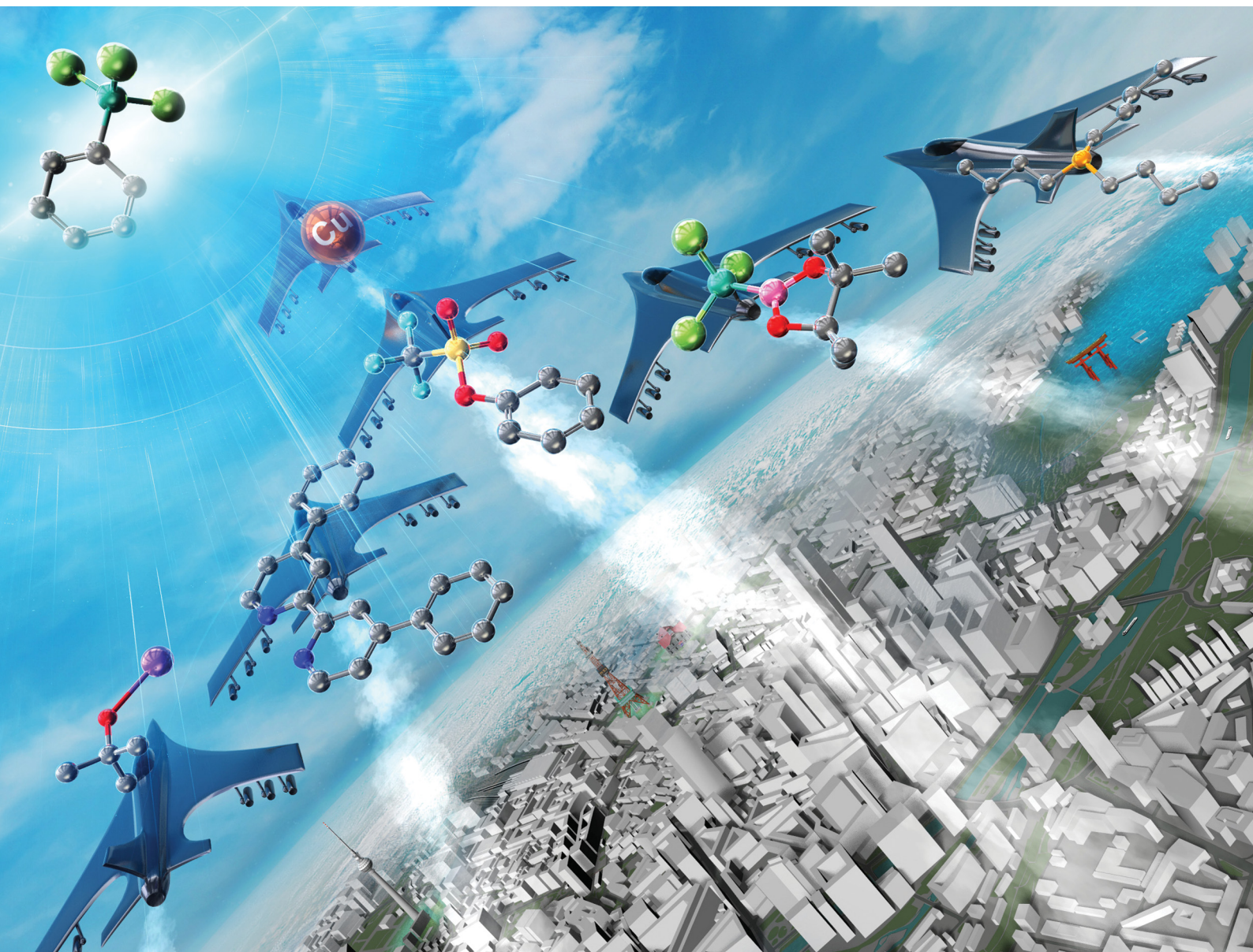


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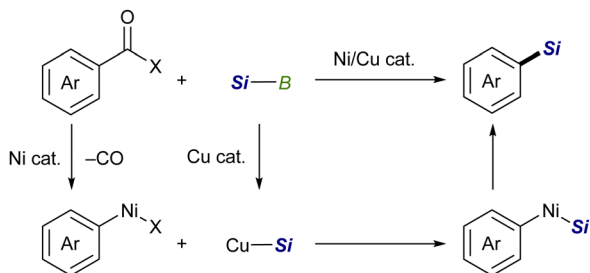
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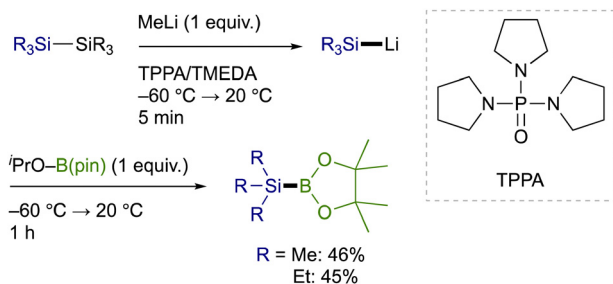
Martin Oestreich, Hiroto Yoshida *et al.*  
Copper-catalyzed silylation of aryl and alkenyl triflates with  
silyboronic esters avoiding base-mediated borylation







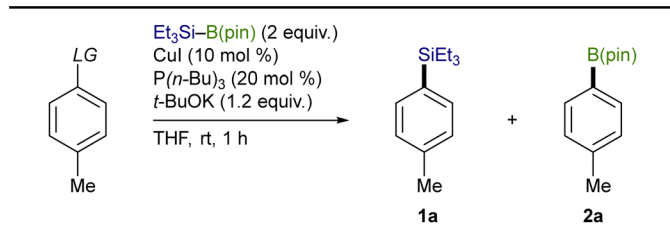
Scheme 2 Cooperative catalytic silylation of aryl electrophiles.



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  $\text{Et}_3\text{Si-B(pin)}$  in the presence of  $\text{CuI-P}(n\text{-Bu})_3$  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  $\text{C}(\text{sp}^2)\text{-Br/I}$  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:  $\text{OSO}_2\text{-CH}_2\text{Cl}$ ), but the silylation did not take place either (entries 3–5).

Table 1 Investigation of a leaving group



Entry	LG	<b>1a</b> <sup>a</sup> (%)	<b>2a</b> <sup>a</sup> (%)
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 <sup>b</sup>	0

<sup>a</sup> GC yield. <sup>b</sup> Isolated yield. Conditions: substrate (0.3 mmol),  $\text{Et}_3\text{Si-B(pin)}$  (0.6 mmol),  $\text{CuI}$  (0.03 mmol),  $\text{P}(n\text{-Bu})_3$  (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  $\text{P}(n\text{-Bu})_3$  (ligand) and found that  $\text{CuI}$  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  $\text{P}(n\text{-Bu})_3$  (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  $\text{C}(\text{sp}^3)\text{-COONPth}$  (entry 12).<sup>7b,11</sup> No desired product was obtained in the absence of the ligands and/or  $\text{CuI}$ , verifying the necessity of the copper catalysis together with the ligand system for the smooth silylation (entries 13 and 14).

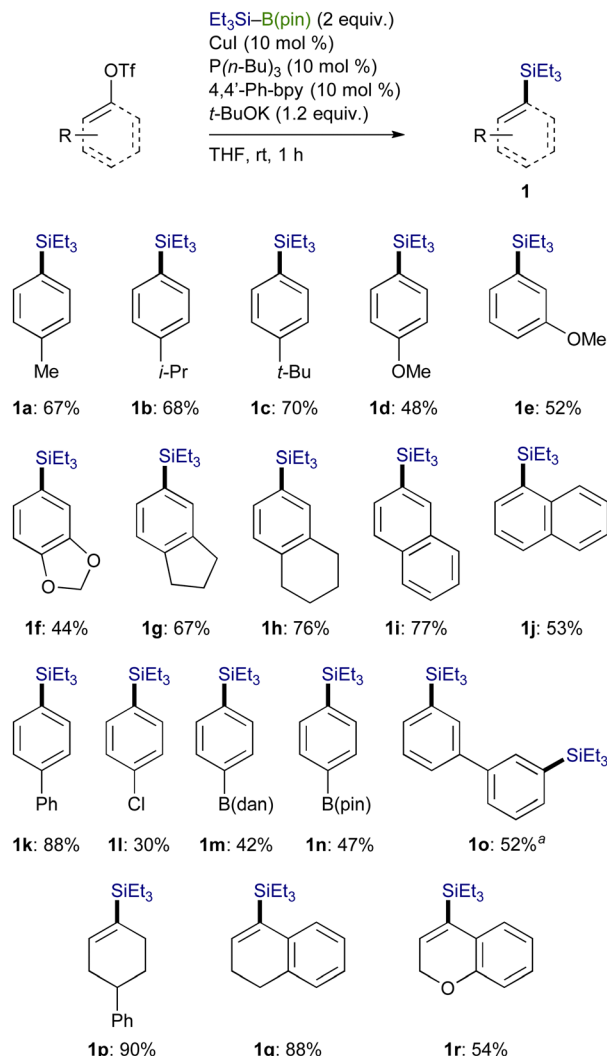
A variety of aryl triflates bearing an electron-donating group could readily undergo the silylation under the optimum conditions to furnish the respective aryl silanes (**1a–1h**) with exclusive chemoselectivity, and borylation-based side-products were not generated at all (Scheme 4). In addition, the 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–SiEt<sub>3</sub> bonds to give **1o**. Furthermore,

Table 2 Optimization of the reaction conditions

Entry	[Cu]	Ligand	Base	GC yield (%)
1	$\text{CuI}$	$\text{P}(n\text{-Bu})_3$	<i>t</i> -BuOK	34 <sup>a</sup>
2	$\text{CuCl}$	$\text{P}(n\text{-Bu})_3$	<i>t</i> -BuOK	29
3	$\text{CuBr}\cdot\text{SMe}_2$	$\text{P}(n\text{-Bu})_3$	<i>t</i> -BuOK	27
4	$\text{CuTc}$	$\text{P}(n\text{-Bu})_3$	<i>t</i> -BuOK	9
5	$\text{CuSCN}$	$\text{P}(n\text{-Bu})_3$	<i>t</i> -BuOK	10
6	$\text{Cu}(\text{MeCN})_4\cdot\text{PF}_6$	$\text{P}(n\text{-Bu})_3$	<i>t</i> -BuOK	7
7	$\text{Cu}(\text{MeCN})_4\cdot\text{BF}_4$	$\text{P}(n\text{-Bu})_3$	<i>t</i> -BuOK	26
8	$\text{CuI}$	$\text{P}(n\text{-Bu})_3$	MeONa	0
9	$\text{CuI}$	$\text{P}(n\text{-Bu})_3$	MeOK	0
10	$\text{CuI}$	$\text{P}(n\text{-Bu})_3$	<i>t</i> -BuOLi	0
11	$\text{CuI}$	$\text{P}(n\text{-Bu})_3$	<i>t</i> -BuONa	Trace
12	$\text{CuI}$	$\text{P}(n\text{-Bu})_3/4,4'\text{-Phbpy}$	<i>t</i> -BuOK	67 <sup>a</sup>
13	$\text{CuI}$	None	<i>t</i> -BuOK	0
14	None	None	<i>t</i> -BuOK	0

<sup>a</sup> Isolated yield. Conditions: *p*-tolyl–OTf (0.3 mmol),  $\text{Et}_3\text{Si-B(pin)}$  (0.6 mmol), copper salt (0.03 mmol), ligand (0.06 mmol), base (0.36 mmol), THF (1 mL), rt, 1 h.



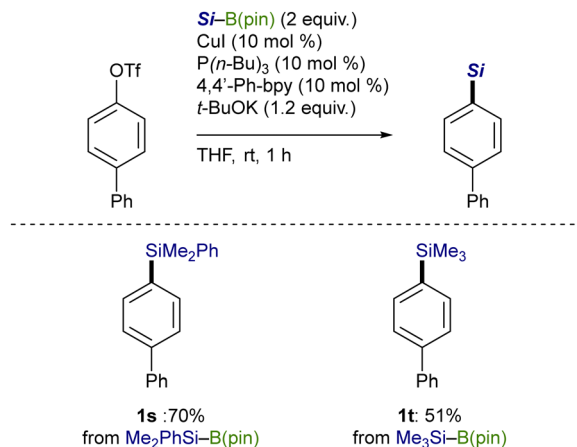


**Scheme 4** Substrate scope on triflates. Conditions: triflate (0.3 mmol),  $\text{Et}_3\text{Si-B(pin)}$  (0.6 mmol), CuI (0.03 mmol),  $\text{P}(n\text{-Bu})_3$  (0.03 mmol), 4,4'-Phbpy (0.03 mmol),  $t\text{-BuOK}$  (0.36 mmol), THF (1 mL), rt, 1 h. <sup>a</sup> Reaction was carried out with a ditriflate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

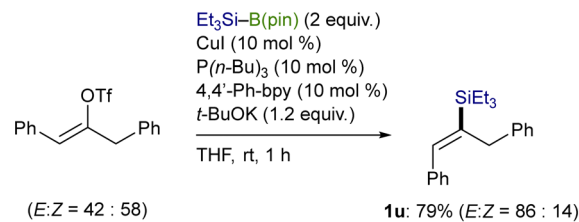
The catalytic silylation was also applicable to  $\text{Me}_2\text{PhSi-B(pin)}$ , giving an arylsilane (**1s**) in 70% yield (Scheme 5). It should be noted that  $\text{Me}_3\text{Si-B(pin)}$ , which can practically be prepared by our method (Scheme 3, *vide supra*), has proven to be convertible into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

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

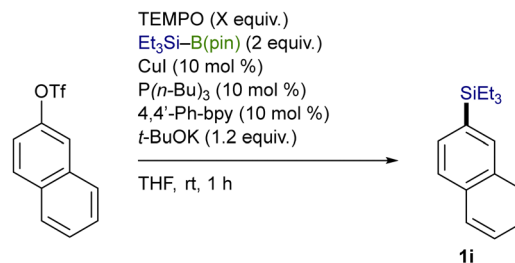


**Scheme 5** Silylation with other silyboronic esters. Conditions: biphenyl-OTf (0.3 mmol), silyboronic ester (0.6 mmol), CuI (0.03 mmol),  $\text{P}(n\text{-Bu})_3$  (0.03 mmol), 4,4'-Phbpy (0.03 mmol),  $t\text{-BuOK}$  (0.36 mmol), THF (1 mL), rt, 1 h.

#### Stereochemistry with an alkenyl triflate



#### Radical trap experiment



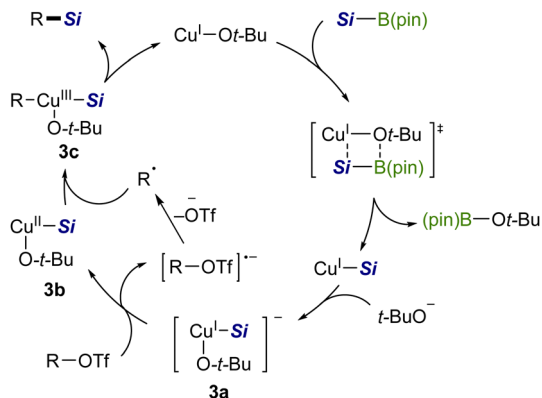
X	Yield of <b>1i</b> (%)
0	77
1.5	52
3.0	39

**Scheme 6** Control experiments.

isomerized before the silylation.<sup>13</sup> 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.<sup>14</sup>

Based on the above results, the silylation would be triggered by the generation of a  $\text{Cu}^{\text{I}}\text{-Si}$  species *via*  $\sigma$ -bond metathesis between a copper alkoxide [ $\text{Cu}^{\text{I}}\text{-O}t\text{-Bu}$ ] and a silyboronic ester (Scheme 7).<sup>7a</sup> 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  $\text{TfO}^-$  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  $\text{Cu}^{\text{III}}$  complex (**3c**).<sup>15</sup> 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;<sup>12e</sup> 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.

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## Conflicts of interest

There are no conflicts to declare.

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