67°C for 24 h on a 20 mmol scale using 0.4 mmol $Pd(OAc)_2$, 0.8 mmol X-phos, 20 mmol chlorides and 10 mmol D_4^V. For details about each substrate please see the Supporting Information. Yields were determined through the isolation of the desired products.



$Am(CH_3OH)_2(NO_3)_3(ClNPy)$ $Cm(CH_3OH)_2(NO_3)_3(ClNPy)$

Figure 1. The optimized structures formed by 2-Cl-Py and Am (Cm).

We further analyzed the Cm-selectivity through density functional theory calculations of the optimized structure, formed by the simplified ligand model (2-Cl-Py) and metal centers (Am, Cm). The Am-N bond length was longer than Cm-N bond length in the optimized structures (Figure 1, 2.843 Å versus 2.832 Å), indicating a weaker interaction between Am and the pyridine ligand. Furthermore, frontier molecular orbital analysis revealed comprehensive interactions between Cl(*p*) orbital and the Cm(*f*) orbital, which was significantly weaker in the Am-system (See the Supporting Information). In addition, the corresponding frontier orbital energy of the Cm complex was significantly lower than that of the Am-complex, and the HOMO-LUMO energy gap of the Cm system was greater, which helped to improve the stability of the Cm complex.

To summarize, we have developed a Pd-catalyzed cross-coupling reaction of aryl halides with organosilicon vinyl reagents. This reaction represents the rare example of a Pd-catalyzed Hiyama vinylation reaction of non-activated aryl chlorides and bromides under mild conditions, in particular, at room temperature. The use of efficient vinyl donors (D_4^V or DVDS) and electron-rich sterically hindered phosphine ligands is crucial. The reaction tolerates a number of synthetically relevant functional groups, including esters, amides, nitryl, cyano, carbonyl, aldehyde, and heteroaryl halides are also good substrates. Furthermore, we also demonstrate that the Pd-catalyzed method is amenable to gram-scale preparative organic synthesis, and the products were used to synthesize pyridine resins, which are promising materials for Am/Cm separation. Finally, we preliminarily evaluated the substituent effect on Am/Cm separating selectivity for pyridine resins. The resin with the electron-withdrawing group (CF_3) exhibited the best selectivity for Am and that with the Cl group showed high selectivity for Cm. The results of this study contribute to the development of new chromatographic materials for the separation of Am and Cm. Follow-up studies are underway in our laboratory.

Experimental Section

Representative procedure (3a, Table 2): In air, $Pd(OAc)_2$(0.01 mmol), and X-phos (0.02 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). TBAF (1 mol/L in THF, 1 mL), 2-chloronaphthalene (0.5 mmol), and D_4^V (0.25 mmol) were added in turn under Argon atmosphere at room temperature. The reaction mixture was stirred at 67 ºC for 24 h, then quenched with H_2O (10 mL). The resulting solution mixture was then extracted with CH_2Cl_2 (3 times, 10 mL each), dried over Mg_2SO_4, filtered through silica gel with copious washings (CH_2Cl_2), concentrated, and purified by column chromatography. The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.

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Keywords: palladium • silicon• cross-coupling • Am/Cm separation • substituent effect

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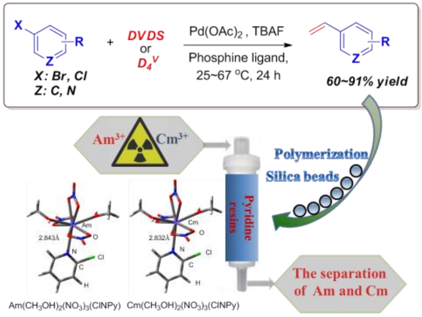
Pd-catalyzed Hiyama vinylation reaction of non-activated aryl chlorides and bromides under mild conditions was achieved. The products of this transformation can be used for Am/Cm separation, an important challenge in nuclear fuel reprocessing.



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