Nickel-Catalyzed Ligand-Free Hiyama Coupling of Aryl Bromides and Vinyltrimethoxysilane

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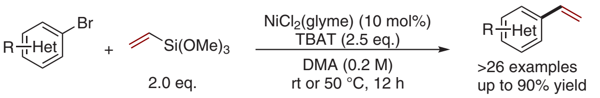


R = ester, ketone, aldehyde, cyanide, amide, sulfonyl, sulfonamide, morpholinyl, etc.

Published as part of the Cluster
Modern Nickel-Catalyzed Reactions

Received: 30.11.2020
Accepted after revision: 31.01.2021

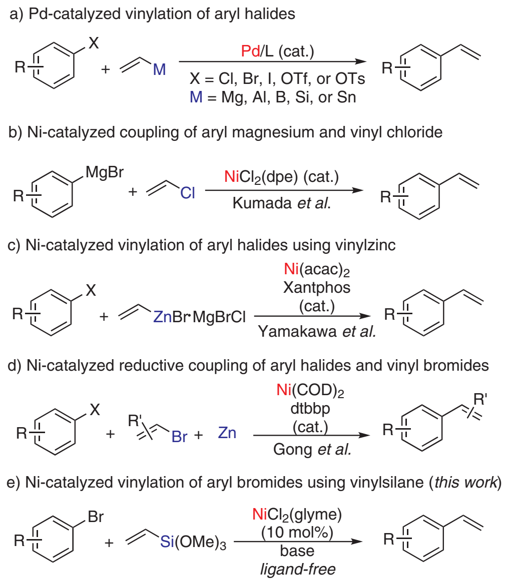
DOI: 10.1055/a-1379-1584; Art ID: st-2020-k0612-c

Abstract We herein disclose the first Ni-catalyzed Hiyama coupling of aryl halides with vinylsilanes. This protocol uses cheap, nontoxic, and stable vinyltrimethoxysilane as the vinyl donor, proceeds under mild and ligand-free conditions, furnishing a diverse variety of styrene derivatives in high yields with excellent functional group compatibility.

Keywords nickel catalysis, vinylation, cross-coupling, Hiyama coupling, ligand-free conditions, vinylsilane, aryl halide

Styrene derivatives represent one of the most important structural units in organic chemistry. Moreover, they serve as versatile synthetic intermediates in various organic transformations, such as olefin metathesis,[1] Heck reaction,[2] hydrofunctionalization,[3] and epoxidation.[4] Besides, they are widely used as monomers for polymer synthesis.[5] The traditional synthetic methods of styrenes include dehydration of alcohols or Hoffman elimination,[6] carbonyl olefination,[7] and semireduction of terminal alkynes.[8] However, these methods, to some extent, are limited by the accessibility of the starting materials, harsh reaction conditions, or the tolerance of functional groups.

In order to address the above-mentioned issues, numerous transition-metal-catalyzed cross-coupling reactions using readily available aryl halides have been developed to access styrenes in the past several decades.[9] For example, Pd-catalyzed vinylation of aryl halides using magnesium-,[10] lithium-,[11] aluminium-,[12] boron-,[13] silicon-,[14] and tin-based[15] vinyl donors has been reported and widely applied to the synthesis of vinyl arenes (Scheme 1a). However, these methods generally suffer from the use of noble metal, expensive and sensitive ligand, and in some cases using toxic or unstable organometallic reagents. Therefore, a mild earth-abundant metal-catalyzed vinylation of aryl halides using stable vinyl donors is highly desirable and yet remains underdeveloped.

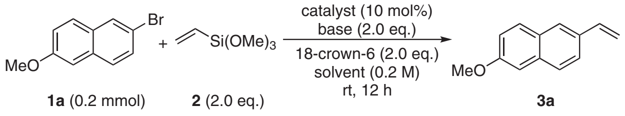


Scheme 1 Pd- or Ni-catalyzed cross-couplings to form styrenes

As the first-row transition metal in the same group as palladium, nickel has attracted much attention from the chemical community due to its earth-abundant, cost-effective characteristics, and numerous nickel-catalyzed reactions have been developed.[16] In 1972, Kumada and co-workers described a pioneering work on Ni-catalyzed cross-coupling reaction of aryl Grignard reagent with vinyl chloride (Scheme 1b).[17] In 2009, Yamakawa and co-workers reported a Ni-catalyzed coupling of vinyl zinc reagents and aryl halides (Scheme 1c).[18] In 2016, Gong and co-workers reported an elegant Ni-catalyzed reductive coupling of aryl halides and vinyl bromides using Zn as the reducing agent (Scheme 1d).[19] We noted that vinylsilanes have the advantages of easy accessibility, low toxicity, and high stability, thus serve as excellent vinyl donors. Although Pd-catalyzed Hiyama coupling of aryl halides with silicon reagents is well-developed,[14,20] the Ni-catalyzed Hiyama cross-coupling reaction is relatively underexplored.[21,22] As far as we know there is no report on the Ni-catalyzed cross-coupling reaction of vinyl silicon reagents with aryl halides. As a part of our continuous interests in nickel catalysis,[23] we herein report a ligand-free Ni-catalyzed Hiyama coupling of aryl halides with vinylsilanes to prepare styrenes (Scheme 1e).

We started our studies by using commercially available vinyltrimethoxysilane (**2**) and aryl bromide **1a** as model substrates and base and 18-crown-6 as activators in the presence of stable divalent nickel catalysts to optimize the reaction conditions (Table 1). We found that inorganic bases such as KOMe, NaOMe, and KO*t*-Bu were effective for the vinylation reaction at ambient temperature (35 °C), affording product **3a** in good yield (ca. 80%, entries 1–4), but KF led to no conversion (entry 5). The use of cyclohexane and dichloromethane as solvent resulted in low or no conversions, but more polar solvents, such as DMF, DMA, dioxane, and THF produced **3a** in high yields (entries 1, 6–10). Among these solvents, DMF is the best choice. The use of different divalent nickel sources gave similar reaction outcomes (entries 11 and 12). Increasing the amount of vinylsilane and base to 2.3 equivalents could improve the yield to 87% (entry 13, 84% isolated yield). The control experiment confirmed that 18-crown-6 is critical to promote the reaction (entry 14).

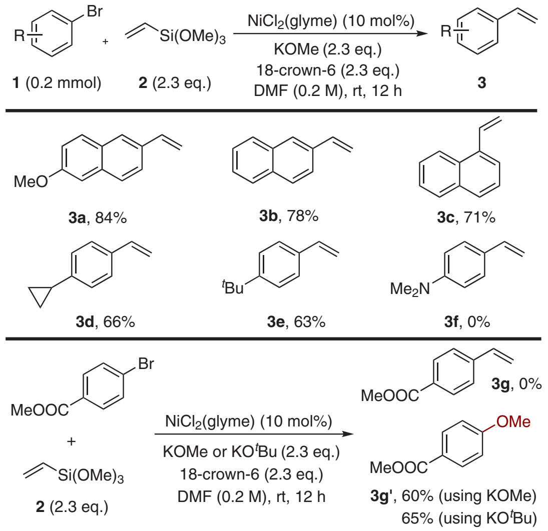
Table 1 Reaction Optimization



Entry	Catalyst	Base	Solvent	Yield (%)^a
1	NiCl$_2$(glyme)	KOMe	THF	80
2	NiCl$_2$(glyme)	NaOMe	THF	74
3	NiCl$_2$(glyme)	KO*t*-Bu	THF	54
4	NiCl$_2$(glyme)	KO*t*-Bu	THF	33
5	NiCl$_2$(glyme)	KF	THF	0
6	NiCl$_2$(glyme)	KOMe	dioxane	75
7	NiCl$_2$(glyme)	KOMe	DMF	83
8	NiCl$_2$(glyme)	KOMe	DMA	76
9	NiCl$_2$(glyme)	KOMe	DCM	0
10	NiCl$_2$(glyme)	KOMe	hexane	37
11	NiBr$_2$(glyme)	KOMe	DMF	80
12	NiCl$_2$	KOMe	DMF	82
13^b	NiCl$_2$(glyme)	KOMe	DMF	87 (84)
14^c	NiCl$_2$(glyme)	KOMe	DMF	<2

[a] Determined by GC using crude samples, the isolated yield is shown in parenthesis.
[b] Using 2.3 equiv of **2**, KOMe, and 18-crown-6.
[c] Without 18-crown-6.

Under the reaction conditions shown in Table 1, entry 13, we examined the preliminary substrate scope of this reaction. As shown in Scheme 2, we found that electronically neutral aryl bromides could furnish the corresponding vinyl arene products in 63–84% yield (**3a–e**). Unfortunately, an electron-rich substrate (**3f**) gave no conversion under ambient temperature or delivered a trace amount of product at elevated temperature (50 °C).



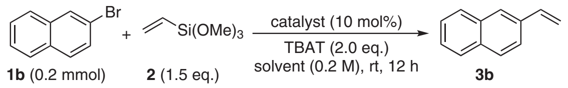
Scheme 2 Preliminary substrate scope

Interestingly, electron-deficient substrates underwent carbon–oxygen (C–O) formation to give an aryl methyl ether (**3g′**) but not the desired vinylation product (**3g**). The use of KO*t*-Bu as the base gave aryl methyl ether (**3g′**) and suggests that the methoxy group in the product results from vinyltrimethoxysilane but not from the base KOMe.[24]

To address this chemoselectivity issue, we felt the use of a more selective silane activator could be required. We noted that tetrabutylammoniumtriphenyldifluorosilicate (TBAT), a commercially available, anhydrous, nonhygroscopic, crystalline solid, was first introduced as a fluoride source by DeShong and co-workers.[25] TBAT was found less basic than tetrabutylammonium fluoride (TBAF) but could more efficiently activate silicon–carbon bonds to generate in situ carbanions to couple with electrophiles.[25,26] Intriguingly, TBAT itself served as a phenylating agent in Pd-catalyzed cross-coupling reactions of aryl halides.[26b] However, in a Ni-catalyzed asymmetric Hiyama coupling of α-bromo esters, TBAT worked as an activator for aryltrimethoxysilane but not as a phenylating agent.[21d]

We next optimized the reaction conditions using TBAT as a nucleophilic activator for the Hiyama coupling of vinylsilane **2** and aryl bromide **1b** in the presence of $NiCl_2$(glyme) catalyst at ambient temperature (35 °C). To our delight, the new conditions afforded the vinylation product **3b** in 68% yield without observing the corresponding phenylation byproduct (TBAT as a phenylating reagent) (Table 2, entry 5). Remarkably, other fluoride sources such as TBAF, KF, NaF, and CsF resulted in no conversions (entries 1–4). A solvent screening suggested DMA is the best solvent, furnishing **3b** in 83% yield (entries 5–9). Other nickel sources, such as $NiBr_2$(glyme) and $NiCl_2$, decreased the yield slightly (entries 10 and 11). However, when increasing the amount of vinyl donor (2.0 equiv) and TBAT (2.5 equiv), the yield could be improved to 87% (83% isolated yield, entry 12). Finally, the reaction was found applicable to aryl iodide and aryl triflate affording **3b** good yields, although aryl chloride and aryl tosylate were unsuitable substrates (entries 13–16).

Table 2 Reaction Optimization

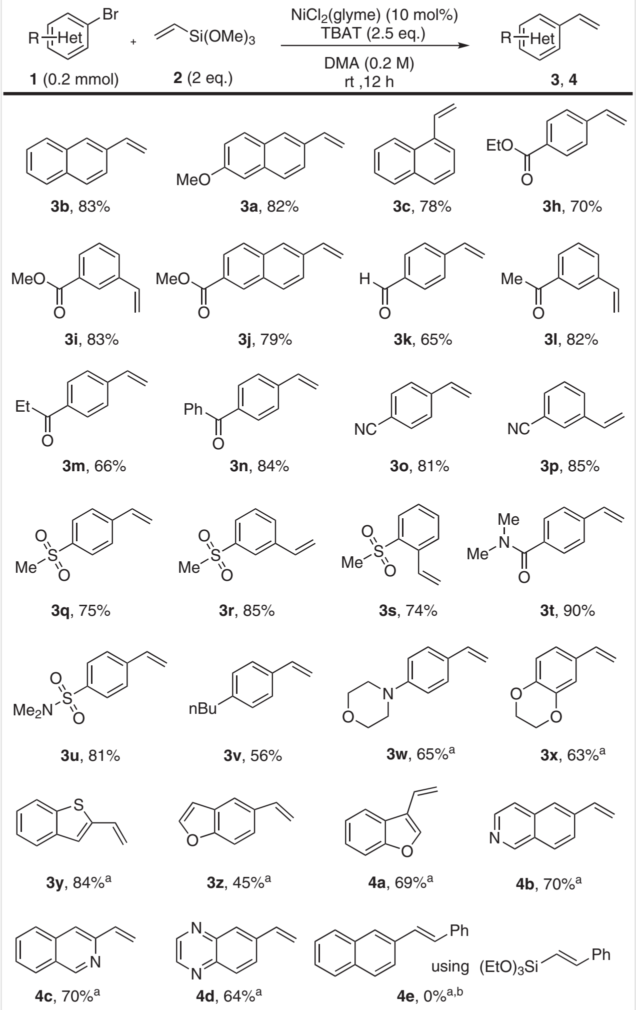


Entry	X	Catalyst	Base	Solvent	Yield (%)^{a}
1	Br	$NiCl_2$(glyme)	KF	dioxane	0
2	Br	$NiCl_2$(glyme)	NaF	dioxane	0
3	Br	$NiCl_2$(glyme)	CsF	dioxane	0
4	Br	$NiCl_2$(glyme)	TBAF	dioxane	0
5	Br	$NiCl_2$(glyme)	TBAT	dioxane	68
6	Br	$NiCl_2$(glyme)	TBAT	THF	75
7	Br	$NiCl_2$(glyme)	TBAT	DCM	20
8	Br	$NiCl_2$(glyme)	TBAT	DMF	74
9	Br	$NiCl_2$(glyme)	TBAT	DMA	83
10	Br	$NiBr_2$(glyme)	TBAT	DMA	67
11	Br	$NiCl_2$	TBAT	DMA	73
12^{b}	Br	$NiCl_2$(glyme)	TBAT	DMA	87 (83)
13^{b}	Cl	$NiCl_2$(glyme)	TBAT	DMA	0
14^{b}	I	$NiCl_2$(glyme)	TBAT	DMA	70
15^{b}	OTf	$NiCl_2$(glyme)	TBAT	DMA	67
16^{b}	OTs	$NiCl_2$(glyme)	TBAT	DMA	11

^{a} Determined by GC analysis. The isolated yield is shown in parenthesis.
^{b} Using 2.0 equiv of **2** and 2.5 equiv of TBAT.

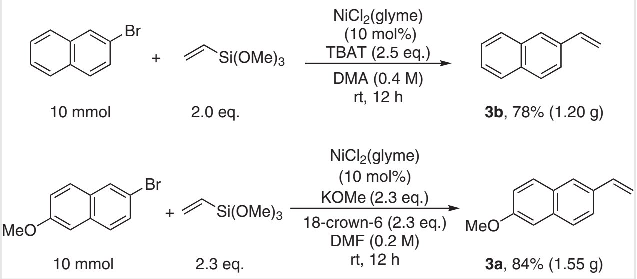
With the optimized reaction conditions in hand, we next surveyed the generality of this novel Ni-catalyzed protocol (Scheme 3). We found that this reaction is not sensitive to steric hindrance; bulky substrates work well (**3c**,**s**).

Notably, electron-deficient aryl bromides that did not work under our initial conditions (Table 1, entry 11) served as suitable substrates, affording the corresponding vinylation products in high yields (**3h**–**u**). The potential biaryl byproduct (TBAT as a phenylating reagent) and the aryl methyl ethers (methoxy migration from silane) were not observed under these mild reaction conditions. A wide variety of functional groups, including esters, aldehydes, ketones, nitriles, sulfone, amides, sulfonamides, ethers, and morpholinyl groups, were compatible (**3a**–**y**). For electron-rich aryl bromides (**3w**–**y**) and heteroaromatic substrates (**3z**–**4e**), the reactions proceeded smoothly when heating the reaction mixtures to 50 °C. Various heterocycles, such as benzothiophene, benzofuran, isoquinoline, and quinoxaline, were all competent substrates, delivering vinyl heteroarenes in good to high yields (**3z**–**4d**). However, an attempt to synthesize β-substituted styrenes using (*E*)-styryltriethoxysilane instead of **2** failed (**4e**).



Scheme 3 Substrate scope. ^{a} Reaction performed at 50 °C. ^{b} Using (*E*)-styryltriethoxysilane instead of **2**.

Finally, we successfully performed two examples of gram-scale reactions. Similar high yields of products were obtained, which highlighting the robustness and practicality of our catalytic method (Scheme 4).



Scheme 4 Gram-scale reactions

In conclusion, we have developed a Ni-catalyzed Hiyama coupling reaction of aryl bromides and vinylsilanes for the first time.[27] The key to the success of the transformation is the use of TBAT as a silane-activating reagent. This protocol uses inexpensive nickel catalyst under ligand-free conditions, employs readily available and stable substrates, displays both high tolerance of functional groups and scale-up capacity.

Funding Information

This work was financially supported by the National Natural Science Foundation of China (NSF, Grant No. 91856111, 21871288, 21690074, 21821002), the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB20000000).

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1379-1584.

References and Notes

(1) (a) Grubbs, R. H. *Tetrahedron* **2004**, *60*, 7117. (b) Ogba, O. M.; Warner, N. C.; Grubbs, R. H. *Chem. Soc. Rev.* **2018**, *47*, 4510.

(2) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.

(3) (a) Chen, J.; Lu, Z. *Org. Chem. Front.* **2018**, *5*, 260. (b) Chen, J.; Guo, J.; Lu, Z. *Chin. J. Chem.* **2018**, *36*, 1075. (c) Fan, W. W.; Li, L.; Zhang, G. Q. *J. Org. Chem.* **2019**, *84*, 5987. (d) Pirnot, M. T.; Wang, Y.-M.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2016**, *55*, 48. (e) Agbossou, F.; Carpentier, J. F.; Mortreux, M. *Chem. Rev.* **1995**, *95*, 2485.

(4) Xia, Q. H.; Ge, H. Q.; Ye, C. P.; Liu, Z. M.; Su, K. X. *Chem. Rev.* **2005**, *105*, 1603.

(5) (a) Hirao, A.; Goseki, R.; Ishizone, T. *Macromolecules* **2014**, *47*, 1883. (b) Goseki, R.; Tanaka, S.; Ishizone, T.; Hirao, A. *React. Funct. Polym.* **2018**, *127*, 94.

(6) Emerson, W. S. *Chem. Rev.* **1949**, *45*, 347.

(7) (a) Maryanoff, B.; Reitz, A. *Chem. Rev.* **1989**, *89*, 863. (b) Bisceglia, J. A.; Orelli, L. R. *Curr. Org. Chem.* **2012**, *16*, 2206.

(8) Chinchilla, R.; Najera, C. *Chem. Rev.* **2014**, *114*, 1783.

(9) Denmark, S.; Butler, C. R. *Chem. Commun.* **2009**, 20.

(10) Bumagin, N. A.; Luzikova, E. V. *J. Organomet. Chem.* **1997**, *532*, 271.

(11) Hornillos, V.; Giannerini, M.; Vila, C.; Fañanás-Mastrala, M.; Feringa, B. L. *Chem. Sci.* **2015**, *6*, 1394.

(12) Schumann, H.; Kaufmann, J.; Schmalz, H.-G.; Bottcher, A.; Gotov, B. *Synlett* **2003**, 1783.

(13) (a) Kerins, F.; O'Shea, D. F. *J. Org. Chem.* **2002**, *67*, 4968. (b) Kesslers, A.; Coleman, C. M.; Charoenying, P.; O'Shea, D. F. *J. Org. Chem.* **2004**, *69*, 7836. (c) Molander, G. A.; Rivero, M. R. *Org. Lett.* **2002**, *4*, 107. (d) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685. (e) Alacid, E.; Najera, C. *J. Org. Chem.* **2009**, *74*, 8191. (f) Civicos, J. F.; Alonso, D. A.; Najera, C. *Adv. Synth. Catal.* **2011**, *353*, 1683.

(14) (a) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918. (b) Itami, K.; Nokami, T.; Yoshidaj, J. *J. Am. Chem. Soc.* **2001**, *123*, 5600. (c) Hosoi, K.; Nozaki, K.; Hiyama, T. *Chem. Lett.* **2002**, *2*, 138. (d) Nakao, Y.; Imanaka, H.; Sahoo, A. K.; Yada, A.; Hiyama, T. *J. Am. Chem. Soc.* **2005**, *127*, 6952. (e) Denmark, S. E.; Sweis, R. F.; Wehrli, D. *J. Am. Chem. Soc.* **2004**, *126*, 4865. (f) Denmark, S. E.; Butler, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 3690. (g) Gordillo, A. L.; Jesus, E. D.; Carmen, L. M. *J. Am. Chem. Soc.* **2009**, *131*, 4584. (h) Premi, C.; Jain, N. *Eur. J. Org. Chem.* **2013**, 5493. (i) Yang, C.-T.; Han, J.; Liu, J.; Li, Y.; Zhang, F.; Yu, H.-Z.; Hu, S.; Wang, X. *Chem. Eur. J.* **2018**, *24*, 10324. (j) Faßbender, S. I.; Molloy, J. J.; Mück-Lichtenfeld, C.; Gilmour, R. *Angew. Chem. Int. Ed.* **2019**, *58*, 18619.

(15) (a) William, J.; Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033. (b) Grasa, G. A.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 119. (c) Littke, A. F.; Schwarz, L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 6343.

(16) For selected reviews on Ni-catalyzed coupling reactions, see: (a) Tasker, S. Z.; Standley, E. A.; Jamison, T. F. *Nature* **2014**, *509*, 299. (b) Moragas, T.; Correa, A.; Martin, R. *Chem. Eur. J.* **2014**, *20*, 8242. (c) Cornella, J.; Zarate, C.; Martin, R. *Chem. Soc. Rev.* **2014**, *43*, 8081. (d) Su, B.; Cao, Z. C.; Shi, Z.-J. *Acc. Chem. Res.* **2015**, *48*, 886. (e) Tobisu, M.; Chatani, N. *Acc. Chem. Res.* **2015**, *48*, 1717. (f) Weix, D. J. *Acc. Chem. Res.* **2015**, *48*, 1767. (g) Gu, J.; Wang, X.; Xue, W.; Gong, H. *Org. Chem. Front.* **2015**, *2*, 1411. (h) Henrion, M.; Ritleng, V.; Chetcuti, M. J. *ACS Catal.* **2015**, *5*, 1283. (i) Choi, J.; Fu, G. C. *Science* **2017**, *356*, eaaf7230. (j) *Modern Organonickel Chemistry*; Tamaru, Y., Ed.; Wiley-VCH: Weinheim, **2006**.

(17) Kiso, Y.; Yamamoto, K.; Tamao, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374.

(18) Yamamoto, T.; Yamakawa, T. *J. Org. Chem.* **2009**, *74*, 3603.

(19) Liu, J.; Ren, Q.; Zhang, X.; Gong, H. *Angew. Chem. Int. Ed.* **2016**, *55*, 15544.

(20) For reviews, see: (a) Monfared, A.; Mohammadi, B.; Ahmadi, S.; Nikpassan, M.; Hosseinian, A. *RSC Adv.* **2019**, *9*, 3185. (b) *Organosilicon Chemistry*; Hiyama, T.; Oestreich, M., Ed.; Wiley-VCH: Weinheim, **2019**. (c) Komiyama, T.; Minami, Y.; Hiyama, T. *ACS Catal.* **2017**, *7*, 631.

(21) For selected examples on coupling reaction of aryl silicon compounds and alkyl halides, see: (a) Lee, J.-Y.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 5616. (b) Powell, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 7788. (c) Lee, J.-Y.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 5616. (d) Dai, X.; Strotman, N. A.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 3302.

(22) For selected examples on coupling reaction of aryl silicon compounds and aryl halides, see: (a) Tang, S.; Takeda, M.; Nakao, Y.; Hiyamaz, T. *Chem. Commun.* **2011**, *47*, 307. (b) Tang, S.; Li, S. H.; Nakao, Y.; Hiyamaz, T. *Asian J. Org. Chem.* **2013**, *2*, 416.

(23) (a) Zhang, W.-B.; Yang, X.-T.; Ma, J.-B.; Su, Z.-M.; Shi, S.-L. *J. Am. Chem. Soc.* **2019**, *141*, 5628. (b) Cai, Y.; Zhang, J.-W.; Li, F.; Liu, J.-M.; Shi, S.-L. *ACS Catal.* **2019**, *9*, 1. (c) Cai, Y.; Ye, X.; Liu, S.; Shi, S.-L. *Angew. Chem. Int. Ed.* **2019**, *58*, 13433. (d) Shen, D.; Zhang, W.-B.; Li, Z.; Shi, S.-L.; Xu, Y. *Adv. Synth. Catal.* **2020**, *362*, 1125. (e) Li, Y.-Q.; Li, F.; Shi, S.-L. *Chin. J. Chem.* **2020**, *38*, 1035. (f) Cai, Y.; Ruan, L.-X.; Rahman, A.; Shi, S.-L. *Angew. Chem. Int. Ed.* **2021**, *60*, in press DOI: 10.1002/anie.202015021. (g) Li, Y.-Q.; Shi, S.-L. *Chin. J. Org. Chem.* **2021**, *41*, in press, DOI: 10.6023/cjoc202101019.

(24) For a similar Pd-catalyzed C–O bond-forming reaction using vinyltrimethoxysilane and electron-deficient aryl halides, see: Milton, E. J.; Fuentes, J. A.; Clarke, M. L. *Org. Biomol. Chem.* **2009**, *7*, 2645.

(25) (a) Pilcher, A. S.; Ammon, H. L.; DeShong, P. *J. Am. Chem. Soc.* **1995**, *117*, 5166. (b) Pilcher, A. S.; DeShong, P. *J. Org. Chem.* **1996**, *61*, 6901.

(26) (a) Brescia, M.-R.; DeShong, P. *J. Org. Chem.* **1998**, *63*, 3156. (b) Mowery, M. E.; DeShong, P. *J. Org. Chem.* **1999**, *64*, 3266.

(27) **General Procedure 1**

In a nitrogen-filled glove box, aromatic halide (0.2 mmol, 1.0 equiv), 18-crown-6 (121.0 mg, 0.46 mmol, 2.3 equiv), KOMe (32.2 mg, 0.46 mmol, 2.3 equiv), $NiCl_2$(glyme) (4.4 mg, 0.02 mmol, 10 mol%), and DMF (1.0 mL) were charged to an 8 mL vial equipped with a magnetic stirrer bar. The vinyltrimethoxysilane (68.0 mg, 0.46 mmol, 2.3 equiv) was added. The vial was removed from the glove box, and the reaction mixture was stirred at rt (35 °C) for 12 h. The reaction mixture was then diluted with EtOAc and washed with water. The organic phase was dried over Na_2SO_4, filtered, and concentrated, and the residue was purified by column chromatography on silica gel to give the product.

2-Methoxy-6-vinylnaphthalene (3a)

Using general procedure 1: white solid, 31.0 mg, yield: 84%. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.66 (m, 3 H), 7.62 (dd, *J* = 8.7, 1.7 Hz, 1 H), 7.19–7.10 (m, 2 H), 6.87 (dd, *J* = 17.6, 10.9 Hz, 1 H), 5.84 (dd, *J* = 17.6, 0.9 Hz, 1 H), 5.30 (dd, *J* = 10.9, 0.9 Hz, 1 H), 3.93 (s, 3 H).

General Procedure 2

In a nitrogen-filled glove box, aromatic halide (0.2 mmol, 1.0 equiv), TBAT (270 mg, 0.5 mmol, 2.5 equiv), $NiCl_2$(glyme) (4.4 mg, 0.02 mmol, 10 mol%), and DMA (1.0 mL) were charged to an 8 mL vial equipped with a magnetic stirrer bar. The vinyltrimethoxysilane (59.1 mg, 0.4 mmol, 2.0 equiv) was added. The vial was removed from the glove box, and the reaction mixture was stirred at rt (35 °C) for 12 h. The reaction mixture was then diluted with EtOAc and washed with water. The organic phase was dried over Na_2SO_4, filtered, and concentrated, and the residue was purified by column chromatography on silica gel to give the product.

2-Vinylnaphthalene (3b)

Using general procedure 2: white solid, 25.5 mg, yield: 83%. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.79 (m, 3 H), 7.76 (s, 1 H), 7.65 (dd, *J* = 8.6, 1.7 Hz, 1 H), 7.50–7.42 (m, 2 H), 6.90 (dd, *J* = 17.6, 10.9 Hz, 1 H), 5.89 (dd, *J* = 17.6, 0.8 Hz, 1 H), 5.35 (dd, *J* = 10.9, 0.8 Hz, 1 H).