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PII: S0040-4039(15)01128-4
DOI: http://dx.doi.org/10.1016/j.tetlet.2015.06.095
Reference: TETL 46487

To appear in: *Tetrahedron Letters*

Received Date: 19 April 2015
Revised Date: 22 June 2015
Accepted Date: 29 June 2015

Please cite this article as: Zhang, H., Wang, C., Li, Z., Wang, Z., Palladium-catalyzed Denitrogenative Hiyama Cross-coupling with Arylhydrazines under Air, *Tetrahedron Letters* (2015), doi: http://dx.doi.org/10.1016/j.tetlet.2015.06.095

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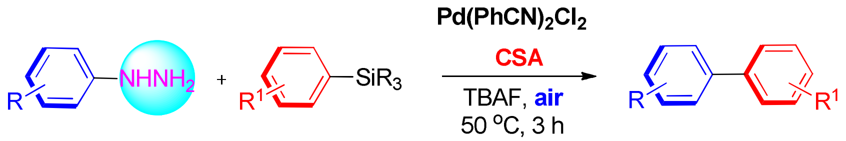

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Abstract

A Pd-catalyzed denitrogenative Hiyama coupling of arylhydrazines and aryl silanes is described under mild conditions. The newly developed catalytic system does not require the use of expensive silver- or copper-based stoichiometric oxidants to obtain diaryl derivatives with high selectivity and reactivity. The reported coupling reactions are very practical as it does not require the protection of inert gas or oxygen and tolerant to the many functional groups.

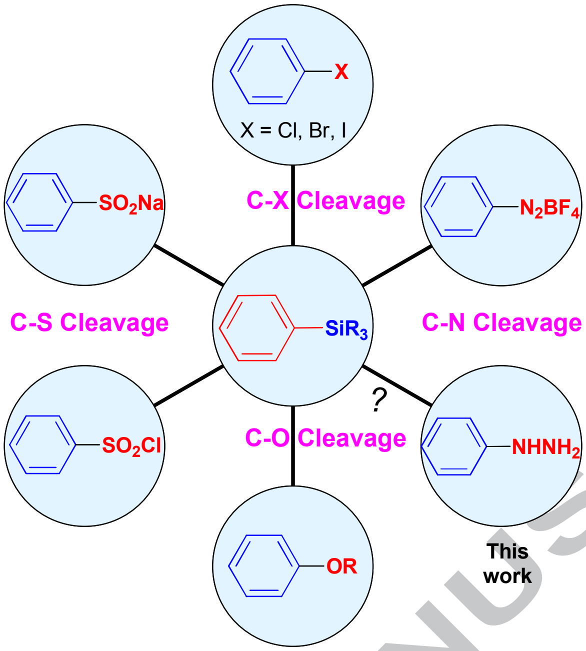
Keywords: denitrogenative coupling, Hiyama cross-coupling, arylhydrazines

Introduction

Transition-metal-catalyzed cross-coupling reactions have provided important innovations for synthetic chemistry over the past decades, were considered to be the most powerful and accurate tools for the construction of carbon–carbon bonds.[1] Consequently, the vast array of reactions has found numerous applications in both industrial and academic settings in the synthesis of complex natural products and biologically active small molecules. Among these modern couplings, the coupling partners can be organic halides/pseudohalides and organometallic reagents. [2] Of these substrates, arylsilanes as transmetalation reagents offer numerous advantages over aryl borates (Suzuki coupling)[3] and aryl stannanes (Stille coupling)[4] in terms of their ready availability, low toxicity, easy workup, good biocompatibility and stability in various chemical media (namely, the Hiyama and Hiyama–Denmark reactions). Also, silicon can be facilely converted into relatively harmless silica by incineration, and all of these points have made Hiyama coupling attractive from environmental and user-friendly points of view. Their environmentally benign nature makes these reagents very attractive to organic chemists.[5]

Traditionally, the Hiyama coupling reaction utilizes arylsilane reagents with aryl halides or triflates for constructing asymmetrical biaryls or multisubstituted alkenes that are structural components of various pharmaceuticals and other functional materials via C-X/C-O cleavage.[6]

(Scheme 1) Thus, There is still a need for broadening the scope of partners to achieve Hiyama-type reactions that are not obtainable through known approaches. Recently, other coupling partners via C-S cleavage have been reported.[7] The cross-coupling of arylsilanes with arylsulfinic salts have been demonstrated by Qi's group and Pd(II) catalytic system was particularly efficient with the assistance of TBAF to obtain biaryls.[8] Zhao et. al. first reported a cross-coupling reaction of arylsilanes with arylsulfonyl chlorides.[9] The Pd(0)-catalyzed reaction was proceeded smoothly with the application of component solvent by 100 °C under N_2. However, the release of SO_2 for these transformation was inevitable which make it environmentally unfriendly. As a consequence, to expand diverse electrophiles has been one of the hot topics in recent years, for the purpose of voiding the productions of deleterious waste and more attractive method of Hiyama coupling was proceeded via the cleavage of C-N bond with the release of nitrogen. In 2011, Qi and coworkers reported a practical carbon-nitrogen bond cleavage procedure for the Hiyama cross-coupling reactions using arenediazonium salts as the electrophilic reagents.[10] Notably, aryl diazonium salts are required to be freshly prepared and need to be kept in storage under zero degree.[11] Another alternative to aryl diazonium salts was recognized as arylhydrazines. Arylhydrazines are low cost, ready availability, chemical stability and extremely valuable compounds in organic chemistry that are widely used for the preparation of numerous N-contained compounds, but little attention has been paid to their use as arylating regents via denitrogenation. Until recently, the efficiency of using arylhydrazines as aryl source in cross-coupling reactions has been witnessed by the oxidative Heck-type with olefins,[12] oxidative radical arylation,[13] Pd-catalyzed Suzuki cross-coupling,[14] etc.[15] However, arylhydrazine as a coupling partner and a potential aryl source via C-N cleavage to form biaryls by Hiyama coupling was rarely reported. In 2014, Kuang et al. [16] reported a single example for the Pd(0)-catalyzed coupling of phenylhydrazine with phenyl triethoxysilane under 100°C in the yield of 62%, which could not rule out the possibility of homocoupling by phenylhydrazine or phenylsilane.[17] Herein, we wish to report a novel approach to obtain diaryl derivatives with high selectivity and reactivity from arylhydrazines and aryl silanes via Pd-catalyzed denitrogenative cross-coupling with selective C-N bond cleavage of arylhydrazines in the presence of CSA (camphorsulfonic acid) under mild conditions.

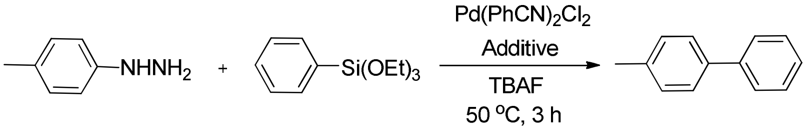


Scheme 1 Pd(II)-catalyzed Hiyama cross-coupling of arylsilane with different coupling partners

Results and Discussion

Owing the low reactivity of these reagents, they typically need to be activated by fluoride in order to generate a more reactive pentacoordinate silicate anion for the transmetalation step. The reaction of *p*-tolylhydrazine with phenyl triethoxysilane was first chosen as a model system for optimization studies (Table 1). Initially, the reaction that was carried out under 50°C for 3 h in the presence of $Pd(PhCN)_2Cl_2$ (5 mol%) as a catalyst in the solution of TBAF (1 M in THF) did not give the desired product (entry 1). Although the addition of bases (such as KOAc) or oxidants (such as AgOAc) as additives to the reaction system also failed to afford 4-methyl-1,1'-biphenyl (entries 2–3), the presence of acetic acid (1 equiv.) was tested and to our delight, afforded the desired biaryl products in 19% yield (entry 4). In this reaction different acids seem play key roles to promote the efficacy. When adding PivOH (2 equiv.) as additives, we were pleased to find that 4-methyl-1,1'-biphenyl was obtained in 68% yield (entry 5). TFA (trifluoroacetic acid) and trichloroacetic acid were observed to diminish the cross-coupling reactions (entries 6–7). The addition of MesCOOH (2,4,6-trimethylbenzoic acid) and oxalate were dramatically lowered the yield (entries 8–9). The attempts to use sulfonic acids as additives were successful. MsOH (methanesulfonic acid) was tested and to our delight, it gave much better results (entry 10). Other sulfonic acids, such as TfOH (trifluoromethanesulfonic acid) and TsOH (4-methylbenzenesulfonic acid) gave a comparable result (entries 11–12). Finally, we test CSA (camphorsulfonic acid) as additive and 91% yield of desired product was isolated without the detection of 4,4'-dimethyl-1,1'-biphenyl by homocoupling. (entry 13)

Table 1 Influence of Additives to the Reaction [a]



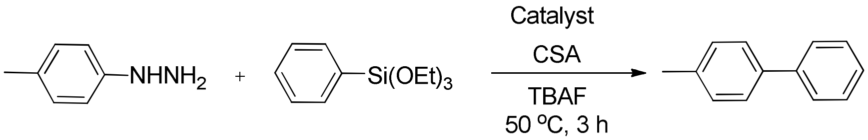
Entry	Additive	Yield(%) [b]
1	-	-
2	KOAc	-
3	AgOAc	-
4	HOAc	19

5	PivOH	68
6	TFA	54
7	trichloroacetic acid	57
8	MesCOOH	35
9	oxalate	10
10	MsOH	81
11	TfOH	77
12	TsOH	83
13	CSA	91

[a]Reaction conditions: *p*-tolylhydrazine (1 mmol), triethoxy(phenyl)silane (1.2 mmol), $Pd(PhCN)_2Cl_2$ (5 mol%), additives (1 mmol), TBAF (1M in THF, 1.0 ml) at 50 °C for 3 hours under air unless otherwise indicated. [b]Isolated coupling yield.

Subsquently, our investigation focused on the effect of transition-metal-catalysts on the model reaction of *p*-tolylhydrazine with phenyl triethoxysilane in TBAF (1M in THF) under 50 °C in the presence of CSA, and the results are summarized in Table 2. Unfortunately, with the use of Ru, Rh and Ni precursors such as $RuCl_2(PPh_3)_3$, $RhCl(PPh_3)_3$ and $NiCl_2(PPh_3)_3$, no desired product was detected (entries 1-3). Various Pd precursors were screened for the reaction. $Pd(OAc)_2$, $PdCl_2$, $PdBr_2$ and PdI_2 were somewhat effective, giving a 78%, 73%, 71% and 74% yield of 4-methyl-1,1'-biphenyl (entries 4-7). Other palladium(II) compounds with phosphine ligands led to higher amounts of desired products (entries 8-11), and the denitrogenative coupling was inhabited with Pd(0) catalysts (entries 12-13). To our delight, $Pd(CH_3CN)_2Cl_2$ served as a catalyst to afford the desired biaryl products in 89% yield (entry 14). Among the tested transition-metal catalysts, $Pd(PhCN)_2Cl_2$ showed the highest catalytic reactivity and the desired product was isolated in 91% yield when the model reaction was performed in TBAF under 50 °C for 3 h (entry 15).

Table 2. Influence of Catalysts to the Reaction [a]



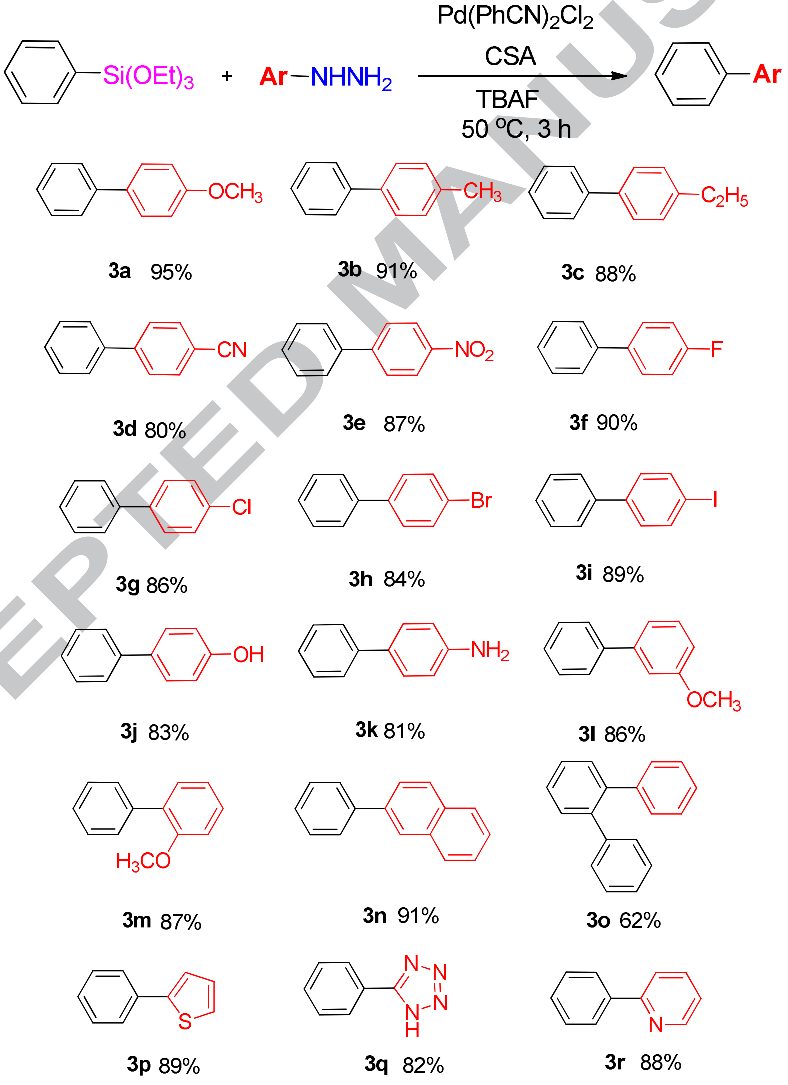
Entry	Catalyst	Yield(%) [b]
1	$RuCl_2(PPh_3)_3$	-
2	$RhCl(PPh_3)_3$	-
3	$NiCl_2(PPh_3)_3$	-
4	$Pd(OAc)_2$	78
5	$PdCl_2$	73
6	$PdBr_2$	71
7	PdI_2	74
8	$PdCl_2(PPh_3)_3$	80
9	$Pd(dppf)Cl_2$	84
10	$PdCl_2(dppb)$	83
11	$PdCl_2(dppe)$	86
12	$Pd(PPh_3)_4$	54
13	$Pd_2(dba)_3$	58
14	$Pd(CH_3CN)_2Cl_2$	89
15	$Pd(PhCN)_2Cl_2$	91

[a]Reaction conditions: *p*-tolylhydrazine (1 mmol), triethoxy(phenyl)silane (1.2 mmol), catalyst (5 mol%), CSA (1 mmol), TBAF (1M in THF, 1.0 ml) uat 50 °C for 3 hours

under air unless otherwise indicated. [b]Isolated coupling yield.

With the optimized conditions in hand, we next set out to explore the scope of the method with respect to this Pd-catalyzed denitrogenative coupling of arylhydrazine with triethoxy(phenyl)silane. Gratifyingly, a variety of arylhydrazine successfully coupled with triethoxy(phenyl)silane. Different functionalities on the phenyl ring of arylhydrazine, whether they were electron-withdrawing or electron-donating groups, are compatible. As shown in Table 3, this reaction was compatible with methoxy, methyl, ethyl, cyano, nitro substituents, and furnished the desired product in good yields (Table 3, 3a-3e). These results implied that the electronic effect is not critical for this transformation. Halogen substituents such as fluoro, chloro, bromo and iodo were tolerated under the optimal reaction conditions, and the desired products were obtained in good yields (Table 3, 3f-3i). To explore the application of this method, we tried other active groups, hydroxyl and amino groups all demonstrated reactivity and the products were isolated in good yield, thus extending the potential applications of the method(Table 3, 3j-3k). The *ortho*- and *meta*-substituted group, such as methoxyl, can also afford a good product yield, thus showing steric hindrance has little effect on the reaction (Table 3, 3l-3m). The naphthyl group also worked well and the desired product was produced in an excellent yield (Table 3, 3n). Biphenyl-2-ylhydrazine could be an optional substrate for preparing *o*-terphenyl in the yield of 62%, which are important precursors in material science (Table 3, 3o). Heteroaromatic substrates, such as 2-thienylhydrazine, 2-pyridylhydrazine and 5-hydrazinyl-1H-tetrazole were tolerated, albeit with good yields (Table 3, 3p-3r).

Table 3. Pd-catalyzed denitrogenative coupling of various arylhydrazine with triethoxy(phenyl)silane [a]



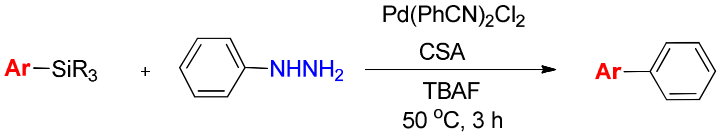
3a 95%
3b 91%
3c 88%
3d 80%
3e 87%
3f 90%
3g 86%
3h 84%
3i 89%
3j 83%
3k 81%
3l 86%
3m 87%
3n 91%
3o 62%
3p 89%
3q 82%
3r 88%

[a] Reaction conditions: arylhydrazines (1 mmol), triethoxy(phenyl)silane (1.2 mmol),

$Pd(PhCN)_2Cl_2$ (5 mol%), CSA (1 mmol),TBAF (1 M in THF, 1.0 ml) at 50 °C for 3 hours under air unless otherwise indicated. [b]Isolated coupling yield.

Encouraged by these promising results, we further applied the optimized reaction conditions to examine the substrate scope of aryl silanes (Table 4). Siloxane having various alkyl substituents, such as methyl and ethyl, afforded the desired products in good yields (Table 4, entries 1-2). Dimethoxydiphenylmethane and diethoxydiphenylmethanewere similarly found to be suitable substrate for this transformation and gave the corresponding biaryls in good yield (Table 4, entries 3-4). Both two phenyl ring could participate in this coupling smoothly. Different functionalities on the phenyl ring of triethoxysilane, whether they were electron-withdrawing or electron-donating groups, are compatible (Table 4, entries 5-6). Meanwhile, phenyl triethoxysilane, bearing a sterically hindered group, such as methyl or chloro at their ortho-positions, also underwent the reaction with good yield (Table 4, entries 7-8). Moderate coupling yield (72% and 75%) were still able to obtain when coupled with naphthyl and pyridinyl (Table 4, entries 9-10).

Table 4. Pd-catalyzed Hiyama cross-coupling reactions of phenylhydrazides with a wide variety of aryl silanes [a]



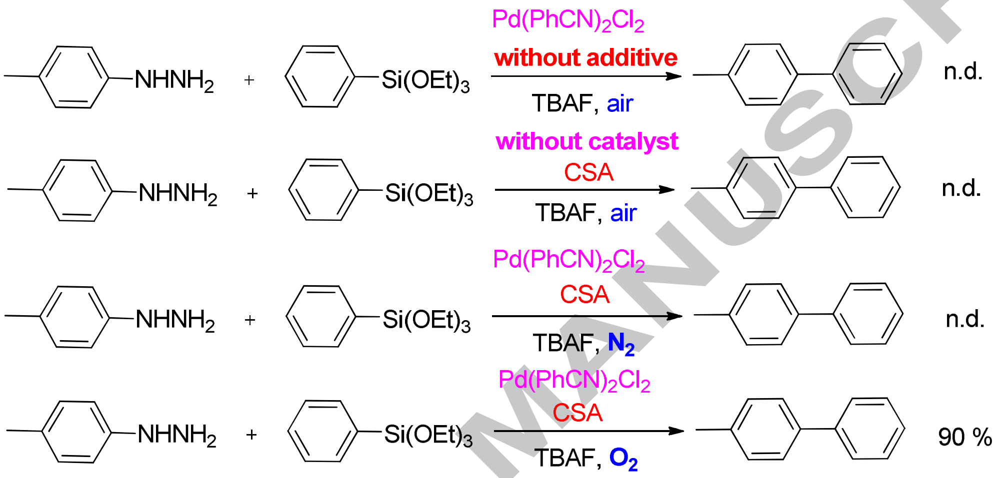
entry	aryl silanes	yield%[b]
1	C_6H_5-$Si(OMe)_3$	92
2	C_6H_5-$Si(OEt)_3$	95
3	$(C_6H_5)_2$-$Si(OMe)_2$	90[c]
4	$(C_6H_5)_2$-$Si(OEt)_2$	93[c]
5	4-$CH_3C_6H_4$-$Si(OEt)_3$	90
6	4-ClC_6H_4-$Si(OEt)_3$	87
7	2-$CH_3C_6H_4$-$Si(OEt)_3$	84
8	2-ClC_6H_4-$Si(OEt)_3$	82
9	1-$C_{10}H_8$- $Si(OEt)_3$	72
10	3-C_6H_5N- $Si(OEt)_3$	75

[a]Reaction conditions: phenylhydrazine (1 mmol), aryl silanes (1.2 mmol), $Pd(PhCN)_2Cl_2$ (5 mol%), CSA (1 mmol), TBAF (1 M in THF, 1.0 ml) at 50 °C for 3 hours under air unless otherwise indicated. [b]Isolated coupling yield. [c]Aryl silanes (0.6 mmol).

Mechanism

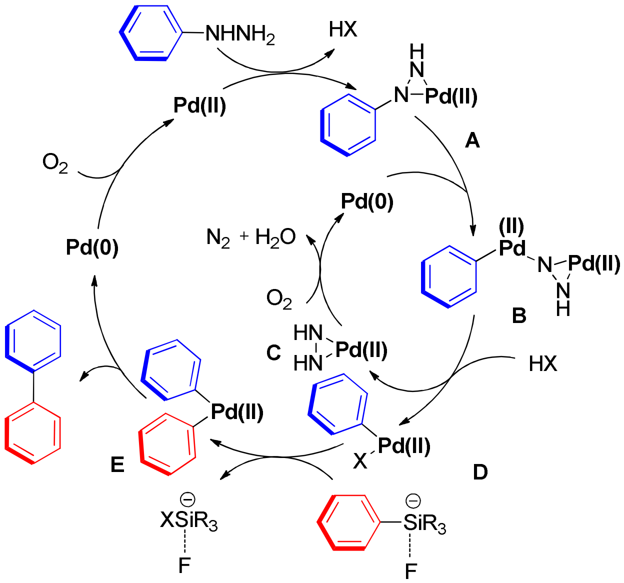
The possible mechanism of the palladium catalytic system was further verified by a series of control experiments (Scheme 2). Both CSA and

$Pd(PhCN)_2Cl_2$ was indispensable to this trasnsformation, which indicate that the reaction proceeded under Pd catalysis and the inversion of palladiaziridine intermediate must be accelerated by acid. On the other side, no desired products were detected under nitrogen and no better yield of biaryls was isolated under oxygen.



Scheme 2 Control Studies for this System

Although the exact mechanism of this reaction is not clear, a proposed pathway exemplified by incorporating one complex from each category A–D, is shown in Scheme 3 and in agreement with the mechanistic proposals for other related reactions. Firstly, the Pd(II) catalyst reacted with arylhydrazines to form an palladiaziridine intermediate A,[15a] which subsequently underwent oxidative insertion of Pd(0) with C-N bond to generate palladium(II)-centered complex B.[18] Protonolysis of complex B with HX resulted in aryl palladium complex C and the palladiaziridine complex D, which is easy to decompose into nitrogen and water when treated with O_2.[12a] The regeneration Pd(0) was concomitantly to formal oxidative insertion to complete the catalytic cycle. The ArPdX species then inserted into Ar-Si bond of aryl silanes via a transmetallation process to form diarylpalladium(II) species E. Finally, reductive elimination from intermediate E generated the cross-coupling product and Pd(0) species, which was reoxidized to Pd(II) by O_2 for its catalytic cycle.



Scheme 3 Proposed mechanism of this reaction

Conclusion

The Pd-catalyzed cross-coupling of the arylhydrazines with aryl silanes has been achieved under mild reaction conditions. The high efficiency and reactivity of the arylhydrazines could be attributed to the formation of the active Pd(II) species via the release of N_2 during the catalytic cycle. The reaction was accelerated by CSA and TBAF. The application of widely available arylhydrazine enables this transformation to be an attractive alternative to the Hiyama-type cross-coupling to dispense with additional ligands and bases.

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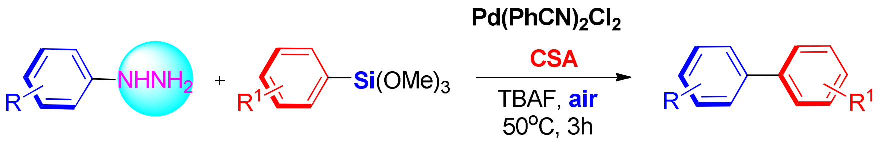
Acknowledgements: This work was supported by the Education Department of Henan Province Natural Science Research Program (13B150274) and the Doctoral Scientific Research Foundation of Zhoukou Normal University(zksybscx201105).

Graphical Abstract



A Pd-catalyzed denitrogenative Hiyama coupling of arylhydrazines and aryl silanes is described. The reported coupling reactions are very practical as it does

not require the protection of inert gas and tolerant to the many functional groups with high selectivity and reactivity.