

Pd-catalyzed intermolecular Si–O formation *via* Si–C activation

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The development of efficient Si–O bond formation reaction with 100% atom-economy, excellent functional group tolerance, and broad scope under mild conditions is highly desired due to the prevalence of silanol, silyl ether, and their derivatives in synthetic chemistry and materials science. Here, we have realized the Pd-catalyzed Si–O formation reaction *via* a Si–C activation approach with 100% atom-economy by employing silacyclobutanes (SCBs) and various hydroxy-containing substrates, including water, alcohols, phenols, and silanols. This protocol features a broad substrate scope, remarkable functional compatibility and mild conditions, providing a series of silanols, silyl ethers in high efficiency. Notably, this protocol could also be used for selective protection of hydroxy functionalities, and for the access of a class of novel polymers containing Si–O main chain. Preliminary mechanistic studies unveiled that this reaction underwent a Pd-catalyzed concerted ring-opening mechanism.

Si–O formation, Si–C activation, palladium, silacyclobutane, silanol, silyl ether

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1 Introduction

Silicon-oxygen bond formation reactions have received tremendous attention due to the prevalence of silanol, silyl ether, and their derivatives in organic chemistry, pharmaceuticals, and materials science [1–11]. Basically, the silicone industry is built upon the silicon-oxygen formation reactions, and the global silicone market size was valued at USD 18.59 billion in 2021. In addition, silyl groups (such as ^tPr₃Si–, ^tBuMe₂Si–, and ^tBuPh₂Si–) are the valuable protecting groups of the hydroxyl functions in synthetic organic chemistry due to their good balance between the stability in the reaction procedure and easy removal afterwards [12,13]. Traditional construction of Si–O bond has been achieved by

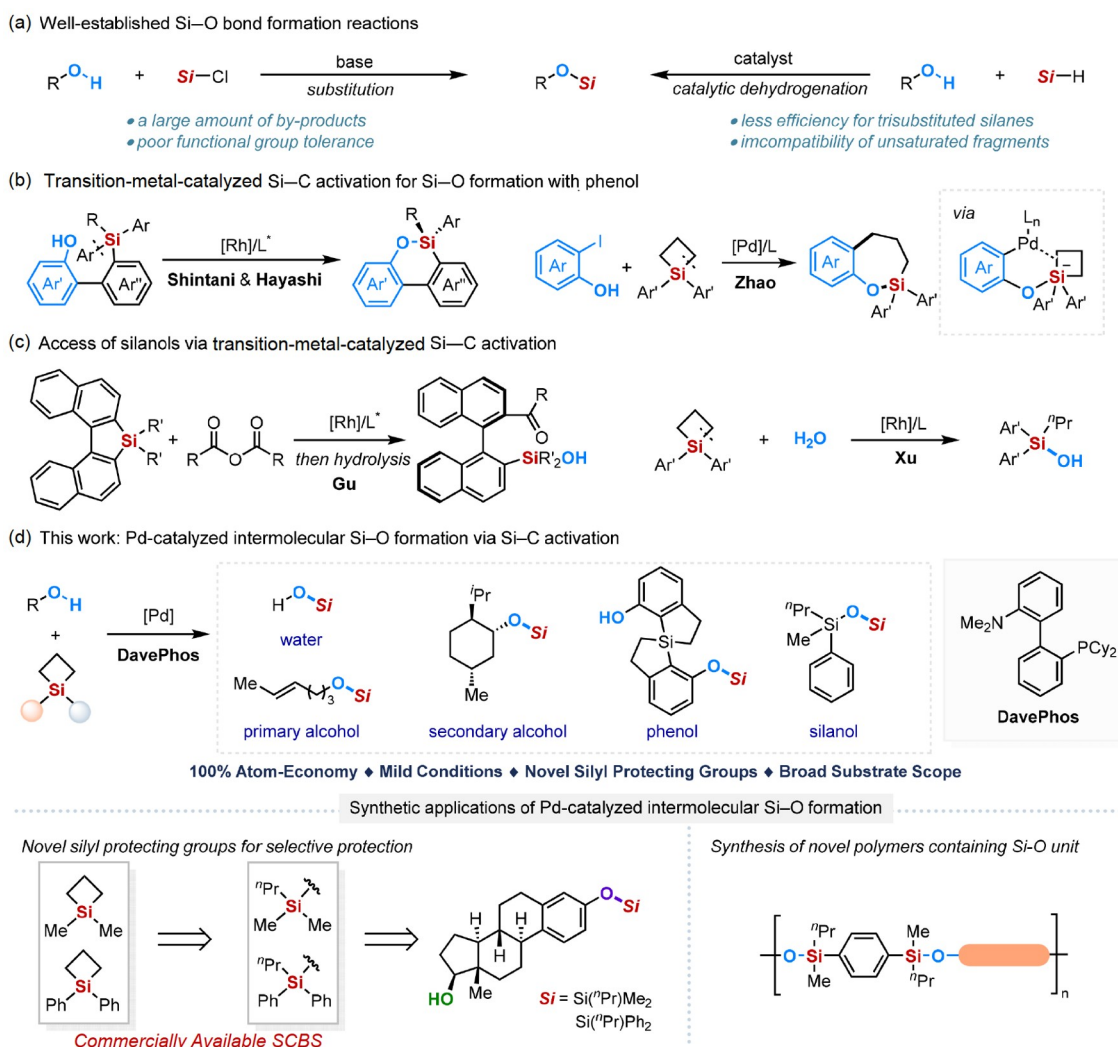
the reaction of hydroxy functionality with moisture-sensitive and corrosive chlorosilanes. This process normally requires the stoichiometric amount of a hydrochloric acid scavenger, resulting in a large number of unwanted wastes, and is not compatible with the base-sensitive functional groups [14–16]. An alternative approach *via* the catalytic dehydrogenative coupling of alcohols with hydrosilanes has merged by virtue of the rapid development of the transition-metal catalysis, where H₂ is the only byproduct [17–26]. However, this process remains several limitations, including the incompatibility with alkenyl and carbonyl groups in most of cases due to the high reactivities of transition-metal-catalyzed hydrosilylation event. Hence, to develop a general approach for the efficient construction of Si–O bond with 100% atom-economy, excellent functional group tolerance and broad scope under mild conditions is highly desired in

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both industry and academic sectors.

Transition-metal-catalyzed silicon-carbon activation has received increasing attention due to the efficient construction of various silicon-containing compounds with remarkable structural diversity [27–30]. For example, silacyclobutanes (SCBs) and their derivatives are known as versatile synthetic blocks to access organosilane compounds *via* various ring-opening or ring expansion reactions [31–52]. However, the efficient formation of Si–O bond *via* the transition metal-catalyzed silicon-carbon activation of SCBs is underdeveloped, and largely limited to silacycles formation [53–63]. For example, Shintani *et al.* [61] reported a Rh-catalyzed synthesis of Si-stereogenic dibenzooxasilines *via* the Si–C(sp²) activation. Recently, Zhao *et al.* [62] have developed Pd-catalyzed ring expansion process of SCBs to produce seven-membered cyclic silyl ether where the hydroxyl group in the substrate assists Si–C(sp³) bond cleavage. The sole example for the preparation of acyclic silanols has been

demonstrated by the Gu's group [63] *via* a Rh-catalyzed aryl-Narasaka acylation of distorted five-membered sila-flyoroenes, in which the chiral silanols were produced by the hydrolysis of the acylated cyclic intermediate. During the preparation of this manuscript, Xu and coworkers [64] also reported an elegant Rh-catalyzed hydrolysis of SCBs with water for the preparation of silanols. Here, we demonstrated the Pd-catalyzed intermolecular Si–O bond formation of various hydroxy-containing substrates *via* a Si–C bond activation approach for the first time (Scheme 1d) [65]. A variety of hydroxy-containing compounds, including water, alcohols, phenols, and silanols, could be silylated by SCBs with 100% atom-economy under mild conditions, thus providing a practical method for the preparation of silyl ethers and silanols. Given 1,1-dimethylsilacyclobutane and 1,1-diphenylsilacyclobutane being commercially available, this protocol provides a highly synthetic useful procedure with remarkable functional group tolerance for the installation of



Scheme 1 (a) Well-established Si–O bond formation reactions. (b) Transition-metal-catalyzed Si–C activation for Si–O formation with phenol. (c) Access of silanols *via* transition-metal-catalyzed Si–C activation. (d) This work: Pd-catalyzed intermolecular Si–O formation *via* Si–C activation (color online).

two novel silyl protection groups (${}^n\text{PrMe}_2\text{Si-}$ and ${}^n\text{PrPh}_2\text{Si-}$) for alcohols and phenols. Detailed studies on the reaction rates with different hydroxyl functionalities indicate our newly established protocol could be employed for the selective protection of polyols bearing complex structures. Furthermore, the versatility of this reaction was demonstrated by the synthesis of a class of novel polymers containing Si–O units. The preliminary mechanistic studies revealed that a concerted ring-opening process might be involved in this reaction, and the kinetic studies indicate the concerted step is the rate-determining step for this reaction.

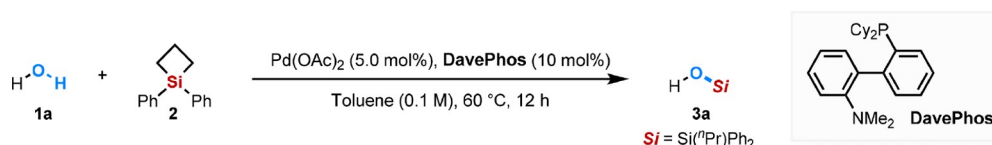
2 Results and discussion

As our continuous interests on developing efficient approaches for the construction of functional organosilanes [66,67], we wondered that the silanols and silyl ethers could be efficiently prepared with 100% atom economy *via* the coupling of SCBs with hydroxy-containing substrates. Hence, we first explored the feasibility of the Si–O formation reaction by conducting the reaction with commercially available 1,1-diphenylsiletane (**2**) and water as the model substrate, due to the importance of silanols in synthetic chemistry [68,69]. After systematic evaluation of the catalyst system, we found a Pd(OAc)₂/DavePhos combination was efficient for this Si–O formation reaction, giving the targeted silanol **3a** in 80% ¹H nuclear magnetic resonance (NMR) yield (entry 1, Table 1), while other transition metal catalysts

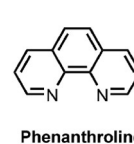
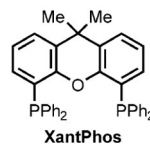
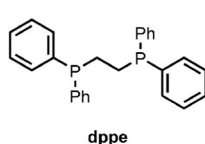
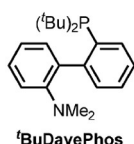
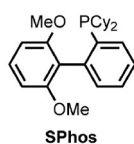
were inefficient under current conditions (for details, see the Supporting Information online). The efficiency of the reaction was decreased when bulkier monophosphine ligands (SPhos or ^tBuDavePhos) were used (entries 9 and 10). Bidentate ligands, such as diphosphine ligands and 1,10-phenanthroline ligand, were also investigated, affording silanol in low to moderate yields (entries 11–14). The screening of the solvents indicated both nonpolar and polar solvents provided the target product **3a** in acceptable yields except for dichloromethane (entries 2–4). The yield was further improved to 94% in a higher concentration with a shorter reaction time (entry 5). Notably, the control experiments indicate both palladium catalyst and DavePhos are essential to the reaction. Without the assistance of a monophosphine ligand, only 6% ¹H NMR yield of desired product was obtained (entries 6 and 7).

Under the optimal reaction conditions, the generality of this Pd-catalyzed Si–O formation reaction *via* Si–C activation was evaluated regarding the hydroxy-containing substrates (Table 2). In general, this protocol was suitable for a wide range of the substrates containing hydroxy functionality, affording the desired silanols and silyl ethers in good to excellent yields. The reaction of **2** with water gave the corresponding silanol **3a** in 85% yield. A variety of alcohols, including primary and secondary alcohols (**1b–1k** and **1l–1p**), underwent this Si–O formation process to afford the corresponding silyl ethers in 70%–97% yields. Although the reaction with tertiary alcohols is not efficient, this protocol could tolerate tertiary silanols (**1q–1t**), probably because the

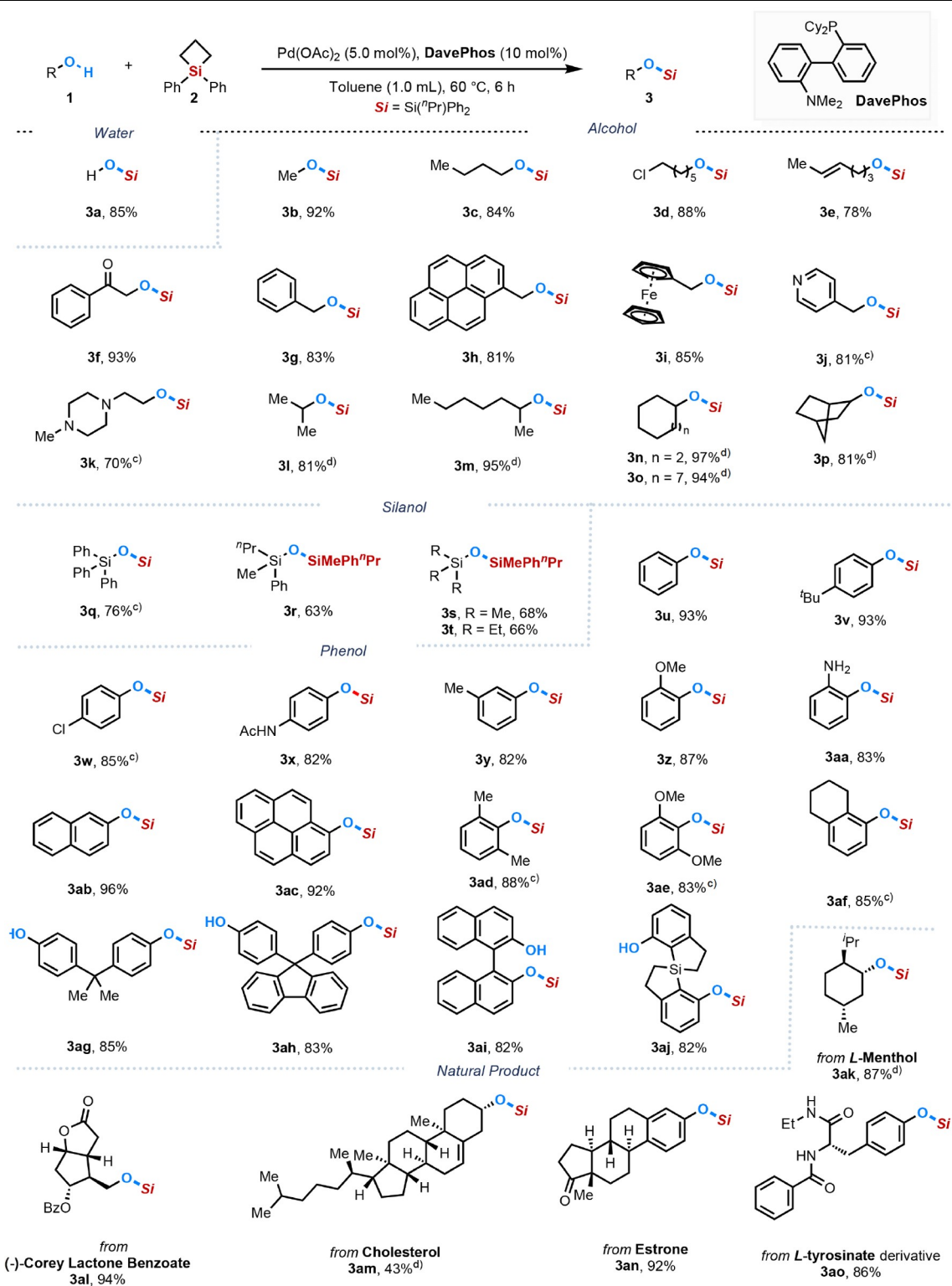
Table 1 Evaluation of reaction parameters^{a),b)}



Entry	Deviation from conditions	Yield (%)	Entry	Ligand	Yield (%)
1	None	80	8	PCy ₃	36
2	Hexane instead of toluene	44	9	SPhos	18
3	DMA instead of toluene	71	10	^t BuDavePhos	42
4	DCM instead of toluene	7	11 ^{c)}	dppe	61
5	Toluene (0.2 M), 6 h	94	12 ^{c)}	dppf	20
6	No Pd(OAc) ₂	<1	13 ^{c)}	XantPhos	6
7	No DavePhos	6	14 ^{c)}	Phenanthroline	37



a) Reaction conditions: **1a** (1.0 mmol, 10 equiv.), **2** (0.1 mmol), Pd(OAc)₂ (1.1 mg, 5.0 mol%), DavePhos (7.9 mg, 10 mol%), toluene (1.0 mL), 60 °C, 12 h. b) Yield was determined by ¹H NMR using CH₂Br₂ as the internal standard. c) Ligand (5.0 mol%) was used.

Table 2 Pd-catalyzed coupling **2** of with water, alcohols, phenols, and silanols^{a),b)}

a) Reaction conditions: **1** (0.2 mmol), **2a** (0.2 mmol, 1.0 equiv.), Pd(OAc)₂ (2.2 mg, 5.0 mol%), DavePhos (7.9 mg, 10 mol%), toluene (1.0 mL), 60 °C, 6 h. b) Isolated yield. c) 100 °C, 12 h. d) Pd(MeCN)₂Cl₂ (2.6 mg, 5.0 mol%), 100 °C, 12 h.

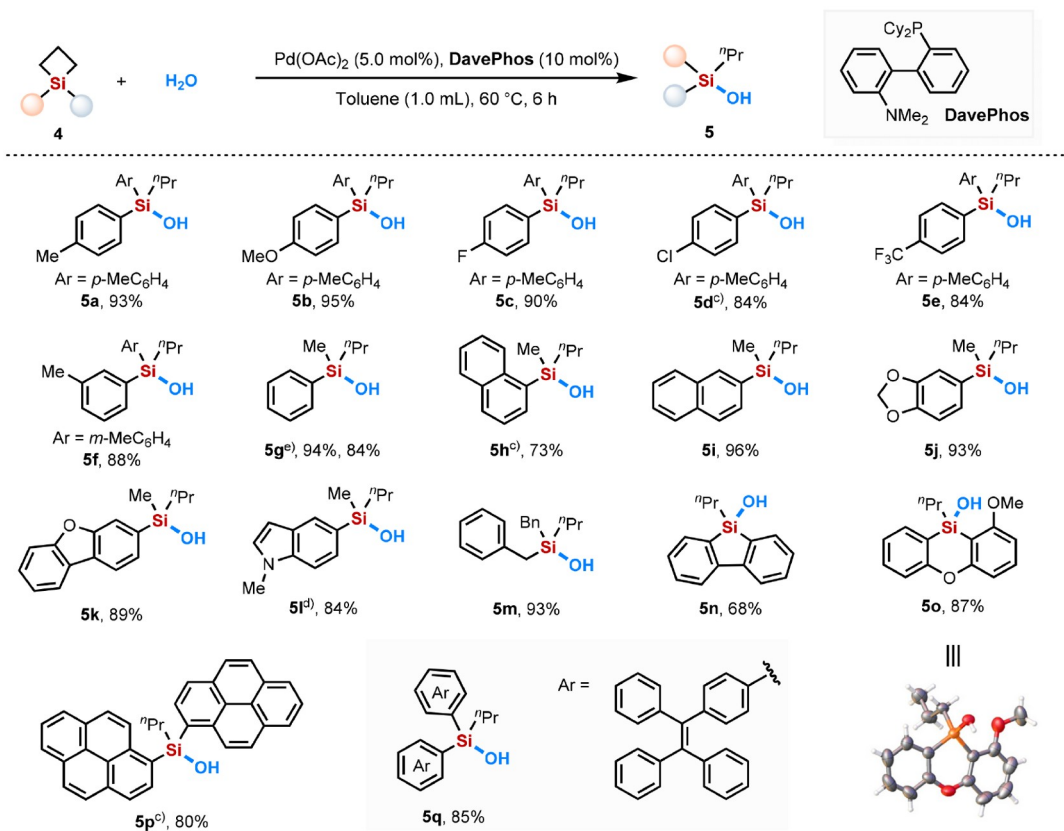
silanols have a looser steric environment in comparison to tertiary alcohols due to the longer Si–C bond (Si–C vs. C–C, ca. 1.87 Å vs. ca. 1.53 Å). It is noteworthy that this protocol

is also suitable for the alcohols bearing basic heterocycles and functionalities, including pyridine (**1j**) and tertiary amine (**1k**), which normally resulted in the corresponding salts

under the typical silyletherification reaction with silyl chlorides. Both various electron-rich and electron-deficient phenols were evaluated, and the electronic properties of phenol derivatives did not significantly affect the efficiency of this reaction. The desired silyl ethers (**3u–3ac**) were obtained in 82%–96% yields. Regarding the bulky *ortho*-disubstituted phenols (**1ad** and **1ae**), a higher temperature was required for maintaining the high reactivity. It should be pointed out that the reactions of the bisphenols (**1ag–1aj**), including BINOL (**1ai**) and SPSiOL (spiro-silabiindane diol, **1aj**) [66] afforded the monosilylated products in 82%–85% yields using 1.0 equiv. of **2**, indicating the high potency for selective protection of symmetric diphenols. Under the established mild conditions, this reaction also shows good functional group compatibility, where the substrates containing methoxy (**1b**, **1ae**), chloro (**1d**, **1w**), alkenyl (**1e**), benzyl (**1g**), amino (**1x**, **1aa**), naphthalene (**1ab**) or pyrenyl (**1ac**) were all tolerated. The generality of the protocol was further demonstrated by conducting this reaction with complex natural products. The silylation of *L*-menthol (**1ak**), (–)-Corey lactone benzoate (**1al**), cholesterol (**1am**), *L*-tyrosinate derivative (**1an**), and estrone (**1ao**) proceeded smoothly to provide the corresponding products with high efficiency.

Next, we turned our attention to check the substrate scope of SCBs with water as the model substrate, which could open a new avenue for efficient preparation of silanols. As shown in Table 3, various 1,1-diarylsilanes with either electron-rich (**4a**, **4b**, **4f**) or electron-deficient (**4c–4e**) aryl group all successfully participated in this Pd-catalyzed Si–O formation reaction in up to 95% yield. The reaction also proceeded smoothly with 1-methyl-1-arylsilanes (**4h–4l**), affording the corresponding silanols containing diverse functional groups such as dibenzo[*b,d*]furan (**5k**) and indole (**5l**). 1,1-Dibenzylsilane (**4m**) was also compatible with this Pd-catalyzed process. It is noteworthy that the C–Si activation happened solely on C(sp³)–Si bond when spiro SCBs containing both C(sp³)–Si and C(sp²)–Si bonds (**4n**, **4o**) were used, giving the cyclic silanols in moderate to good yields. Polyaromatic pyrene and tetraphenylethylene (TPE) fragments are key scaffolds widely presented in organic optoelectronic materials. The introduction of the Si–O unit in such molecules might alter the photophysical properties. SCBs attached with pyrene (**4p**) or TPE (**4q**) reacted with water efficiently, providing a new approach for the construction of silicon-oxygen containing optoelectronic materials. Notably, the access of Si-stereogenic silanols *via* this Pd-catalyzed Si–O formation reaction has also been preliminarily evaluated

Table 3 Scope of SCBs^{a),b)}

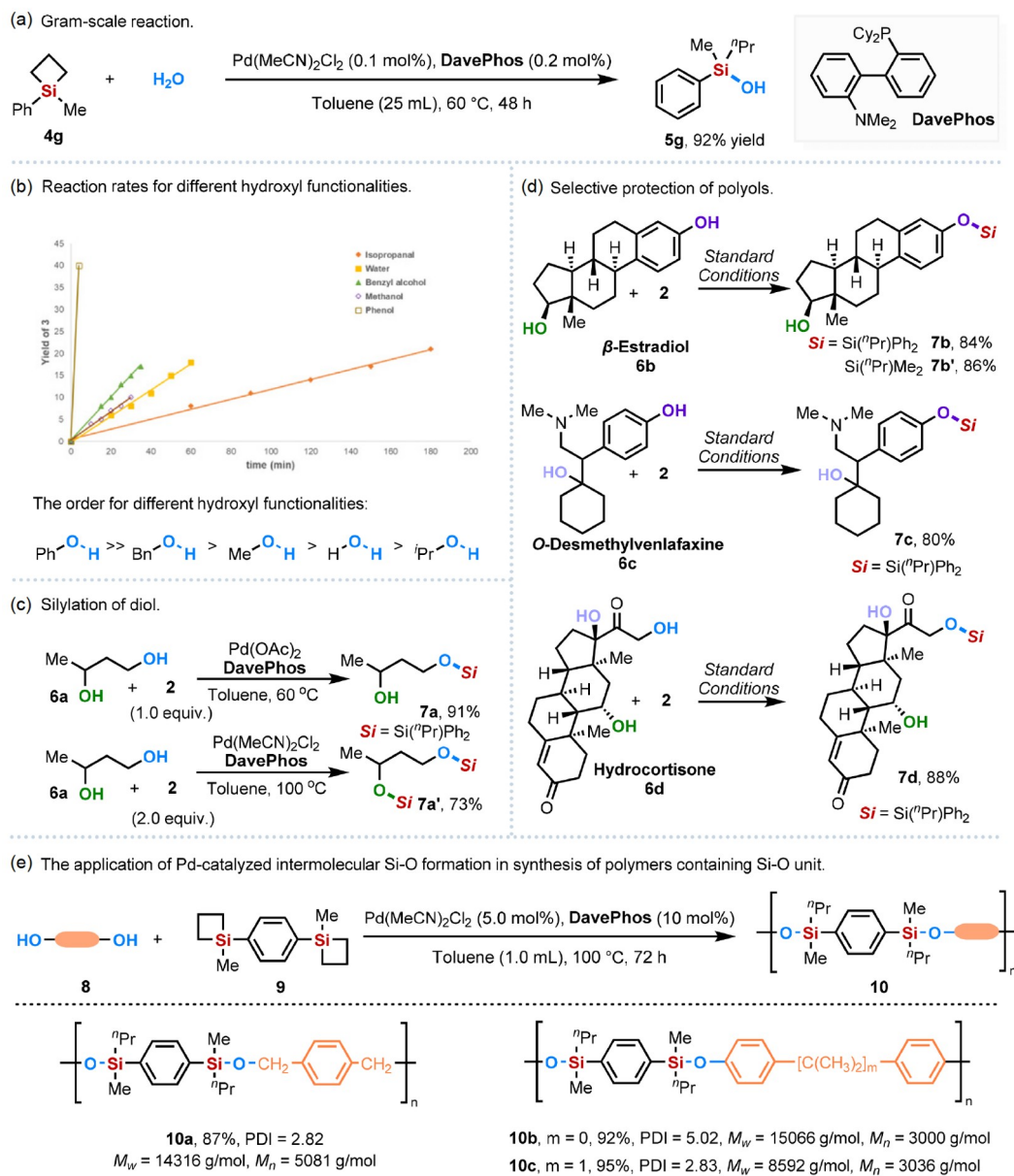


a) Reaction conditions: **4** (0.2 mmol, 1.0 equiv.), water (0.2 mmol, 1.0 equiv.), $\text{Pd}(\text{OAc})_2$ (2.2 mg, 5.0 mol%), DavePhos (7.9 mg, 10 mol%), toluene (1.0 mL), 60 °C, 6.0 h. b) Isolated yield. c) 100 °C, 12 h. d) 100 °C, 8.0 h. e) The reaction was conducted on 10 mmol scale.

by using chiral ligands or *L*-menthol, and only less than 5% *ee* was obtained (for details, see the [Supporting Information online](#)).

To demonstrate the scalability of this method, we have conducted the reaction on 5.0 mmol scale with 0.1 mol% of Pd(MeCN)₂Cl₂ as the metal precursor. To our delight, the desired product **5g** was obtained in 92% yield with a prolonged reaction time (48 h). Given the importance of silyl protection group in organic synthesis, the development of efficient Si–O formation reaction with remarkable functional group tolerance under mild conditions might also lead to the development of novel silyl protection groups [13–18]. With commercially available 1,1-diphenylsilylacyclobutane as the silyl source, we first investigated the reaction rates with re-

gard to various hydroxy functionalities. The exploration of the order of the reaction rates with different alcohols and phenols will provide a guiding principle for selective protection using our newly developed Si–O formation reaction. As listed in [Scheme 2b](#), the order of the reaction rates for different hydroxy functionalities with 1,1-diphenylsilylacyclobutane **2** is PhOH ≫ BnOH > MeOH > H₂O > *i*PrOH. Based on this principle, the selective protection of polyols containing different hydroxy functionalities has been achieved ([Scheme 2c and d](#)). With β-estradiol (**6b**) containing both phenolic hydroxyl and alcoholic hydroxyl groups as substrate, the silylations of either commercially available SCBs (**2** or 1,1-dimethylsiletane) were occurred selectively on phenolic hydroxy, delivering the corresponding products



Scheme 2 Gram-scale reaction and applications of Pd-catalyzed intermolecular Si–O formation (color online).

(**7b** and **7b'**) in high selectivity. The similar selective protection of *o*-desmethylvenlafaxine (**6c**) has also been realized using our protocol. For the polyols including different alkyl hydroxy groups, the less sterically hindered hydroxy group could be selectively protected (**6d**). Moreover, the silylation on the primary alcohol of **7a** was realized in high yield with the secondary alcohol untouched under the standard conditions using 1.0 equiv. of **2**, and the full protection could also be achieved by slightly modifying the reaction conditions using Pd(MeCN)₂Cl₂ as the catalyst at higher temperatures.

To further demonstrate the synthetic utility of this newly developed methodology, we performed the polymerization reaction by using diols and bis-SCBs, which could provide a novel polymer containing the Si–O units (Scheme 2e). The polymerization reaction was conducted between **9** containing two SCB fragments and the diol (**8**), and the high conversions were reached under our reaction conditions at a higher temperature (100 °C). The high *M_w* values (14,316 and 15,066 g/mol) were reached when 1,4-benzenedimethanol (**8a**) or (1,1'-biphenyl)-4,4'-diol (**8b**) was used as the hydroxyl source. The Si–O–C linkages in the polymers are susceptible in acidic condition which has potential utilization

for triggered degradation in biomedicine [70].

To better understand the reaction mechanism, the reaction was first performed with CD₃OD under the standard reaction conditions (Figure 1a). The deuterium on the product **3b-d** only appeared at the terminal position of ⁿPr group, revealing no β-H elimination occurred during the ring-opening process. The parallel kinetic isotope effect (KIE) experiments indicated that the O–H cleavage might be involved in the rate-determining step (*k_H*/*k_D* = 2.61/1.0) (Figure 1b). Furthermore, the kinetic studies were conducted, showing that this reaction is first order in alcohol, SCB and palladium catalyst, which indicated that both substrates and catalyst were all involved in the rate-determining step (Figure 1c). The reaction process was also monitored by ¹H NMR. The fact that no detection of Si–Pd–C species when the reaction was heated at 60 °C without alcohol and after the addition of alcohol might rule out that the reaction was initiated by oxidative addition of Pd(0) to SCB or alcohol, although the reason for the inertia of SCBs in the presence of Pd catalyst is unclear. According to the aforementioned mechanistic experiments, a proposed reaction pathway was depicted in Figure 1e. The Pd(0) species was formed by the *in-situ* re-

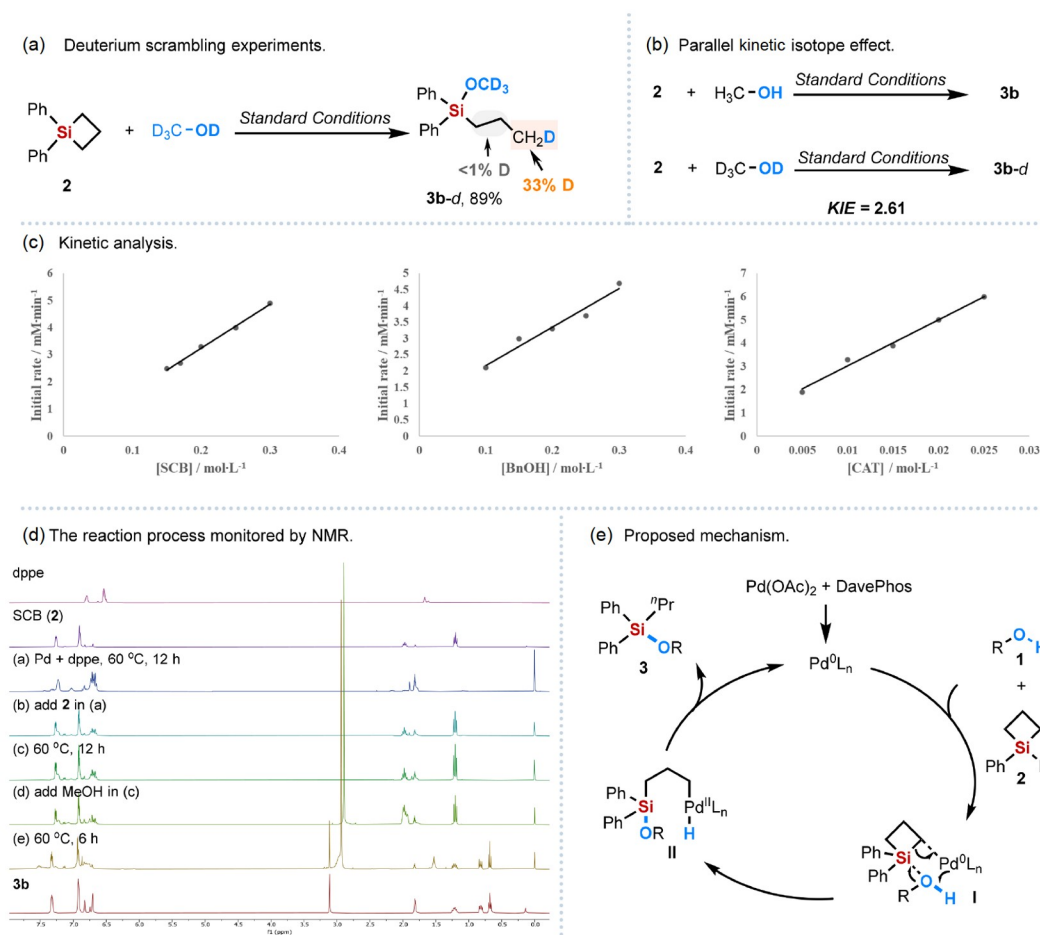


Figure 1 (a) Deuterium scrambling experiments. (b) Parallel KIE. (c) Kinetic analysis. (d) The reaction process monitored by NMR. (e) Proposal mechanism (color online).

duction of Pd(OAc)₂ in the presence of phosphine ligand, which could coordinate with both alcohol and SCB. Next, the concerted ring-opening process was proceeded to deliver the intermediate **II**, which underwent reductive elimination to give the final product **3** and release Pd(0) species. Given the observation of secondary kinetic effect in alcoholic O–H cleavage, the concerted hydroxy group assisted ring-opening process was the rate-determining step in this reaction.

3 Conclusions

In summary, we have demonstrated a Pd-catalyzed intermolecular Si–O bond formation reaction *via* a C–Si activation approach using SCBs as silicon source. The present catalytic system is compatible with various types of hydroxy functionalities, including water, alcohols, silanols, and phenols. This reaction features 100% atom-economy, a broad substrate scope, and mild conditions. Moreover, selective protection of complex compounds containing multiple types of hydroxy functionalities has been realized with commercially available SCBs, providing a synthetically useful protecting strategy with novel silyl protecting groups in organic synthetic chemistry. This protocol has also been valued in the synthesis of the novel polymers bearing Si–O units, indicating the potential utilization in materials science.

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Conflict of interest The authors declare no conflict of interest.

Supporting information The supporting information is available online at chem.scichina.com and link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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