Rhodium(III)-Catalyzed C–H Vinylation of Arenes: Access to Functionalized Styrenes

Jun Zhou,[a,b] Xin Li,[a] Gang Liao,[a] and Bing-Feng Shi*,[a]

ABSTRACT An effective method has been developed for the Rh(III)-catalyzed direct vinylation of arenes to give functionalized styrenes, using vinyltriethoxysilane as a convenient and inexpensive vinyl source. A wide variety of substrates, including 1-aryl-2-pyrrolidinones, anilines, benzamides and ketones, were compatible with this reaction. Moreover, this method can be applied to the two-step synthesis of functionalized indoles. Mechanistic investigation reveals that the reaction probably proceeds through an oxidative Heck/desilylation pathway.

KEYWORDS C-H Activation, Vinylation, Rhodium, Styrenes, Vinyltriethoxysilane

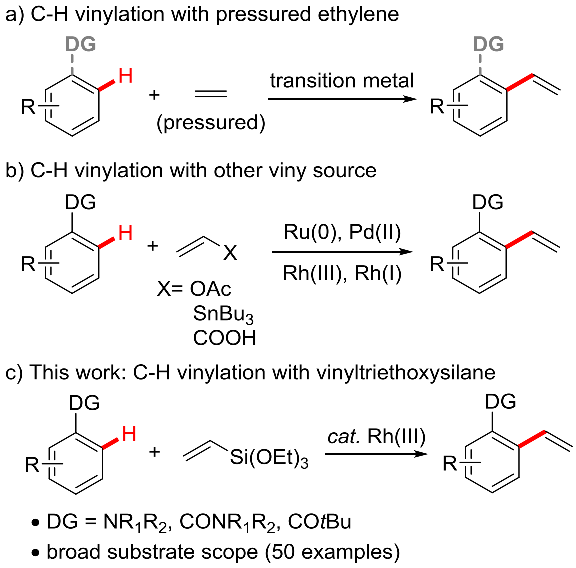
Introduction

Functionalized styrenes are important building blocks for organic synthesis and the polymer industry.[1] Classically, they are prepared by elimination reactions (mainly via dehydration of alcohols or dehydrohalogenation of halides),[2] carbonyl alkenylation (by using P, Si, or Ti-based reagents),[3] or the semihydrogenation of terminal alkynes.[4] One of the most useful methods is the transition metal-catalyzed cross-coupling of aryl and vinyl units (eg. aryl electrophiles with vinylmetallic reagents, vinyl electrophiles with arylmetallic reagents, or aryl electrophiles with ethylene or its synthons).[5] However, extra steps are needed to prepare the prefunctionliazed coupling partners and undesired waste salts are generated. Therefore, the direct oxidative coupling of arenes with ethylene or its synthons is a more attractive strategy.

Recently, significant efforts have been devoted to the synthesis of vinylarenes through oxidative coupling of arenes with alkenes.[6] Since the pioneering work by Fujiwara and coworkers on the Pd-catalyzed oxidative arylation of ethylene for the production of styrenes,[7] styrene synthesis via direct coupling with ethylene has been extensively investigated (Scheme 1a).[8] Although ethylene is the most atom efficient vinylation reagent, the use of pressured and flammable ethylene gas is still relatively inconvenient on laboratory-scale.[7,8] More recently, elegant studies by the groups of Kakiuchi,[9] Kuang,[10] Ellman,[11] Wei,[12] and Dong[13] have successfully demonstrated that vinyl acetate could be used as vinyl source in the directed C-H vinylation of arenes. Cheng and coworkers reported the Rh(III)-catalyzed vinylation of benzamides using tributyl(vinyl)sannane as vinylation reagent.[14] Xu and Fan reported a Rh(I)-catalyzed decarbonylative C-H vinylation of arenes with acrylic acid as an efficient ethylene surrogate (Scheme 1b).[15] Although these elegant examples have significantly broadened the scope of the vinylation reactions, the survey of more easy to handle and readily available ethylene surrogates with broad substrate scope for oxidative vinylation of arenes is still in high demand.

Herein, we describe a Rh(III)-catalyzed vinylation of aromatic C-H bonds with vinyltriethoxysilane, which is nontoxic, commercially available and ease of operation.[16] A wide variety of substrates, including 1-aryl-2-pyrrolidinones, anilines, benzamides and ketones, were compatible with this reaction, providing a general and efficient strategy to access functionalized styrenes (Scheme 1c).

Scheme 1 Synthesis of styrenes via transition-metal-catalyzed C-H vinylation



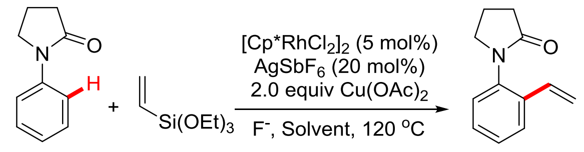
Results and Discussion

We initially applied our previously reported conditions[17] for the oxidative coupling 1-Phenyl-2-pyrrolidinone (**1**) with vinyltriethoxysilane. To our delight, the vinylation product **2** was obtained in 40% yield (Table 1, entry 1). Considering the important role of the fluoride source in the activation of organosilicon reagents, we then investigated various fluoride reagents (entries 2-6). The yield increases to 63% when NaF was used instead (entry 6). Solvent effects played a significant role in the reaction and DCE was found to be the most suitable solvent (entries 6-11). Further optimization revealed that LiF was the optimal (entry 12). The yield dramatically increases to 90% when prolonging the reaction time to 36 h (entry 13). Other commercially available vinylsilanes, such as DVDS (divinyl-tetramethyldisiloxane, entry 14, 35%) and D_4^v (1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane, entry 15, 23%), were ineffective.

---

[a] Department of Chemistry, Zhejiang University, Hangzhou 310027,China.
[b] School of Chemistry and Biological Engineering, Changsha University of Science & Technology, Changsha 410114, China.
E-mail: bfshi@zju.edu.cn

Table 1 Optimization of reaction conditions [a, b]



1 2

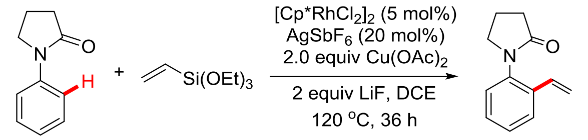
Entry	F^-	t (h)	Solvent	Yield(%)[b]
1	-	24	DCE	40[c]
2	TBAF•3H_2O	24	DCE	trace
3	CsF	24	DCE	trace
4	AgF	24	DCE	32
5	KF	24	DCE	45
6	NaF	24	DCE	63
7	NaF	24	DME	5
8	NaF	24	THF	trace
9	NaF	24	*t*-AmylOH	trace
10	NaF	24	MeOH	trace
11	NaF	24	Dioxane	trace
12	LiF	24	DCE	78
13	LiF	36	DCE	90
14[d]	LiF	36	DCE	35
15[e]	LiF	36	DCE	23

[a] Reactions were carried out with **1** (0.2 mmol), vinyltriethoxysilane (0.6 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2$ (0.4 mmol) and fluoride reagent (0.4 mmol) in 2 mL solvent for 24 h. [b] Isolated Yield. [c] Starting material **1** was recovered in 50% yield. [d] Using DVDS instead, DVDS = divinyl-tetramethyldisiloxane. [e] Using D_4^v instead, D_4^v = 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane.

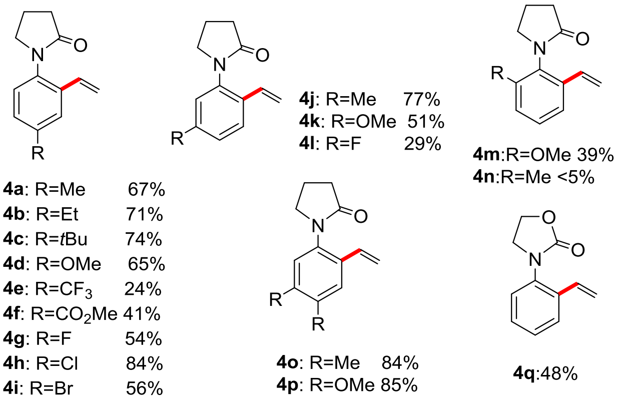
With the optimized conditions in hand, we further investigated the compatibility of various 1-aryl-2-pyrrolidinones (Table 2). A variety of functional groups, including methoxy (**4d**, **4k**, **4p** and **4m**), trifluoromethyl (**4e**), ester (**4f**), fluoro (**4g** and **4l**), chloro (**4h**), and bromo (**4i**), were well tolerated, providing great opportunities for further elaborations. Electronic effect can greatly affect the reactivity. In general, substrates bearing electron-donating groups (**4a**-**d**, **4j**-**k**) gave higher yields than those bearing electron-withdrawing groups (**4e**-**g**, **4i** and **4l**). The reaction is also very sensitive to steric effect, as substitutes in the *ortho*-position of the directing group significantly inhibit the reactivity (**4m**, 39%; **4n**, <5%). Moreover, 4,5-disubstituted substrates were olefinated effectively to give even higher yields (**4o**-**p**). In addition, 3-phenyl-2-oxazolidinone is also an effective substrate, affording the desired vinylation product in moderate yield (**4q**, 48%).

Arenes and heteroarenes with other kinds of directing groups (DGs) were tested. Pivalamides were also compatible with this vinylation protocol (Table 3). Pivalamides bearing both electron-donating and electron-withdrawing groups on the aromatic rings reacted smoothly to give the desired vinylation products in moderate yields (**6b**-**6l**). Moreover, disubstituted substrates were also vinylated effectively to give the corresponding products (**6j**-**6l**). To our delight, the vinylation happened not only on simply arenes but also on heteroarenes, including quinolines (**6m**) and pyridines (**6n**-**o**), albeit in relatively low yields (20%-32%). In addition, 1,2,3,4-tetrahydroquinoline **5p** could also be vinylated using acetamide as DG. It is worth mentioning that the low yields was largely due to the decomposition. We have hypothesized that the possible dimerization and/or polymerization of the vinylation products might be the problem. However, the addition of various commonly used radical inhibitors, such as PTZ (phenothiazine), BHT (2,6-di-*tert*-butyl-4-methylphenol), TBC (4-*tert*-butylcatechol), and hydroquinone, didn't give any improvement.[18]

Table 2 Substrates Scope: 1-Phenyl-2-pyrrolidinones [a, b]



3 4



4a: R=Me 67%
4b: R=Et 71%
4c: R=*t*Bu 74%
4d: R=OMe 65%
4e: R=CF_3 24%
4f: R=CO_2Me 41%
4g: R=F 54%
4h: R=Cl 84%
4i: R=Br 56%

4j: R=Me 77%
4k: R=OMe 51%
4l: R=F 29%

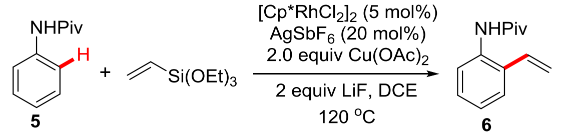
4m:R=OMe 39%
4n:R=Me <5%

4o: R=Me 84%
4p: R=OMe 85%

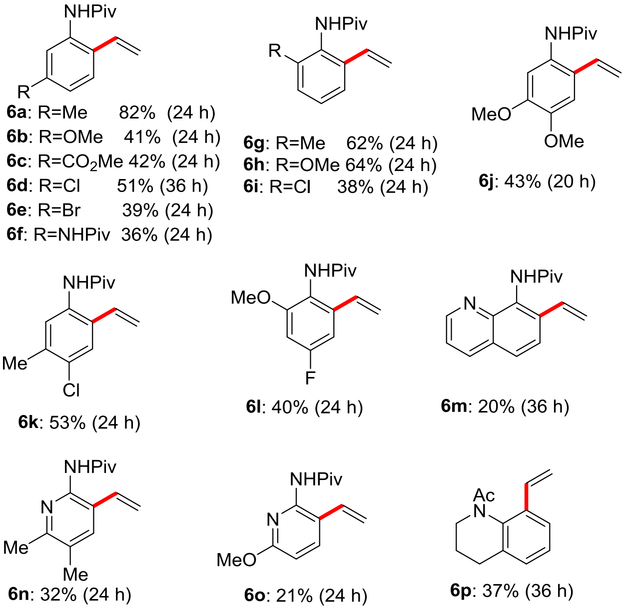
4q:48%

[a] Reactions were carried out with **3** (0.2 mmol), vinyltriethoxysilane (0.6 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mo l%), $Cu(OAc)_2$ (0.4 mmol) and LiF (0.4 mmol) in 2 mL DCE for 36 h. [b] Isolated Yield.

Table 3 Substrates Scope: Pivalamides [a, b]



5 6



6a: R=Me 82% (24 h)
6b: R=OMe 41% (24 h)
6c: R=CO_2Me 42% (24 h)
6d: R=Cl 51% (36 h)
6e: R=Br 39% (24 h)
6f: R=NHPiv 36% (24 h)

6g: R=Me 62% (24 h)
6h: R=OMe 64% (24 h)
6i: R=Cl 38% (24 h)

6j: 43% (20 h)

6k: 53% (24 h)

6l: 40% (24 h)

6m: 20% (36 h)

6n: 32% (24 h)

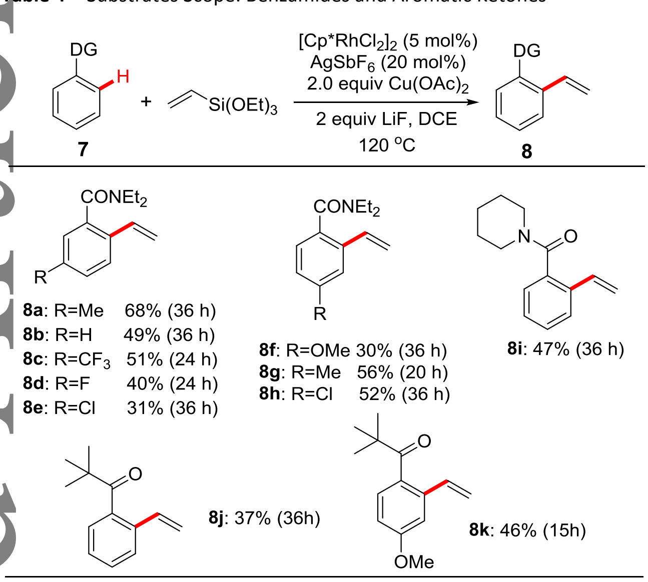
6o: 21% (24 h)

6p: 37% (36 h)

[a] Reactions were carried out with **5** (0.4 mmol), vinyltriethoxysilane (1.2 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), $Cu(OAc)_2$ (0.8 mmol) and LiF (0.8 mmol) in 2 mL DCE. [b] Isolated Yield.

The success of the vinylation reaction of anilines led us to extend the method developed to substrates bearing other DGs. Benzamides were found to be compatible with this reaction, affording the vinylation products in moderate yields (Table 4). A broad range of important functional groups, such as trifluoromethyl, halogens (F and Cl), and methoxy, were well tolerated. The yield remains to be moderate regardless of whether the benzamides bearing electron-withdrawing or electron-donating groups. To our delight, ketones, generally considered as weakly coordinating substrates, were also viable (**8j**-**8k**).

Table 4 Substrates Scope: Benzamides and Aromatic Ketones [a, b]



8a: R=Me 68% (36 h)
8b: R=H 49% (36 h)
8c: R=CF_3 51% (24 h)
8d: R=F 40% (24 h)
8e: R=Cl 31% (36 h)

8f: R=OMe 30% (36 h)
8g: R=Me 56% (20 h)
8h: R=Cl 52% (36 h)

8i: 47% (36 h)

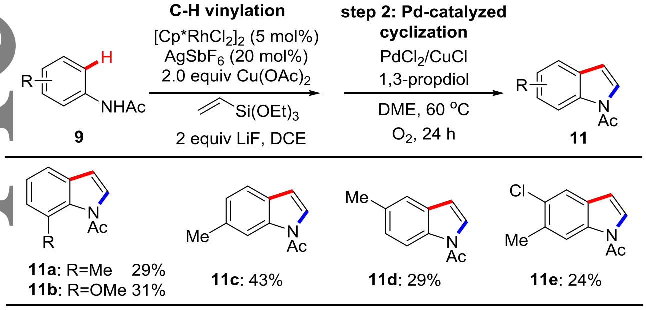
8j: 37% (36h)

8k: 46% (15h)

[a] Reactions were carried out with **7** (0.4 mmol), vinyltriethoxysilane (1.2 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), $Cu(OAc)_2$ (0.8 mmol) and LiF (0.8 mmol) in 2 mL DCE. [b] Isolated Yield.

Furthermore, we found that *N*-acylindoles could be synthesized through a two-step sequence involving the Rh-catalyzed C-H vinylation of acetanilides **9** with vinyltriethoxysilane followed by Pd-catalyzed cyclization (Table 5).[19]

Table 5 Synthesis of Indoles [a, b]



11a: R=Me 29%
11b: R=OMe 31%

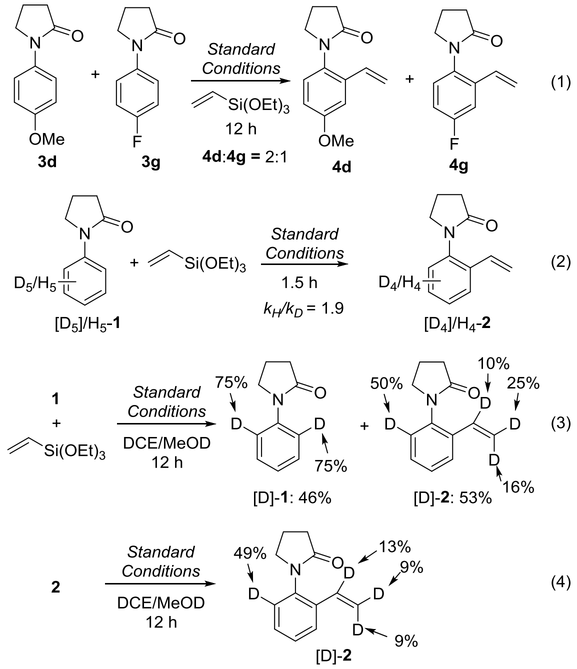
11c: 43%

11d: 29%

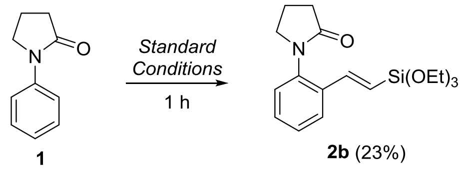
11e: 24%

[a] Reaction Conditions. Step 1: **9** (0.4 mmol), vinyltriethoxysilane (1.2 mmol), $[Cp^*RhCl_2]_2$ (5 mmol %), $AgSbF_6$ (20 mmol %), $Cu(OAc)_2$ (0.8 mmol) and LiF (0.8 mmol) in 2 mL DCE. Step 2: $PdCl_2$ (0.04 mmol), CuCl (0.4 mmol) and 1,3-propdiol (0.4 mmol) in 2 mL of DME. [b] Isolated Yield in two steps.

To investigate mechanism of the rhodium(III)-catalyzed C-H vinylation reaction, a series of experiments were conducted. Intermolecular competition experiments between **3d** and **3g** showed that electron-rich *N*-aryl-pyrrolidinone **3d** was transformed preferentially (Eq 1). To determine the rate-determining step of the catalytic cycle, the deuterium kinetic isotope effect was measured (eq 2). Therefore, $[d_5]$-**1** was prepared and submitted to the standard conditions together with **1**. A k_H/k_D value of 1.9 was observed, indicating that the cleavage of the C-H bond might be involved as the rate-determining step. Subsequently, to check the reversibility of the C-H activation step, reactions of **1** with vinyltriethoxysilane were carried out in the presence of MeOD as co-solvent, 75% deuterium incorporation in [D]-**1** and 50% deuterium incorporation in [D]-**2a** was observed, suggesting that the C-H bond activation step is reversible (eq 3). We also observed that partial deuterium incorporation was detected on ethylene moiety of product [D]-**2**. The vinylation product **2** was then subjected to the standard conditions with MeOD as co-solvent, deuterium incorporation into the ethylene moiety was also detected (eq 4).



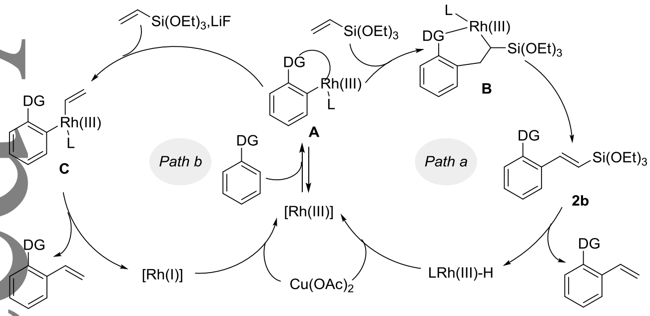
We further tried to monitor the reaction by GC-MS to identify possible intermediates. A peak with mass value of 349 was detected when the reaction proceeded for 1 hour, which was identical to the Heck-type product **2b** and further confirmed by ^1H and ^{13}C NMR analysis (eq 5). The Heck-type product **2b** could be readily transferred to the vinylation product **2** under the standard reaction conditions. These results indicated that **2b** might be a possible intermediate and an oxidative Heck coupling/desilylation sequence might be involved.



(5)

From these results and precedents,[6f-g, 11,22], we depict a plausible mechanistic pathway for this rhodium(III)-catalyzed C-H vinylation (Path a, scheme 2). Arene undergoes a reversible C-H activation to form rhodacycle **A**, followed by migratory insertion of the C-Rh bond into the double bond of vinyltriethoxysilane to generate a seven-membered metallacycle **B**. Subsequent β-hydride elimination gives Heck-type product **2b**, which undergoes desilylation[23] to afford the desired vinylation product. Oxidation of rhodium-hydride with copper acetate closes the catalytic cycle. While we believe the above mentioned Heck-type mechanistic pathways are most likely to be involved, a Rh(III)-catalyzed C-H activation/Hiyama coupling pathway cannot be completely ruled out (Path b).[20,21]

Scheme 2 Plausible mechanism.



Conclusions

In summary, we have developed an expeditious method to access functionalized styrenes through direct Rh(III)-catalyzed C–H vinylation. Vinyltriethoxysilane serves as an inexpensive and convenient vinyl source for a range of substrates. Moreover, this method can be applied to the two-step synthesis of functionalized indoles. Mechanistic investigation reveals that the reaction probably proceeds through an oxidative Heck/desilylation pathway.

Experimental

To 20 mL Schlenck tube was added 1-phenyl-2-pyrrolidinone **1** (0.2 mmol, 1.0 equive), vinyltriethoxysilane (0.6 mmol, 3.0 equive), $[Cp^*RhCl_2]_2$ (5 mmol %), $AgSbF_6$ (20 mmol %), $Cu(OAc)_2$ (0.4 mmol), LiF (0.4 mmol) and DCE (2 mL), the solution was stirred at 120 °C for 36 h. After cooling to room temperature, H_2O (2 mL) was added and stirred for 5 min. The resulting mixture was extracted with DCM. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography to give the vinylation product **2**.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

Acknowledgement

Financial support from the NSFC (21572201, 21772170), the National Basic Research Program of China (2015CB856600), and the Fundamental Research Funds for the Central Universities (2018XZZX001-02) is gratefully acknowledged.

References

[1] (a) Agbossou, F.; Carpentier, J.-F.; Mortreaux, A. *Chem. Rev.*, **1995**, *95*, 2485; (b) *The Chemistry of Double-Bonded Functional Groups*, Ed.: Patai, S., Wiley, New York, **1997**; (c) Grubbs, R. H. In *Handbook of Metathesis*, Ed.: Grubbs, R. H., Wiley-VCH, Weinheim, **2003**; (d) *Modern Styrenic Polymers: Polystyrenes and Styrenic Copolymers*, Eds.: Scheirs, J.; Priddy, D. B., John Wiley & Sons, Chichester, UK, **2003**; (e) *Comprehensive Asymmetric Catalysis*, Eds.: Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H. Springer-Verlag, Heidelberg, **1999**, vol. I–III. For recent examples on the application of styrene in alkene difunctionalization, see: f) Liu, Y.; Hu, B.; Zhang, X. *Chin. J. Chem*. **2017**, *35*, 307; g) Cui, T.-L.; Li, X.-H.; Chen, J.-S. *Chin. J. Chem*. **2017**, *35*, 577; h) Zhang, Y.; Wang, M.; Cao, P.; Liao, J. *Acta Chim. Sinica* **2017**, *75*, 794; i) Han, E.; Guo, Y.; Chen, Q. *Chin. J. Org. Chem.* **2017**, *37*, 1714; j) Babu, K.R.; Chen, S.; Li, Y.; Bao, H. *Chin. J. Org. Chem*. **2017**, *37*, 1160.

[2] (a) Wu, J.-C.; Gong, L.-B.; Xia, Y.; Song, R.-J.; Xie, Y.-X.; Li, J.-H. *Angew. Chem. Int. Ed.* **2012**, *51*, 9909; (b) Murphy, S. K.; Park, J.-W.; Cruz, F. A.; Dong, V. M. *Science* **2015**, *347*, 56.

[3] (a) Larock, R. C.; In *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*, VCH, Weinheim, **1989**, pp. 17,132, and 173; (b) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863.

[4] (a) Wienhöfer, G.; Westerhaus, F. A.; Jagadeesh, R. V.; Junge, K.; Junge, H.; Beller, M. *Chem. Commun.*, **2012**, *48*, 4827; (b) Cao, H.; Chen, T.; Zhou, Y.; Han, D.; Yin, S.-F.; Han, L.-B. *Adv. Synth. Catal.* **2014**, *356*, 765.

[5] For a review, see: Denmark, S. E.; Butler, C. R. *Chem. Commun*. **2009**, 20.

[6] For reviews on the oxidative C-H alkenylation, see: (a) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633; (b) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem. Int. Ed.* **2009**, *48*, 5094; (c) Satoh, T.; Miura, M. *Chem. Eur. J.* **2010**, *16*, 11212; (d) Le Bras, J.; Muzart, J. *Chem. Rev.* **2011**, *111*, 1170; (e) Yu, D.-G.; Li, B.-J.; Shi, Z.-J. *Tetrahedron* **2012**, *68*, 5130; (f) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. *Chem. Rev.* **2012**, *112*, 5879; (g) Patureau, F. W.; Wencel-Delord, J.; Glorius, F. *Aldrichimic Acta* **2012**, *45*, 31; (h) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651; (i) Zhou, L.; Lu, W.; *Chem. Eur. J.* **2014**, *20*, 634; (j) Ma, W.; Gandeepan, P.; Li, J.; Ackermann, L. *Org. Chem. Front.* **2017**, *4*, 1435; (k) Manikandan, R.; Jeganmohan, M. *Chem. Commun.* **2017**, *53*, 8931.

[7] (a) Fujiwara, Y.; Noritani, I.; Danno, S.; Asano, R.; Teranishi, S. *J. Am. Chem. Soc.* **1969**, *91*, 7166; (b) Moritani, I.; Fujiwara, Y. *Synthesis*, **1973**, 524.

[8] (a) McKeown, B. A.; Gonzalez, H. E.; Friedfeld, M. R.; Brosnahan, A. M.; Gunnoe, T. B.; Cundari, T. R.; Sabat, M. *Organometallics* **2013**, *32*, 2857; (b) Yamada, T.; Sakakura, A.; Sakaguchi, S.; Obora, Y.; Ishii, Y. *New J. Chem.* **2008**, *32*, 738; (c) Hong, P.; Yamazaki, H. *J. Mol. Catal.* **1984**, *26*, 297; (d) Weissman, H.; Song, X.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 337; (e) Vaughan, B. A.; Webster-Gardiner, M. S.; Cundari, T. R.; Gunnoe, T. B. *Science* **2015**, *348*, 421; (f) Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 9982; (g) Rakshit, S.; Grohmann, C.; Besset, T.; Glorius, F. *J. Am. Chem. Soc.*

2011, *133*, 2350; For vinylation of preformed palladacycles, see: (h) Horino, H.; Inoue, N. *J. Org. Chem.* **1981**, *46*, 4416.

[9] (a) Matsuura, Y.; Tamura, M.; Kochi, T.; Sato, M.; Chatani, N.; Kakiuchi, F. *J. Am. Chem. Soc.* **2007**, *129*, 9858; (b) Ogiwara, Y.; Tamura, M.; Kochi, T.; Matsuura, Y.; Chatani, N.; Kakiuchi, F. *Organometallics* **2014**, *33*, 402.

[10] Liu, W.; Li, Y.; Xu, B.; Kuang, C. *Org. Lett.* **2013**, *15*, 2342.

[11] Otley, K. D.; Ellman, J. A. *Org. Lett.* **2015**, *17*, 1332.

[12] Mei, S.-T.; Jiang, K.; Wang, N.-J.; Shuai, L.; Yuan, Y.; Wei, Y. *Eur. J. Org. Chem.* **2015**, 6135.

[13] Li, S.-S.; Wang, C.-Q.; Lin, H.; Zhang, X.-M.; Dong, L. *Org. Biomol. Chem.* **2016**, *14*, 229.

[14] Prakash, S.; Muralirajan, K.; Cheng, C.-H. *Chem. Commun.* **2015**, *51*, 13362.

[15] Xu, J.; Chen, C.; Zhao, H.; Xu, C.; Pan, Y.; Xu, X.; Li, H.; Xu, L.; Fan, B. *Org. Chem. Front.* **2018**, *5*, 734.

[16] For selected reviews on Rh-catalyzed C-H functionalization, see: (a) Yang, Y.; Li, K.; Cheng, Y.; Wan, D.; Li, M.; You, J. *Chem. Commun.* **2016**, *52*, 2872; (b) Li, S.-S.; Qin, L.; Dong, L. *Org. Biomol. Chem.* **2016**, *14*, 4554; (c) Ye, B.; Cramer, N. *Acc. Chem. Res.* **2015**, *48*, 1308; (d) Wencel-Delord, J.; Patureau, F. W.; Glorius, F. *Top. Organomet. Chem.* **2015**, *55*, 1; (e) Song, G.; Li, X. *Acc. Chem. Res.* **2015**, *48*, 1007; (f) Kuhl, N.; Schröder, N.; Glorius, F. *Adv. Synth. Catal.* **2014**, *356*, 1443; (g) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624.

[17] Zhou, J.; Li, B.; Hu, F.; Shi, B.-F. *Org. Lett.* **2013**, *15*, 3460.

[18] Smith, C. R.; RajanBabu, T. V. *Tetrahedron* **2010**, *66*, 1102

[19] (a) Kasahara, A.; Izumi, T.; Murakami, S.; Miyamoto, K.; Hino, T. *J. Heterocyclic. Chem.* **1989**, *26*, 1405; (b) Zhang, H.-J.; Lin, W.; Su, F.; Wen, T.-B. *Org. Lett.* **2016**, *18*, 6356.

[20] For early examples on C-H activation/Hiyama coupling, see: (a) Yang, S.; Li, B.; Wan, X.; Shi, Z. *J. Am. Chem. Soc.* **2007**, *129*, 6066; (b) Zhou, H.; Xu, Y.-H.; Chung, W.-J.; Loh, T.-P. *Angew. Chem. Int. Ed.* **2009**, *48*, 5355; (c) Liang, Z.; Yao, B.; Zhang, Y. *Org. Lett.* **2010**, *12*, 3185; (d) Chen, K.; Li, H.; Li, Y.; Zhang, X.-S.; Lei, Z.-Q.; Shi, Z.-J. *Chem. Sci.* **2012**, *3*, 1645; e) Hachiya, H.; Hirano, K.; Satoh, T.; Miura, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 2202; f) Senthilkumar, N.; Parthasarathy, K.; Gandeepan, P.; Cheng, C.-H. *Chem. Asian J.* **2013**, *8*, 2175.

[21] Other organosilanes, including arylsiloxanes and allylsiloxanes, were unreactive under the standard reaction conditions.

[22] (a) Qi, X.; Li, Y.; Bai, R.; Lan, Y. *Acc. Chem. Res*. **2017**, *50*, 2799; (b) Liu, S.; Qi, X.; Bai, R.; Lan, Y. *Catal. Sci. Technol*., **2018**, *8*, 1645; (c) Yu, S.; Liu, S.; Lan, Y.; Wan, B.; Li, X. *J. Am. Chem. Soc.* 2015, *137,* 1623; (d) Luo, Y.; Liu, S.; Xu, D.; Qu, L.-B.; Luo, X.; Bai, R.; Lan,Y. *J. Organomet. Chem.* 2018, *864,* 148.

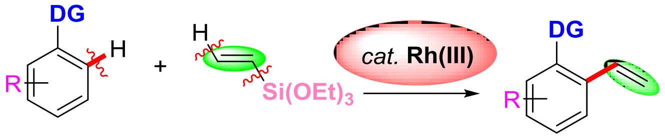
[23] Sumida, Y.; Kato, T.; Yoshida, S.; Hosoya, T. *Org. Lett.* 2012, *14*, 1552.

(The following will be filled in by the editorial staff)
Manuscript received: XXXX, 2018
Revised manuscript received: XXXX, 2018
Accepted manuscript online: XXXX, 2018
Version of record online: XXXX, 2018

Entry for the Table of Contents

Page No.

Rhodium(III)-Catalyzed C–H Vinylation of Arenes: Access to Functionalized Styrenes



- DG = NR_1R_2, $CONR_1R_2$, CO^tBu
- broad substrate scope (**50** examples)

J. Zhou, X. Li, G. Liao, B.-F. Shi*

An effective Rh(III)-catalyzed direct vinylation of arenes has been developed for the synthesinons of functionalized styrenes, using vinyltriethoxysilane as a convenient and inexpensive vinyl source. The reaction is compatible with a wide range of directing groups and various functional groups.