Synthetic Methods

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Rhodium-Catalyzed Tandem Cyclization/Si–C Activation Reaction for the Synthesis of Siloles**

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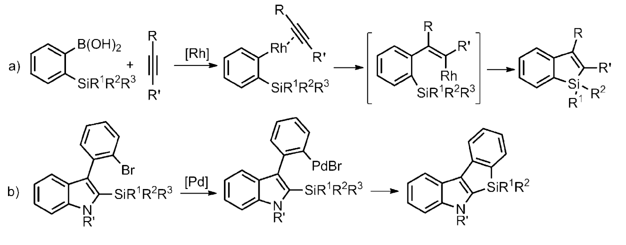
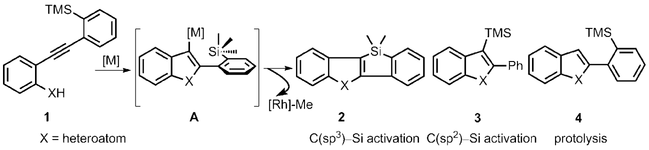
Abstract: *Siloles represent an important emerging class of photoluminescent materials. Reported herein is a new synthetic strategy involving a tandem cyclization/Si–C activation reaction featuring high efficiency, wide substrate scope, and practical utility. This method enabled the first synthesis of benzofuran siloles as well as rapid access to conjugated siloles. During the course of the study we also uncovered an unusual yet general Si–C(sp^2) activation in the presence of π acids.*

Siloles have found wide applications in light-emitting materials, fluorescent probes, thin-film transistors and solar cells because of their unique optical and electronic properties.[1–6] Introduction of a heteroatom or an aryl group is frequently explored to modify the light-absorbing and light-emitting behavior of the parent siloles.[2b] In this context, facile synthesis and easy derivation of silole scaffolds remain important both in synthetic and material chemistry. Traditional syntheses of siloles often require stoichiometric organic lithium or magnesium reagents, and thus limited the choice of functional groups on the substrates. In answer to this challenge, remarkable advances have been made toward the catalytic synthesis of siloles.[7–14] Among them, the most recent syntheses involving catalytic activation of Si–C bonds were conceptually inspiring, thus featuring high efficiency and intriguing reactivity.[11–12] Specifically, Chatani and co-workers reported facile Si–C bond activation reactions catalyzed by in situ generated Rh–C(sp^2) species by transmetalation between aryl boronic acids or esters and alkynes (Scheme 1 a).[11b,c] As a valuable alternative, Xi and co-workers discovered that Pd^0 underwent oxidative addition to aryl bromides, thus leading to efficient activation of Si–C bonds in both an inter- and intramolecular fashion (Scheme 1 b).[12] Despite this progress, additional investigations on silole synthesis through Si–C bond activation would not only expand the synthetic toolbox, but also provide insight into the mechanistic aspects associated with this useful yet less explored process.



Scheme 1. Recent breakthrough in catalytic Si–C(sp^3) activation.

Inspired by these pioneering works, we were intrigued by the possibility of accessing siloles by tandem cyclization/Si–C bond activation reactions (Scheme 2). At the heart of this design is the new strategy to generate a M–C(sp^2) species capable of Si–C bond activation, which is distinct from the previous transmetalation or oxidative insertion pathways (Scheme 1). Briefly, we anticipated that the intramolecular cyclization[15] of the aniline derivative **1** would generate such an organometallic intermediate (**A**). Subsequent selective activation of the Si–C(sp^3) bond would provide the desired indole [3,2-*b*] silole **2**. However enticing this proposal might appear, it was conceived to have three major challenges: 1) the cyclization reaction requires a Lewis-acidic (electron-deficient) metal catalyst, while subsequent Si–C bond activation is best achieved with an electron-rich metal species;[16] 2) the protodemetalation of **A** (undesired) and [Rh]-Me (desired for catalyst turnover) are two competing pathways. The protonation of **A** might prevail because of its inherent higher basicity relative to that of the intermediate [Rh]–Me;[17] 3) very little is known about the selectivity in rhodium-catalyzed activation of different Si–C bonds.[11] In this particular case, the relatively electron-rich nature of **A** might favor oxidative addition of the Si–C(sp^2) bond,[18] thus leading to the undesired silicon-group-transfer product **3** upon reductive elimination.



Scheme 2. The tandem cyclization/Si–C activation strategy. TMS = trimethylsilyl.

With these considerations in mind, we commenced our study using the methylsulfonyl-protected aniline derivative **1a** as the model substrate (Table 1). It is important to point out that one advantage of this strategy lies in the easy access to the substrate of type **1a** by standard Sonogashira coupling reactions between widely available alkynes and aryl halides.

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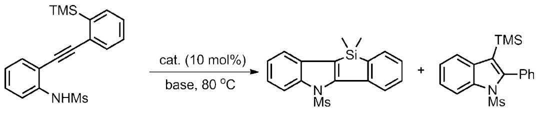
Table 1: Screening of the reaction conditions.[a]



1a **2a** **3a**

Entry	Cat.	Base	Solvent	Yield (**2a**/**3a**)[b]
1	CuOTf	DABCO	1,4-dioxane	n.d.
2	$PdCl_2$	DABCO	1,4-dioxane	n.d.
3	$[\{Ir(cod)Cl\}_2]$	DABCO	1,4-dioxane	n.d.
4	$[Ru(cod)Cl_2]$	DABCO	1,4-dioxane	n.r.
5	$[\{Rh(cod)Cl\}_2]$	DABCO	1,4-dioxane	32 (3:1)
6	$[\{Rh(cod)Cl\}_2]$	DABCO	toluene	23 (5:1)
7	$[\{Rh(cod)Cl\}_2]$	*t*BuONa	1,4-dioxane	trace
8	$[\{Rh(cod)Cl\}_2]$	DMAP	1,4-dioxane	<10
9	$[\{Rh(cod)Cl\}_2]$	DBU	1,4-dioxane	0
10	$[\{Rh(cod)Cl\}_2]$	DABCO	toluene/H_2O	<10
11	$[\{Rh(cod)Cl\}_2]$	DABCO	toluene/ethanol	44 (4:1)
12	$[\{Rh(cod)Cl\}_2]$	DABCO	toluene/octanol	65 (7:1)
13	$[\{Rh(cod)Cl\}_2]$	DABCO	mesitylene/octanol	60 (8:1)
14[c]	$[\{Rh(cod)Cl\}_2]$	DABCO	toluene	40 (<5:95)

[a] **2a** (0.1 mmol), base (2.0 equiv), catalyst (10 mol%) and degassed solvent (0.5 mL, for entries 10–13, 100 uL of the proton source was added) in a N_2 flushed glove box, 80°C for 24 h. [b] Yield of isolated products. **2a**/**3a** determined by ^1H NMR spectroscopy. [c] 3,3-dimethylacrolein (5.0 equiv) was added. cod = 1,5-cyclooctadiene, DABCO = 1,4-diazobicyclo[2.2.2]octane, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, DMAP = 4-(*N*,*N*-dimethylamino)pyridine, Ms = methanesulfonyl, n.d. = not determined, n.r. = no reaction, Tf = trifluoromethanesulfonyl.

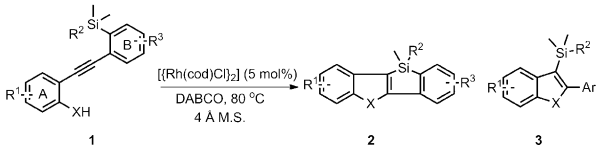
We first tested a number of catalysts (entries 1–5) using DABCO (2.0 equiv) as the base and 1, 4-dioxane as the solvent. Disappointingly, the more cationic CuOTf and $PdCl_2$ only gave the byproduct **4a** (entries 1 and 2). In these two cases, the protodemetalation took place before any Si–C activation could be observed, probably because of the aforementioned lability of **A**. In light of this, heavy late-transition metals, which are thought to form more stable M–C bonds,[19] were then examined (entries 3–5). However, $[\{Ir(cod)Cl\}_2]$ only gave a complex mixture with no desired product detected (entry 3), and no reaction took place with $[Ru(cod)Cl_2]$ (entry 4). To our delight, with $[\{Rh(cod)Cl\}_2]$ the desired Si–C bond activation products (e.g. **2a** and **3a**) could be obtained in a low combined yield (32%). The selectivity for Si–C(sp^3) over Si–C(sp^2) bond activation was also moderate (**2a**/**3a** = 3:1; entry 5). When the solvent was changed to the less-polar toluene, the selectivity improved to 5:1 but the yield decreased to 23% (entry 6). In both cases the low yields of Si–C bond activation products were due to the undesired protodemetalation of **A**, a process which generated the hydroamination product **4a** predominantly.

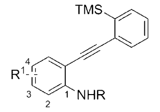
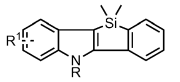
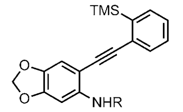
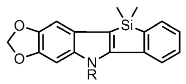
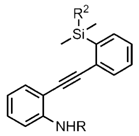
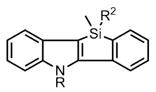
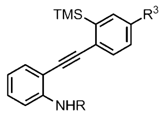
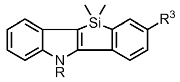
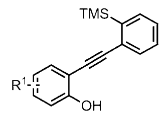
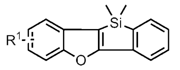
To circumvent the undesired protodemetalation, we tested various bases with the notion that decreasing the acidity of the reaction mixture might favor the Si–C bond activation pathway (Table 1, entries 7–9). With the strong base *t*BuONa, very low conversion of the substrate was observed (entry 7). A similar observation was made with DMAP (entry 8). In the presence of another strong base DBU, full conversion of **1a** was achieved, however, the only obtained product was the protodemetalation byproduct **4a** (entry 9). Since the reaction pathway had no clear dependence on the pK_a value of the bases, factors governing the competing protodemetalation/Si–C bond activation are likely more complicated than the rate of the Rh–C(sp^2) protolysis. In other words, the bases could also act as a ligand to the rhodium and influence the rate of the Si–C bond activation in terms of both electronic and steric effects.[20]

During the screening process, we observed that the yield of product **2a** was closely related to the catalyst loading, thus hinting at a difficult catalyst turnover. Accordingly, we attempted to use external proton sources to facilitate the protonation of the Rh–Me intermediate (Scheme 2; Table 1, entries 10–14). We were cautious that this might lead to escalated protodemetalation of **A**. However, as indicated in our experiments with the base additive, the key lies in alternating the competition between the desired catalyst turnover and the undesired protodemetalation of **A**. Water has been known to help rhodium catalyst turnover, however in our case it resulted in a diminished yield (entry 10). After extensive experimentation, we identified that addition of ethanol could improve the yield to 44% without apparent change in the ratio of **2a**/**3a** (4:1; entry 11). Satisfyingly, both the yield (65%) and the selectivity (**2a**/**3a** = 7:1) were further improved when *n*-octanol was employed (entry 12). A similar result was obtained in the less-polar solvent mesitylene (entry 13). Very interestingly, when the π acid 3,3-dimethylacrolein (5.0 equiv) was used instead of alcohols, the selectivity for Si–C(sp^3) over Si–C(sp^2) bond activation was reversed, thus leading exclusively to the silicon transfer product **3a** (entry 14; see the Supporting Information). We further identified that 2-trifluoromethyl phenylsulfonyl is the optimal protecting group of the indole nitrogen atom after extensive screening (see the Supporting Information), such that the reaction proceeded smoothly under milder reaction conditions (5 mol% catalyst at 80°C) to afford **3a** in 82% yield.

With the optimized reaction conditions and protecting group, we investigated the substrate scope as summarized in Table 2. First, we studied the substituent effect on ring A (entries 1–7). Both electron-withdrawing (entry 3) and electron-donating (entries 1, 2, and 4–6) groups on ring A were well tolerated, thus giving good yields of the desired silole products with high selectivity. The piperonyl substrate **1g** also reacted smoothly to furnish **2g** in 66% yield with excellent selectivity (16:1; entry 7). In addition, the structure of **2g** was unambiguously determined by single-crystal X-ray diffraction.[21] Second, we examined the silicon moiety with ethyl, *n*-butyl, and isopropyl substitutions (entries 8–10). To our great delight, in all three cases the Si–Me bond was preferentially cleaved to give the corresponding unsymmetrical siloles in good yields. We then turned our attention to the substitution on ring B (entries 11–14). Notably, regardless of their stereoelectronic difference, all the four cases produced the desired siloles in moderate to good yields with uncompromised selectivity. It is worth mentioning that our method enabled the first synthesis of benzofuran siloles, which are predicted to possess interesting properties.[22] Thus, when *t*BuONa (1.0 equiv) was used in place of *n*-octanol, the phenolic substrates **1o** (entry 15) and **1p** (entry 16) were successfully

Table 2: Substrate scope.[a]



Entry	Substrate	Product	Yield[b]	2/3[c]
				
1	R^1 = H, R = Ms (**1a**)	**2a**	65	7:1
2	R^1 = H (**1b**)	**2b**	82(50)[d]	10:1(0:1)[d]
3	R^1 = 3-F (**1c**)	**2c**	69	8:1
4	R^1 = 3-Me (**1d**)	**2d**	67	10:1
5	R^1 = 3-OMe (**1e**)	**2e**	75	11:1
6	R^1 = 4-Me (**1f**)	**2f**	54	5:1
				
7	**1g**	**2g**	66	19:1
				
8	R^2 = Et (**1h**)	**2h**	77(34)[d]	8:1(0:1)[d]
9	R^2 = *n*Bu (**1i**)	**2i**	79	9:1
10	R^2 = *i*Pr (**1j**)	**2j**	61	8:1
				
11	R^3 = Me, (**1k**)	**2k**	71	5:1
12	R^3 = *t*Bu, (**1l**)	**2l**	65	5:1
13	R^3 = C(O)*n*Bu, (**1m**)	**2m**	52	11:1
14[e]	R^3 = Cl, (**1n**)	**2n**	57	8:1
				
15[f]	R^1 = H (**1o**)	**2o**	54(50)[d]	18:1(0:1)[d]
16[f]	R^1 = 3-OMe (**1p**)	**2p**	41(61)[d]	16:1(0:1)[d]

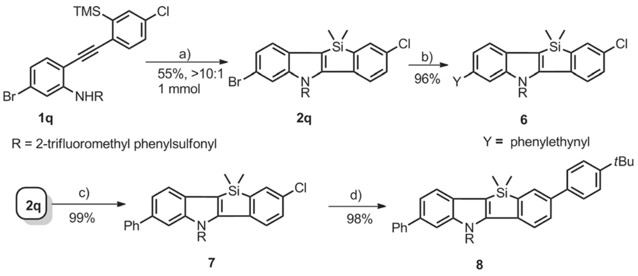
[a] Standard conditions, R = 2-trifluoromethanesulfonyl except for **1a** where R = Ms [b] Yields of isolated products [%]. [c] Determined by ^{1}H NMR analysis. [d] 3,3-dimethylacrolein (1.0 equiv) were added instead of *n*-octanol, the yields and ratios of **2/3** are shown within the parentheses. [e] 10 mol% catalyst was used. [f] *t*BuONa (1.0 equiv) was added, the reaction was carried out in toluene (1 mL), please see the Supporting Information. M.S. = molecular sieves.

converted into the siloles **2o** and **2p**, respectively, with excellent selectivities (18:1 and 16:1).

To prove the utility of our method in fluorescent material research, larger scale preparation as well as the removal of the protecting group was pursued (see the Supporting Information). As an illustration, 5 mmol of **1b** (2.37 g) was successfully converted into the silole product **2b** in 76% yield upon isolation with a greater than 20:1 selectivity. After screening a panel of reaction conditions, the 2-trifluoromethyl phenylsulfonyl group was cleanly cleaved using Mg foil with the assistance of NH_4Cl, thus furnishing the unprotected silole **5** in 91% yield (for the structure of **5**, see **2b** but with R = H)), which could serve as a good starting point to further functionalize the N atom. Our preliminary data suggested that the representative silole products (**2d**, **2e**, **2g**, **2o**, **2p**, **3**, **5**) exhibit interesting light-emitting properties which warrant further investigation (see Table S1 in the Supporting Information).

The π-acid effect observed with **1a** (entry 14, Table 1) was proven to be a general phenomenon as illustrated by various other substrates (**1b**, **1h**, **1o** and **1p**). As shown in Table 2 (entries 2, 8, 15 and 16), the selective Si–C(sp^2) activation led to the products **3b**, **3h**, **3o**, and **3p** with excellent selectivity and in moderate yields (34–61%). The single-crystal X-ray structure of **3b** was also obtained to unambiguously determine its identity.[21] To the best of our knowledge this represents the first case wherein selective cleavage of both Si–C(sp^3) and Si–C(sp^2) could be achieved with the same metal catalyst, thus leading to the synthesis of two types of valuable fluorescent materials under subtly different reaction conditions.

One potential advantage of this method is its compatibility with aryl halides as it does not involve an oxidative-addition pathway under rhodium catalysis.[23] We demonstrated such an advantage in the synthesis of the conjugated siloles **6**–**8** as depicted in Scheme 3. Again, the substrate **1q**, containing preinstalled halogens (Br and Cl), was readily synthesized. Satisfyingly, the desired product **2q** was obtained in good yield with high selectivity under the reaction conditions on a 1 mmol scale. Subsequent Sonogashira coupling provided the phenylethynyl-substituted silole **6** in 96% yield with the aryl chloride intact. Alternatively, sequential Suzuki–Miyaura coupling reactions first with phenylbronic acid then with *para-tert*-butyl phenylbronic acid elaborated the product **2q** into the functionalized siloles **7** and **8** in excellent yield and chemoselectivity.[24,8b] Given the versatility of the preinstalled halogen functionality, this



Scheme 3. Syntheses of conjugated indole siloles. Reagents and conditions: a) Standard conditions, 10 mol% cat.; b) phenylacetylene, Et_3N, $[Pd(PPh_3)_2Cl_2]$ (5 mol%), CuI (1 mol%), 50 °C; c) $PhB(OH)_2$ (1.5 equiv), $Pd(OAc)_2$ (10 mol%), Sphos (20 mol%), K_3PO_4 (3 equiv), toluene, 50 °C; d) 4-*t*BuPhB$(OH)_2$ (1.5 equiv), $Pd(OAc)_2$ (10 mol%), Sphos (20 mol%), K_3PO_4 (3 equiv), toluene, 90 °C.

method should find applications in the syntheses of other conjugated siloles.

We propose the mechanism of the selective activation of Si–C bonds based on our experimental findings and recent work[25] (Figure 1). As shown in the central box, ligand exchange of the precatalyst [{Rh(cod)Cl}$_2$] (**D1**) with DABCO (annotated as [N]) gave rise to [Rh(cod)-(DABCO)Cl] (**D2**). Species **D2** was successfully detected by HRMS ($[M+H]^+ = 359.0757$; see the Supporting Information) after careful experimentation. Dissociation of a Cl$^-$ from **D2** would lead to the cationic, coordinative unsaturated [Rh(cod)(DABCO)]$^+$ (**D3**) which serves as the active catalyst for the cyclization. Depending on the additive (e.g., *n*-octanol or 3,3-dimethylacrolein), the resulting indole–Rh intermediate **A** or $\mathbf{A}_{\pi\ \text{acid}}$ could then undergo oxidative insertion to either Si–C bond as depicted, thus leading to intermediates **B** or **C**, respectively. Reductive elimination of **B** would produce the final product **2** as well as [Rh(cod)(DABCO)Me] (**D4**). Protodemetalation of **D4** with the aid of *n*-octanol then regenerates the active catalyst **D3** and concludes the catalytic cycle. Based on our observations, this step was the turnover-limiting step of the tandem reactions. In contrast, reductive elimination of **C** would give the silicon-transfer product **3** and the corresponding Rh–Ar species (not shown). Unlike [Rh-(cod)(DABCO)Me], the more liable Rh–Ar could undergo facile protonation possibly by the DABCO conjugated acid to regenerate the active catalyst **D3**.

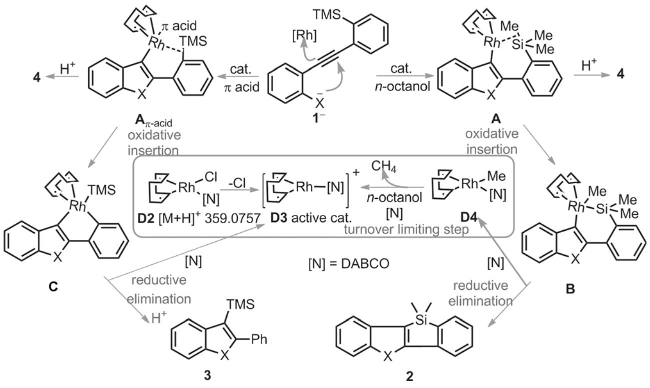


Figure 1. Proposed mechanism for the selective Si–C activation.

In conclusion, we have developed a new method for the rapid synthesis of structurally diverse siloles, including the first examples of benzofuran siloles, through a rhodium(I)-catalyzed cyclization/Si–C bond activation sequence. During our efforts to reconcile the different demands of these two processes, we discovered that external proton source is beneficial for the catalyst turnover. Divergent selectivity for Si–C(sp^3) and Si–C(sp^2) bond activation was achieved depending on subtly different additives, thus underscoring interesting mechanistic aspects of rhodium-catalyzed Si–C activation.[25] We further demonstrated the advantage of this method in the synthesis of halogenated siloles which allows rapid derivation. Further work concerning the mechanistic implications, the enantioselective synthesis of chiral siloles, as well as light emitting siloles are currently ongoing in our group.

Experimental Section

The substrate **1** (0.1 mmol), DABCO (0.1 mmol), [{Rh(cod)Cl}$_2$] (5 mol %), and degassed solvent (toluene/1-octanol, 0.5:0.1 mL) were added to a screw-capped tube in a N$_2$ flushed glove box. The tube was capped and removed from the glove box and the reaction mixture was heated at 80 °C for 12 h. The reaction mixture was filtered, washed with ethyl ether, and concentrated under vacuum. The resulting mixture was directly subjected to silica gel column chromatography (eluent: hexanes/EtOAc 100:1).

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[21] CCDC 948123 (**2g**) and 979513 (**3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. (Also see SI)

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