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DEVELOPMENT OF THE REACTION CONDITIONS OF A SUZUKI-MIYAURA CROSS COUPLING REACTION CATALYSED BY Ag-Pd ALLOY NANOPARTICLE PHOTOCATALYST

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Abstract

To increase product yield, percentage conversion, and catalyst recovery ease, the reaction parameters required for a successful Suzuki Miyaura cross-coupling process were optimized. To form new carbon-carbon bonds, 3-Indotoluene and Phenylboronic acid were cross-coupled using synthesized Ag-Pd Alloy Nanoparticle photocatalysts. Reaction conditions namely reaction base, solvent, wavelength, light intensity and reaction atmosphere were individually optimized by comparative analysis to find out the best set of parameters that will result in a cross-coupling product with high yield and high percentage conversion. Mix solvent of Dimethylformamide and water in the ratio of 3:1 was determined as the best solvent for the cross-coupling carried out in this research as a percentage conversion of 96% was achieved. Potassium carbonate (K_2CO_3) was the reaction base that gave better reaction yield and percentage conversion than the other bases that were tested in this research, also Argon as the reaction atmosphere gave better results than another reaction environment, while light intensity and light sources with shorter wavelength (less than 500nm) are favorable as the gave better percentage conversion, due to their ability in activating the Alloy Nano-particle Photo-catalysts that was used in this research. Findings from this research work suggest that for an effective and efficient Suzuki-Miyaura cross-coupling reaction, K_2CO_3, Dimethylformamide and water in the ratio of 3:1, argon, and a light source with high intensity and shorter wavelength are the appropriate reaction conditions.

1.0 INTRODUCTION

When two different molecular entities are brought together by the production of a new carbon-carbon or carbon-heteroatom bond, the process is known as a cross-coupling reaction [1, 2, 3]. Palladium, nickel, or copper are examples of transition metal catalysts that are frequently used in these reactions to help couple organic substrates [1, 2, 4]. Because they make complex compounds that would have been challenging to manufacture, cross-coupling reactions have emerged as a crucial technique in organic synthesis [3, 5].

The Suzuki-Miyaura coupling, so named after its creators, Akira Suzuki and Ei-Ichi Miyaura, is a well-known cross-coupling reaction [5,6,7]. In this reaction, an organic halide and an organo-boron molecule combine with a palladium catalyst to produce a biaryl compound [2,3,6,7].

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This newly formed biaryl compound came about as a result of the coupling of a carbon atom from the organo-boron and another carbon atom from the organic halide. The synthesis of medicines, agrochemicals, and various organic reagents is accomplished through the widespread usage of this reaction in both academia and industry [6,8,9,10]. The Heck reaction is a noteworthy example of a cross-coupling reaction. It was identified by Richard F. Heck, Ei-ichi Negishi, and Akira Suzuki. It entails coupling an alkene and an aryl or vinyl halide in the presence of a palladium catalyst [1, 2, 5]. The selective and regulated formation of carbon-carbon bonds is facilitated by the Heck reaction [1, 3]. In a similar vein, cross-coupling reactions also include vinylation and arylation processes such as the Stille and Sonogashira couplings [8,11]. In these reactions, an organic halide is coupled with an organotin or organosilicon molecule to create vinyl or aryl compounds, respectively [1,3,4]. The Buchwald-Hartwig amination is a notable instance of cross-coupling in which a palladium catalyst is used to couple an amine with an aryl halide. The production of medications and other chemicals containing nitrogen has made considerable use of this reaction [3,4]. The oxidative addition of an aryl hydroxide to a palladium complex Pd(0) initiates the general mechanism of the palladium-catalyzed Suzuki Miyaura cross-coupling reaction, forming an intermediate Aryl-palladium (II). Subsequently, the generated Biaryl-palladium complex undergoes a rapid reductive elimination after trans-metalation with a boronic acid. The formation of the Biaryl (coupling product) and the regeneration of the palladium Pd(0) complex are the outcomes of the reductive elimination [1,2,4,5,6]. An illustration of the mechanism is shown in Figure 1.

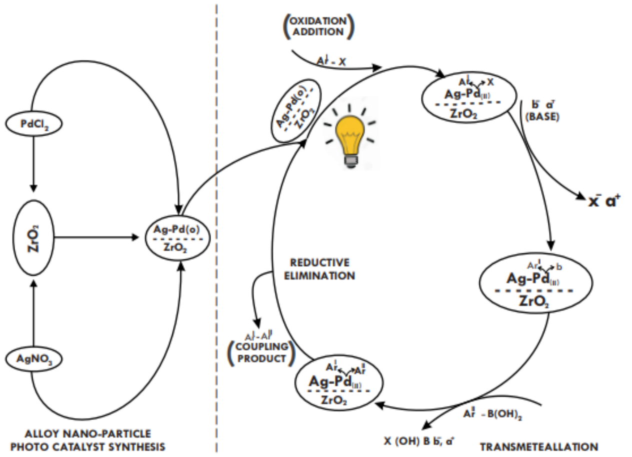

Figure 1: Cycle for a Suzuki-Miyaura cross coupling reaction

A cross-coupling reaction needs to meet several requirements to be successful [2,12]. These requirements are essentially the same for all cross-coupling reactions, with the only real variations being in the type of substrate or the precise coupling that needs to be done [12,13, 14]. For a Suzuki-Miyaura cross-coupling reaction, the reaction condition includes the catalysts system, base, reaction solvent, reaction atmosphere, and temperature [1,7]. Since the Suzuki-Miyaura reaction normally involves an Organo-halides and an organometallic compound (both as substrate) with a catalysts system, the other reaction conditions namely reaction base, reaction solvent, reaction atmosphere and temperature can be optimized to achieve increased reaction yield, high percentage conversion or ease of removing the catalysts from the coupling product [1,7,15,16].

Ag–Pd alloy nanoparticle photocatalysts offer significant advantages over conventional catalyst systems in Suzuki–Miyaura cross-coupling reactions due to their enhanced catalytic efficiency and stability [7]. The incorporation of silver into the palladium nanoparticle structure leads to a synergistic electronic interaction that modifies the d-band structure of palladium, facilitating more efficient oxidative addition and reductive elimination steps, which are crucial for the cross-coupling reaction [3.7]. This synergy results in higher turnover frequencies and improved reaction rates compared to catalysts based on pure Pd or traditional homogeneous systems. Additionally, the alloying helps control the size and dispersion of the nanoparticles, increasing the surface area and availability of active sites, thereby further enhancing catalytic performance [7]. Beyond catalytic efficiency, Ag–Pd alloy nanoparticles are more stable and cost-effective [2;5;6]. The presence of silver reduces the tendency of palladium to aggregate or leach during reactions, leading to improved durability and reusability of the catalyst over multiple cycles [7]. Since palladium is an expensive metal, partially substituting it with silver lowers the overall material cost without sacrificing performance [7]. Furthermore, their heterogeneous nature allows for easy separation from reaction mixtures, making them more practical for industrial applications. The Ag–Pd alloy system also demonstrates better tolerance to a wide range of functional groups and reaction conditions, including operation in aqueous or mild environments, which broadens the substrate scope and makes the process more environmentally friendly [1,3,5,6].

The development (optimization) of the reaction condition is done to achieve several objectives, one of them is an increased yield, the primary goal of optimization is often to maximize the yield of the desired product [3]. Fine-tuning reaction conditions can result in a higher conversion of starting materials to the desired coupling product [3,16,17]. Improved Selectivity is another reason for Optimization, optimization can enhance the selectivity of the reaction, reducing the formation of undesired by-products or side reactions [3]. This is crucial for obtaining a purer final product [1,17]. Optimized conditions may expand the range of substrates that can participate in the Suzuki coupling [12,18]. This is particularly important for the applicability of the reaction to a variety of organic compounds [12]. Efficient optimization may allow for the reduction of the amount of expensive catalyst required for the reaction, leading to cost savings without compromising the efficiency of the process [1,2,20,21]. Optimization can accelerate the reaction rate, reducing the overall reaction time [22,27,30]. This can increase process efficiency overall and is advantageous for practical concerns in large-scale synthesis. Additional advantages of optimization include reduced adverse effects, the viability of scaling up, operational safety, cost-effectiveness, and repeatability [1,2,3,4,14,18,19,20,22, 23]. As a result, the Suzuki-Miyaura cross-coupling reaction conditions are optimized to increase efficiency, selectivity, and applicability, which makes the procedure more useful and affordable for a range of synthetic applications.

2.0 EXPERIMENTAL SECTION

2.1 Materials

Reagents of analytical standard namely, AgNO3, PdCl2, ZrO2, NaHB4, HCl, K2C03, KOH, DMF, Na3P04, NaF, DMSO, NaOH, KI, Na2CO3, aqueous lysine, 3-Iodotoluene, Phenylboronic acid and Ethanol were used in this research and were all obtained from Merck.

2.2 Methodology

Alloy Nanoparticle photocatalyst was synthesized in this work, for use as the catalyst system for the Suzuki-Miyaura coupling between Phenylboronic acid and Iodotoluene. Subsequently, the Factors necessary for an efficient Suzuki-Miyaura cross-coupling of Phenylboronic acid and 3-Indotoluene (with the synthesized Nano particle photocatalysts as the catalysts system) were optimized. These factors include the Reaction solvent, the reaction environment (atmosphere), the base, light intensity and wavelength. Each factor was individually optimized with the view of looking for the perfect type or condition that would result in a greater percentage conversion and yield.

2.3 Synthesis of the Ag-Pd Alloy Nanoparticle Photocatalysts

The Nano-particle photo-catalysts were synthesized from AgNO3 and PdCl2 solutions. 31ml of 0.02M of AgNO3 and 56.3ml of 0.02M PdCl2 aqueous solution were mixed in a 250ml beaker, thereafter 4g of ZrO2 powder was added into the same beaker while stirring magnetically. 40ml aqueous lysine of 1M was added with vigorous stirring for 30 minutes. After 30 minutes of vigorous stirring, 20ml, 0.65M of NaHB4 was added in a dropwise manner for 25 minutes followed by 20ml, 0.6M HCl. After the combination was let to stand for a full day, the solid was separated by centrifugation, cleaned with ethanol and water, and then allowed to dry at 60 degrees Celsius. Now, the dehydrated solid served as the alloy's catalyst.

2.4 Characterization of the Ag-Pd Alloy Nanoparticle Photocatalysts

The synthesized Ag-Pd alloy nanoparticle photocatalysts were characterized for uniformity via TEM, surface area using the BET method, light absorptivity using UV-VIS spectrometry, and elemental compositions via ICP-OES.

2.5 Development of Reaction Conditions

To perform the Suzuki-Miyaura cross-coupling of 3-iodotoulene with phenylboronic acid, Ag-Pd Alloy Nano-particle Photocatalysts were synthesized. Each reaction condition necessary for a successful coupling was optimized individually to determine the best (type/condition) that will give optimum reaction yield. Mixing 1 mmol of 3-iodotoluene, 1.5 mmol of phenylboronic acid, and 50 mg of the alloy nanoparticle photo-catalysts in a 25 ml round-bottom flask is the first step in the general cross-coupling process. In addition, the base and the preferred solvent were added to the flask. After magnetic swirling and sealing the flask with a rubber septum lid, it was placed inside a chamber. The chamber was then irradiated with LED floodlights under the environment of choice. The reaction chamber was maintained at 300C using an air conditioner system during the 6-hour reaction time for each reaction. To get rid of the catalysts, 2-milliliter aliquots were collected after 6 hours, centrifuged, and filtered using a Millipore filter (0.45um). For product composition analysis, the filtrates were examined.

3.0 RESULTS AND DISCUSSION

This section of the research shows the results obtained on the characterization of the synthesized Ag-Pd Alloy nanoparticle photocatalysts and the optimization of reaction conditions. The reaction base, reaction atmosphere, solvent, light wavelength and intensity were individually optimized with the view of finding the best condition for the Suzuki-Miyaura cross-coupling reaction carried out in this research.

3.1 Characterization of the Synthesised Ag-Pd Alloy Nanoparticle Photocatalysts

The transmission electron microscope image of the synthesized nanoparticles photocatalysts as indicated in Figure 2 shows that the Ag-Pd metals are uniformly distributed on the zirconium oxide support with an average diameter of less than 8 nm. The images show a neat crystallographic arrangement of the Ag-Pd metals on the surface of the catalyst support, this means that the catalyst will have numerous active sites for reactions and all the surface area of the catalysts can be used for reaction. The inductively coupled plasma optical emission spectroscopy (ICP-OES) result further gives credence to the type and amount of metal present in the nanoparticle photocatalysts, from the results obtained show that the elemental composition of Ag and Pd in the alloy is 2710.22 ppb and 3160.20 ppb respectively. The value obtained for the BET surface area of the alloy nanoparticles photocatalyst (reported in m2g -1) is very similar to that of the pure ZrO2 which was found to be 11.10m2g-1 indicating that, loading of the silver, palladium or a mixture of both metals on the ZrO2 support base does not have a significant effect on the surface area of the ZrO2. One of the great advantages nanoparticles have when being used as a catalyst is their large surface area [2,4,78], the surface area of the catalysts synthesized in this research is quite large, hence providing enough site for catalytic activities.

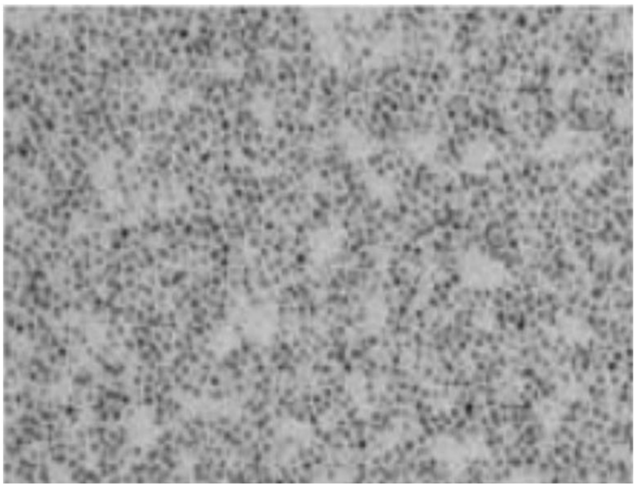

Figure 2: TEM image of alloy nanoparticle photocatalyst with a particle diameter of 8nm

3.2 Reaction Solvent

In the Suzuki cross-coupling process between phenyl-boronic acid and 3-iodotoluene, several solvents (including proptic and aprotic) were employed as the reaction solvents in an attempt to identify the solvent or solvent mixture that yields a high percentage conversion and stable coupling product. For every different solvent that was used, other reaction conditions were kept constant.

Table 1: Different solvent/solvent mixture used and their corresponding percentage conversion

S/N	Base	Reaction Solvent	Reaction Environment	% Conversion
1	$K_2 C0_3$	DMF	Ar	19
2	$K_2 C0_3$	DMSO	Ar	27
3	$K_2 C0_3$	ETHANOL	Ar	48
4	$K_2 C0_3$	DMF: H_2O (3:1)	Ar	96
5	$K_2 C0_3$	ETHANOL: H_2O (1:1)	Ar	73
6	$K_2 C0_3$	DMSO: H_2O (3:1)	Ar	82

Table 1 shows the different solvent/solvent mixtures used and the corresponding percentage conversion that was obtained. N-dimethylformamide (DMF) and Dimethysuifoxide (DMSO) which are all polar aprotic solvents gave a poor percentage conversion hence low yield of coupling products. While a mixture of the polar aprotic solvent DMF and water in the ratio of 3:1 gave an excellent yield of about 96% conversion. Another mix of solvents like ethanol and water (ratio 1:1), DMSO and water (ratio 3:1) gave relatively good percentage conversion and stable coupling product. Interestingly when the polar protic solvent ethanol was used alone it gave a decent percentage conversion value which was higher than the polar aprotic DMF AND DMSO but lower than the mix solvent of DMF: Water and Ethanol: Water. The effectiveness of the mixed solvent that involves water, for example, DMF: Water to drive the Suzuki cross-coupling reactions is due to the propensity of the reactants and bases to dissolve faster in water, hence a higher rate of reaction in the aqueous medium leading to a greater percentage conversion and higher yield of the coupling products [12, 27 30]. This higher rate of reaction in the aqueous medium results in a greater percentage conversion and higher yield of the coupling products. As a result, it was discovered that the optimal solvent to drive the Suzuki cross-coupling reaction involving the synthesized alloy nanoparticle photo-catalyst utilized in this work was a 3:1 mixture of DMF and water.

3.3 Reaction Base

The Suzuki cross-coupling reaction can be achieved with a variety of bases [7,13,23,31,32], as Table 2 illustrates. The goal of this section of the research was to determine which base would function best in the Suzuki cross-coupling reaction that was conducted in this paper.

The result as shown in Table 2 reveals that K2CO3 when used alongside Dimethylformamide (DMF) and

Water in a ratio of 3:1 gives an excellent yield of 96% conversion. KI and NaF which are weak bases showed poor activity (4% and 6% percentage conversion) and selection problems were encountered when used for cross-coupling reaction in an identical condition as that involving K2CO3 as the reaction base. Table 2 also shows that Na3PO4 gave a good activity for the coupling reaction with 85% percentage conversion, while the application of Na2CO3 as the coupling base gave a fairly good result. Apart from good values obtained for percentage conversion of reactants to product when potassium carbonate is used as the base for the reaction, the subsequent high degree of stability of the cross-coupling product, high purity of the product and zero homo-coupling product are other advantages of potassium carbonate offers when been use as base for the Suzuki-Miyaura cross-coupling reaction [20.26.35].

Table 2: Different base and their respective percentage conversion

S/N	Reaction Solvent	Reaction Environment	Base	% Conversion
1	DMF: H_2O (3:1)	Ar	K_2CO_3	96
2	DMF: H_2O (3:1)	Ar	KI	4
3	DMF: H_2O (3:1)	Ar	Na_2CO_3	83
4	DMF: H_2O (3:1)	Ar	NaOH	71
5	DMF: H_2O (3:1)	Ar	KOH	84
6	DMF: H_2O (3:1)	Ar	NaF	6
7	DMF: H_2O (3:1)	Ar	Na_3P0_4	85

3.4 Reaction Atmosphere

As Table 3 illustrates, the environment in which a Suzuki cross-coupling reaction occurs affects both the yield and the percentage conversion [7,23,26,34, 35]. A higher percentage conversion was obtained when the reaction occurred in an inert gas environment like Argon, precisely 96% conversion was obtained. Among the three different environments in which the Suzuki cross-coupling reaction was carried out in this work, the oxygen environment shows the least promise with less than 30% percent conversion and an excessive amount of homo-coupling product was detected on analysis of the product using GC-MS, while the natural Air atmosphere gave a better percentage conversion (46%) than oxygen, but less than the inert gas. Therefore, it can be deduced from the evidence in this work that an inert environment promotes the Suzuki cross-coupling reaction when Ag-Pd nanoparticle photocatalysts are being used. The reaction atmosphere can significantly affect the mechanism of a Suzuki–Miyaura cross-coupling reaction because the presence or absence of oxygen or other reactive gases can influence the oxidation state and stability of the palladium catalyst, which is central to the catalytic cycle. In an inert atmosphere (such as argon), the palladium species remain in their active zero or +2 oxidation states, facilitating smooth oxidative addition, transmetalation, and reductive elimination steps. However, in the presence of oxygen or moisture from air, the palladium catalyst can be oxidized to higher, less active oxidation states or form palladium oxides or hydroxides, which disrupt the catalytic cycle and reduce the overall efficiency of the reaction. Thus, controlling the atmosphere ensures the catalyst remains in its most active form and prevents side reactions or catalyst deactivation.

Table 3: Different reaction environment and the percentage conversion obtained

S/N	Base	Reaction Environment	Reaction Solvent	% Conversion
1	$K_2 C0_3$	Ar	DMF: H_2O (3:1)	96%
2	$K_2 C0_3$	0_2	DMF: H_2O (3:1)	21%
3	$K_2 C0_3$	Air	DMF: H_2O (3:1)	46%

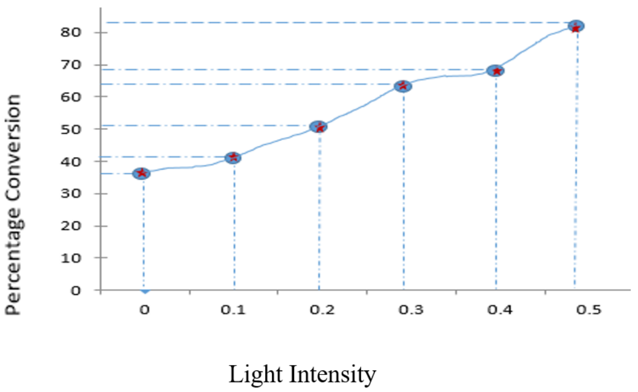

Figure 3: Relationship between percentage conversion of reactants and light intensity

3.5 Light Intensity and Wavelength

The photocatalytic nature of the Nano-particle photo-catalysts synthesized in this research implies that the activity of the catalysts is triggered by light. To investigate the effect of light and light intensity on the percentage conversion of the Suzuki reaction carried out in this research, two separate reactions were done in identical reaction conditions but one was done in the presence of light and the other in the dark. Figure 3 illustrates the impact of light irradiation on the percentage conversion. There is a significant difference in the percent conversion between the dark and light-irradiated reactions. The conversion value obtained when the reaction was done in the dark was referred to as thermal conversion because the conversion was affected mainly by heat. Also, a linear relationship between light intensity and percent conversion was observed, this is so because as the intensity of the light irradiation was increased from 0.1, 0.2, 0.3 to 0.5 the percent conversion also increased as seen in Figure 3. The increase in percent conversion as the light irradiation intensity increases is possibly due to an increase in the electrons population with a higher energy level which in turn creates a strong electromagnetic environment around the Nanoparticle Photo-catalysts [22,36,37,38,39, 40,41].

The effect of the wavelength of the light on percentage conversion was also investigated by using different light sources with inherent different wavelengths. Figure 4 shows that shorter wavelength induces stronger absorption by electrons in the nanoparticle Photo-catalysts hence generating more electrons with a higher energy level which in turn drives the reaction to a higher percentage conversion.

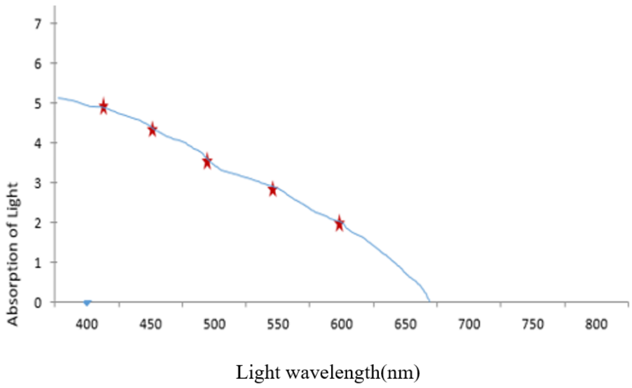

Figure 4: Relationship between light wavelength and amount of light absorbed by reacting substrate

4.0 CONCLUSION

Looking through the reaction conditions (base, solvent, atmosphere, light wavelength and intensity) for the Suzuki-Miyaura cross-coupling reaction that was optimized in this research, it is safe to conclude that an increase in reaction yield, percentage conversion and overall reaction success is directly tied to the type of reaction condition adopted for a particular cross-coupling reaction. The Suzuki-Miyaura cross-coupling was catalyzed by an alloy nanoparticle photo-catalyst system in this study, which is why light intensity and wavelength were optimized. The success of the cross-coupling reaction in this study is largely dependent on light, both in terms of wavelength and intensity, due to the photocatalyst's need for light for activation.

Light source with shorter wavelengths (less than 500nm) was found to be effective in activating the photo-catalysts, this could largely be due to the presence of Silver as a major component of the Alloy. The rapid dissolution of the reaction substrate in the reaction solvent is a key factor that determines reaction percentage conversion and the overall success of the reaction. The most effective solvent for the specific Suzuki cross-coupling reaction used in this study was determined to be a solvent mixture consisting of dimethylformamide (DMF) and water in a 3:1 ratio. This combination produced a 96% percentage conversion value with no side reactions or homo-coupling products. Carrying out the cross-coupling reaction adopted in this research in an argon environment was found to be more profitable looking at the percentage conversion value (96%) and the conversion value when the reaction was done in an oxygen or air environment (21% and 46% respectively). When compared to the other bases that were tested in this study, potassium carbonate turns out to be a superior reaction base. 96% was the percentage conversion number that K2CO3 yielded, which is significantly greater than the values found for the other bases that were tested in this study. Thus, it can be said that when the Suzuki-Miyaura cross-coupling reaction is carried out in an argon environment with potassium carbonate as the base, DMF and water in a 3:1 ratio as a solvent, and a light source with a wavelength of less than 500 nm, the best performance values are obtained in terms of reaction yield, present conversion, and limited side reaction. This reaction is catalyzed by nanoparticle photocatalysts. Therefore, for an efficient Suzuki-Miyaura cross-coupling reaction, an Ag-Pd alloy nanoparticle photocatalyst is recommended as the catalyst system, while for a greater percentage conversion of reactants to products in a Suzuki-Miyaura cross-coupling reaction, the application of K2CO3, Argon, high-intensity light with a short wavelength and a solvent mixture of DMF: H2O in ratio 3:1 as reaction condition is suggested.

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