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Dual photoredox nickel-catalyzed silylation of aryl/heteroaryl bromides using hydrosilanes†

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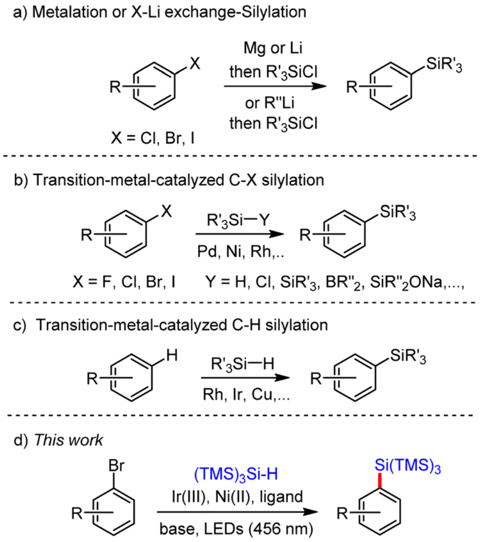
Dual Ni and Ir catalysis enables the preparation of arylsilanes having a $(TMS)_3Si$ substituent from the corresponding aryl bromides and $(TMS)_3SiH$ at 30 °C using visible-light irradiation. This protocol avoids strong bases, high temperature and air and moisture sensitive silyl reagents, providing the expected arylsilanes in moderate to good yields. The reaction was shown to proceed through a silyl radical, likely generated by hydrogen atom abstraction from $(TMS)_3SiH$ by a bromide radical.

Arylsilanes have found widespread utility in organic synthesis and materials chemistry due to their unique reactivity and properties.[1] They may also serve as versatile intermediates in organic transformations, including electrophilic *ipso* substitution,[2] Heck,[3] and Hiyama–Denmark cross-coupling reactions.[4] These transformations enable the introduction of aryl groups onto diverse substrates, making arylsilanes valuable building blocks for the synthesis of complex organic molecules. Arylsilanes exhibit remarkable stability, the C–Si bond being highly resistant to oxidation and hydrolysis, allowing for synthetic manipulations under harsh conditions without compromising the integrity of the C–Si bond. In addition to their synthetic utility, their unique properties, such as thermal stability and low toxicity, make them suitable for use in polymers and electronic materials.[5] Overall, arylsilanes offer a valuable toolbox for synthetic chemists, providing versatile reactivity, stability, and tunable properties. Their applications span across diverse fields, including synthesis, materials science, and pharmaceutical research,[6] making them important components in modern organic chemistry.[1,2]

The traditional approach of building arylsilanes involves the metalation through a Barbier-type reaction or lithium–halogen exchange using an organo-lithium reagent followed by a silylation of the resulting aryl-Mg(Li) intermediate (Scheme 1a).[1,7] This strategy however has several drawbacks, including low functional group tolerance, harsh reaction conditions, and requires the use of air- and moisture sensitive reagents. Transition-metal silylation of aryl halides has offered an attractive alternative to this strategy, allowing the C_{sp^2}–Si bond formation starting from a broad variety of aryl(heteroaryl) halides and various silylating agents (Scheme 1b).[8] Amongst these reagents hydrosilanes and silylboranes, have found a widespread use although the former tends to provide various amount of reduced products, while the latter are air and moisture sensitive. Disilanes have also been used, but suffer from a low reactivity of the Si–Si bond, which activation requires strong bases and high temperature. Recently sodium silanolates and silylsilanolates were designed to address some of these issues.[9]

Friedel–Crafts C–H silylation is a powerful technique, which is however restricted to electron-rich arenes and heteroarenes such as indoles and pyrroles.[10] Recently, transition metal-catalyzed



Scheme 1 Cross-coupling reactions between aryl halides or arenes and silylating reagents.

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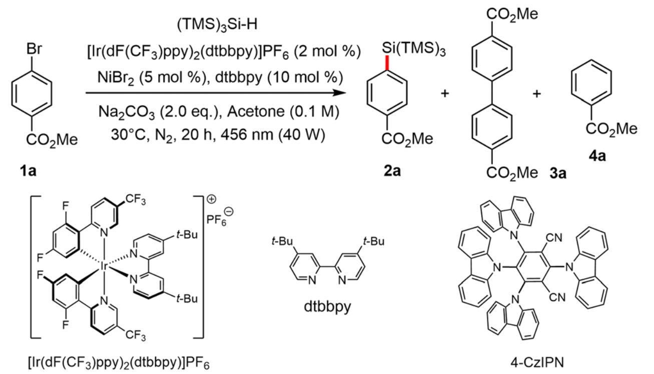
cross-dehydrogenative coupling between arenes/heteroarenes and hydrosilanes to deliver arylsilanes has grown in popularity (Scheme 1c).[11] Iridium, ruthenium and rhodium complexes were shown to exhibit efficient catalytic activities in C–H silylation.[12] However, the following challenges nevertheless continue to exist: (1) low regioselectivity; (2) need for directing groups, noble metal catalysts, and hydrogen acceptors. More recently, Liu and co-workers disclosed a radical mediated site-selective aryl/heteroaryl C–H silylation in the presence of Cu_2O catalyst, a peroxide, and a hydrosilane.[13] This strategy exhibits exceptional *para*-selectivity. However, large excess of peroxide, hydrosilane, and high temperatures are required. Finally, unactivated arenes and heteroarenes were recently silylated using silyldiazenes under transition-metal free conditions.[14] In this context, we recently uncovered a photoredox mediated dual Ir/Ni catalysis[15] for the construction of arylsilanes, which proceeds at room temperature, using readily available tristrimethylsilylsilane ($(TMS)_3SiH$)[16] as the silicon source and aryl bromides as aryl precursors (Scheme 1d).

The process was optimized using methyl-4-bromobenzoate **1a** as model substrate and TMS_3SiH as the silicon source. Following extensive screening, we discovered that $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ as a photocatalyst and $NiBr_2$ as a synergistic catalyst, sodium carbonate (Na_2CO_3) as the base at room temperature in acetone, delivered the product in reasonable yield (entry 1). Several solvents were also used to optimize the reaction conditions (SI), but "green" (dry) acetone proved to be the best. Two side-products were identified, including biaryl **3a** and the debrominated adduct **4a**, which could be easily discarded upon chromatography. Stronger inorganic bases, such as K_2CO_3 and K_3PO_4 were tested, but led to decomposition of the starting material and to very low yield in **2a** (entries 2 and 3). The organic base 2,6-lutidine efficiently yielded the corresponding product, albeit in a slightly lower yield (entry 4). The nature of the Ni(II) catalyst was also studied. $NiCl_2$·glyme, $NiBr_2$·glyme, and $NiBr_2$ all afforded comparable yields. $NiBr_2$ being the cheapest available, it was retained for the remaining part of the study (entries 1, 5 and 6). Next, several ligands were also screened, with dtbbpy providing the best yields (entries 7 and 8). Interestingly, when 5,5′-CF_3-bpy was employed as a ligand, the self-coupling product **3a** was the main product with a 47% yield (entry 9). The amount of $(TMS)_3SiH$ in the reaction proved to be crucial as shown with the better yield obtained when 3 equivalents was used (entry 10). Under these optimized conditions, absence or traces of **2a** were observed when the reaction was performed in the absence of a catalyst (entry 11), light (entry 12) or base (entry 13). The target product was then produced in 45% yield when the organic photocatalyst 4-CzIPN was utilized in place of $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (entry 14). Other silanes including $PhMe_2SiH$ were tested, but led to much lower yields (<10%) under these conditions. Aryl chlorides were also used as precursors but were found to be poorly reactive.

Table 1 Optimization of the Ni/Ir cross coupling between arylbromide **1a** and $(TMS)_3SiH$



Entry	Deviation from standard conditions[a]	Yield[c] (%) 2a	Yield[c] (%) 3a	Yield[c] (%) 4a
1	None	44	5	12
2	K_2CO_3	<10	—	—
3	K_3PO_4	<10	—	—
4	2,6-Lutidine	37	4	36
5	$NiCl_2$·glyme	42	16	30
6	$NiBr_2$·glyme	44	17	20
7	bpy	38	24	25
8	4,4′-OMe-bpy	21	6	32
9	5,5′-CF_3-bpy	17	47	11
10	$(TMS)_3SiH$ (3 eq.)	62	11	14
11[b]	No catalyst [Ir]	0	0	0
12[b]	No light	0	0	0
13[b]	No base	Traces	Traces	Traces
14[b]	4-CzIPN instead of [Ir]	45	7	11

[a] Standard conditions: $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (2 mol%), $NiBr_2$ (5 mol%), dtbbpy (10 mol%), Na_2CO_3 (2 eq.), **1a** (0.2 mmol, 1 eq.), $(TMS)_3SiH$ (0.4 mmol, 2 eq.), dry acetone (2.0 mL), Kessil 40 W LEDs (456 nm), 30 °C, 20 h. [b] $(TMS)_3SiH$ (0.6 mmol, 3 eq.). [c] ^1H NMR yields of **2a**, **3a**, and **4a** using mesitylene as an internal standard.

Having established the optimal conditions (Table 1, entry 10), various bromides were then submitted to the Ir/Ni cross-coupling process. The corresponding arylsilanes were generated in moderate to good yields, as shown in Scheme 2. Benzene rings with electron-deficient substituents, including esters and ketones as in **2a**, **2b** and **2p–r**, nitriles (**2c**, **2d**), amides (**2h**, **2i**, **2s**), sulfones (**2j**), halogens (**2f**, **2g**), and trifluoromethyl groups (**2e**), reacted smoothly. Interestingly, the method is compatible with the presence of acidic protons as in **2h**, **2i** or **2s**. The formation of *ortho*-cyanoarylsilane **2d** in only moderate yield demonstrates that steric hindrance around the reacting center may be a limiting factor. On the other hand, attempting the reaction with methyl 2-bromobenzoate as the substrate did not result in any reaction (ESI†). Certain electron-donating substituents, such as methyl (**2n**), ethyl (**2m**), and *t*-butyl (**2o**), are also compatible with this system, although the yield is lower, most likely due to the ease with which electron-rich aromatic rings are oxidized by the Ir photocatalyst in its excited-state. Benzylic positions as in **2i** remains however intact. It is worth noting that derivatives of certain natural products (**2p–s**) exhibit efficient reactivity, yielding the desired product in moderate to good yields. To our satisfaction, although the yield was modest, we found that heteroaromatics (*i.e.* **2t–v**) were also appropriate substrates for this reaction conditions. Finally, we attempted to extend the methodology to alkyl bromides. Primary alkyl bromides were thus shown to react to afford the corresponding products (**2w–y**) in moderate yields.

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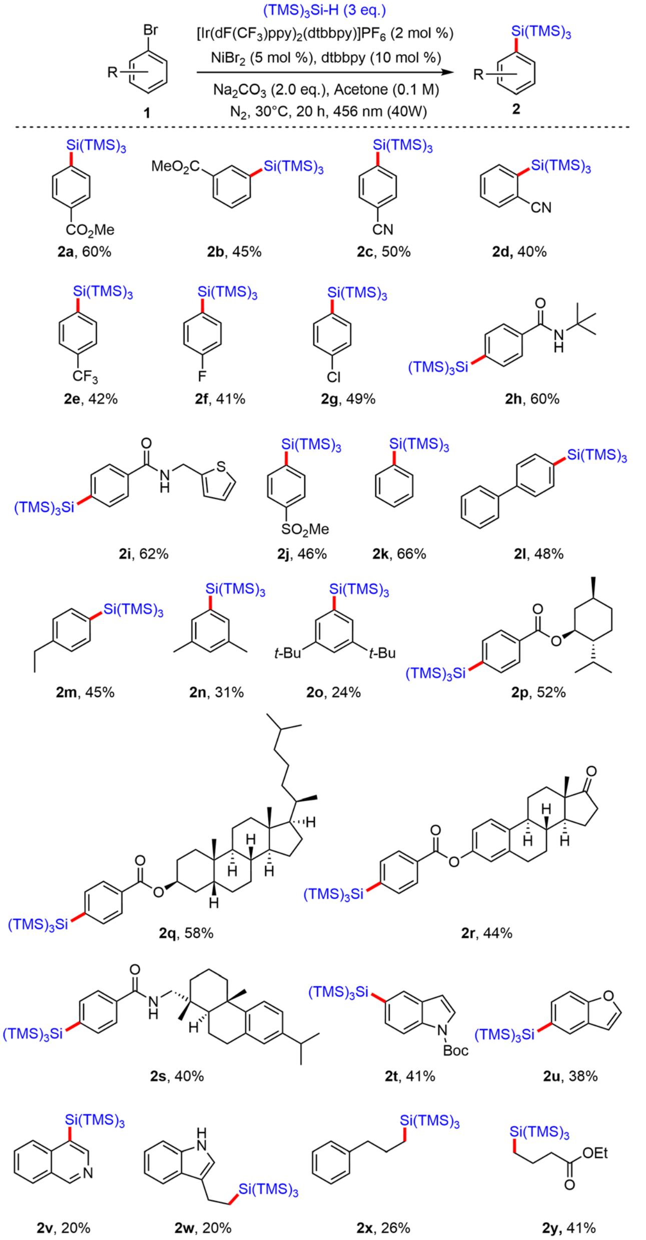
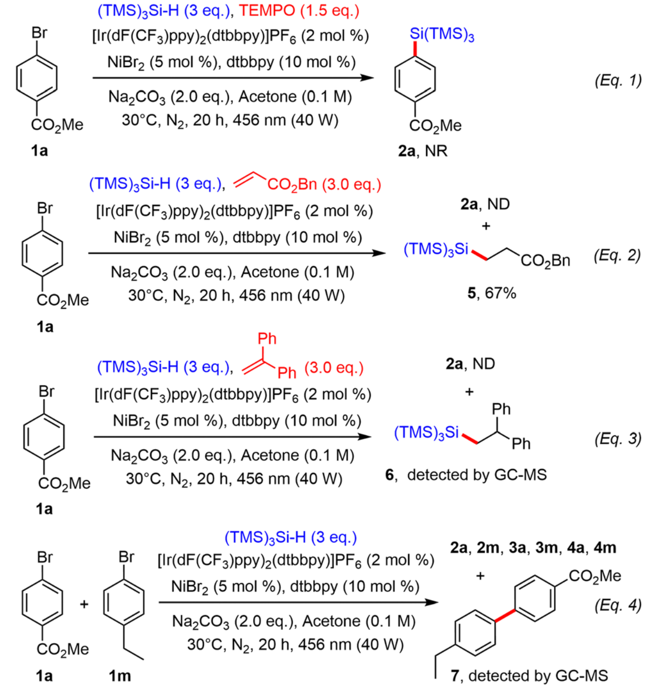


Scheme 2 Scope of the Ir/Ni-catalyzed cross-coupling process between bromoarenes **1** and (TMS)$_3$SiH.



Scheme 3 Mechanistic studies.

Preliminary mechanistic investigations were also performed. For instance, when the reaction between **1a** and (TMS)$_3$SiH under the optimal conditions above was repeated in the presence of TEMPO, no reaction occurred, indicating the occurrence of radical species during the process (Scheme 3, eqn (1)). Benzyl acrylate was then added to the standard reaction mixture as a radical trap. Under these conditions, the target product **2a** was not detected, but addition product **5** was isolated in good yield, diagnostic of the formation of a silyl radical, which is known to add efficiently onto electron-poor olefins (Scheme 3, eqn (2)).[17] When the reaction was repeated in the presence of 1,1-diphenylethylene, the desired product **2a** was not formed, but the hydrosilylation product **6** could be detected by GC-MS, confirming the presence of a silyl radical (Scheme 3, eqn (3)). Finally, when both aryl bromides **1a** and **1m** were mixed together under the above dual catalytic system, arylsilanes **2a** and **2m**, reduced products **4a** and **4m** but also homocoupling products **3a** and **3m** were detected by GC-MS. Heterobiaryl coupling product **7** was also found, suggesting the formation of aryl radicals during the process (Scheme 3, eqn (4)).[18]

Based on these experimental evidences and literature precedent using similar dual catalytic systems,[15b] a plausible mechanism was proposed (Fig. 1). The Br$^-$ issued from NiBr$_2$ is oxidized by Ir(III)* in its excited-state, under blue-light irradiation, to give Br$^\bullet$ and Ir(II).[15b] Oxidation of electron-rich aryl bromides by Ir(III)* may compete with this step, explaining the lower yield with these arenes (ESI†). Br$^\bullet$ then abstracts a hydrogen from the silane to afford the silyl radical **I**.[17] Meanwhile, the Ni(I) is reduced by the resulting Ir(II) into Ni(0) and the photoactivable Ir(III). Oxidative addition of aryl bromide **1** onto the Ni(0) complex provides the Ni(II) species **II** and Br$^-$. The silyl radical **I** then reacts with **II**, leading to the Ni(III) complex **III**, the reductive elimination of which affording the final coupling product **2**. Interestingly, the silyl radical might also abstract a bromine atom for aryl bromide **1** and afford an aryl radical **IV**,[18] which could enter into the Ni catalytic cycle, reacting for instance with **II** to provide after reductive elimination a biaryl **3**. Such a pathway would explain the formation of **3a** (Table 1). The same aryl radical **IV** may react further with (TMS)$_3$SiH to furnish reduction product **4**.[16,19] Abstraction of the bromide from **1** to generate unstable aryl radical **IV**, is likely a slower pathway as compared with the reaction of the (TMS)$_3$Si radical **I** with intermediate **II**.[19]

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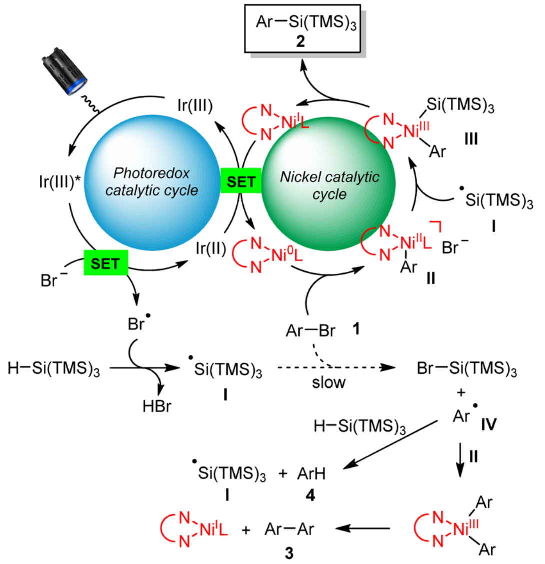

Fig. 1 Dual catalytic system. Suggested mechanism.

In summary, we report here on a new silylation process of arylbromides using simple $(TMS)_3SiH$. The combination of the $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ complex and $NiBr_2$/dtbpy catalyst was shown to trigger the formation of aryl/heteroaryl/alkyl silanes using commercially available $(TMS)_3SiH$ as a silicon source.[16,17] This approach exhibits good functional group tolerance, regardless of their electronic properties, leading to the desired products with moderate to satisfying yields. In addition, not only aryl bromides and heteroaryl bromides, but also primary alkyl bromides can serve as suitable substrates. This strategy offers a complementary method to access these synthetically important synthons, avoiding strongly basic organo-lithiums and sensitive chlorosilanes. It also offers an entry for the late stage functionalization of pharmaceutically relevant compounds[20] and access to silicon isosteres through the so-called "silicon-switch" strategy.[21] Work in now under way to further extend this method to other aryl derivatives and silanes.

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Conflicts of interest

There are no conflicts to declare.

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