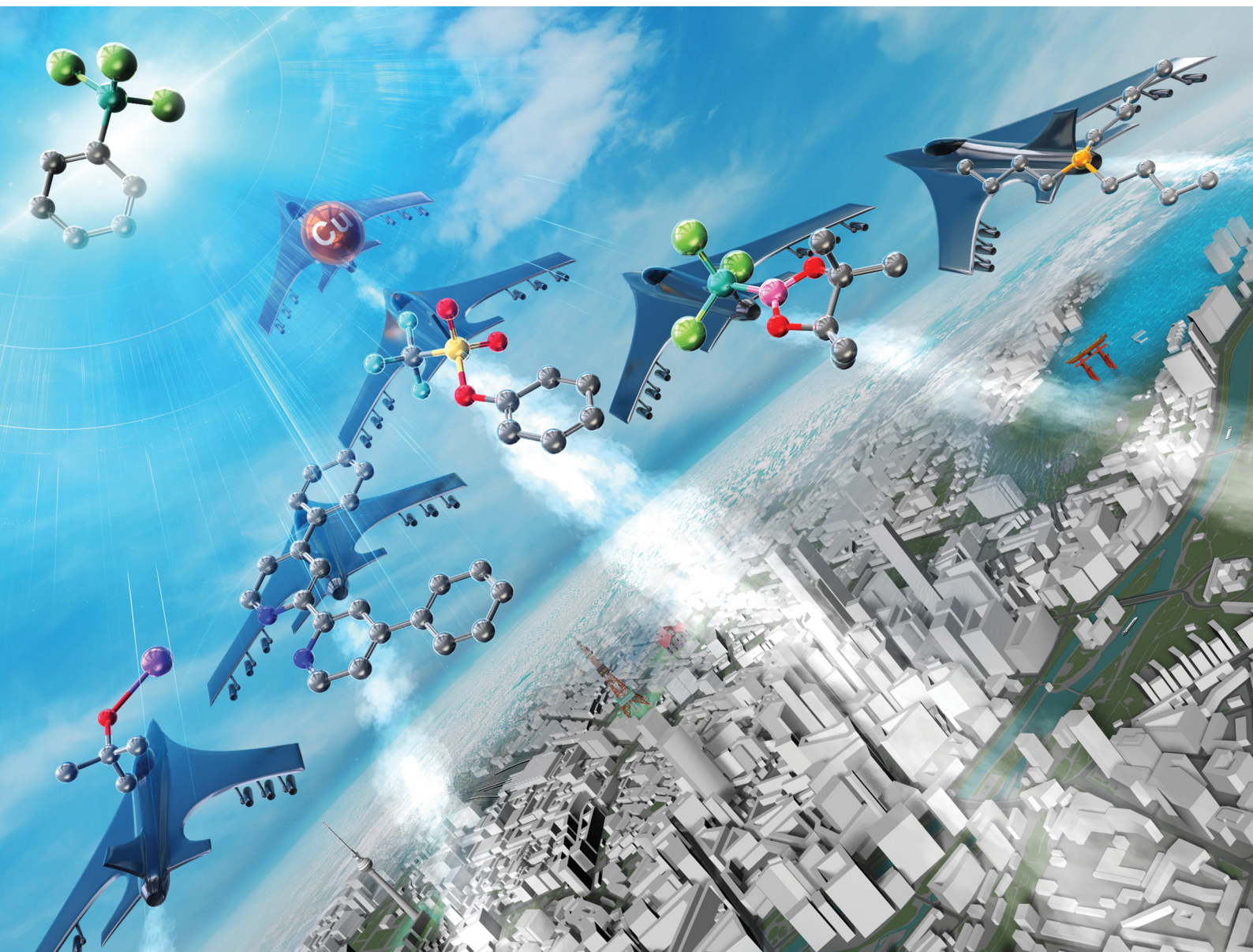


ChemComm

Chemical Communications

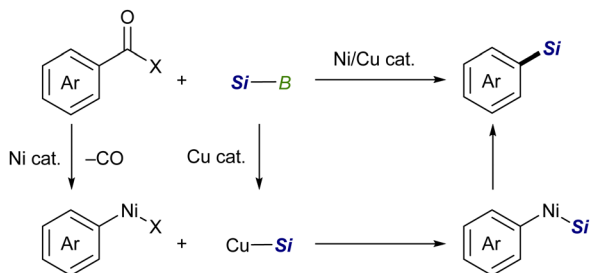
rsc.li/chemcomm



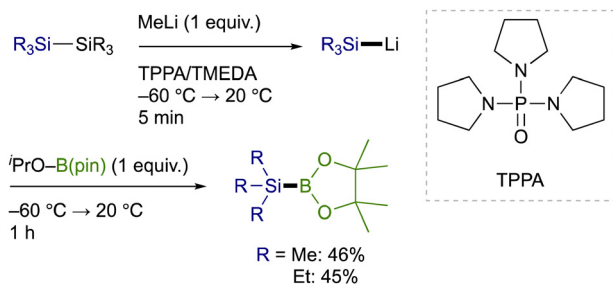
ISSN 1359-7345

COMMUNICATION

Martin Oestreich, Hiroto Yoshida *et al.*
Copper-catalyzed silylation of aryl and alkenyl triflates with
silylboronic esters avoiding base-mediated borylation



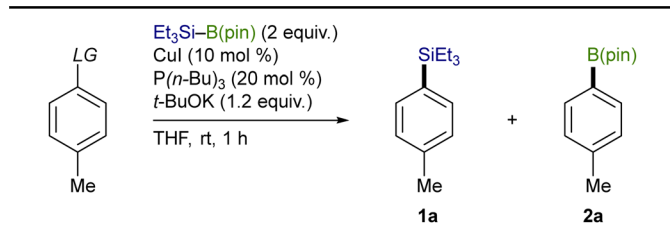
Scheme 2 Cooperative catalytic silylation of aryl electrophiles.



Scheme 3 Synthesis of trialkylsilylboronic esters via TPPA-assisted generation of trialkylsilyl lithium reagents.

base-mediated borylation while exhibiting enough reactivity toward a Cu-Si species. As was expected, the reactions of *p*-tolyl bromide/iodide with Et₃Si-B(pin) in the presence of CuI-P(*n*-Bu)₃ as a catalyst afforded *p*-tolyl-B(pin) (**2a**) as the major product, showing that chemoselective installation of a silicon functionality is indeed difficult with C(sp²)-Br/I bonds even under copper catalysis (Table 1, entries 1 and 2). On the other hand, the borylation was completely suppressed with *N*-hydroxyphthalimide ester (COONPth) or such pseudohalides as mesylate (OMs) and chloromethane sulfonate (OMc: OSO₂-CH₂Cl), but the silylation did not take place either (entries 3–5).

Table 1 Investigation of a leaving group



Entry	LG	1a ^a (%)	2a ^a (%)
1	I	13	28
2	Br	15	38
3	COONPth	0	0
4	OMs	0	0
5	OMc	0	0
6	OTs	18	0
7	OTf	34 ^b	0

^a GC yield. ^b Isolated yield. Conditions: substrate (0.3 mmol), Et₃Si-B(pin) (0.6 mmol), CuI (0.03 mmol), P(*n*-Bu)₃ (0.06 mmol), *t*-BuOK (0.36 mmol), THF (1 mL), rt, 1 h.

Finally, the desired silylation was found to proceed exclusively by employing tosylate (OTs) or triflate (OTf) as leaving groups to provide **1a** in 18% and 34% yield, respectively (entries 6 and 7).

Using an OTf moiety as the better leaving group, we next carried out the silylation with various copper salts in the presence of *t*-BuOK (base) and P(*n*-Bu)₃ (ligand) and found that CuI was optimal (Table 2, entries 1–7). The use of *t*-BuOK turned out to be indispensable for the silylation, and thus reactions with other alkoxides of lower basicity were totally unsuccessful (entries 8–11). Among the ligands surveyed, the combined use of P(*n*-Bu)₃ (10 mol%) and 4,4'-diphenyl-2,2'-bipyridine (4,4'-Phbpy) (10 mol%) proved to be the most effective as was the case of our previously reported Cu-catalyzed silylation of C(sp³)-COONPth (entry 12).^{7b,11} No desired product was obtained in the absence of the ligands and/or CuI, verifying the necessity of the copper catalysis together with the ligand system for the smooth silylation (entries 13 and 14).

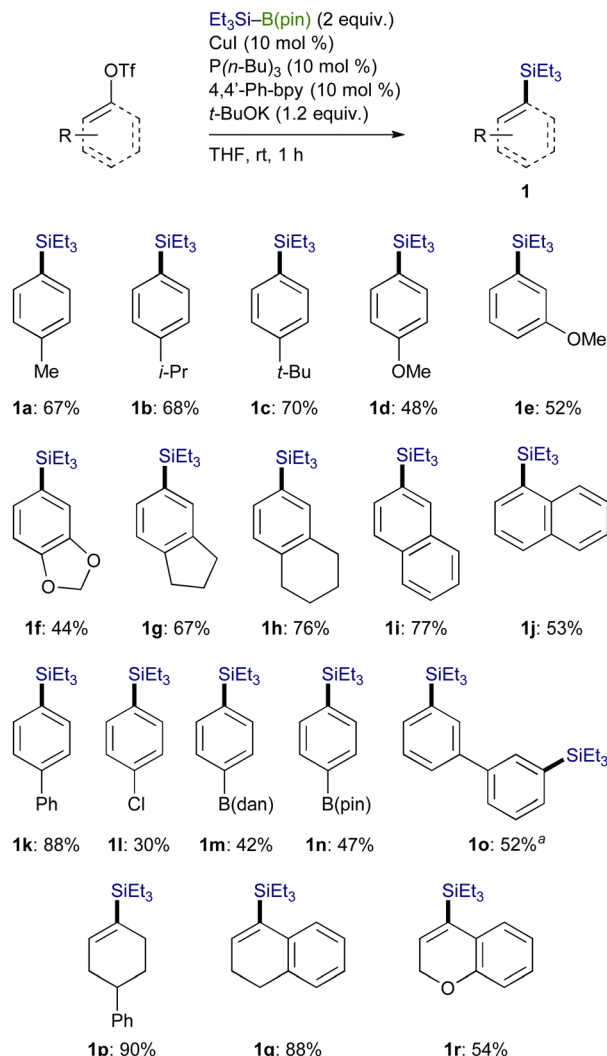
A variety of aryl triflates bearing an electron-donating group could readily undergo the silylation under the optimum conditions to furnish the respective aryl silanes (**1a–1h**) with exclusive chemoselectivity, and borylation-based side-products were not generated at all (Scheme 4). In addition, the reaction of naphthyl and biphenyl triflates also took place to afford the corresponding arylsilanes (**1i–1k**) in moderate to good yields. Although the silylation of functionalized aryl triflates with Cl, B(dan) (dan: naphthalene-1,8-diaminato), and B(pin) (pin: pinacolato) also proceeded under the present reaction conditions, the yield became somewhat lower (**1l–1n**). The reaction was applicable to a bis-triflate, whose C-OTf bonds could both be transformed into C-SiEt₃ bonds to give **1o**. Furthermore,

Table 2 Optimization of the reaction conditions

Entry	[Cu]	Ligand	Base	GC yield (%)
1	CuI	P(<i>n</i> -Bu) ₃	<i>t</i> -BuOK	34 ^a
2	CuCl	P(<i>n</i> -Bu) ₃	<i>t</i> -BuOK	29
3	CuBr·SMe ₂	P(<i>n</i> -Bu) ₃	<i>t</i> -BuOK	27
4	CuTc	P(<i>n</i> -Bu) ₃	<i>t</i> -BuOK	9
5	CuSCN	P(<i>n</i> -Bu) ₃	<i>t</i> -BuOK	10
6	Cu(MeCN) ₄ ·PF ₆	P(<i>n</i> -Bu) ₃	<i>t</i> -BuOK	7
7	Cu(MeCN) ₄ ·BF ₄	P(<i>n</i> -Bu) ₃	<i>t</i> -BuOK	26
8	CuI	P(<i>n</i> -Bu) ₃	MeONa	0
9	CuI	P(<i>n</i> -Bu) ₃	MeOK	0
10	CuI	P(<i>n</i> -Bu) ₃	<i>t</i> -BuOLi	0
11	CuI	P(<i>n</i> -Bu) ₃	<i>t</i> -BuONa	Trace
12	CuI	P(<i>n</i> -Bu) ₃ /4,4'-Phbpy	<i>t</i> -BuOK	67 ^a
13	CuI	None	<i>t</i> -BuOK	0
14	None	None	<i>t</i> -BuOK	0

^a Isolated yield. Conditions: *p*-tolyl-OTf (0.3 mmol), Et₃Si-B(pin) (0.6 mmol), copper salt (0.03 mmol), ligand (0.06 mmol), base (0.36 mmol), THF (1 mL), rt, 1 h.



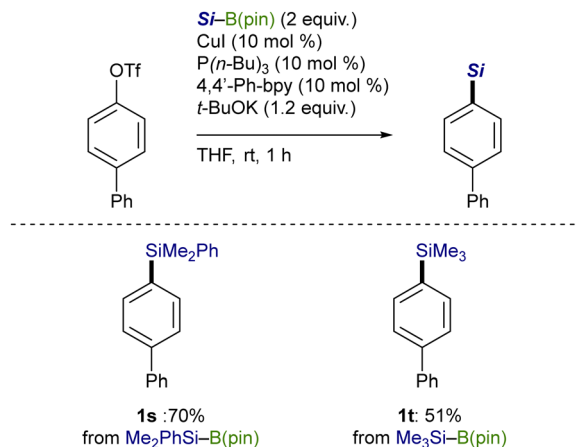


Scheme 4 Substrate scope on triflates. Conditions: triflate (0.3 mmol), $\text{Et}_3\text{Si-B(pin)}$ (0.6 mmol), CuI (0.03 mmol), $\text{P}(n\text{-Bu})_3$ (0.03 mmol), 4,4'-Phbpy (0.03 mmol), $t\text{-BuOK}$ (0.36 mmol), THF (1 mL), rt, 1 h. ^a Reaction was carried out with a ditriflate (0.15 mmol).

alkenyl triflates, readily prepared from the respective ketones, could also participate in the present reaction, providing good yields of various alkenylsilanes (**1p–1r**).

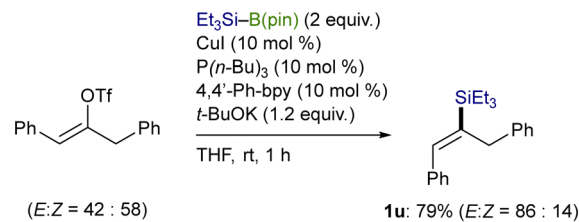
The catalytic silylation was also applicable to $\text{Me}_2\text{PhSi-B(pin)}$, giving an arylsilane (**1s**) in 70% yield (Scheme 5). It should be noted that $\text{Me}_3\text{Si-B(pin)}$, which can practically be prepared by our method (Scheme 3, *vide supra*), has proven to be convertible into the corresponding product (**1t**) in a straightforward manner, providing an alternative approach for the Me_3Si -installing process.¹²

As depicted in Scheme 6, control experiments were conducted to gain mechanistic insights into the $\text{C}(\text{sp}^2)\text{-Si}$ bond-forming process. The stereochemical outcome with an acyclic alkenyl triflate (isomeric ratio = 58 : 42) indicates that a radical pathway would be operative in the present substitution: (*E*)-alkenylsilane (**1u**) became enriched through a stereoconvergent pathway, where an alkenyl radical intermediate rapidly

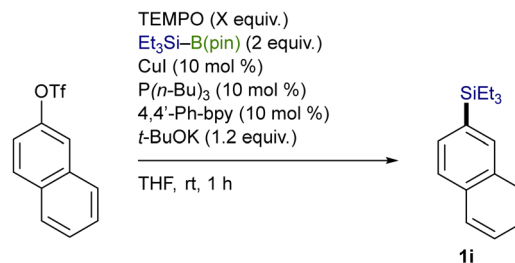


Scheme 5 Silylation with other silyboronic esters. Conditions: biphenyl-OTf (0.3 mmol), silyboronic ester (0.6 mmol), CuI (0.03 mmol), $\text{P}(n\text{-Bu})_3$ (0.03 mmol), 4,4'-Phbpy (0.03 mmol), $t\text{-BuOK}$ (0.36 mmol), THF (1 mL), rt, 1 h.

Stereochemistry with an alkenyl triflate



Radical trap experiment



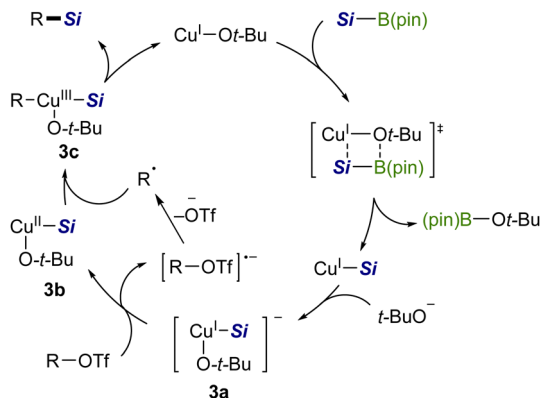
X	Yield of 1i (%)
0	77
1.5	52
3.0	39

Scheme 6 Control experiments.

isomerized before the silylation.¹³ Besides, the addition of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), a radical scavenger, to the reaction of 2-naphthyl triflate reduced the yields of **1i** as the amount of TEMPO increased, which also supports the possibility of the radical pathway.¹⁴

Based on the above results, the silylation would be triggered by the generation of a $\text{Cu}^{\text{I}}\text{-Si}$ species *via* σ -bond metathesis between a copper alkoxide [$\text{Cu}^{\text{I}}\text{-O}t\text{-Bu}$] and a silyboronic ester (Scheme 7).^{7a} Then $t\text{-BuO}^-$ coordinates to $\text{Cu}^{\text{I}}\text{-Si}$ to provide an





Scheme 7 A proposed catalytic cycle.

electron-rich silylcuprate species $[t\text{-BuO-Cu}^{\text{I}}\text{-Si}]^-$ (**3a**), which may serve as a single-electron reductant for an aryl/alkenyl triflate. The resulting radical anion then releases TfO^- of good leaving ability to generate an isomerizable free radical (cf. Scheme 6), which readily recombines with $[t\text{-BuO-Cu}^{\text{II}}\text{-Si}]$ (**3b**), affording a Cu^{III} complex (**3c**).¹⁵ Finally, **3c** undergoes reductive elimination to provide a $\text{C}(\text{sp}^2)\text{-Si}$ product with the regeneration of the copper alkoxide.

In conclusion, we have demonstrated for the first time that $\text{C}(\text{sp}^2)$ electrophiles undergo selective silylation with silylboronic esters under copper-only catalysis by using a triflate moiety as an optimal leaving group, which leads to the exclusive formation of various aryl/alkenyl-silanes with complete suppression of undesired base-mediated borylation. Moreover, the mechanistic studies suggested that the present silylation may involve a radical pathway. A similar silylation of aryl and alkenyl carbamates under iron catalysis was reported by the Feng group;^{12e} however, the present silylation is a meaningful expansion of the reactivity as this proceeds under milder conditions and permits the use of easily accessible triflates as substrates. Further studies on the catalytic utilization of silylboronic esters as well as on details of the reaction mechanism are in progress.

S. K., M. O., and H. Y. designed the study. M. N. and T. Y. aided in interpreting the results. H. Y. supervised the project. S. K. collected all data and wrote the manuscript with support from M. O. and H. Y. All authors have approved the final version of the manuscript.

This work was supported by the Natural Science Center for Basic Research and Development, Hiroshima University (NBARD-00001). S. K. acknowledges the JSPS fellowship for young scientists, JSPS KAKENHI grant number JP20J14589 and JSPS Overseas Challenge Program for Young Researchers.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 For reviews on the chemistry of silylboranes, see: (a) J. Feng, W. Mao, L. Zhang and M. Oestreich, *Chem. Soc. Rev.*, 2021,

- 50, 2010; (b) M. Oestreich, E. Hartmann and M. Mewald, *Chem. Rev.*, 2013, **113**, 402; (c) T. Ohmura and M. Sugimoto, *Bull. Chem. Soc. Jpn.*, 2009, **82**, 29.
- 2 For a review on the reactions of silylcopper species, see: W. Xue and M. Oestreich, *ACS Cent. Sci.*, 2020, **6**, 1070.
- 3 For the seminal works with alkynes, see: (a) T. Fujihara, Y. Tani, K. Semba, J. Terao and Y. Tsuji, *Angew. Chem., Int. Ed.*, 2012, **51**, 11487; (b) F. Meng, H. Jang and A. H. Hoveyda, *Chem. - Eur. J.*, 2013, **19**, 3204.
- 4 For the seminal works with carbonyl compounds, see: (a) C. Kleeberg, E. Feldmann, E. Hartmann, D. J. Vyas and M. Oestreich, *Chem. - Eur. J.*, 2011, **17**, 13538; (b) J. Plotzitzka and C. Kleeberg, *Inorg. Chem.*, 2017, **56**, 667.
- 5 For the seminal works with allylic electrophiles, see: (a) D. J. Vyas and M. Oestreich, *Angew. Chem., Int. Ed.*, 2010, **49**, 8513; (b) L. B. Delvos, D. J. Vyas and M. Oestreich, *Angew. Chem., Int. Ed.*, 2013, **52**, 465; (c) C. K. Hazra, E. Irran and M. Oestreich, *Eur. J. Org. Chem.*, 2013, 4903; (d) M. Takeda, R. Shintani and T. Hayashi, *J. Org. Chem.*, 2013, **78**, 5007; for the seminal works with propargylic electrophiles, see: (e) D. J. Vyas, C. K. Hazra and M. Oestreich, *Org. Lett.*, 2011, **13**, 4462.
- 6 For ionic reactions with alkyl electrophiles, see: (a) J. Scharfbier and M. Oestreich, *Synlett*, 2016, 127; (b) J. Scharfbier, H. Hazrati and M. Oestreich, *Org. Lett.*, 2017, **19**, 656; (c) J. Scharfbier, B. M. Gross and M. Oestreich, *Angew. Chem., Int. Ed.*, 2020, **59**, 1577.
- 7 For radical reactions with alkyl electrophiles, see: (a) W. Xue, Z.-W. Qu, S. Grimme and M. Oestreich, *J. Am. Chem. Soc.*, 2016, **138**, 14222; (b) W. Xue and M. Oestreich, *Angew. Chem., Int. Ed.*, 2017, **56**, 1164; for a review, see: (c) S. Bähr, W. Xue and M. Oestreich, *ACS Catal.*, 2019, **9**, 16.
- 8 (a) E. Yamamoto, K. Izumi, Y. Horita and H. Ito, *J. Am. Chem. Soc.*, 2012, **134**, 19997; (b) E. Yamamoto, K. Izumi, Y. Horita, S. Ukigai and H. Ito, *Top. Catal.*, 2014, **57**, 940; (c) E. Yamamoto, S. Ukigai and H. Ito, *Chem. Sci.*, 2015, **6**, 2943; (d) R. Uematsu, E. Yamamoto, S. Maeda, H. Ito and T. Taketsugu, *J. Am. Chem. Soc.*, 2015, **137**, 409; (e) E. Yamamoto, K. Izumi, R. Shishido, T. Seki, N. Tokodai and H. Ito, *Chem. - Eur. J.*, 2016, **22**, 17547; for a review, see: (f) E. Yamamoto, S. Maeda, T. Taketsugu and H. Ito, *Synlett*, 2017, 1258.
- 9 (a) L. Guo, A. Chatupheeraphat and M. Rueping, *Angew. Chem., Int. Ed.*, 2016, **55**, 11810; (b) X. Pu, J. Hu, Y. Zhao and Z. Shi, *ACS Catal.*, 2016, **6**, 6692; (c) S.-C. Lee, L. Guo, H. Yue, H.-H. Li and M. Rueping, *Synlett*, 2017, 2594; (d) X. Wang, Z. Wang and Y. Nishihara, *Chem. Commun.*, 2019, **55**, 10507; (e) W. Srimontree, L. Guo and M. Rueping, *Chem. - Eur. J.*, 2020, **26**, 423.
- 10 S. Kamio, T. Imagawa, M. Nakamoto, M. Oestreich and H. Yoshida, *Synthesis*, 2021, 4678.
- 11 For the effects of other ligands and full optimization of the reaction conditions, see ESI^\dagger for details.
- 12 For the seminal works on catalytic Me_3Si -installation reactions, see: (a) H. Matsumoto, S. Nagashima, K. Yoshihiro and Y. Nagai, *J. Organomet. Chem.*, 1975, **85**, C1; (b) D. Azarian, S. S. Dua, C. Eaborn and D. R. M. Walton, *J. Organomet. Chem.*, 1976, **117**, C55; (c) H. Matsumoto, K. Yoshihiro, S. Nagashima, H. Watanabe and Y. Nagai, *J. Organomet. Chem.*, 1977, **128**, 409; (d) L. J. Gooßen and A. S. Ferwan, *Synlett*, 2000, 1801; for recent works on constructing $\text{C}(\text{sp}^2)\text{-SiEt}_3$ bonds with $\text{Et}_3\text{Si-B}(\text{pin})$, see: (e) J. Zhang, Y. Zhang, S. Geng, S. Chen, Z. Liu, X. Zeng, Y. He and Z. Feng, *Org. Lett.*, 2020, **22**, 2669; (f) J. Jia, X. Zeng, Z. Liu, L. Zhao, C.-Y. He, X.-F. Li and Z. Feng, *Org. Lett.*, 2020, **22**, 2816.
- 13 Less steric repulsion between a Ph group of the *cis*-alkenyl radical and an incoming **3b** may determine the stereoselectivity.
- 14 The naphthyl moiety was not trapped by TEMPO while a $\text{Et}_3\text{Si-TEMPO}$ adduct was generated as a side-product. In sharp contrast to the results obtained with TEMPO, the addition of 9,10-dihydroanthracene, a known radical scavenger, hardly influenced the course of the silylation, implying that an ionic mechanism involving direct σ -bond metathesis between Cu-SiEt_3 and aryl/alkenyl triflates might still be conceivable.
- 15 For our previous reports on similar copper-catalyzed borylations of alkyl, alkenyl and aryl halides with diborons, see: (a) H. Yoshida, Y. Takemoto, S. Kamio, I. Osaka and K. Takaki, *Org. Chem. Front.*, 2017, **4**, 1215; (b) H. Yoshida, S. Kamio and I. Osaka, *Chem. Lett.*, 2018, **47**, 957.

