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Concise Report

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Rhodium-Catalyzed Intermolecular C–H Silylation of Indoles with Silacyclobutanes

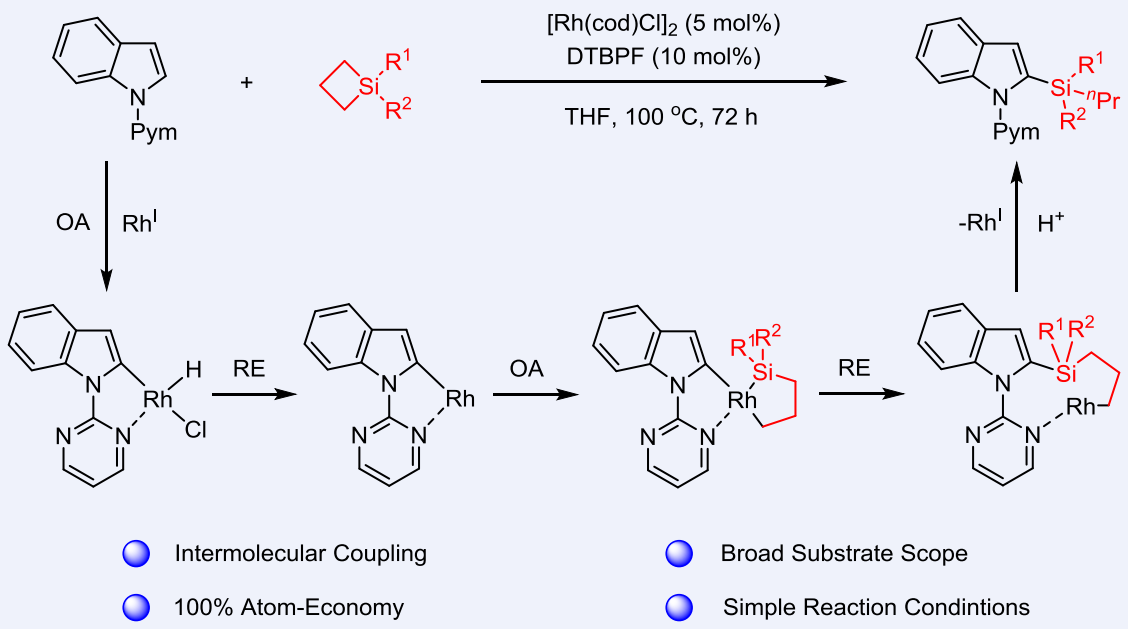
Shengbo Xu,[a] Mengxia Gong,[a] Fen Wang,*[,a] and Xingwei Li*[,a,b]

[a] *School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, Shaanxi 710062, China*
[b] *Institute of Molecular Science and Engineering, Institute of Frontier and Interdisciplinary Sciences, Shandong University, Qingdao, Shandong 266237, China*

Keywords

Rhodium | C–H bond activation | Indole | Silacyclobutane | Silylation

Comprehensive Summary



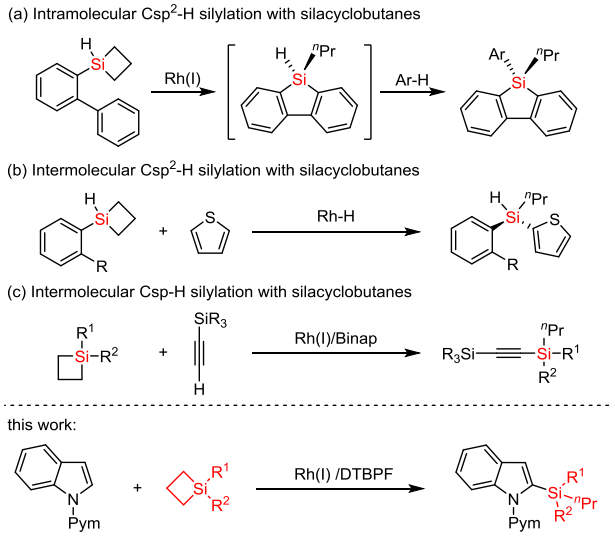
Silylation of C–H bond has been established to be an important strategy toward construction of complex organosilicons. Still, the state-of-the-art is mostly limited to intramolecular reactions or limited to employment of thiophenes or reactive arene reagents. Herein, rhodium-catalyzed intermolecular C–H silylation of indoles has been realized using silacyclobutanes as a silylating reagent, affording a variety of C2-silylated indoles. This chelation-assisted C–H silylation system proceeds well with a broad substrate scope with 100% atom-economy.

*E-mail: fenwang@snnu.edu.cn; lixw@snnu.edu.cn

Background and Originality Content

Organosilicons are a large class of main group organic compounds that have found increasing applications in organic synthesis,[1] materials science,[2] and pharmaceutical chemistry.[3] Their broad utility has sustained a continuing interest in synthesis, making this a vibrant and enduring research topic. Meanwhile, metal-catalyzed C–H activation has recognized as a powerful strategy toward efficient construction of *C*-heteroatom bonds from readily available feedstocks.[4] Notably, significant efforts have been devoted to the C–H bond silylation owing to the availability of substrates and excellent step- and atom-economy.[5] In many studies, organosilicons with a Si–H, Si–Si, or Si-B bond have been applied as silylating reagents in C–H bond silylation under iridium, ruthenium, and rhodium catalysis. In 1954, four-membered silacyclobutanes (SCBs) were first introduced by Sommer and Baum.[6] In comparison to other organosilicons, SCBs have been extensively developed as useful reagents in the ring-opening or ring-expansion reactions due to their inherent ring strain.[7] In particular, intramolecular and intermolecular ring-opening or ring-expansion of SCBs with alkynes,[8] olefins,[9] carbene precursors,[10] allenes,[11] small-ring systems[12] and other coupling partners has been described.[13] However, very limited studies have focused on the aryl C–H silylation using silacyclobutanes. He and co-workers reported intramolecular aryl C–H silylation with silacyclobutanes under the catalysis of Rh(I)/TMS-segphos, which likely proceeds through a six-membered silacyle (Scheme 1a).[14] Furthermore, He and co-workers expanded this reaction to tandem desymmetrization of Si–H in SCBs followed by intermolecular dehydrogenative silylation to construct chiral tetraorganosilicons.[15] Significantly, they also realized intermolecular C–H silylation of Si–H type silacyclobutanes with heteroarenes (Scheme 1b).[16] Intermolecular C(sp)–H silylation with silacyclobutanes has been developed.[17] Nevertheless, C–H silylation reactions have been predominantly limited to employment of arenes and thiophene substrates, while the reactivity of other heteroarenes remains unclear. Given the tremendous abundance of reports on directing group-assisted aryl C(aryl)–H functionalization,[18] we wonder whether this strategy could be applied to address the challenge of silylation of other classes of (hetero)arenes. Herein, we reported the rhodium-catalyzed intermolecular C2-selective silylation of indoles with silacyclobutanes.

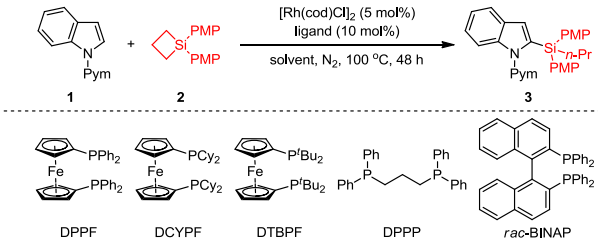
Scheme 1 C–H silylations with silacyclobutanes



Results and Discussion

We commenced our study by examining the reaction between 1-(pyrimidin-2-yl)-1*H*-indole (**1**) and 1,1-bis(4-methoxyphenyl)silacyclobutane (**2**) in the presence of $[Rh(cod)Cl]_2$ and DPPF in toluene at 100 °C for 12 h under N_2. The desired silylation product **3** was obtained in 36% yield, and extending the reaction time to 48 h resulted in increased isolated yield to 52% (Table 1, entry 1). After the screening of a series of phosphine ligands, DTBPF was found to give the desired product in 61% yield (entries 2–5). Subsequently, we investigated the solvent effect. The reaction was almost inhibited when DCE, PhCl, and MeCN were utilized as the solvents (Table 1, entries 6–8). THF gave a more favorable outcome (79%, entry 15), while other solvents such as dioxane, EtOAc, *p*-xylene, MTBE, PhOMe, and DME gave inferior results (26%–76%, entries 9–14). Upon extending the reaction time to 72 h, the yield increased to 84% (entry 16). Our control experiments also indicated air-sensitivity of this system.

Table 1 Optimization of reaction conditions[a]



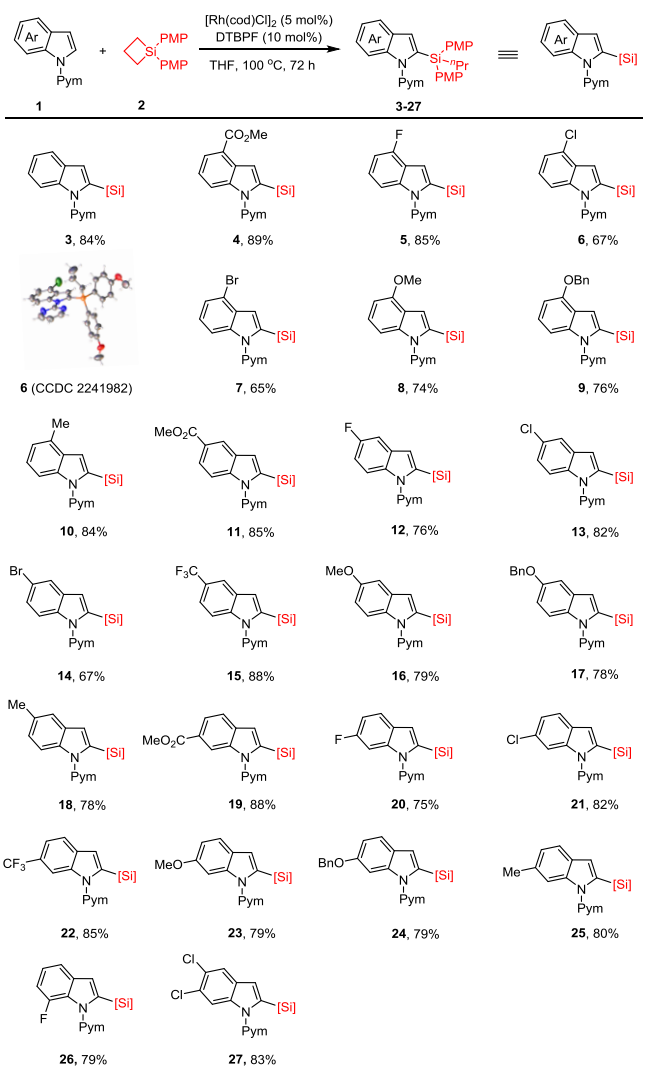
Entry	Ligand	Solvent	Yield[b]/%
1	DPPF	toluene	36[c], 52[d]
2	DPPP	toluene	46
3	BINAP	toluene	57
4	DCYPE	toluene	42
5	DTBPF	toluene	61
6	DTBPF	DCE	trace
7	DTBPF	PhCl	trace
8	DTBPF	MeCN	trace
9	DTBPF	dioxane	26
10	DTBPF	EtOAc	73
11	DTBPF	*p*-xylene	76
12	DTBPF	MTBE	63
13	DTBPF	PhOMe	60
14	DTBPF	DME	71
15	DTBPF	THF	79
16	DTBPF	THF	84[d]

[a] Reaction conditions are as follows: **1** (0.2 mmol), **2** (0.4 mmol), $[Rh(cod)Cl]_2$ (5 mol%), and ligand (10 mol%) in solvent (1 mL) under N_2 at 100 °C for 48 h. [b] Isolated yield. [c] Reaction time: 12 h. [d] Reaction time = 72 h. PMP = *p*-methoxyphenyl. Pym = 2-pyrimidyl.

With the optimal reaction conditions established, the scope of *N*-substituted indoles was next investigated, as illustrated in Scheme 2. A diverse array of electron-donating, -withdrawing, and halogen groups at the C4, C5 or C6 position of the indole ring were compatible, providing **4**–**25** with good yields ranging from 67% to 88%. The structure of compound **6** was confirmed by X-ray crystallography (CCDC 2241982). 7-Fluoroindole afforded corresponding product **26** in 79% yield. Particularly, 5,6-dichloro substituted indole also served as an viable substrate, generating the desired product **27** in 83% yield.

Next, the scope of symmetrical diaryl-substituted silacyclobutanes was examined, as presented in Scheme 3. Since the silicon of silacyclobutanes can be either mono- or diaryl-substituted, the corresponding products can be divided into unsymmetric and asymmetric. Regarding diaryl-substituted silacyclobutanes, various functional groups at the 4-position of phenyl were found to be

Scheme 2 Scope with respect to the indoles[a]

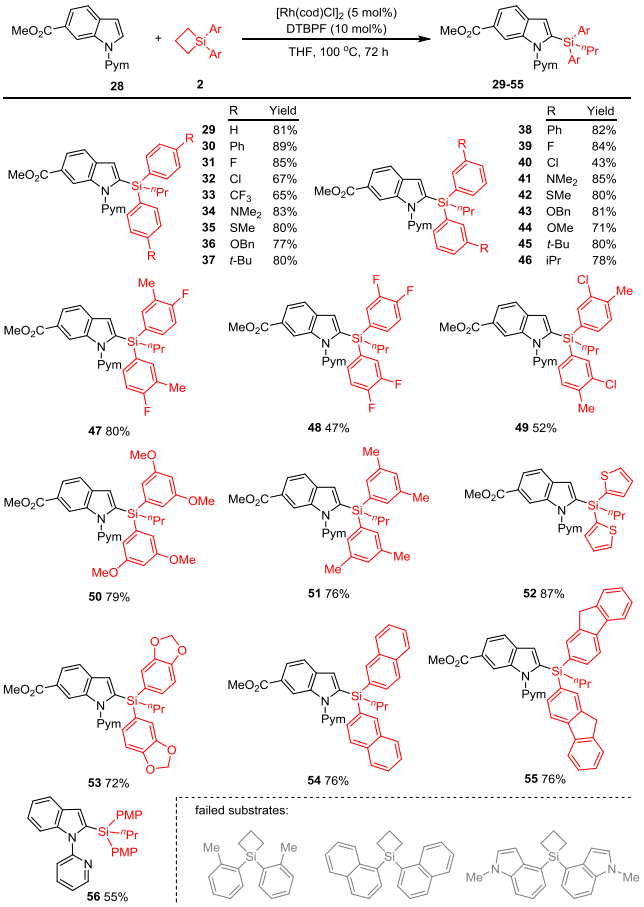


[a] Reaction conditions are as follows: **1** (0.2 mmol), **2** (0.4 mmol), $[Rh(cod)Cl]_2$ (5 mol%), and DTBPF (10 mol%) in THF (1 mL) under N_2 at 100 °C for 72 h. Isolated yields.

suitable for this transformation, including phenyl (**30**, 89%), halo (**31**, 85%; **32**, 67%), trifluoromethyl (**33**, 65%), dimethylamino (**34**, 83%), methylsulfanyl (**35**, 80%), benzyloxy (**36**, 77%), and *tert*-butyl (**37**, 80%). The *meta*-substituted phenyl groups on silicon substrate exhibited efficient reactivity, providing target products with moderate to excellent yields (**38**–**46**, 43%–85%). Furthermore, disubstituted silicon substrates were found to be tolerated, affording the corresponding products in generally good yields (**47**, 80%; **48**, 47%; **49**, 52% **50**, 79%; **51**, 76%). Importantly, dithiophene-substituted silacyclobutane reacted to furnish **52** in 87% yield. Meanwhile, the 3,4-methylenedioxyphenyl-substitted SCB reacted to give **53** in 72% yield. The reaction also tolerated 2-naphthy or 2-fluorenyl group in the SCB (**54** and **55**). *N*-Pyridyl-indole also reacted smoothly with **2** to provide the desired product **56** in 55% yield. However, 2-methylphenyl, 1-naphthyl and 4-indolyl substituted silacyclobutanes failed to react under the standard conditions.

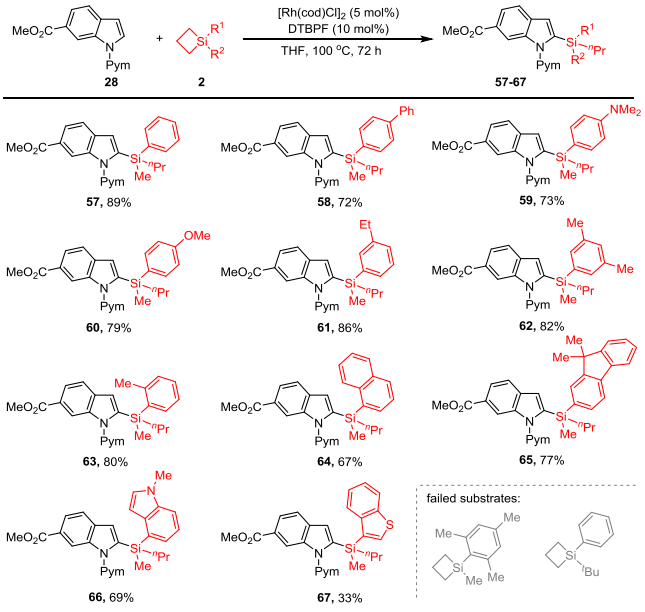
The scope of mono aryl-substituted silacyclobutanes was further investigated (Scheme 4). Several substituted phenyl groups were well tolerated (**57**–**62**, 72%–89%). Interestingly, 2-methylphenyl and 1-naphthyl substituted aryl silacyclobutanes all reacted smoothly with the indole, providing **63** and **64** in moderate yields. 9,9-Dimethylfluorenyl-based silacyclobutanes reacted to give **65** in 77% yield. It was observed that heteroaryl silacyclobutanes also

Scheme 3 Scope with respect to the diaryl-substituted si-lacyclobutanes[a]



[a] Reaction conditions are as follows: **28** (0.2 mmol), **2** (0.4 mmol), $[Rh(cod)Cl]_2$ (5 mol%), and DTBPF (10 mol%) in THF (1 mL) under N_2 at 100 °C for 72 h. Isolated yields.

Scheme 4 Scope with respect to the monoaryl-substituted silacyclobutanesa[a]



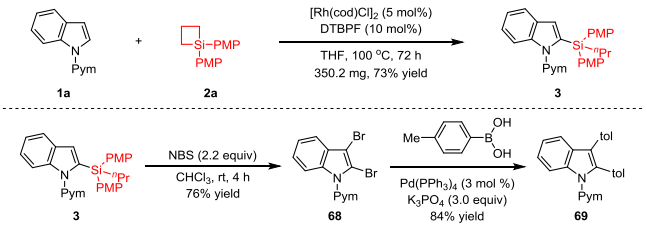
[a] Reaction conditions are as follows: **28** (0.2 mmol), **2** (0.4 mmol), $[Rh(cod)Cl]_2$ (5 mol%), and DTBPF (10 mol%) in THF (1 mL) under N_2 at 100 °C for 72 h. Isolated yields.

provided the desired products **66** and **67**. However, 2,4,6-trimethylphenyl and *tert*-butyl monoaryl-substituted silacyclobutanes

failed to participate in the reaction.

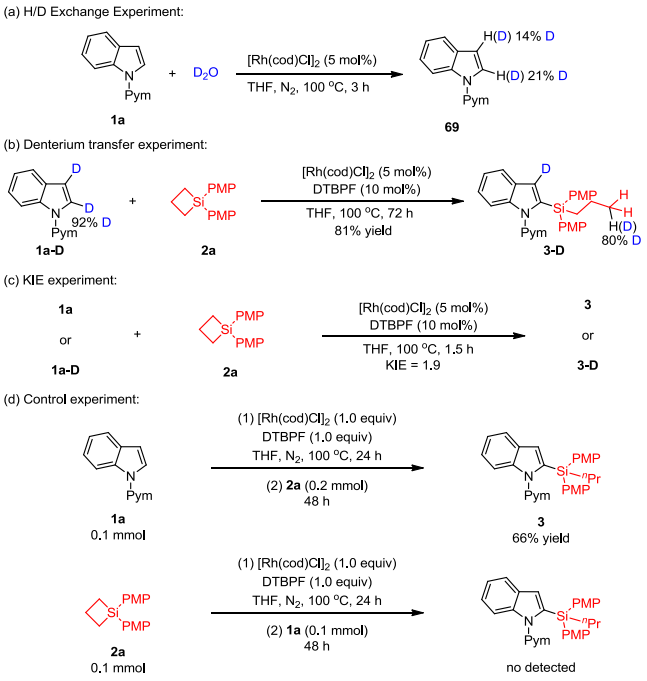
To briefly demonstrate the practicality of this reaction system, the synthetic utility of a representative silylation indole has been performed (Scheme 5). A scaled-up (1 mmol) synthesis of **3** was carried out, affording product **3** with 73% yield. Upon treatment with NBS, the 2,3-dibromo product **68** was obtained with moderate yield. The Suzuki coupling of **68** with *p*-tolylboronic acid produced a 2,3-di-*p*-tolyl indole **69** in good yield.

Scheme 5 Derivatization of representative products



A series of experiments were performed to explore the reaction mechanism (Scheme 6). Initially, H/D scrambling was observed at the C2 and C3 positions of indole using D_2O as deuterium source when treated with **1a** for 3 h in the presence of the catalyst (Scheme 6a). This indicated the C–H activation step is reversible under the standard reaction conditions. Subsequently, the reaction of deuterated indole **1a-D** and SCB **2a** proceeded smoothly under standard conditions, affording the desired product **3-D** in 81% yield. Deuteration (80% D) occurred exclusively at the terminal carbon atom of ^{n}propyl group of **3-D**, suggesting that β-hydride elimination in the Rh-alkyl group is not involved (Scheme 6b). Thirdly, in order to gain more insights into the C–H activation, we conducted kinetic isotope effect (KIE) measurements from the parallel reactions between the (deuterated) indole and SCB **2a** (Scheme 6c). The measured KIE was 1.9, indicating that the cleavage of the aryl C–H bond is probably involved in the turnover-limiting process or occurs prior to the turnover-limiting step.[19] Finally, in order to investigate whether the initiation step of the reaction is rhodium-catalyzed C–H bond activation or oxidative addition between the rhodium catalyst and silacyclobutane, two sets of control experiments were designed for study

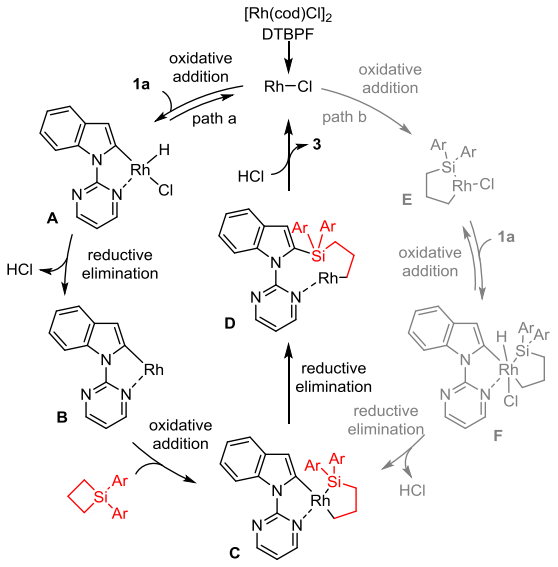
Scheme 6 Mechanistic studies



(Scheme 6d). The experimental results demonstrated that in the first set of experiments, the silylated product **3** was obtained with a yield of 66%, whereas in the second set of experiments, no silylated indole product was detected. This finding indicates that the initiating step of the reaction is the rhodium-catalyzed C–H bond activation process, rather than the oxidative addition between the catalyst and silacyclobutane. Additionally, it suggests that the reaction between the C–H bond and Rh-Si intermediate is relatively difficult, whereas the polymerization between Rh-Si complexes is more facile.[20]

Based on our preliminary mechanistic studies and literature reports, a plausible mechanism is proposed in Scheme 7. Initially, coordination of the phosphine ligand gives an active Rh^I-Cl species, followed by cyclometallation of the indole, generating a five-membered rhodium(III) hydride **A** (Scheme 7, path a). Subsequently, reductive elimination of HCl gives Rh(I) species **B**. The transformation to a five-membered silametallacycle **C** occurs via oxidative addition of SCB. C-Si reductive elimination and subsequent protonolysis by HCl then furnish the target product together with regeneration of the Rh(I) catalyst. The control experiment results indicated that the mechanism of Path a is more probable. An alternative pathway is also postulated, involving Si–C oxidative addition to afford a Si-Rh-Cl species **E**, followed by C–H bond oxidative addition of indole to afford Rh^{IV}-Cl intermediate **F**, and subsequent reductive elimination then produces a common intermediate **C**.

Scheme 7 Proposed mechanism



Conclusions

In conclusion, we have reported a rhodium-catalyzed intermolecular C–H silylation of indoles with SCB. The catalytic system proceeds with high regioselectivity with relatively high efficiency and good substrate compatibility, affording a variety of silylated indoles. This new C–H silylation system expands the application of SCB in synthesis of functionalized heterocyclic compounds.

Experimental

A vial (8 mL) was charged with **1a** (0.2 mmol, 1.0 equiv), $[Rh(cod)Cl]_2$ (5 mol%), **2a** (0.4 mmol, 2.0 equiv), and DTBPF (10 mol%), THF (1.0 mL) was then added in the glovebox with N_2 atmosphere and the mixture was stirred at 100 °C in heating block for 72 h. The reaction mixture was concentrated under reduced pressure, and then purified by flash chromatography on silica gel

(petroleum ether/EtOAc, 30 : 1) to give the corresponding product **3**.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.70290.

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The Authors

Left to Right: Shengbo Xu, Mengxia Gong, Fen Wang, Xingwei Li

