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A Pincer Ruthenium Complex for Regioselective C–H Silylation of Heteroarenes

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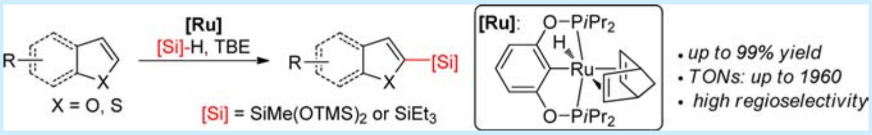
Supporting Information



ABSTRACT: A pincer Ru(II) catalyst for the highly efficient undirected silylation of *O*- and *S*-heteroarenes with $(TMSO)_2MeSiH$ and Et_3SiH is described, producing heteroarylsilanes with exclusive C2-regioselectivity, good functional-group tolerance, and high turnover numbers (up to 1960). The synthetic utility of the silylated products is demonstrated by Pd-catalyzed Hiyama–Denmark cross-coupling under mild conditions. One-pot, two-step silylation and coupling procedures have been also developed.

Due to their stability, low toxicity, and ease of manipulation, heteroarylsilanes are useful building blocks in organic synthesis.[1] Moreover, these compounds have found application in the manufacture of organic optoelectronic materials[2] and in the pharmaceutical sector.[3] The classical method for the preparation of heteroarylsilanes involves the reaction of organometallic species with suitable silicon electrophiles.[4] However, this method suffers from low functional-group tolerance, formation of waste inorganic salts, and a multistep synthetic sequence. Recently, methods for catalytic silylations of C–H[5] and carbon–halide[5d,6] bonds without directing groups have been developed for the synthesis of heteroarylsilanes. The former is of particular interest because of the high atom and step economy and environmentally benign nature.

Although the C–H silylation of arenes has a long history,[7,8] the silylation of heteroarenes without directing effects was reported much more recently. In 2005, Ishiyama and Miyaura reported the C–H silylation of five-membered heteroarenes using an Ir complex of the 2-*tert*-butyl-1,10-phenanthroline ligand (3 mol %).[9] The reactions used tetrafluorodisilane $(tBuF_2Si)_2$ as the silane reagent and a large excess of heteroarenes (10 equiv relative to silane) were required. Falck and Lu employed a similar Ir catalyst ligated by 4,4′-di-*tert*-butyl-2,2′-bipyridine (10 mol % of Ir) for the C–H silylation of *N*-, *S*-, and *O*-heteroarenes with Et_3SiH (3 equiv) using norbornene (NBE) as the hydrogen acceptor.[10] Building on their earlier work on Rh-catalyzed C–H silylation of arenes and heteroarenes with $(TMSO)_2MeSiH$,[7e] Hartwig and co-workers reported an Ir complex of the 2,4,7-trimethyl-1,10-phenanthroline ligand (2.2 mol %) that enables C–H silylation of heteroarenes with the same hydrosiloxane.[7f] The Ir catalyst exhibits broader functional-group tolerance compared to the Rh catalyst.[7e,f] During the preparation of this manuscript, Pilarski and co-workers disclosed that $RuH_2(CO)(PPh_3)_3$ (5 mol %) catalyzes the C–H silylation of heteroarenes with Et_3SiH using amine directing groups. The process required an excess of silane (5–10 equiv) and hydrogen acceptor (5–10 equiv NBE) for high conversions. This system also effects undirected C–H silylation of indoles and benzofurans, but it is inactive for the silylation of benzothiophene.[11] Earth-abundant metal catalysts, such as KO*t*Bu,[12] iron,[13] and copper[14] catalysts, have also been developed for C–H silylations of heteroarenes with alkyl- or aryl-substituted silanes; however, these systems in general showed inferior efficiency and limited substrate scope in comparison with the precious metal catalyst systems.

As detailed above, with a few exceptions offered by Hartwig[7e,f] and Ishiyama/Miyaura,[9,15] most existing catalytic systems employ alkyl/aryl silanes as the reagents, and thus, the resultant silylation products have limited synthetic utilities because the lack of electronegative substitution at the silicon atom renders them unsuitable for Hiyama–Denmark coupling[16] or Tamao oxidation reactions.[17] Moreover, despite the significant advances,[7e,f,9–14,18] there is need for improvement in known catalyst systems with regard to activity, as these systems necessitate relatively high catalyst loadings. Our contribution to this field is to improve the catalytic efficiency for the silylation reactions and to produce synthetically useful heteroarylsilanes utilizing readily available and low-cost silanes.

In early 2016, our laboratory reported the synthesis of new pincer Ru(II) hydrido olefin complexes. Possibly in part due to their high thermostability, these pincer Ru(II) complexes exhibit higher productivity than the previously reported Ru catalysts for alkane dehydrogenations.[19] We hypothesized that these robust pincer Ru complexes could be effective for

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Table 1. Evaluation of Ruthenium Catalysts for the Silylation of Benzofuran[a]

entry	[Ru] (mol %)	silane	solvent	t/h	yield (%)[b]
1	**1** (0.5)	$(TMSO)_2MeSiH$	toluene	6	99
2	**1** (0.5)	$(TMSO)_2MeSiH$	*n*-hexane	6	99
3	**1** (0.5)	$(TMSO)_2MeSiH$	none	6	97(96)
4[c]	**1** (0.5)	$(TMSO)_2MeSiH$	none	6	49[d]
5	**1** (0.05)	$(TMSO)_2MeSiH$	none	24	96(95)
6[e]	**1** (0.25)	Et_3SiH	none	24	98(98)
7	none	$(TMSO)_2MeSiH$	none	6	0
8	$Ru_3(CO)_{12}$ (0.5)	$(TMSO)_2MeSiH$	none	6	3
9	$[Cp^*RuCl_2]_2$ (0.5)	$(TMSO)_2MeSiH$	none	6	<5
10	(cod)Ru(2-methylallyl)$_2$ (0.5)	$(TMSO)_2MeSiH$	none	6	10
11	$Ru(acac)_3$ (0.5)	$(TMSO)_2MeSiH$	none	6	4

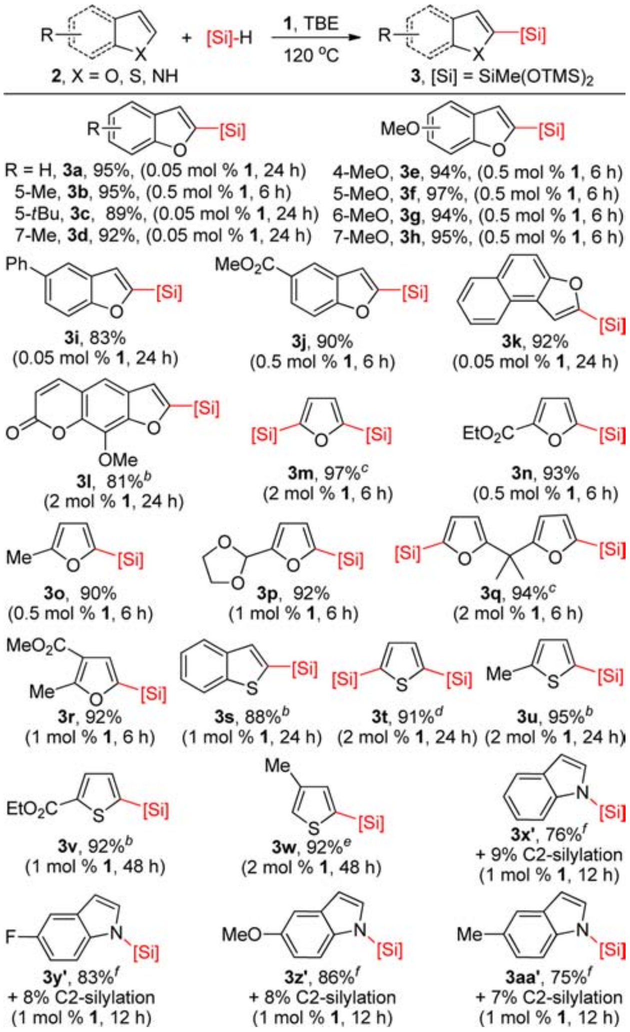
[a] Reaction conditions: **2a** (1.0−20 mmol), $(TMSO)_2MeSiH$ (1 equiv) or Et_3SiH (1.5 equiv), [Ru] (0.05−0.5 mol %), *tert*-butylethylene (TBE, 1 equiv) at 120 °C, 6−24 h. [b] Determined by ^1H NMR analysis of the crude reaction mixture using mesitylene as an internal standard. Values in the parentheses are the yields of isolated products. [c] Without TBE. [d] 2,3-Dihydrobenzofuran obtained in 47% yield. [e] With 1.2 equiv of TBE.

functionalizations of C(sp^2)−H bonds. Herein we report that the bis(phosphinite)-based pincer Ru complex is highly active for undirected C−H silylation of *O*- and *S*-heteroarenes with $(TMSO)_2MeSiH$ and Et_3SiH with high regioselectivity. The reaction is scalable by using a minimal amount of the catalyst (0.05 mol %). Furthermore, the silylation products are amenable to Hiyama−Denmark cross-coupling reactions, and a one-pot, two-step silylation and cross-coupling protocol is described.

The silylation of benzofuran **2a** with $(TMSO)_2MeSiH$ using the pincer Ru complex **1**, (POCOP)RuH(NBD) (NBD = norbornadiene), as the catalyst, was selected as the model reaction. The results are summarized in Table 1. A practical catalytic silylation should avoid using the heteroarene or the silane in excess. To our delight, using *tert*-butylethylene (TBE, 1 equiv) as the hydrogen acceptor, the reaction of **2a** with 1 equiv of $(TMSO)_2MeSiH$ and 0.5 mol % of **1** in toluene or *n*-hexane at 120 °C formed the C2-silylation product **3a** in quantitative yield after 6 h (entries 1 and 2). The dehydrogenative silylation reaction also occurred smoothly under solvent-free conditions (97% yield, entry 3). The reaction without TBE gave 49% **3a** and 47% 2,3-dihydrobenzofuran (entry 4), suggesting that benzofuran itself can serve as the hydrogen acceptor. Reducing the catalyst loading to 0.05 mol % and extending the reaction time to 24 h afforded **3a** in 96% yield (entry 5). This Ru catalyst is also effective for the silylation of **2a** with Et_3SiH (entry 6). Triethylsilane appeared to be less reactive than $(TMSO)_2MeSiH$ under the catalytic conditions; however, the silylation product **4a** was obtained in high yield when 1.5 equiv of Et_3SiH and 0.25 mol % of **1** were applied. The control experiment without **1**, but with TBE, did not form the silylation product (entry 7). For comparison, we also examined several common Ru complexes for the silylation reaction. $Ru_3(CO)_{12}$ has been reported for the silylation of C(sp^2)−H[8] and C(sp^3)−H[20] bonds in substrates with directing groups. However, the silylation of **2a** using $Ru_3(CO)_{12}$ (0.5 mol %) at 120 °C after 6 h gave 3% **3a** (entry 8). The reactions using Ru(II) and Ru(III) complexes, $[Cp^*RuCl_2]_2$, (cod)Ru(2-methylallyl)$_2$, and $Ru(acac)_3$, gave low yields of **3a** (entries 9−11).

Next, the substrate scope of the silylation reactions was explored utilizing **1** as the catalyst (Scheme 1). All of the reactions were performed neat. For the reactions with $(TMSO)_2MeSiH$ as the reagent, a variety of benzofuran derivatives bearing electron-donating and -withdrawing groups underwent C2-silylations to

Scheme 1. Silylations of Heteroarenes with $(TMSO)_2MeSiH$[a]



[a] Reaction conditions: **1** (0.05−2.0 mol %), **2** (0.5−10 mmol), $(TMSO)_2MeSiH$ (1 equiv), TBE (1 equiv) at 120 °C. Yields shown are of isolated products unless otherwise noted. [b] TBE (1.5 equiv). [c] $(TMSO)_2MeSiH$ (2 equiv), TBE (2 equiv). [d] $(TMSO)_2MeSiH$ (2 equiv), TBE (3 equiv). [e] $(TMSO)_2MeSiH$ (1.5 equiv), TBE (1 equiv). [f] $(TMSO)_2MeSiH$ (2 equiv), TBE (1.2 equiv).

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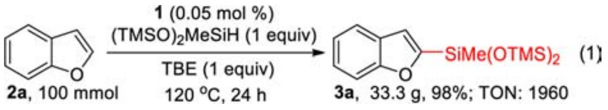
form the corresponding silylation products in high isolated yields (**3a**–**l**). Most reactions employed 0.5 mol % of the Ru catalyst, but five examples using only 0.05 mol % of **1** were demonstrated to proceed with high yields (**3a**, **3c**, **3d**, **3i**, **3k**). Benzofurans with substituents at C4–C7 positions were all selectively silylated at the C2 position (**3e**–**h**). The reaction of methoxsalen produced the desired product **3l** in 81% yield, while the *α*,*β*-unsaturated ester moiety remained intact during the silylation process. Furan and its derivatives were efficiently silylated at the C2 positions. The disilylation products (**3m**, **3q**) were obtained in high isolated yields when furan and 2,2-di(2-furyl)propane were treated with 2 equiv of silane and TBE.

S-Heteroarenes are also suitable substrates for the silylation, although higher catalyst loadings were used relative to reactions of *O*-heteroarenes (Scheme 1). For instance, the reaction of benzothiophene with 1 mol % **1** afforded the silylated product **3s** in 88% yield. Similar to furan, thiophene underwent disilylation to form **3t** in 91% yield. The thiophenes with Me and ester substituents at the 2-poisition gave the corresponding products (**3u**, **3v**) in high yields. In addition, the substrate with a Me group at the 3-poisition undergoes regioselective silylation at the 5-position with no detectable evidence for silylation at the 2-position (**3w**). We attribute the high regioselectivity to the sensitivity of the sterically hindered pincer Ru complex to the steric effect of the substrate.

In contrast to the selective C2-silylations with *O*- and *S*-heteroarenes, the Ru-catalyzed silylation of indoles with $(TMSO)_2MeSiH$ resulted in selective formation of the *N*-silylation products (**3x′**–**3aa′**, >75%), albeit with accompanying C–H silylation, giving the C2-silylation products as the minor products (<10%, see Scheme 1).

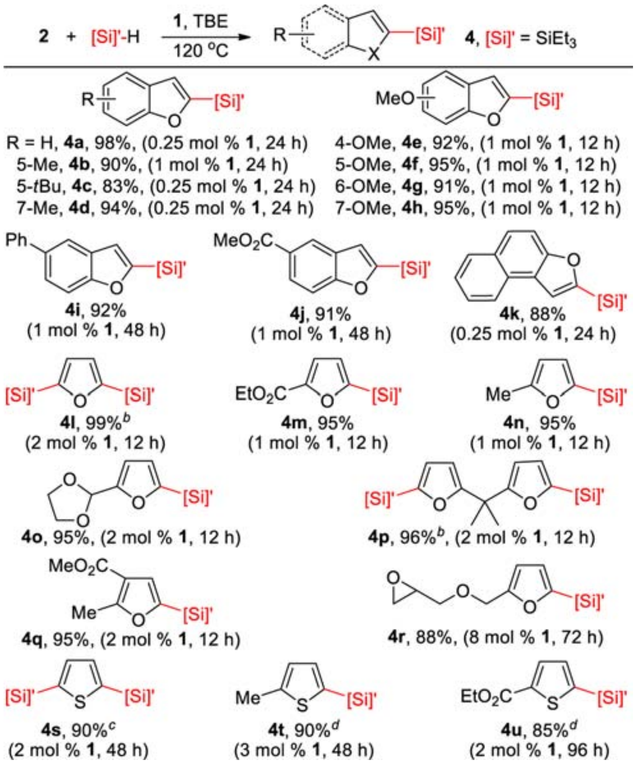
The reactions using triethylsilane Et_3SiH as the silylating reagent display a wide substrate scope similar to those using $(TMSO)_2MeSiH$ (Scheme 2). However, the processes are slower than those with $(TMSO)_2MeSiH$ and thus require higher catalyst loadings. Nevertheless, most reactions of *O*-, *S*-heteroarenes with Et_3SiH provided the desired products (**4**) in >90% isolated yields. Ester (**4j**, **4m**, **4q**, **4u**), ether (**4e**–**4h**), acetal (**4o**), and epoxide (**4r**) functional groups can be tolerated.

Having established a highly active catalyst for the silylation, we sought to develop procedures to conduct this transformation at a large scale. Using 0.05 mol % of **1**, the reaction of **2a** (100 mmol) with $(TMSO)_2MeSiH$ (100 mmol) afforded **3a** in nearly quantitative yield (98%, 33.3 g) with a turnover number (TON) of 1960. To the best of our knowledge, this represents the highest TON obtained by any metal-catalyzed silylation of heteroarenes (eq 1).



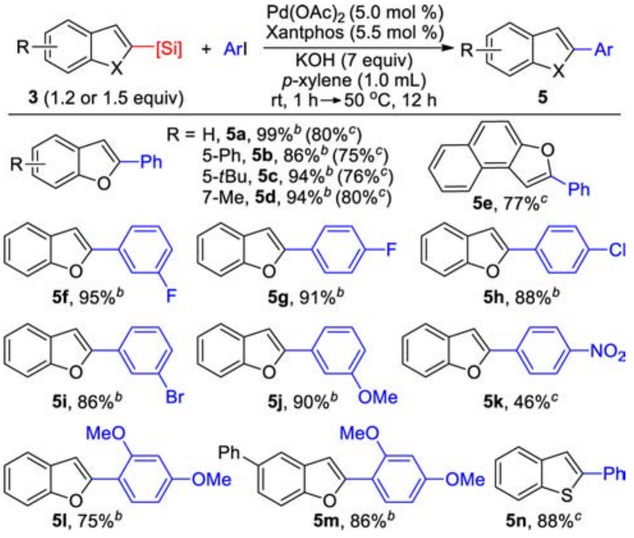
The synthetic value of the heteroarylsilane products **3** that contain Si–O bonds is demonstrated by their applications to Pd-catalyzed Hiyama–Denmark cross-coupling reactions (Scheme 3).[21] Using $Pd(OAc)_2$/Xantphos (5 mol %) as the catalyst and KOH as the base (7 equiv), the couplings between heteroarylsilanes **3** and various aryl iodides in *p*-xylene occurred under mild conditions (50 °C) to afford the products in good to high yields. A variety of functionalities, including nitro, chloro, and bromo groups in the electrophiles, were found to be compatible under the reaction conditions.

Scheme 2. Silylations of Heteroarenes with Et_3SiH[a]



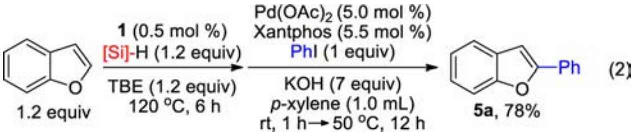
[a]Reaction conditions: **1** (0.25–8.0 mol %), **2** (0.5–2.0 mmol), Et_3SiH (1.5 equiv), TBE (1.2 equiv) at 120 °C. Yields shown are of isolated products. [b]Et_3SiH (3 equiv), TBE (3 equiv). [c]Et_3SiH (3 equiv), TBE (2.4 equiv). [d]Et_3SiH (1.5 equiv), TBE (1.5 equiv).

Scheme 3. Hiyama–Denmark Cross-Couplings of the Heteroarylsilanes with Iodobenzenes[a]



[a]Reaction conditions: **3** (1.2–1.5 equiv), ArI (0.2–0.3 mmol), $Pd(OAc)_2$ (5.0 mol %), Xantphos (5.5 mol %), KOH (7 equiv), *p*-xylene (1.0 mL). Yields shown are of isolated products. [b]**3** (1.5 equiv). [c]**3** (1.2 equiv).

Given the high conversions of heteroarenes to the silylation products and the low loadings of the Ru catalyst, we envisioned that the crude silylation products could be applied to the sequential cross-coupling reaction without purification. Indeed, the heteroarylsilane **3a**, generated *in situ* from the Ru-catalyzed silylation of **2a**, reacted with PhI in the presence of the Pd catalyst to form **5a** in good yield (eq 2).



(2)

In summary, a highly efficient ruthenium complex has been developed for the undirected C2-selective silylation of *O*- and *S*-heteroarenes with (TMSO)$_2$MeSiH and Et$_3$SiH. High conversions and high TONs (~2000) can be achieved using low catalyst loadings. Moreover, a mild and practical protocol has been described for the Hiyama–Denmark coupling of heteroarylsilanes with aryl iodides.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02857.

Experimental procedures and product characterization (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375. (b) Pierrat, P.; Gros, P.; Fort, Y. *Org. Lett.* **2005**, *7*, 697. (c) Suzawa, K.; Ueno, M.; Wheatley, A. E. H.; Kondo, Y. *Chem. Commun.* **2006**, 4850. (d) Denmark, S. E.; Baird, J. D. *Chem. - Eur. J.* **2006**, *12*, 4954. (e) Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A. *Science* **2012**, *337*, 1644.

(2) (a) Kumagai, T.; Itsuno, S. *Macromolecules* **2002**, *35*, 5323. (b) Bai, D.; Han, S.; Lu, Z.-H.; Wang, S. *Can. J. Chem.* **2008**, *86*, 230. (c) Zhang, F.; Wu, D.; Xu, Y.; Feng, X. *J. Mater. Chem.* **2011**, *21*, 17590.

(3) (a) Franz, A. K. *Curr. Opin. Drug Discovery Dev.* **2007**, *10*, 654. (b) Franz, A. K.; Wilson, S. O. *J. Med. Chem.* **2013**, *56*, 388.

(4) (a) Denmark, S. E.; Neuville, L. *Org. Lett.* **2000**, *2*, 3221. (b) Crich, D.; Grant, D. *J. Org. Chem.* **2005**, *70*, 2384. (c) Nakano, M.; Shinamura, S.; Sugimoto, R.; Osaka, I.; Miyazaki, E.; Takimiya, K. *Org. Lett.* **2012**, *14*, 5448.

(5) For reviews, see: (a) Cheng, C.; Hartwig, J. F. *Chem. Rev.* **2015**, *115*, 8946. (b) Yang, Y.; Wang, C. *Sci. China: Chem.* **2015**, *58*, 1266. (c) Sharma, R.; Kumar, R.; Kumar, I.; Singh, B.; Sharma, U. *Synthesis* **2015**, *47*, 2347. (d) Xu, Z.; Huang, W.-S.; Zhang, J.; Xu, L.-W. *Synthesis* **2015**, *47*, 3645.

(6) Selected examples of catalytic silylation of heteroaryl halides: (a) Murata, M.; Suzuki, K.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **1997**, *62*, 8569. (b) Manoso, A. S.; DeShong, P. *J. Org. Chem.* **2001**, *66*, 7449. (c) Murata, M.; Ishikura, M.; Nagata, M.; Watanabe, S.; Masuda, Y. *Org. Lett.* **2002**, *4*, 1843. (d) Denmark, S. E.; Kallemeyn, J. M. *Org. Lett.* **2003**, *5*, 3483. (e) Yamanoi, Y. *J. Org. Chem.* **2005**, *70*, 9607. (f) Hamze, A.; Provot, O.; Alami, M.; Brion, J.-D. *Org. Lett.* **2006**, *8*, 931. (g) McNeill, E.; Barder, T. E.; Buchwald, S. L. *Org. Lett.* **2007**, *9*, 3785. (h) Yamanoi, Y.; Taira, T.; Sato, J.-i.; Nakamula, I.; Nishihara, H. *Org. Lett.* **2007**, *9*, 4543. (i) Yamanoi, Y.; Nishihara, H. *J. Org. Chem.* **2008**, *73*, 6671. (j) Kurihara, Y.; Nishikawa, M.; Yamanoi, Y.; Nishihara, H. *Chem. Commun.* **2012**, *48*, 11564. (k) Kurihara, Y.; Yamanoi, Y.; Nishihara, H. *Chem. Commun.* **2013**, *49*, 11275. (l) Yamamoto, Y.; Matsubara, H.; Murakami, K.; Yorimitsu, H.; Osuka, A. *Chem. - Asian J.* **2015**, *10*, 219.

(7) (a) Gustavson, W. A.; Epstein, P. S.; Curtis, M. D. *Organometallics* **1982**, *1*, 884. (b) Sakakura, T.; Tokunaga, Y.; Sodeyama, T.; Tanaka, M. *Chem. Lett.* **1987**, *16*, 2375. (c) Ishikawa, M.; Okazaki, S.; Naka, A.; Sakamoto, H. *Organometallics* **1992**, *11*, 4135. (d) Ishiyama, T.; Sato, K.; Nishio, Y.; Miyaura, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 5346. (e) Cheng, C.; Hartwig, J. F. *Science* **2014**, *343*, 853. (f) Cheng, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2015**, *137*, 592.

(8) (a) Kakiuchi, F.; Matsumoto, M.; Sonoda, M.; Fukuyama, T.; Chatani, N.; Murai, S.; Furukawa, N.; Seki, Y. *Chem. Lett.* **2000**, *29*, 750. (b) Kakiuchi, F.; Igi, K.; Matsumoto, M.; Chatani, N.; Murai, S. *Chem. Lett.* **2001**, *30*, 422. (c) Kakiuchi, F.; Igi, K.; Matsumoto, M.; Hayamizu, T.; Chatani, N.; Murai, S. *Chem. Lett.* **2002**, *31*, 396. (d) Kakiuchi, F.; Matsumoto, M.; Tsuchiya, K.; Igi, K.; Hayamizu, T.; Chatani, N.; Murai, S. *J. Organomet. Chem.* **2003**, *686*, 134.

(9) Ishiyama, T.; Sato, K.; Nishio, Y.; Saiki, T.; Miyaura, N. *Chem. Commun.* **2005**, 5065.

(10) Lu, B.; Falck, J. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 7508.

(11) Devaraj, K.; Sollert, C.; Juds, C.; Gates, P. J.; Pilarski, L. T. *Chem. Commun.* **2016**, *52*, 5868.

(12) (a) Toutov, A. A.; Liu, W.-B.; Betz, K. N.; Fedorov, A.; Stoltz, B. M.; Grubbs, R. H. *Nature* **2015**, *518*, 80. (b) Toutov, A. A.; Liu, W.-B.; Betz, K. N.; Stoltz, B. M.; Grubbs, R. H. *Nat. Protoc.* **2015**, *10*, 1897.

(13) (a) Sunada, Y.; Soejima, H.; Nagashima, H. *Organometallics* **2014**, *33*, 5936. (b) Ito, J.-i.; Hosokawa, S.; Khalid, H. B.; Nishiyama, H. *Organometallics* **2015**, *34*, 1377. (c) Yin, Q.; Klare, H. F. T.; Oestreich, M. *Angew. Chem., Int. Ed.* **2016**, *55*, 3204.

(14) Gu, J.; Cai, C. *Chem. Commun.* **2016**, *52*, 10779.

(15) Note that the disilane (tBuF$_2$Si)$_2$ applied in the Ishiyama/Miyaura system is commercially unavailable.

(16) Denmark, S. E.; Regens, C. S. *Acc. Chem. Res.* **2008**, *41*, 1486.

(17) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694.

(18) (a) Klare, H. F. T.; Oestreich, M.; Ito, J.-i.; Nishiyama, H.; Ohki, Y.; Tatsumi, K. *J. Am. Chem. Soc.* **2011**, *133*, 3312. (b) Curless, L. D.; Clark, E. R.; Dunsford, J. J.; Ingleson, M. J. *Chem. Commun.* **2014**, *50*, 5270. (c) Wuebbolt, S.; Oestreich, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 15876. (d) Minami, Y.; Komiyama, T.; Hiyama, T. *Chem. Lett.* **2015**, *44*, 1065. (e) Sabat, N.; Slavetinska, L. P.; Hocek, M. *Tetrahedron Lett.* **2015**, *56*, 6860. (f) Lee, K.-s.; Katsoulis, D.; Choi, J. *ACS Catal.* **2016**, *6*, 1493. (g) Ma, Y.; Wang, B.; Zhang, L.; Hou, Z. *J. Am. Chem. Soc.* **2016**, *138*, 3663. (h) Chen, Q.-A.; Klare, H. F. T.; Oestreich, M. *J. Am. Chem. Soc.* **2016**, *138*, 7868.

(19) Zhang, Y.; Fang, H.; Yao, W.; Leng, X.; Huang, Z. *Organometallics* **2016**, *35*, 181.

(20) (a) Kakiuchi, F.; Tsuchiya, K.; Matsumoto, M.; Mizushima, B.; Chatani, N. *J. Am. Chem. Soc.* **2004**, *126*, 12792. (b) Li, W.; Huang, X.; You, J. *Org. Lett.* **2016**, *18*, 666.

(21) Hartwig and co-workers have reported cross-couplings between arylsilanes and ary iodides using a Pd catalyst generated from Pd(OAc)$_2$ and bis(dicyclohexylphosphino)ethane and KOSiMe$_3$ as the base. See refs 7e and 7f.