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Synthesis of Diazine-Based Dendrimer Supported Pd/Co Bimetallic Nanoparticles and Catalytic Activity for Sonogashira Coupling Reactions

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ABSTRACT

A moisture-stable diazine-based dendrimer assisted heterogeneous bimetallic Pd/Co nanoparticles (NPs) was synthesized which showed a simple, profitable and environmentally sustainable operation for the Sonogashira reactions under copper and solvent-free conditions with regained easily and recycled four times without substantial activity loss. Furthermore, the dendrimer was analyzed by IR, ^1H NMR, ^{13}C NMR, and elemental analysis whereas the Pd/Co bimetallic NPs was characterized by EDX, TGA & DSC, and XRD techniques.


Keywords: Bimetallic nanoparticles (NPs), Diazines; Dendrimer and Sonogashira reaction.

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Introduction

Bimetallic nanoparticles (NPs) are an important class of catalysts. Bimetallic nanoparticles can be divided into three main types based on their mixing template: hetero-structures, core-shell arrangements, and intermetallic or alloy structures [1]. Bimetallic alloy NPs among these types are very vital nanomaterials due to their various implementation in a wide range of catalytic reactions, including catalytic alcohol oxidation, C-C bond forming reactions [2–9]. The introduction of a second metal is an impactful strategy to modify geometric and electronic frameworks of nanoparticles to facilitate their catalytic activity and sensitivity.

However, a major issue is the stability of nanoparticles in different reactions forming carbon-carbon bonds. Dendrimer can be used as a template for controlling the size, stability, and solubility of nanoparticles to overcome this problem [10, 11]. For the usual reasons, dendrimers are suitable guests for metal nanoparticles, specifically for catalytic mechanisms: (i) nanoparticles are stabilized by encapsulation within the dendrimer and do not agglomerate; (ii) embedded nanoparticles are known to have steric effects, which means that a significant part of their surface is non-passive and accessible for catalytic reactions [12-18].

In addition, a great deal of attention has recently been given to the coupling reaction of terminal alkynes and aryl halides catalyzed by Pd catalysts [19-21]. Li et al. [22, 23] reported recently a new approach containing hollow Pd/Co alloy nano-spheres as a catalyst for 80 °C solvent Sonogashira reactions in water with 4–9 h reaction times.

Nevertheless, most of the methods described require anhydrous solvents, inert gas, long reaction times and costly and toxic reagents. There is a little study in the literature on the synthesis of bimetallic NPs supported with diazine-based dendrimer and the development of their heterogeneous catalytic interest in cross-coupling reactions. Here we have shown

synthesis and characterization and the uses as catalyst in the sonogashira coupling reaction of a new class of dendrimer assisted heterogeneous Pd/Co bimetallic NPs wherein synthetic route is phosphine-ligand-free conditions with recovered easily and recycled a few times without substantial activity loss.

Experimental

Materials and Methods

All the solvents such as DMF, DMSO, CH₃CN, and THF were purchased from Aldrich and used as received. Shimadzu FTIR 8400S Fourier Transform Spectrophotometer (400-4000 cm⁻¹) with KBr pellets was used to take the IR spectra. ¹H NMR and ¹³C NMR spectra were recorded at 500 MHz and 100 MHz, respectively, on a JEOL AL 300/BZ instrument and also ¹H NMR (400 MHz, Bruker) and ¹³C NMR (100 MHz, Bruker). Analytical thin layer chromatography (TLC) was silica gel 60 F 254 coated on 25 TCC aluminum sheets (20 × 20 cm). Silica gel column chromatographic separations were made on silica gel 60 N (neutral, 40-100 μm). 2, 4, 6-triaminopyrimidine; acetyl chloride and CoCl₂·6H₂O, PdCl₂ were purchased from Aldrich. TG and DSC data were taken by a thermogravimetric analyzer (NETZSCH STA 449F3) from 26 to 600 °C under a nitrogen atmosphere using aluminum oxide crucible at a heating rate of 10 k/min and at a flow rate of 40 and 60 mL/min. The JEOL-JSM-7600F was used to determine the EDX of the nanoparticle. Particle size and phase identification were discovered with a PANANALYTICAL x-ray diffractometer. Determination of C/H/N of dendrimer was done using a "2400 CHN Elemental Analyzer" by Perkin Elmer.

Synthesis of 2,4,6-Tris (di-acetamido)-1,3-diazine 3

The mixture of 0.2 g (0.00159 mol) 2,4,6-Triaminopyrimidine, 3 mL of acetyl chloride was added in 5 mL of DMF and the reaction mixture was stirred at room temperature for around 2 hours in a 250 mL round bottom flask. The reaction was observed by TLC. After complete

conversion of the reactants into products, the reaction was stopped by adding distilled water. Then the reaction mixture was extracted with CHCl_3 . After the elimination of the solvent, the product was crystallized by using ethanol and the required compound **3** was white crystalline solid, m. p. 130-132 °C, odorless and 96 % of yield. IR (KBr): ν_{max} 3030, 1684, 1674, 1620, 1359 and 1293 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): 2.53(s, 18H), 8.22 (s, 1H) ppm. ^{13}C NMR (100 MHz, D_2O): 68.23, 88.33, 98.57, 151.82 and 160.44 ppm. Anal. Calcd. for $\text{C}_{16}\text{H}_{19}\text{N}_5\text{O}_6$; C 50.93, H 5.08, N 18.56; found: C 50.85, H 5.00, N 18.45

Synthesis of dendrimer compound **3** assisted Pd/Co bimetallic NPs **4**

We pursued a sequential loading technique to synthesize bimetallic Pd / Co nanoparticles. In a usual test, 0.200 g 2,4,6-Tris (di-acetamido)-1,3-diazine **3** (0.00053 mol), 0.00096 g PdCl_2 , were dissolved in CH_3CN (8 mL) and also added $\text{NH}_2\text{-NH}_2\text{.H}_2\text{O}$ (1.5 mmol) in a round bottom flask cautiously and stirred the mixture at 1 h at 90 °C. Then 0.020 g of $\text{CoCl}_2\text{.6H}_2\text{O}$ (0.00085 mol) and $\text{NH}_2\text{-NH}_2\text{.H}_2\text{O}$ slightly more than the equivalent amount of copper salt was introduced to the reaction combination. The NaOH solution (0.3 M) was gradually introduced to the reaction mixture in order to preserve pH 11 and the suspension was strongly boiled for 2 hours with a special stirring cap. The black residue was discovered after the reaction combination had been settled. The residue was filtered after the reaction mixture was centrifuged (3000 rpm for 10 min), washed with double distilled water and acetone and dried overnight at 110 °C in an oven.

Catalytic application of Pd/Co bimetallic NPs **4** for Sonogashira Reaction

A Round Bottom flask was loaded with 1.0 mmol aryl halide, 1.3 mmol phenylacetylene, 1.0 mol Pd / Co bimetallic NPs **4**, Et_3N (1.3 mL) as a foundation and CH_3CN (10 mL) as a solvent under the inert environment. The mixture was then stirred at 90 °C for 2 hours and the reaction was observed by TLC. At the end of the reaction,

the residue of the product was obtained with CHCl_3 (20 ml) and purified by chromatography with silica gel using ethyl acetate and hexane (8:1).

Synthesis of 1- (2- (4-methoxyphenyl) ethynyl) benzene **12**, [24]

Solid white product was obtained, m.p. 55-58 °C (lit. 57 °C); ^1H NMR (400 MHz): δ 3.72 (s, 3H); 6.89 (d, 2H, $J=8.8$ Hz); 7.34 (t, $J=10.8$ Hz, 3H); 7.35 (d, 2 H, $J=8.8$ Hz); 7.45 (d, 2H, $J=8.0$ Hz), ^{13}C NMR (100 MHz, CDCl_3): δ 55.52, 93.24, 113.24, 115.21, 123.38, 128.49, 129.49, 132.04, 133.94, 160.98

Synthesis of 1-(2-p-tolyethynyl)benzene **13**, [25]

Solid colorless product was obtained, m.p. 70-72 °C (lit. 71 °C); ^1H NMR (400 MHz): δ 2.32(s, 3 H); 7.21 (d, 2H, $J= 8.8$ Hz); 7.33 (t, 3H, $J= 5.6$ Hz); 7.34 (d, 2H, $J=8.4$ Hz); 7.55 (d, 2H, $J= 8.0$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 92.52, 93.14, 120.21, 122.24, 128.28, 128.49, 128.98, 132.04, 133.94, 139.14

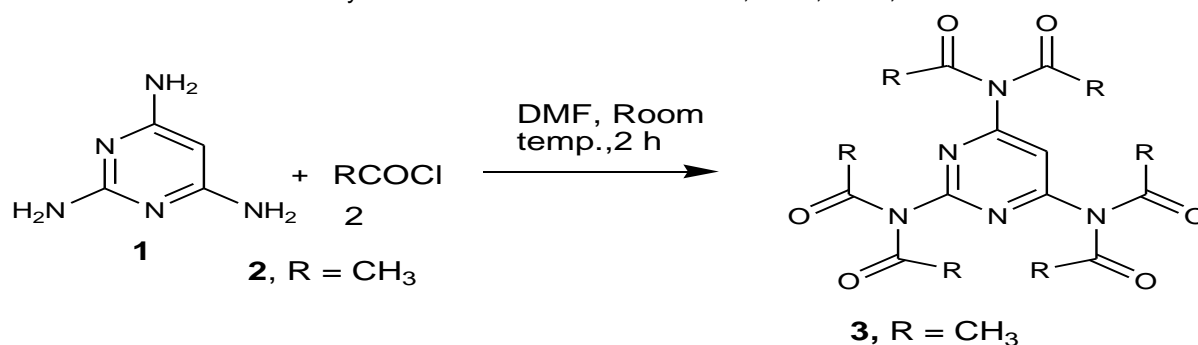
Synthesis of 4-(2-phenylethynyl)phenol **14**, [25]

Solid product was obtained, m.p. 123-125 °C; ^1H NMR (CDCl_3 , 400 MHz): δ 5.07 (s, 1 H, OH); 6.74 (d, 2H, $J=8.8$ Hz); 7.28-7.36 (m, 3 H); 7.44 (d, $J= 8.8$, 2H); 7.54 (d, $J=8.8$, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 93.92, 114.14, 115.31, 123.98, 128.48, 129.04, 133.94, 134.44, 159.52.

Results and Discussion

Synthesis and characterization

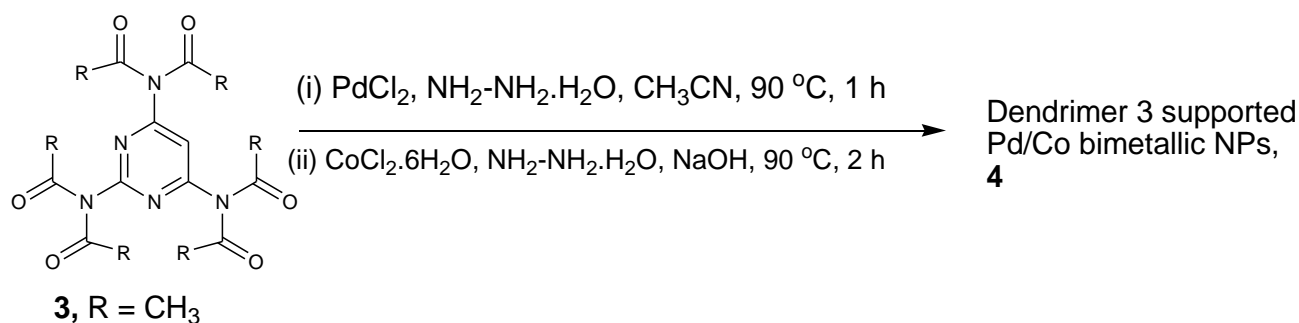
Dendrimer **3** was synthesized by the reaction of 0.2 g (0.00159 mol) 2,4,6-Triaminopyrimidine **1** with acetyl chloride **2** (3 mL) in anhydrous DMF at room temperature for 2 hrs under an inert atmosphere (Scheme 1). The improvement of the reaction was monitored by thin layer chromatography (TLC) and after the end of the reaction, the reaction mixture was extracted with chloroform and recrystallization with ethanol gave the product **3**. The product was analyzed by using IR, ^1H NMR, ^{13}C NMR (S1-S3 in the supporting information).



Scheme 1. Synthesis of dendrimer 3

The existence of peaks within the range of 3000-3100 cm^{-1} and 1670-1760 cm^{-1} showed the C-H, C=O groups respectively, while the C=N group was identified by a band at 1585-1620 cm^{-1} . The peaks of 1310-1360 cm^{-1} and 1240-1350 cm^{-1} respectively verified the presence of groups of C=C and C-N. Here it is noteworthy that there is no band for N-H close to 3400–3250 cm^{-1} which has been shown to have altered 1° amino group

of triaminopyrimidine into a group of 3° amido group. The required dendrimer 3 was also proved by ^1H NMR and ^{13}C NMR spectra. There is no NH or NH_2 band ^1H NMR, which has been further demonstrated to be compound 3's framework. In addition, the results of elemental analysis of the amount of carbon, nitrogen, and hydrogen ensured the structure of compound 3.

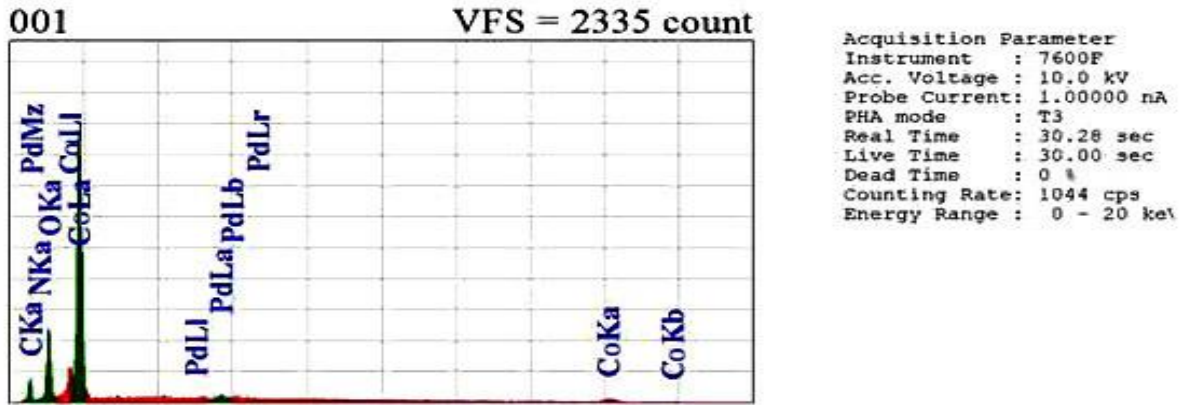


Scheme 2. Synthesis of Pd/Co bimetallic NPs 4

The entirely dendrimer-based diazine supported Pd / Co bimetallic NPs 4 was synthesized using a sequential loading approach (Scheme 2) and thus further characterized by various physicochemical methods which include EDX, XRD, TGA, and DSC. EDX analysis identified the presence of palladium and cobalt, and cobalt was 53.75 percent of the mass and palladium 11.40 percent of the synthetic Pd/Co bimetallic NPs (Figure 1).

The XRD graphs (Figure 2) further described the particle shape and size of the Pd-Co bimetallic NPs 4. Three prominent peaks at 44.2°, 52.35° and 76° were attributed (111), (110) and (220)

peaks of FCC Cobalt nanoparticles and correlated with the JCPDS standard powder diffraction card Co_FCC JCPDS #15-0806. [26] while the two basic peaks at 2theta (o) values of 43.50 and 46.30 correspond to (111), (200) planes of Palladium respectively those characterized the formation of FCC Palladium nanoparticle and in comparison with well-known powder diffraction card of JCPDS, Palladium report no (46—1043) [27], (figure 2). As a result, these results were found in Pd-Co bimetallic NP's FCC framework. The Pd-Co bimetallic NP 4 XRD template represents the average 18.50 nm particle size calculated through the Debye-Scherrer equation.



ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.0837

Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation	K
C K*	0.277	14.02	0.25	33.48				5.6763
N K*	0.392	1.61	0.15	3.30				1.7853
O K	0.525	19.22	0.34	34.44				21.5728
Co L	0.930	53.75	0.63	20.87				67.8324
Pd L*	2.838	11.40	0.30	7.91				3.1331
Total		100.00		100.00				

Figure 1. EDX of Pd/Co bimetallic NPs

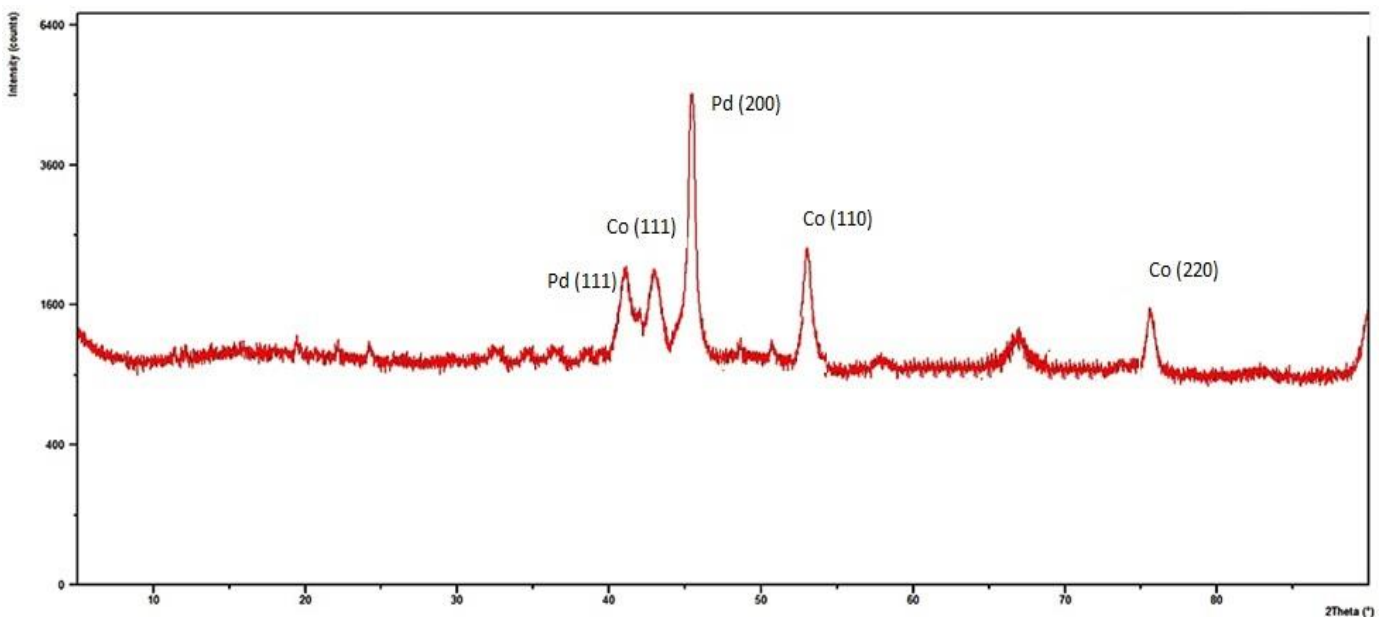


Figure 2. XRD pattern of Pd/Co bimetallic NPs 4

Thermal constancy is the main characteristic for a catalyst to maintain their activity in extended periods of reaction. TG and DSC techniques evaluated the thermal stability of the Pd/Co bimetallic NP 4 at temperatures between 26 ° C and 600 ° C under the atmospheric air (Figure 4). The content of a specific nanoparticle 4 element varies with its composition and structure and is calculated within the thermo-gravimetric graph depending on the weight decrease of these parts.

From the TG curve, it was recorded that compound 4's overall weight loss from 300 ° C to 340 ° C and the compound's DSC figures were almost comparable to the TG figures. The compound 4 melting point in the DSC value was revealed at approximately 300 ° C from the endothermic curve. The final decomposition step confirmed the ash residue of the compound about 15.50 %.

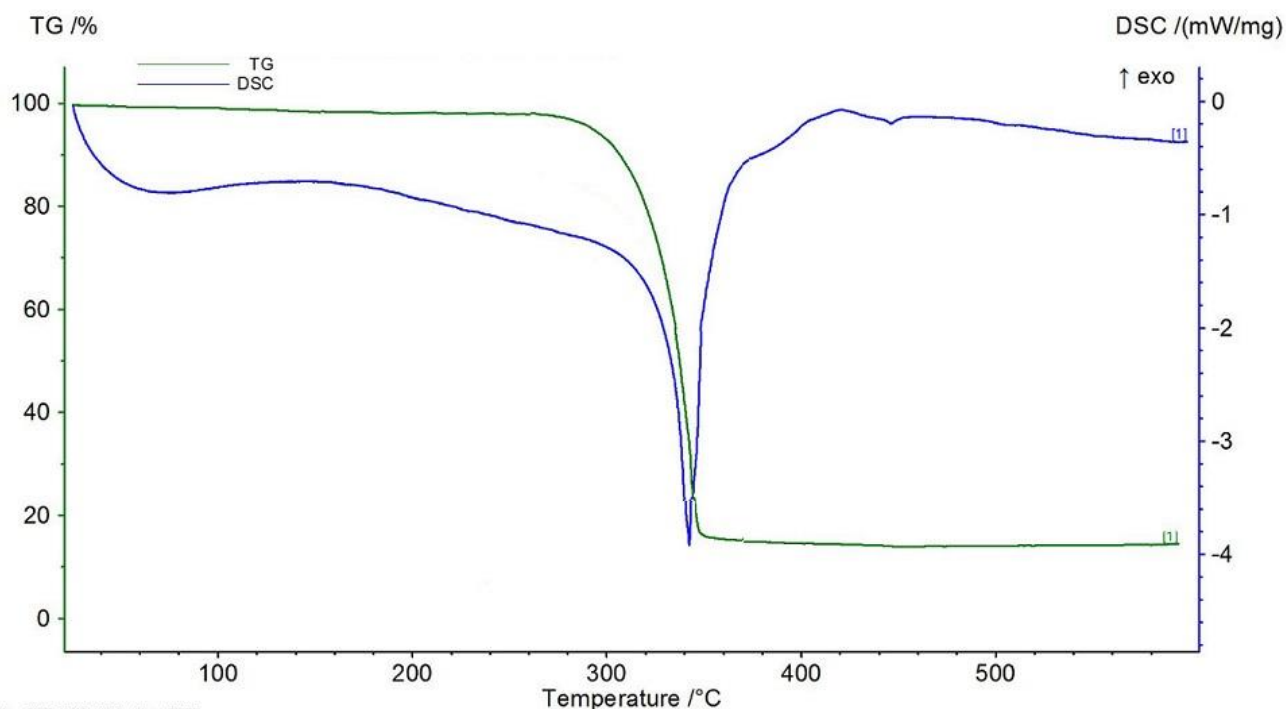


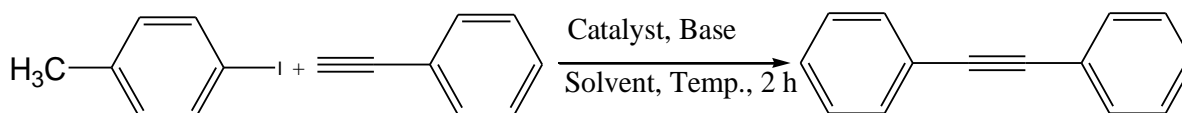
Figure 3. TG& DSC curves of Pd/Co bimetallic NPs 4

Catalytic performance

In Sonogashira reaction of aryl halides with terminal alkynes, the catalytic effect of the Pd / Co bimetallic 4 catalyst was investigated. A typical reaction between the reaction of 4-iodotoluene and phenylacetylene was tested including the solvent reaction temperature and catalyst loading, to evaluate the optimized reaction conditions. This reaction yielded very small rates with water as the solvent and various bases such as Na_2CO_3 , K_2CO_3 , $^t\text{BuOK}$, Et_3N , and KOH (Table 1, entries 1–5) in the presence of 0.3 mol % Pd / Co NPs 4 at 70 °C for 2 hour. While, in the presence of 0.5 mol % catalyst 4, the solvent was modified to DMF or THF including the use of selected bases at temperature at 80 °C (Table 1, entries 6–10), the yields had improved. Curiously, by enhancing the temperature of the reaction to 90 °C and

catalyst to 1.0 mol % , the highest outcomes with yields of 90 % were obtained by the use of Et_3N as a base CH_3CN as a solvent (Table 1, section 11). As a result, 1.0 mol % of the catalyst, Et_3N as a base and CH_3CN as a solvent at 90 °C at 2 hours were identified as maximally efficient and optimized reaction conditions (Table 1, Entry 11).

In fact, we usually aim to investigate the overall catalytic system activity that had to catalyze reactions with an outstanding type of aryl halides and diverse terminal acetylene (Table 2). The results showed with the familiar method that aryl halides iodo-derivatives (Table 2, Entries 1, 3 and 5) showed better Sonogashira reactivity than bromo-derivatives (Table 2, Entries 2, 4 and 6). The formation of Glaser-type alkyne homo-coupling products had not been detected.

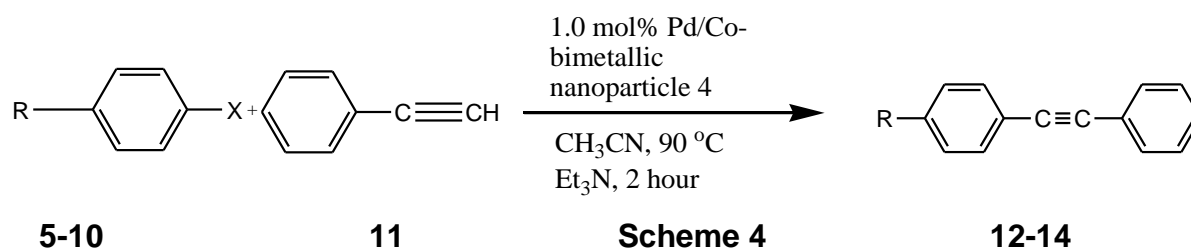


Scheme 3.

Table 1. Optimization of reaction condition for the Sonogashira coupling of 4-iodo toluene and phenylacetylene catalyzed by Pd/Co bimetallic NPs 4

Entry	Cat (mol%)	Base	Solvent	Temp. (°C)	Yield (%)
1	0.3	Na ₂ CO ₃	H ₂ O	70	14
2	0.3	K ₂ CO ₃	H ₂ O	70	12
3	0.3	^t BuOK	H ₂ O	70	15
4	0.3	N(Et) ₃	H ₂ O	70	17
5	0.3	KOH	H ₂ O	70	11
7	0.5	KOH	DMF	70	20
8	0.5	^t BuOK	THF	80	30
9	0.5	Et ₃ N	THF	80	45
10	0.5	KOH	DMF	80	60
11	1.0	Et ₃ N	CH ₃ CN	90	90

Reaction conditions: Aryl halide (1mmol), phenylacetylene (1.3 mmol), catalyst (1.0 mol%), base (1.3 mmol), solvent (10 mL), 90 °C, 2 hrs, under inert atmosphere, Yield% was calculated based on aryl halide.

**Table 2. Sonogashira coupling reaction of different aryl chlorides with phenylacetylene catalyzed by Pd/Co bimetallic NP 4**

Entry	R	X	product	Yield%
1	5, CH ₃	5, I	12	95
2	6, CH ₃	6, Br	12	90
3	7, OCH ₃	7, I	13	94
4	8, OCH ₃	8, Br	13	91
5	9, OH	9, I	14	90
6	10, OH	10, Br	14	87

Yield% was calculated based on aryl halide. All NMR data of the synthesized compounds were compared with literature data.

Recyclability and reusability of Pd/Co bimetallic NPs 4

We also examined the recyclability and reusability of the Pd-Co bimetallic NPs 4 towards the coupling reaction between 4-iodo toluene and phenylacetylene. After the reaction of each catalytic run, the residue of Pd-Co bimetallic

nanoparticle 4 was recovered from the reaction mixture by filtration, washed thoroughly with water followed by acetone, and then dried under vacuum. The recovered catalyst 4 was used for consecutive runs and exhibited minimum decrease in the yield % of products revealed in the following table.

Table 3- Recyclability of Pd/Co bimetallic NPs 4 of the coupling reaction between 4-iodo toluene and phenylacetylene

Entry	Run	Time	Yield
1	Fresh	2 h	95
2	1	2 h	93
3	2	2 h	92
4	3	2 h	90
5	4	2 h	88

Conclusion

In short, diazine-based dendrimer supported heterogeneous Palladium-Cobalt bimetallic nanoparticles were synthesized through a sequential loading method. The results of all analysis (EDX, XRD, TG& DSC) has revealed its high thermal stability and nano-shaped structure, as well as this nanoparticle, was found excellent heterogeneous catalytic activity in the carbon-carbon cross-coupling reaction such as Sonogashira cross-coupling reaction in which the synthetic route was copper iodide and phosphine ligand-free. The catalyst was easily recovered and reused at least four times without any significant loss of catalytic activity. Moreover, additional applications of this heterogeneous catalytic activity in diverse C–C coupling reactions like as Heck, Suzuki coupling are being investigated.

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Conflicts of Interest: The authors confirm no conflicts of interest.

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Supporting Informations

IR spectra of 2, 4, 6-Tris (di-acetamido)-1, 3 diazine 3

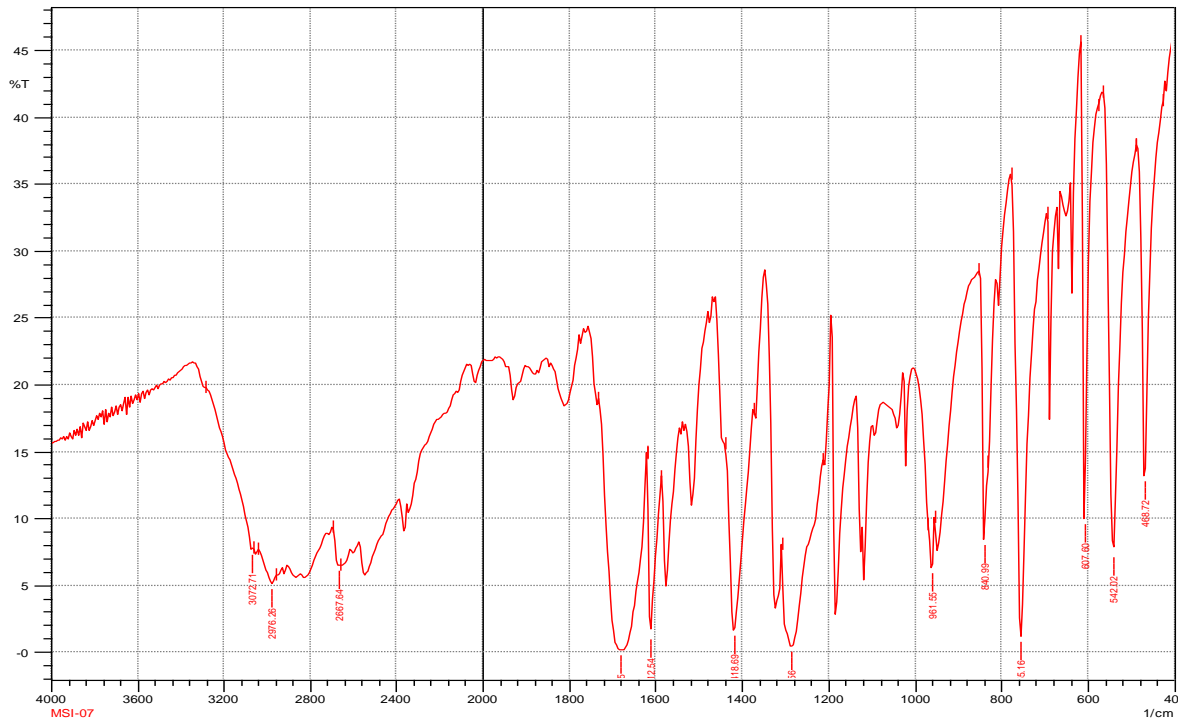


Fig. S1

¹H NMR spectra of 2, 4, 6-Tris (di-acetamido)-1, 3 diazine 3

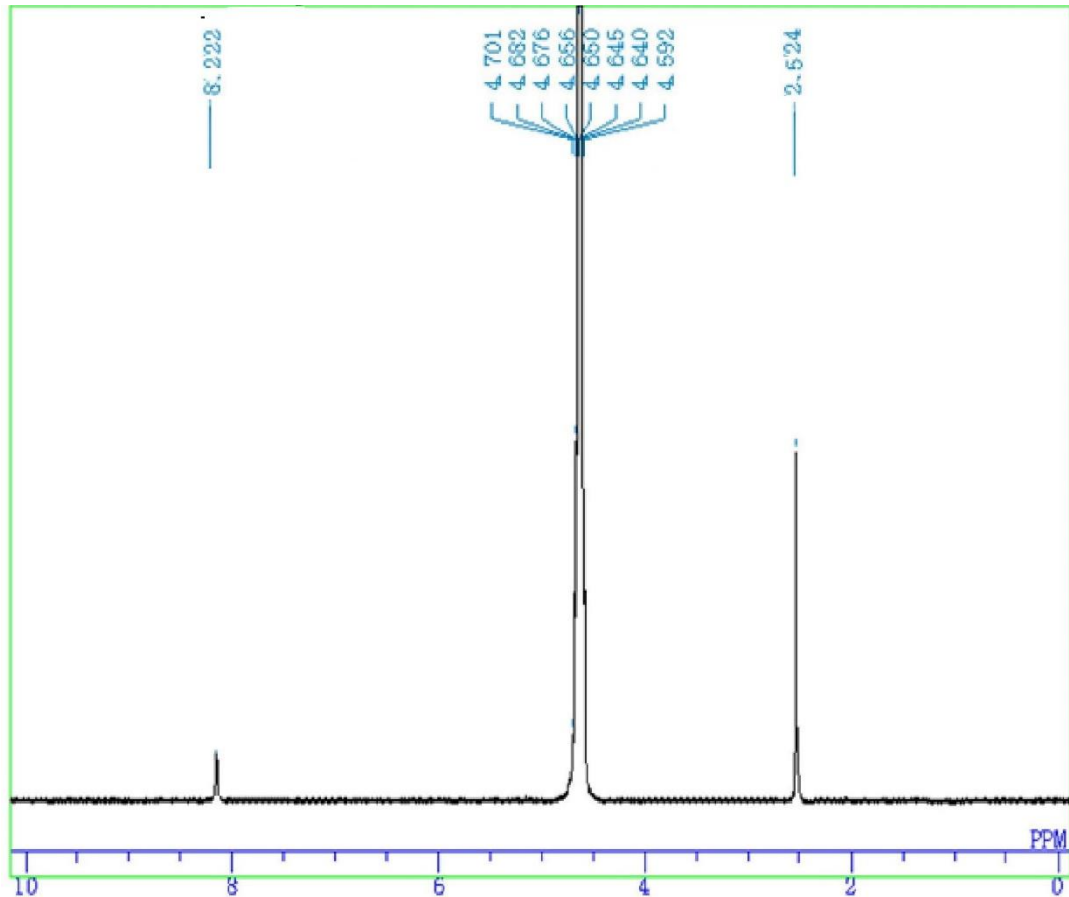


Fig. 2

¹³C NMR spectra of 2, 4, 6-Tris (di-acetamido)-1, 3 diazine 3

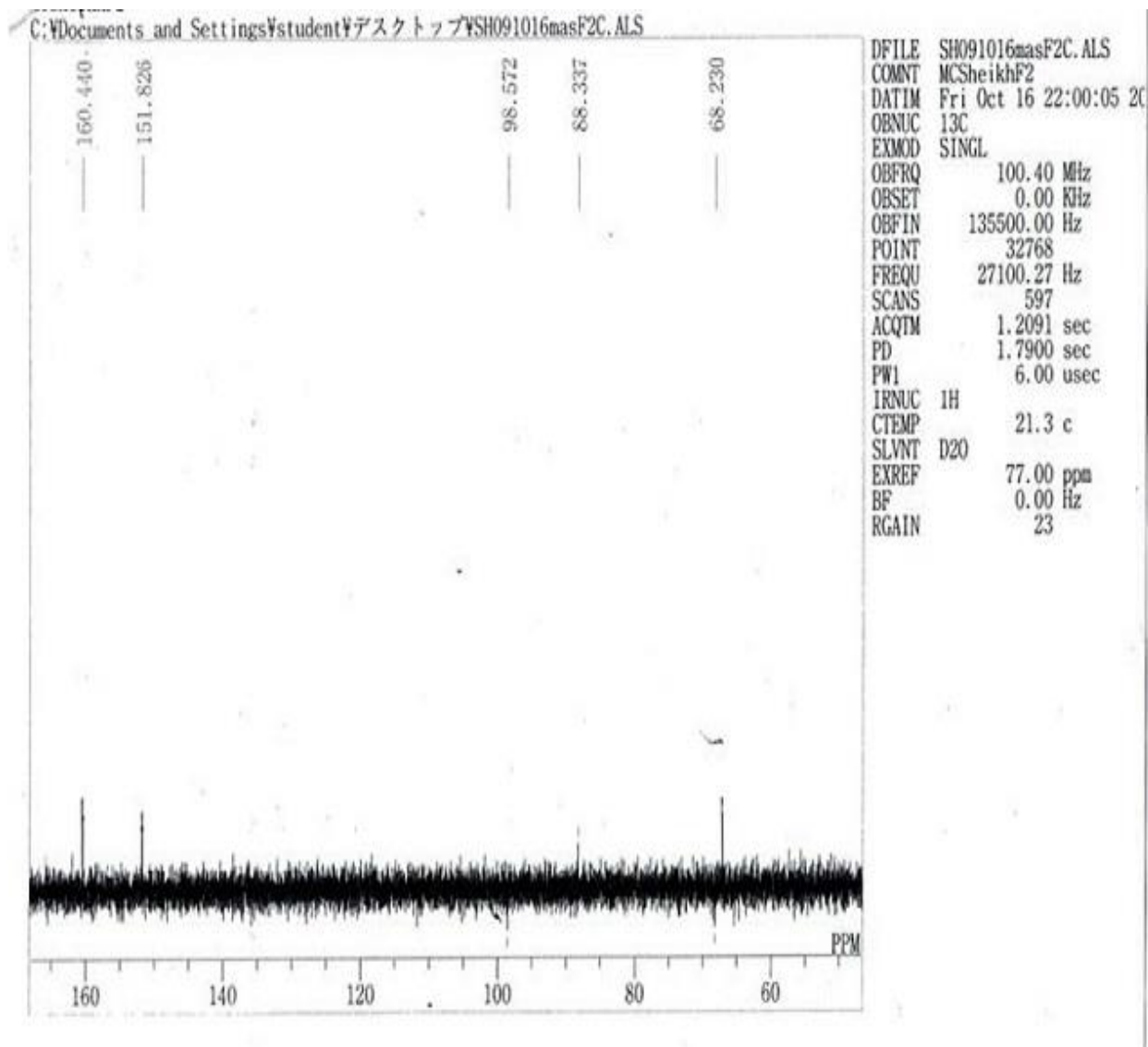


Fig. 3