

Sonogashira coupling of arenediazonium salts: discovery and developments

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Dedicated to my beloved teacher Professor Dipakranjan Mal to celebrate his 70th birthday

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Abstract

Colourful chemistry: Arenediazonium salts represent efficient, common, easily available aryl surrogates from inexpensive anilines and show higher reactivity compare to aryl halides and triflates towards various cross-coupling reactions. We have disclosed the Sonogashira coupling of arenediazonium salts in 2010; afterward, several groups successfully developed various protocols for this reaction. This mini-review describes the discovery and progress of the alkylation of arenediazonium salts in due time, highlights the strengths and weaknesses of each protocol.



Keywords: Arenediazonium salt, Sonogashira coupling, alkylation, cross-coupling, C-C bond formation

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1. Introduction

In 2010, the Nobel Prize in chemistry recognized the invention of strategies for the palladium-catalyzed construction of carbon-carbon bonds through the so-called cross-coupling reactions. In organic chemistry, the development of new carbon-carbon bonds is of key significance and a requirement for the synthesis of medicinally important compounds, polymers, and various functional materials. The palladium-catalyzed cross-coupling reaction is a reliable method for the C-C bond formation. In this context, aryl or vinyl halides or triflates have found broad utility as electrophilic coupling partners. Recently, considerable attention has been focused on the metal-catalyzed coupling reactions that incorporate arenediazonium tetrafluoroborate salts as aryl electrophilic components.¹ Aryl diazonium salts have been discovered in the middle of the 19th century by Johann Peter Grieffs, who was working on azo compounds as dyes and pigments.² They are a class of super electrophiles with the common structure of R-N₂X, where R is an aryl or heteroaryl fragment and X is a weakly nucleophilic organic or inorganic anion. Some diazonium salts are commercially available; however, the high nucleofuge properties of the diazonium salts make these compounds potentially hazardous, especially on large scale. By the way, whenever aryl diazonium salts have been involved in several industrial processes, including a Heck-Matsuda reaction for the preparation of herbicide Prosulfuron at Syngenta^{3, 4} safety issues hampered further developments. Indeed, the stability of aryl diazonium salts is mostly dependent on the associated counterion, although the aryl structure should also be considered. For instance, while aryl diazonium chlorides⁵ and acetates are unstable above 0 °C, their tetrafluoroborate,⁶ tosylate,⁷ and disulfonamide^{8,9} counterparts are usually more stable and isolable as crystalline salts. Arenediazonium salts are good aryl halide surrogates so one can take full advantage of several of their important features.¹⁰ First, arenediazonium salts can be easily synthesized from the corresponding anilines with high yields.¹¹ Second, the arenediazonium salts are more reactive than the corresponding aryl halides in the palladium-catalyzed Heck

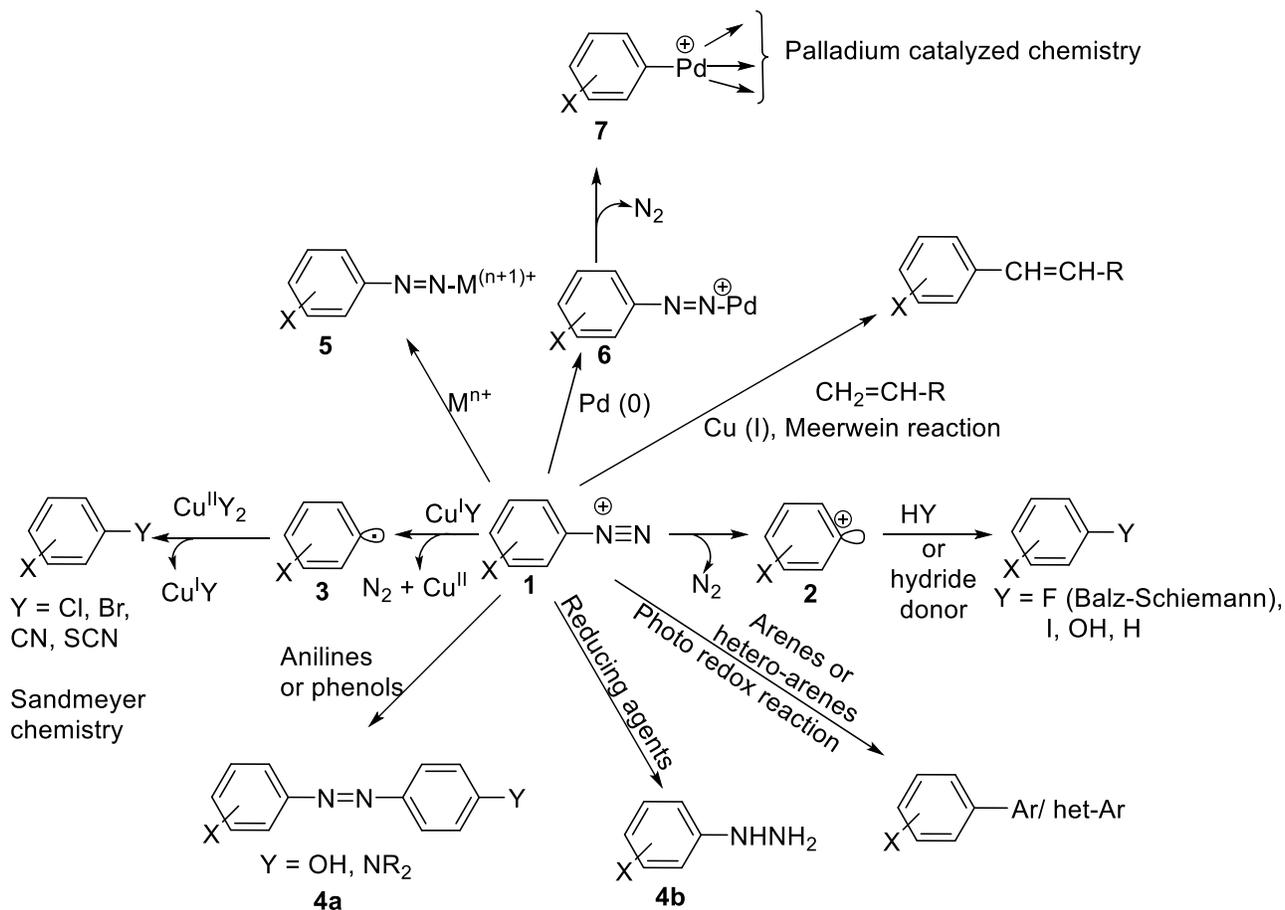
and Suzuki reactions.^{12,13} Third, palladium-catalyzed reactions can usually be carried out at lower temperature (between 20 and 50 °C) than the typical Heck and Suzuki reactions (over 100 °C), and they can also be carried out without added extra base or salt (such as silver chloride or thallium ethoxide),^{14,15} which extend the reaction scope to substrates with sensitive functional groups. Fourth, using arenediazonium salts high chemo- and regioselectivity can be achieved in the coupling reactions. Fifth, in the cross-coupling reaction of arenediazonium salts the leaving group N₂ does not interfere with the reaction mixture. Thus, the development of an arenediazonium salt that can be used in the metal-catalyzed coupling reaction could both accelerate the synthesis of valuable organic molecules and reduce the steps involved in the synthesis of pharmaceuticals and agrochemicals.¹⁰

Arenediazonium salts are prepared by the reaction of anilines with a source of nitrite.¹⁶ When the diazotization reaction is performed in water, sodium nitrite and a strong acid are required according to the stoichiometry of equation 1. Since the nature of the counterions of arenediazonium salt is of utmost importance for their stability as well as reactivity, the choice of acid in the diazotization process is most significant. Diazotization of anilines in organic solvents is accomplished by reaction of the aniline with an organic nitrite (equation 2).¹¹

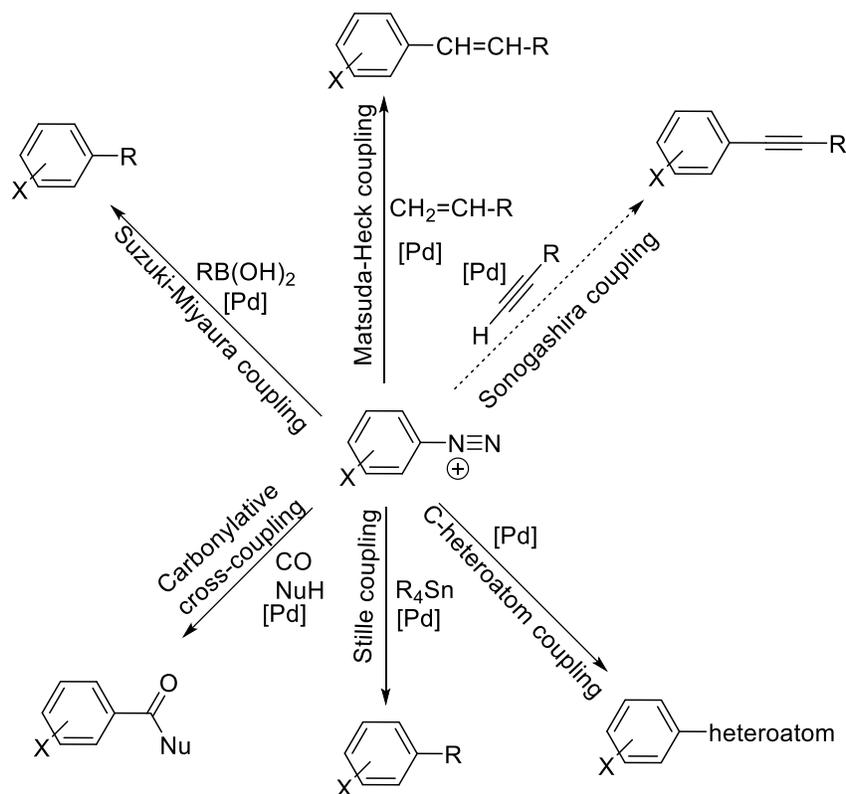


The common reactions of arene diazonium salts are shown in Scheme 1. Its use is limited due to the low stability of arene cations **2**, generated from **1** through nitrogen elimination.¹ Elimination of dinitrogen is frequently induced by single electron transfer (SET) from a low-valence metal, usually Cu(I).^{1,17} Generation of the relatively stable arene free radical **3** induces introduction of several nucleophilic anions (chloride, bromide, cyanide, thiocyanate: Sandmeyer chemistry) probably through an aromatic radical-anion intermediate¹⁷ with the recovery of the low-valence metal that acts catalytically. Coupling of arene diazonium salts with highly nucleophilic aniline derivatives or phenolates provides coloured diazo compound **4a**, commonly known as azo dye. They constitute the most numerous family of commercially available dyes.² Certain reducing agents (Na₂SO₃, SnCl₂/HCl, Zn/NiCl₂) preserve the N-N bond to afford arylhydrazines **4b**. It is little understood that cations **1** can coordinate metals to give species **5** where the oxidation number of the metal (M) has been increased by two units. Palladium(0) gives this type of reaction producing, initially, cation **6** and, finally, arenepalladium cation **7** (Scheme 1).

Although typical palladium-catalyzed cross-couplings like Matsuda-Heck,¹⁸⁻²⁰ Suzuki-Miyaura,²¹⁻²³ carbonylative couplings,²⁴ Stille,²⁵ C-heteroatom²⁶⁻²⁸ couplings, etc in which diazonium salts have been used as electrophilic partners instead of the more usual halides or oxygen-based electrophilic components are known in the literature, Sonogashira-type cross-coupling of arenediazonium salts is not being reported before our work (Scheme 2). For years, however, the Sonogashira reaction²⁹ has remained a staple of organic synthesis due to the efficiency with which aryl alkynes and conjugated enynes, which are prevalent intermediates for the synthesis of a diverse array of natural products,³⁰⁻³³ pharmaceuticals, and molecular organic materials, are accessible.³⁴⁻³⁶



Scheme 1. Reaction of arenediazonium salts.



Scheme 2. Cross-Coupling of arenediazonium salts.

2. Early Attempt

Sengupta and Sadhukhan attempted the Sonogashira coupling of arenediazonium salts for the first time, but they were unable to succeed.³⁷ In the course of their investigation on palladium-catalyzed reactions of arenediazonium salts, they had introduced the “iodoarenediazonium salts (III)” **8** (Figure 1) as a new class of aromatic substrates for differential Heck and cross-coupling reactions. They commented in their published communication³⁷ in the year 1998 that “A limitation of the synthon III arises from the fact that arenediazonium salts do not participate in Sonogashira-type couplings with terminal acetylenes.”

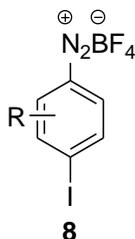
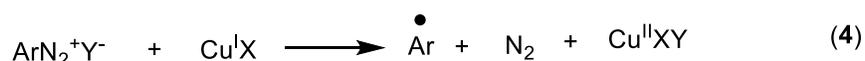
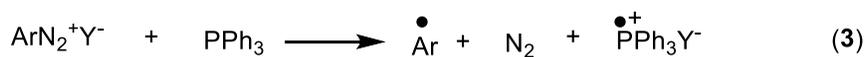


Figure 1. Synthon III.

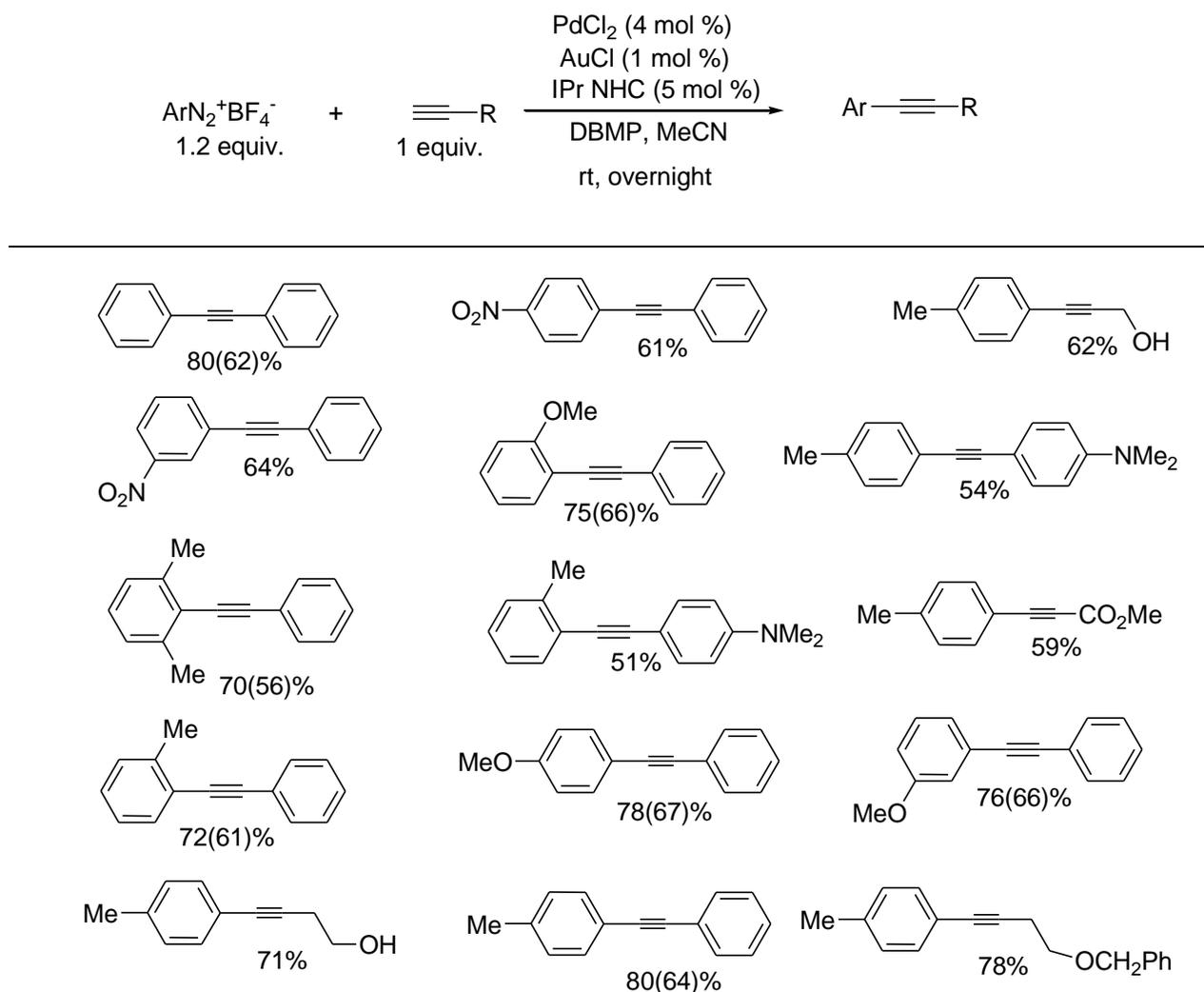
Presumably, there are two main reasons for the absence of arenediazonium salts in Sonogashira couplings: firstly, phosphines such as Ph_3P cannot be a ligand of choice in Pd-catalyzed cross-coupling reactions with diazonium salts as it is known to transfer an electron to the latter to afford the arene radical and the cation radical of Ph_3P (equation 3)¹; the arene radical then abstracts a hydrogen atom, mainly from alcoholic solvents or moisture, to give the overall reduction products Ar-H, whereas the cation radical of Ph_3P is finally converted to $\text{O}=\text{PPh}_3$. Secondly, elimination of N_2 is frequently induced by single electron transfer (SET) from a low-valence metal, usually, Cu(I) which was used in traditional Sonogashira coupling as co-catalyst (equation 4),^{1,17} as described in scheme 1.



3. Discovery of Sonogashira Coupling of Arenediazonium Salts

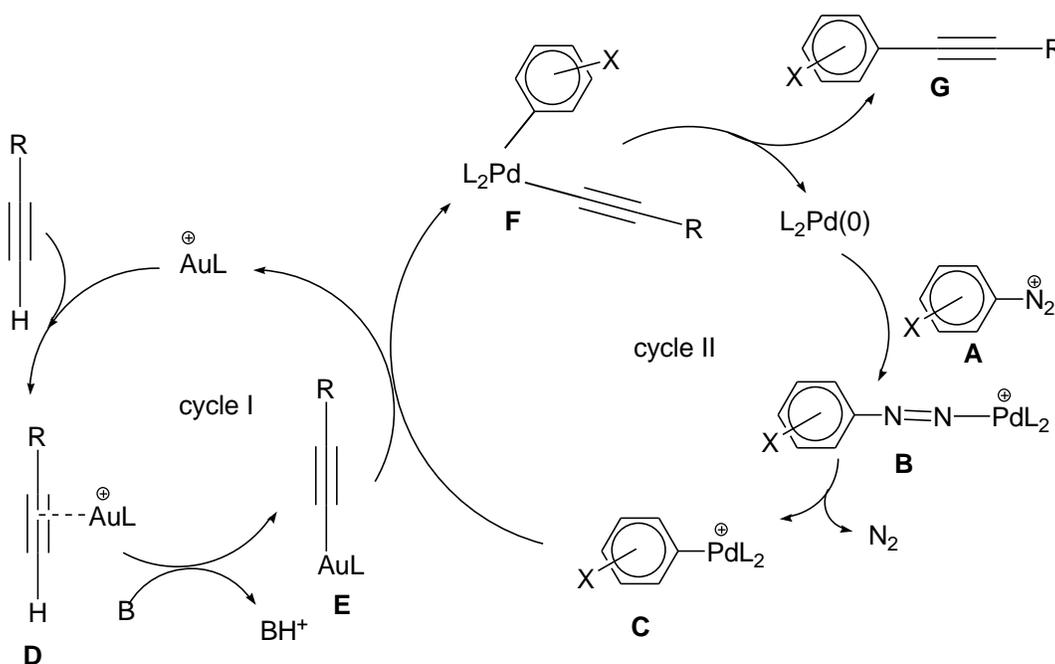
Although traditionally the palladium catalysts for the Sonogashira coupling of aryl or vinyl halides contain phosphine ligands, in case of an uneventful Sonogashira reaction with arenediazonium salts, we must avoid the use of phosphine-based ligands on palladium. Similarly, the other metal required for the transmetalation step should have high oxidation potential and be compatible with arenediazonium salts. It occurred to us that the other coinage metal, namely gold fulfills these criteria. In the previous work, we have found the efficacy of the catalytic combination $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{AuCl}(\text{PPh}_3)$ in Sonogashira coupling of aryl and heteroaryl halides.^{38,39} We felt that a similar combination devoid of phosphine ligands may be the catalyst of choice for the Sonogashira coupling of arenediazonium salts. Indeed, we have successfully developed the protocol for the first Sonogashira coupling of arenediazonium salts using a Pd-Au dual catalytic system.⁴⁰ In our method, 1 mol% AuCl has been used as co-catalyst combined with 4 mol% PdCl_2 in the coupling of arenediazonium salts with terminal alkynes, a process carried out in the presence of

ligand bis-2,6-diisopropylphenyl dihydroimidazolium chloride (IPr NHC) (5 mol%) and base 2,6-di-tert-butyl-4-methylpyridine (DBMP) in acetonitrile solvent. The reaction proceeds smoothly at room temperature to afford various alkynylated products in good yields. The synthetic efficiency of this reaction was studied with a variety of electronically and structurally diverse arenediazonium salts and acetylenes. Electron neutral, electron-rich as well as electron-deficient arenediazonium salts were successfully coupled with both aryl and alkyl acetylenes to afford desired arylated alkynes in good yields (Scheme 3). Sterically hindered arenediazonium salts are also coupled nicely in our protocol. Because *N,N*-dimethylanilines readily undergo azo-coupling with arenediazonium salts, cross-coupling of arenediazonium salts with alkynes containing an *N,N*-dimethylanilino group is a challenging task, such couplings are achievable under these conditions. Various functional groups like nitro, alcohol, benzyl ether, methoxy, methyl, ester, *N,N*-dimethylanilino, etc are tolerated in this method. *ortho*-Substituted arenediazonium salts and sterically hindered 2,6-dimethyl benzene diazonium salts also nicely coupled with alkynes. Our method was found to be useful for the one-pot direct in situ diazotization and cross-coupling reaction starting from anilines. The yields indicated in parenthesis in scheme 3 are obtained directly from aniline in one-pot diazotization and cross-coupling reactions.

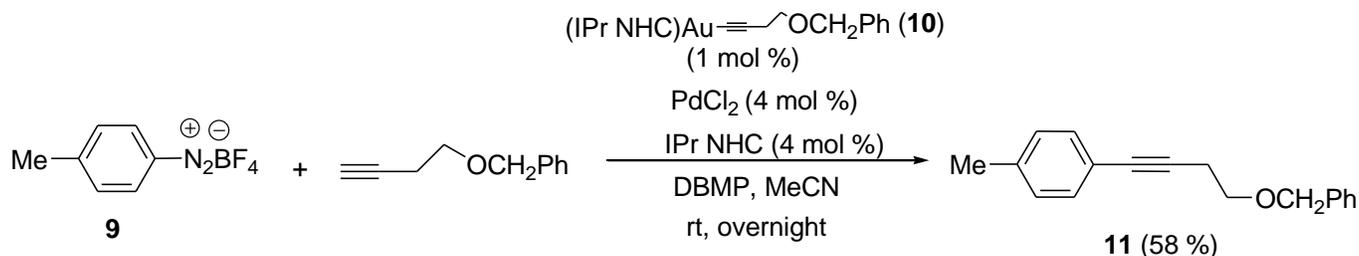


Scheme 3. First Sonogashira coupling of arenediazonium salts.

A plausible mechanism for the Sonogashira coupling of arenediazonium salts using the Pd-Au dual catalytic system⁴¹⁻⁵⁹ is shown in Scheme 4. This reaction presumably occurs in three stages:³⁴ firstly, the cation **A** can coordinate the in situ generated palladium(0) to give initially cation **B** and finally, arene-palladium cation **C**, in which the palladium(0) has increased its oxidation number by two units. The second stage involves the transmetalation of the in situ generated alkynylgold species **E**, formed by initial coordination of gold to the alkyne followed by abstraction of a proton from **D** by the base, to the palladium species **F**. The last step is the obvious reductive elimination to yield the product **G** and regeneration of palladium(0) complex. To support the proposed mechanism, coupling of **9** was carried out as usual, but instead of AuCl the preformed gold acetylide **10** (1 mol%) was used as the source of gold catalyst. This reaction furnished the desired coupled product **11** in 58% isolated yield (Scheme 5).



Scheme 4. A proposed mechanism for Sonogashira coupling of arenediazonium salts.



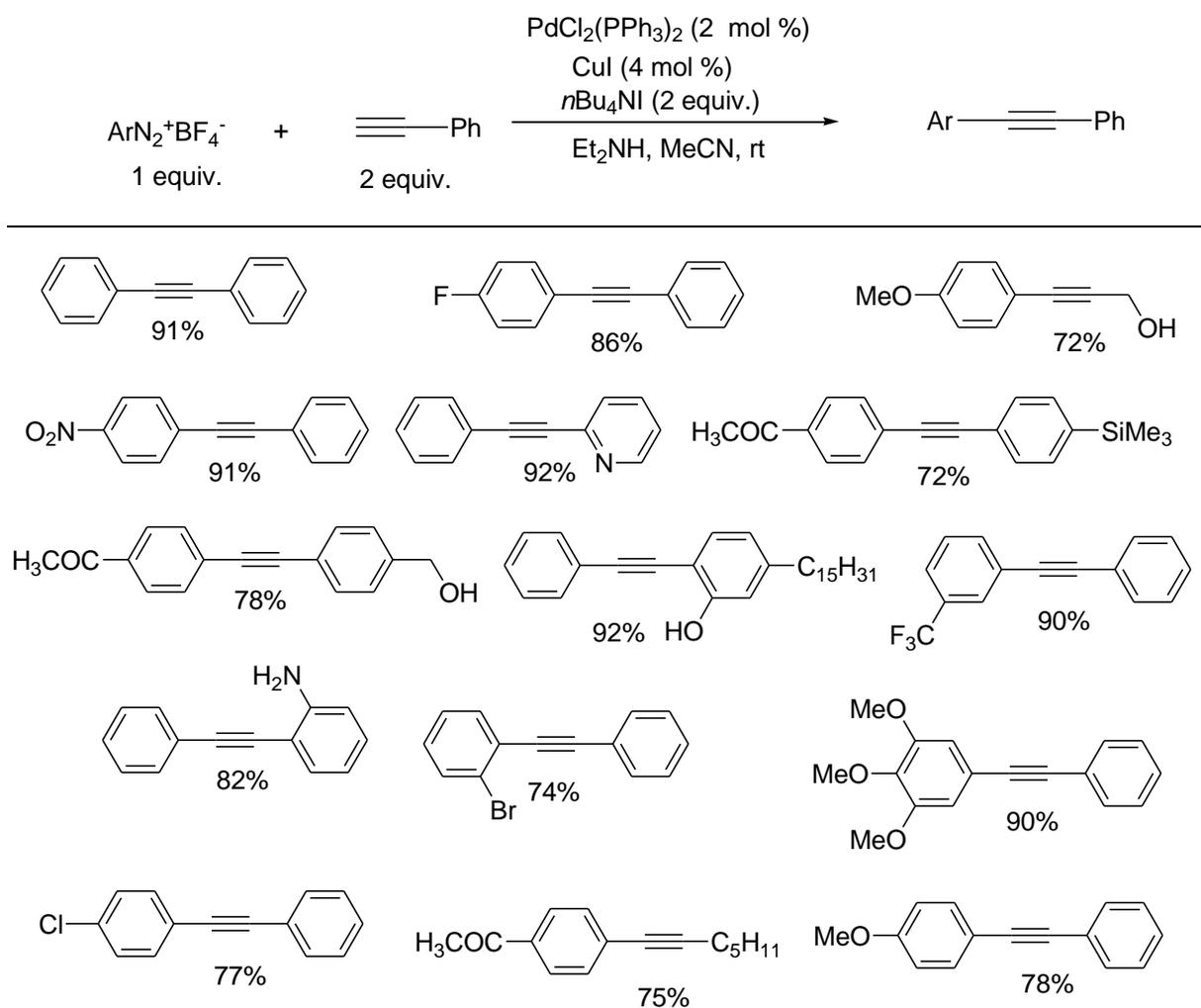
Scheme 5. Sonogashira coupling using preformed alkynylgold as the catalyst.

4. Developments

4.1. Cachhi and coworkers protocol for Sonogashira coupling of arenediazonium salts (2010)

After our pioneering work on Sonogashira coupling of arenediazonium salts, Cacchi et al.⁶⁰ reported the Sonogashira coupling of arenediazonium salts using classical catalytic systems, e.g. PdCl₂(PPh₃)₂, CuI, and

amine base (Et_2NH) in presence of two equivalents of iodide source ($n\text{Bu}_4\text{NI}$). Two equivalents of terminal acetylenes are required with respect to arenediazonium salts to obtain satisfactory yields. The method provides moderate to good yields of the coupled products. The one-pot diazonium salt preparation followed by Sonogashira coupling is possible in this protocol (Scheme 6). The mechanism for this alkynylation reaction, according to this group, involves the initial iododediazoni-ation of the arenediazonium salt, followed by the formation of a σ -aryl palladium iodide by oxidative addition, subsequent reaction of σ -aryl palladium iodide with copper acetylide that is formed in situ, and reductive elimination of the resultant σ -alkyne- σ -aryl palladium complex to give the cross-coupling product with the regeneration of active catalyst species.

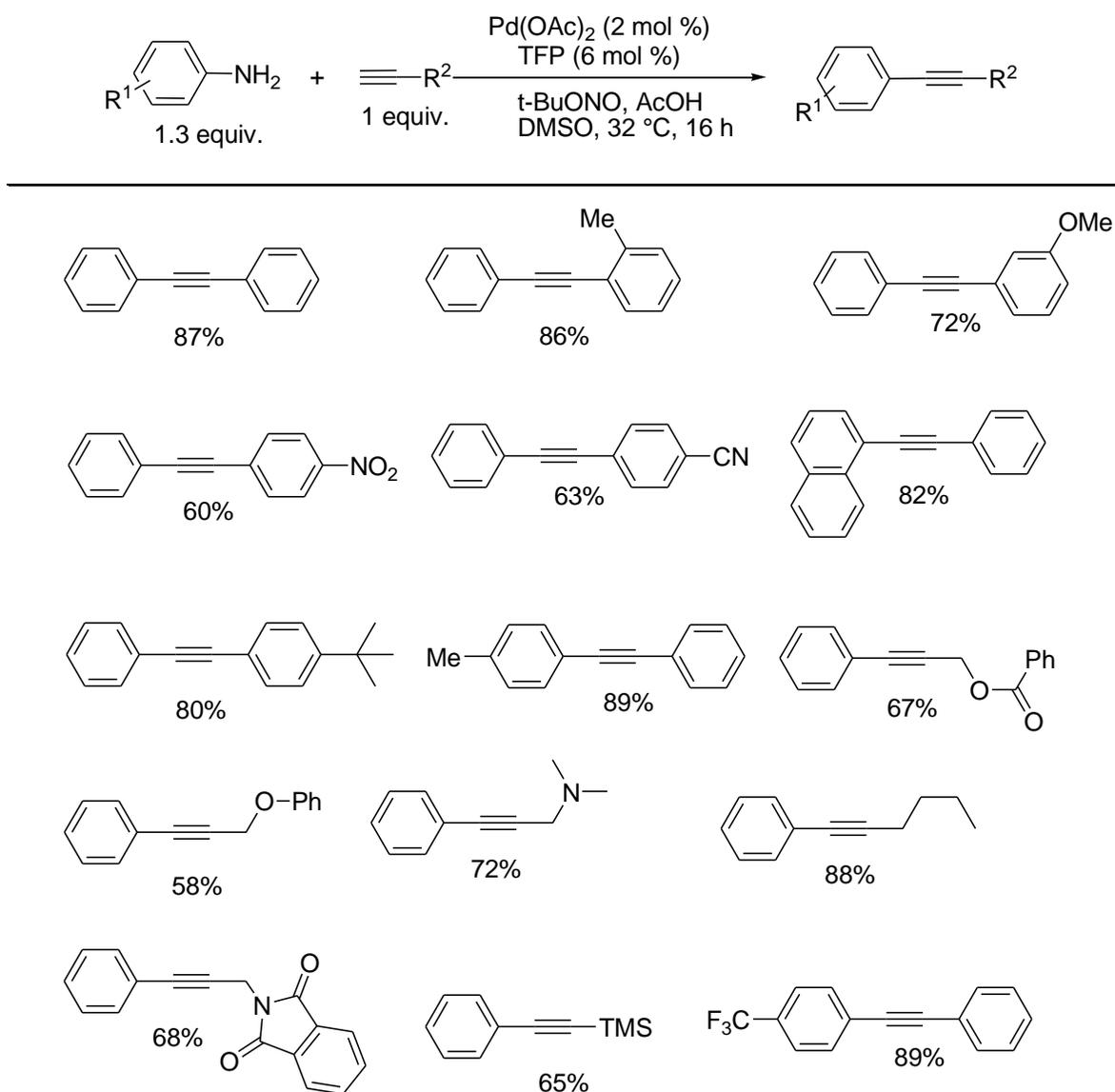


Scheme 6. One-pot iododediazoni-ation and Sonogashira coupling of arenediazonium salts.

In the true sense, this method is not an example of direct Sonogashira coupling of arenediazonium salts. In this method, the coupling reaction occurs in two stages: firstly aryl iodides are formed via iododediazoni-ation, and secondly regular Sonogashira coupling of generated aryl iodides gives the coupled products. Thus, it is an example of a domino iododediazoni-ation-Sonogashira cross-coupling sequence. This method suffers from several weaknesses, the reason to use aryl diazonium salts is to avoid the use of the more expensive aryl iodides. In this method, two equivalents of $n\text{Bu}_4\text{NI}$ are needed, and these are sometimes more costly than aryl iodides themselves. Additionally, this method will not be beneficial if the terminal acetylene is either difficult to make or expensive, since additional amount of acetylene is required to get success in this protocol.

4.2. Beller and coworkers protocol for Sonogashira coupling of arenediazonium salts (2011)

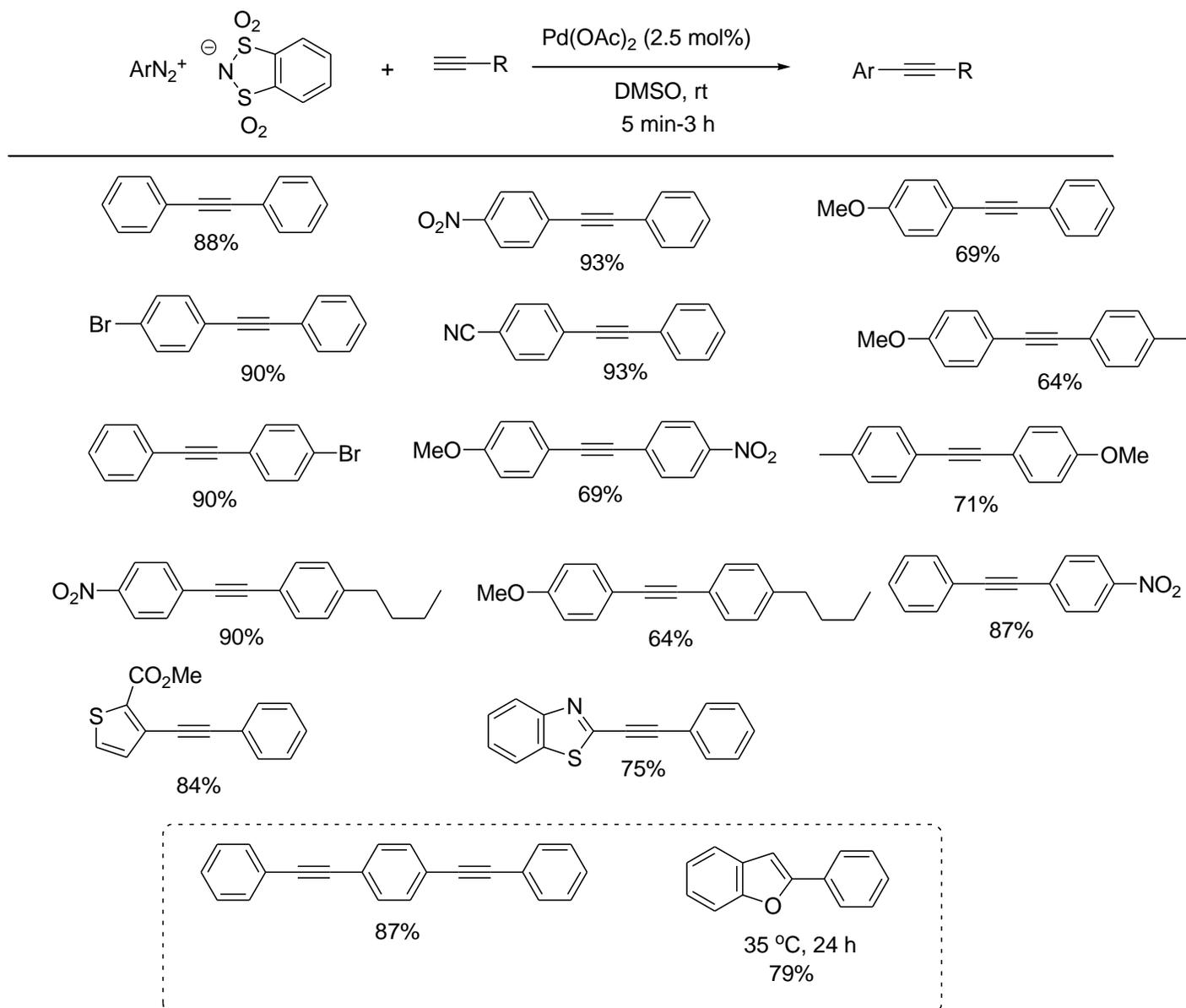
In 2011, Beller et al.'s reported a mild and expedient protocol for the Sonogashira coupling of in situ generated arenediazonium salts with alkynes to afford diverse arylated alkynes. This method is of course more direct and allows a general and convenient palladium-catalyzed Sonogashira coupling of arenediazonium salts to give the internal aryl alkynes in good yields (Scheme 7).⁶¹ In this method Pd(OAc)₂ is used as a catalyst and a tri-heteroarylphosphane, namely a tri(2-furyl)phosphane (TFP) as ligand. Both electron-donating substituents and electron-withdrawing groups in arenediazonium salts are tolerated in this method. Not only the arenediazonium salts, but a large number of aryl, alkyl, and trimethylsilyl acetylenes have also participated under this protocol. Base or co-catalyst was not required in this condition. Interestingly, thermally unstable propargyl alcohol derivatives such as phenyl propargyl ether, propargyl benzoate, etc were successfully coupled and provide the desired products in moderate to good yields. However, Sonogashira coupling of arenediazonium salts with alkynes bearing an *N,N*-dimethylanilino group, e.g. 4-ethynyl-*N,N*-dimethylaniline, which is well tolerated in Pd-Au dual catalytic condition,⁴⁰ is ineffective in this method.



Scheme 7. Palladium-catalyzed Sonogashira coupling of in situ generated arenediazonium salts.

4.3. Dughera and coworkers protocol for Sonogashira coupling of arenediazonium salts (2014)

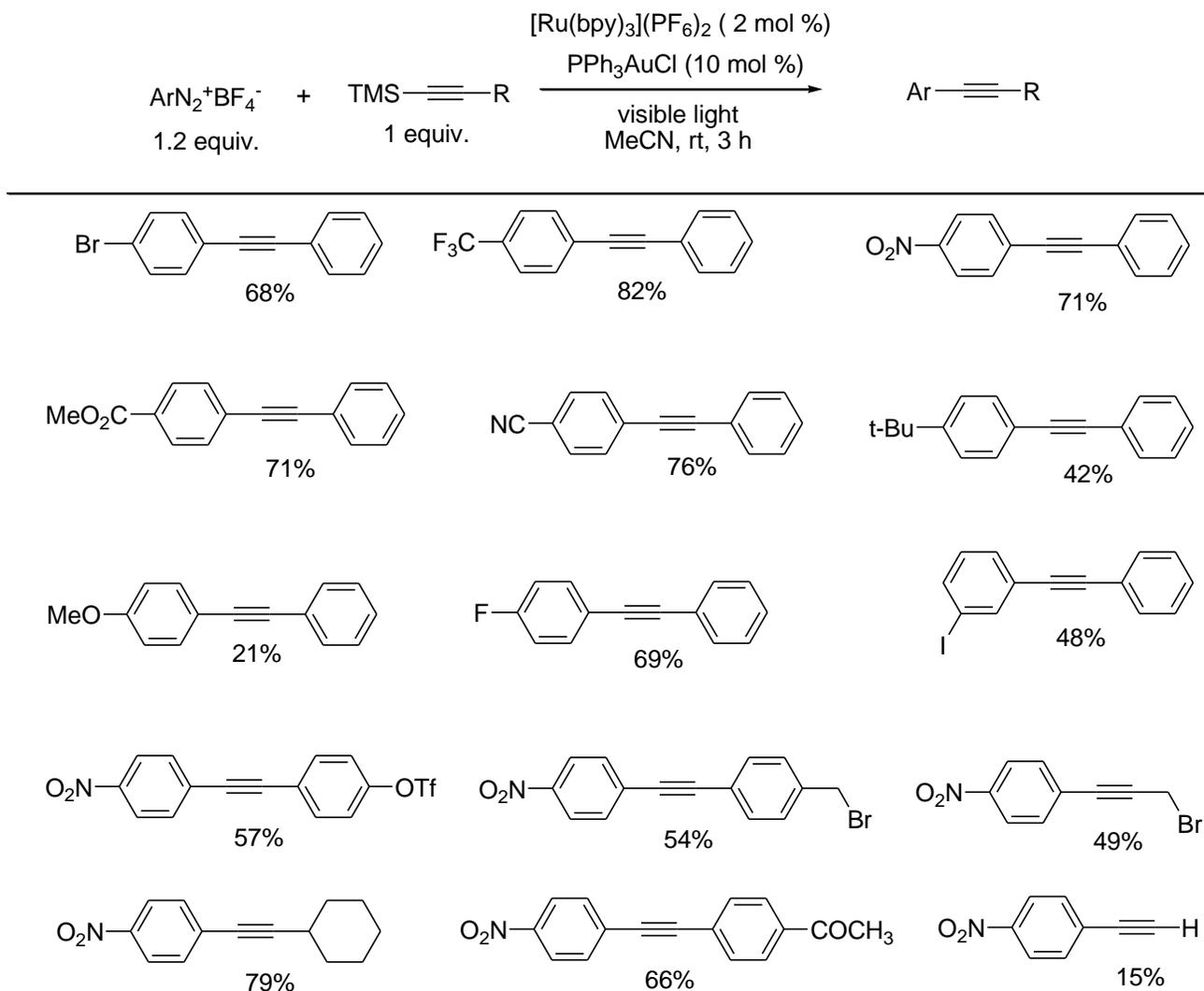
In 2014, Dughera and co-workers have reported a protocol for the palladium-catalyzed Sonogashira coupling of arenediazonium O-benzenedisulfonimides under copper and phosphane-free conditions (Scheme 8).⁶² Application of Arenediazonium O-benzenedisulfonimides which are easy to prepare and shows comparatively higher stability with respect to arenediazonium halides made this protocol more user-friendly. Notably, base, ligand, or co-catalyst was not required in this protocol. The high yield and cleanness of the reactions are the merits of this method. Mechanistic investigation shows that DMSO and the anion of O-benzenedisulfonimides play fundamental roles in the generation of actual Pd(0) catalyst. It also revealed that DMSO plays a vital role in the mechanistic cycle to increase the reactivity of alkyne. Aromatic rings containing two diazonium groups also participate in cross-coupling under these conditions. Benzene-1,4-bis(diazonium) O-benzenedisulfonimide coupled successfully in presence of two equivalents of phenylacetylene to afford the bis-alkyne product in good yield (shown in dashed box). Interestingly, coupling of 2-hydroxybenzene diazonium salt with phenylacetylene provides 2-phenylbenzofuran in satisfactory yield through the spontaneous cyclization of initially formed 1-(2-hydroxyphenyl)-2-phenylacetylene.



Scheme 8. Sonogashira coupling of arenediazonium o-benzenedisulfonimides.

4.4. Toste and coworkers protocol for Sonogashira coupling of arenediazonium salts (2016)

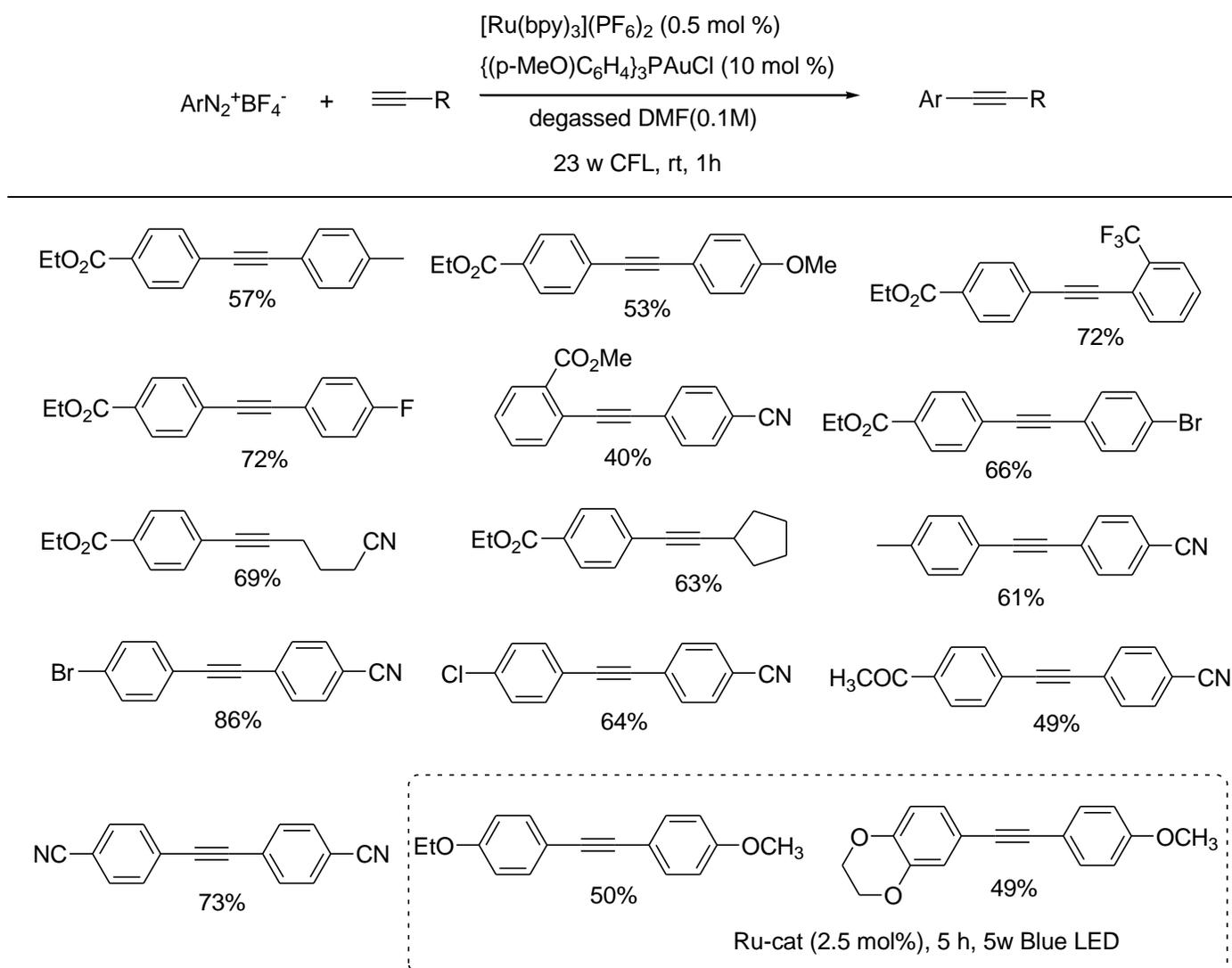
Alkynylation of arenediazonium tetrafluoroborates with alkynyl trimethyl silanes under dual photoredox and gold-catalyzed methods was described by Troste et al. in 2016 (Scheme 9).⁶³ Mechanistic insight revealed that the reaction undergoes in three steps, firstly; via visible light-mediated oxidative addition of arenediazonium salts. Then, gold-catalyzed transmetalation of alkynyl trimethyl silane through the generation of gold acetylide intermediate and lastly, reductive elimination of aryl-alkynyl complex to furnished the desired product. Notably, aryl halides that are susceptible to the Sonogashira coupling are well tolerated in this protocol which helps for further functionalization. Since the base is not required in this coupling procedure, alkynylation can be feasible for the arenediazonium salts containing base-sensitive functional groups. Interestingly, both tetrafluoroborate and tosylate diazonium salts were found to be effective coupling partners compared to hexafluorophosphate salts and the latter provide the desired product with low yield. Furthermore, just a trace amount of the coupling product was isolated when terminal alkyne was used instead of alkynyltrimethylsilanes. These findings show that transmetalation from the organosilane is crucial for the present coupling reaction for high efficiency. After the completion of reaction, the presence of stoichiometric amounts of trimethylsilyl fluoride were detected in the reaction mixture by analyzing ¹H NMR spectra of crude product. Mild experimental conditions and high functional group toleration, as well as high yields of the coupled products, are the merits of this method.



Scheme 9. Alkynylation of arenediazonium salts with alkynyl trimethyl silanes.

4.5. Glorius and coworkers protocol for Sonogashira coupling of arenediazonium salts (2016)

Glorius and co-workers have reported an efficient method for the arylation of terminal alkynes employing arenediazonium salts under a dual gold/photo redox catalytic system (Scheme10).⁶⁴ Both electronically and structurally diverse aryl alkynes were synthesized using aryl or alkyl acetylenes under mild, base-free reaction conditions using visible light from a household light bulb or in presence of sunlight. Large substrate scope, room temperature reaction, high functional group toleration are the merits of this protocol. Since halogenated substrates are well tolerated, this protocol may be beneficial in the design of cross-coupling sequences. Interestingly, Au(I)/Au(III) redox cycles were employed without using external oxidants in this strategy.

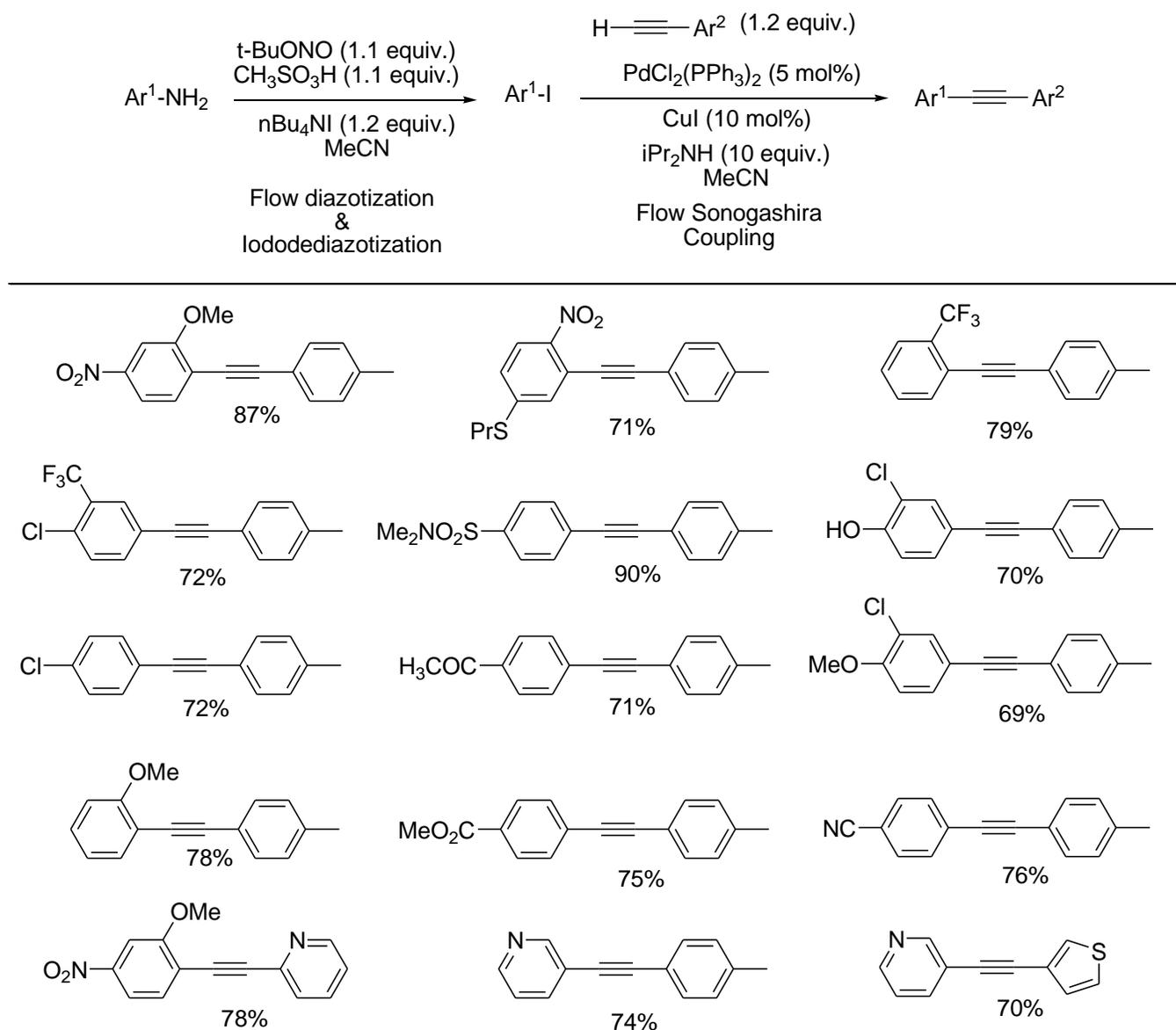


Scheme 10. Alkynylation of arenediazonium salts using gold/photo redox catalytic system.

4.6. Organ and coworkers protocol for Sonogashira coupling of arenediazonium salts (2016)

Organ and coworkers have outlined a flow process for the conversion of a wide range of commercially available aryl amines into biarylacetylene compounds in high yield (Scheme11).⁶⁵ It follows the sequential diazotization, Sandmeyer reaction, and Sonogashira coupling strategy to furnish the coupled products. This process offered a high-yielding, versatile method for the conversion of cheap anilines into valuable internal aryl alkynes. They have also developed software to control the flow of the aryl iodide segment to the cross-

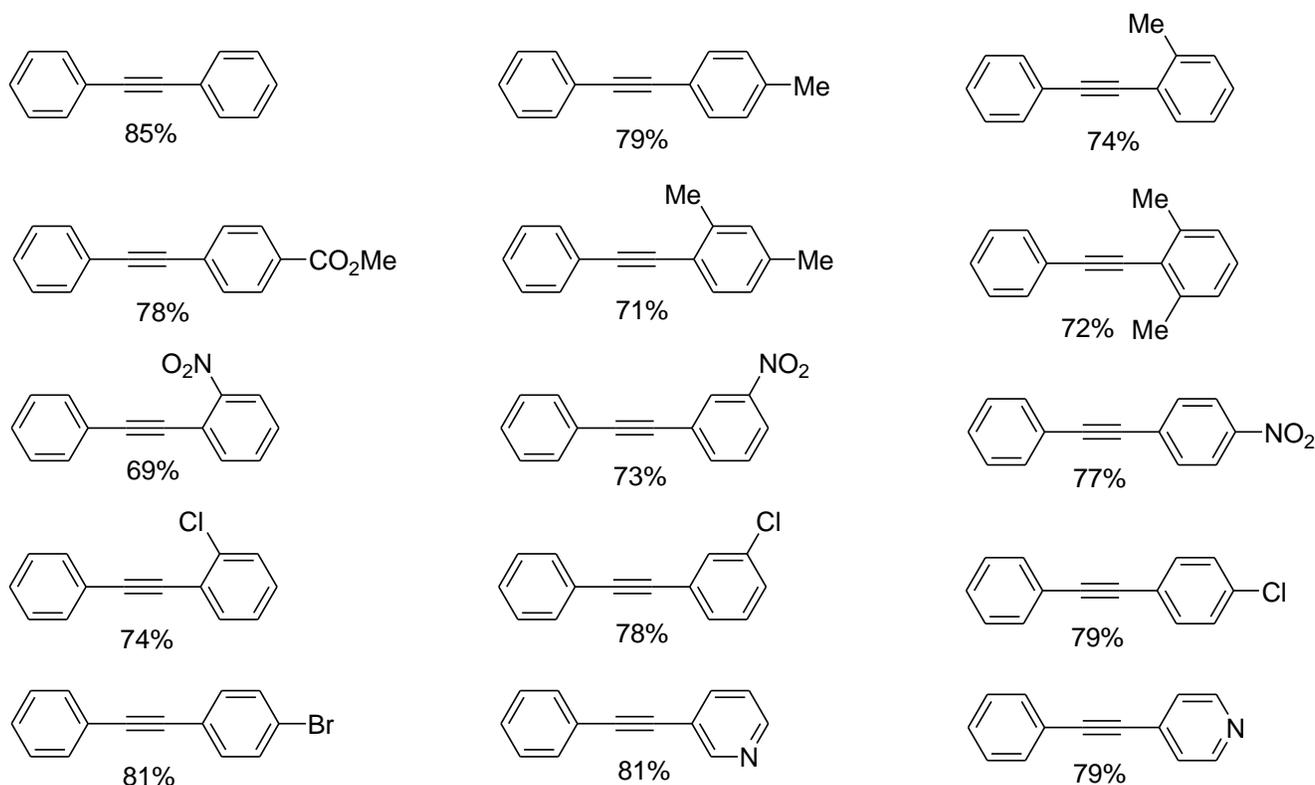
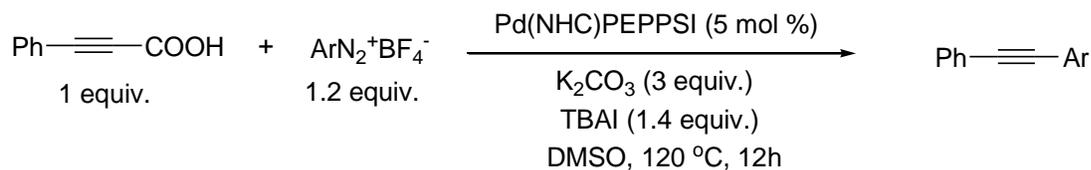
coupling reactors with the help of an automated continuous-flow unit which was controllable by that software.



Scheme 11. Sonogashira coupling under flow conditions.

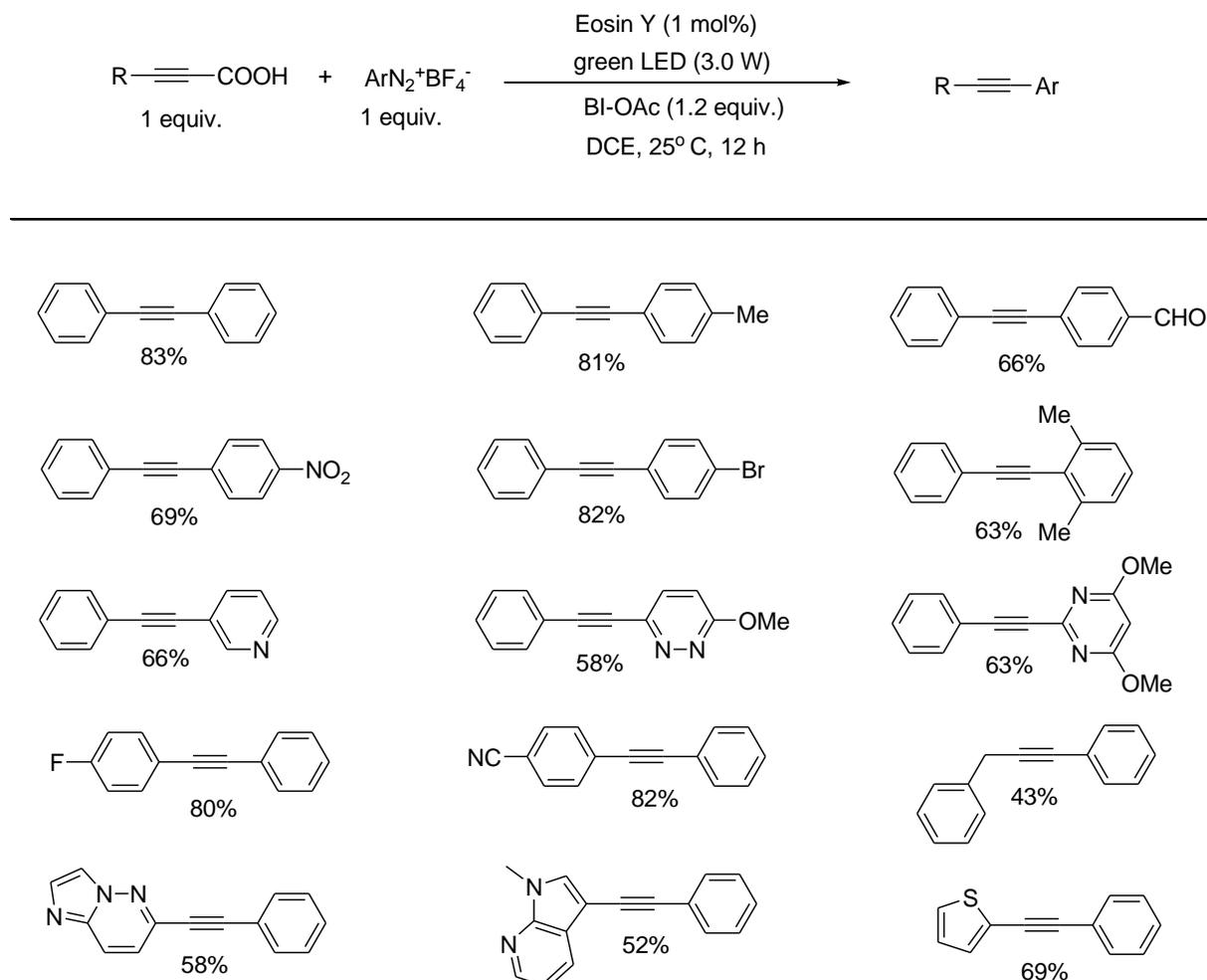
4.7. Nagarkar and coworkers protocol for Sonogashira coupling of arenediazonium salts (2017)

In 2017, Nagarkar and co-workers described an effective N-heterocyclic carbene-based Pd complex catalyzed decarboxylative Sonogashira coupling reactions with diazonium salts in ligand and co-catalyst free conditions (Scheme 12).⁶⁶ The Pd(NHC)PEPSI is a pre-catalyst that is not only air and moisture stable, but also efficiently catalyzes the alkynylation reaction at lower loading. Different aryl and heteroaryl diazonium salts perform sp^2 - sp cross-coupling reactions with alkynyl carboxylic acid to offer moderate to good yields of various internal acetylenes. This methodology was successfully used to Sonogashira coupling of heteroaryl diazonium salts of 4-amino pyridine, 3-amino pyridine, and benzo[*d*]thiazol-2-amine with phenyl propiolic acid to produce heteroaryl-substituted acetylene products in high yields. Thus diazonium salt serve as an effective, easily accessible, and economical aryl surrogates over traditional aryl halides and triflates.



Scheme 12. Decarboxylative Sonogashira coupling of arenediazonium salts.

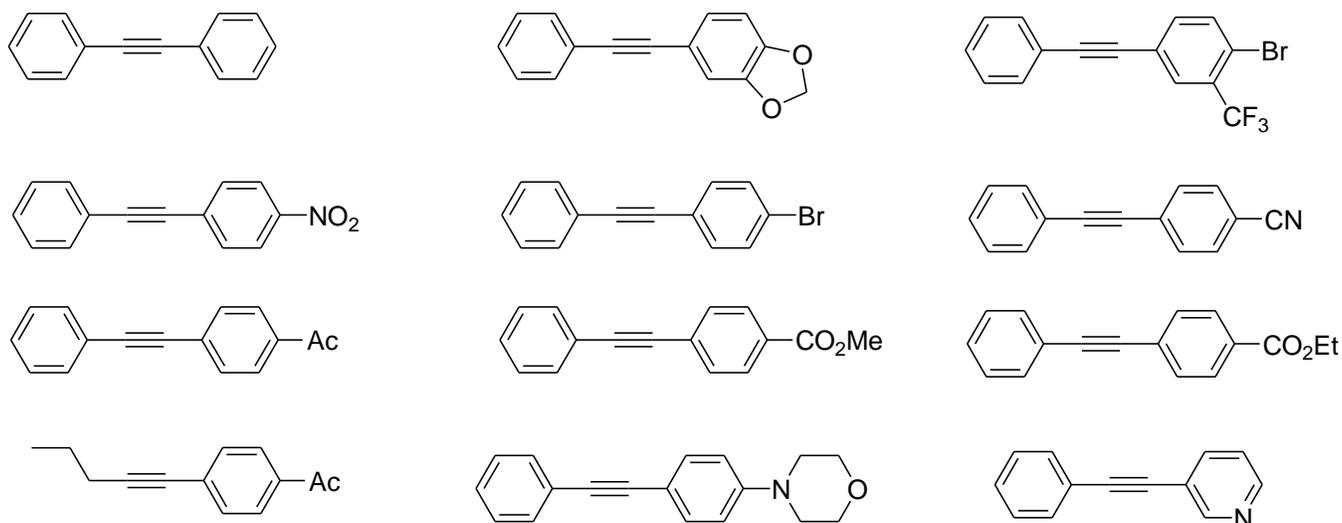
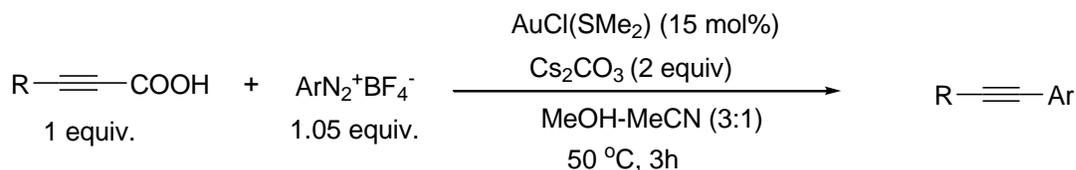
The authors also reported the synthesis of symmetrical alkynes using propiolic acid as an alkyne source under newly optimized conditions (Scheme 13). They used organic base DBU in DMSO instead of inorganic bases K_2CO_3 or Cs_2CO_3 at 90 °C. In contrast to asymmetrical coupling, the electronic effect played a more important role in symmetrical coupling than steric hindrance, since diazonium salts containing electron-donating substituents such as 2-methyl, 2,6-di-methyl, and 4-methyl easily undergo coupling reaction and provide the desired products in excellent yield. Likewise, diazonium salts containing mild electron-withdrawing substituents (halides) also gave the coupling product in good yield. On the other hand, the coupling reaction of arenediazonium salts containing electron-withdrawing functional groups (2-nitro, 4-nitro) and heteroaryl diazonium salts were found to be unsuccessful under this experimental conditions.



Scheme 14. Visible light-catalyzed decarboxylative alkylation of arenediazonium salts.

4.9. Chi and coworkers protocol for Sonogashira coupling of arenediazonium salts (2020)

In 2020, Abrams and Chi accidentally discovered a decarboxylative Sonogashira coupling of isolated arenediazonium tetrafluoroborate salts with alkynyl carboxylic acid in presence of the gold(I) catalyst $\text{AuCl}(\text{Me}_2\text{S})$ and base Cs_2CO_3 under mild conditions (Scheme 15).⁶⁸ The reaction affords highly functionalized diaryl alkynes in low yield from various structurally diverse arene diazonium salts. Authors did not reported the actual isolated yields of each final product instead of a general yield 25-30%. Although these reactions are not much sensitive to electronic nature of function groups present in arene diazonium salts, but lower rate of reaction was observed in case of coupling of sterically hindered ortho-substituted diazonium salts with alkynoic acids. Since the reaction yielded several by-products among them two major by-products are hydrodediazonation and Ullmann coupling product. They have prilimarily proposed that the reaction proceed through a radical pathway via the generation of arene radical.

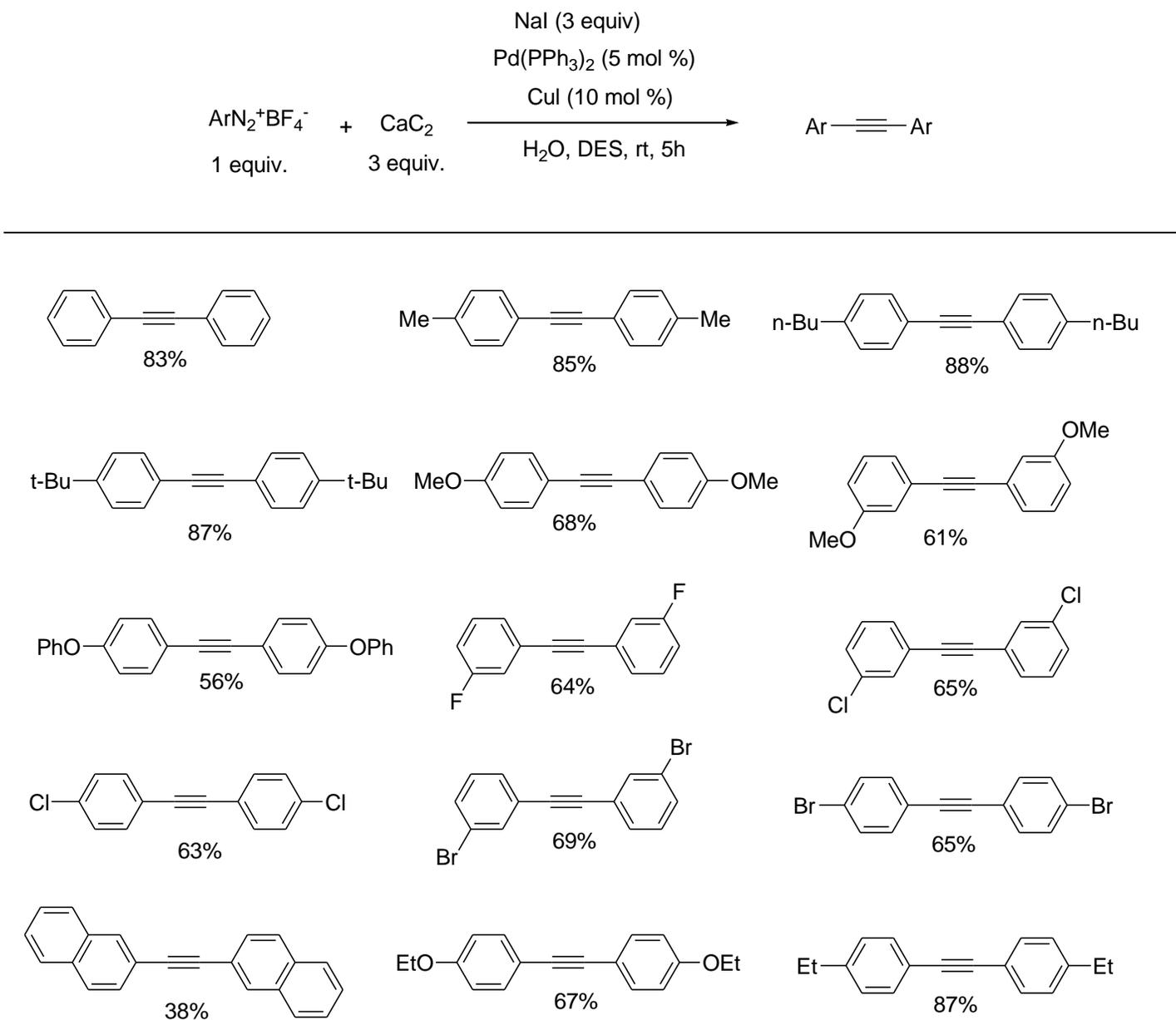


N.B. All yields were consistent in nature and ranged from 25 to 30% .

Scheme 15. Gold(I)-catalyzed alkylation of arenediazonium salts with alkynoic Acids

4.10. Li and coworkers protocol for Sonogashira coupling of arenediazonium salts (2021)

In 2021, Li et al. reported an effective process for the Sonogashira coupling of aryl diazonium salts through domino iododediazotiation-Sonogashira coupling strategy (Scheme 16). In their method calcium carbide was used as a source of acetylene and the reaction was performed in a deep eutectic solvent (DES).⁶⁹ Mixture of choline chloride and urea in 1:2 ratio was used as DES here. Electronically and structurally diverse diarylethyne were synthesized at ambient temperature with good yields. This method has several benefits such as the use of calcium carbide as cheap and convenient to handle alkyne sources and the solvent used that is non-toxic, non-volatile, and reusable, mild and open-air reaction conditions, and an easy work-up procedure. This method is useful for the gram-scale synthesis of diaryl acetylenes. This approach offers a strong alternative to access diarylacetylenes, and will broaden the scope of uses of calcium carbide in organic synthesis.



Scheme 16. Alkynylation of arenediazonium salts by using CaC_2 as an alkyne source

5. Conclusions

In conclusion, the details about the discovery of Sonogashira coupling of arenediazonium salts and the developments of various protocols were described briefly in this mini-review. To get a deep insight into the reaction path of all the methods, considerable discussion on the mechanism of each reaction was included. The strengths and weaknesses of each protocol were thoroughly highlighted in this article. It can be expected that the chemistry involving in situ formation of diazonium salts from anilines and its application as cheap, environment friendly, and secure alternative to aryl halides for the construction of carbon-carbon as well as carbon-heteroatom bonds will continue to attract the attention of synthetic chemists in the coming years. Although the cross-dehydrogenative coupling (CDC),⁷⁰⁻⁷² cross-coupling hydrogen evolution reaction (CCHER),⁷³⁻⁷⁶ and electrochemical oxidative cross-coupling⁷⁷⁻⁸¹ reactions are growing strategies for direct C-H

alkynylation, application of diazonium salts for Sonogashira coupling provides a good alternative for the easy and user-friendly synthesis of diarylacetylenes.

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Author's Biographie



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