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Recent advances and prospects in palladium-catalyzed Hiyama coupling reaction

S. Sivakumar,[a] Thaipparambil Aneeja,[b] and Gopinathan Anilkumar[a,b*]

[a] *Institute for Integrated Programmes and Research in Basic Sciences (IIRBS), Mahatma Gandhi University, Priyadarsini Hills P O, Kottayam, Kerala, 686560, India*
[b] *School of Chemical Sciences, Mahatma Gandhi University, Priyadarsini Hills, Kottayam, Kerala, INDIA 686560*
E-mail: anilgi1@yahoo.com anil@mgu.ac.in

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Abstract

Palladium-catalyzed Hiyama coupling reaction became an astonishing area in organic chemistry. Palladium has been widely used as a catalyst in organic synthesis due to its good functional group tolerance and mild reaction condition. This review focuses on the recent advancements in Pd-catalyzed Hiyama coupling reactions and covers literature up to mid-2022.

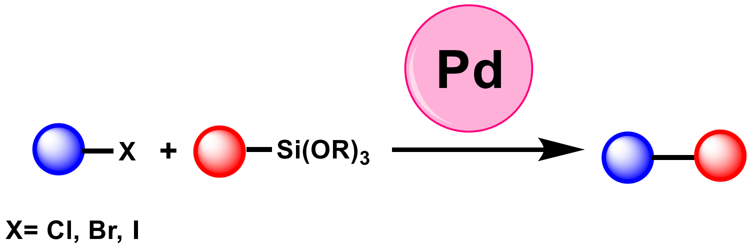

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Table of Contents

1. Introduction

Cross-coupling reactions have emerged as important tools for the construction of carbon-carbon and carbon-heteroatom bonds.[1] In 1972, Kumada and Tamao developed the nickel-catalyzed cross-coupling reaction between Grignard reagents and organic halides.[2] From then onwards, a wide range of organometallic reagents involving lithium, aluminium, zinc, tin etc. have been exploited as coupling partners and received much acceptance among researchers.[3-5] However, the instability, air and moisture sensitivity of these compounds and the production of a large amount of halogen wastes demanded a better coupling partner in cross-coupling reactions.[6]

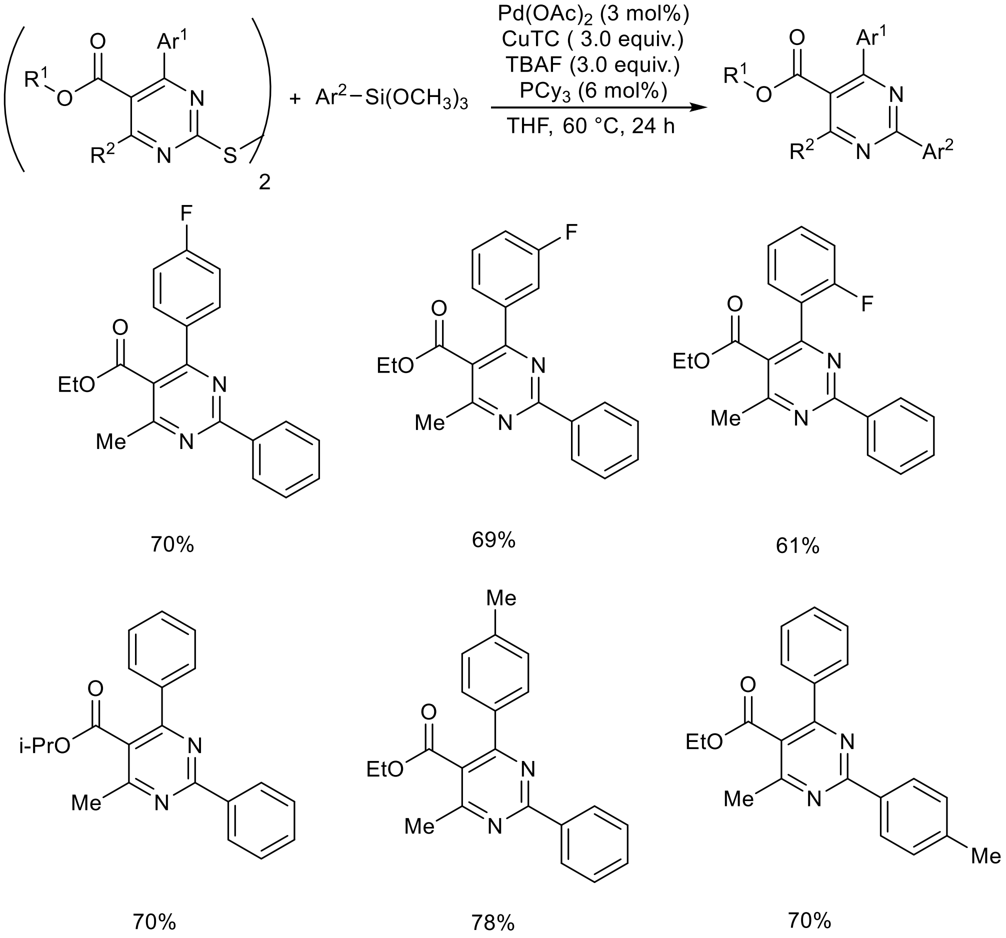
In this direction, organosilicon compounds were identified as an attractive coupling partner in cross-coupling reactions due to their less toxicity, high stability, good functional group tolerance and natural abundance.[7-9] Hiyama and co-workers were the first to explore the efficiency of organosilicon compounds in cross-coupling reactions.[10] Over the past decades, Hiyama cross-coupling reactions have achieved tremendous progress. This reaction has been widely exploited for the formation of Csp^2-Csp bonds. Transition metals such as Pd, Ni, Cu etc. have been widely utilized as catalysts in cross-coupling reactions.[11-14] However, palladium has always fascinated scientists owing to its mild reaction conditions and good functional group tolerance.[15]

Due to the continuous interest in this area, the Hiyama coupling has been reviewed before,[16,17] and the latest one appeared in 2017.[18] Herein, we summarize the recent advances in palladium-catalyzed Hiyama coupling covering the literature from 2017 to 2022. For simplicity and brevity, the topic has been classified into two sections as Hiyama reaction using homogeneous and heterogeneous palladium catalysis. Homogeneous palladium catalysis is further categorized based on the ligand used.

2. Homogeneous palladium catalysis

2.1 Phosphine ligand

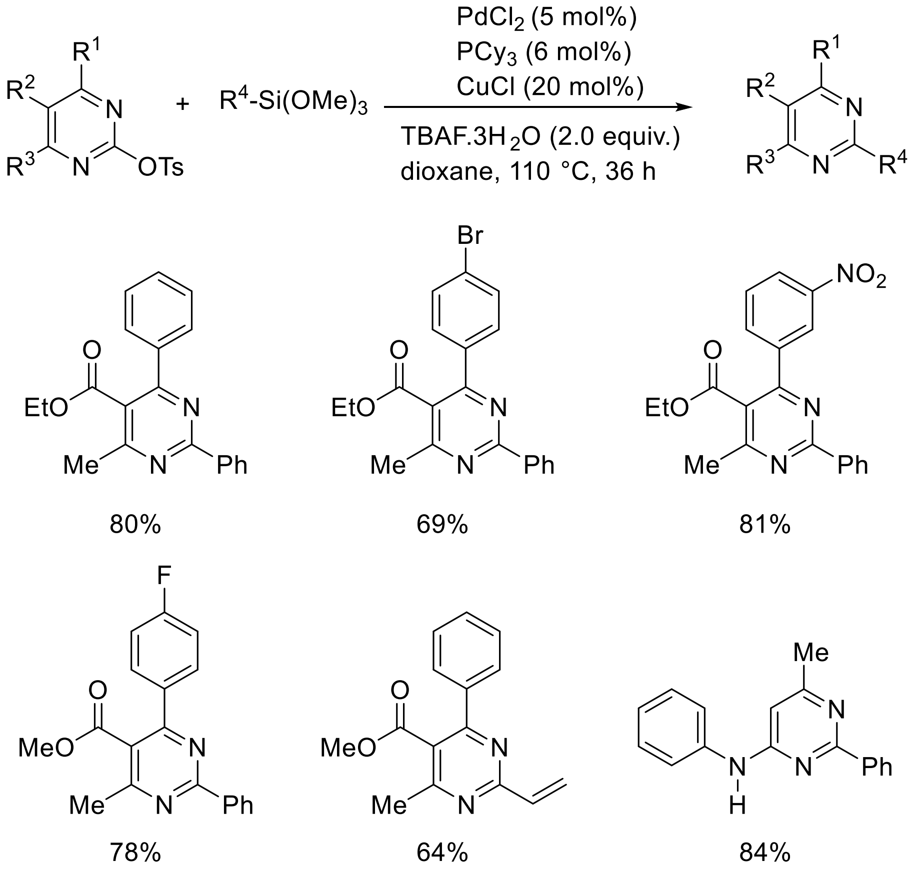
Wang *et al.* in 2017 disclosed a new palladium-catalyzed protocol for generating C–C bonds using dihetaryl disulfides as electrophiles in Hiyama cross-coupling reaction with arylsilanes.[19] The optimized condition includes the use of 3 mol% $Pd(OAc)_2$ as the catalyst, 3.0 equiv. copper(I)thiophene-2-carboxylate as additive, 3.0 equiv. TBAF, 6 mol% PCy_3 as ligand in THF at 60 °C (Scheme 1). They found that *para*-substituted aryldisulphides gave coupling products in good yields irrespective of the substituent. At the same time, *ortho* substitution led to a slight decrease in the yield due to steric hindrance. Disulphides with *meta* substituted phenyls yielded between *ortho* and *para*-substituted ones.



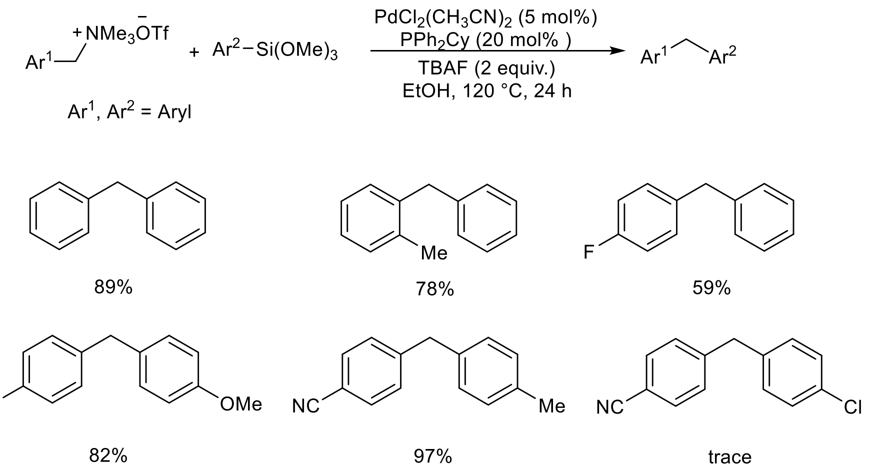
Scheme 1. Hiyama cross-coupling reaction of dihetaryl disulfides with arylsilanes.

They also reported a Hiyama coupling between pyrimidin-2-yl tosylates and trimethoxy(phenyl)silane to obtain C2 arylated products.[20] The coupling occurred best in the presence of 5 mol% of $PdCl_2$, 20 mol% CuCl, PCy_3 as ligand, and TBAF as the base in dioxane solvent at 110 °C (Scheme 2). The method offers good tolerance for various substituted pyrimidin-2-yl tosylates. Trimethoxyvinylsilane gave the desired product in moderate yields, and aromatic amino pyrimidin-2-yl tosylates also gave the coupling products. They also reported a similar coupling between 2-chloro pyrimidines and organosilanes.[21]

Zhao *et al.* in 2019 reported a palladium-catalyzed Hiyama cross-coupling of arylsilanes with benzyltrimethylammonium salts for the first time.[22] In this methodology, C(sp^2)-C(sp^3) bond formation occurs via cleavage of the C-N bond. They studied the substrate scope of this method under the optimized condition ($PdCl_2(CH_3CN)_2$ (5 mol%), PPh_2Cy (20 mol%), TBAF (2 equiv.) in EtOH at 120 °C for 24 h) (Scheme 3). They found that both electron-donating and electron-withdrawing groups on the benzylammonium salts gave the coupling products in moderate to good yields. While trimethoxyarylsilanes with electron-donating groups gave a good yield of the coupling products, *p*-chloro-substitution gave only a trace of the expected product.

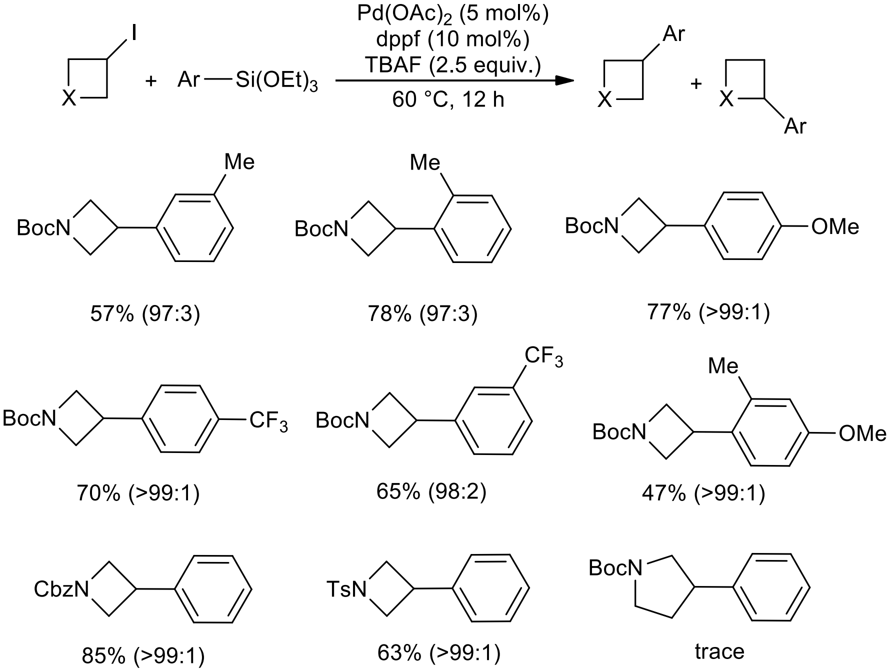


Scheme 2. Hiyama coupling between pyrimidin-2-yl tosylates and trimethoxy(phenyl)silane.



Scheme 3. Palladium-catalyzed Hiyama cross-coupling of arylsilanes with benzyltrimethylammonium salts.

In 2019, Hiyama cross-coupling of 3-iodoazetidine and arylsilanes catalyzed by palladium under mild conditions was reported by Liu and co-workers.[23] The optimized reaction condition was established as 5 mol% $Pd(OAc)_2$ as the catalyst, 10 mol% dppf as ligand, and 2.5 equiv. TBAF as fluoride source at 60 °C for 12 h (Scheme 4). Both electron-withdrawing and electron-donating groups in the *para* position in the aryl siloxanes gave higher yields than those at *meta* positions, while substituents in the *ortho* position gave moderate yields, indicating steric effects to play a role.

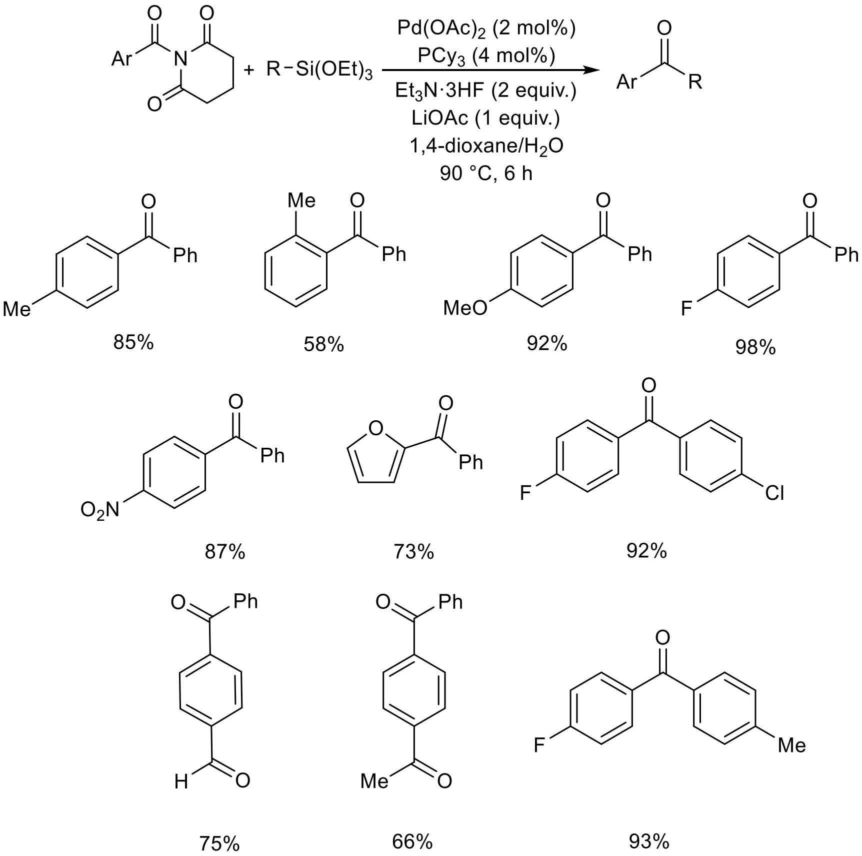


Scheme 4. Hiyama cross-coupling of 3-iodoazetidine and arylsilanes.

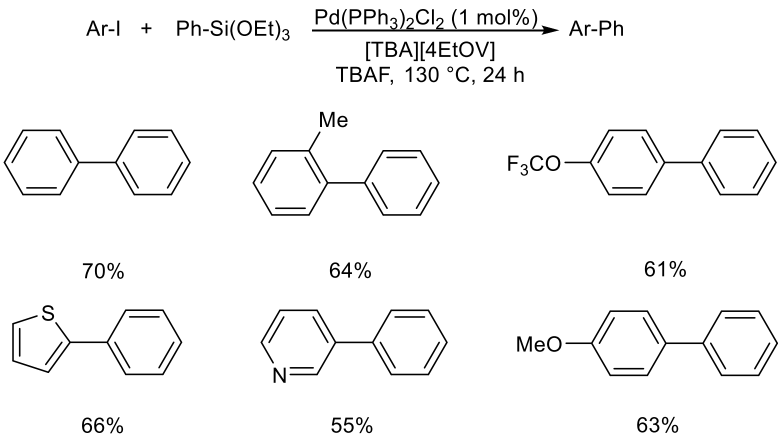
In 2020 Lee *et al.* reported the first Hiyama type coupling reaction involving amides, where N-acylglutarimides were reacted with aryl siloxanes to get the corresponding aryl ketones.[24] The optimal conditions for obtaining the Hiyama cross-coupling product was found to be 2 mol% Pd(OAc)$_2$ and 4 mol% PCy$_3$ in 1,4-dioxane/H$_2$O in the presence of Et$_3$N·3HF and LiOAc (Scheme 5). Substrate scope studies showed that *ortho*-substituted *N*-benzoylglutarimide gave relatively low product yield, indicating a lower reactivity due to steric effects. This reaction showed broad functional group tolerance. Control experiment studies using equal amounts of both substrates indicated that *N*-benzoylglutarimides with mesomerically electron-withdrawing substituents provided higher yields than those with mesomerically electron-donating substituents. Contrastingly, for triethoxy(phenyl)silanes, higher yields were obtained when the substituents were electron-donating rather than electron-withdrawing.

In 2020 Mika *et al.* showed that a biomass-derived ionic liquid, tetrabutylphosphonium 4-ethoxyvalerate ([TBP][4EtOV]), could be used as a solvent for Hiyama coupling between aryl iodides and organosilanes.[25] The optimized condition includes the use of Pd(PPh$_3$)$_2$Cl$_2$ (1 mol%) and tetra-*n*-butylammonium fluoride (TBAF) in [TBP][4EtOV] at 130 °C for 24 h (Scheme 6). Aryl iodides with electron-donating and electron-withdrawing groups performed well and afforded the desired products in good yields. The use of environment-friendly ionic liquid further enhances the significance of this method.

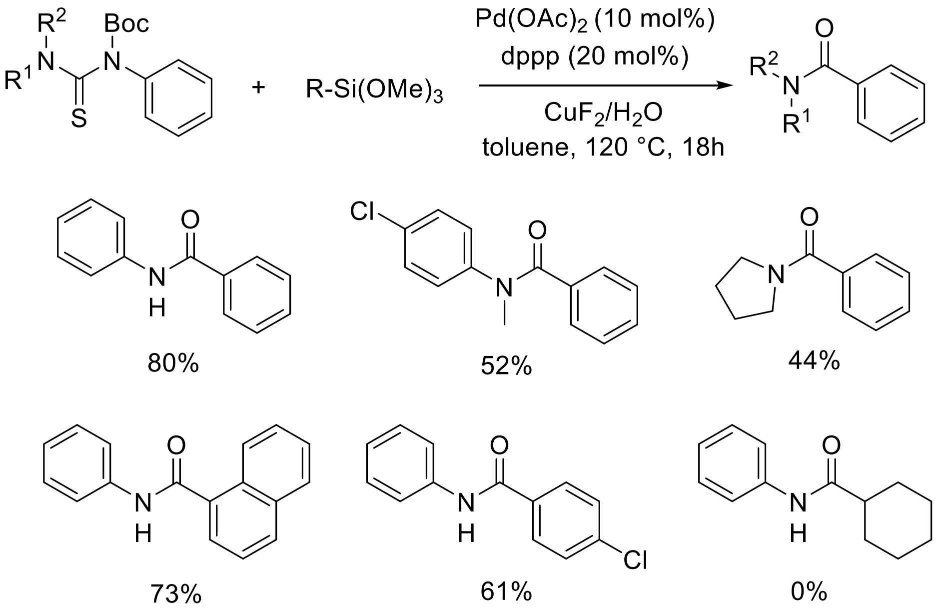
He *et al*. reported a Palladium-catalyzed desulfurative Hiyama coupling via a selective C-N bond cleavage of thiourea and trimethoxy(phenyl)silane to obtain an amide.[26] The optimized conditions for the reaction is 10 mol% Pd(OAc)$_2$, 20 mol% dppp, CuF$_2$ (2 equiv.), H$_2$O (1 equiv.), arylsilane (2 equiv.) in toluene at 120 °C for 18 h (Scheme 7). Substrate scope was explored, and electron-neutral and electron-rich substrates on both thioureas and silanes gave the coupling products in moderate to good yields. Alkylsilanes did not provide the desired products. Good functional group tolerance of this method allows for the production of a variety of amides, thus enhancing the practical utility.



Scheme 5. Hiyama coupling of various substituted N-acylglutarimides and arylsiloxanes.

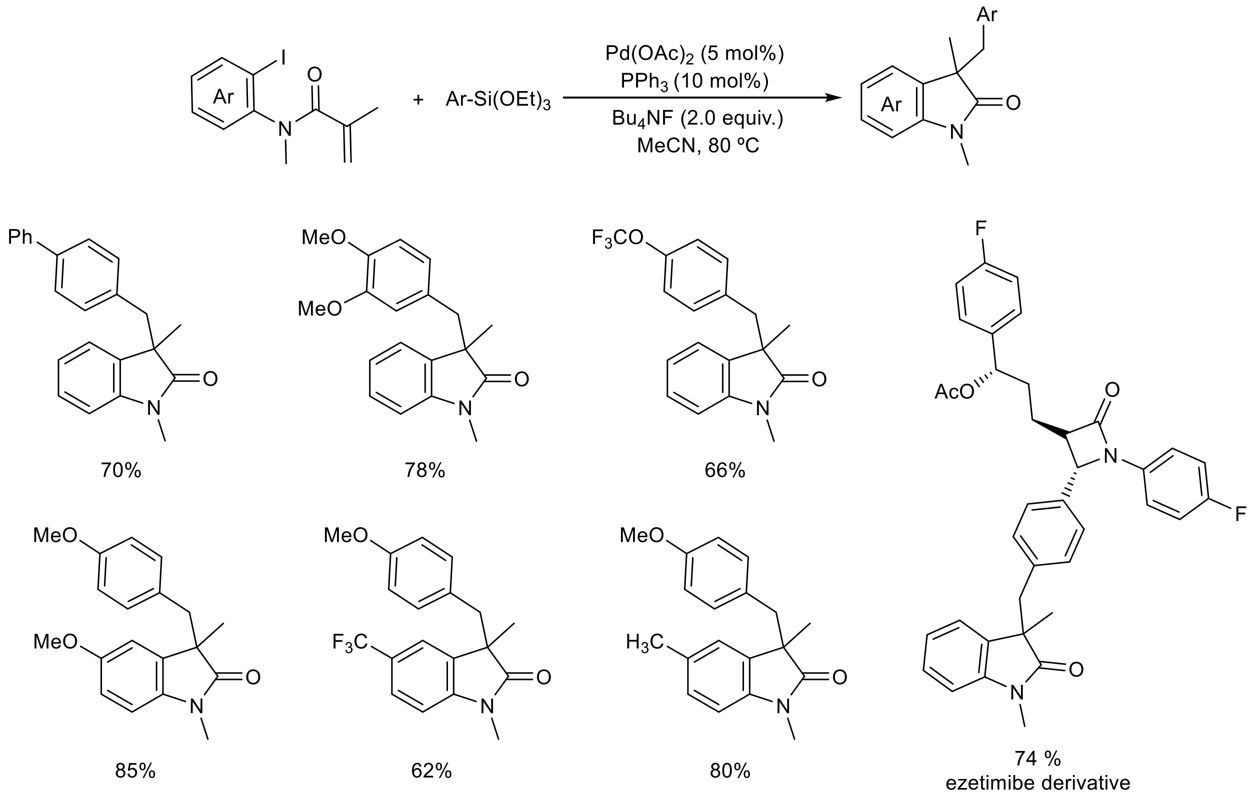


Scheme 6. Hiyama coupling of aryl iodides and organosilanes in [TBP][4EtOV] solvent.



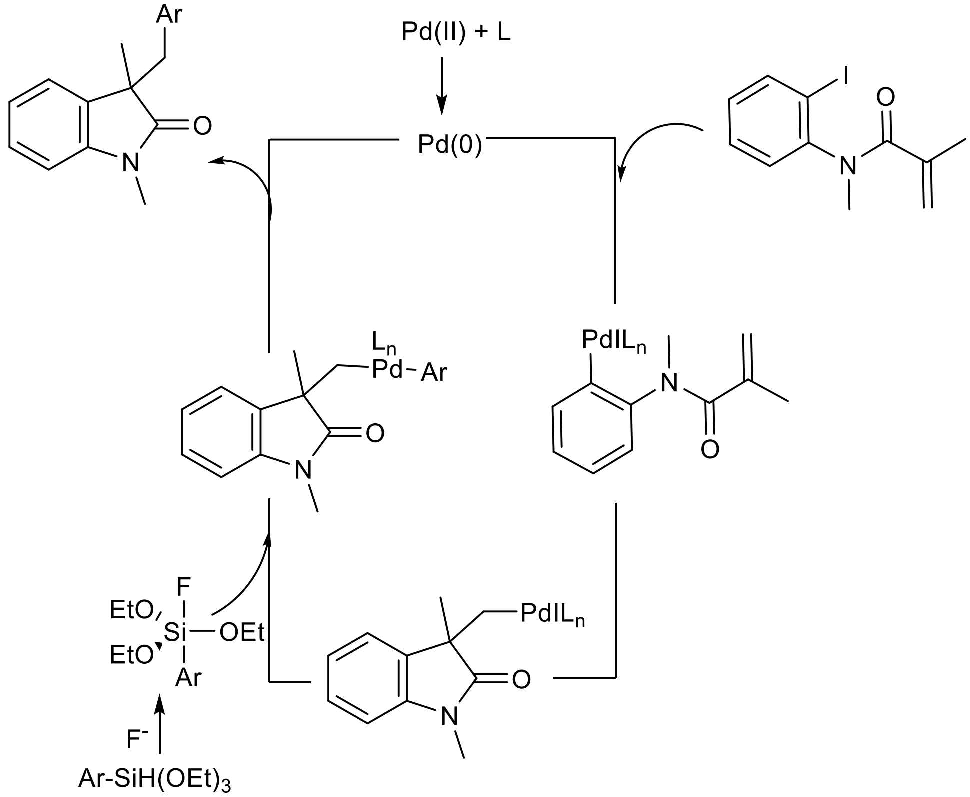
Scheme 7. Desulfurative Hiyama coupling of thiourea and trimethoxy(phenyl)silane.

Wu *et al.* disclosed a domino Heck cyclization/Hiyama cross-coupling of aryl-tethered alkenes with arylsilanes catalyzed by palladium.[27] The reactions afforded the best results when 5 mol% $Pd(OAc)_2$ was used as the catalyst, 10 mol% PPh_3 as ligand, Bu_4NF as the fluoride source in MeCN at 80 °C for 12 h (Scheme 8).



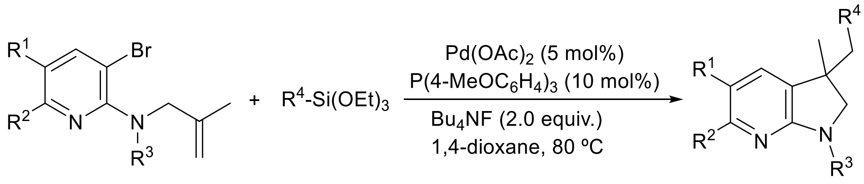
Scheme 8. Palladium catalyzed cascade Heck cyclization/Hiyama coupling of aryl-tethered alkenes with arylsilanes

Substrate scope studies showed that both electron-donating substituents like methoxy and electron-withdrawing substituents like trifluoromethoxy on arylsilanes gave the desired products in good yields. Aryl-tethered unactivated alkenes also performed well in this reaction. The application prospect of this method was demonstrated by the synthesis of oxindole functionalized ezetimibe in 74% yield. The proposed mechanism proceeds via the oxidative addition of Pd(0) to the carbon–halogen bond followed by carbopalladation and transmetallation resulting in an intermediate which undergoes reductive elimination to give the desired product and Pd(0) (Scheme 9).



Scheme 9. Mechanism for the palladium catalyzed cascade Heck cyclization/Hiyama coupling of aryl-tethered alkenes with arylsilanes.

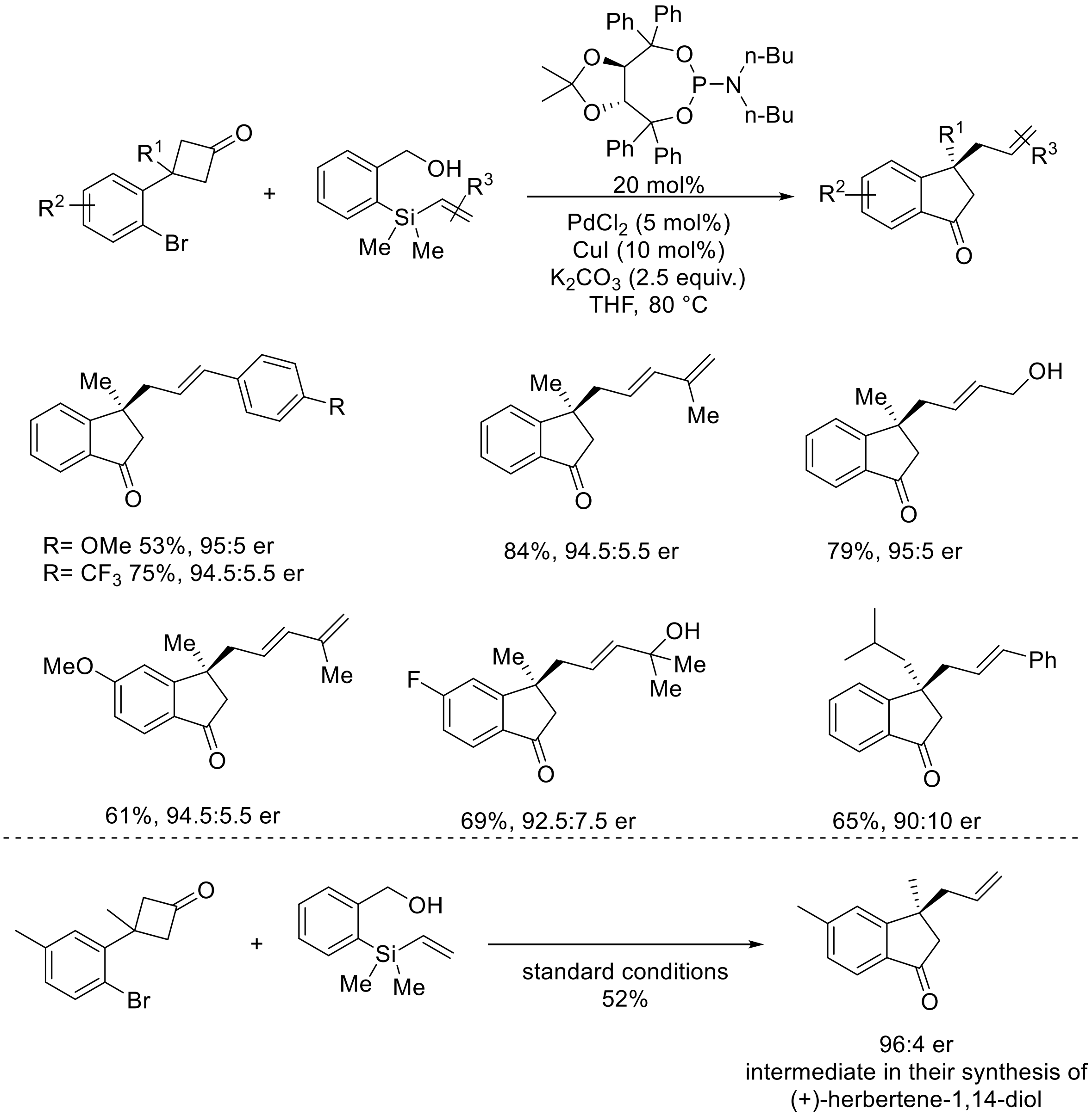
Later they disclosed a method for synthesizing (hetero)aryl functionalized 3,3-disubstituted azaindoline derivatives employing the same method to substituted aminopyridine and arylsilanes.[28] This reaction afforded the best results when 5 mol% $Pd(OAc)_2$ was used as catalyst, in 1,4-dioxane (Scheme 10). In this method electron-rich $P(4\text{-}MeOC_6H_4)_3$ was employed as the ligand and Bu_4NF was used for activating the inert C–Si bond. From substrate scope studies, it was discovered that both electron-rich and electron-deficient *p*-arylsilanes gave the desired azaindolines in moderate to good yields. Heteroarylsilanes, di-and trisubstituted arylsilanes were also tolerated well in this method. Concerning the N-substituents on the precursors, tosyl, benzyl- and methyl-protected aminopyridines gave the coupling products with various arylsilanes in good yield.



R^1	R^2	R^3	R^4	yield (%)
H	H	Ts	Ph	67
H	H	H	Ph	trace
H	H	Ts	4-PhC_6H_4	66
H	H	Ts	4-ClC_6H_4	53
H	H	H	3,4-$(OMe)_2C_6H_3$	61
H	H	Bn	3-$CF_3C_6H_4$	74
H	H	Bn	2-thienylsilane	77
Me	H	Ts	Ph	69
H	Me	Ts	4-$OMeC_6H_4$	61

Scheme 10. Palladium catalyzed synthesis of (hetero)aryl functionalized 3,3-disubstituted azaindoline derivatives.

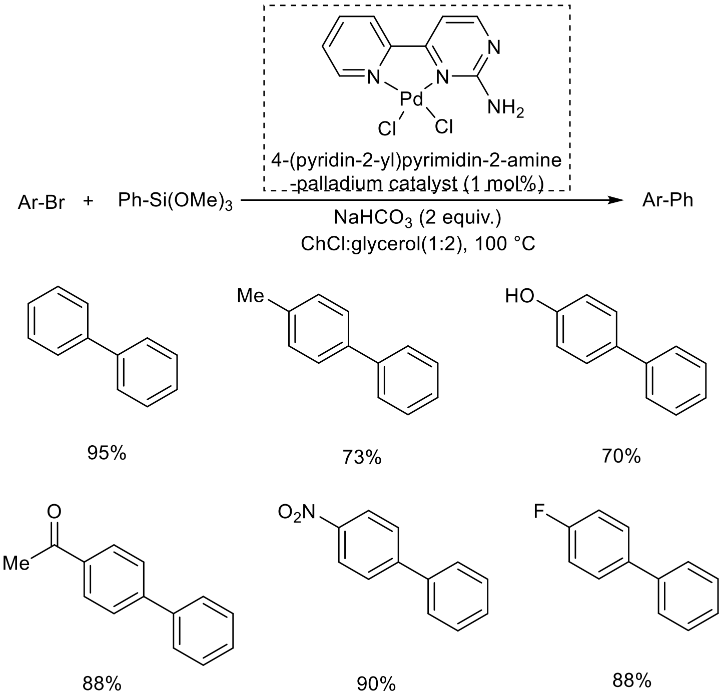
Xu *et al*. in 2022 reported a method for synthesizing 1-indanones by a Pd-catalyzed enantioselective domino ring-opening/Hiyama coupling of cyclobutanones with the bench-stable alkenyl-[2-(hydroxymethyl)phenyl]dimethylsilanes.[29] The resulting 1-indanones fancy a versatile alkenyl group and an all-carbon quaternary center. The best reaction condition was 5 mol% $PdCl_2$, 10 mol% CuI, and the use of a TADDOL-derived phosphoramidite ligand and K_2CO_3 base in dried THF at 80 °C (Scheme 11). In the alkenyl part of the silane, various substituents, like aryl, diene and hydroxyl were tolerated well with excellent enantioselectivity. They performed the reaction using cyclobutanone with variously substituted (CH_3, OMe, F, and Cl) phenyl moiety and obtained the desired product in good yields. They also used this methodology in a key step in the asymmetric total synthesis of (+)-herbertene-1,14-diol.



Scheme 11. Domino ring-opening/Hiyama coupling of cyclobutanones with alkenyl-[2-(hydroxymethyl)phenyl]dimethylsilanes.

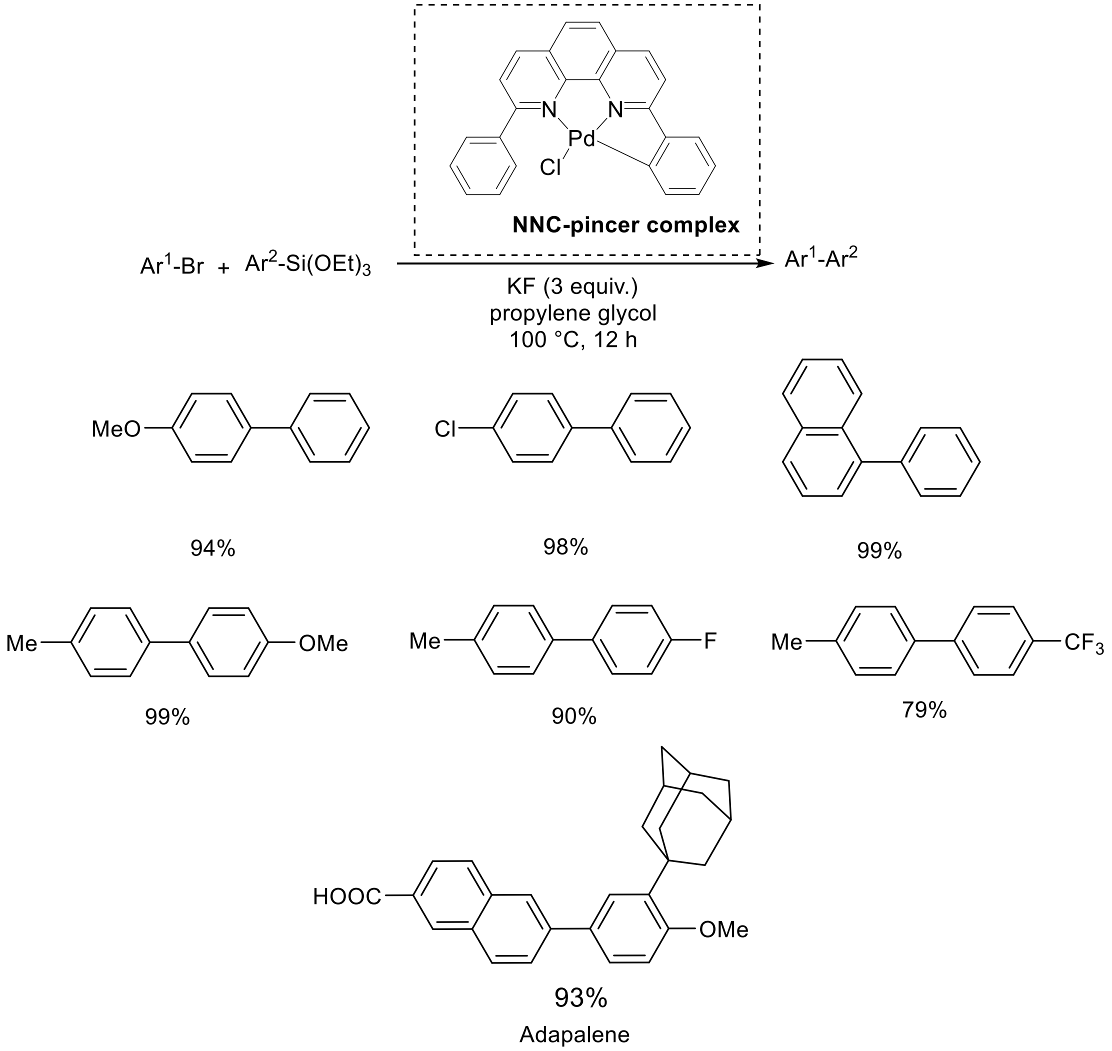
2.2. Nitrogen based ligand

In 2019 Ramón *et al.* reported a new amino-4-(2-pyridinyl)pyrimidine-palladium complex as a pre-catalyst for cross-coupling reactions which was highly efficient for Hiyama coupling reactions (Scheme 12).[30] Good yields of the required products were obtained irrespective of the substituents on aryl bromide. For the Hiyama reaction, the catalyst could be recycled for up to 5 consecutive cycles without any loss of activity or efficiency. This palladium pre-catalyst was also shown to catalyze Suzuki-Miyaura, Heck-Mizoroki and Sonogashira coupling reactions. Usage of the environmentally friendly deep eutectic solvent (DES) choline chloride + glycerol adds value to this method.



Scheme 12. Hiyama coupling catalyzed by the amino-4-(2-pyridinyl)pyrimidine-palladium catalyst.

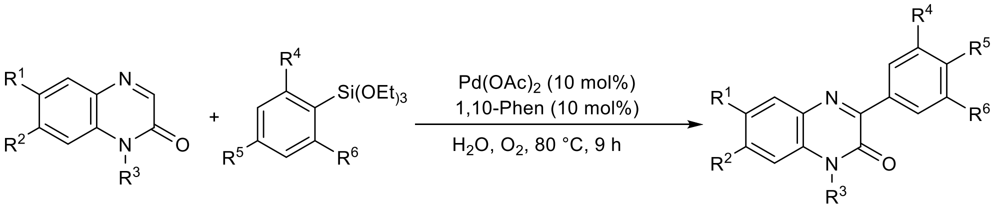
A palladium NNC-pincer complex as a catalyst for the Hiyama coupling reaction of aryl bromides with aryl(trialkoxy)silanes was developed by Uozumi and co-workers.[31] In situ-formation of glycol-derived pentacoordinate spirosilicate intermediates from aryl(trialkoxy)silanes played a critical role in the coupling. Optimization studies were carried out using 4-bromotoluene and trimethoxy(phenyl)silane as model substrates. Various aryl bromides were reacted with trimethoxy(phenyl)silane under the optimized conditions (palladium NNC-pincer complex (5 mol ppm), KF (3 equiv.) in propylene glycol at 100 °C) and found that both electron-donating and electron-withdrawing substituents gave the coupling products in high yields (Scheme 13). Sterically hindered 1-naphthyl bromide and heteroaromatic bromides were also well-tolerated in this reaction. The reaction was also amenable to electron-rich and electron-neutral arylsilanes. They also carried out the reaction using electron-deficient triethoxyarylsilanes and observed that a higher amount of catalyst was required for affording the desired products in good yields. The synthesis of adapalene on a gram scale and the derivatization of some drug molecules via this method proved the synthetic applicability of this method.



Scheme 13. Hiyama coupling catalyzed by palladium NNC-pincer complex.

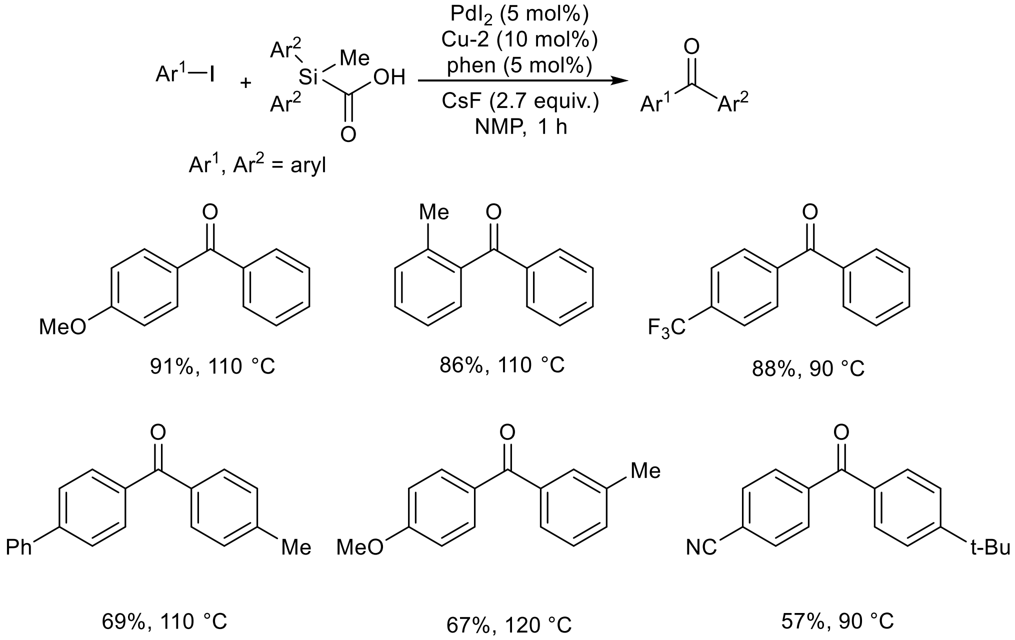
In 2020 Wu *et al.* described a palladium catalyzed method for direct coupling of quinoxalin-2-ones with aryl siloxanes in water using O_2 as the oxidant.[32] The best results were afforded when 10 mol% $Pd(OAc)_2$ was used as the catalyst and 10 mol% 1,10-phenanthroline as ligand (Scheme 14). Substrate scope studies showed that N-protected quinoxalin-2(1*H*)-ones, were effective for this reaction rather than the N-unsubstituted ones which failed to give the desired product. Moreover, aryl siloxanes with strong electron-withdrawing group at *para*-position failed to achieve the desired product.

Lian and co-workers developed a new methodology for the carbonylative Hiyama-Denmark cross-coupling reaction.[33] In this reaction, the CO precursor, methyl diphenylsilanecarboxylic acid, provides CO for carbonylation. The bifunctional reagent eliminates the need for an external carbon monoxide supply. The optimized reaction conditions for this method was found as 5 mol% PdI_2 as the catalyst, 10 mol % ((thiophene-2-carbonyl)oxy)copper, Cu-2, as co-catalyst, 5 mol% phenanthroline as ligand, 1.8 equiv. of methyl diphenylsilanecarboxylic acid as CO source, 2.7 equiv. of CsF as an additive, and NMP as solvent at 110 °C for 1 h (Scheme 15). Substrate scope studies showed that this new method exhibited good functional group tolerance and provided good yields for both electron-rich and electron-deficient aryl iodides.



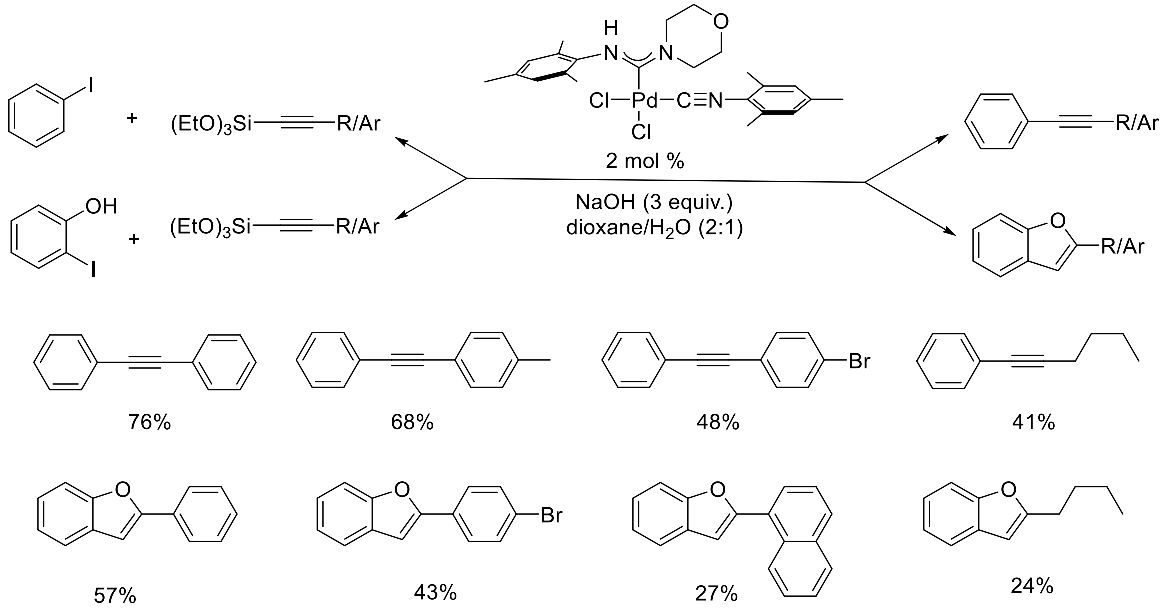
R^1	R^2	R^3	R^4	R^5	R^6	yield (%)
H	H	Me	H	H	H	87
Me	Me	Me	H	H	H	59
H	H	Bn	H	H	H	77
H	H	4-FC_6H_4	H	H	H	71
H	H	H	H	H	H	ND
H	H	Me	H	F	H	50
H	H	Me	H	Cl	H	13
H	H	Me	Me	Me	Me	9
H	H	Me	H	OMe	H	75

Scheme 14. Palladium catalyzed coupling of quinoxalin-2-ones with aryl siloxanes



Scheme 15. Palladium catalyzed carbonylative Hiyama-Denmark cross-coupling reaction.

Ghosh and coworkers reported the first Hiyama coupling and one-pot tandem Hiyama alkynylation/cyclization catalyzed by Palladium(II) acyclic diaminocarbene (ADC) complexes.[34] Hiyama coupling reaction of iodobenzene with triethoxysilylalkynes was carried out under the optimized conditions of 2 mol% Pd catalyst, 3 equiv. NaOH in 1,4-dioxane: H_2O (2:1) medium at 80 °C to obtain the products in moderate to good yields (Scheme 16). Higher yields were obtained for the aryl triethoxysilylalkyne compared to aliphatic alkyne silyl ether reagents. Hiyama coupling reaction followed by cyclization of iodophenol with triethoxysilylalkynes was also carried out under identical conditions to obtain various benzofuran compounds in moderate yields.

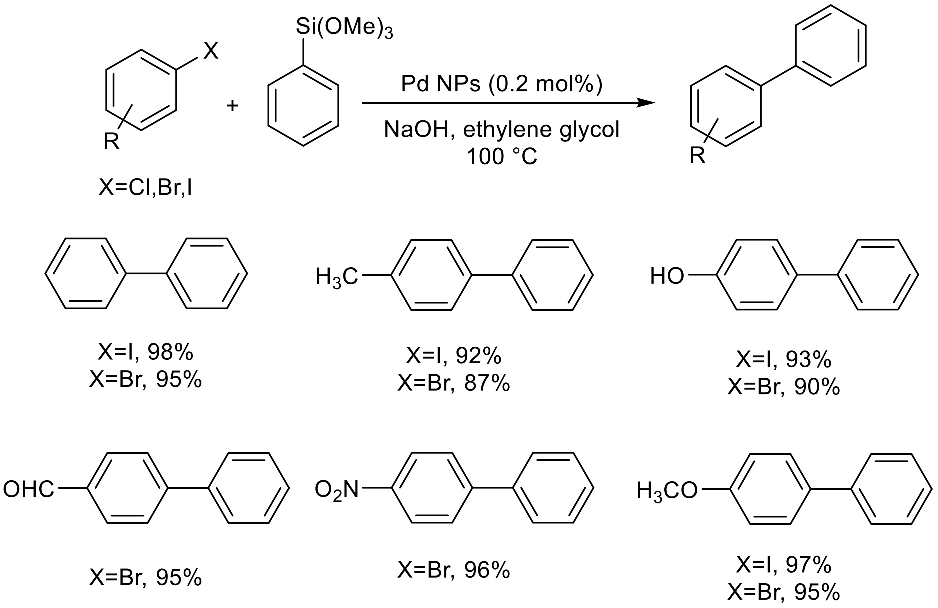


Scheme 16. Hiyama reactions and tandem Hiyama alkynylation/cyclization catalyzed by ADC complexes.

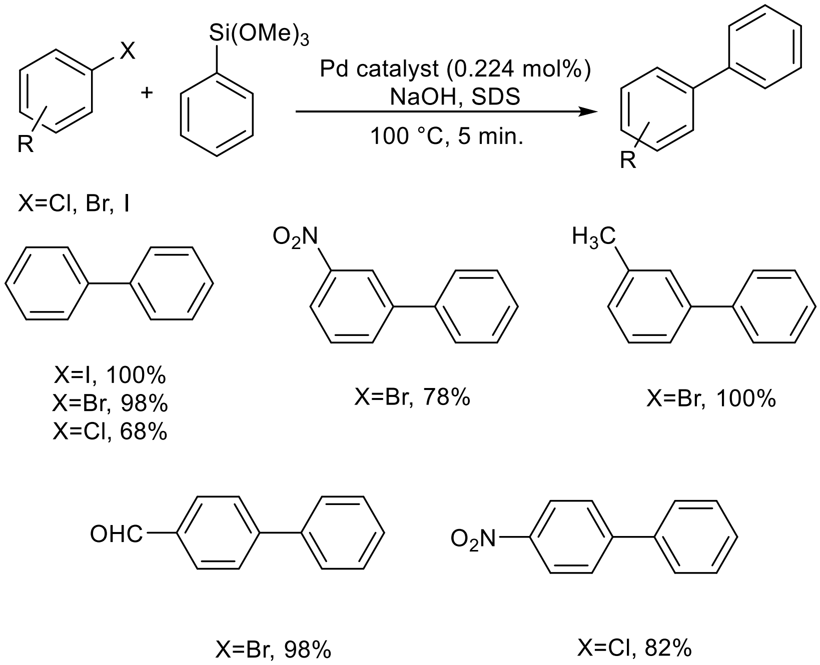
3. Heterogeneous Palladium Catalysis

Patil *et al.* biogenically synthesized palladium nanoparticles (Pd NPs) and characterized them using techniques including TEM, XRD and TGA. The Pd NPs were used as catalyst for Hiyama cross-coupling of various aryl halides with trimethoxy(phenyl)silane.[35] The optimum condition for this reaction was found as 0.2 mol % of Pd catalyst, 3 equiv. NaOH, at 100 °C in ethylene glycol (Scheme 17). Substrate scope studies on the aryl halides indicated that both electron-donating and electron-withdrawing groups gave excellent yields. The yields obtained were comparable with or better than the previously reported catalysts. The other benefits were that the reaction was carried out under fluoride-free conditions and ligand-free circumstances under air and avoided toxic chemicals that were usually employed in Hiyama reactions. The Pd NPs could be recycled up to ten times with only a small drop in the activity. In addition to Hiyama coupling, the catalyst was also good for the cyanation of aryl halides.

A new nanocatalyst, $Fe_3O_4@SiO_2$/APTMS/Pd(cdha)$_2$ was prepared by stabilizing Pd(cdha)$_2$ on the surface of $Fe_3O_4@SiO_2$/APTMS core–shell nanocatalyst support, where APTMS = 3-aminopropyltrimethoxysilane and cdha = bis(2-chloro-3,4-dihydroxyacetophenone), and characterized using FT-IR, XRD, SEM and used as a catalyst in the fluoride-free Hiyama cross-coupling reaction of aryl halides with trimethoxy(phenyl)silane in water by Karami and co-workers.[36] The optimized condition for the reaction was realized as 0.224 mol% Pd catalyst, sodium dodecyl sulfate, NaOH in water at 100 °C for 5 min. (Scheme 18). The reaction offered good functional group tolerance. Aryl halides with both electron-withdrawing and electron-donating substituents gave the coupling products in good yields. Aryl chlorides afforded the desired products in lower yields compared to aryl bromides and aryl iodides. The catalyst could be reused up to 4 times without considerable activity loss and was found to have good stability and exhibited comparable yields with other palladium catalysts available. The major advantages of this method include low catalyst loading, short reaction time, high turnover frequency, easy separation of the magnetic catalyst and fluoride-free conditions.

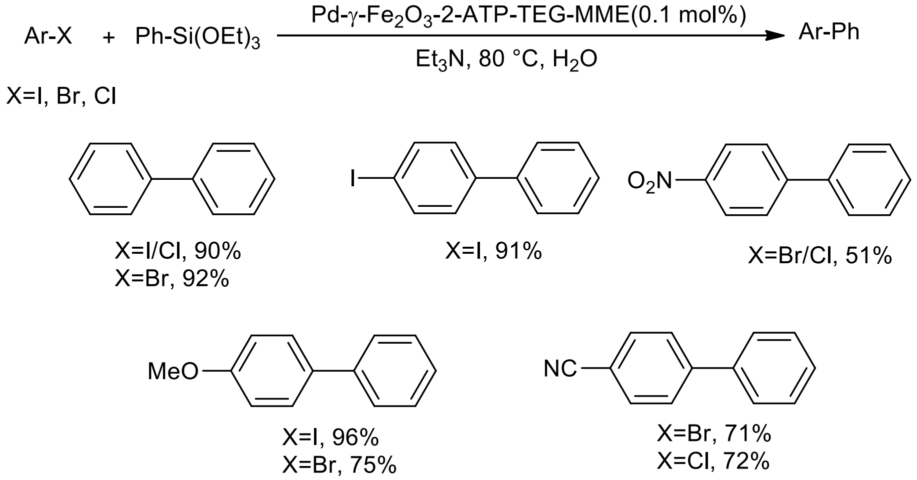


Scheme 17. Pd NP catalyzed Hiyama cross-coupling of aryl halides with trimethoxy(phenyl)silane.



Scheme 18. Palladium catalyzed fluoride-free Hiyama cross-coupling reaction of aryl halides with trimethoxy(phenyl)silane.

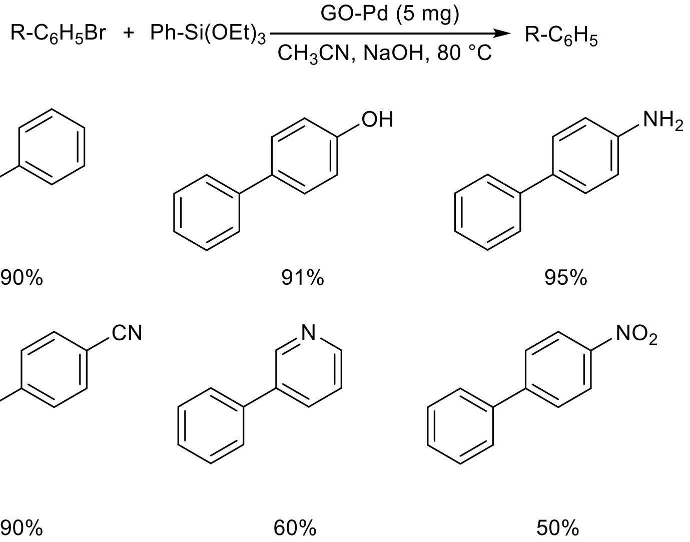
Sobhani and co-workers have synthesized and characterized a novel Pd heterogeneous catalyst, Pd-γ-Fe_2O_3-2-ATP-TEG-MME, where 2-ATP is 2-aminothiophenol and TEG-MME is triethylene glycol monomethyl ether. The catalyst is water-dispersible and recyclable by magnetic separation.[37] This catalyst was found efficient in the Hiyama cross-coupling reaction of halobenzenes with triethoxy(phenyl)silane, and coupling products were achieved in good yields except when electron-withdrawing NO_2 group was present (Scheme 19). The reaction did not require any fluoride activation of the aryl silanes. This catalyst can be reused up to 9 times without considerable loss in reactivity. The scalability of the process was tested, and the desired product was obtained in 88% yield. Compared with other reported Pd catalysts in water, Pd-γ-Fe_2O_3-2-ATP-TEG-MME was the most efficient catalyst for the C-C coupling reactions of aryl halides.



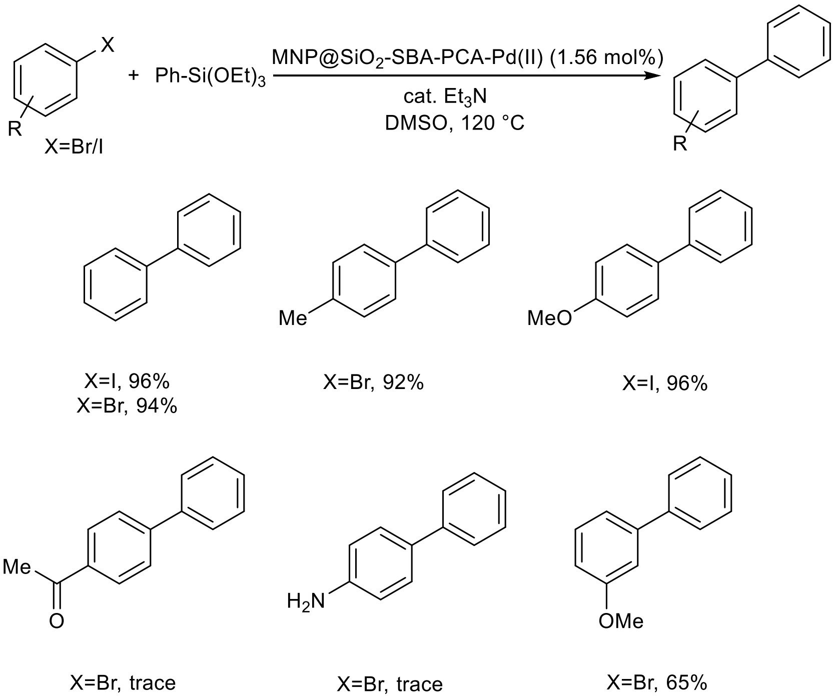
Scheme 19. Hiyama cross-coupling reaction of halobenzenes with triethoxy(phenyl)silane catalyzed by Pd-γ-Fe_2O_3-2-ATP-TEG-MME.

Sharma *et al.* synthesized GO-Pd, a recyclable heterogeneous nanocatalyst by immobilizing Pd nanoparticles on Schiff base-functionalized graphene-oxide (GO).[38] GO-Pd showed high catalytic activity in Hiyama and other coupling reactions. They utilized bromobenzene and trimethoxy(phenyl)silane as the model substrates, and the optimized condition includes 5 mg of GO-Pd as the catalyst for 1 mmol substrate, NaOH as a base, acetonitrile as solvent at 80 °C (Scheme 20). The substrate scope studies indicated that the electronic nature of substituents on bromobenzene does not influence the yield of the reaction. The catalyst could be reused for up to six cycles without remarkable loss of catalytic activity.

A new Pd(II) supported catalyst MNP@SiO_2-SBA-PCA-Pd(II), was prepared by embedding magnetite nanoparticles between SBA-15 channels and silylating them with N-(3-(trimethoxysilyl)propyl)picolinamide (TMS-PCA), and complexing with PD(II). This catalyst was found to have having high activity in the Hiyama and Heck coupling reactions, was synthesized and characterized by Mansoori and co-workers.[39] The efficiency of the new catalyst in Hiyama coupling was studied for the coupling between iodobenzene and triethoxy(phenyl)silane. Various aryl halides smoothly underwent this reaction under the optimized conditions of 1.56 mol% catalyst, Et_3N as the base, in DMSO at 120 °C (Scheme 21). This system offered conversions similar to the previously reported Pd catalysts. The catalyst could be easily separated by magnetic means and recycled and reused up to 5 times without significant loss in reactivity.

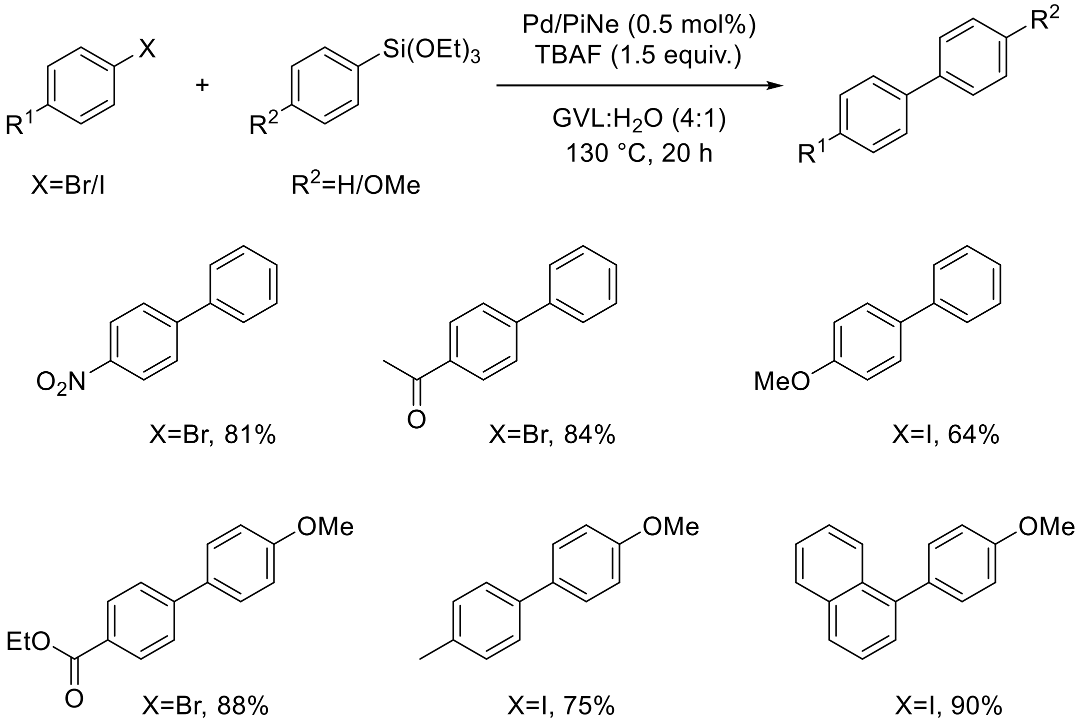


Scheme 20. Hiyama coupling of aryl bromines and trimethoxy(phenyl)silane catalyzed by GO-Pd.



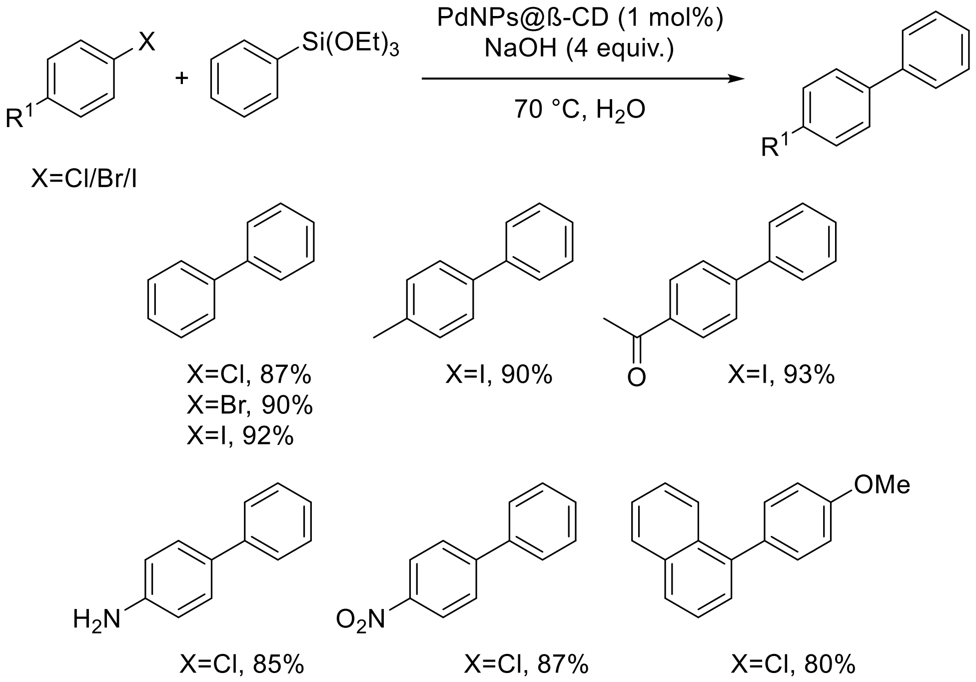
Scheme 21. Hiyama coupling between aryl halides and triethoxy(phenyl)silane catalyzed by Pd(II) supported catalyst, MNP@SiO_2-SBA-PCA-Pd(II).

Vaccaro and co-workers converted pine needle urban waste into low-cost support (PiNe) to immobilize Pd nanoparticles.[40] The prepared Pd/PiNe heterogeneous catalyst exhibit excellent activity in Hiyama coupling in the biomass-derived solvent γ-valerolactone(GVL). The optimized conditions for the hiyama coupling were realized as 0.5 mol% Pd/PiNe catalyst, 1.5 equiv. TBAF in GVL: H_2O (4:1) solvent system (Scheme 22). The coupling products of different aryl bromides and iodides with various silanes were obtained in good yields. The use of biomass-derived solvent GVL and catalyst support derived from pine needles adds value to this method.



Scheme 22. Pd/PiNe catalyzed Hiyama coupling of aryl halides and arylsilanes.

Bazgir *et al*. prepared and characterized a reusable catalyst PdNPs@β-CD, Palladium decorated β-cyclodextrin, as a suitable catalyst for synthesizing biaryls through Hiyama coupling in water.[41] The Hiyama reaction of triethoxy(phenyl)silane with aryl halides under the optimized conditions of 1 mol% PdNPs@β-CD, 4 equiv. NaOH at 70 °C gave the coupling products in good yields (Scheme 23). The catalyst was also used in Ullmann and Suzuki couplings. The green conditions for the reaction, the easy recovery, and the reusability of the catalyst are highlights of this method.



Scheme 23. Hiyama reaction of triethoxy(phenyl)silane with aryl halides catalyzed by PdNPs@β-CD.

4. Conclusions

This review summarizes the recent developments in palladium catalyzed Hiyama coupling reactions. Hiyama coupling has emerged as a powerful strategy for the synthesis of wide variety of organic compounds. Cross-coupling reactions using organosilicon compounds has been identified as an efficient method owing to the less-toxic, high stability and good functional group tolerance characteristics of this compound.

From this review, it is understood that a large number of methods prefer aryl or vinylsilanes with trialkoxy substituent at the silicon atom as the coupling partner. Moreover, the most frequently used ligands are phosphine ligands. Most of the reported methods employ a palladium catalyst with an activator for the silicon reagent i.e. a fluoride source (commonly Bu_4NF or CsF). Some of the reported works includes fluoride-free approaches and further exploration in this field is certainly required. The wide scope of this reaction indicates the need to explore more on palladium-catalyzed Hiyama coupling reaction in future.

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Authors' Biographies

S. Sivakumar was born in Kerala, India. Currently he is a final year student of the five-year Integrated Master of Science Programme at the Institute for Integrated Programmes and Research in Basic Sciences (IIRBS), Mahatma Gandhi University, Kottayam. He has qualified GATE in 2022. His research interests are in the areas of organic synthesis and transition metal catalysis.

T Aneeja was born in Chittariparamba, Kannur, Kerala, India. She obtained her B.Sc. degree from Kannur University (Nirmalagiri college, Kuthuparamba) in 2016 and her M.Sc. degree from the Department of Applied Chemistry, CUSAT in 2018. She passed the CSIR-UGC National Eligibility Test 2019 for a research fellowship. Currently she is pursuing her doctoral research under the guidance of Dr G. Anilkumar in the School of Chemical Sciences, Mahatma Gandhi University, Kottayam.

Gopinathan Anilkumar was born in Kerala, India and took his Ph. D in 1996 from Regional Research Laboratory (renamed as National Institute for Interdisciplinary Science and Technology NIIST-CSIR), Trivandrum with Dr. Vijay Nair. He did postdoctoral studies at University of Nijmegen, The Netherlands (with Professor Binne Zwanenburg), Osaka University, Japan (with Professor Yasuyuki Kita), Temple University, USA (with Professor Franklin A. Davis), Leibniz-Institüt für Organische Katalyse (IfOK), Rostock, Germany (with Professor Matthias Beller) and Leibniz-Institüt für Katalyse (LIKAT), Rostock, Germany (with Professor Matthias Beller). He was a senior scientist at AstraZeneca (India). Currently he is Professor in Organic Chemistry at the School of Chemical Sciences, Mahatma Gandhi University in Kerala, India. His research interests are in the areas of organic synthesis, medicinal chemistry, heterocycles and catalysis. He has published more than 150 papers in peer-reviewed journals, 7 patents, three book chapters and edited two books entitled "*Copper Catalysis in Organic Synthesis*" (Wiley-VCH, 2020) and "*Green Organic Reactions"* (Springer, in press). He has received Dr. S Vasudev Award from Govt. of Kerala, India for best research (2016) and Evonik research proposal competition award (second prize 2016). His h-index is 35.