

Palladium Organo-Mineral Complex Fixed on Fe₃O₄@Arginine Magnetic Nanoparticles: an Effective Catalyst for Heck Reaction

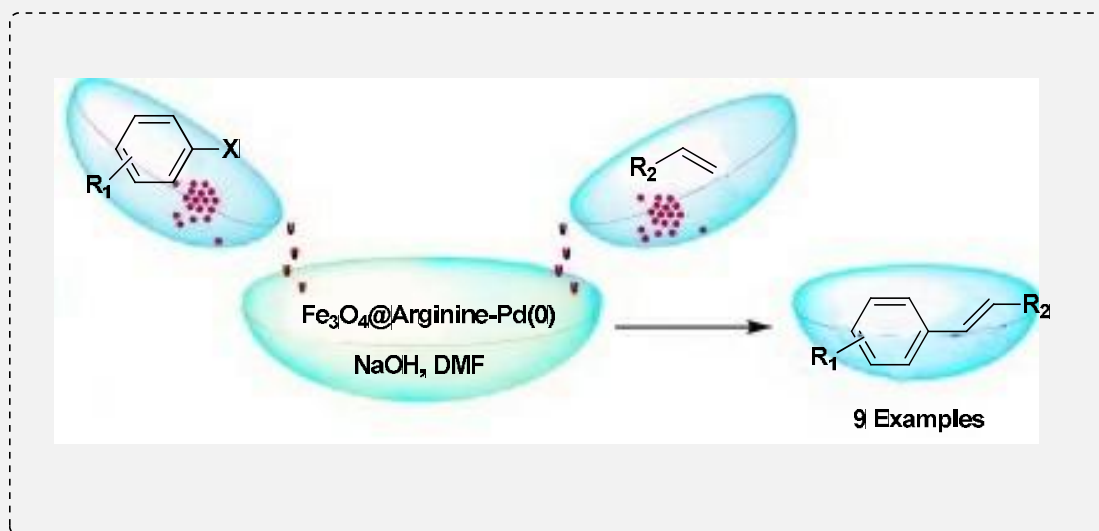
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ABSTRACT: Heck reactions are effective and practical instruments for the synthesis of organic molecules. The palladium catalyst facilitates this reaction, which results in the formation of a C-C cross-pair bond. Due to difficulties in reusing the catalyst and removing the palladium catalyst and ligand from the end product, palladium catalyst application in homogenous reaction systems is restricted. As a result, numerous solid species, including silica, chitosan, arginine, and palladium catalyst, have been produced. Science and technology have placed more of an emphasis on adapting in recent years to be more environmentally friendly and to use sustainable materials and processes. A range of electron-rich and electron-poor olefin substrates have been effectively converted into the target products with high yields in this study thanks to the preparation of a straightforward heterogeneous palladium complex, which has been employed as an excellent catalyst for the Heck cross-coupling reaction.



KEYWORDS: Heck reactions, Homogenous, Arginine, Silica, Olefin.

Introduction

When contrasted to materials with coarser grains, nanomaterials typically have unique characteristics [1]. According to the quantum mechanism, materials exhibit peculiar features that can alter attributes including conductivity, heat transfer, melting temperature, optical, and magnetic characteristics when their size is down to less than 100 nm [2]. Smaller nanoparticles have unique features because they increase the volume fraction of atoms' surfaces [3]. Constructing nanoparticles with magnetic

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characteristics has drawn a lot of interest lately. Particles that are autonomous, up to 100 nm in size, and possess magnetic components are known as magnetic nanoparticles [4]. Because of their tremendous potential for usage in a variety of industries, including advanced production, medical, energy, and food, and their ease of separation using an external magnetic field, magnetic nanoparticles have garnered the most attention among other types of nanoparticles [5]. Because of their large effective surface area, chemical activity, and magnetic dipole interactions, magnetic nanoparticles are prone to oxidation and aggregation. Under typical circumstances, the surface of nanoparticles is prone to oxidation, which significantly influences their characteristics [6]. Several coating and protection techniques use nanoparticles to preserve their special qualities and prevent unwanted oxidation. Among them are coatings made of carbon, silica, metal, and organic polymers. Fe_3O_4 is an example of an iron oxide and magnetic iron nanoparticle [7].

A catalyst with an extremely wide active surface can be produced by nanotechnology [8]. In contrast to catalytic nanoparticles, which have a larger size relative to the catalyst, the active surface of nanocatalysts is always smaller than that of a homogeneous catalyst, despite the fact that their active surface is significantly higher than that of conventional catalysts [9]. Homogeneous materials are easily separated and do not dissolve in the reaction solution [10]. Nanocatalysts are a bridge between homogeneous and heterogeneous catalysts because of their high active surface and capacity to separate the catalyst at the end of the reaction. Magnetic separations are a strong, quick, highly effective, and efficient technique for products and catalysts as compared to traditional separations [11]. An external magnet can be used to efficiently separate catalysts bound on supported magnetic nanoparticles from the reaction fluid, eliminating the need for laborious processes like centrifugation and filtering. Furthermore, a noteworthy characteristic of magnetic nanoparticles is their appropriately changed surface, which offers a large region of increased activity functionalized magnetic catalysts [12]. By adjusting the size of pores and particles, nanocatalysts can be used to increase activity and selectivity. They can also increase efficiency by reacting more molecules in a given amount of time than conventional catalysts since they have a higher surface area [13]. The capacity to separate, extract, recycle, and reuse nanocatalysts was mentioned as a way to lower production costs when using them in place of precious metal catalysts [14].

A significant area of research in recent years has been the application of metal nanoparticle-based heterogeneous and homogeneous catalysts [15]. In that area, heterogeneous catalysts in which the nanocatalysts are adhered to a solid surface represent one of the biggest obstacles. Palladium nanoparticles have found extensive use in organic synthesis, particularly in cross-couplings like Suzuki, Heck, Style, and Sonagashira [16]. As a result, these materials have become highly recognized in the field of nanocatalysts [17]. Given the widespread application of these materials, it is evident how important these nanocatalysts are from a commercial and practical standpoint due to their ease of separation from the desired product following the reaction and their capacity to be reused without experiencing a major loss of catalytic activity [18]. Palladium nanoparticle collection on the surface of a suitable substrate has been the subject of numerous research. Palladium nanoparticles can be absorbed by iron and iron oxides, which is why this team has looked into them [19].

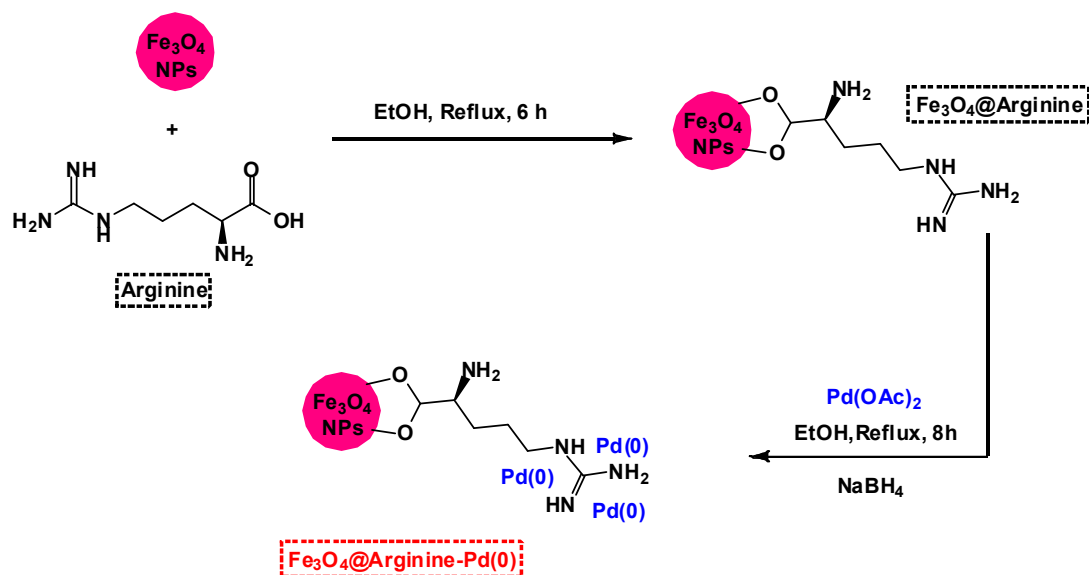
Palladium may catalyze a variety of reactions, but the Heck reaction and its associated chemistry are particularly noteworthy [20]. Heck and Mizoroki separately discovered the Heck-Mizoroki reaction in the

late 1960s, and Heck developed it in the 1970s [21]. This reaction developed to the point where it became one of the most fundamental reactions in organic chemistry, particularly in the ten to fifteen years after it first appeared [22]. Heck reactions are among the most important chemical reactions because they can involve a lot of functional groups. Complex molecule synthesis is done with organic materials [23]. This is a C-C coupling process that takes place in the presence of a palladium catalyst and involves an olefin with at least one hydrogen and an aryl halide, alkenyl halide, or triflate [24]. The Heck reaction's efficiency and quickness are determined by a number of factors. We can list the catalyst, aryl halide, and leaving group as some of these components [25]. Heck reactions are frequently catalyzed by $\text{Pd}_2(\text{dba})_2$, $\text{Pd}(\text{PPh}_3)_2$, and several palladium+2 salts. However, palladium acetate is the palladium combination that is most frequently employed in this reaction [26]. This is because palladium acetate is more soluble in organic solvents. Aryl iodides have an activity several times higher than that of aryl bromides, and these aryl halides are utilized in Heck reactions [27]. Because the catalyst is unstable at these high temperatures and the reaction takes a considerably higher temperature to complete, aryl chlorides are utilized less frequently [28]. The type of aryl halide utilized in this reaction is also crucial; if an electron-less alkene is employed, electron-less arenes will yield the greatest outcomes [29]. In this case, spatial variables are especially crucial. For instance, the spatial barrier created by ortho substitutions slows down reaction times [30].

This study reports on the stability of palladium metal via organic molecule binding on magnetic nanoparticles covered in silica gel. The IR and SEM spectroscopic methods have been used to identify this magnetic nanocatalyst. Because of its magnetic feature, the produced catalyst easily facilitates the carbon-carbon coupling reaction in the Heck reaction and makes its separation at the end of the process very easy.

■ Results and Discussion

$\text{Fe}_3\text{O}_4@$ Arginine-Pd(0) nanocomposites can be conceptually synthesized as **Scheme 1** illustrates. Several spectroscopic methods were used to characterize the structure of the $\text{Fe}_3\text{O}_4@$ Arginine-Pd(0) nanocatalyst.



Scheme 1. Experimental details of the fabrication of $\text{Fe}_3\text{O}_4@$ Arginine-Pd(0) nanocatalyst.

FT-IR spectroscopy

Figure 1 shows the FT-IR measurement of $\text{Fe}_3\text{O}_4@$ Arginine-Pd(0) nanocatalyst. The presence of an antisymmetric stretching vibration of Si-O-Si and the absorption peak of NH groups at 3240 cm^{-1} in the compound's infrared spectrum are indicative of the presence of a SiO_2 layer around each Fe_3O_4 nanoparticle. The samples' spectra show the aliphatic C-H stretching of methylene groups, which is represented by the peak at roughly $2856\text{--}2924\text{ cm}^{-1}$. These findings suggest that L-arginine is immobilized on the $\text{Fe}_3\text{O}_4@$ SiO_2 surface.

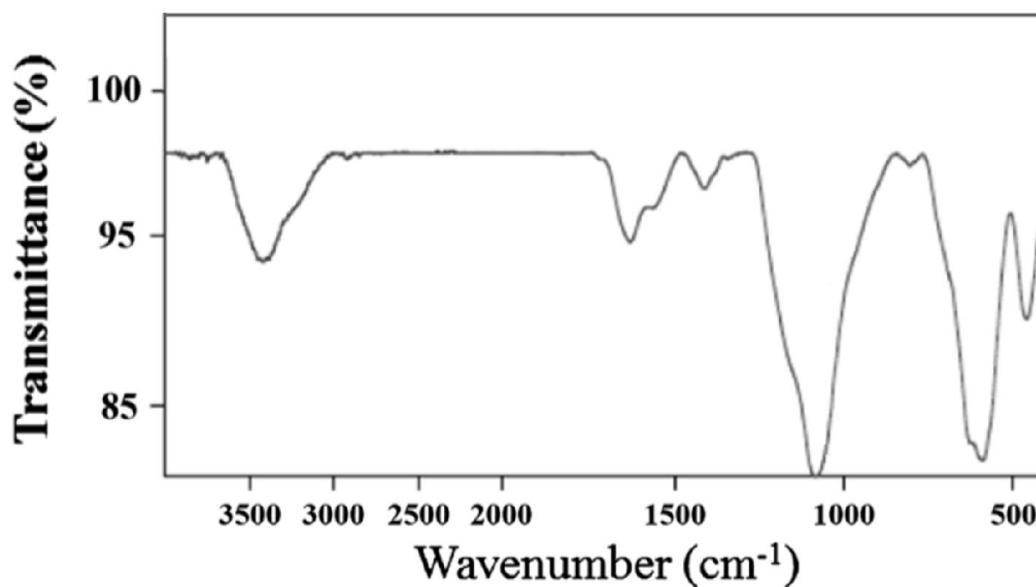


Figure 1. FT-IR spectroscopy of $\text{Fe}_3\text{O}_4@$ Arginine-Pd(0) nanomaterial.

SEM analysis

The dispersion and morphology of Fe₃O₄@Arginine-Pd(0) nanomaterial were further characterized by SEM (**Figure 2**). Fe₃O₄@Arginine-Pd(0) nanomaterial with almost spherical morphology that can be recognized are placed together and dispersed on the surface. In addition, the size of the synthesized particles is 40 nm to 60 nm, which indicates that they are nano-sized.

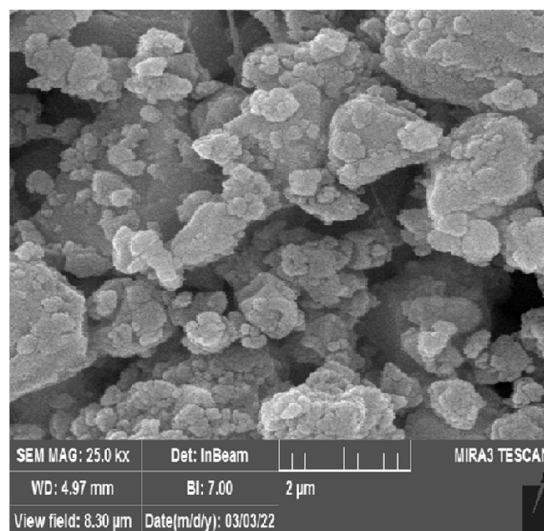


Figure 2. SEM image of Fe₃O₄@Arginine-Pd(0) nanomaterial.

First, we used the reaction between iodobenzene and styrene to optimize the reaction conditions. Among the bases we tried, NaOH produced the best results and yield. Following optimization, the synthesized catalyst utilizing a NaOH base, 80 °C, and an hour of time produced the best results (**Table 1**). The best yield was found when the electron-withdrawing substitution was on aryl halide, for example, when we employed different aryl iodide derivatives after optimizing the reaction's general conditions. Good yields were obtained when aryl iodide was used with electron-donating substitution. An extended response time was attained. Styrene was readily linked from the iodine side when the starting material contained both iodine and bromine. Moreover, alkenes with more electrons than those with less electrons produced larger yields. Aryl iodides with orthogonal substitution produced less than the para position due to the steric hindrance in the ortho and meta positions (**Table 2**).

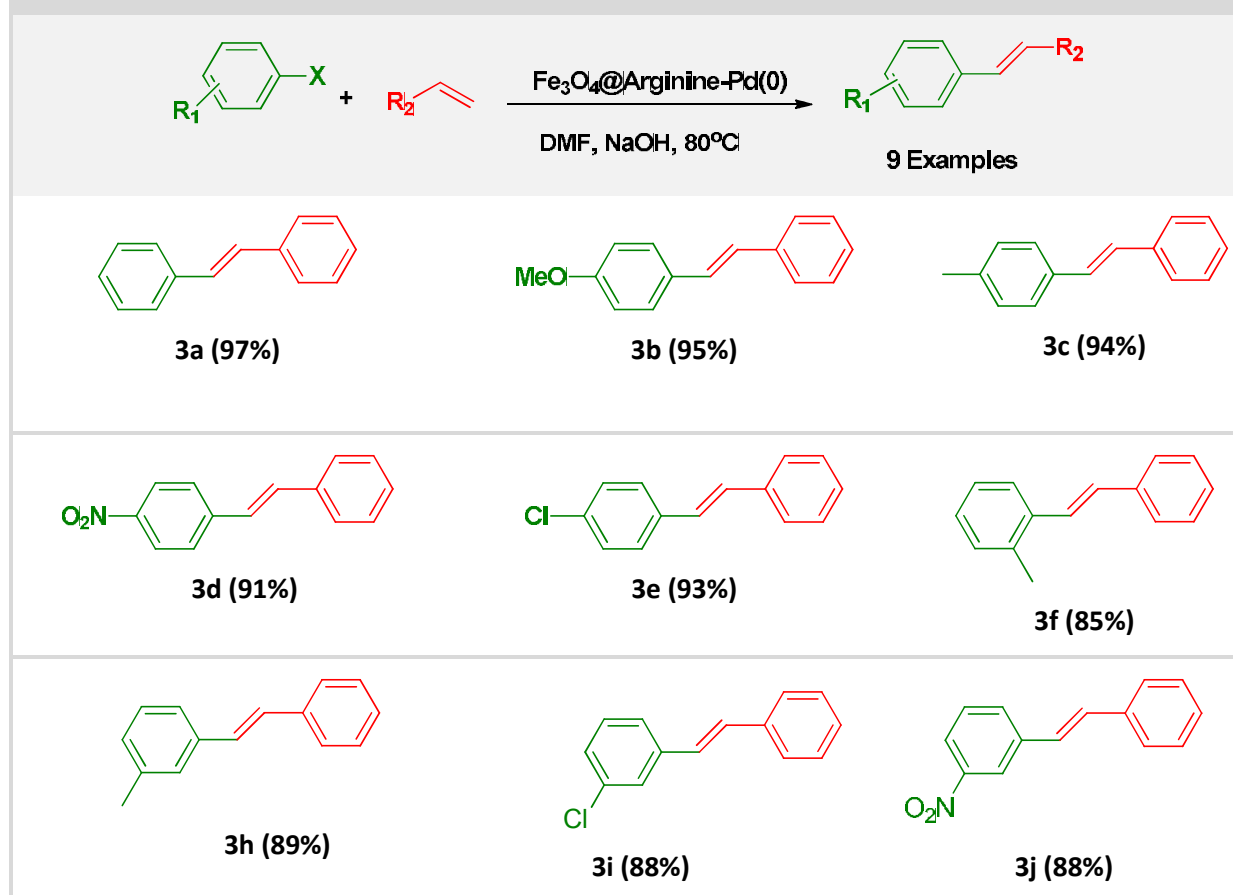
Table 1. Optimization parameters for Heck reactions ^a

Entry	Catalyst (mol%)	Base	Solvent	Time (min)	Yield (%) ^a
1	--	NaOH	DMF	120	No

2	5	NaOH	DMF	60	32
3	10	NaOH	DMF	60	57
4	15	NaOH	DMF	60	76
5	20	NaOH	DMF	60	69
6	30	NaOH	DMF	60	97
7	30	KOH	DMF	60	82
8	30	K ₂ CO ₃	DMF	60	91
9	30	Na ₂ CO ₃	DMF	60	39
10	30	NaOH	PEG	60	89
11	30	NaOH	EtOH	60	63
12	30	NaOH	CCl ₄	60	21
13	30	NaOH	THF	60	58
14	30	NaOH	Hexane	30	35

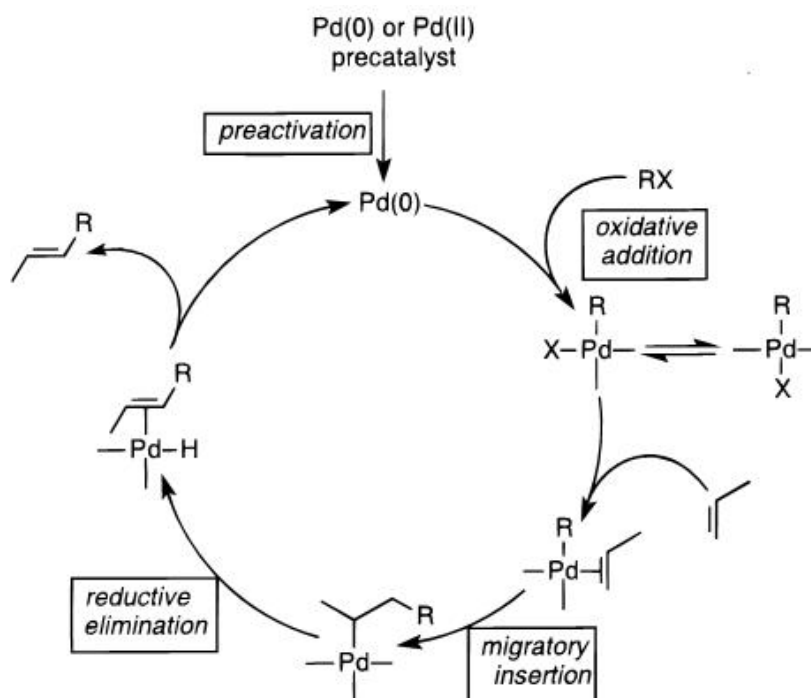
^a Isolated yields

Table 2. Reaction of derivatives for (E)-1,2-diphenylethene.



The mechanism of this reaction is shown in **scheme 1**. Based on that, At first, aryl halide (Ar-X) is placed

on palladium during an oxidation-addition reaction and ArXPdL_2 is formed. Then, due to the increase of the alkene group, it is placed on palladium. In the next step, due to the removal of beta hydride, HPdXL_2 is formed from the complex is separated and the product is released. In order to reduce palladium (+2) to palladium (0) and return it to the reaction cycle, a suitable base is used, which enters the cycle by removing HX palladium (0).



Scheme 1. The general mechanism of Heck reaction.

Conclusion

With the synthesized catalyst, we were able to accomplish the entire reaction in this project with a very tiny quantity of palladium, make a variety of compounds, and then easily separate the catalyst at the end. As demonstrated by tests, the palladium catalyst immobilized on Fe_3O_4 exhibits remarkable efficiency in catalyzing cross-coupling reactions and the production of C-C bonds between iodobenzene and different alkenes while taking into account the best possible reaction conditions. Heck reaction products have a high efficiency, which is highly helpful and efficient in the industry of preparing materials for the synthesis of organic compounds, as demonstrated by the products with ^1H NMR system.

Experimental

High purity chemicals were purchased from Fluka and Merck. The melting points in the capillary tube were determined using the Electrothermal 9100 device. FTIR spectrum was recorded by VERTEX 70 device (Bruker). ^1H and ^{13}C NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at frequencies of 300.13 and 75.46 MHz and on a BRUKER DRX-400 AVANCE spectrometer at frequencies of

400.22 and 100.63 MHz, respectively. Determination of purity Products and reaction monitoring were performed by TLC on polygram silica gel SILG/UV 254 plates.

Preparation of Fe₃O₄@Arginine-Pd(0) Catalyst

First, magnetic iron nanoparticles were synthesized using previous methods [2]. In the next step, Fe₃O₄@Arginine-Pd(0) nanocomposite was successfully synthesized through the reaction of Fe₃O₄-NPs with arginine in ethanol solvent under reflux conditions for 6 hours. Finally, palladium acetate (II) (PdOAc)₂ was successfully immobilized on the Fe₃O₄@Arginine-Pd(0) ligand in ethanol solvent under reflux conditions for 8 hours in the presence of NaBH₄.

General Conditions for Heck Reaction

We added 1 mmol of aryl halide and 2 mmol of alkene along with 3 mmol of base and 03.0 g of catalyst in a test tube along with 3 ml of DMF. The reaction mixture was stirred under a temperature of 100 °C for 2 hours. We followed the progress of the reaction with TLC thin layer chromatography. After the completion of the reaction, we separated the catalyst from the reaction solution with the help of a magnet. We separated the product from the reaction solution by adding water.

Supplementary Information

(E)-1-methyl-4-styrylbenzene (3c): White solid (94% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.52 (d, J = 7.1 Hz, 2H, ArH), 7.45 (d, J = 8.3 Hz, 2H, ArH), 7.38 (t, J = 7.2 Hz, 2H, ArH), 7.25 (d, J = 7.3 Hz, 1H, ArH), 7.18 (d, J = 7.6 Hz, 2H, ArH), 7.08 (d, J = 4.7 Hz, 2H, CH), 2.33 (s, 3H, CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃) δ 137.8, 137.1, 134.6, 129.7, 128.9, 127.3, 127.2, 126.3, 126.1, 21.3 ppm. mp: 118 - 120 °C.

(E)-1-chloro-3-styrylbenzene (3i): White solid (88% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.52 (d, J = 7.6 Hz, 3H, ArH), 7.39 (t, J = 7.7 Hz, 3H, ArH), 7.28 (t, J = 7.8 Hz, 2H, ArH), 7.24 (d, J = 8.2 Hz, 1H, ArH), 7.13 (d, J = 6.2 Hz, 1H, CH), 7.08 (d, J = 6.3 Hz, 1H, CH) ppm. ¹³C NMR (150 MHz, CDCl₃) δ 139.7, 137.4, 134.5, 130.2, 129.4, 128.6, 128.1, 127.7, 127.3, 126.5, 126.3, 124.8 ppm. mp: 75 -77 °C.

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