



New insight in Hiyama cross-coupling reactions: Decarboxylative, denitrogenative and desulfidative couplings

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ABSTRACT

In this mini-review, recent advances and developments in the decarboxylative, denitrogenative, and desulfidative Hiyama-type cross-coupling reaction from 2011 up present are studied. This review focused mainly on mechanistic aspects of Hiyama cross-coupling reactions.

1. Introduction

Transition metal-catalyzed cross-coupling reactions have been used as an essential tool for the formation of various carbon-carbon [1] and carbon-heteroatom [2] bonds with high atom economy under mild reaction conditions. Among the various C-C cross-coupling reactions, the Hiyama coupling is one of the most attractive methods to create C(sp²)-C(sp²) bonds, which widely used in many industrial processes, including pharmaceuticals and fine chemicals. Traditionally, this reaction utilizes aromatic silanes as nucleophilic partners with aryl halides or triflates as electrophilic partners for constructing biaryl derivatives that are structural components of various pharmaceuticals and natural products *via* C-X/C-O cleavage [3, 4]. Nevertheless, even aryl chlorides are widely available commercially, they have very low reactivity in coupling reactions. Moreover, aryl bromides and iodides are expensive and some of the structurally targeted reagents may not be readily accessible. Furthermore, most of the aryl halides are environmentally toxic compounds and causing a variety of safety and health problems [5]. Aryl triflates are very good electrophilic reagents in most

coupling reactions. However, they are unstable, expensive, and release potentially genotoxic triflic acid (CF₃SO₃H) as a by product [6]. Thus, there is still a need for broadening the scope of electrophilic partners to achieve Hiyama-type reactions that are not obtainable through known approaches. Recently, various coupling partners with the release of CO₂, SO₂, and N₂ gases (instead of toxic halogens of triflic acid) have been reported [7]. These include: carboxylic acids, arenesulfonyl chlorides, sodium arenesulfonates, arenediazonium salts, and arenehydrazines. Although a number of significant advances in the decarboxylative, denitrogenative, and desulfidative Hiyama-type cross-coupling reactions have studied from 2011 to present, a focus-review on this interesting field seems to be worthy, following of our recent reviews [8-18]. Herein, we will highlight the most important developments in the arena of Hiyama-type cross-coupling reactions between organosilane and titled coupling partners. In this mini review, we have classified these reactions based on the type of coupling partners (Figure 1) with special emphasis on the mechanistic aspects of the reactions.

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2. Decarboxylative Hiyama Couplings

Transition metal-catalyzed decarboxylative cross-coupling reactions have recently emerged as a powerful strategy to form various carbon-carbon [19] and carbon-heteroatom [20] bonds from carboxylic acids with loss of CO₂. A significant advantage of this reaction is the usage of available, inexpensive, and low toxic carboxylic acids and is far less air and moisture sensitive in comparison to conventional organometallic reagents [21].

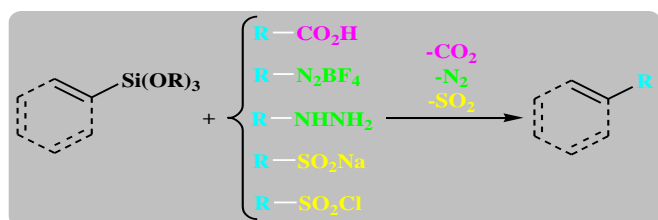


Fig. 1 Hiyama-type decarboxylative, denitrogenative, and desulfidative cross-coupling reactions.

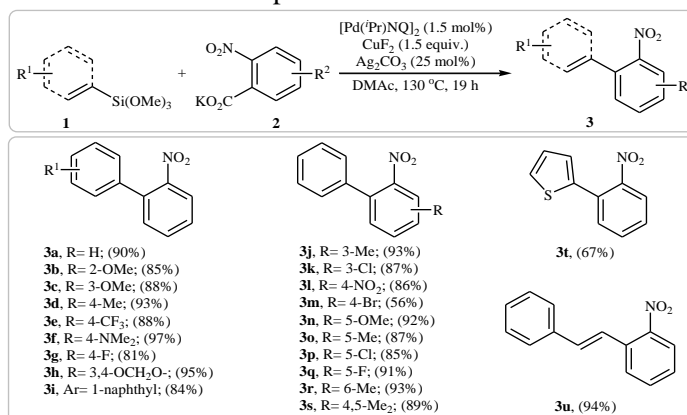
This strategy allows for the highly regioselective coupling of carboxylic acids with various electrophiles as well as nucleophiles [22]. The first example of decarboxylative Hiyama cross-coupling reaction between siloxanes and carboxylic acids was reported by Katayev, Exner, and Gooßen in 2015; a broad range of trimethoxysilanes **1** (aryl, heteroaryl, and vinyl silanes) were reacted with various ortho-nitro substituted aryl carboxylates **2** at 130 °C in the presence of [Pd(IPr)NQ]₂/Ag₂CO₃/CuF₂ combination as a catalytic system in Dimethylacetamide and afforded the corresponding biaryls **3** in high to excellent yields (Scheme 1) [23]. The results showed that the yields in this reaction were slightly dependent on the electronic characters of the substituents on the 2-nitrobenzoic acids. Generally, both electron-donating and electron-withdrawing groups in the phenyl ring periphery of aryl carboxylates were well tolerated. For silanes, the order of reactivity is aryl silanes ≈ vinyl silanes > heteroaryl silanes. Noteworthy, the reaction can be easily scaled up to produce multigram quantities of the product without sacrificing the yield or outcome of the methodology. The authors nicely applied their protocol for the synthesis of 1H-indazole and carbazole.

The mechanism proposed to explain this transformation start with the decarboxylation of carboxylate **2** by metal catalyst through the intermediate **A**, leading to the formation of the organometallic intermediate **B**. Subsequently, the reaction of the Pd(II) with intermediate **B** yields intermediate **C**. Its transmetalation with organosilane **1** forms the palladium complex **D** along with [BXS₃(OMe)₃]⁻. Finally, the reductive elimination of the intermediate **D** affords the expected products **3**.

Shortly afterwards, Kim, Lee and their co-workers developed a beautiful and highly efficient Ni-catalyzed

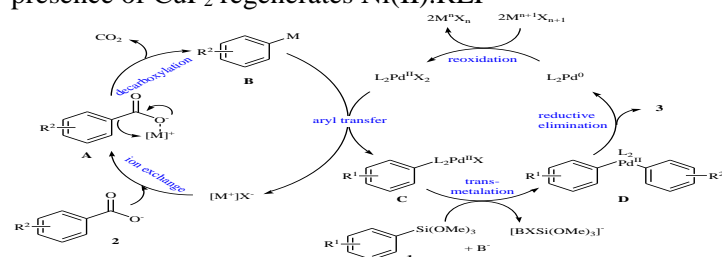
Hiyama-type decarboxylative coupling reaction between aryl silanes **4** and propiolic acids **5** for the construction of biologically important tolanses **6** (Scheme 3) [24].

The best conversion efficiency was obtained for the reactions containing Ni(acac)₂ (10 mol%), 1,10-phen (10 mol%), CuF₂ (1 equiv.) and CsF (1 equiv.) in DMSO at 120 °C under air atmosphere.

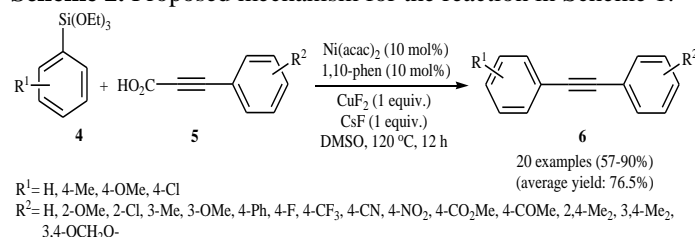


Scheme 1. Pd-catalyzed C-C coupling of organosilanes **1** with aryl carboxylates **2**.

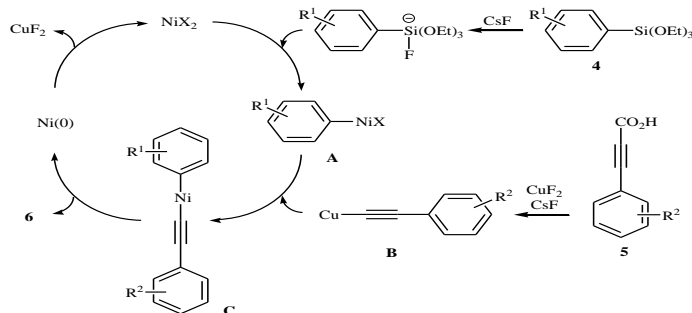
A variety of sensitive functional groups including fluoro, chloro, cyano, nitro, ketone, ether and ester functionalities are well tolerated by the reaction conditions. The protocol was also successfully extended to the bicyclic and heteroaromatic substrates. However, alkyl-substituted propiolic acids failed to give the corresponding products under this reaction condition. The author proposed mechanism for this coupling reaction, which is represented in Scheme 4. It consists of the following key steps: (i) initial formation of aryl Ni complex **A** via reaction of arylsilane **4** with Ni(II) in the presence of CsF; (ii) decarboxylation of alkynyl carboxylic acid **5** with Cu to give the alkynyl copper complex **B** as well as carbon dioxide; (iii) transmetalation of aryl Ni complex **A** and alkynyl copper complex **B** forms the aryl alkynyl Ni complex **C**; (iv) reductive elimination of intermediate **C** provides the target product **3**; and (v) oxidation of Ni(0) in the presence of CuF₂ regenerates Ni(II).REF



Scheme 2. Proposed mechanism for the reaction in Scheme 1.

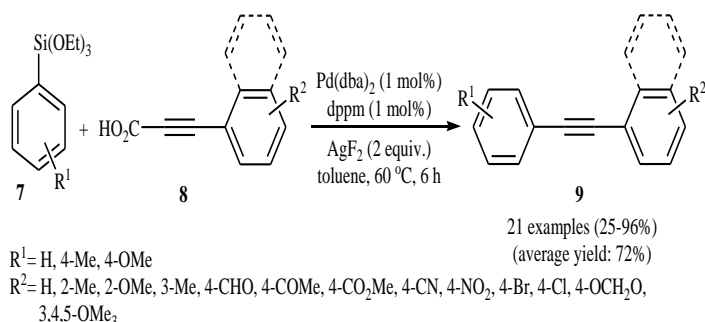


Scheme 3. Ni(II)-catalyzed decarboxylative coupling between aryl silanes **4** and propiolic acids **5**.



Scheme 4. Mechanism of the formation of tolanes **6**.

In 2016, the group of Lee reported an analogous protocol for the Hiyama-type decarboxylative coupling of arylsilanes **7** with aryl alkynyl carboxylic acids **8** (Scheme 5) [25]. In their optimization study, the authors found that the use of Pd(dba)₂/dppm/AgF₂ combination as catalytic system in toluene gave the best results. Examination of the scope of the reaction revealed that a range of propiolic acids bearing both electron-withdrawing and electron-donating groups and a series of electron-rich arylsilanes afforded the corresponding tolanes **9** in almost fair to excellent yields. However, electron-poor arylsilanes and heteroarylsilanes failed to enter into this coupling reaction.



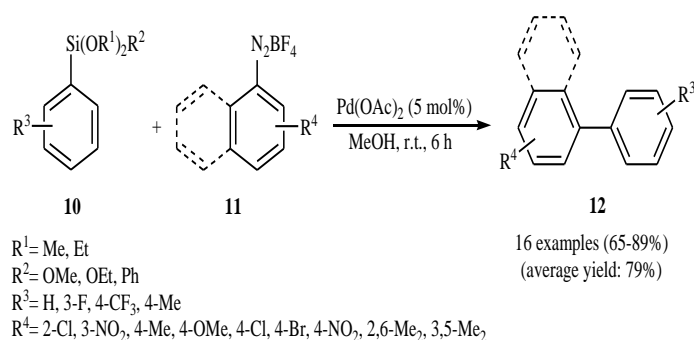
Scheme 5. Lee's synthesis of tolanes **9**.

3. Denitrogenative Hiyama Couplings

In this section, we describe the current literature on denitrogenative Hiyama cross-coupling reactions between C-N₂ and C-Si bonds. These lead to the formation of a C-C bond in a green and high yielding procedure. The coupling of organosilanes with arenediazonium salts are discussed first. This is followed by coupling of organosilanes with arylhydrazine derivatives.

In 2011, Qi and co-workers reported the first example of denitrogenative Hiyama cross-coupling of organosilanes with arenediazonium salts [26]. They showed that arylsilanes **10** underwent relatively rapid C-C cross-coupling with various arenediazonium salts **11** in the presence of 5 mol% of commercially available Pd(OAc)₂ as a catalyst in MeOH to provide the corresponding biaryls **12** in good to high yields. Interestingly, the electronic and steric characters of the substituents in the phenyl ring periphery of both organosilanes and arenediazonium salts had remarkably little effect on the rate of the reaction. Various substrates

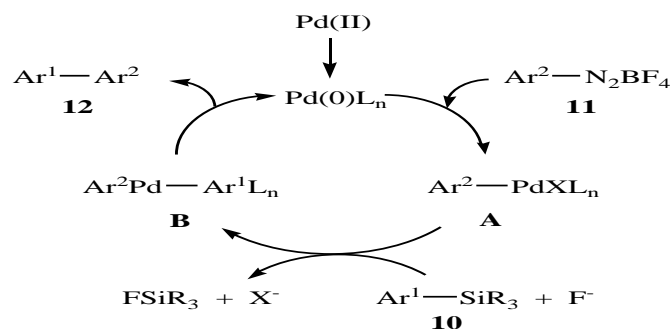
were examined involving electron-donating and withdrawing groups in the *ortho*, *meta* and *para* positions according to Scheme 6. It should be mentioned that other palladium catalyst such as PdCl₂, PdI₂, PdCl₂(dppf), PdCl₂(PPh₃)₃, Pd(PCy₃)₂Cl₂, Pd(PPh₃)₄, and Pd₂(dba)₂ were also found to promote this denitrogenative coupling but in lower yields. According to the author proposed mechanistic pathway, this reaction is believed to proceed through an oxidative addition/transmetalation/reductive elimination sequential process (Scheme 7). Based on the theoretical studies, it was found that the transmetalation is the rate-limiting step for this reaction and both AcO⁻ and BF₄⁻ anions may be involved in the direct reaction with the silicon atom.



Scheme 6. Denitrogenative coupling of arylsilanes **10** with arenediazonium salts **11**.

With the objective of designing a greener procedure to biaryls through denitrogenative Hiyama coupling reaction, the same authors were able to demonstrate that a range of functionalized biaryls **15** could be obtained from the reaction of organosilanes **13** with arenediazonium salts **14** in the most significant green solvent, water, employing Pd(OAc)₂ as catalyst and tetra-*n*-butylammonium fluoride (TBAF) as an additive at room temperature [27].

Under optimized conditions [Pd(OAc)₂ (5 mol%), TBAF (75%, 0.8 equiv.), H₂O, 6 h], the expected biaryls **15** were obtained in good to high yields (Table 1). The reaction showed good functional group tolerance, including fluoro, chloro, bromo, alkoxy and nitro functionalities that would allow further elaboration of the coupling products.

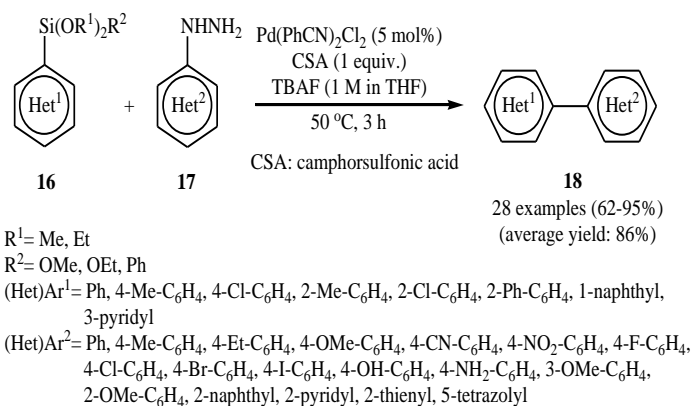
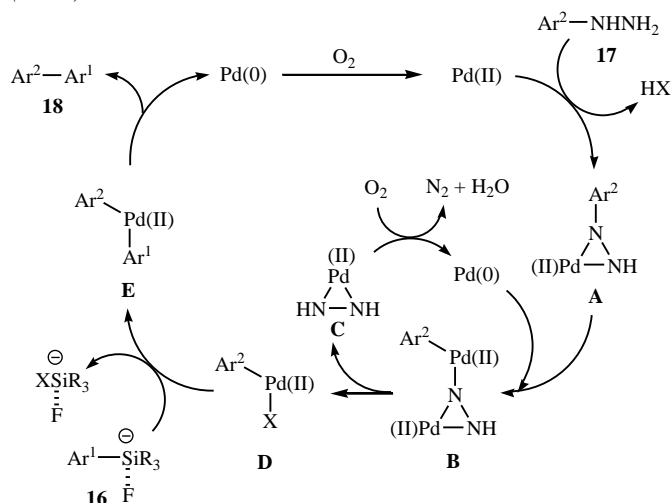


Scheme 7. Mechanism that accounts for the formation of biaryls **12**.

Table 1. Synthesis of functionalized biaryls **15** via the Pd-catalyzed cross-coupling of organosilanes **13** with arenediazonium salts **14**.

$\text{R}^2\text{-Si}(\text{R}^3)_3 + \text{R}^1\text{-N}_2\text{BF}_4 \xrightarrow[\text{H}_2\text{O, r.t., 6 h}]{\text{Pd}(\text{OAc})_2 (5 \text{ mol}\%), \text{TBAF} (0.6 \text{ equiv.})} \text{R}^1\text{-R}^2$				
Entry	R ¹	R ²	R ³	Yield (%)
1	4-Me-C ₆ H ₄	Ph	OEt	83
2	4-Me-C ₆ H ₄	Ph	OMe	82
3	4-Me-C ₆ H ₄	4-Me-C ₆ H ₄	OMe	84
4	4-Me-C ₆ H ₄	3-F-C ₆ H ₄	OMe	80
5	4-Me-C ₆ H ₄	4-CF ₃ -C ₆ H ₄	OMe	73
6	Ph	Benzo[d]thiazol-2-yl	OMe	81
7	Ph	Benzo[d]oxazol-2-yl	OMe	78
8	4-OMe-C ₆ H ₄	Ph	OEt	73
9	4-Cl-C ₆ H ₄	Ph	OEt	80
10	4-Br-C ₆ H ₄	Ph	OEt	82
11	4-NO ₂ -C ₆ H ₄	Ph	OEt	65
12	3-NO ₂ -C ₆ H ₄	Ph	OEt	70
13	2-Cl-C ₆ H ₄	Ph	OEt	74
14	2,6-Me ₂ -C ₆ H ₃	Ph	OEt	69
15	1-Naphthyl	Ph	OEt	70
16	Phenanthren-9-yl	Ph	OEt	66

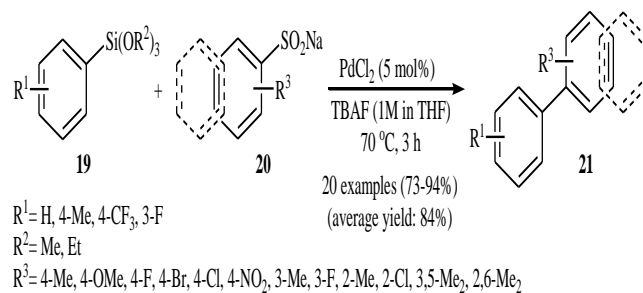
In 2015, Zhang's research team reported an elegant Pd-catalyzed denitrogenative Hiyama cross-coupling reaction of aryl silanes **16** with arylhydrazines **17** into unsymmetrical biaryls **18** employing Pd(PhCN)₂Cl₂/CSA/TBAF combination as the catalytic system [28]. The reaction was carried out under air at 50 °C, tolerated many functional groups and provided the expected biaryls in good to almost quantitative yields (Scheme 8). It should be mentioned that the presence both catalyst and additive is crucial for the outcome of the reaction, no coupling product was observed in the absence of any of them. As shown in Scheme 9, this reaction proceeds along the similar mechanistic pathway that described for the coupling of organosilanes with arenediazonium salts. It is noted that Kuang and co-workers reported a single example for the Pd-catalyzed coupling of phenyl triethoxysilane with phenylhydrazine under 100 °C in the yield of 62% [29].

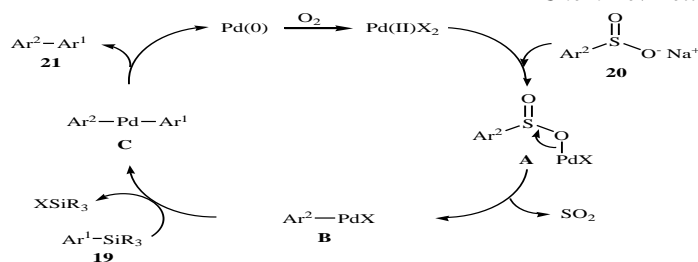
**Scheme 8.** Pd(II)-catalyzed C-C bond formation of aryl silanes **16** with arylhydrazines **17** reported by Zhang.**Scheme 9.** Mechanistic explanation of the synthesis of biaryls **18**.

4. Desulfitative Hiyama Couplings

In recent years, RSO₂R' derivatives, such as RSO₂Na or RSO₂Cl have been successfully employed as versatile electrophilic partners, *via* extrusion of SO₂, in various cross-coupling reactions [30]. Advantages of these coupling partners are that many of them are commercially available and easy to handle. Moreover, they give access to alternative regioisomers.

The possibility of desulfitative Hiyama cross-coupling of organosilanes with arenedisulfonates was first realized by Qi and co-workers in 2013, who synthesized a series of functionalized biaryls **21** from the reaction of aryl siloxanes **19** with sodium arenedisulfonates **20** in the presence of PdCl₂ as the catalyst and TBAF as an additive in THF under air [31]. This Pd(II)-catalyzed desulfitative coupling reaction tolerated both the electron-rich as well as electron-poor arenedisulfonates and various substituted aryl silanes and afforded the expected biaryls in more than 94% yields (Scheme 10). The mechanistic pathway of this coupling is shown in Scheme 11, and involves the initial formation of the ArS(=O)OPdX reactive intermediate **A** *via* the reaction of PdCl₂ catalyst with starting arenedisulfonate **20**. Next, expulsion of SO₂ from this intermediate leading to the ArPdX intermediate **B**, which then undergoes transmetalation with organosilane **19** to produce intermediate **C**. Finally, reductive elimination of this intermediate affords the expected coupling products **21**.

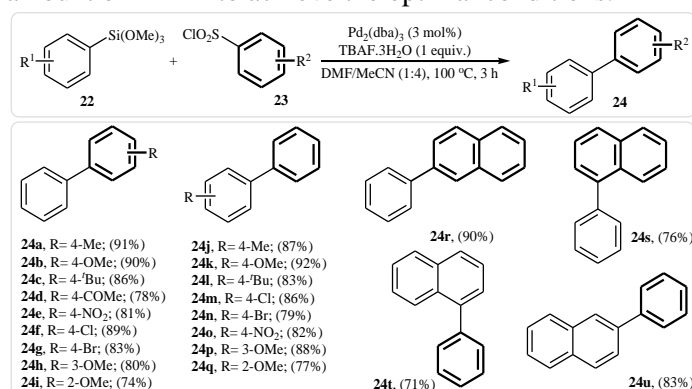
**Scheme 10.** Desulfitative coupling of aryl siloxanes **19** with sodium arenedisulfonates **20**.



Scheme 11. Mechanistic proposal for the reaction in Scheme 10.

Subsequently, Zhao and co-workers published an efficient methodology for the synthesis of a library of biaryls **24** through desulfitative Hiyama-type coupling of trimethoxyphenylsilanes **22** with arylsulfonyl chlorides **23** under an inert atmosphere [32]. Considering the catalyst, additive, and solvent, the optimized conditions of this C-C cross-coupling reaction involved using $\text{Pd}_2(\text{dba})_3$ as a catalyst, $\text{TBAF}\cdot 3\text{H}_2\text{O}$ as an additive, and DMF/MeCN (1:4) as the solvent at 100 °C for 3 h. The optimized protocol tolerated many important functional groups, such as chloro, bromo, acetyl, methoxy, and nitro functionalities and provided the expected biaryls in good to excellent yields (Scheme 12). According to the authors proposed mechanism, this reaction proceeds along the similar mechanistic pathway that described in Scheme 11.

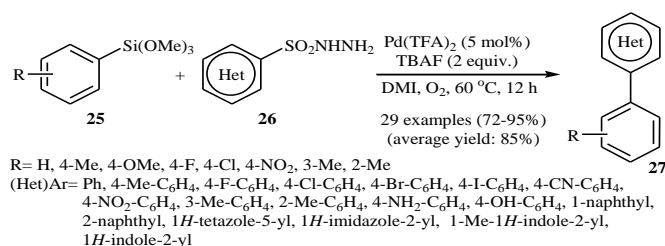
Inspired by these works, in 2015, the group of Zhou developed an elegant and efficient approach to the synthesis of biaryls **27** via a facile palladium-catalyzed desulfitative Hiyama cross-coupling of trimethoxyphenylsilanes **25** with arylsulfonyl hydrazides **26** under an atmosphere of oxygen [33]. Amount 5 mol% of commercially available $\text{Pd}(\text{TFA})_2$ was utilized as the catalyst in the solvent 1,3-dimethyl-2-imidazolidinone (DMI) with an over-stoichiometric amount of TBAT to achieve the optimal conditions.



Scheme 12.-Synthesis of biaryls **24**.

In the reported methodology, arylsulfonyl hydrazides with both electron-donating and electron-withdrawing groups on the aromatic ring substituent were found to react smoothly and provided functionalized biaryls **27** in good to excellent yields (Scheme 13). Noteworthy, this desulfitative coupling reaction is equally effective for

both aromatic and heteroaromatic sulfonyl hydrazides. The proposed mechanism for this transformation is shown in Scheme 14. Initially Pd(0) is oxidized to Pd(II), which by reaction with the sulfonyl hydrazide **26** and β -elimination of a palladium hydride to give a sulfonyldiimine **B**. This intermediate reacts with catalyst to give another reactive Pd(II) intermediate **C** that release N_2 and SO_2 to produce a new arylpalladium(II) intermediate **D**. This intermediate involved in arylation with the silanes **25** to give, after reductive elimination, the final biaryl **27** and recovering the Pd(0) precatalyst.

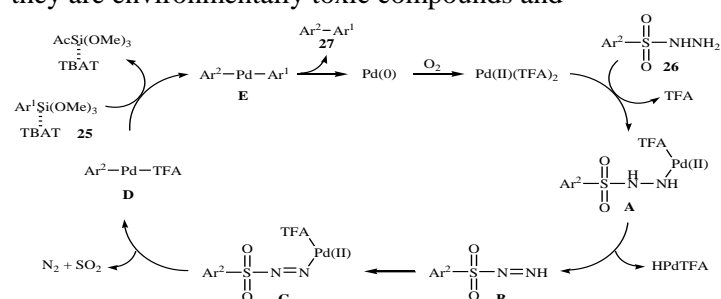


Scheme 13. Pd-catalyzed Hiyama-type cross-coupling of trimethoxyphenylsilanes **25** with arylsulfonyl hydrazides **26**.

5. Conclusions

The Hiyama cross-coupling reaction comprise one of the most efficient methods for the construction of C(sp²)-C(sp²) bonds. The organosilicon reagents used as nucleophilic partners are of low cost, low toxicity, easy to prepare and handle, and highly stable to a variety of reaction conditions.

Although these reagents are commercially available, they are environmentally toxic compounds and



Scheme 14. Plausible mechanism for the formation of **27**.

causing a variety of safety and health problems. Moreover, aryl bromides and iodides are expensive and some of the structurally targeted reagents may not be readily accessible. Thus, there is still a need for broadening the scope of electrophilic partners to achieve Hiyama-type reactions that are not obtainable through known approaches. Transition metal-catalyzed decarboxylative, desulfitative and denitrogenative cross-coupling reactions have recently emerged as a new and important category of organic transformations that find many applications in the construction of various carbon-carbon and carbon-heteroatom bonds. As illustrated, a variety of carboxylic acids, arenediazonium salts, arenhydrazines, and sulfinic acid derivatives have been developed as the alternative coupling partners for the

Hiyama coupling. High selectivity, yields and availability of starting materials are the key features of these novel and green reactions. Hopefully, this review motivates researchers to further study in this interesting research arena.

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