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Borane-Catalyzed Selective Hydrosilylation of Internal Ynamides Leading to β-Silyl (*Z*)-Enamides

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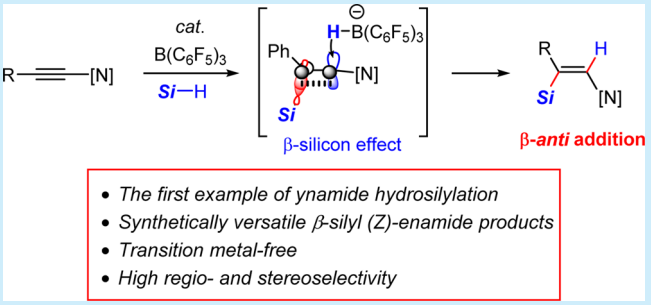
Supporting Information

ABSTRACT: We have developed a borane-catalyzed regio- and stereoselective hydrosilylation of internal ynamides for the first time. The scope of ynamide substrates and silane reactants was broad under mild reaction conditions, affording synthetically versatile β-silyl (*Z*)-enamide products. The observed stereoselectivity was reasoned to be due to the β-silicon effect on a postulated ketene iminium intermediate.



Vinylsilanes are versatile compounds that serve as an important synthetic building unit.[1] In fact, they are frequently utilized in a broad range of transformations, including Tamao−Fleming oxidation, electrophilic substitution, and cross-coupling reactions.[2] Among various preparative methods for vinylsilanes, hydrosilylation of alkynes is one of the most straightforward, convenient, and atom-economical procedures.[3] While transition-metal catalysts such as platinum, ruthenium, rhodium, or iridium have been well studied for the hydrosilylation of alkynes (Scheme 1a),[4] control of regio- and/or stereoselectivity is often problematic.[5] In this context, unsymmetrical internal alkynes are especially challenging substrates. As a result, several approaches have been investigated to improve the limitations:[6] intramolecular hydrosilylation,[7] the use of polarized alkynes,[8] or the presence of internal directing groups.[9]

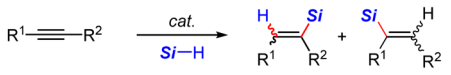
Lewis acids have been shown to be effective for the hydrosilylation of alkynes, wherein Lewis acidic metal species are initially inserted into triple bonds and then transmetalation by silanes is followed to afford vinylsilane products. For instance, Molander and Yamamoto independently reported organoaluminum or yttrium-catalyzed hydrosilylation of alkynes.[10] Although these procedures were successfully applied to internal alkynes as well as terminal ones, there is room to improve the regioselectivity. In addition, compatibility of labile functional groups was rather insufficient mainly due to the acidic nature of the metal species (Scheme 1a).[11]

We herein report the borane-catalyzed selective hydrosilylation of ynamides for the first time (Scheme 1b). The scope was found to be broad with high functional group tolerance under mild conditions. Moreover, the reaction occurs with excellent regio- and stereoselectivity to afford synthetically valuable β-silyl (*Z*)-enamide products. Based on the mechanistic studies, including computational calculations, the β-silicon effect was hypothesized to be responsible for the observed excellent stereoselectivity.

We commenced our study by monitoring a test reaction of a representative ynamide **1a** with diethylsilane (2.0 equiv) in the presence of $B(C_6F_5)_3$ catalyst (5 mol %) in chloroform-*d* (Table 1). The progress of hydrosilylation was checked by ^{1}H NMR spectroscopy. The hydrosilylation reaction proceeded with moderate efficiency at room temperature to afford β-silyl (*Z*)-enamide **2a** (66% ^{1}H NMR yield after 24 h, entry 1).

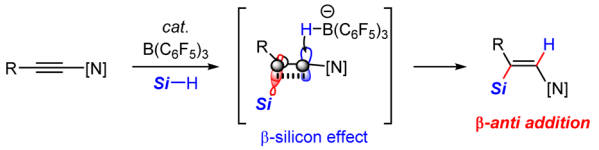
Scheme 1. Hydrosilylation of Unsymmetrical Internal Alkynes

a. Catalysis by transition metals or Lewis acids



- *Selectivity issue in regio- and stereo-control*
- *Limitation in functional group compatibility*

***b. Present Study**: Borane-catalyzed hydrosilylation of ynamides*



- *The first example of ynamide hydrosilylation*
- *Synthetically versatile β-silyl (Z)-enamide products*
- *Transition metal-free*
- *High regio- and stereoselectivity*

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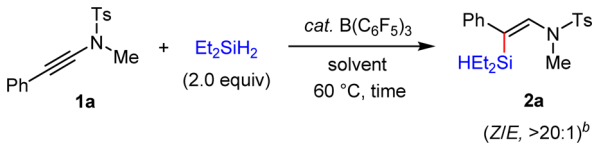
Table 1. Optimization of Reaction Conditions[a]



entry	$B(C_6F_5)_3$ (mol %)	solvent	time (h)	yield[b] (%)
1[c]	5	$CDCl_3$	24	66
2	5	$CDCl_3$	6	94
3	**3**	**$CDCl_3$**	**6**	**96**
4[d]		$CDCl_3$	24	NR
5[e]	3	$CDCl_3$	24	71
6	3	toluene-d_8	24	79
7	3	THF-d_8	24	NR

[a]Conditions: **1a** (0.2 mmol), diethylsilane (2.0 equiv), and $B(C_6F_5)_3$ catalyst in $CDCl_3$ (0.8 mL). [b]Determined by ^1H NMR analysis of the crude mixture (internal standard: mesitylene). [c]At 25 °C. [d]At 80 °C. [e]Diethylsilane (1.1 equiv).

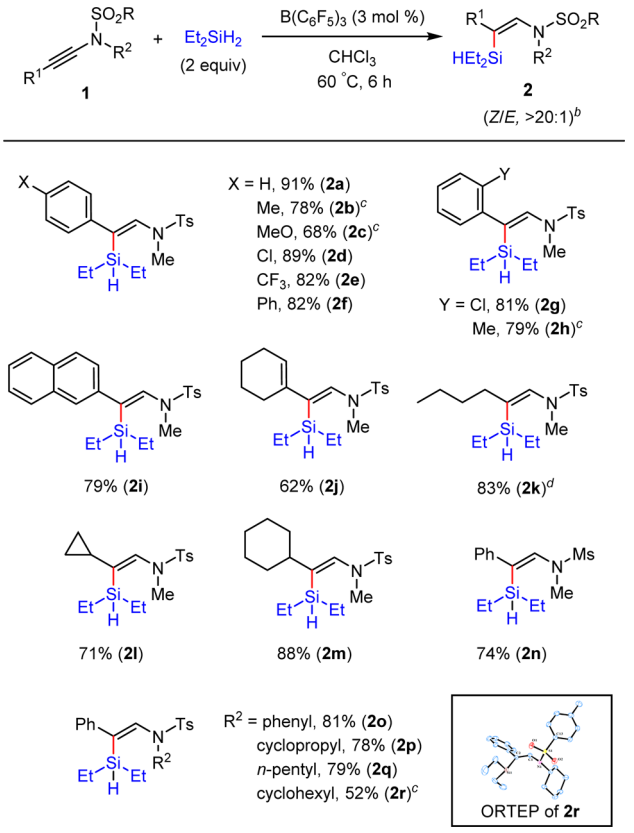
Importantly, the isolated product was determined to display complete control of regio- and stereoselectivity as determined by NMR spectroscopy (see the Supporting Information for details). This result was significant in that while $B(C_6F_5)_3$ was known to catalyze hydrosilylation of unsaturated bonds such as olefins, carbonyls, imines, carboxylic acids, and nitriles,[12] only limited examples of internal alkynes were known to undergo the borane-catalyzed hydrosilylation.[13] Therefore, we determined to optimize the present hydrosilylation further by evaluating various reaction parameters.

The hydrosilylation efficiency was significantly improved by running the reaction at higher temperature even with lower catalyst loading and in shorter time, and excellent product yield was obtained in 6 h at 60 °C using 3 mol % of $B(C_6F_5)_3$ catalyst (entry 3). No reaction was observed in the absence of borane species (entry 4). The product yield was slightly decreased with the use of 1.1 equiv of silylating reagent (entry 5). Solvents other than chloroform were less effective in the current hydrosilylation of ynamide (entries 6 and 7).

With the above optimized reaction conditions in hand, we next explored the scope of *N*-sulfonyl ynamides (Scheme 2). Substrates bearing various *para*-substituents in the phenylacetylenic moiety smoothly underwent the desired hydrosilylation leading to the corresponding *β*-silyl (*Z*)-enamides in high yields (**2a**–**f**), which displayed complete control of regio- and stereoselectivity. Notably, the reaction efficiency was not affected by the electronic variation, and substrates having either electron-donating (Me or OMe) or -withdrawing substituents (Cl or CF_3) were hydrosilylated in good yields. The presence of *ortho* substituents in the phenyl moiety of ynamides did not give any detrimental effect on the desired reaction (**2g** and **2h**). Ynamide derivatives having naphthyl or alkenyl side chains were also viable for the present hydrosilylation to furnish the corresponding products (**2i** and **2j**, respectively). In the latter case, in particular, the olefinic double bond remained intact to prove that the present hydrosilylation is highly chemoselective.

When alkyl ynamides were subjected to the standard conditions, the desired hydrosilylation also took place smoothly with complete control of regio- and stereoselectivity. For instance, butyl-, cyclopropyl-, and cyclohexyl ynamides were all reacted to afford the corresponding *β*-silyl (*Z*)-enamides in good yields (**2k**–**m**). Replacement of the *N*-tosyl (Ts) group with the *N*-mesyl (Ms) did not hamper the reactivity and selectivity (**2n**).

Scheme 2. Substrate Scope of Ynamides[a]



[a]Conditions: substrate (0.2 mmol), silane (2.0 equiv), and $B(C_6F_5)_3$ (3 mol %) in $CHCl_3$ (0.8 mL) at 60 °C. [b]Determined by ^1H NMR analysis of the crude mixture (internal standard: mesitylene). [c]For 12 h at 60 °C. [d]For 0.5 h at 25 °C.

In addition, variation of *N*-substituents in substrates from *N*-methyl to phenyl, cyclopropyl, *n*-pentyl, or cyclohexyl was compatible with the present conditions to afford the corresponding products in satisfactory yields (**2o**–**r**). The structure of **2r** was confirmed by X-ray crystallographic analysis. On the other hand, the reaction of acetylenic terminal ynamides and internal *N*-acyl ynamides was unsuccessful, and the desired vinylsilanes were not obtained.

The scope of silanes was next briefly examined (Scheme 3). Diphenylsilane, as another type of secondary hydrosilane in addition to dietheylsilane, worked well in the current reactions, still displaying excellent regio- and stereoselectivity (**2s**). Tertiary silylating reagents such as dimethylphenylsilane, triethylsilane, and benzyldimethylsilane were all efficient for the present hydrosilylation (**2s**–**v**). However, the reaction with triisopropylsilane or diethoxymethylsilane was ineffective even at elevated temperature.

The synthetic utility of the present $B(C_6F_5)_3$-catalyzed hydrosilylation of ynamides was briefly examined. The reaction procedure was convenient to carry out on a gram scale with slightly lower loading of catalyst, still maintaining the high efficiency and excellent selectivity (eq 1). In addition, the silyl group in the obtained vinylsilane products was easily removed by silver fluoride, affording synthetically versatile (*E*)-enamide **3** without scrambling the double bond (eq 2). The structure of **3** was confirmed by X-ray crystallographic analysis (see the Supporting Information).

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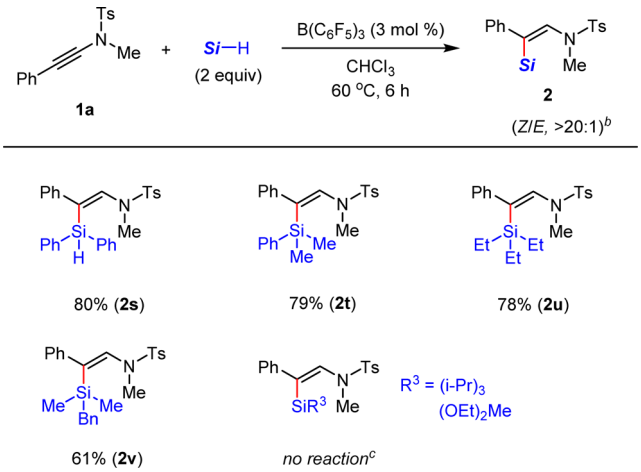
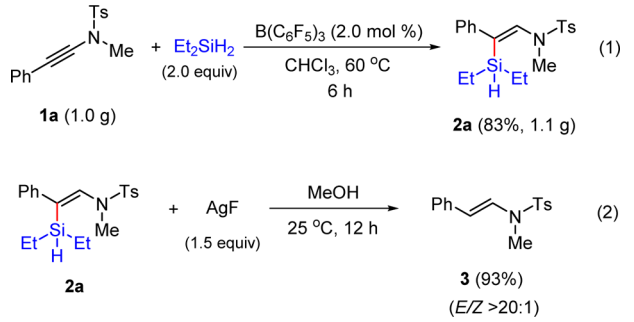
Scheme 3. Substrate Scope of Silanes[a]

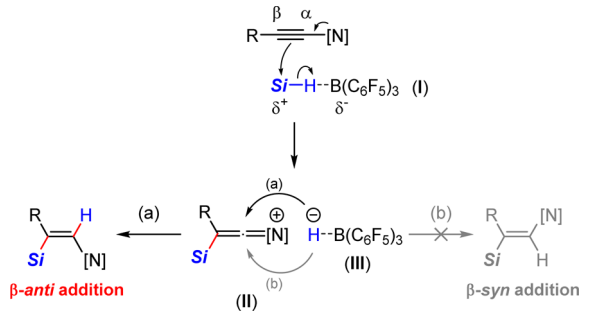


[a]Conditions: **1a** (0.2 mmol), silane (2.0 equiv), and $B(C_6F_5)_3$ (3 mol %) in $CHCl_3$ (0.8 mL) at 60 °C. [b]Determined by ^1H NMR analysis of the crude mixture (internal standard: mesitylene). [c]At 80 °C for 12 h.



We wondered about the rationale on the observed regio- and stereoselectivity in the present borane-catalyzed hydrosilyation of ynamides. In accordance with the precedents to form a borane-silane adduct **I** in situ,[14] the first step is believed to be a selective addition of ynamide to the silylium species, leading to ketene iminium species **II** (Scheme 4).[15] A subsequent hydride attack to

Scheme 4. Mode of the Present Hydrosilylation of Ynamides



the assumed intermediate **II** by borohydride **III** can proceed via two paths: (a) to the opposite side from the silyl group or (b) to the same side relative to the silyl moiety. While experimental results showed the exclusive formation of β-silyl (*Z*)-enamide products indicating the preference of path (a), computational calculations on this process were performed.

Calculations based on the density functional theory (DFT) showed that in a reaction of the presupposed ketene iminium intermediate (**INT**) with borohydride the solution-phase free energy barriers differ 3.1 kcal/mol between *anti*-addition (10.8 kcal/mol) and *syn*-addition (13.9 kcal/mol, Figure 1). This difference in the free energy barriers ($\Delta\Delta G^{\ddagger}$) is in reasonably good agreement with the experimental results, suggesting that the *anti*-addition path will be predominant.

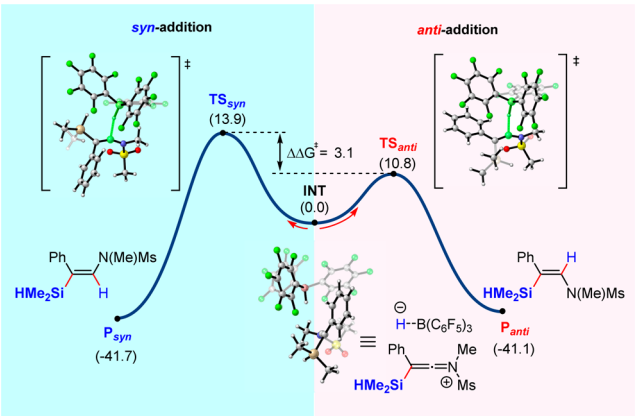


Figure 1. Relative energetics in the product-determining transition states [values in the parentheses are the relative free energies in kcal/mol; color code: H (white), B (pink), C (gray), N (purple), O (red), F (green), Si (gold), and S (yellow)].

Analysis of the geometry-optimized structure of ketene iminium species provided an additional insight into the reason for the observed stereoselectivity (Figure 2). The difference in

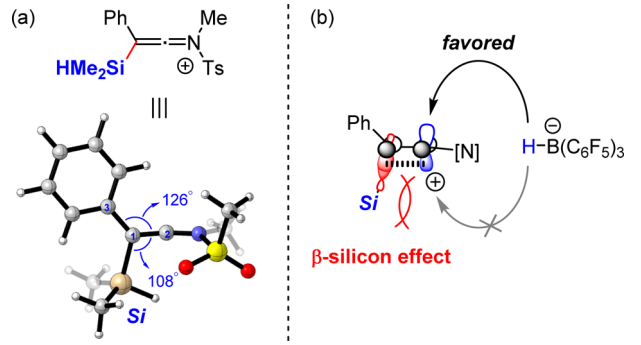


Figure 2. (a) Geometry-optimized structure of ketene iminium species and (b) schematic presentation of β-silicon effect.

dihedral angles between Si−C(1)−C(2) and C(3)−C(1)−C(2) was determined to be 18°. This geometrical bias can be attributed to the β-silicon effect to overlap the C(1)−Si and empty p-orbital of a carbocationic C(2) atom.[16] This alignment will accordingly decrease the dihedral angle of Si−C(1)−C(2) relative to that of C(3)−C(1)−C(2),[17] thus favoring the borohydride attack to ketene iminium species via the sterically more accessible *anti*-addition path.

In conclusion, the $B(C_6F_5)_3$-catalyzed highly regio- and stereoselective hydrosilylation of ynamides has been developed to deliver synthetically versatile β-silyl (*Z*)-enamide products. The scope of ynamides and silanes was broad, and the reaction proceeds efficiently under mild and convenient conditions. The observed stereoselectivity was rationalized to result from a β-silicon effect of a postulated ketene iminium intermediate.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03485.

Complete experimental details and relevant spectra for all important compounds (PDF)
Crystallographic data for **2r** (CIF)
Crystallographic data for **3** (CIF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Corey, J. Y. *Chem. Rev.* **2011**, *111*, 863. (b) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375. (c) Marciniec, B. *Catalysis of hydrosilylation of carbon-carbon multiple bonds: Recent progress*; Springer: New York, 2002.

(2) (a) Blumenkopf, T. A.; Overman, L. E. *Chem. Rev.* **1986**, *86*, 857. (b) Bunlaksananusorn, T.; Rodriguez, A. L.; Knochel, P. *Chem. Commun.* **2001**, 745. (c) Denmark, S. E.; Liu, J. H. C. *Angew. Chem., Int. Ed.* **2010**, *49*, 2978. (d) Denmark, S. E.; Pan, W. *Org. Lett.* **2001**, *3*, 61. (e) Denmark, S. E.; Regens, C. S. *Acc. Chem. Res.* **2008**, *41*, 1486. (f) Fleming, I.; Henning, R.; Plaut, H. *J. Chem. Soc., Chem. Commun.* **1984**, 29. (g) Nakao, Y.; Hiyama, T. *Chem. Soc. Rev.* **2011**, *40*, 4893. (h) Tamao, K.; Akita, M.; Maeda, K.; Kumada, M. *J. Org. Chem.* **1987**, *52*, 1100. (i) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694. (j) McAdam, C. A.; McLaughlin, M. G.; Cook, M. J. *Org. Chem. Front.* **2015**, *2*, 510. (k) McIntosh, M. C.; Weinreb, S. M. *J. Org. Chem.* **1991**, *56*, 5010.

(3) (a) Lim, D. S. W.; Anderson, E. A. *Synthesis* **2012**, *44*, 983. (b) Trost, B. *Science* **1991**, *254*, 1471.

(4) (a) Chaulagain, M. R.; Mahandru, G. M.; Montgomery, J. *Tetrahedron* **2006**, *62*, 7560. (b) De Bo, G.; Berthon-Gelloz, G.; Tinant, B.; Markó, I. E. *Organometallics* **2006**, *25*, 1881. (c) Gallenkamp, D.; Fürstner, A. *J. Am. Chem. Soc.* **2011**, *133*, 9232. (d) Iglesias, M.; Sanz Miguel, P. J.; Polo, V.; Fernández-Alvarez, F. J.; Pérez-Torrente, J. J.; Oro, L. A. *Chem. - Eur. J.* **2013**, *19*, 17559. (e) Na, Y.; Chang, S. *Org. Lett.* **2000**, *2*, 1887. (f) Trost, B. M.; Ball, Z. T.; Laemmerhold, K. M. *J. Am. Chem. Soc.* **2005**, *127*, 10028. (g) Zhou, H.; Moberg, C. *Org. Lett.* **2013**, *15*, 1444.

(5) (a) Belger, C.; Plietker, B. *Chem. Commun.* **2012**, *48*, 5419. (b) Itami, K.; Mitsudo, K.; Nishino, A.; Yoshida, J.-i. *J. Org. Chem.* **2002**, *67*, 2645. (c) McBee, J. L.; Escalada, J.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 12703. (d) Mo, Z.; Xiao, J.; Gao, Y.; Deng, L. *J. Am. Chem. Soc.* **2014**, *136*, 17414. (e) Sanada, T.; Kato, T.; Mitani, M.; Mori, A. *Adv. Synth. Catal.* **2006**, *348*, 51. (f) Wu, W.; Li, C.-J. *Chem. Commun.* **2003**, 1668. (g) Zuo, Z.; Yang, J.; Huang, Z. *Angew. Chem., Int. Ed.* **2016**, *55*, 10839. (h) McLaughlin, M. G.; Cook, M. J. *Chem. Commun.* **2011**, *47*, 11104. (i) Tojo, S.; Isobe, M. *Tetrahedron Lett.* **2005**, *46*, 381. (j) Yong, L.; Kirleis, K.; Butenschön, H. *Adv. Synth. Catal.* **2006**, *348*, 833.

(6) (a) Berthon-Gelloz, G.; Schumers, J.-M.; De Bo, G.; Markó, I. E. *J. Org. Chem.* **2008**, *73*, 4190. (b) Ding, S.; Song, L.-J.; Chung, L. W.; Zhang, X.; Sun, J.; Wu, Y.-D. *J. Am. Chem. Soc.* **2013**, *135*, 13835. (c) Rooke, D. A.; Ferreira, E. M. *J. Am. Chem. Soc.* **2010**, *132*, 11926.

(7) (a) Denmark, S. E.; Pan, W. *Org. Lett.* **2002**, *4*, 4163. (b) Marshall, J. A.; Yanik, M. M. *Org. Lett.* **2000**, *2*, 2173. (c) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2003**, *125*, 30.

(8) (a) Ding, S.; Song, L.-J.; Wang, Y.; Zhang, X.; Chung, L. W.; Wu, Y.-D.; Sun, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 5632. (b) Hamze, A.; Provot, O.; Alami, M.; Brion, J.-D. *Org. Lett.* **2005**, *7*, 5625. (c) Song, L.-J.; Ding, S.; Wang, Y.; Zhang, X.; Wu, Y.-D.; Sun, J. *J. Org. Chem.* **2016**, *81*, 6157. (d) Stork, G.; Jung, M. E.; Colvin, E.; Noel, Y. *J. Am. Chem. Soc.* **1974**, *96*, 3684. (e) Sumida, Y.; Kato, T.; Yoshida, S.; Hosoya, T. *Org. Lett.* **2012**, *14*, 1552. (f) Sun, J.; Deng, L. *ACS Catal.* **2016**, *6*, 290. (g) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2004**, *126*, 13942.

(9) (a) Huang, K.-H.; Isobe, M. *Eur. J. Org. Chem.* **2014**, *2014*, 4733. (b) Kawasaki, Y.; Ishikawa, Y.; Igawa, K.; Tomooka, K. *J. Am. Chem. Soc.* **2011**, *133*, 20712.

(10) (a) Holthausen, M. H.; Mehta, M.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2014**, *53*, 6538. (b) Molander, G. A.; Retsch, W. H. *Organometallics* **1995**, *14*, 4570. (c) Pérez, M.; Hounjet, L. J.; Caputo, C. B.; Dobrovetsky, R.; Stephan, D. W. *J. Am. Chem. Soc.* **2013**, *135*, 18308. (d) Sudo, T.; Asao, N.; Gevorgyan, V.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 2494. (e) Sudo, T.; Asao, N.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 8919.

(11) (a) Asao, N.; Sudo, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 7654. (b) Kato, N.; Tamura, Y.; Kashiwabara, T.; Sanji, T.; Tanaka, M. *Organometallics* **2010**, *29*, 5274.

(12) (a) Blackwell, J. M.; Morrison, D. J.; Piers, W. E. *Tetrahedron* **2002**, *58*, 8247. (b) Blackwell, J. M.; Sonmor, E. R.; Scoccitti, T.; Piers, W. E. *Org. Lett.* **2000**, *2*, 3921. (c) Gandhamsetty, N.; Jeong, J.; Park, J.; Park, S.; Chang, S. *J. Org. Chem.* **2015**, *80*, 7281. (d) Gandhamsetty, N.; Joung, S.; Park, S.-W.; Park, S.; Chang, S. *J. Am. Chem. Soc.* **2014**, *136*, 16780. (e) Gandhamsetty, N.; Park, S.; Chang, S. *J. Am. Chem. Soc.* **2015**, *137*, 15176. (f) Gevorgyan, V.; Rubin, M.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2001**, *66*, 1672. (g) Kim, Y.; Chang, S. *Angew. Chem., Int. Ed.* **2016**, *55*, 218. (h) Oestreich, M.; Hermeke, J.; Mohr, J. *Chem. Soc. Rev.* **2015**, *44*, 2202. (i) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440. (j) Rubin, M.; Schwier, T.; Gevorgyan, V. *J. Org. Chem.* **2002**, *67*, 1936. (k) Gandhamsetty, N.; Park, J.; Jeong, J.; Park, S.-W.; Park, S.; Chang, S. *Angew. Chem., Int. Ed.* **2015**, *54*, 6832. (l) Simonneau, A.; Oestreich, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 11905. (m) Süsse, L.; Hermeke, J.; Oestreich, M. *J. Am. Chem. Soc.* **2016**, *138*, 6940.

(13) (a) Curless, L. D.; Ingleson, M. J. *Organometallics* **2014**, *33*, 7241. (b) Keess, S.; Simonneau, A.; Oestreich, M. *Organometallics* **2015**, *34*, 790.

(14) (a) Hermeke, J.; Mewald, M.; Oestreich, M. *J. Am. Chem. Soc.* **2013**, *135*, 17537. (b) Houghton, A. Y.; Hurmalainen, J.; Mansikkamäki, A.; Piers, W. E.; Tuononen, H. M. *Nat. Chem.* **2014**, *6*, 983. (c) Nikonov, G. I.; Vyboishchikov, S. F.; Shirobokov, O. G. *J. Am. Chem. Soc.* **2012**, *134*, 5488. (d) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090. (e) Rendler, S.; Oestreich, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 5997.

(15) (a) DeKorver, K. A.; Li, H.; Lohse, A. G.; Hayashi, R.; Lu, Z.; Zhang, Y.; Hsung, R. P. *Chem. Rev.* **2010**, *110*, 5064. (b) Evano, G.; Coste, A.; Jouvin, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 2840.

(16) (a) Dallaire, C.; Brook, M. A. *Organometallics* **1990**, *9*, 2873. (b) Dallaire, C.; Brook, M. A. *Organometallics* **1993**, *12*, 2332. (c) Lambert, J. B.; Chelius, E. C. *J. Am. Chem. Soc.* **1990**, *112*, 8120. (d) Lambert, J. B.; Emblidge, R. W.; Malany, S. *J. Am. Chem. Soc.* **1993**, *115*, 1317. (e) Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 2020. (f) Lambert, J. B.; Wang, G. T.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838. (g) Pitt, C. G. *J. Organomet. Chem.* **1973**, *61*, 49. (h) Sommer, L. H.; Dorfman, E.; Goldberg, G. M.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 488.

(17) (a) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496. (b) Zhang, W.; Stone, J. A.; Brook, M. A.; McGibbon, G. A. *J. Am. Chem. Soc.* **1996**, *118*, 5764.

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