

Short Communication

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Photoredox/nickel dual-catalyzed reductive C(sp²)–Si cross-coupling

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Abstract

Nickel-catalyzed cross-electrophile coupling of carbon-electrophiles and silicon-electrophiles has recently emerged as a powerful tool for C–Si bond formations to synthesize highly valuable organosilanes. This reductive coupling strategy eliminates the manipulation of highly reactive organometallic reagents, thereby leading to a good functional group tolerance and a high step economy. However, the reported reductive C–Si couplings have to use stoichiometric amounts of Zn or Mn dust as a reductant, which somehow limits the synthetic application. Herein, we reported a novel cross-electrophile coupling of aryl halides with chlorosilanes enabled by dual photoredox/nickel catalysis. Instead of using metallic reductants, a mild and readily available α -silylamine is selected as a reliable organic reductant. Various vinyl chlorosilanes and chlorohydrosilanes were coupled smoothly. This new catalytic protocol offers an alternative approach for facile synthesis of organosilanes.

Keywords: Organosilanes, reductive coupling, organic reductants, photoredox catalysis, nickel catalysis, chlorosilanes



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INTRODUCTION

Organosilanes are a class of important building blocks in organic synthesis, which also have broad applications in material science and medicinal chemistry^[1-5]. Due to the importance of these compounds, substantial efforts have been devoted to the development of efficient methodologies for the synthesis of organosilanes^[6-8]. Transition metal-catalyzed C–Si coupling has been developed as a powerful synthetic tool for the preparation of organosilanes [Figure 1]^[9,10]. Traditional synthesis involves the reaction of silyl electrophiles Si–X (X = Cl, Br, I, *etc.*) with organometallic reagents C–M (M = Mg, Li, B, *etc.*)^[11-14] [Figure 1A(i)]. An opposite direction relies on the coupling of Si–M reagents with C–X^[15-18] [Figure 1A(ii)]. Despite tremendous advances, these protocols typically require the handling of highly reactive and basic organometallic reagents, thus suffering from limited functional group tolerance and experimental safety issues. In addition, the coupling of organic halides with hydrosilanes has also been developed as a useful method for the formation of organosilanes^[19-22] [Figure 1A(iii)]. However, this synthetic process is commonly complicated by the annoyed reductive dehalogenation due to the strong reductive ability of hydrosilanes. Therefore, the exploration of novel and efficient C–Si coupling strategy for accessing organosilanes^[23-25] by using readily available chemicals under mild conditions is highly desirable.

Over the past decade, transition metal-catalyzed cross-electrophile coupling between two electrophiles has received considerable attention^[26-29]. This novel and convenient coupling strategy bypasses the pre-preparation and handling of highly reactive organometallic reagents, leading to a high atom- and step-economy and broad functional group tolerance. Cross-electrophile coupling has significantly progressed in organic synthesis for the construction of C–C bonds, while the successful applications of reductive strategy in C–Si coupling are rarely reported^[30,31] [Figure 1A(iv)]. Duan *et al.* demonstrated the first nickel-catalyzed cross-electrophile coupling of vinyl/aryl electrophiles with chlorosilanes using Mn as a reductant^[32]. Further endeavors have been devoted to the expansion of substrate types and exploration of new transformations by the researchers^[33-38], Zhang and Oestreich^[39], and others^[40-43]. These attractive syntheses make an important contribution to the area of C–Si coupling. Despite the impressive advancements, the requirement of stoichiometric amounts of metal reductants (Mn or Zn) would hinder the practical application due to the substantial disposal of metal salts. Therefore, exploring a catalytic strategy that uses mild organic reductants instead of metallic reductants in C–Si coupling is meaningful.

Based on our previous studies on metallaphotoredox-catalyzed organic reductant-mediated cross-electrophile coupling reactions^[44-48], we reported herein a photoredox/nickel dual-catalyzed reductive C–Si coupling of aryl halides and chlorosilanes by applying silylamine as a potential organic reductant [Figure 1B]. This novel catalytic platform obviates the necessity of metallic reductants and shows good tolerance for both chlorosilanes and chlorohydrosilanes, thus providing a complementary approach to synthesize organosilanes via reductive C–Si coupling.

EXPERIMENTAL

The reactions were set up in a N₂-filled glovebox. An oven-dried vial equipped with a stir-bar was added aryl bromide **1a** (0.20 mmol, 1.0 equiv.), Ir(ppy)₃ (1.3 mg, 2.0 μmol, 0.010 equiv.), 5,5'-diMeppy (7.4 mg, 40 μmol, 0.20 equiv.), NiI₂ (6.4 mg, 20 μmol, 0.10 equiv.). Then, *N,N*-Dimethylacetamide (DMAc, 0.10 M, 2.0 mL), reductant α -silylamine (69 mg, 0.40 mmol, 2.0 equiv.) and chlorodimethyl(vinyl)silane **2a** (0.60 mmol, 3.0 equiv.) were added. The vial was sealed and removed from the glovebox, then irradiated with a 1.5 W blue light-emitting diode (LED) lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 24 h. After the completion of the reaction, the crude reaction mixture was indicated by thin layer chromatography, and then purified through column chromatography on silica gel (petroleum ether:dichloromethane = 100:1 as eluent) to afford pure product **3**.

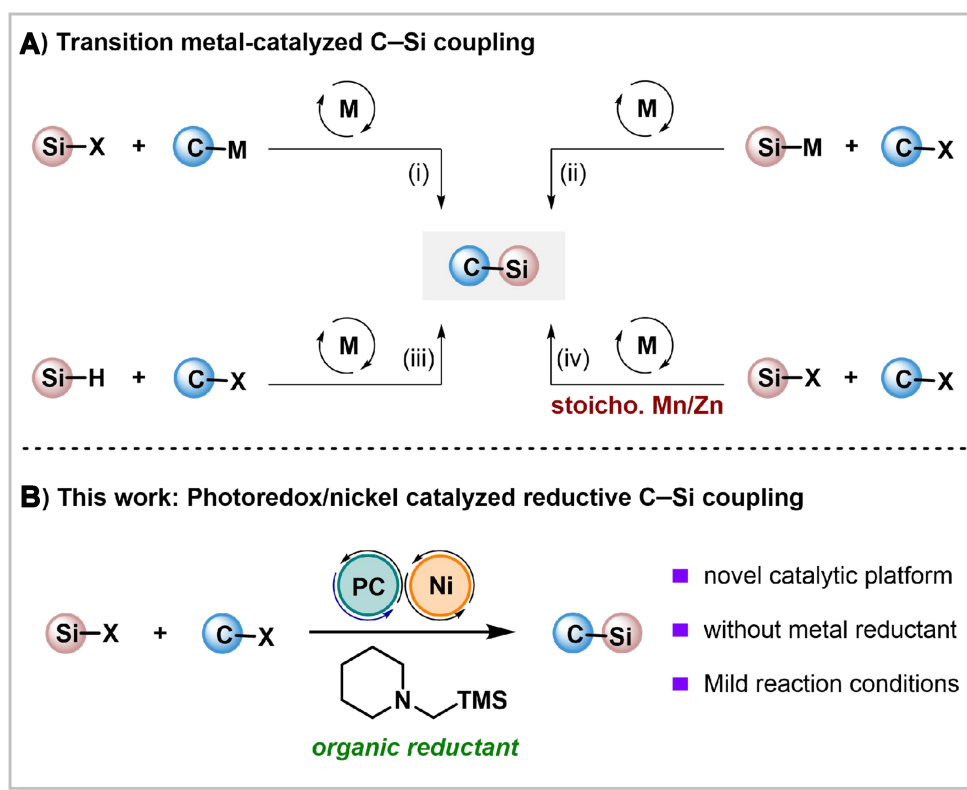


Figure 1. Profile of transition metal-catalyzed C–Si coupling.

RESULTS AND DISCUSSION

Based on this design, we initiated our study of the reductive C–Si coupling with methyl 4-bromobenzoate (1a) and chlorodimethyl(vinyl)silane (2a) in the presence of 1 mol% Ir(ppy)₃ (Tris[2-phenylpyridine]iridium) as a photocatalyst, NiI₂ (10 mol%) as a nickel catalyst. After a systematic investigation, we were pleased to find that the reaction could proceed smoothly to afford the desired coupling product (3) in 64% gas chromatography (GC) yield (with 62% isolated yield) when using 5,5'-diMeppy (5,5'-dimethyl-2,2'-dipyridine) (20 mol%) as a ligand, α -silylamine as an organic reductant, and performing the reaction in aprotic polar solvent DMAc under 1.5 W blue LED irradiation for 24 h (Table 1, entry 1). Other solvents were unable to facilitate the reaction or showed less efficiency [Supplementary Materials]. NiI₂ was found to be the most efficient catalyst after screening a sort of nickel catalyst. Besides, photocatalyst has a significant influence on the reactivity and the organic photosensitizer 4-CzIPN [1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene] could only provide 28% of GC yield (entry 2). Subsequently, other types of ligands were examined and 5,5'-diMeppy was proven to be the most efficient for the reaction (entry 6). Based on our previous discovery of α -silylamine as a potent organic reductant in carbonyl reductive coupling^[44,45], we noticed that the organic reductants should greatly influence the reaction efficiency. Indeed, several other commonly used organic reductants such as Hantzsch ester (HE), triethylamine (Et₃N), and tetrakis(dimethylamino)ethylene (TDAE) showed no reactivity here (entries 3–5). Control experiments revealed that nickel, photocatalyst, and visible light are all indispensable for the reaction (entries 7–8).

With the optimal reaction conditions determined, we then investigated the scope generality of the reductive C–Si coupling. First, the substrate scope of the aryl electrophiles was studied by reactions with 2a [Figure 2].

Table 1. Optimization of the reaction conditions^a

Entry	Deviation from the standard condition	Yield (%) ^b
1	None	64 (62) ^c
2	4-CzIPN as photocatalyst	28
3	HE as reductant	0
4	Et ₃ N as reductant	0
5	TDAE as reductant	0
6	4,4'-dtbbpy as ligand	37
7	without Ni catalyst	0
8	without light or photocatalyst	0

^aUnless otherwise noted, the reaction was carried out at 0.1 mmol scale with **1a** (0.1 mmol), **2a** (0.3 mmol); ^bYields were determined by GC with *n*-tridecane as an internal standard; ^cIsolated yield. ppy: 2-phenylpyridine; 5,5'-diMeppy: 5,5'-dimethyl-2,2'-dipyridine; DMAc: *N,N*-dimethylacetamide; 4,4'-dtbbpy: 4,4'-di-*tert*-butyl-2,2'-dipyridine; cod: 1,5-cyclooctadiene; 4-CzIPN: 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene; HE: Hantzsch esters; TDAE: tetrakis(dimethylamino)ethylene.

Aryl electrophiles irrespective of aryl bromides, iodides, and triflates were valid carbon-electrophiles to undergo reductive C–Si coupling, affording the desired coupling products in moderate yields. Aryl halides with different electronic and steric natures of substituents have no significant influence on the reactivity. Not only electron-withdrawing groups (3–8) but also electron-donating groups (9–12) reacted smoothly. Aryl bromides bearing a *para*-, *meta*-, or sterically congested *ortho*-substituted ester group successfully engaged in the reaction to deliver the corresponding products (3–5). The reaction tolerated a variety of functional groups such as CN (6), amide (7), and chloride (8). Particularly noted, the coupling process could even tolerate a boron group, a synthetic versatile functionality for further cross-coupling (13). Besides phenyl bromides, 2-bromonaphthalene and 1-bromonaphthalene were proved to be suitable substrates (15–16). Gratifyingly, heteroaryl bromides such as 5-bromobenzo[*d*][1,3]dioxole (17) and 3-bromothiophene (18) successfully participated in the reaction to give the expected products.

Furthermore, we turned our attention to investigating the substrate scope of chlorosilanes [Figure 3]. Vinyl chlorosilanes containing different substituents such as chloro(methyl)(phenyl)(vinyl)silane and chlorodiphenyl(vinyl)silane were tolerated well (19–20). Specially, chlorotri(vinyl)silane could be incorporated into the reaction to deliver tri(vinyl)phenylsilane in a good yield (21). Probably due to the enhanced coordination ability of vinylchlorosilane to the nickel catalyst, chlorosilanes without vinyl-substituent have failed to deliver any desired products. Chlorohydrosilanes are a kind of very challenging substrates in transition-metal-catalyzed silylation via selective Si–Cl cleavage as the bond dissociation energy of Si–Cl bond is higher than that of Si–H bond. Zhao *et al.* reported the first example of nickel-catalyzed reductive C–Si coupling of chlorohydrosilanes via selective Si–Cl bond cleavage in the aid of Mn as reductant^[34]. To explore the feasibility of chlorohydrosilanes in our developed photoredox/nickel dual

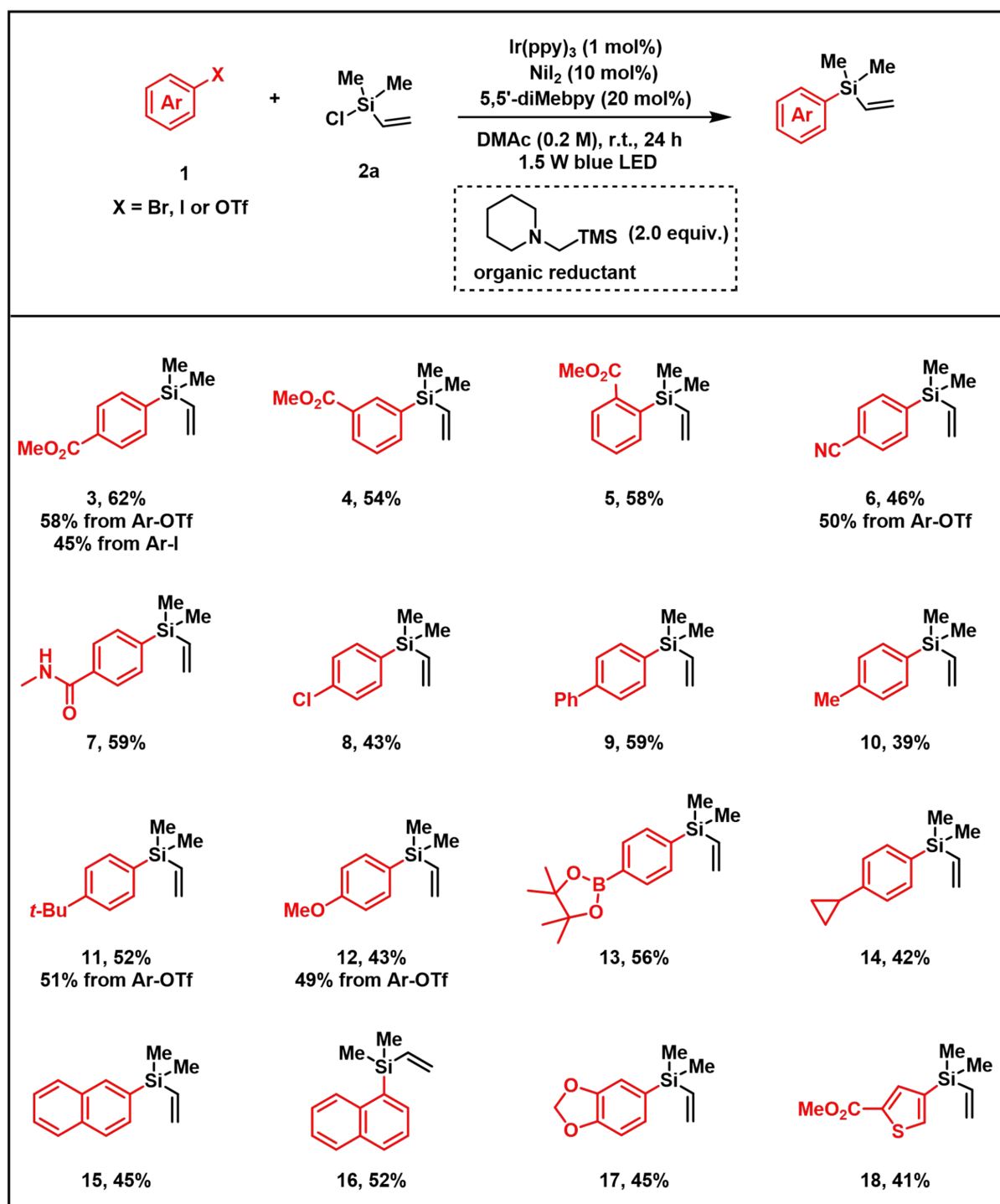


Figure 2. Substrate scope of C–Si coupling with respect to aryl electrophiles. Reaction conditions: 1 (0.2 mmol), 2a (0.6 mmol, 3.0 equiv.). Isolated yields.

catalytic system, we further optimized the reaction conditions. To our delight, after slightly adjusting the ligand to 3,4,7,8-Me₄Phen and using a mixed solvent system, the coupling of chlorodiphenylsilane with different aryl halides could afford triphenylsilanes in moderate yields (22–24).

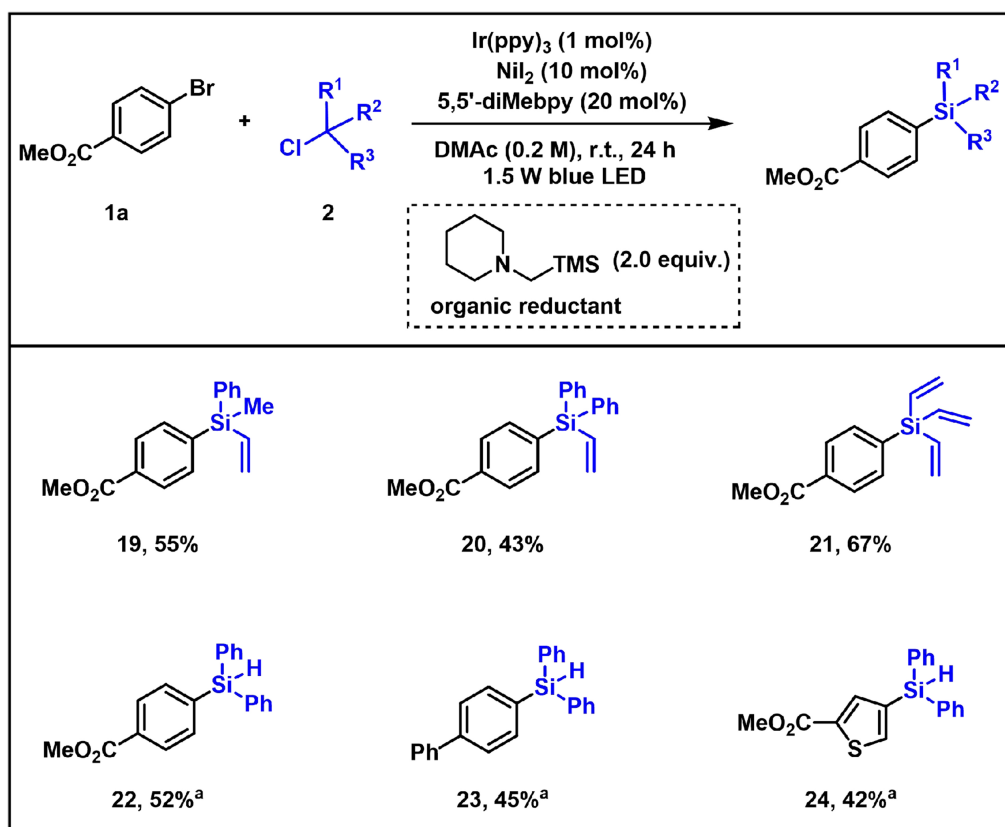


Figure 3. Substrate scope of C–Si coupling with respect to chlorosilanes. Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol, 3.0 equiv.). Isolated yields. ^aMeCN/DMAc: 7:3 (0.1 M), 3,4,7,8-tetramethyl-1,10-phenanthroline (20 mol%) was used. DMAc: *N,N*-dimethylacetamide.

To demonstrate the scalability of this reaction, Hiyama cross-coupling of product **3** with 2-bromo-5-(trifluoromethyl)pyridine was attempted in the presence of 5 mol% $\text{Pd(PPh}_3)_4$ and 1.0 equiv. of CuI as a promotor, the reaction proceeded smoothly to get aryl-heteroaryl coupled product **25** in 63% isolated yield [Figure 4A]. In order to gain insight into the mechanism, several control experiments were conducted [Supplementary Materials]. The C–Si coupling process was suppressed once adding (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) as a radical scavenger [Figure 4B], and the aminomethyl radical-captured product was determined by electrospray ionization high-resolution mass spectrometry (ESI-HRMS), which suggested a radical pathway for the reaction in some extent. Even Ni^0 pre-catalyst such as Ni(cod)_2 could catalyze the standard reaction to afford **3** in a comparable yield [Figure 4C], this indicated that the reaction might initiate via an oxidative addition of Ni^0 species. However, when performing the reaction with stoichiometric amounts of Ni(cod)_2 under dark conditions, no desired C–Si coupling product was observed [Figure 4D], suggesting the necessity of a photocatalytic process to regulate the valence of a nickel catalyst. Moreover, we synthesized ArNi^{II} complex and performed the control experiment with stoichiometric ArNi^{II} complex. The reaction of the ArNi^{II} complex with **2a** could also afford product **3** in 37% yield, indicating that ArNi^{II} is likely a real reaction intermediate [Figure 4E]. Light on-off experiment revealed that the reaction requires persistent irradiation [Figure 4F]. Stern-Volmer quenching experiment was performed and the result showed that **1a** or **2a** has no obvious quenching effect, while the nickel complex, rather than α -silylamine, has the most efficient quenching effect on the photoexcited photocatalyst [Figure 4G].

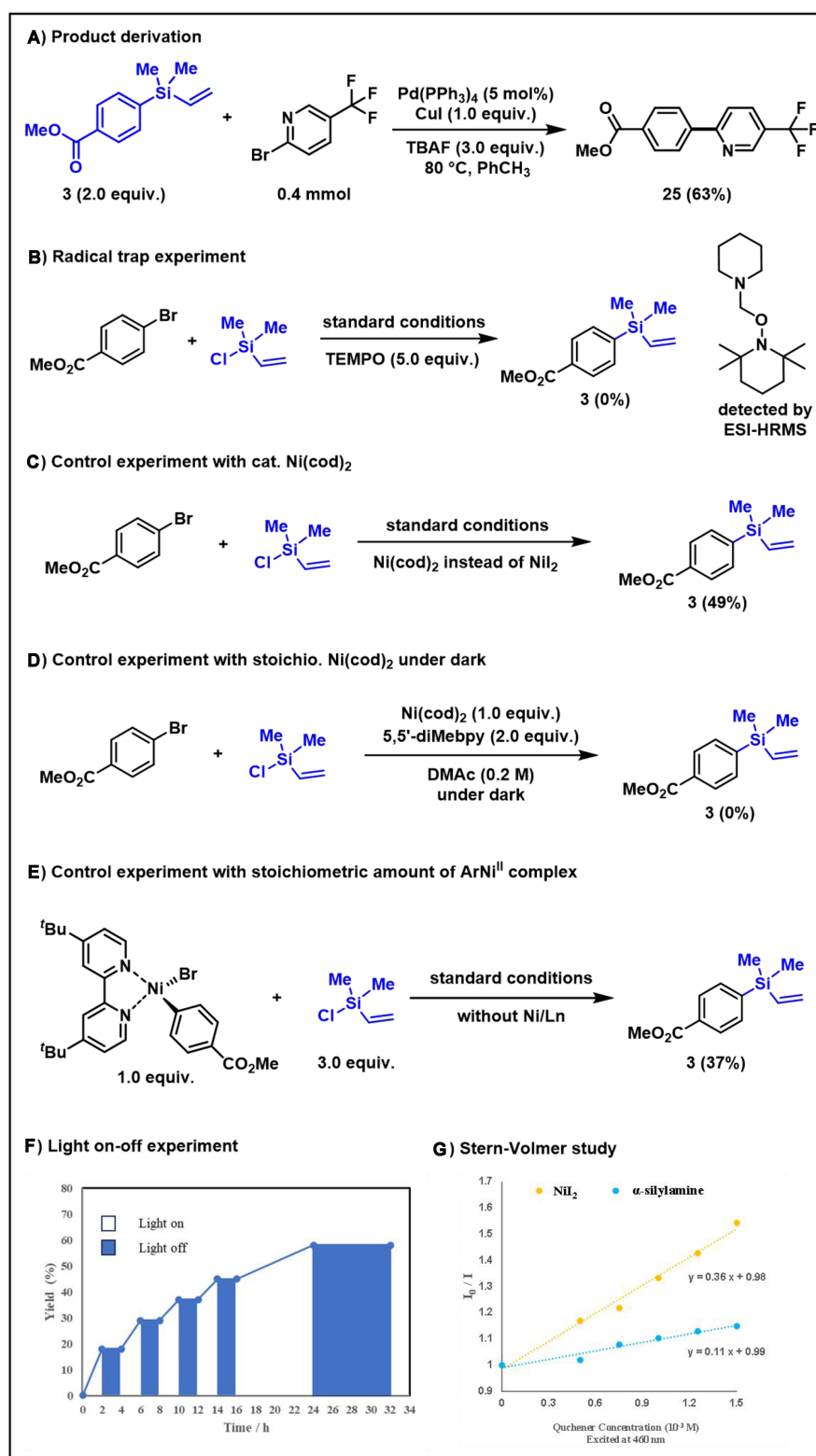


Figure 4. Synthetic application and mechanistic studies.

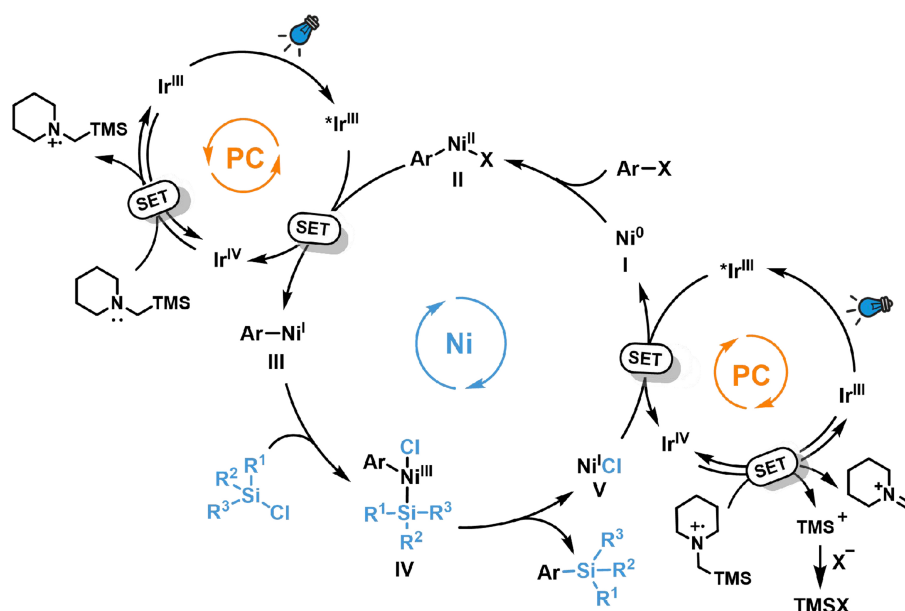


Figure 5. Proposed mechanism.

Based on the above-performed experiments and previous reports^[32,39], a plausible mechanism for the photoredox-assisted nickel-catalyzed reductive C-Si coupling was depicted in Figure 5. Ni^0 undergoes an oxidative addition of aryl halide forms a $\text{ArNi}^{\text{II}}\text{X}$ [$E_{\text{red}} \text{Ni}^{\text{II}}/\text{Ni}^{\text{I}} = -1.17 \text{ V}$ vs. saturated calomel electrode (SCE)]^[49], which is reduced by PC^* ($E_{1/2} \text{Ir}^{\text{IV}}/\text{Ir}^{\text{III}} = -1.73 \text{ V}$ vs. SCE)^[50] via a single-electron transfer (SET) to get a ArNi^{I} complex, which further oxidized by chlorosilane to form ArNi^{III} , final reductive elimination of ArNi^{III} affords C-Si coupling product and generates the Ni^{I} , which undergoes a second SET with PC^* and regenerates Ni^0 catalyst^[51-53]. On the other hand, the oxidative state of PC ($E_{1/2} \text{Ir}^{\text{IV}}/\text{Ir}^{\text{III}} = +0.77 \text{ V}$ vs. SCE)^[50] is reduced to its ground state by α -silylamine ($E_{1/2}^{\text{ox}} = +0.71 \text{ V}$ vs. SCE)^[54] completing both catalytic cycles.

CONCLUSION

In summary, we have reported a synergistic photoredox/nickel catalytic protocol for reductive cross-coupling of aryl electrophiles and chlorosilanes. α -Silylamine is identified as a potent organic reductant to replace metal reductants for reductive C-Si coupling. The reaction tolerances a generally broad scope of chlorosilanes and (hetero)aryl halides. Further studies on mechanistic investigation and synthetic application are underway in this lab.

DECLARATIONS

Authors' contributions

Performing the experiments and data analysis: Liu, J.

Directing the project and writing the manuscript: Yuan, W.

Availability of data and materials

The raw data supporting the findings of this study are available within this Article and its [Supplementary Materials](#). Further data are available from the corresponding authors upon reasonable request.

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Conflicts of interest

Both authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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