

## A Mild Synergistic Ni/Cu-Catalyzed Silylation via C–O Cleavage

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Supporting Information Placeholder

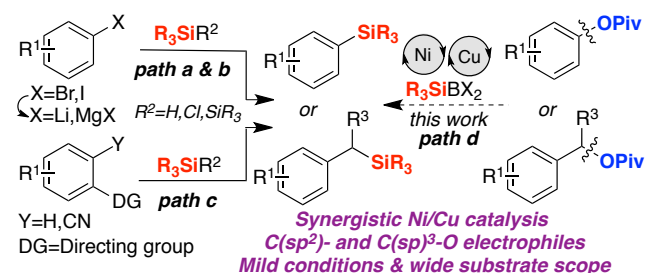
**ABSTRACT:** A synergistic Ni/Cu-catalyzed silylation of unactivated C–O electrophiles derived from simple alcohols is described. This transformation is characterized by its wide scope and mild conditions, thus providing a direct access to synthetically versatile silylated compounds. The protocol allows for the coupling of C(sp<sup>2</sup>)–O and even C(sp<sup>3</sup>)–O bonds with similar efficiency.

Synergistic catalysis has recently received a considerable interest for designing unconventional synthetic strategies that are unattainable by other means.<sup>1</sup> Among these, the synergistic use of Pd and Cu catalysts has shown to be particularly effective in methodologies that have changed the landscape of organic synthesis, such as the Sonogashira-Hagihara coupling<sup>2</sup> or the Wacker-Tsuji oxidation,<sup>3</sup> among others. While Ni catalysts play a dominant role in the cross-coupling arena,<sup>4</sup> it comes as a surprise that a synergistic effect of Ni and Cu catalysts has been virtually unexplored in homogeneous catalysis.<sup>5</sup> Therefore, the discovery of new protocols within this field might lead to novel synthetic routes towards advanced intermediates, counterintuitive at first sight, thus increasing our organic chemist's repertoire.

In recent years, the utilization of C–O electrophiles has received considerable attention due to their lack of toxicity and the readily availability of phenol as compared to commonly employed organic halides.<sup>6</sup> Unlike the use of activated aryl sulfonates, a limited knowledge has been acquired when employing simpler aryl esters via catalytic C–O cleavage. This is probably due to the high activation barrier for C–O cleavage, the proclivity of esters towards hydrolysis under strong basic conditions and the site-selectivity issues in the presence of multiple C–O reaction sites.<sup>6</sup> Despite the advances realized, the vast majority of C–O bond-cleavage reactions are restricted to the formation of C–C bonds. Indeed, the development of catalytic C–heteroatom bond-forming reactions remains an elusive task in the cross-coupling arena when utilizing unactivated C–O bonds.<sup>7</sup> We envisioned that organic silanes, valuable synthetic interme-

diates of considerable interest in medicinal and material science,<sup>8</sup> could be within reach by a C–Si bond-forming event from unactivated C–O electrophiles under certain reaction conditions. Such a method would constitute an alternative to classical metal/halogen exchange (Scheme 1, path a),<sup>9</sup> the use of organic halides as coupling partners (path b)<sup>10</sup> and C–H<sup>11a–e</sup> or C–CN functionalization techniques<sup>11e–f</sup> that are conducted at high temperatures<sup>11</sup> and using *ortho*-directing groups<sup>11a–e</sup> (path c). As part of our ongoing studies in this field,<sup>12</sup> we report herein the discovery of a synergistic effect of Ni and Cu catalysts that allows for a C–Si bond-forming reaction via cleavage of unactivated C–O bonds in ester derivatives (path d).<sup>13</sup> The method is distinguished by its mild conditions, robustness and wide substrate scope, including the formation of particularly elusive C(sp<sup>3</sup>)–Si bonds,<sup>14</sup> and without compromising its application profile.

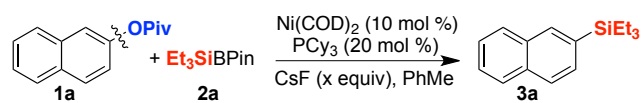
### Scheme 1. Synthesis of Aryl and Aliphatic Silanes



We began our investigations by examining the reactivity of **1a** using nickel catalysts (Table 1).<sup>15,16</sup> While silylboranes have extensively been employed for promoting silylborylation of unsaturated C–C bonds,<sup>17</sup> to the best of our knowledge their utilization en route to aryl silanes has not been explored. As shown in entry 3, we found promising results when employing readily available **2a**,<sup>18</sup> Ni(COD)<sub>2</sub> as the catalyst and PCy<sub>3</sub> as the supporting ligand. In line with our studies in the field, we found that the absence of COD had a deleterious impact on reactivity (entries 1 and 2), suggesting that non-innocent ancillary ligands might stabilize the active species within the catalytic cycle.<sup>12</sup> As anticipat-

ed,<sup>17</sup> additives played a crucial role by activating the Si–B bond (entries 4, 5). As shown in entries 6–8, the inclusion of AgF or CuF<sub>2</sub> was particularly effective for our purposes, suggesting the intermediacy of MSiEt<sub>3</sub> species (M= Ag (I), Cu (II)).<sup>19</sup> Importantly, the combination of CuF<sub>2</sub> and CsF allowed for the reaction to occur at 50 °C in 2 h reaction time (entry 13). A simple filtration of the crude mixture through a plug of Celite® was necessary, thus greatly simplifying the workup. Interestingly, the counterion and oxidation state of the additives utilized were found to be critical factors for success (entries 10–12). Control experiments in which the Ni catalyst was omitted resulted in no product formation, suggesting that both Ni and Cu cooperatively assist the C–O bond-cleavage/C–Si bond-forming event (entry 14). Although silylboranes have been recently used as a platform for preparing aryl boronic esters,<sup>18,20</sup> not even traces of C–B bond-formation were detected by NMR spectroscopy of the crude reaction mixture, thus showing the distinctive features of our catalytic protocol.

**Table 1. Optimization of the Reaction Conditions<sup>a</sup>**



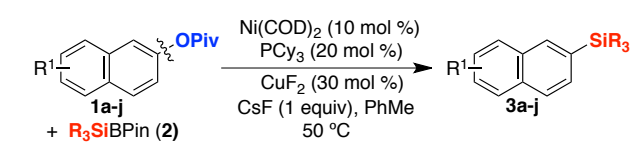
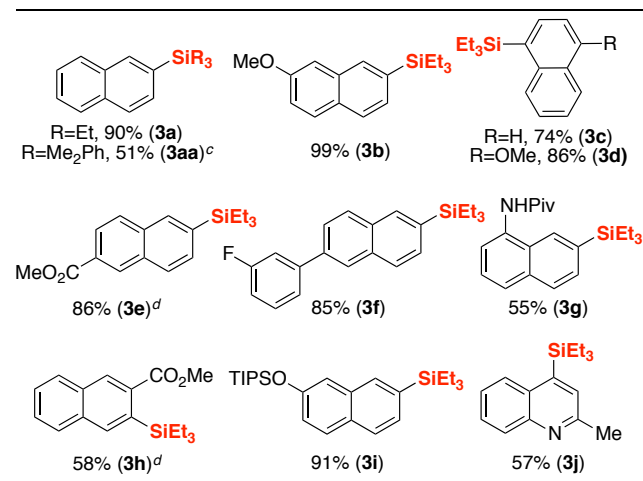
Entry	Ni catalyst	CsF (x)	Additive (mol %)	T (°C)	3a (%) <sup>b</sup>
1	Ni(PCy <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )	0	–	130	0
2	NiCl <sub>2</sub> (PCy <sub>3</sub> ) <sub>2</sub>	0	–	130	1 <sup>c</sup>
3	Ni(COD) <sub>2</sub>	0	–	130	24
4	Ni(COD) <sub>2</sub>	0	K <sub>3</sub> PO <sub>4</sub> (100)	130	39
5	Ni(COD) <sub>2</sub>	0	CsF (30)	130	44
6	Ni(COD) <sub>2</sub>	0	AgF (30)	130	56
7	Ni(COD) <sub>2</sub>	0	CuF <sub>2</sub> (30)	130	61
8	Ni(COD) <sub>2</sub>	0	CuF <sub>2</sub> (30)	110	56
9	Ni(COD) <sub>2</sub>	1	CuF <sub>2</sub> (30)	110	88 (85) <sup>d</sup>
10	Ni(COD) <sub>2</sub>	1	CuBr <sub>2</sub> (30)	110	0
11	Ni(COD) <sub>2</sub>	1	CuSO <sub>4</sub> (30)	110	76
12	Ni(COD) <sub>2</sub>	1	CuI (30)	110	0
<b>13</b>	<b>Ni(COD)<sub>2</sub></b>	<b>1</b>	<b>CuF<sub>2</sub> (30)</b>	<b>50</b>	<b>94 (90)<sup>d,e</sup></b>
14	Ni(COD) <sub>2</sub>	1	CuF <sub>2</sub> (30)	50	0

<sup>a</sup> Reaction conditions: **1a** (0.25 mmol), **2a** (0.30 mmol), Ni(COD)<sub>2</sub> (0.025 mmol), PCy<sub>3</sub> (0.05 mmol) in toluene (2.0 mL), 15 h. <sup>b</sup> GC yields using decane as an internal standard. <sup>c</sup> Zn (0.25 mmol) was used. <sup>d</sup> Isolated yield. <sup>e</sup> 2 h reaction time.

Next, we turned our attention to study the preparative scope of our reaction. As shown in Table 2, the outcome was largely insensitive to changes in the electronic nature of the substrates utilized, obtaining the desired compounds in excellent yields using **2a** as coupling counterpart. Interestingly, we found that the coupling of **2aa** resulted in moderate yields of **3aa**, hence showing the superior activity of **2a**.<sup>21</sup> The chemoselectivity profile of the method is nicely illustrated by the fact that ethers (**3b** and **3d**), esters (**3e** and **3h**), amides (**3g**) or silyl ethers (**3i**) were perfectly tolerated under our opti-

mized protocol. As shown for **3h**, the reaction was not seriously hampered by the presence of *ortho*-substituents, although slightly higher temperatures were required in this case. While C(sp<sup>2</sup>)–F bonds are prone to oxidative addition in the presence of Ni catalysts with PCy<sub>3</sub> as supporting ligand,<sup>22</sup> we found that such motifs remained intact under our reaction conditions (**3f**). Similarly, the presence of nitrogen-containing heterocycles did not interfere with the productive C–Si bond-forming reaction (**3j**).

**Table 2. Ni-catalyzed Silylation of Naphthyl Pivalates<sup>a, b</sup>**

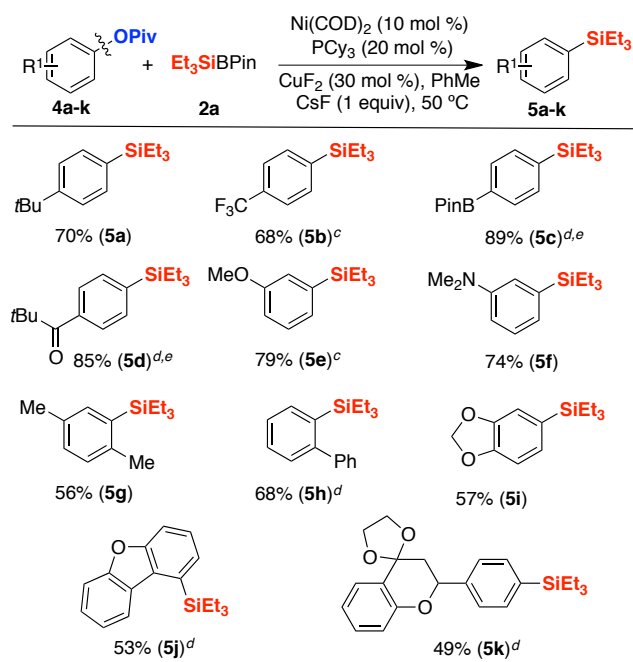



<sup>a</sup> Reaction conditions: **1** (0.50 mmol), **2a** (0.60 mmol), Ni(COD)<sub>2</sub> (10 mol %), PCy<sub>3</sub> (20 mol %), CuF<sub>2</sub> (30 mol %), CsF (1 equiv) in toluene (3.0 mL) at 50 °C. <sup>b</sup> Isolated yields, average of at least two independent runs. <sup>c</sup> PhMe<sub>2</sub>SiBpin (**2aa**) was utilized. <sup>d</sup> Reaction conducted at 80 °C.

A closer look into the literature data indicates that the inclusion of p-extended systems greatly accelerates the rate of C(sp<sup>2</sup>)–O bond-cleavage reactions.<sup>23</sup> Encouraged by the findings in Table 2, we speculated that our mild synergistic Ni/Cu-catalyzed silylation event could be even extended to the use of simpler, yet challenging, phenyl pivalates. As shown in Table 3, this was indeed the case, and a wide variety of phenyl pivalates, regardless of the electronic effects on the aryl ring, could be coupled in high yields (**5a–5k**). It is worth noting that the coupling of phenyl and naphthyl pivalates (Tables 2 and 3) operates under otherwise identical reaction conditions, an observation that demonstrates the robustness and generality of our synergistic Ni/Cu-catalyzed event. In analogy with the results in Table 2, the presence of *ortho*-substituents did not hinder the C–Si bond-forming reaction (**5g**, **5h**). Likewise, a number of functional groups such as boronic esters (**5c**), ketones (**5d**), amines

(5f), acetals (5i, 5k) and heteroaromatics (5j) could also be equally accommodated in good to excellent yields.

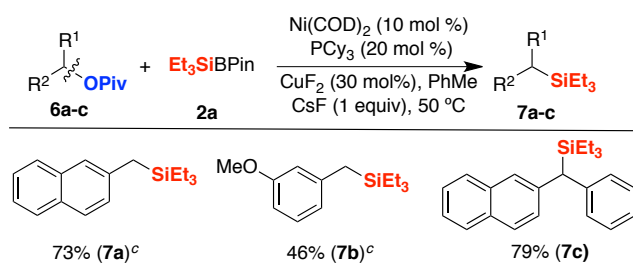
**Table 3. Ni-catalyzed Silylation of Phenyl Pivalates<sup>a, b</sup>**



<sup>a</sup> As for Table 2. <sup>b</sup> Isolated yields, average of at least two independent runs. <sup>c</sup> GC yields using decane as an internal standard due to volatility issues. <sup>d</sup> Reaction conducted at 80 °C. <sup>e</sup> 2a (1.0 mmol) and CsF (1.70 equiv).

To the best of our knowledge, a catalytic carbon-heteroatom bond-forming reaction via the cleavage of unactivated  $\text{C}(\text{sp}^3)\text{-O}$  bonds has no precedents in the literature.<sup>24</sup> Gratifyingly, we observed that primary and even secondary benzylic pivalates could be cross-coupled with 2a in good yields (Table 4). Importantly, no re-optimization of the reaction conditions was required, a rather valuable finding that demonstrates the outcome of our method. Overall, we believe the results shown in Tables 2-4 nicely illustrate the excellent reactivity and the wide application profile of our synergistic Ni/Cu-catalyzed  $\text{C}(\text{sp}^2)\text{-}$  and  $\text{C}(\text{sp}^3)\text{-O}$  bond-cleavage protocol, suggesting that other conceivable synergistic scenarios might be discovered in the near future.

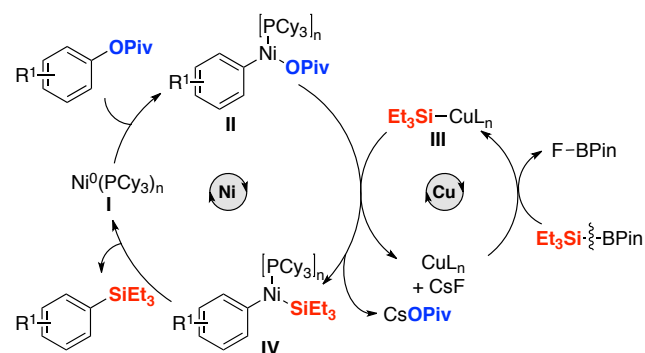
**Table 4.  $\text{C}(\text{sp}^3)\text{-O}$  Cleavage/ $\text{C-Si}$  bond-formation<sup>a, b</sup>**



<sup>a</sup> As for Table 2. <sup>b</sup> Isolated yields, average of at least two independent runs. <sup>c</sup> Reaction conducted at 80 °C.

Although a detailed mechanistic picture requires further studies, we tentatively propose that two catalytic cycles operate simultaneously in a synergistic fashion (Scheme 2). Thus, we favor a scenario consisting of an initial oxidative addition of the  $\text{C}(\text{sp}^2)\text{-O}$  bond to  $\text{Ni}(0)$  (**II**).<sup>25</sup> Then, a transmetalation event facilitated by in-situ generated **III**,<sup>26,27</sup> followed by a reductive elimination delivers the final product while recovering back the active  $\text{Ni}(0)\text{L}_n$  catalytic species **I**. Whether other mechanistic pictures come into play<sup>28</sup> or the reaction involves single-electron transfer processes is subject of ongoing studies in our laboratory.

### Scheme 2. Mechanistic Proposal



In summary, we have discovered a synergistic Ni/Cu-catalyzed  $\text{C-Si}$  bond-forming reaction via  $\text{C}(\text{sp}^2)\text{-}$  and even  $\text{C}(\text{sp}^3)\text{-O}$  bond-cleavage.<sup>29</sup> This study suggests that other synergistic scenarios might lead to the foundation of new discoveries within the field of Ni-catalyzed cleavage of unactivated  $\text{C-O}$  bonds. The wide substrate scope, mild reaction conditions, robustness and generality of the method suggest that this protocol can be a powerful alternative to existing methodologies for preparing organic silanes from readily available precursors. Further mechanistic studies and other synergistic events are currently underway in our laboratories.

### ASSOCIATED CONTENT

**Supporting Information.** Experimental procedures and spectral data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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#### Funding Sources

No competing financial interests have been declared.

### ACKNOWLEDGMENT

We thank ICIQ Foundation, the European Research Council (ERC-277883) and MICINN (CTQ2012-34054) for financial support. Johnson Matthey, Umicore and Nippon

Chemical Industrial are acknowledged for a gift of metal and ligand sources. Dr. N. Cabello at ICIQ and X. Ribas from UdG are acknowledged for HRMS as well as insightful mechanistic discussions.

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