Organic LETTERS

Letter

pubs.acs.org/OrgLett

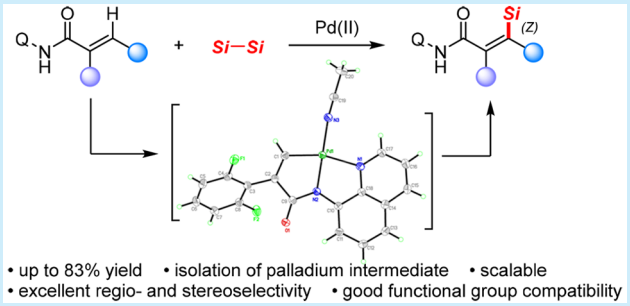
Stereoselective Synthesis of *Z*-Vinylsilanes via Palladium-Catalyzed Direct Intermolecular Silylation of C(sp^2)−H Bonds

Jin-Long Pan,[†] Chao Chen,[†] Zhi-Gang Ma,[†] Jia Zhou,[†] Li-Ren Wang,[§] and Shu-Yu Zhang*[,†,‡]

[†]School of Chemistry and Chemical Engineering, [‡]Key Laboratory for Thin Film and Microfabrication of Ministry of Education, and [§]Zhiyuan College, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

Supporting Information

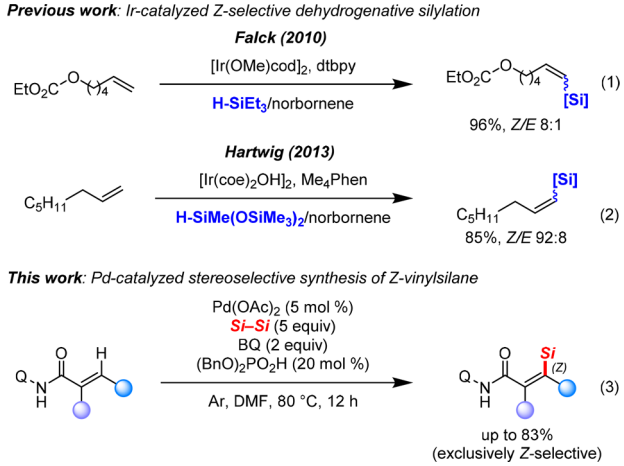
ABSTRACT: An efficient and convenient palladium-catalyzed direct intermolecular silylation of C(sp^2)−H bonds by using disilanes as the silicon source with the assistance of a readily removable bidentate directing group is reported. This strategy provided a regio- and stereoselective protocol for exclusive synthesis of *Z*-vinylsilanes with reasonable to excellent yields and good functional group compatibility. Silylation of the isolated palladacycle intermediate revealed the *Z*-stereoselective pathway. Moreover, the practicality and effectiveness of this method were illustrated by a gram-scale experiment and further functionalization of the silylation product.



Vinylsilanes,[1] an important class of valuable building blocks in organic chemistry, are widely applied in organic synthesis (Hiyama−Denmark coupling, Tamao−Fleming oxidation, etc.), polymer chemistry, and medicines.[2,3] Numerous classical transformations have been developed for the formation of the vinylsilane compounds, such as hydrosilylation,[4a−d] silylmetalation,[4e,f] metathesis,[4g,h] silyl-Heck coupling,[4i,j] silylative coupling,[4k,l] dehydrogenative silylation,[4m,n] etc.[4o−r] Among these, the transition-metal-catalyzed direct selective conversion of the C(sp^2)−H bond of alkenes to the corresponding vinylsilanes is one of the most attractive synthetic approaches due to its high efficiency and directness.[5−7] However, one of the main drawbacks of the C−H silylation reaction for the formation of vinylsilanes is that stereoselectivity-related issues must always be addressed (*Z*/*E* mixture) in this reaction.[8]

In past decades, significant advances have been made in the direct silylation or hydrosilylation of C(sp^2)−H bonds to *E*-selective vinylsilanes.[9] Nonetheless, direct regio- and stereoselective silylation of terminal alkene C(sp^2)−H bonds to prepare the *Z*-vinylsilanes remains a great challenge in synthetic chemistry.[10] In 2010, Falck reported that $[Ir(OMe)(cod)]_2$/dtbpy catalyzed the *Z*-selective, dehydrative silylation of terminal alkenes to give 7:1−10:1 *Z*/*E* vinylsilanes (Scheme 1, eq 1).[11a] In 2013, Hartwig reported that the use of Ir-catalyzed, 3,4,7,8-tetramethyl-1,10-phenathroline (Me_4phen) as ligand is better for the highly *Z*-selective (*Z*/*E* up to 92:8) dehydrogenative silylation of terminal alkenes (Scheme 1, eq 2).[11b,c] Obviously, the development of more efficient and novel *Z*-vinylsilane formation methods is an intensively investigated field that is still a focus of synthetic chemistry research. Our continuous interest and effort has been directed toward the development of efficient and selective unactivated C−H functionalizations and their applications in the synthesis of natural biological products.[12] We describe herein an efficient palladium-catalyzed C(sp^2)−H silylation for a stereoselective synthesis of *Z*-vinylsilanes under mild conditions (Scheme 1, eq 3). This method offers a practical and environmentally friendly strategy for the rapid synthesis of *Z*-stereoselective vinylsilanes from simple starting materials.

Scheme 1. Synthetic Approaches to *Z*-Vinylsilanes via Direct C(sp^2)−H Silylation of Alkenes



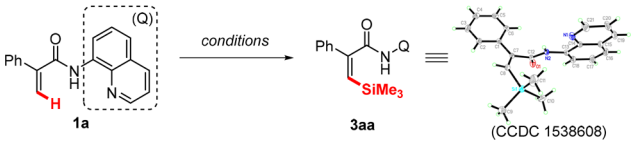
In our previous study,[12d] we found that environmentally benign 1,4-benzoquinone (BQ) can act as a nonmetal oxidant, replacing the stoichiometric metal oxidants Ag_2CO_3[13a,b] and AgOAc.[13c] Encouraged by these results, we began our investigation of silylation of vinylic C(sp^2)−H bonds by examining the reactivity of 2-phenyl-*N*-(quinolin-8-yl)-

Received: August 10, 2017

DOI: 10.1021/acs.orglett.7b02486
Org. Lett. XXXX, XXX, XXX−XXX

acrylamide (**1a**)[14] with hexamethyldisilane (HMDS, **2a**) as the silylation partner. After an initial screening of the catalysts and oxidants, optimization studies employing $Pd(OAc)_2$ as the catalyst with nonmetal oxidant BQ were performed, and the results are summarized in Table 1. A detailed screening of

Table 1. Optimization of Reaction Conditions[a]



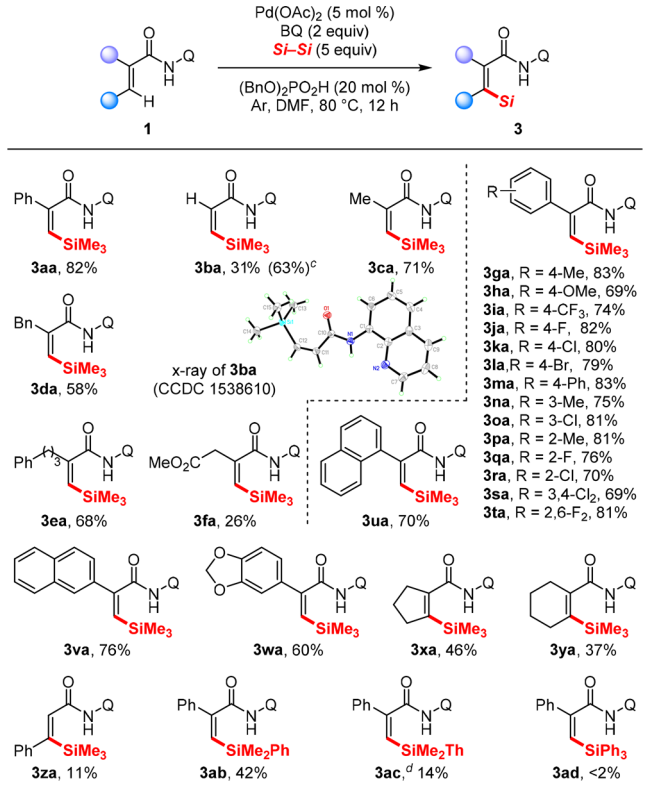
entry	reagents (equiv), temp (°C), and solvent	yield[b] (%)
1	BQ (2), 80, 1,4-dioxane	14
2	BQ (2), 80, toluene	19
3	BQ (2), 80, MeCN	8
4	BQ (2), 80, DMF	83
5	BQ (2), Na_2CO_3 (0.2), 80, DMF	79
6[c]	BQ (2), 4 Å MS, 80, DMF	77
7	BQ (2), PivOH (0.2), 80, DMF	84
8	BQ (2), $MesCO_2H$ (0.2), 80, DMF	33
9	BQ (2), L-proline (0.2), 80, DMF	62
10	BQ (2), *s*-BINA-PO_2H (0.2), 80, DMF	74
11	BQ (2), $(BnO)_2PO_2H$ (0.2), 80, DMF	90 (82)[d]
12	BQ (2), $(PhO)_2PO_2H$ (0.2), 80, DMF	84
13	BQ (2), $(BnO)_2PO_2H$ (0.2), 60, DMF	66
14	BQ (2), $(BnO)_2PO_2H$ (0.2), 100, DMF	89
15[e]	BQ (2), $(BnO)_2PO_2H$ (0.2), 80, DMF	64
16[f]	Ag_2CO_3 (2), $CaSO_4$ (2), 130, 1,4-dioxane	20
17[f]	Ag_2CO_3 (2), $NaHCO_3$ (2), LiOAc (0.5),*s*-BINA-PO_2H (0.3), 125, toluene	32

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.0 mmol), $Pd(OAc)_2$ (5 mol %), and additive (20 mol %) in solvent (1.0 mL) at the indicated temperature for 12 h. [b]Yields were determined by ^1H NMR analysis of the crude reaction mixture. [c]4 Å MS (30 mg) was used. [d]Isolated yield. [e]$Pd(OAc)_2$ (2 mol %) was used. [f]$Pd(OAc)_2$ (10 mol %) was used.

various solvents revealed that the solvent was a very important parameter and that the silylation reaction was sluggish in 1,4-dioxane, toluene, and MeCN (Table 1, entries 1−3), while it could be notably improved to give the desired product **3aa** in good yield when DMF was used as the solvent at 80 °C (Table 1, entry 4). To promote the circulation of this reaction system, further studies surveyed a series of additives (Table 1, entries 5−12). Significantly, the use of a catalytic amount of $(BnO)_2PO_2H$[12a] in the reaction system gave a slightly enhanced yield (Table 1, entry 11). We speculate that phosphate may facilitate the dissociation of palladium from Pd−Si intermediate to accelerate catalyst turnover in this context.[12c] Variation of the temperature was not beneficial for the silylation reaction (Table 1, entries 13 and 14). In addition, reducing catalyst loading from 5 to 2 mol % resulted in a significant decrease of the yield (Table 1, entry 15). Stoichiometric Ag_2CO_3 as oxidant was not applied successfully to **1a** (Table 1, entries 16[13a] and 17[13b]). Finally, the combination of HMDS (5 equiv), $Pd(OAc)_2$ (5 mol %), BQ (2 equiv), and $(BnO)_2PO_2H$ (20 mol %) in DMF at 80 °C for 12 h was found to be the optimal system for the palladium-catalyzed silylation of **1a** to exclusively afford the product **3aa** with 82% isolated yield (the stereochemistry of **3aa** was unambiguously confirmed by X-ray crystallography).

With the optimal conditions in hand, the scope and limitations of our silylation protocol were investigated (Scheme 2). *α,β*-Unsubstituted acrylamide **1b** showed a poor reactivity

Scheme 2. Substrate Scope[a,b]



[a]Reaction conditions: **1** (0.2 mmol), **2** (1.0 mmol), $Pd(OAc)_2$ (5 mol %), BQ (0.4 mmol), $(BnO)_2PO_2H$ (20 mol %), DMF (1.0 mL), at 80 °C for 12 h. [b]Isolated yield. [c]Reaction conditions: **1b** (0.2 mmol), **2a** (1.0 mmol), $Pd(OAc)_2$ (5 mol %), BQ (0.4 mmol), 3 Å MS (30 mg), DMF (1.0 mL), at 110 °C for 12 h. [d]Th = thiophene-2-yl.

with a yield of 31% under the optimal conditions. An improved yield of 63% for **3ba** could be achieved when 3 Å MS was used instead of $(BnO)_2PO_2H$ at 110 °C. As depicted in Scheme 2, *α*-substituted acrylamides bearing methyl, benzyl, and 3-phenylpropyl groups were readily silylated in 58−71% yields (**3ca**−**ea**). Exceptionally, itaconic acid derivative **3fa** was afforded in a low yield. Irrespective of electronic properties or substitution patterns in the aryl ring, a variety of *α*-aryl acrylamides with different substituents were able to smoothly undergo the silylation reaction and provided the corresponding silylation products in good to excellent yields (**3ga**−**wa**). In addition, *β*-substituted *E*-acrylamides could be utilized to afford the silylation products (**3xa**−**za**) in low to moderate yields. Obviously, the conversion is sensitive to the *β*-substituted groups since it is difficult for the higher steric hindrance to form the stabilized palladacycle intermediates. We then sought to investigate the scope of the organosilicon sources. Compared to HMDS (**2a**), $(Me_2PhSi)_2$ (**2b**) and $(Me_2ThSi)_2$ (**2c**) were less reactive, affording **3ab** and **3ac**, respectively. When $(Ph_3Si)_2$ was used as the organosilicon source, no desired product (**3ad**) was isolated because of steric effects. Notably, stereoselectivity in favor of *Z* silylation of acrylamides was excellent throughout, and no *E*-silylation products were observed.

DOI: 10.1021/acs.orglett.7b02486
Org. Lett. XXXX, XXX, XXX−XXX

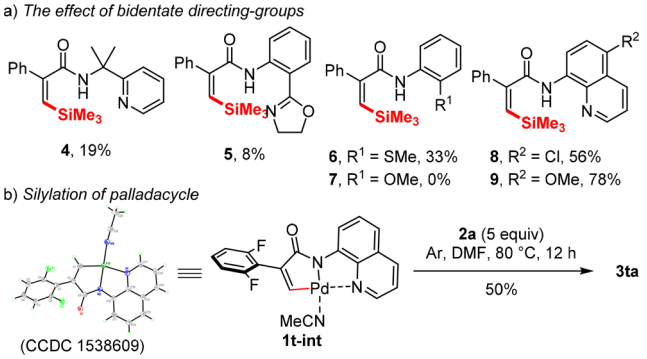
To gain preliminary insight into the mechanism, a primary kinetic isotope effect (~1.0) was obtained (see the Supporting Information), which indicated that the palladation was not the rate-limiting step in this C−H silylation reaction. We next examined the effect of other directing groups carefully (Scheme 3a). The corresponding silylation products containing an *N,N*-bidentate directing group 2-pyridinyl isopropyl (PIP)[15a] **4** or 2-oxazolinyl (Oxa)[15b] **5** or an *N,S*-bidentate directing group[15c] **6** could be isolated with much lower yields. Nevertheless, the desired product with an *N,O*-bidentate group could not be afforded under standard conditions. When the 5-position of 8-aminoquinoline was substituted with Cl, the modification would dramatically decrease the reactivity. Interestingly, 5-OMe-substituted 8-aminoquinoline retained good directing activity, providing the corresponding silylation product in a similar yield. Based on these results, we believe that the *N,N*-bidentate directing group[16] plays a critical role in this Pd-catalyzed *Z*-selective C−H silylation reaction. Fortunately, the 5-membered palladium complex **1t-int** via vinyl C(sp^2)−H bond activation was isolated, which can be used to react with HMDS to give the desired silylation product **3ta** in 50% yield (Scheme 3b). The X-ray determined structure of **1t-int** can effectively explain and describe the *Z*-stereoselectivity of vinylsilanes.

On the basis of our experimental results and previous reports,[12,13,15] we proposed a plausible reaction mechanistic pathway as shown in Scheme 4. First, Pd(II) species **A** was afforded by initial chelation of 2-phenylacrylamide **1a** with Pd(II) catalyst followed by ligand exchange. The key palladacycle intermediate **B** was produced via a C−H concerned metalation−deprotonation (CMD) process. Subsequently, intermediate **C** was formed by insertion of the Si−Si bond and simultaneous transfer of trimethylsilyl group. Finally, a reductive elimination and a final protonation of the amide gave the desired silylation product **3aa** with the generation of Pd(0) species, which will be reoxidized to Pd(II) with the assistance of 1,4-benzoquinone to continue the catalytic cycle.

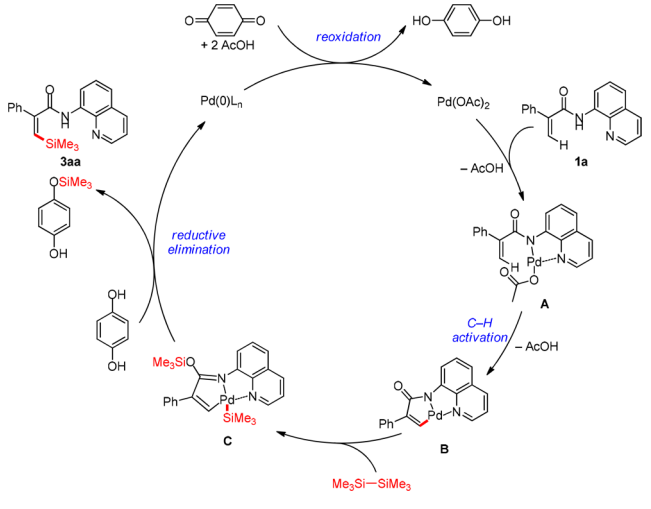
To prove both the practicality and effectiveness of this method in organic synthesis, the silylation reaction was scaled up to 5 mmol (1.37 g) under the optimal conditions by the synthesis of **3aa** (Scheme 5a). Gratifyingly, the auxiliary can be readily removed by a two-step sequence to afford the corresponding methyl ester **10** (Scheme 5a). To demonstrate the application of the *Z*-vinylsilanes prepared by our C−H silylation, a high stereoselectivity *Z*-configured *α,β*-unsaturated ester **11** was prepared via *ipso*-iodination/Suzuki−Miyaura cross-coupling reaction (Scheme 5b).

In summary, we have developed an efficient and convenient palladium-catalyzed direct intermolecular silylation reaction of acrylamides with disilanes, providing a protocol to exclusively generate *Z*-vinylsilanes with reasonable to excellent yields. A broad range of functional groups was proved to be well-tolerated by this strategy. The silylated products can be obtained on a preparative scale, and the auxiliary can be readily removed. Further application of this approach in the synthesis of natural products such as lythridine[17a] and vertine[17b] is currently under investigation.

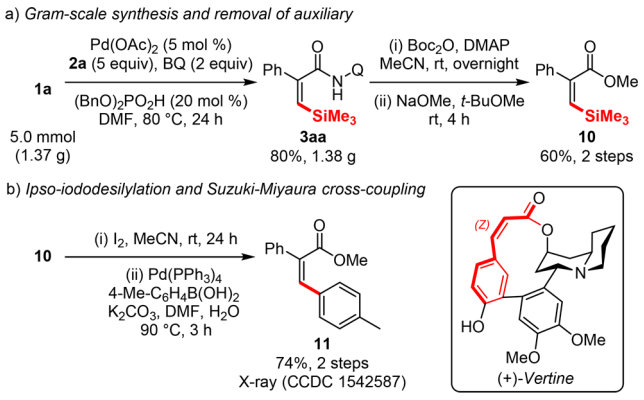
Scheme 3. Mechanistic Studies



Scheme 4. Proposed Catalytic Cycle



Scheme 5. Synthetic Applicability



■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02486.

Experimental procedures, NMR spectra, and X-ray and analytical data for all new compounds (PDF)
X-ray data for compound **3aa** (CIF)
X-ray data for compound **3ba** (CIF)
X-ray data for compound **1t-int** (CIF)
X-ray data for compound **11** (CIF)

DOI: 10.1021/acs.orglett.7b02486
Org. Lett. XXXX, XXX, XXX−XXX

AUTHOR INFORMATION

Corresponding Author

*E-mail: zhangsy16@sjtu.edu.cn.

ORCID

Jin-Long Pan: 0000-0002-1085-4566
Shu-Yu Zhang: 0000-0002-1811-4159

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the "Thousand Youth Talents Plan", NSFC (21672145), the Shuguang program from Shanghai Education Development Foundation and Shanghai Municipal Education Commission, and startup funds from Shanghai Jiao Tong University.

REFERENCES

(1) For recent selected reviews, see: (a) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375. (b) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063. (c) Denmark, S. E.; Liu, J.-H. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 2978. (d) Nakao, Y.; Hiyama, T. *Chem. Soc. Rev.* **2011**, *40*, 4893. (e) Martin, S. E. S.; Watson, D. A. *Synlett* **2013**, *24*, 2177.

(2) (a) Tamao, K.; Ishida, N.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2120. (b) Hirabayashi, K.; Mori, A.; Hiyama, T. *Tetrahedron Lett.* **1997**, *38*, 461. (c) Denmark, S. E.; Regens, C. S. *Acc. Chem. Res.* **2008**, *41*, 1486. (d) Sore, H. F.; Galloway, W. R. J. D.; Spring, D. R. *Chem. Soc. Rev.* **2012**, *41*, 1845.

(3) (a) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988. (b) Rappoport, Z.; Apeloig, Y. *Chemistry of Organosilicon Compounds*; Wiley-VCH: New York, 2001. (c) Rochow, E. G. *Silicon and Silicones*; Springer-Verlag: New York, 1987.

(4) For selected references for preparation of vinylsilanes, see: (a) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2001**, *123*, 12726. (b) Na, Y.; Chang, S. *Org. Lett.* **2000**, *2*, 1887. (c) Kim, Y.; Dateer, R. B.; Chang, S. *Org. Lett.* **2017**, *19*, 190. (d) Mutoh, Y.; Mohara, Y.; Saito, S. *Org. Lett.* **2017**, DOI: 10.1021/acs.orglett.7b02477. (e) Suginome, M.; Nakamura, H.; Ito, Y. *Chem. Commun.* **1996**, 2777. (f) Nakamura, S.; Uchiyama, M.; Ohwada, T. *J. Am. Chem. Soc.* **2004**, *126*, 11146. (g) Marciniec, B.; Lewandowski, M.; Bijpost, E.; Małecka, E.; Kubicki, M.; Walczuk-Guściora, E. *Organometallics* **1999**, *18*, 3968. (h) Marciniec, B.; Kownacki, I.; Kubicki, M. *Organometallics* **2002**, *21*, 3263. (i) McAtee, J. R.; Martin, S. E. S.; Ahneman, D. T.; Johnson, K. A.; Watson, D. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 3663. (j) Martin, S. E. S.; Watson, D. A. *J. Am. Chem. Soc.* **2013**, *135*, 13330. (k) Szudkowska-Frątczak, J.; Marciniec, B.; Hreczycho, G.; Kubicki, M.; Pawluć, P. *Org. Lett.* **2015**, *17*, 2366. (l) Takeuchi, R.; Yasue, H. *Organometallics* **1996**, *15*, 2098. (m) Bokka, A.; Jeon, J. *Org. Lett.* **2016**, *18*, 5324. (n) Hirano, K.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 6094. (o) Rooke, D. A.; Ferreira, E. M. *J. Am. Chem. Soc.* **2010**, *132*, 11926. (p) Lim, D. S. W.; Anderson, E. A. *Org. Lett.* **2011**, *13*, 4806. (q) Li, L.; Ye, X.; Wu, Y.; Gao, L.; Song, Z.; Yin, Z.; Xu, Y. *Org. Lett.* **2013**, *15*, 1068. (r) Zhang, L.; Hang, Z.; Liu, Z. Q. *Angew. Chem., Int. Ed.* **2016**, *55*, 236.

(5) (a) Noels, A. F.; Hubert, A. J. In *Industrial Applications of Homogeneous Catalysis*; Mortreux, A., Petit, F., Eds.; Kluwer: Amsterdam, 1985. (b) Marciniec, B.; Gulinski, J.; Urbaniak, W.; Kornetka, Z. W. *Comprehensive Handbook on Hydrosilylation*; Marciniec, B., Ed.; Oxford University Press: New York, 1992.

(6) For recent reviews about C−H silylation, see: (a) Yang, Y.; Wang, C. *Sci. China: Chem.* **2015**, *58*, 1266. (b) Sharma, R.; Kumar, R.; Kumar, I.; Singh, B.; Sharma, U. *Synthesis* **2015**, *47*, 2347. (c) Cheng, C.; Hartwig, J. F. *Chem. Rev.* **2015**, *115*, 8946.

(7) For recent selected references of C−H silylation, see: (a) Cheng, C.; Hartwig, J. F. *Science* **2014**, *343*, 853. (b) Li, Q.; Driess, M.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2014**, *53*, 8471. (c) Toutov, A. A.; Liu, W.-B.; Betz, K. N.; Fedorov, A.; Stoltz, B. M.; Grubbs, R. H. *Nature* **2015**, *518*, 80. (d) Toutov, A. A.; Liu, W.-B.; Betz, K. N.; Stoltz, B. M.; Grubbs, R. H. *Nat. Protoc.* **2015**, *10*, 1897. (e) Zhang, Q.-W.; An, K.; Liu, L.-C.; Yue, Y.; He, W. *Angew. Chem., Int. Ed.* **2015**, *54*, 6918. (f) Wübbolt, S.; Oestreich, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 15876. (g) Murai, M.; Takami, K.; Takeshima, H.; Takai, K. *Org. Lett.* **2015**, *17*, 1798. (h) Lee, K.; Katsoulis, D.; Choi, J. *ACS Catal.* **2016**, *6*, 1493. (i) Yin, Q.; Klare, H. F. T.; Oestreich, M. *Angew. Chem., Int. Ed.* **2016**, *55*, 3204. (j) Ma, Y.; Wang, B.; Zhang, L.; Hou, Z. *J. Am. Chem. Soc.* **2016**, *138*, 3663. (k) Chen, Q.-A.; Klare, H. F. K.; Oestreich, M. *J. Am. Chem. Soc.* **2016**, *138*, 7868.

(8) For selected references, see: (a) Denmark, S. E.; Wang, Z. *Org. Lett.* **2001**, *3*, 1073. (b) Wu, W.; Li, C.-J. *Chem. Commun.* **2003**, 1668. (c) Roy, A. K. *Adv. Organomet. Chem.* **2007**, *55*, 1. (d) Belger, C.; Plietker, B. *Chem. Commun.* **2012**, *48*, 5419. (e) Konno, T.; Taku, K.; Yamada, S.; Moriyasu, K.; Ishihara, T. *Org. Biomol. Chem.* **2009**, *7*, 1167. (f) Atienza, C. C. H.; Diao, T.; Weller, K. J.; Nye, N. A.; Lewis, K. M.; Delis, J. P. G.; Boyer, J. L.; Roy, A. K.; Chirik, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 12108.

(9) For recent reviews, see: (a) Marciniec, B. *Coord. Chem. Rev.* **2005**, *249*, 2374. (b) Du, X.; Huang, Z. *ACS Catal.* **2017**, *7*, 1227. For recent selected references, see: (c) Dong, H.; Jiang, Y.; Berke, H. *J. Organomet. Chem.* **2014**, *750*, 17. (d) Wang, X.; Nakajima, M.; Serrano, E.; Martin, R. *J. Am. Chem. Soc.* **2016**, *138*, 15531. (e) Gu, J.; Cai, C. *Chem. Commun.* **2016**, *52*, 10779.

(10) Komiyama, T.; Minami, Y.; Hiyama, T. *ACS Catal.* **2017**, *7*, 631.

(11) (a) Lu, N.; Falck, J. R. *J. Org. Chem.* **2010**, *75*, 1701. (b) Cheng, C.; Simmons, E. M.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2013**, *52*, 8984. (c) Cheng, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2015**, *137*, 592.

(12) (a) Zhang, S.-Y.; He, G.; Nack, W. A.; Zhao, Y.; Li, Q.; Chen, G. *J. Am. Chem. Soc.* **2013**, *135*, 2124. (b) Zhang, S.-Y.; Li, Q.; He, G.; Nack, W. A.; Chen, G. *J. Am. Chem. Soc.* **2013**, *135*, 12135. (c) Zhang, S.-Y.; Li, Q.; He, G.; Nack, W. A.; Chen, G. *J. Am. Chem. Soc.* **2015**, *137*, 531. (d) Pan, J.-L.; Li, Q.-Z.; Zhang, T.-Y.; Hou, S.-H.; Kang, J.-C.; Zhang, S.-Y. *Chem. Commun.* **2016**, *52*, 13151. (e) Zhang, T.-Y.; Lin, J.-B.; Li, Q.-Z.; Kang, J.-C.; Pan, J.-L.; Hou, S.-H.; Chen, C.; Zhang, S.-Y. *Org. Lett.* **2017**, *19*, 1764. (f) Bai, H.-Y.; Ma, Z.-G.; Yi, M.; Lin, J.-B.; Zhang, S.-Y. *ACS Catal.* **2017**, *7*, 2042.

(13) (a) Kanyiva, K. S.; Kuninobu, Y.; Kanai, M. *Org. Lett.* **2014**, *16*, 1968. (b) Liu, Y.-J.; Liu, Y.-H.; Zhang, Z.-Z.; Yan, S.-Y.; Chen, K.; Shi, B.-F. *Angew. Chem., Int. Ed.* **2016**, *55*, 13859. (c) Chen, C.; Guan, M.; Zhang, J.; Wen, Z.; Zhao, Y. *Org. Lett.* **2015**, *17*, 3646.

(14) Pioneering work using 8-aminoquinoline as an *N,N*-bidentate directing group: Zaitsev, V. G.; Shabashov, D.; Daugulis, O. *J. Am. Chem. Soc.* **2005**, *127*, 13154.

(15) (a) Chen, F.-J.; Zhao, S.; Hu, F.; Chen, K.; Zhang, Q.; Zhang, S. Q.; Shi, B.-F. *Chem. Sci.* **2013**, *4*, 4187. (b) Giri, R.; Maugel, N.; Foxman, B. M.; Yu, J.-Q. *Organometallics* **2008**, *27*, 1667. (c) Shabashov, D.; Daugulis, O. *J. Am. Chem. Soc.* **2010**, *132*, 3965.

(16) Recent reviews about the N,N-bidentate directing group: (a) Corbet, M.; De Campo, F. *Angew. Chem., Int. Ed.* **2013**, *52*, 9896. (b) Rouquet, G.; Chatani, N. *Angew. Chem., Int. Ed.* **2013**, *52*, 11726. (c) Daugulis, O.; Roane, J.; Tran, L. D. *Acc. Chem. Res.* **2015**, *48*, 1053. (d) He, G.; Wang, B.; Nack, W. A.; Chen, G. *Acc. Chem. Res.* **2016**, *49*, 635.

(17) (a) Rumalla, C. S.; Jadhav, A. N.; Smillie, T.; Fronczek, F. R.; Khan, I. A. *Phytochemistry* **2008**, *69*, 1756. (b) Ferris, J. P.; Boyce, C. B.; Briner, R. C. *J. Am. Chem. Soc.* **1971**, *93*, 2942.

DOI: 10.1021/acs.orglett.7b02486
Org. Lett. XXXX, XXX, XXX−XXX