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# Copper-driven formation of siloxanes *via* dehydrocoupling between hydrosilanes and silanols†

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In this study, we introduce a method for directly synthesizing various siloxanes from hydrosilanes and silanols under ambient conditions. This process relies on the use of Stryker's reagent ($[(PPh_3)CuH]_6$) as the first copper catalyst, enabling this specific cross-dehydrogenative coupling. This method stands out for its exceptional chemoselectivity, making it a superb alternative to established catalytic systems. It operates under mild conditions yet maintains high process efficiency. Throughout the investigation, we demonstrated the potential for modifying the resulting hydrosiloxanes through alcoholysis to produce silyl ethers and *via* hydrosilylation to yield functionalized siloxanes.

## Introduction

Siloxanes represent a category of compounds defined by a sequence of alternating silicon and oxygen atoms. The mentioned Si–O–Si motif is widely encountered in nature, although the synthetically derived combinations revolutionized industry.[1–6] This was driven by the versatility of siloxanes, which are used, among other things, as sealants, adhesives, coatings, plastics, cosmetics, *etc.*[7–13] In synthetic chemistry, siloxanes and silyl ethers also serve as very important reagents and building blocks.[14–22]

Regardless of their structure, chain length, or shape, the main method leading to the formation of Si–O–Si sequences is associated with the process of chlorosilane hydrolysis (Fig. 1a).[2] Despite many significant advantages, mainly related to the wide availability of substrates, these methods are accompanied by numerous limitations. This becomes particularly critical in instances where the synthesis of unsymmetrical compounds or complex structures with particular functional groups is envisaged. This, in turn, led scientists to begin searching for alternative synthetic methods replacing chlorosilanes, and using silanols in combination with an appropriate silylating agent.[2,23,24] Consequently, a series of methods based on coupling reactions were developed, where instead of a corrosive byproduct such as HCl, dihydrogen (dehydrogenative coupling),[25–32] alkene (dealkenative coupling),[33,34] or alkyne[35] (dealkynative coupling) is obtained. Additionally, the possibility of functionalizing existing siloxanes, for example through hydrosilylation of tetramethyldisiloxane, has also been demonstrated.[36–39] Among the aforementioned methodologies, the approach based on the dehydrocoupling reaction between silanols and hydrosilanes appears to be the most extensively explored, particularly concerning the potential util-

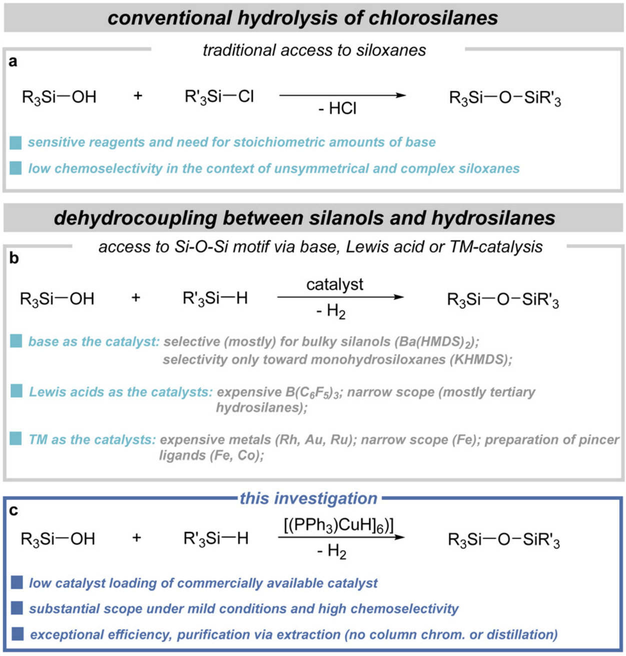

**Fig. 1** Context of the investigation.

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ization of the released dihydrogen (Fig. 1b). Among the strategies for selective SiO–H/Si–H dehydrocoupling, approaches involving the utilization of strong bases,[27,28,31] Lewis acids,[40–47] 4d/5d metal catalysts,[25,48] and increasingly prevalent 3d metal complexes have emerged.[26,30,32] Each type of catalyst has its own advantages and disadvantages. One of the main limitations of base-catalyzed protocols is the challenge of achieving desired chemoselectivity. When using Lewis acids, we are restricted to the costly tris(pentafluorophenyl) borane and primarily the use of tertiary silanes. Catalysts based on noble metals are very expensive, so the focus is primarily on utilizing 3d metal complexes. Of notable interest is the employment of cobalt complexes featuring NNN-type[30] and PNP-type[32] pincer ligands. However, the preparation of the ligands themselves can be considered a drawback. Copper compounds have shown effectiveness in synthesizing silyl ethers,[49–54] yet they have not been applied to the production of siloxanes. Within this context, pivotal methodologies, as relevant to this study, have been pioneered by Schubert and Lorenz, leveraging Stryker's reagent ($[(PPh_3)CuH]_6$) to obtain diverse alkoxysilanes and silanols.[54,55] Moreover, there exists a sole example where copper compounds have been applied during the synthesis of siloxanes.[29] However, in this scenario, reactions must be performed with copper(II) triflate at 80 °C, where mechanistic studies show that silyl triflate molecules, formed *in situ*, are the true catalytic species.

Considering the precedent research by Schubert and Lorenz,[54] as well as our expertise in forging of Si–O bonds, we embarked on an investigation into the application of commercially available (triphenylphosphine)copper hydride hexamer, known as Stryker's reagent,[56–59] within the field of siloxane synthesis (Fig. 1c). It is worth adding here that, until now, this compound and its variations with different phosphine ligands have been used as very useful (pre)catalysts in a range of synthetic processes.[60–64] Our initial hypothesis posited that this easily accessible copper cluster would serve as an exceptionally useful catalyst for the dehydrocoupling between silanols and hydrosilanes, thus circumventing the necessity for intricate pincer ligands commonly utilized in prior instances involving 3d metal complexes. Thus, this approach would yield a catalytic system based on copper, which is much more abundant in nature than cobalt. This endeavor resulted in the development of a highly efficient methodology for siloxane synthesis. Moreover, we substantiated the practical viability of our approach through scaled-up experimentation and exemplification of further product modification *via* subsequent alcoholysis and hydrosilylation reactions.

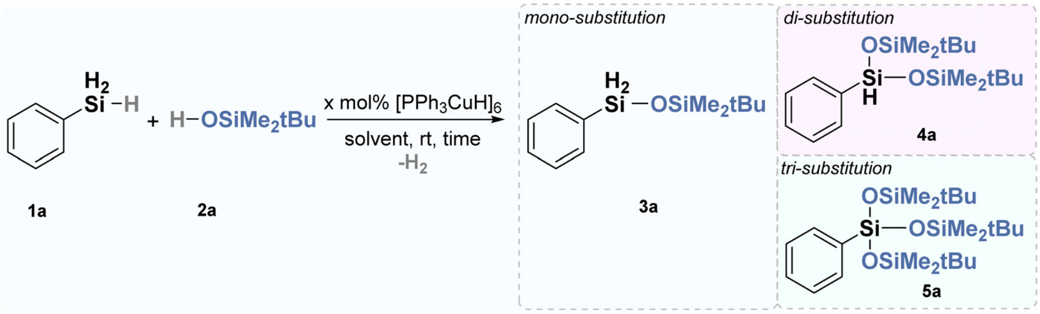
## Results and discussion

In Table 1, we compared the initial findings from our investigation into the dehydrogenative coupling reaction involving phenylsilane (**1a**) and *tert*-butyldimethylsilanol (**2a**). These comparisons were important for optimizing the entire process. This is particularly significant in terms of chemoselectivity. The use of primary silane may lead, depending on the reagent ratio, to the substitution of one, two, or even three silanol molecules. Theoretically, this may yield three distinct products: disiloxane, trisiloxane, and a branched variant. Hence, it is crucial to establish reaction conditions that ensure selectivity and facilitate straightforward isolation of the desired products. It should be noted that due to the sensitivity of all reagents (substrates and catalyst), they were stored in a glovebox and each reaction was set up there. Subsequently, the sealed vials were removed from the glovebox and mixed for a predetermined duration. We initiated our research by examining how the catalyst affects the progression of the dehydrocoupling reaction. Firstly, two tests were carried out (entries 1 and 2). In both tests, all reagents were mixed for 20 hours without the catalyst present. One test maintained the reaction in a closed vial (entry 1), while the second vial after being set up in the glovebox was opened briefly and exposed to air, then sealed again and mixed for the specified duration (entry 2). Both tests affirmed the necessity of a copper catalyst for the reaction to proceed, prompting us to continue our research with its inclusion. Across all experiments (entries 3–12), it became evident that a catalyst amount as low as 0.125 mol% is sufficient. Any further reduction in catalyst amount began to impact the conversion rate of the substrates. Additionally, these experiments revealed the versatility of conducting the reaction in either an argon atmosphere or in air. The presence of air only shortens the duration of the process compared to carrying out the entire reaction in an argon atmosphere (entries 5 and 6). This observation aligns with the pioneering findings of Lorenz and Schubert, who similarly noted the expedited reaction rate in the presence of air.[54]

Next, by conducting the reaction in toluene with 0.125 mol% of the catalyst and a reagent ratio of **1a** : **2a** = 2 : 1, we achieved efficient and highly selective synthesis, exclusively yielding the disiloxane product **3a** (entry 9). Subsequently, we explored the possibility of substituting two molecules of silanol to obtain the corresponding trisiloxane. Once again, toluene proved to be the most effective solvent (entry 13). Interestingly, despite increasing the amount of silanol in the system (entry 14) and simultaneously increasing the catalyst amount, we did not observe the substitution of a third silanol molecule. Subsequent studies, to be discussed later, indirectly suggest that steric effects likely play a crucial role in preventing the substitution of the third molecule of this bulky silanol. Finally, we investigated the impact of simple copper salts on the progression of this reaction (entries 15 and 16). Both copper(II) chloride and copper(II) acetate demonstrated limited activity in the dehydrocoupling process, yielding only traces of the desired products (less than 3%).

With the optimized conditions in hand, we carried out experiments utilizing different hydrosilanes and silanols to showcase the wide-ranging utility of our protocol. Our reaction conditions demonstrated effectiveness across a diverse array of primary and secondary silanes in the process of mono-dehydrogenative coupling (Fig. 2). It has been shown that various silanols, including those containing bulky groups like isopro-

**Table 1** Optimization studies for a copper-catalyzed dehydrogenative silylation of phenylsilane with *tert*-butyldimethylsilanol[a]



| Entry | Variation of conditions | Catalyst loading (mol%) | Molar ratio [**1a**] : [**2a**] | Conversion of **1a** or **2a**[i] [%]; {isolated yield}; | Selectivity[j] [%] [**3a**] : [**4a**] : [**5a**] |
|---|---|---|---|---|---|
| 1 | No catalyst[a] | — | 1 : 1 | 0 | — |
| 2 | No catalyst[b] | — | 1 : 1 | 0 | — |
| 3 | In toluene[c] | 0.25 | 1 : 1 | 99 (**2a**) | 91 : 9 : 0 |
| 4 | In toluene[d] | 0.25 | 1 : 1 | 99 (**2a**) | 60 : 40 : 0 |
| 5 | In toluene[c] | 0.125 | 1 : 1 | 99 (**2a**); {**3a**, 80%} | 90 : 10 : 0 |
| 6 | In toluene[d] | 0.125 | 1 : 1 | 99 (**2a**); {**3a**, 79%} | 92 : 8 : 0 |
| 7 | In toluene[d] | 0.125 | 1.5 : 1 | 99 (**2a**); {**3a**, 82%} | 98 : 2 : 0 |
| 8 | In hexane[e] | 0.125 | 1.5 : 1 | 99 (**2a**); {**3a**, 81%} | 97 : 3 : 0 |
| 9 | In toluene[d] | 0.125 | 2 : 1 | 99 (**2a**); {**3a**, 87%} | 99 : 1 : 0 |
| 10 | In hexane[e] | 0.125 | 2 : 1 | 99 (**2a**); {**3a**, 84%} | 99 : 1 : 0 |
| 11 | In acetonitrile[f] | 0.125 | 2 : 1 | 99 (**2a**); {**3a**, 86%} | 95 : 5 : 0 |
| 12 | In 2-methyltetrahydrofuran[g] | 0.125 | 2 : 1 | 65 (**2a**) | 97 : 3 : 0 |
| 13 | In toluene[d] | 0.25 | 1 : 2 | 99 (**1a**); {**4a**, 92%} | 0 : 100 : 0 |
| 14 | In toluene[e] | 0.25 | 1 : 3 | 99 (**1a**) | 0 : 100 : 0 |
| 15 | $CuCl_2$ instead of $[(PPh_3)CuH]_6$[h] | 2 | 1 : 2 | 3 (**1a**) | 0 : 100 : 0 |
| 16 | $Cu(OAc)_2$ instead of $[(PPh_3)CuH]_6$[h] | 2 | 1 : 2 | 2 (**1a**) | 0 : 100 : 0 |

[a] All reaction conditions: **1a** (1 eq.), **2a** (1 eq.), toluene (0.25 mL), rt, under argon atmosphere, 20 h. [b] All reaction conditions: **1a** (1 eq.), **2a** (1 eq.), toluene, rt, under air atmosphere, 20 h. [c] Under argon atmosphere, 20 h. [d] Under air atmosphere, 30 min. [e] Under air atmosphere, 1 h. [f] Under air atmosphere, 3 h. [g] Under air atmosphere, 6 h. [h] Under air atmosphere, in toluene, 20 h. [i] Conversion of **1a** or **2a** determined by GC. [j] Selectivity of [mono-sub] : [di-sub] : [tri-sub] products determined by GC.

pyl, are reactive under the studied conditions. All of them easily undergo coupling with phenylsilane or *p*-tolylsilane to give dihydrosiloxanes (**3a–3k**) in very good yields (76–99%). In the case of trimethylsilanol, a significant excess of **1a** was needed (10.0 eq.). Otherwise, we observed the formation of di-substituted product.

At this point, a brief comparison can be made between the previously known methods of synthesizing dihydrosiloxanes and the method described in this article. Because the authors of all discussed studies often used various reagents and reaction conditions, often focusing on different aspects, this comparison is very general in nature. However, the obtained results are highly satisfactory. Firstly, comparable numbers of products were achieved as when using Au catalyst,[25] and more than with cobalt complexes.[30,32] In the protocol where $Ba(HMDS)_2$ was used as a catalyst,[27] only bulky silanols were investigated, resulting in the production of dihydrosiloxanes. However, there is insufficient knowledge about the potential synthesis of dihydrosiloxanes from non-hindered silanols in the presence of a barium base. However, when a similar catalyst like KHMDS was used, no product containing the $SiH_2$ motif was observed. Even after altering the substrate ratio, the reaction did not exclusively yield dihydrosiloxanes.[31]

Following that, we advanced to examine various secondary hydrosilanes (Fig. 2). In this scenario, irrespective of the substituents' character around the silicon atom – aliphatic or aromatic – the anticipated monohydrosiloxane products (**3g–3k**) were consistently acquired with good yields, ranging between 80–98%.

This notable outcome sets apart our method from, for instance, the one utilizing KHMDS, which exclusively yields products of double dehydrogenative coupling.[31] Finally, we wanted to verify whether suitable tertiary hydrosilanes would undergo a single dehydrogenative coupling reaction leading to unsymmetrical disiloxanes. The initial test using a combination of dimethylphenylsilane and trimethylsilanol as reagents resulted in the desired product **3l** with a yield of 90%. This sets apart the copper-catalyzed method from those employing cobalt complexes with PNP-type ligands.[32] In the latter, it was impossible to carry out the dehydrogenative coupling of any tertiary hydrosilane. However, attempts to expand the scope to include more sterically hindered silanols were unsuccessful. The main reason undoubtedly lies in steric hindrance. This is evidenced by the possibility of only attaching trimethylsilanol – the smallest of the investigated molecules.

Equipped with prior knowledge of the mono-dehydrogenative coupling reaction, we launched investigations into the sub-

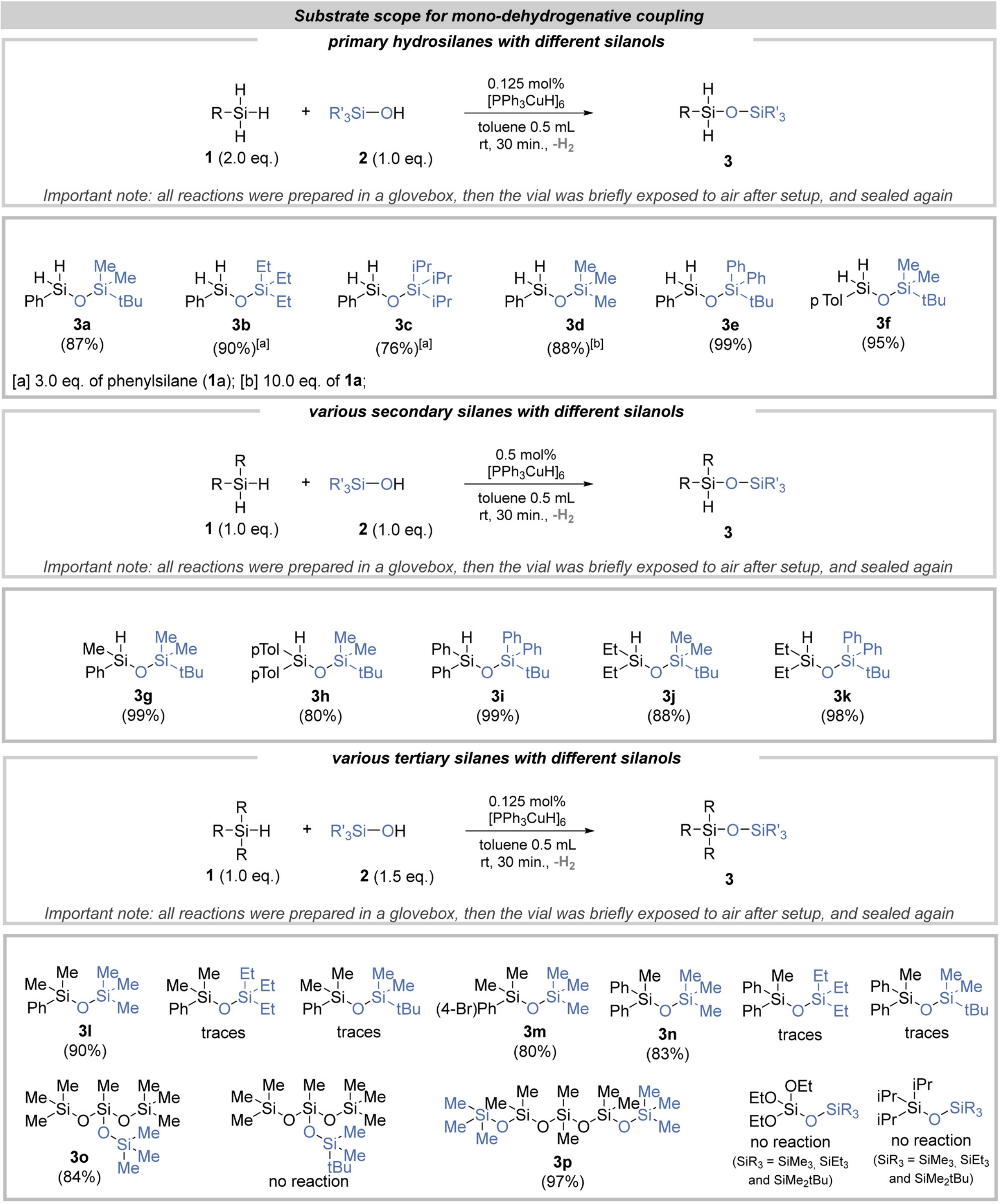


**Fig. 2** Substrate scope for mono-dehydrogenative coupling reaction between various silanes and silanols.

strate's compatibility in the double dehydrogenative coupling reaction (Fig. 3). In the case of various primary hydrosilanes, the situation was quite clear, and a series of monohydrosiloxanes **4a–4i** was obtained (with yields up to 99%). Secondary hydrosilanes displayed a distinct pattern: only reactions employing the least sterically hindered trimethylsilanol resulted in the formation of products *via* double dehydrogenative coupling (products **4j–4l**). Conversely, when bulkier sila-

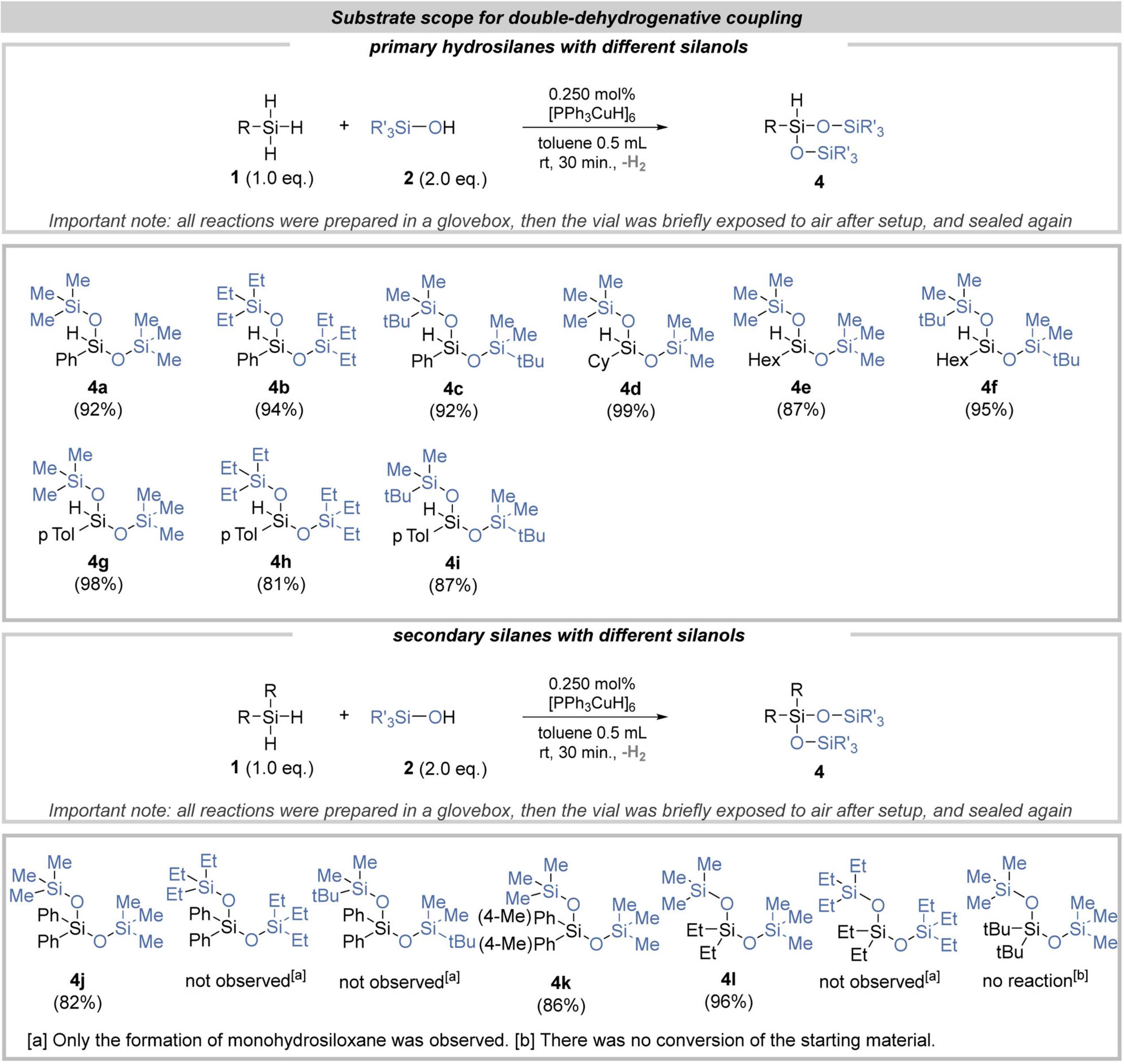


**Fig. 3** Substrate scope for double-dehydrogenative coupling reaction between various silanes and silanols.

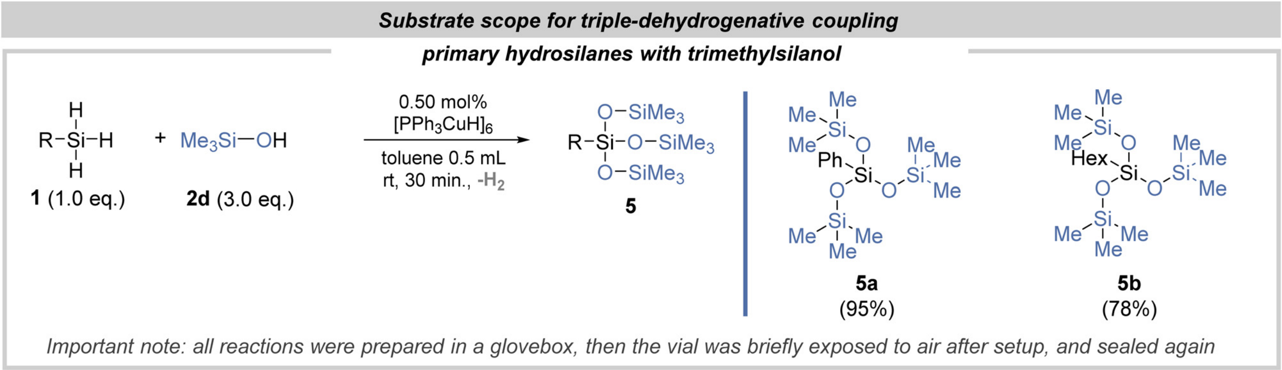


**Fig. 4** Substrate scope for triple-dehydrogenative coupling reaction between aliphatic and aromatic hydrosilane and trimethylsilanol.

nols were utilized, only products of mono-dehydrogenative coupling were detected. Notably, di-*tert*-butylsilane stood as a unique case, failing to react with any silanol due to its inherent steric hindrance. Finally, we also investigated whether it was possible to obtain a product of triple dehydrogenative coupling in the case of primary hydrosilanes (Fig. 4). It turned out that in combination with the least sterically hindered trimethylsilanol, branched siloxanes were successfully obtained (Fig. 4). Unfortunately, endeavors to selectively synthesize siloxanes from two distinct silanols yielded no success (Fig. 5). In pursuit of this, previous products **3a** and **4c** were subjected to reactions with trimethylsilanol. Upon analysis of

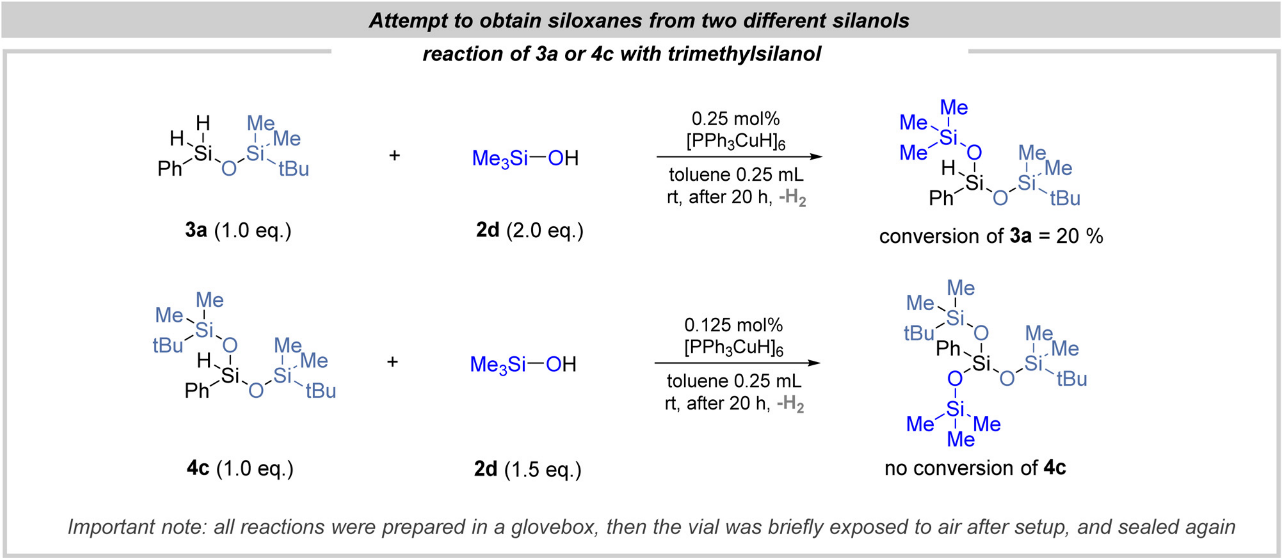


**Fig. 5** Unsuccessful attempt to synthesize siloxanes from two different silanols.

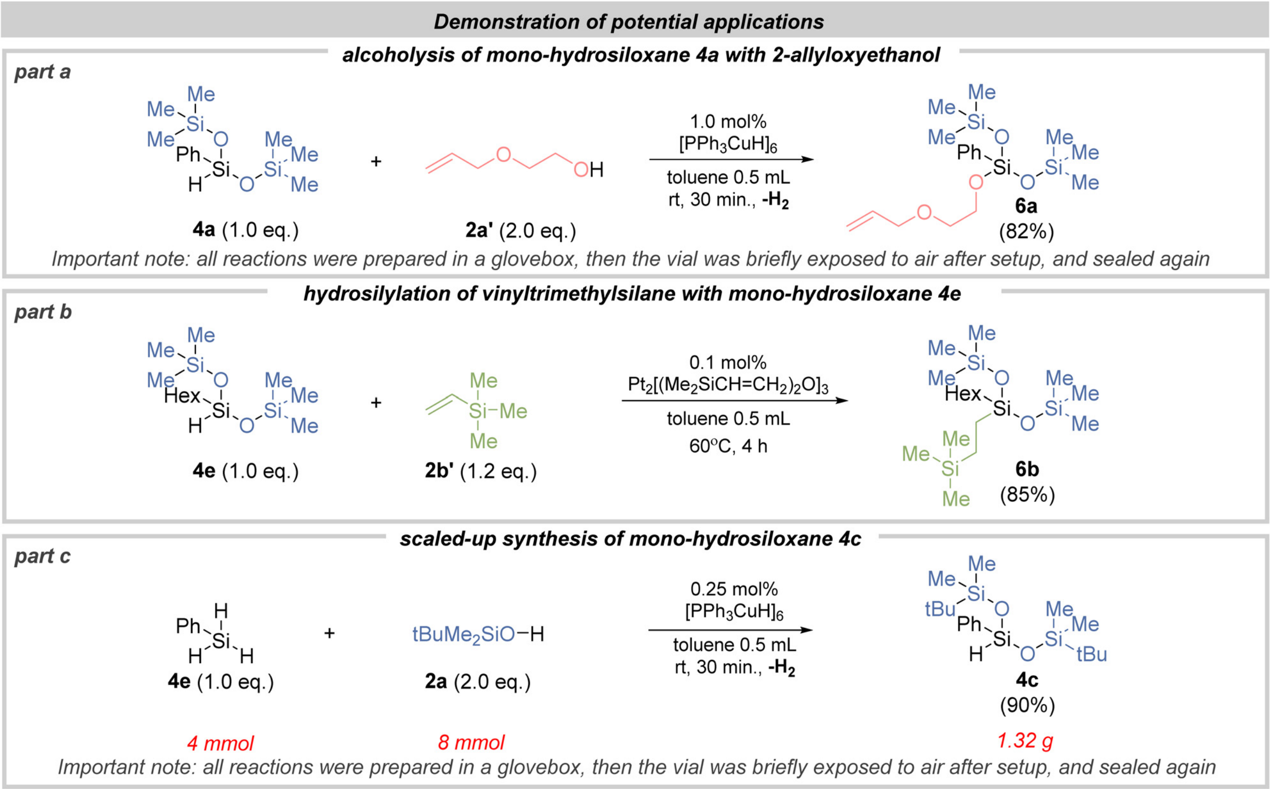


**Fig. 6** Potential pathways for derivatization and scale-up of the reaction.

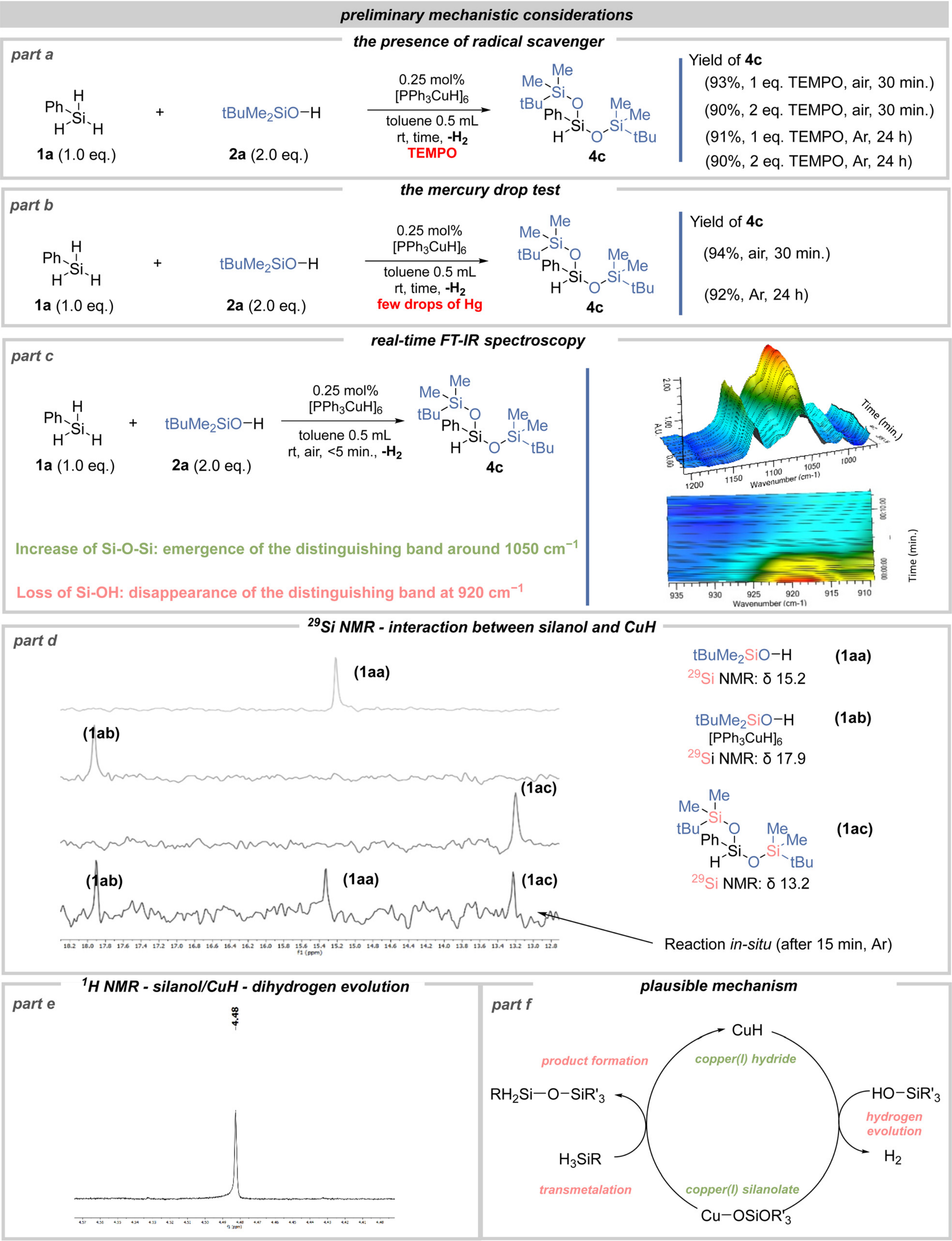


**Fig. 7** Mechanistic studies.

the post-reaction mixture, the anticipated product originating from **3a** was detected; however, the conversion of the starting substrates was notably low (20%). This is particularly intriguing considering the anticipation of a substantially higher conversion in this scenario.

In the subsequent phase, our aim was to illustrate the potential for functionalizing the hydrosiloxanes we had synthesized (Fig. 6). Initially, drawing on research by Schubert and Lorenz,[54] we performed alcoholysis of the previously obtained product **4a** using the same catalyst. This process yielded a silyl ether **6a** (Fig. 6, *part a*). Following this, we focused on employing product **4e** in a hydrosilylation process with platinum as the catalyst (Fig. 6, *part b*). Platinum-based catalysts are widely utilized and studied in this field.[65–67] The reaction of product **4e** with vinylsilane resulted in the formation of product **6b** with 85% yield. These reactions collectively highlight the significant application potential of the hydrosiloxanes obtained in our study. Furthermore, we successfully demonstrated the scalability of the original siloxane synthesis reaction by conducting it on an 8-fold larger scale (Fig. 6, *part c*).

Next, to get some mechanistic insights into copper catalysis, we carried out some of preliminary experiments (Fig. 7). Initially, we conducted tests involving the radical scavenger – TEMPO (Fig. 7, *part a*).[32] We observed no significant changes in the siloxane synthesis process, regardless of the atmosphere (air or argon) or the amount of TEMPO used (1.0 or 2.0 eq.). This suggests that the process may not proceed *via* a radical mechanism. Subsequently, a mercury drop test was performed to determine the nature of the catalysis, whether homogeneous or heterogeneous (Fig. 7, *part b*).[68–70] Once again, irrespective of the atmosphere, the reaction proceeded in the presence of mercury, indicating homogeneous catalysis.

Additionally, Stryker's reagent, characterized by its brick-red color and utilized in all reactions, exhibited excellent solubility in solvents like benzene or toluene. Analysis of its solution in benzene-$d_6$ *via* $^1$H NMR spectroscopy confirmed the existence of a copper–hydrogen bond (broad signal at 3.51 ppm).[71] Then, we employed real-time *in situ* FT-IR spectroscopy to observe the reaction system. The kinetic profiles derived from the silylation of phenylsilane with *tert*-butyldimethylsilane at room temperature substantiated a swift vanishing (within less than 5 minutes) of the distinctive peak at 920 cm$^{-1}$ attributed to the Si–OH functionalities, accompanied by a concomitant increase in the intensity of the Si–O–Si band at 1050 cm$^{-1}$ (Fig. 7, *part c*). Moreover, the instrumentation indicated the exothermic nature of the reaction. Then, an attempt was made to verify the catalytic system using NMR spectroscopy. The behaviour of phenylsilane and *tert*-butyldimethylsilanol in the presence of Stryker's reagent was monitored using both $^1$H and $^{29}$Si NMR (Fig. 7, *part d* and *e*). The visible change was observed for the silicon atom of the *tert*-butyldimethylsilanol molecule. Under normal conditions, the signal from this silicon atom appears at 15.2 ppm. Investigating the same molecule but in the presence of a copper complex showed a shift in the signal to 17.9 ppm. Both of these signals appeared in the spectrum recorded after 15 minutes of the reaction between *tert*-butyldimethylsilanol and phenylsilane, with an observed signal from the reaction product **4c** also at 13.2 ppm (Fig. 7, *part d*). Furthermore, using $^1$H NMR, the evolution of hydrogen was demonstrated (signal at 4.48 ppm; Fig. 7, *part e*), which was also observed visually in the case of each reaction (formation of gas bubbles, particularly vigorous upon opening the vial to the air). Given that the NMR analysis of the phenylsilane/catalyst mixture revealed no discernible changes in the spectrum, in contrast to the silanol/catalyst system, and drawing from prior literature indicating that copper hydrides typically undergo protonolysis in the presence of alcohols or weak acids to produce $H_2$ gas,[49,72,73] we propose a plausible mechanism outlined in Fig. 7 (*part f*). In the initial step, Stryker's reagent goes through protonolysis, which forms a copper–silanolate complex and releases hydrogen. Subsequently, the copper complex undergoes transmetalation, resulting in product formation and the regeneration of copper(I) hydride. It has been indirectly demonstrated that the silanolate form of the complex and its size play a crucial role in driving the reaction forward. Hence, when using the smallest silanol, trimethylsilanol, even trisubstitution reactions were achievable. However, even a minor alteration to triethylsilanol promptly stops the reaction at the disubstitution stage.

Finally, the acceleration of the reaction in the presence of oxygen (air), compared to under argon, is not well understood and requires further experimentation. Schubert[54] and Riant[74] observed the same effect with copper hydrides, presenting a challenging and interesting problem to solve.

## Conclusions

In summary, we have documented the first copper-catalyzed cross-dehydrogenative coupling between hydrosilanes and silanols under remarkably gentle conditions (room temperature), without the need for additional activators or specialized pincer ligands. In this study, commercially available Stryker's reagent proved to be an effective catalyst with just 0.125 mol% loading. This resulted in a catalytic system that is not only straightforward and easily accessible but also significantly more competitive compared to previously used – more expensive gold or cobalt-based systems. Consequently, a range of products including unsymmetrical disiloxanes, symmetrical trisiloxanes, and branched siloxanes were synthesized. This also encompasses hydrosiloxanes containing free Si–H groups, which offer further functionalization potential, as demonstrated through alcoholysis and hydrosilylation processes. Moreover, the employed catalytic system allows for scalability, enhancing the practicality of this approach. Mechanistic investigations highlight the homogeneous nature of the catalysis and the absence of free radicals. Consequently, a proposed mechanism revolves around the formation of a copper–silanolate complex followed by its transmetalation with hydrosilanes.

## Data availability

The ESI contains general information, synthetic procedures, characterization data and spectra of the obtained products.

The authors have cited additional references within the ESI.† [75–86]

## Author contributions

Methodology, K. K.; Synthesis of products – K. K., M. M., K. Ł.; Formal analysis, K. K., M. M., K. Ł.; writing—original draft preparation, K. K. and Q. B.; visualization, K. K. and Q. B.; supervision, K. K.; funding acquisition, K. K. All authors reviewed the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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