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Synthesis of Triazine-Based Dendrimer Assisted Pd-Cu Bimetallic Nanoparticles and Catalytic Activity for C-C Coupling Reactions

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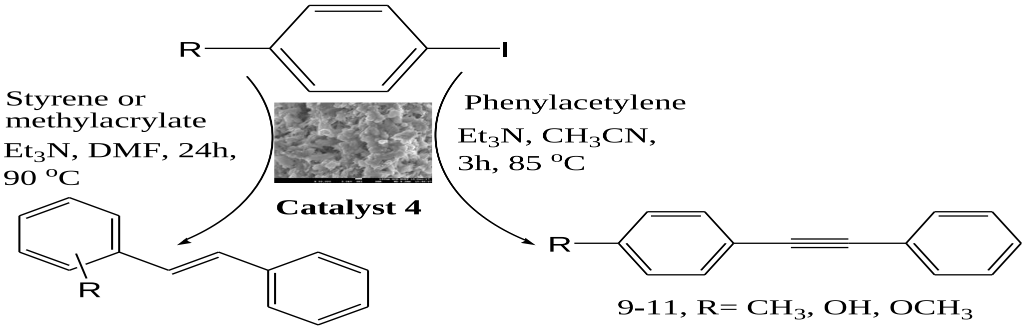
Abstract Triazine-based dendrimer assisted Pd-Cu bimetallic nanoparticles (NPs) were synthesized through the sequential loading method from the dendrimer which was prepared by the reaction of 2,4,6-triamino-1,3,5-triazine with benzoyl chloride in DMF at 80°C at 8 hrs. The dendrimer was characterized by IR, NMR, and elemental analysis. SEM and EDX of Pd-Cu bimetallic NPs demonstrated nanosized spherical surface morphology as well as the existence of palladium ions, and copper ions in the nanoparticles whereas TGA and DSC confirmed good thermal stability of the nanoparticles, in addition, XRD data and the analysis of TEM revealed the average 18.50 nm nano shape FCC structure of the particles. These NPs were found to be the effective heterogeneous a catalyst for the C-C cross-coupling reactions such as Heck, Sonogashira in excellent yields. The high stability, reusability, and heterogeneity of recovered catalyst was also observed by further analysis (SEM, EDX, XRD, TEM and leaching study).



16-18, R= *O*-CH_3, *P*-OH, *P*-OCH_3

9-11, R= CH_3, OH, OCH_3

Cat. 4 = Pd-Cu bimetallic nanoparticle

Keywords Bimetallic nanoparticles (NPs), Triazine, Dendrimer, phenylacetylene, Heck and Sonogashira reaction

1. Introduction

Bimetallic nanoparticles, composed of two different metals, often display stepped forward catalytic performances and applications in numerous industrial processes, on the whole in fuel industries or environmental catalytic approaches, and more recently in C–C cross-coupling reactions [1]. Bimetallic catalysts constitute an interesting magnificence of catalysts due to the fact one metal can tune and/or alter the catalytic properties of the alternative because of the electronic and structural interactions [2]. On the other hand, several metal-catalyzed cross-coupling reactions require the presence of another metal either as a co-catalyst or to help manipulate the general manner such as Sonogashira reaction among an aryl halide and terminal alkynes calls for an aggregate of Pd and Cu as the catalysts, in which Cu+ plays a catalytic role in shifting the alkynyl groups to Pd [3]. The splendid redox properties of the Pd/Cu method are due to the electron donor and acceptor individual of Cu and Pd, respectively [4,5]. The prominent “Cu-effect” within the Pd-catalyzed cross-coupling reaction [6,7] has enhanced the improvement of several heterogeneous bimetallic NPs the use of commercially to be had insoluble polymeric help and has been used efficaciously in various cross-coupling reactions [8-14]. The main disadvantages of

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the Sonogashira reaction has been idea-about to rise up from the high price of palladium catalyst and its low reusability, the residual contamination of a poisonous palladium species (the main downside in the synthesis of pharmaceuticals), and consequently the utilization of copper salt sensitive to oxygen that elicited a side reaction, i.e., oxidative homocoupling of the alkyne substrates (the so-referred to as Glaser-coupling reaction) [15-17]. In addition, many improved protocols for Suzuki–Miyaura [18-20] and Heck [21] couplings have been reported with the use of bimetallic Pd-Cu NPs. Our research has been centered at the event of an additional green, extra price, and additional simply formulated catalyst which can be active enough to perform the carbon-carbon coupling reaction under moderate conditions.

Furthermore, Bimetallic DENs used as catalysts have discovered numerous crucial applications, and research pursuits have already progressed far beyond the improvement of the synthetic method to synthesize the designed dendrimer templated nanoparticles [22]. Because of the synthesis of DENs with the dendrimer as the template has the following benefits: (1) the products have for the most component an undistinguishable composition and shape since the dendrimers template themselves and construct properly-defined nanoparticle replicas; (2) the probabilities for the nanoparticles to agglomerate during the catalytic reactions are declined substantially as they're stabilized and encapsulated within the dendrimers; (3) the impact of the catalytic active nanoparticles in the reactions may be aided considering the fact that the most portions at the surface of the nanoparticles are unpassivated. That is due to the fact the combination of nanoparticles in the dendrimers is specially induced by means of steric outcomes; (4) the branches of the dendrimer will play a characteristic of being a selective gate to control the entrance of the substrate to the catalytic nanoparticles inside the dendrimers; and (5) the periphery functional portions of the dendrimer can be tailored to adjust the miscibility of the DENS with the continuous phase and in addition to help in connecting to the surfaces and different polymers [23-37].

However, to the great of our knowledge, there's less report to be had inside the literature for the synthesis of bimetallic NPs impregnated on triazine-based dendrimer and the exploration of their heterogeneous catalytic interest in cross-coupling reactions. Here we record the synthesis and characterization of a new elegance of heterogeneous Pd/Cu bimetallic dendrimer assisted that have proven efficient catalytic activity for the Heck and the Sonogashira cross-coupling reaction without using CuI as co-catalyst under phosphine-ligand-free conditions with high recyclability.

2. Materials and Methods

2.1. Materials

All reactions involving air- and moisture-sensitive conditions were carried out in a dry nitrogen atmosphere. Unless otherwise noted, all reagents were reagent grade, and were used without purification. Dehydrated DMF, DMSO, CH_3CN and THF were used as reaction solvent. These solvents were purchased from Aldrich and used as received. De-ionized water was used in the experiment where required. Analytical thin layer chromatography (TLC) was silica gel 60 F 254 coated on 25 TCC aluminum sheets (20 × 20 cm). Silica gel column chromatography separations were performed on silica gel 60 N (neutral, 40-100 μM). 2, 4, 6-triamino-1, 3, 5-triazine, benzoyl chloride and $CuCl_2.nH_2O$, $H_2N\text{-}NH_2.H_2O$, $PdCl_2$ were purchased from Aldrich and were directly used without further purification. K_2CO_3, NaOH, Cs_2CO_3, KOH, Na_2CO_3, Et_3N, K^tOBu (Sigma-Aldrich), and $MgSO_4$ (Sigma-Aldrich) and also in the coupling reactions, styrene, methyl acrylate phenylacetylene were used (Sigma-Aldrich).

2.2. Instrumentations

Melting points were determined by open capillary tubes by a melting point apparatus (Model BUCHI, B-540). The IR spectra were taken on a Shimadzu FTIR 8400S Fourier Transform. Infrared Spectrophotometer (400-4000 cm^{-1}) with KBr pellets. ^{1H} NMR and ^{13}C NMR spectra were recorded at 500 MHz and 100 MHz, respectively, on a JEOL, JNM-ECZ 500 MHz instrument and also ^1H NMR (400 MHz, Bruker) and ^{13}C NMR (100 MHz, Bruker). Chemical shifts were given relative to TMS. Mass spectra (MS) were measured by using AXIMA-CFR, Shimadzu/Kratos TOF Mass spectrometer. Elemental analyses were carried out with a Fisons EA 1108 CHNS-O apparatus. Analytical thin layer chromatography (TLC) was silica gel 60 F 254 coated on 25 TCC aluminum sheets (20 × 20 cm). Silica gel column chromatography separations were performed on silica gel 60 N (neutral, 40-100 μM). The thermal behavior of Pd/Cu NP was determined by a thermo gravimetric analyzer (NETZSCH STA 449F3) from 26℃ to 600℃. TG and DSC data were obtained under a nitrogen atmosphere by using aluminum oxide crucible at a heating rate of 10 k/min and at a flow rate of 40 and 60 ml/min. SEM and EDX of Pd/Cu bimetallodendrimer NPs 4 were taken by the JEOL-JSM-7600F. Particle size and phase identification were performed with a PANANALYTICAL x-ray diffractometer. TEM analysis was performed by Philips CM12 transmission electron microscope (operating at 200 KeV). The leaching study was done by Perkin Elmer ELAN DRC E ICP/MS.

2.3. Synthesis

Synthesis of 2, 4, 6-Tris (di-benzamido)-1, 3, 5-Triazine 3

Benzoyl chloride **2** (1.45 g, 9.54 mmol) was in turn added to a solution of 2, 4, 6-triamino-1, 3, 5-Triazine **1** (0.2 g, 1.59 mmol) in DMF (10 ml). The solution was degassed and stirred for 8 hrs at 80 ^oC under a nitrogen atmosphere. The advancement of the reaction was checked by TLC. At the start of the reaction, the reactant mixture was a clear solution and progressively it was transformed into white solid. When the reaction was completed, distilled water was added and the white solid product was separated, washed with sodium bicarbonate solution by using Buchner funnel in addition as finally refined by re-crystallization with ethyl alcohol and was obtained the preferred product 3.

White crystalline solid, m. p. 195-197 °C, odorless and 95% of yield. IR (KBr): δ max 3052.19, 2976.31, 1712.20, 1615.69, 1415.69, 1360.20 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.45 (t, 12H, Ar-H, *J* =7.5 Hz), 7.62 (t, 6H, Ar-H, *J*=6.5 Hz), 8.15 (d, 12H, Ar-H, *J*=7.0 Hz).^{13}C NMR (100 MHz, $CDCl_3$): δ 128.60, 129.46, 130.34, 133.94, 144.75 and 172.77 ppm. Anal. Calcd. (%) for $C_{45}N_6H_{30}O_6$: C, 71.99; H, 4.03; N, 11.19. Found: C, 71.90; H, 4.00; N, 11.10.

Synthesis of dendrimer templated Pd-Cu bimetallic nanoparticles 4

The effective development of a diversity of the synthetic techniques for the preparation of bimetallic dendrimer nanocatalysts is key advances in recent years. Among the various methods, mostly three routes of preparing the bimetallic dendrimer nanocatalysts are commonly used which includes co-complexing, partial displacement, and sequential reduction [38]. Here we followed the sequential reduction method to synthesize Cu/Pd nanoparticles. The dendrimer of 0.113 g 2, 4, 6-Tris (di-benzamido)-1, 3, 5-Triazine 3 (0.15 mmol), 0.00095 g $PdCl_2$, NH_2-NH_2.H_2O (1.5 mmol) was stirred in CH_3CN (10 mL) in a round bottom flask at 85℃ for 1 h. Then 0.025 g $CuCl_2$.$2H_2O$ (Pd-Cu weight ratio of 1:26) and NH_2-NH_2.H_2O were added to the reaction mixture dropwise with a little more than the equivalent amount of copper salt. The NaOH solution (0.3 M) was slowly added to the reaction mixture to maintain pH 10 and the suspension was stirred vigorously for 2.5 hours using a magnetic stirring bar at 100℃. After settling the reaction mixture, the black residue was obtained. The residue was filtered after centrifugation (4000 r.p.m. for 10 min) of the reaction mixture, washed with double distilled water and acetone and dried overnight in an oven at 130℃.

Catalytic performance of Pd-Cu bimetallic nanoparticle 4 for Sonogashira Reaction

General method: A Round Bottom flask was charged with 1.0 mmol of aryl iodide, 1.2 mmol of phenylacetylene, 1.5 mol % of Pd-Cu bimetallic NP 4, Et_3N (2 mL) as a base and CH_3CN (5 mL) as a solvent under the nitrogen atmosphere. The mixture was then stirred at 85℃ for 3 hours, and the reaction was checked by TLC. After the reaction was completed, the mixture was extracted with $CHCl_3$ (15 mL). The organic layer dried with $MgSO_4$ was separated, filtered and concentrated to supply crude product purified by silica gel column chromatography using ethyl acetate and hexane (6:1) to produce preferred pure products under reduced pressure.

Synthesis of 1-(2-p-tolylethynyl)benzene 9, [38]

Solid colorless product was obtained, yield: 91%, m.p. 71-73℃ (lit. 71℃); ^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 10, [38]

Solid product was obtained, yield: 95%, m.p. 124-126℃; ^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.

Synthesis of 1-(2-(4-methoxyphenyl)ethynyl)benzene 11

Solid white product was obtained, yield: 97 %, m.p. 57-59℃ (lit. 57℃); ^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.

Catalytic performance of Pd-Cu bimetallic nanoparticle 4 for Heck Reaction

In an R.B flask under nitrogen atmosphere, a mixture of aryl iodide (1 mmol) with styrene or methylacrylate (1.2 mmol), Pd-Cu bimetallic nanoparticle 4 (1.5 mol %) and triethylamine (1.2 mL) was stirred in DMF (5 mL). The solution was heated for 24 hours at 90℃. The progress of the reaction was detected with the TLC chromatography (n-hexane/ethyl acetate 1:1). The reaction mixture was evaporated to dryness under reduced pressure after the desired transformation of the reaction was obtained and the residue was extracted with chloroform. The chloroform extract was washed with distilled water, dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure and purified by silica gel column chromatography using ethyl acetate and hexane (3:1) to provide the desired products.

Synthesis of (E)-Methyl 3-o-tolylacrylate 16

White solid product, Yield: 96%, IR (KBr): δ max 2950.32, 1722.32, 1639.35, 1267.27, 1220.20, 1172.21, 980.30, 764.27. ^1H NMR (400 MHz, $CDCl_3$), δ 2.48 (s, 3H); 3.84 (s, 3H); 6.46 (d, 1H, *J*=16.0 Hz); 7.35-7.68 (m, 3H); 7.83-7.98 (m, 1H); 8.33 (d, *J*=8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.66, 51.56, 118.46, 126.17, 126.61, 130.11, 130.75, 133.56, 137.66, 142.46, 167.36.

Synthesis of trans stilbene 17, [39]

White solid product, Yield: 94%, Colourless Solid was found and melting point was 74-76℃, IR (KBr): δ max 3027, 1600.35, 1496, 1452.24, 1319.36, 1267.27, 962.35, 909.25, 733.74. ^1H NMR (400 MHz, $CDCl_3$), δ 7.02 (s, 2 H), 7.35 (dd, 1 H, *J*=1.2 Hz, 7.2 Hz), 7.43 (dd, 4 H, *J*=9.2 Hz, 7.2 Hz), 7.63 (dd, 4H, *J*=1.2 Hz, 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 126.56, 127.61, 128.11, 128.85, 137.46.

Synthesis of (E)-methyl 3-(4-methoxyphenyl)acrylate 18

White solid product, yield: 97%, m. p. 135-137 °C, IR (KBr): δ max 2960.74, 1601.35, 1511.24, 1319.35, 1251.27, 1179.75, 1031.15, 966.36, 812.25. ^{1}H NMR (400 MHz, $CDCl_3$), δ 3.88 (s, 3H); 6.37 (d, 2H, *J*=8.0 Hz); 6.57 (d, 1H, *J*=16 Hz); 6.86 (d, 1 H, *J*=16 Hz); 6.39-6.29 (m, 1H); 7.58 (t, 2H, *J*=7.2 Hz); 7.94 (t, 4 H, *J*=9.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.31, 114.29, 126.32, 126.76, 127.26, 127.86, 128.33, 128.77, 130.22, 137.34, 159.40.

3. Results and Discussion

3.1. Synthesis and Characterization

Dendrimer **3** was directly synthesized by a reaction of 2, 4, 6-triamino-1, 3, 5-Triazine **1** (1.59 mmol) with benzoyl chloride **2** (9.54 mmol) in anhydrous DMF at 80°C for 8 h in a nitrogen atmosphere (Scheme 1). The movement of the reaction was detected by thin layer chromatography (TLC) and after complete transformation of the reaction, the dendrimerized product was found by purification of the solid reaction mixture with recrystallization. The product was analyzed by IR, ^{1}H NMR, ^{13}C NMR (S1-S3 in the supporting information).

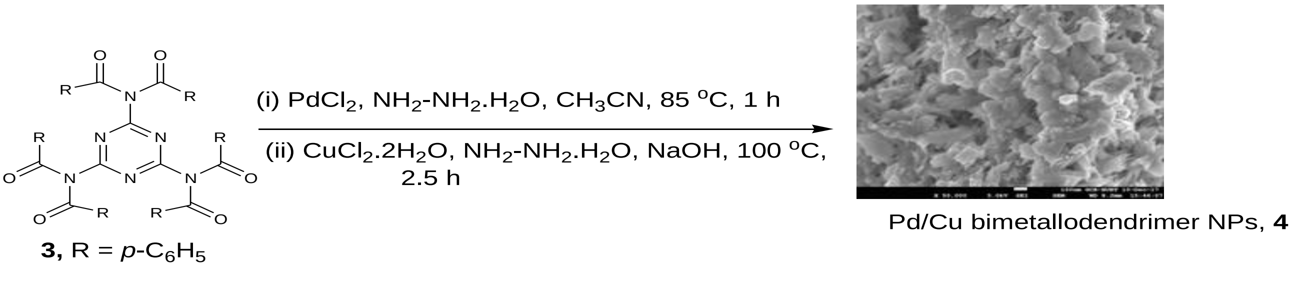
IR peaks revealed the existence of required compound 3 groups. The presence of peaks in the range of 3000-3100 cm^{-1} and 1680-1760 cm^{-1} suggested the C-H, C= O groups respectively, while the C= N group was directed by a strong absorption band at 1580-1620 cm^{-1}. The peaks of 1300-1360 cm^{-1} and 1250-1335 cm^{-1} respectively confirmed the presence of groups of C= C and C-N. Here it is noteworthy that in the region around 3400–3250 cm^{-1} there is no band for N-H specifying that 1° amino group of triaminotriazine was converted into 3° amido group. The selected dendrimer 3 was identified in ^{1}H NMR and ^{13}C NMR spectra. There is no NH or NH_2 group ^{1}H NMR peak, which was further established the structure of compound **3**.

The triazine based dendrimer assisted Pd/Cu bimetallic nanoparticle 4 was synthesized by sequential loading method (Scheme 2) and also characterized by various physicochemical techniques including SEM, EDX, XRD, TGA and DSC analysis. The SEM images of the Pd/Cu bimetallic nanoparticle 4 displays the spherical size of the particle and also dendritic leaf shape (Fig. 1).

The existence of Palladium and Copper was identified from EDX analysis, and Copper was 64.78% of mass and Palladium was 2.54% of mass of synthesized NPs (Fig. 2). The EDX results also indicted that the sequential loading method is very effective for preparing the Pd/Cu bimetallic nanoparticle in which Pd/Cu ratio is almost same used Pd/Cu ratio. The particle structures of Pd/Cu bimetallic nanoparticle were further characterized by the XRD patterns (Fig. 3).

The three basic peaks at 2 theta$^{(o)}$ values of 43.20, 50.60, and 74.20 degrees corresponding to (111), (200), and (220) copper planes were found respectively, characterizing the formation of FCC copper nanoparticles and correlated with standard JCPDS powder diffraction card, Copper file no (04—0836) [40], while another three basic peaks at 2 theta$^{(o)}$ values of 40.10 and 46.10 were observed those characterized the formation of FCC Palladium nanoparticle and compared with standard powder diffraction card of JCPDS, Palladium file no (46—1043) [41], (Fig. 3). Consequently, these results were revealed in the Pd-Cu bimetallic nanoparticle 4 FCC structure. Pd-Cu bimetallic nanoparticle 4 XRD patterns indicate the average 18.50 nm particle size calculated by Debye-Scherrer formula.

Scheme 1. Synthesis of dendrimer **3**



Scheme 2. Synthesis of Pd-Cu bimetallic nanoparticle **4**

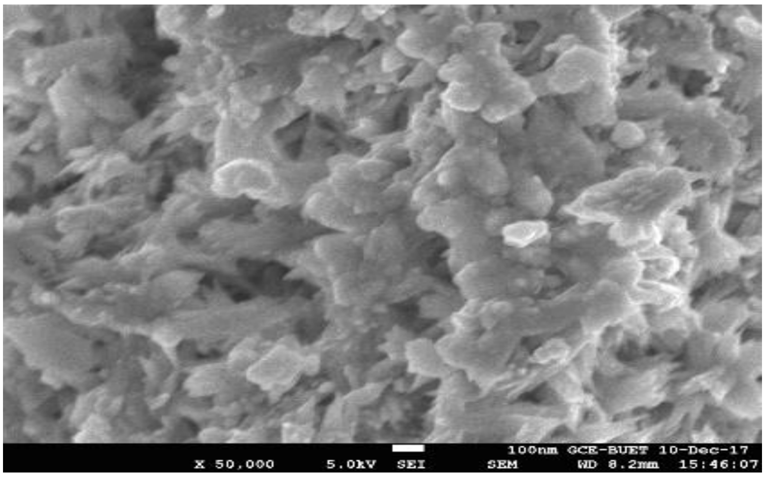
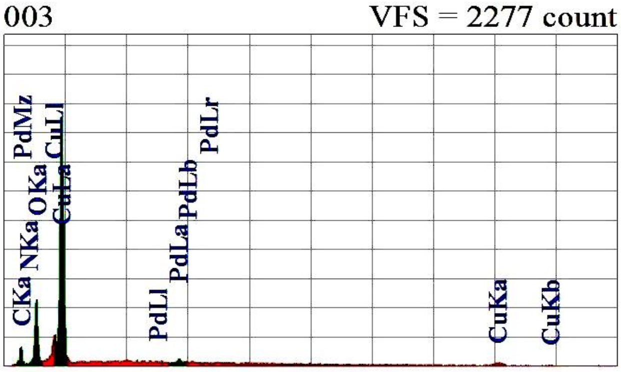


Figure 1. SEM images of the nanoparticle 4



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Acquisition Parameter
Instrument    : 7600F
Acc. Voltage  : 10.0 kV
Probe Current: 1.00000 nA
PHA mode      : T3
Real Time     : 30.26 sec
Live Time     : 30.00 sec
Dead Time     : 0 %
Counting Rate: 1020 cps
Energy Range :  0 - 20 ke\
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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.0836
Element         (keV)    Mass%    Sigma    Atom%  Compound    Mass%  Cation          K
 C K*           0.277    13.42     0.26    33.19                                5.2668
 N K*           0.392     0.26     0.11     0.56                                0.2934
 O K            0.525    18.99     0.34    35.26                               22.0098
Cu L            0.930    64.78     0.66    30.28                               70.0941
Pd L*           2.838     2.54     0.29     0.71                                2.3359
Total                   100.00            100.00
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Figure 2. EDX analysis of the nanoparticle **4**

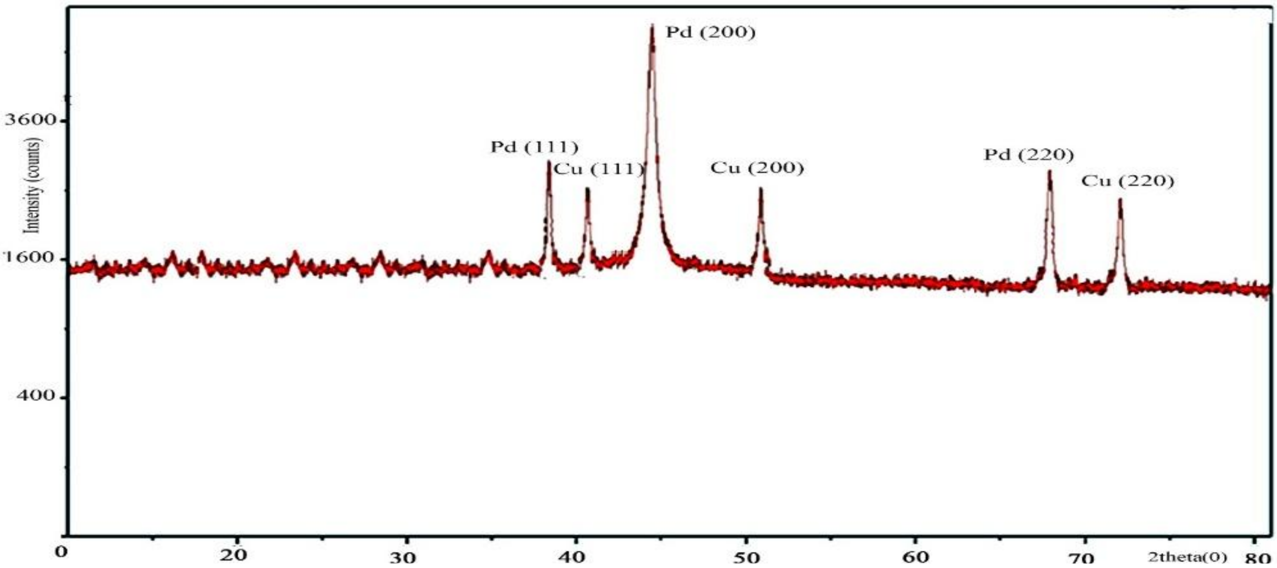


Figure 3. XRD of Pd-Cu bimetallic nanoparticle **4**

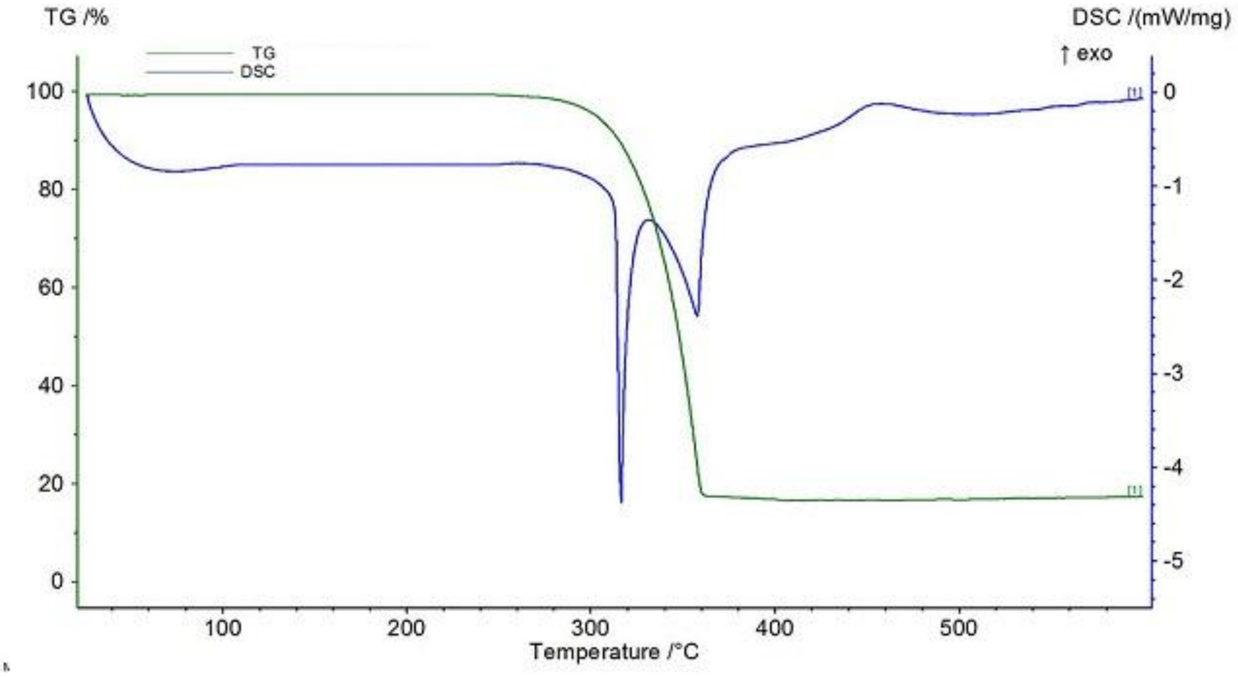


Figure 4. DSC& TGA of Pd-Cu bimetallic nanoparticle **4**

TEM was used to determine the size distribution and percentage of the average size of the synthesized nanoparticles. The TEM images of pure and recovered bimetallic Pd-Cu NPs 4 have been shown in Figure 8 (a, b). The size distribution of the synthesized bimetallic Pd-Cu NPs 4 was found in the range 17–20 nm (Figure 8.a). The average particle size was observed at 18.50 nm from TEM analysis that supported the XRD results calculated by Debye-Scherrer formula.

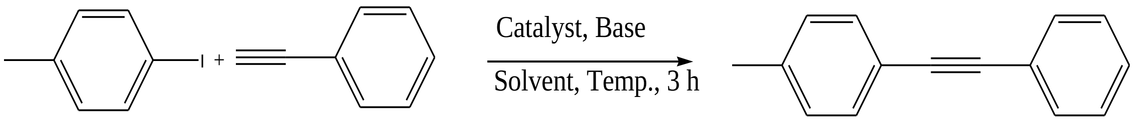
Thermal constancy is a key factor in maintaining the activity of catalysts in elongated reaction time. For industrial applications that require high thermal action, thermally stable catalysts are solely important. TG and DSC techniques examined the thermal stability of the Pd-Cu bimetallic nanoparticle 4 at temperatures between 26℃ and 600℃ in the nitrogen atmosphere (Fig. 4). The content of a particular nanoparticle 4 component changes with its composition and structure and is determined in the thermogravimetric graph based on the weight loss of these components. The actual weight loss of compound 4 from 315℃ to 360℃ from the TG curve was recorded. The DSC values of the compound were almost similar to those of TG values. In the DSC curve of Pd / Cu bimetallic nanoparticle 4, the sharp endothermic curve above 315℃ indicated the melting point. The final decomposition step had shown ash residue of the compound 17.50%.

3.2. Catalytic Performance of Pd/Cu Bimetallic Nanoparticle 4 in Sonogashira and Heck Reaction

In the case of Pd-Cu bimetallic NPS, the synergistic effect between palladium and copper showed astonishing efficiency for the various carbon-carbon cross-coupling reactions [42]. In the synergistic mechanism, the energy gap between HOMO and LUMO comes closer by two metal catalyst stimulating both nucleophile and electrophile simultaneously [43].

The catalytic activity of synthesized Pd-Cu bimetallic nanoparticle 4 catalyst was studied in Sonogashira alkynylation reaction of aryl halides with terminal alkynes.

A typical reaction between the reaction of 4-iodotoluene and phenylacetylene and the impact of various factors along with the solvent, reaction temperature and catalyst loading was studied due to the determination of optimized reaction conditions. This reaction gave very low yields with water as the solvent and distinctive bases together with Na_2CO_3, K_2CO_3, t-BuOK, Et_3N, and K_3PO_4 (Table 1, entries 1–5) in the presence of 0.5 mol % Pd-Cu bimetallic NP 4. The yields were advanced with the help of changing the solvent to DMF and using different bases (Table 1, entries 6–10) in the presence of a 1 mol % catalyst. Curiously, by increasing the temperature of the reaction to 85℃ and catalyst to 1.5 mol %, the best results with a yield of 91% were obtained by using Et_3N as a base, CH_3CN as a solvent (Table 1, entry 11). However, with a view to confirming approximately catalyst loading, this reaction was performed in the presence of 2.0 mol % and 1.0 mol % of catalyst 4 and results showed the formation of preferred products in 92% and 80% yield respectively (Table 1, entries 12 and 13). For this reason, we selected 1.5 mol % of catalyst, Et_3N as base and CH_3CN as solvent at 85 ℃ at 3h for maximum efficiency and optimized reaction conditions (Table 1, Entry 11).



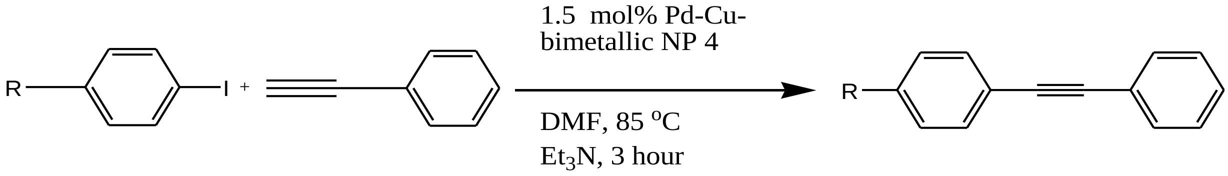
Scheme 3. Optimization of Pd-Cu bimetallic nanoparticle 4 catalyzed between 4-iodotoluene and phenylacetylene

Table 1. Optimization of reaction condition for the Sonogashira coupling of 4-iodotolouene and phenylacetylene catalyzed by Pd-Cu bimetallic nanoparticle 4

Entry	Cat (mol%)	Base	Solvent	Temp. (°C)	Yield (%)
1	0.5	K_2CO_3	H_2O	60	10
2	0.5	K_2CO_3	H_2O	60	8
3	0.5	*t*-BuOK	H_2O	60	11
4	0.5	$N(Et)_3$	H_2O	60	10
5	0.5	$K_3PO_4{\cdot}3H_2O$	H_2O	60	8
7	1.0	K_2CO_3	DMF	60	20
8	1.0	*t*-BuOK	DMF	60	30
9	1.0	Et_3N	DMF	60	40
10	1.0	$K_3PO_4{\cdot}3H_2O$	DMF	60	36
11	1.5	Et_3N	CH_3CN	85	91
12	2.0	Et_3N	CH_3CN	85	92
13	1.0	Et_3N	CH_3CN	85	80

Reaction conditions: 4-iodotolouene (1mmol), phenylacetylene (1.2 mmol), catalyst (1.5 mol%), base (1.2 mmol), solvent (5 mL), 85 ^{o}C, 3h, under nitrogen atmosphere, Yield% was calculated based on aryl halide.

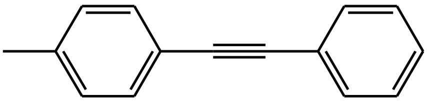
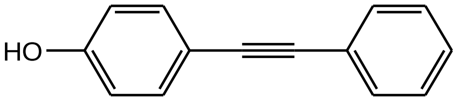
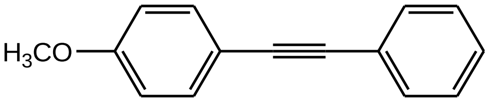
Scheme 4. Sonogashira coupling between differents aryl halides and phenylacetylene catalyzed by Pd-Cu NPs 4.



5-7 **8** **9-11**

Scheme 4

Table 2. Sonogashira coupling reaction of different aryl chlorides with phenylacetylene catalyzed by Pd-Cu bimetallic NP 4

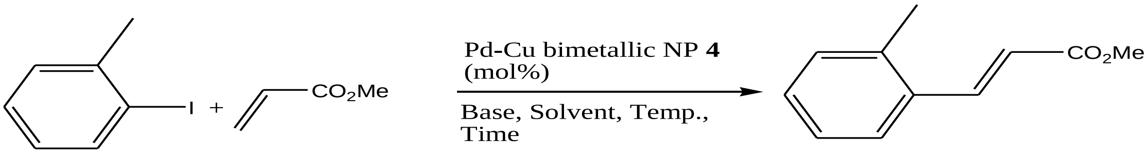
Entry	R	Product	Yield%
1	4, CH_3	8 	91
2	5, OH	9 	95
3	6, OCH_3	10 	97

Yield% was calculated based on aryl halide.

We tend to explore the overall activity of the catalytic system used to catalyze the reactions with three different types of aryl iodide and sundry terminal acetylene (Table 2) in addition to studies. The selectivity of the catalyst 4 was another vital advantage. NMR spectra showed excessive purity of catalytic system products. It was not found the formation of Glaser-type alkyne homo-coupling products.

Likewise, due to optimization the Heck reaction conditions, a series of reactions under various combinations of bases, solvents, and temperatures, using Pd-Cu bimetallic NP 4 as catalyst.

The coupling product was not produced when the coupling reaction was occurred using 1.5 mol% Pd-Cu bimetallic NP 4 as a catalyst, methyl acrylate (1.2 mmol) and o-iodo toluene (1 mmol) in CH_3CN, DMF or DMSO (5 mL) and at temperature (room temperature to 40℃) in the presence of NaOH, Na_2CO_3 or KOH, K_2CO_3 (1.2 equivalent) at 24 h (Scheme 5, Table 3, entries 1-5). Fascinatingly, in the presence of Et_3N and DMF at 60℃ at 20 h, the reaction showed the progress of 50 % yield with 2.0 mol % of catalyst 4. (Table 3, entry 6). Furthermore, the use of other bases containing K_2CO_3, KO^tBu and in the presence of the solvents, methanol, toluene or DMF at 90℃, the coupling products were found above 60% yield (Table 3, entries 7-9). The best result was observed whilst 1.5 mol% of the catalytic system 4 and Et_3N, as a base, and solvent DMF was used under the nitrogen atmosphere at 90℃ at 24 h for Heck coupling reaction (Table 3, entry 10). A wide variety of olefins and different aryl iodides were selected for cross-coupling to produce the corresponding 1, 2-disubstituted olefins under these optimized Heck reaction conditions. (Table 4, entries 1-3)



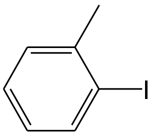
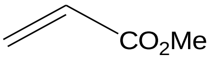
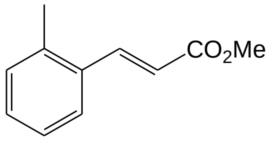
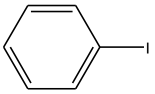
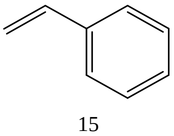
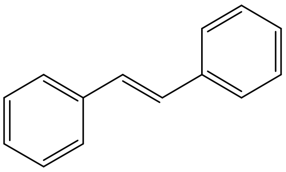
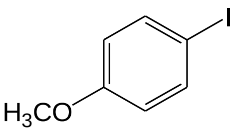
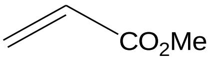
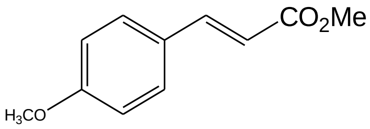
Scheme 5. Optimization of the Pd-Cu bimetallic NP 4 catalyzed Heck reaction between *o*-iodo toluene and methyl acrylate

Table 3. Optimization of the Pd-Cu bimetallic NP 4 catalyzed Heck reaction between *o*-iodo toluene and methyl acrylate

Entry	Time (h)	Base	Temp (℃)	Solvent	Catalyst, 3 (mol%)	Yield (%)
1	24	NaOH	RT	CH_3CN	1.5	-
2	24	Na_2CO_3	RT	DMSO	1.5	-
3	24	KOH	RT	DMF	1.5	-
4	24	KOH	40	CH_3CN	1.5	-
5	24	K_2CO_3	40	DMSO	1.5	-
6	20	Et_3N	60	DMF	2.0	50
7	24	K_2CO_3	90	CH_3OH	1.5	60
8	26	KO^tBu	90	$CH_3C_6H_5$	1.5	70
9	24	K_2CO_3	90	DMF	1.5	75
10	24	Et_3N	90	DMF	1.5	90

Reaction conditions: *o*-iodo toluene (1 mmol) and methyl acrylate (1.2 mmol), base (1.2 mmol), 24 hours, Temp. 90 °C, Yields% was calculated on the basis of *o*-iodo toluene.

Table 4. Heck coupling reaction of different aryl chlorides with different olefins catalyzed by Pd-Cu bimetallic NP 4

Entry	Aryl halides	Olefins	products	Yield%
1	 11	 14	 15	96
2	 12	 15	 16	94
3	 13	 14	 17	97

Yield% was calculated based on aryl iodides.

The Sonoghasira and Heck products were analyzed by IR, ^{1}HNMR, ^{13}CNMR as well as also all data were compared with authentic literature values [38, 39], (Figures S4-S17 in the supporting information).

3.3. Reusability and Stability of Recovered Pd-Cu Bimetallic NPs 4

The recyclability of Pd-Cu bimetallic NPs 4 to the coupling reaction between 4-iodotoluene and phenylacetylene was also studied (Table 5). After the reaction, black Pd-Cu bimetallic NP 4 was simply recovered from the reaction mixture after each catalytic run by centrifugation, filtration, thoroughly washed with water followed by acetone, and then dried under vacuum.

Table 5. Recyclability of Pd-Cu bimetallic NPs 4 of the coupling reaction between 4-iodotoluene and phenylacetylene

Entry	Run	Time (h)	Yield %
1	Fresh	3	98
2	1	3	96
3	2	3	94
4	3	3	90
5	4	3	88

The stability of structure and shape of the recovered Pd-Cu bimetallic NP 4 after five catalytic run was examined by SEM, EDX XRD and TEM analysis. Catalyst SEM images showed retained surface morphology (Fig. 5) as well as Pd (2.42%) and Cu (63.17%) from EDX analysis (Fig. 6) were found.

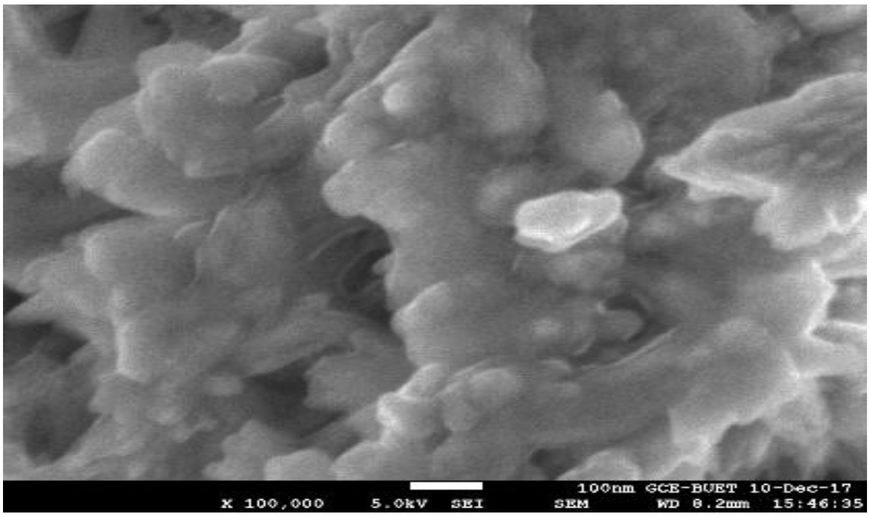
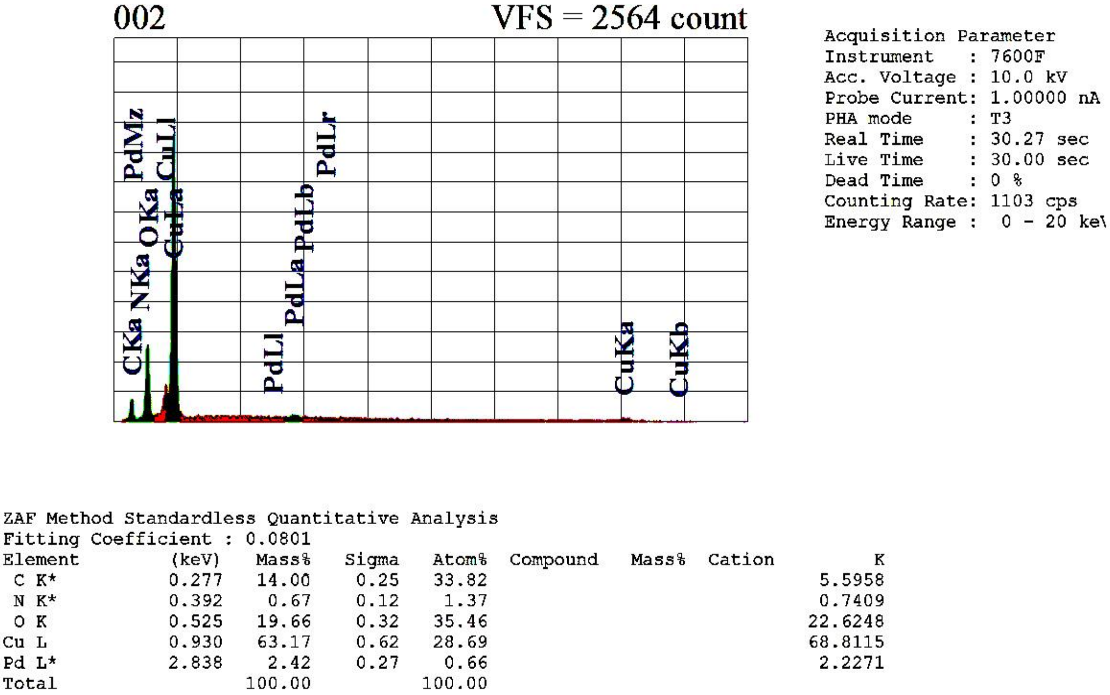


Figure 5. SEM image of the recovered NP 4



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Live Time     : 30.00 sec
Dead Time     : 0 %
Counting Rate: 1103 cps
Energy Range :  0 - 20 ke\
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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.0801
Element        (keV)   Mass%   Sigma   Atom%  Compound   Mass%  Cation          K
 C K*          0.277   14.00    0.25   33.82                               5.5958
 N K*          0.392    0.67    0.12    1.37                               0.7409
 O K           0.525   19.66    0.32   35.46                              22.6248
Cu L           0.930   63.17    0.62   28.69                              68.8115
Pd L*          2.838    2.42    0.27    0.66                               2.2271
Total                 100.00          100.00
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Figure 6. EDX analysis of the recovered NP 4

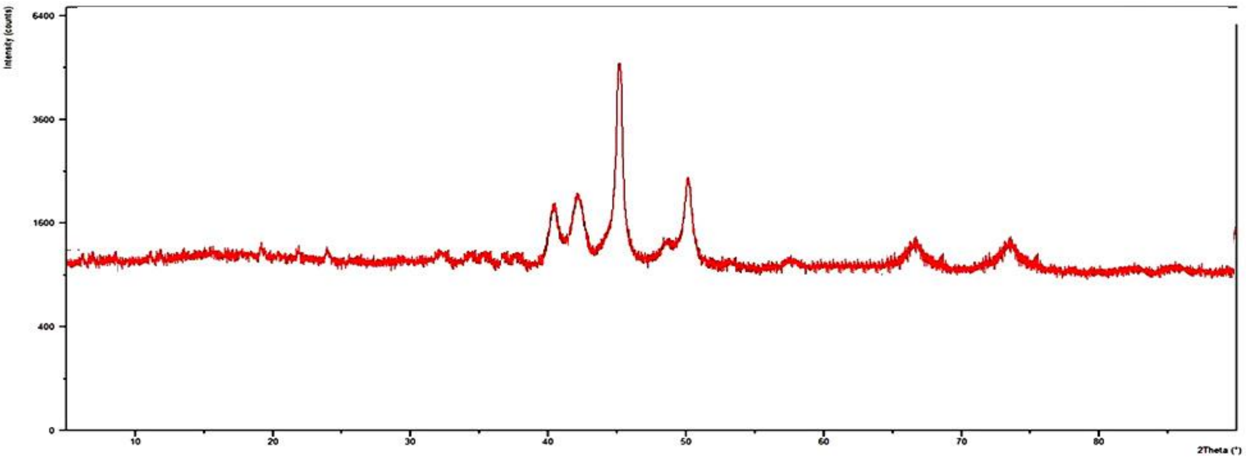


Figure 7. XRD analysis of the recovered NP 4

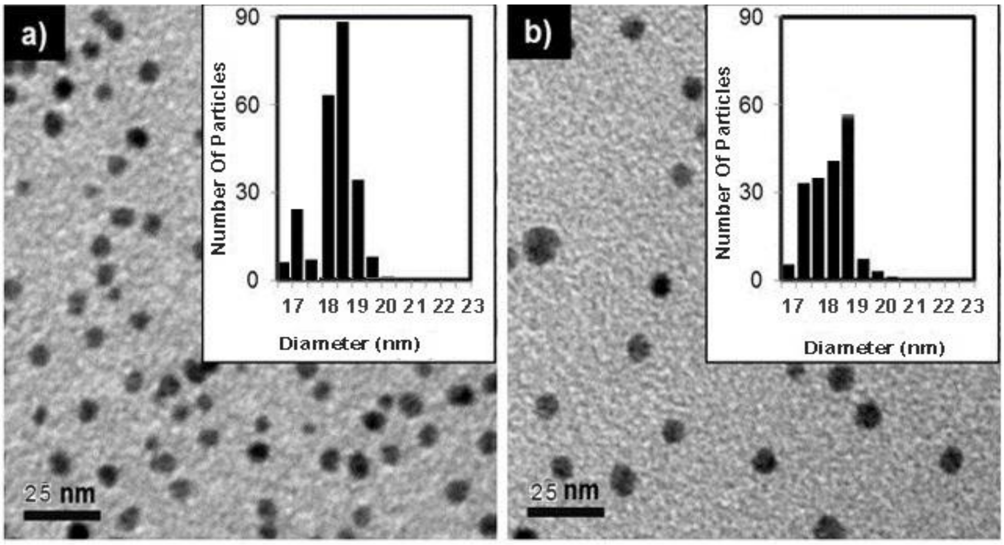


Figure 8. TEM analysis of the pure Pd-Cu bimetallic NPs 4 (Fig. 8a) and recovered NP 4 (Fig. 8b)

The peaks at 2 theta$^{(o)}$ values of 42.50, and 50.00 degrees corresponding to (111), and (200) planes of copper as well as 2 theta$^{(o)}$ values of 40.40, and 45.00 degrees corresponding to (111), (200) planes of Palladium were observed respectively and those confirmed that the FCC structure of the recovered nanoparticles 4 (Fig 7) and the TEM analysis results indicated the average particle size of the recovered catalyst 4 (Fig 8.b).

In addition, the catalyst's leaching study was performed due to checking heterogeneity. The reaction mixture was analyzed by ICP-MS after isolation of the catalyst and only 0.14 ppm of copper was observed in the reaction mixture. All the results of analysis proved the high stability and reusability of the catalyst 4.

4. Conclusions

In summary, we have synthesized triazine-based dendrimer assisted heterogeneous Palladium-Copper bimetallic nanoparticles by sequential loading method. Because of its low rate, however, most effective palladium with bimetallic nanocatalyst and fantastically valuable, recoverable, reusable, a small amount of palladium salt was used as copper salt. All analytical consequences (SEM, EDX, XRD, TG&DSC, TEM and leaching study) verify their heterogeneous catalytic activity in the carbon-carbon cross-coupling reaction such as Heck, Sonogashira and the synthetic route used to be also discovered to be phosphine ligand-free. Further applications of this heterogeneous catalytic activity in a number of C–C coupling reactions such as Stile, Suzuki coupling are being investigated.

ACKNOWLEDGMENTS

We thank the Ministry of Science and Technology, Dhaka, Bangladesh (National Science & Technology Fellowship Program 2018-2019, Ph.D. Fellowship, No- 39.00.0000.012. 002.03.18. 25, Code No-1260101-120005100-3821117) and the University of Engineering and Technology of Bangladesh (BUET), Dhaka, Bangladesh for providing financial support for our research work.

Supporting Information

IR spectra of 2, 4, 6-Tris (di-benzamido)-1, 3, 5-triazine 3

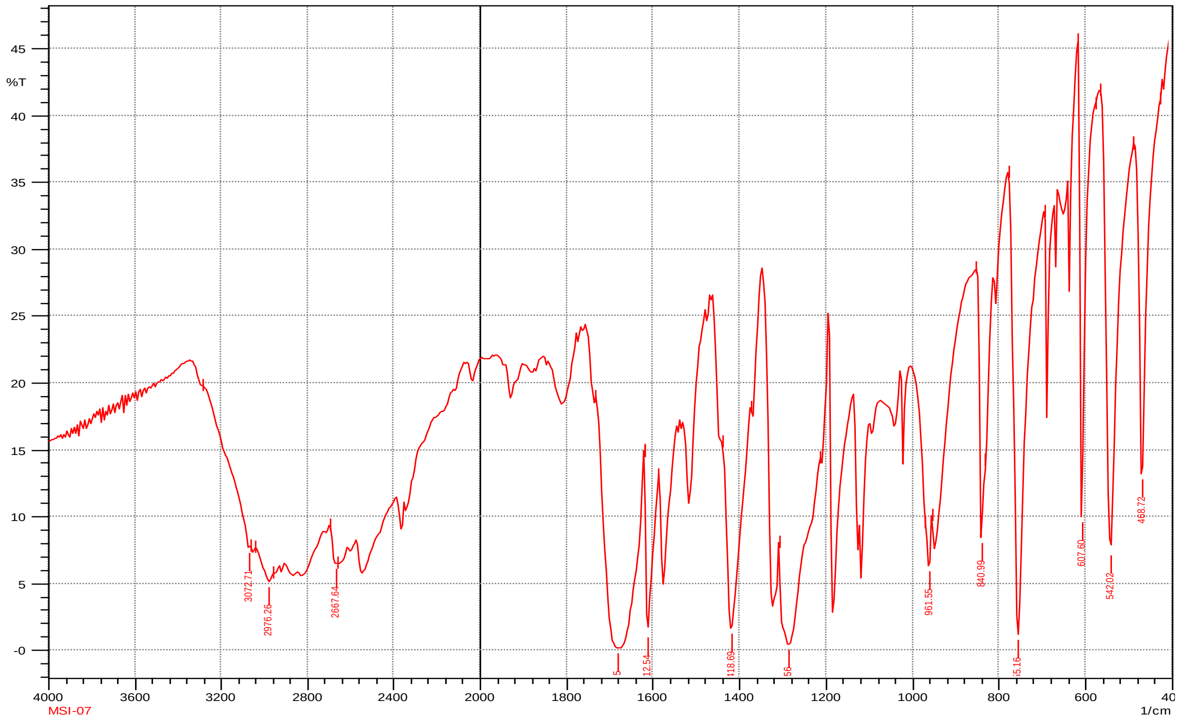


Figure S1

^{1}H NMR spectra of 2, 4, 6-Tris (di-benzamido)-1, 3, 5-Triazine 3

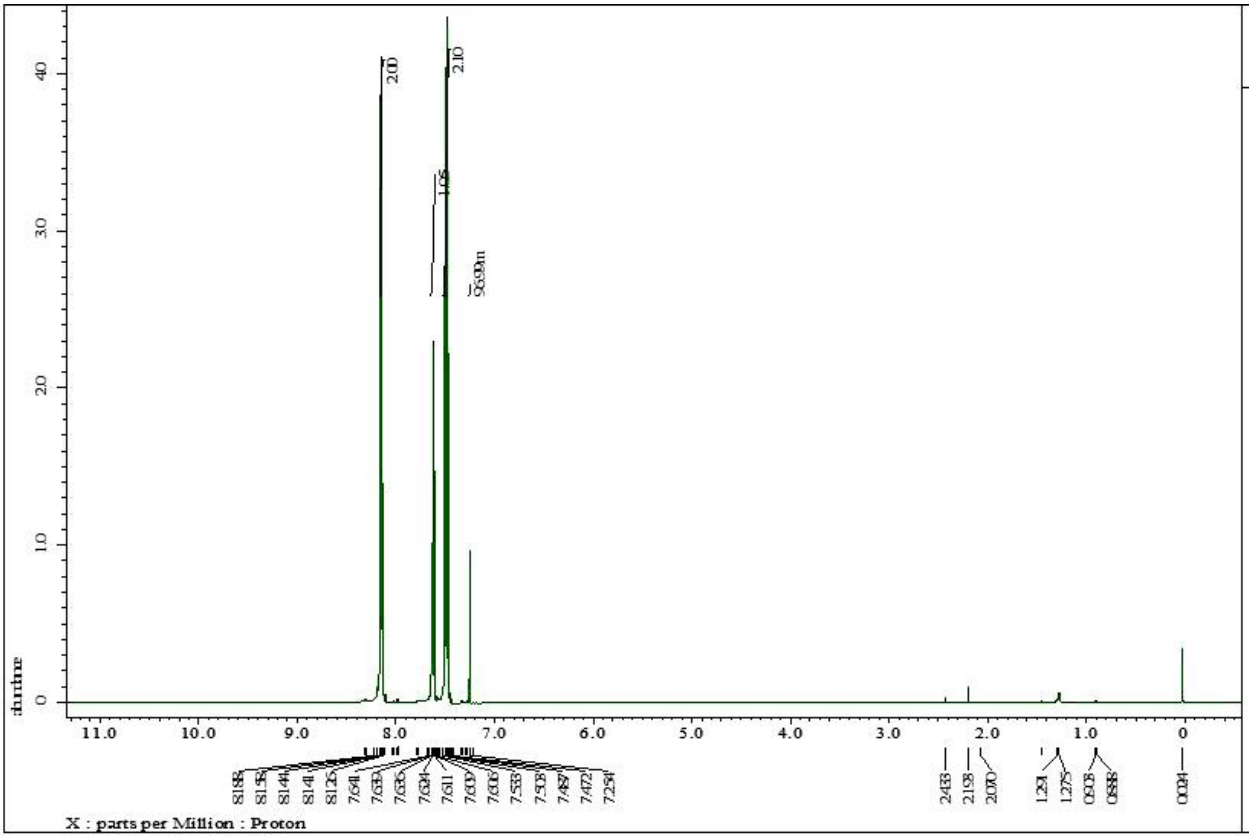


Figure S2

^{13}C NMR of 2, 4, 6-Tris (di-benzamido)-1, 3, 5-triazine 3

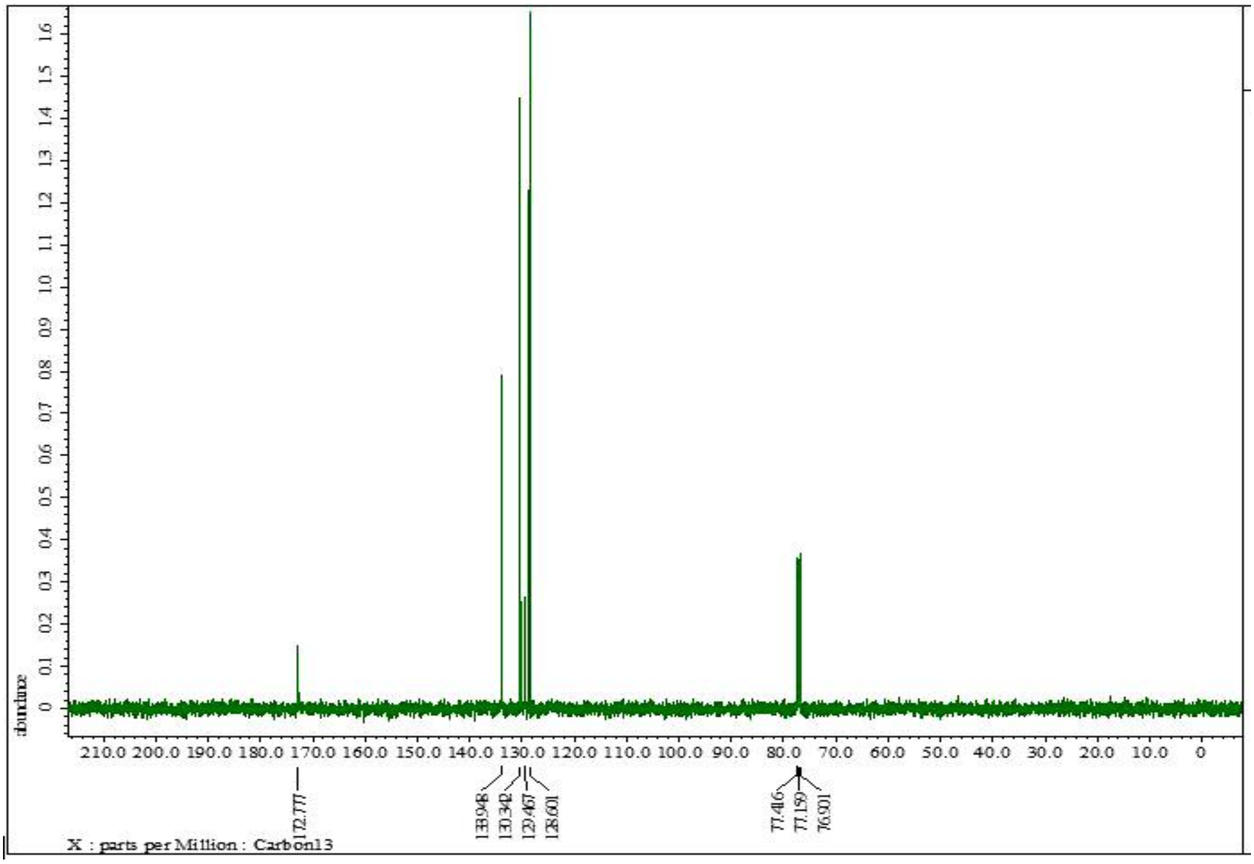
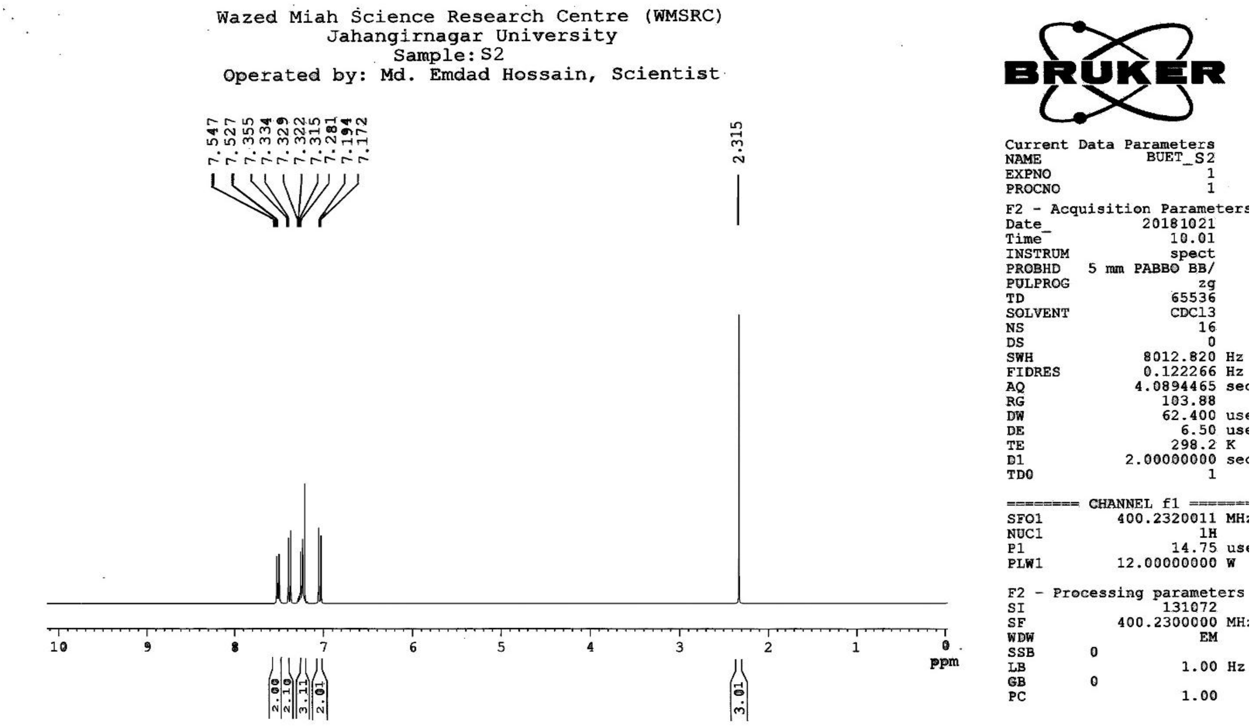


Figure S3

^{1}H NMR of 1-(2-p-tolylethynyl)benzene **9**



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RG                 103.88
DW                 62.400 us
DE                   6.50 us
TE                  298.2 K
D1             2.00000000 se
TD0                     1

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PLW1          12.00000000 W

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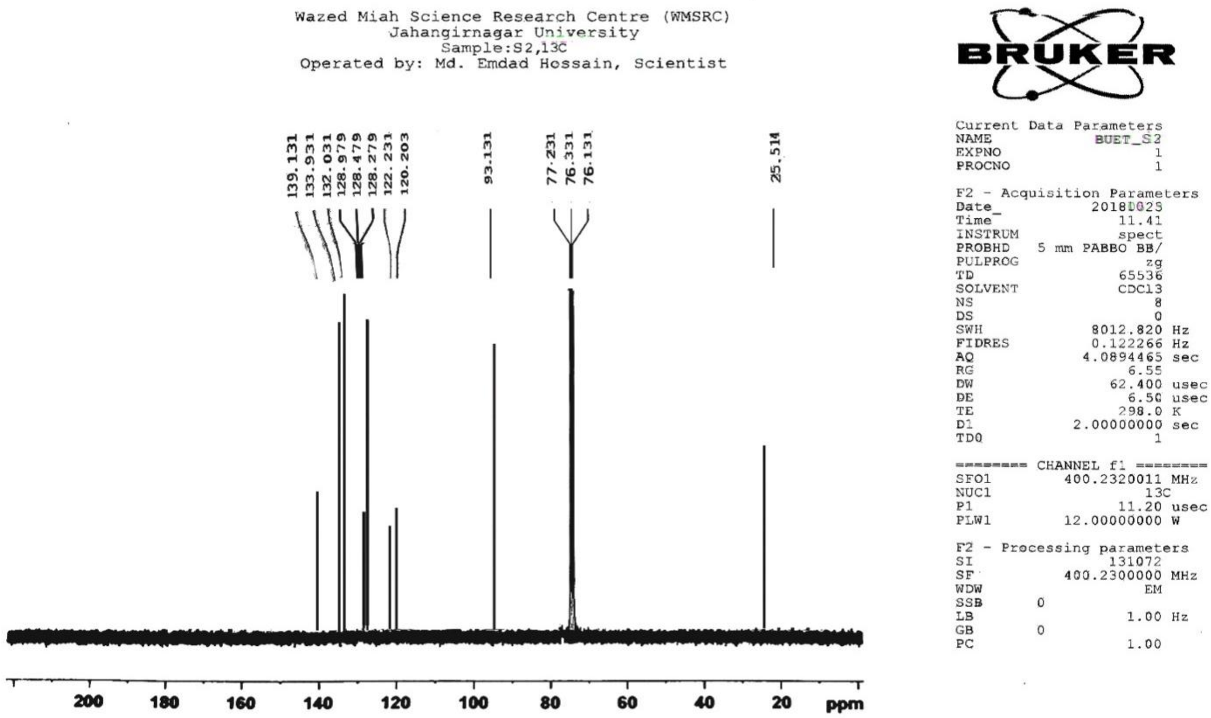
Figure S4

^{13}C NMR of 1-(2-p-tolylethynyl)benzene **9**


Wazed Miah Science Research Centre (WMSRC)
Jahangirnagar University
Sample:S2,13C
Operated by: Md. Emdad Hossain, Scientist

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RG                   6.55
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DE                   6.50 usec
TE                  298.0 K
D1             2.00000000 sec
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NUC1                    13C
P1                  11.20 usec
PLW1          12.00000000 W

F2 - Processing parameters
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WDW                    EM
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LB                   1.00 Hz
GB       0
PC                   1.00
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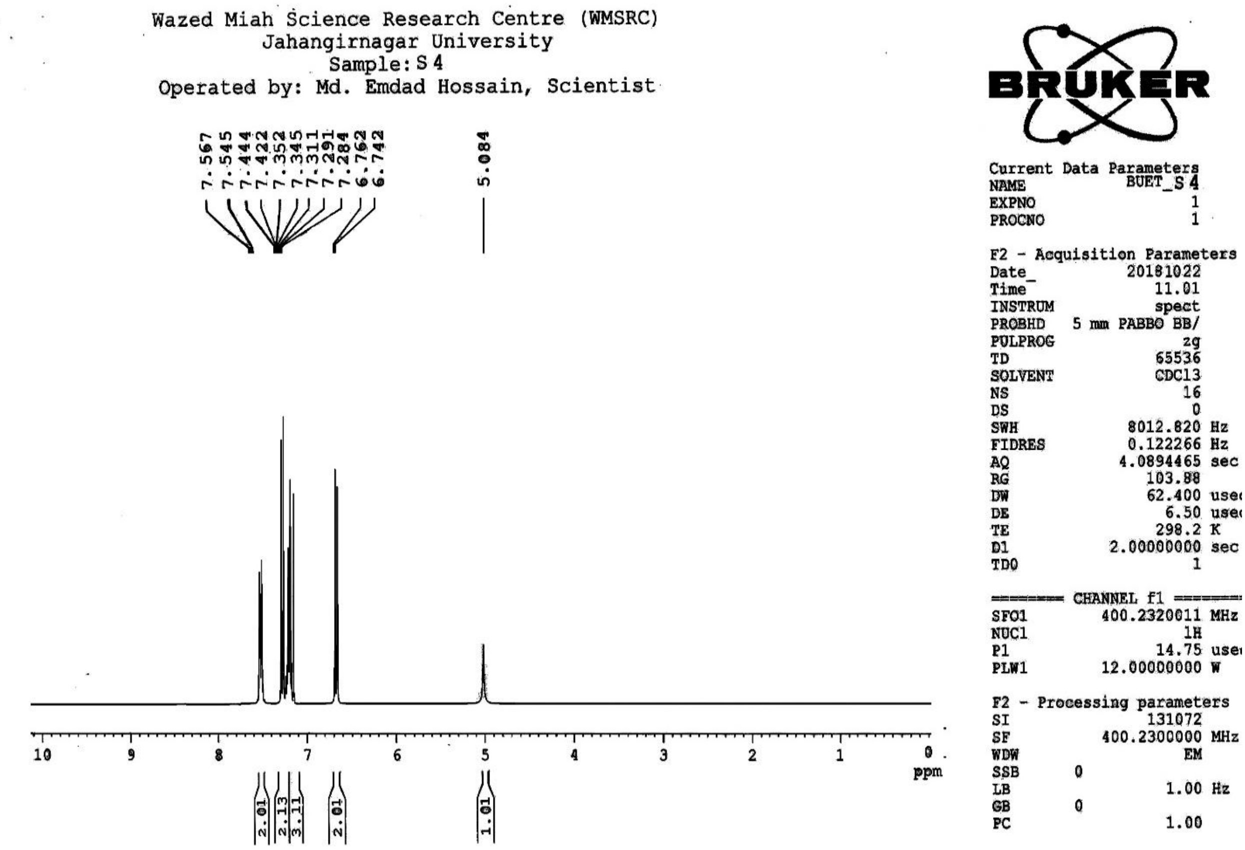
Figure S5

^{1}H NMR of 4-(2-phenylethynyl)phenol **10**


Wazed Miah Science Research Centre (WMSRC)
Jahangirnagar University
Sample: S 4
Operated by: Md. Emdad Hossain, Scientist

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PROCNO                  1

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DW                 62.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
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NUC1                     1H
P1                  14.75 usec
PLW1          12.00000000 W

F2 - Processing parameters
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PC                   1.00
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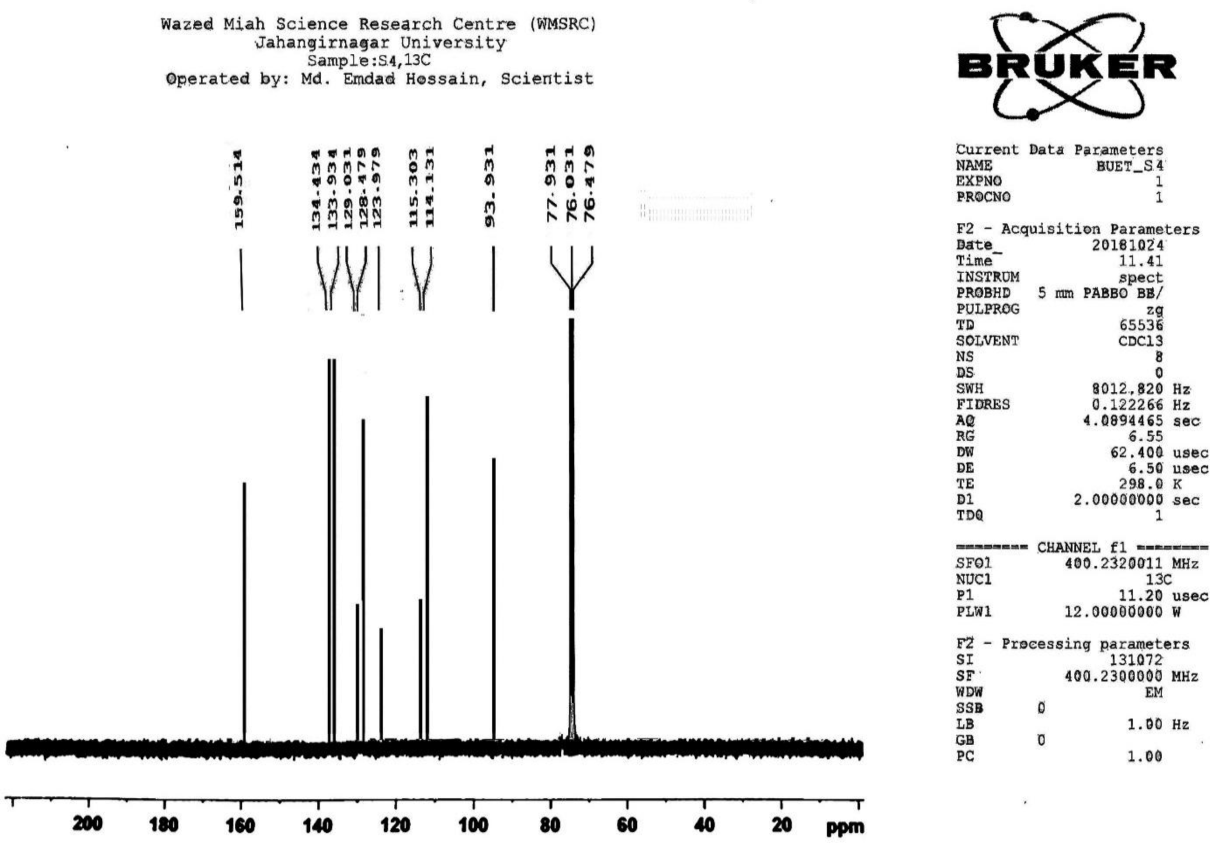
Figure S6

^{13}C NMR of 4-(2-phenylethynyl)phenol **10**


Wazed Miah Science Research Centre (WMSRC)
Jahangirnagar University
Sample:S4,13C
Operated by: Md. Emdad Hossain, Scientist

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PROCNO                 1

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======== CHANNEL f1 ========
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PLW1         12.00000000 W

F2 - Processing parameters
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GB       0
PC                  1.00
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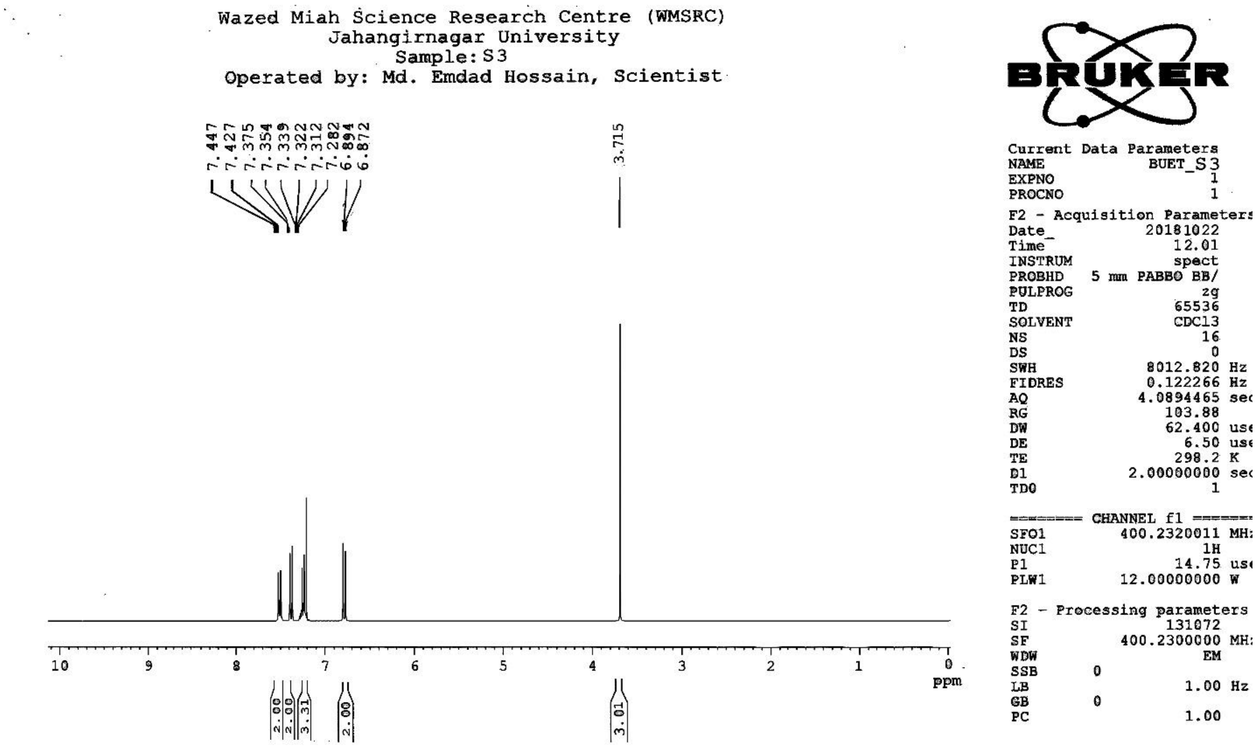
Figure S7

^{1}H nmr of 1-(2-(4-methoxyphenyl)ethynyl)benzene **11**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Jahangirnagar University
Sample: S3
Operated by: Md. Emdad Hossain, Scientist

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PROCNO                 1
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PULPROG               zg
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DS                     0
SWH             8012.820 Hz
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RG                103.88
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TE                 298.2 K
D1            2.00000000 se
TD0                    1

======= CHANNEL f1 ======
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NUC1                  1H
P1                 14.75 us
PLW1         12.00000000 W

F2 - Processing parameters
SI                131072
SF           400.2300000 MH
WDW                   EM
SSB      0
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GB       0
PC                  1.00
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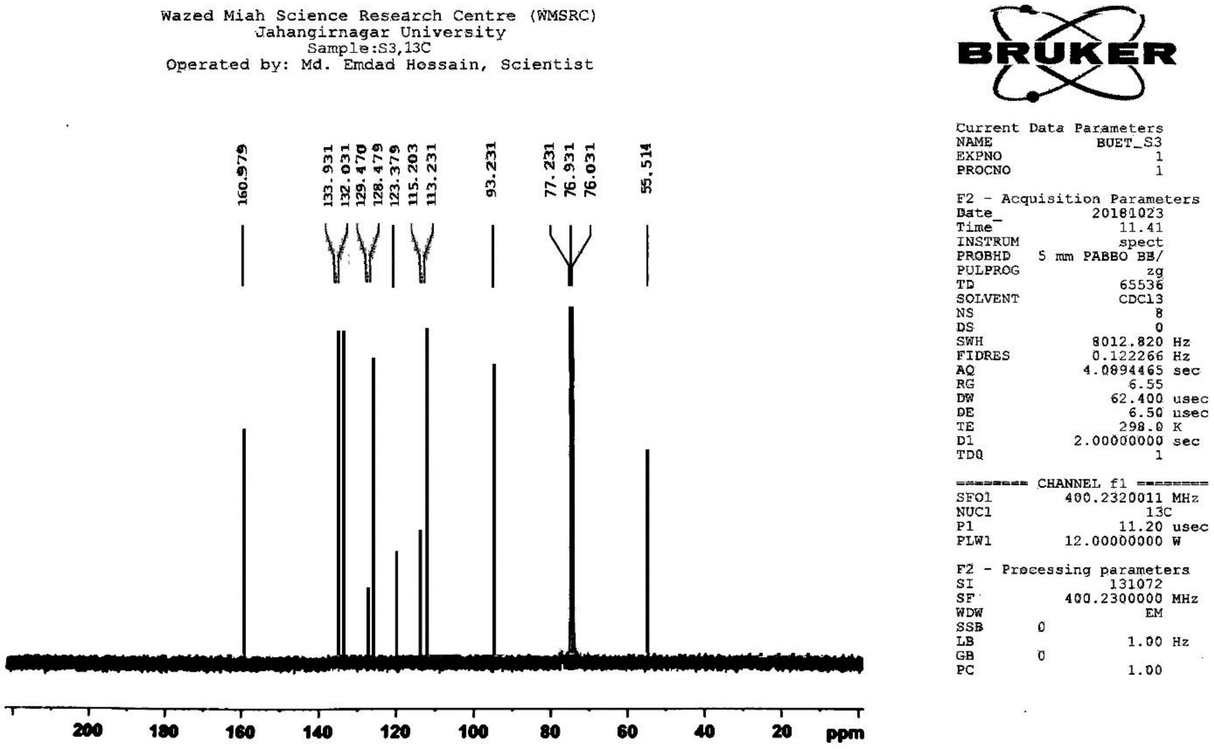
Figure S8

^{13}C nmr of 1-(2-(4-methoxyphenyl)ethynyl)benzene **11**



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Wazed Miah Science Research Centre (WMSRC)
         Jahangirnagar University
             Sample:S3,13C
  Operated by: Md. Emdad Hossain, Scientist
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PROCNO                   1

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PULPROG                 zg
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FIDRES            0.122266 Hz
AQ               4.0894465 sec
RG                    6.55
DW                  62.400 usec
DE                    6.50 usec
TE                   298.0 K
D1              2.00000000 sec
TDQ                      1

======== CHANNEL f1 ========
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NUC1                   13C
P1                   11.20 usec
PLW1           12.00000000 W

F2 - Processing parameters
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WDW                     EM
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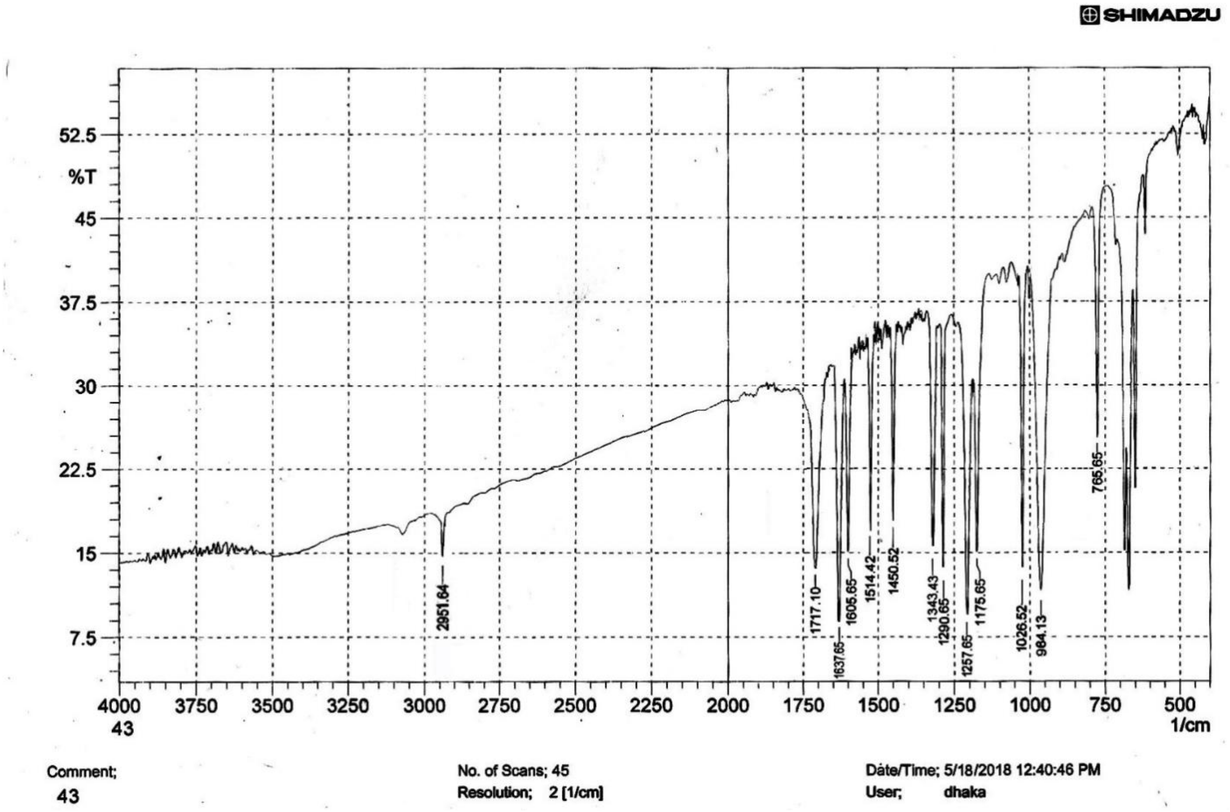
Figure S9

IR of (E)-methyl 3-o-tolylacrylate **16**



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Date/Time; 5/18/2018 12:40:46 PM
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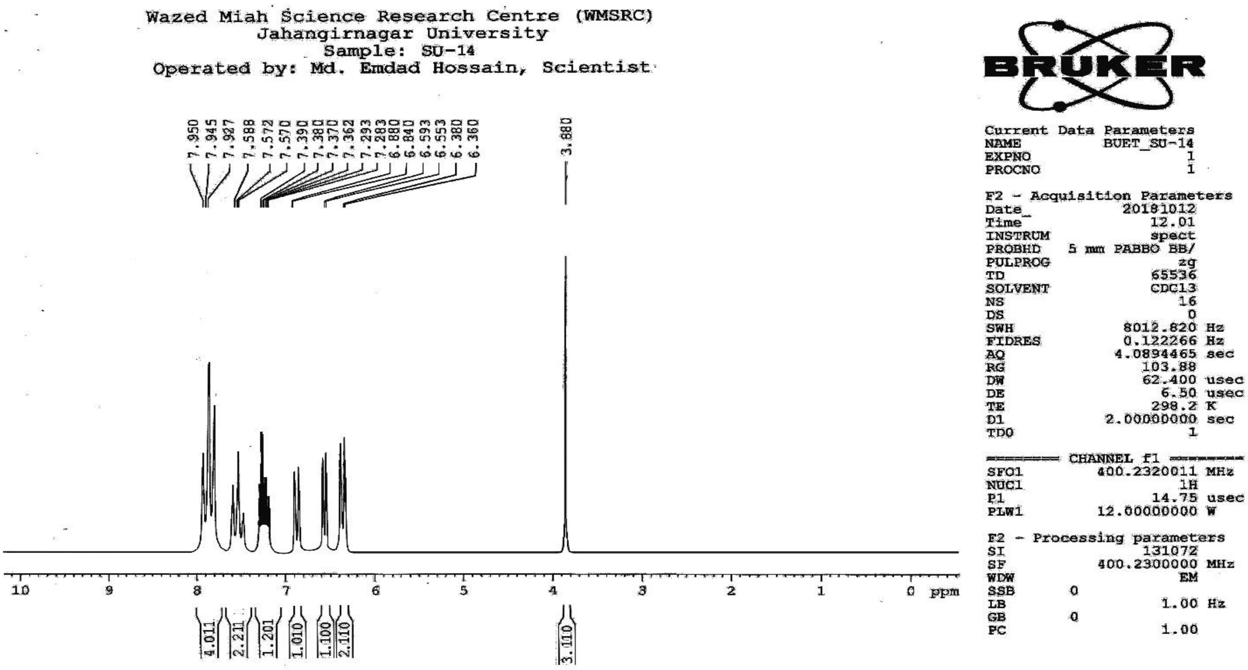
Figure S10

^{1}H nmr of (E)-methyl 3-o-tolylacrylate **16**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Jahangirnagar University
Sample: SU-14
Operated by: Md. Emdad Hossain, Scientist

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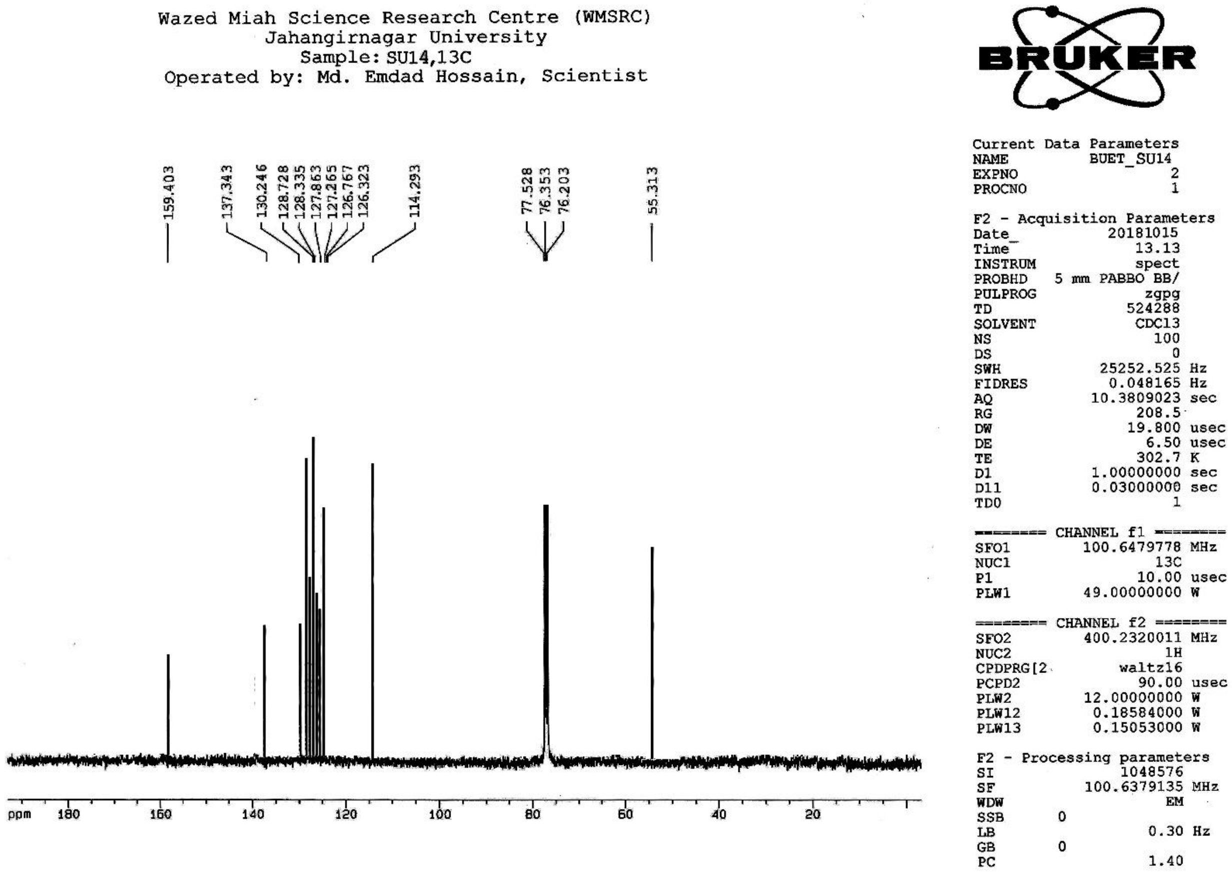
Figure S11

^{13}C nmr of (E)-methyl 3-o-tolylacrylate **16**


Wazed Miah Science Research Centre (WMSRC)
Jahangirnagar University
Sample: SU14,13C
Operated by: Md. Emdad Hossain, Scientist

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PLW1          49.00000000 W

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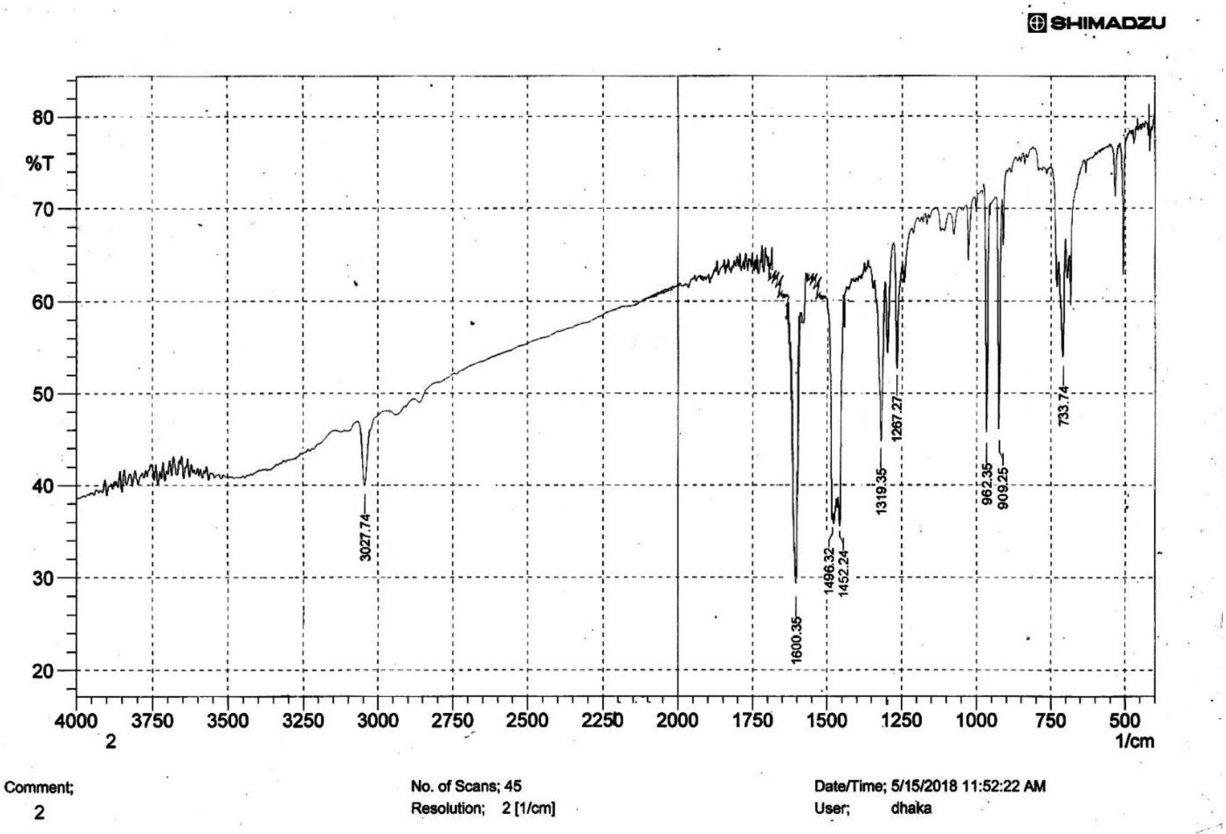
Figure S12

IR of Transstillbene **17**



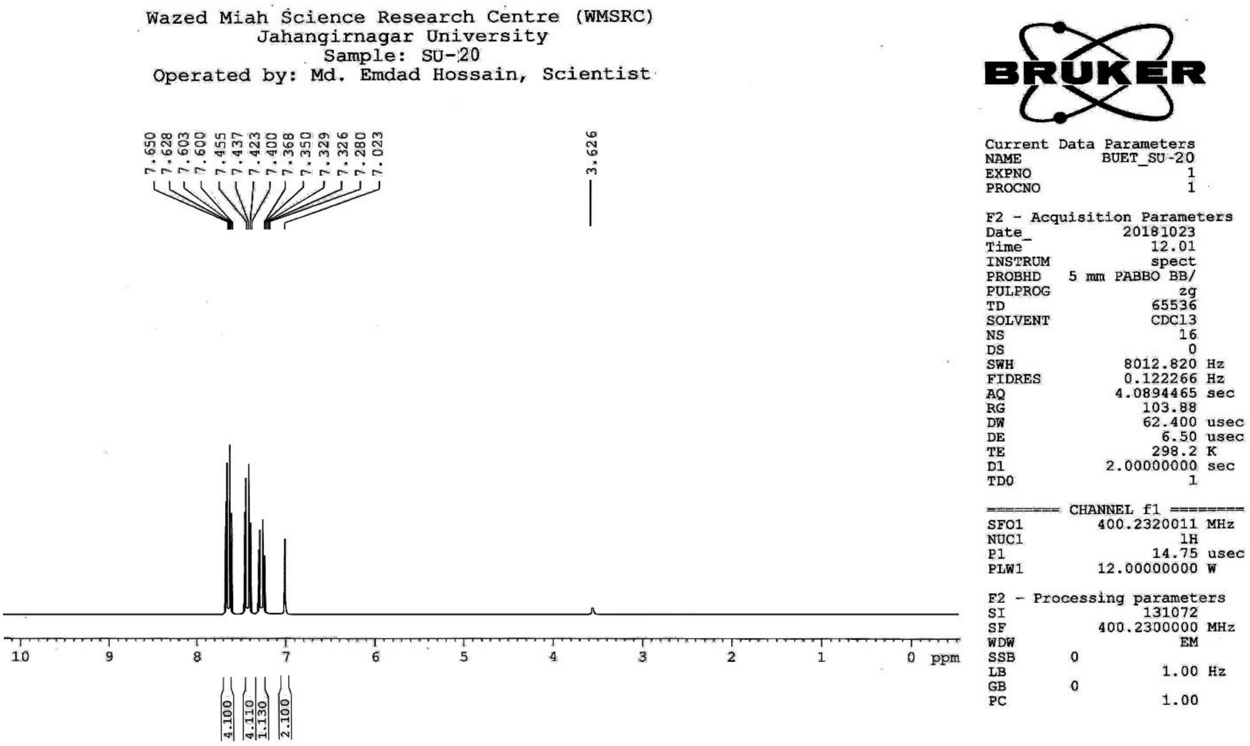
Comment;
2

No. of Scans; 45
Resolution; 2 [1/cm]

Date/Time; 5/15/2018 11:52:22 AM
User; dhaka

Figure S13

^{1}H nmr of trans stilbene **17**



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Wazed Miah Science Research Centre (WMSRC)
         Jahangirnagar University
             Sample: SU-20
 Operated by: Md. Emdad Hossain, Scientist
```

```
Current Data Parameters
NAME           BUET_SU-20
EXPNO                   1
PROCNO                  1

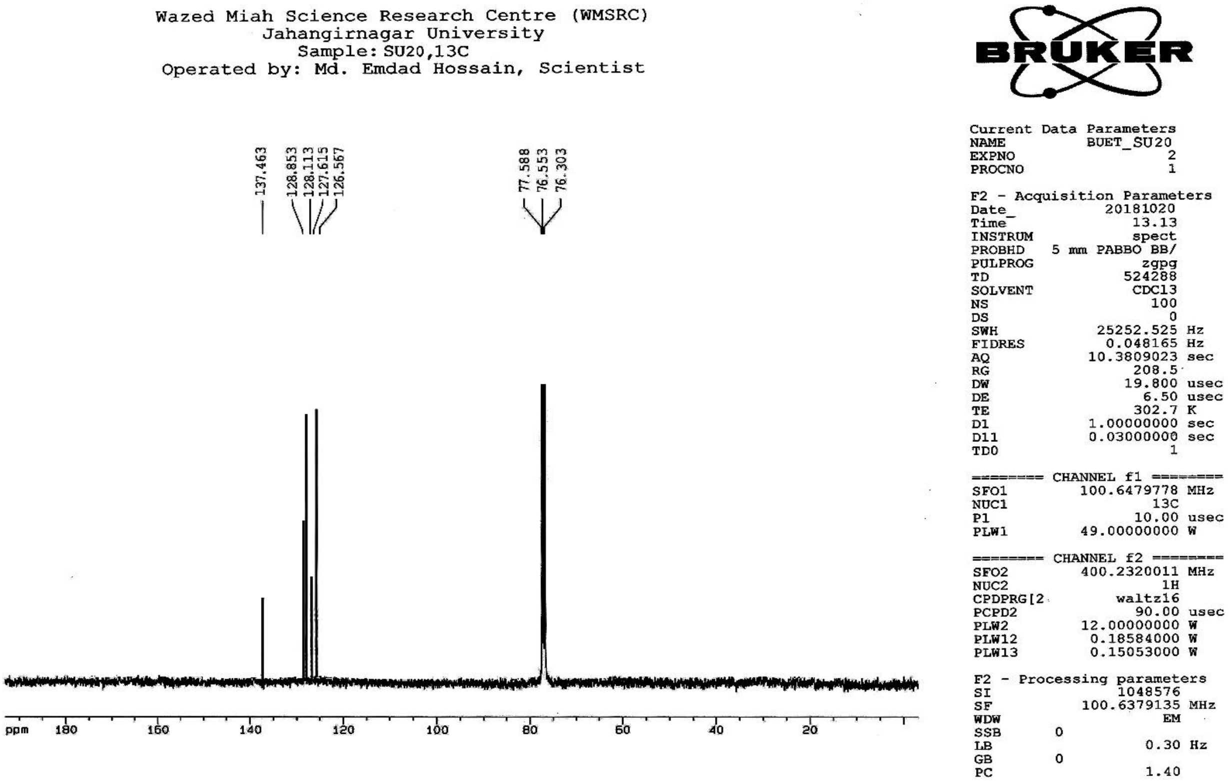
F2 - Acquisition Parameters
Date_            20181023
Time                12.01
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894465 sec
RG                 103.88
DW                 62.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.2320011 MHz
NUC1                   1H
P1                  14.75 usec
PLW1          12.00000000 W

F2 - Processing parameters
SI                 131072
SF            400.2300000 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.00
```

Figure S14

^{13}C nmr of trans stilbene **17**



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Wazed Miah Science Research Centre (WMSRC)
        Jahangirnagar University
          Sample: SU20,13C
 Operated by: Md. Emdad Hossain, Scientist
```
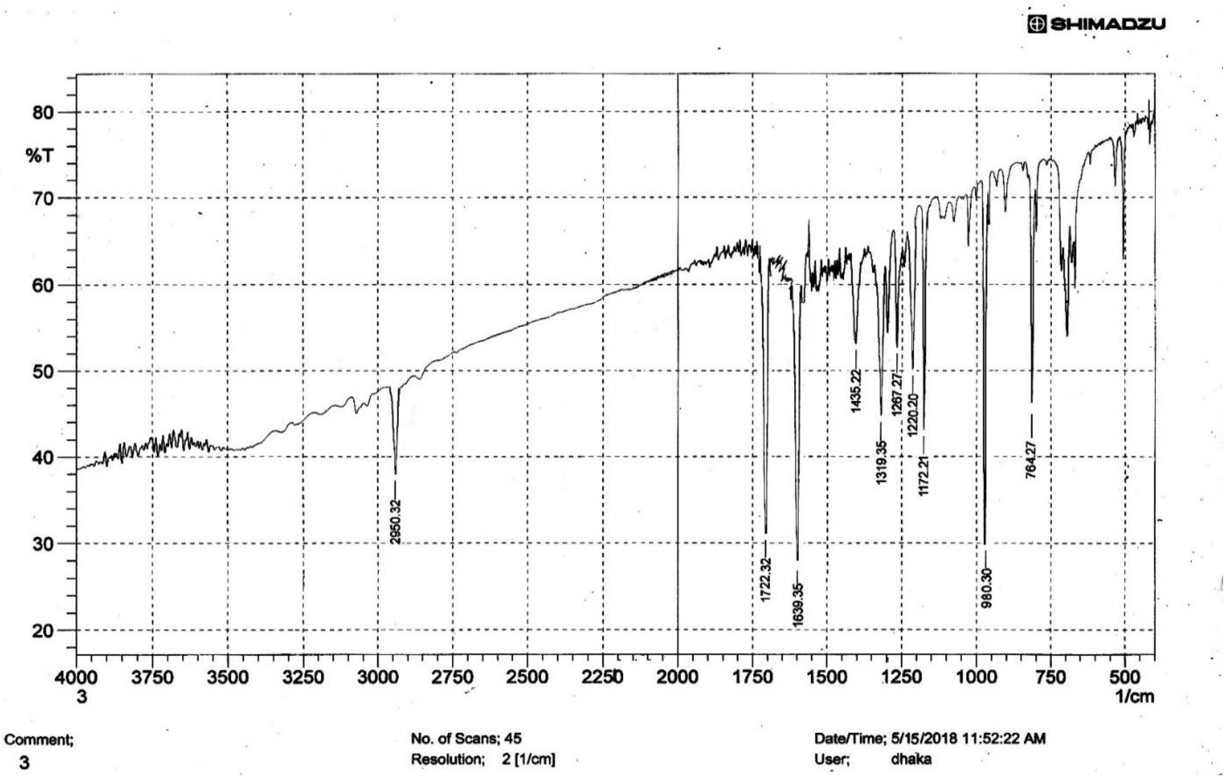

```
Current Data Parameters
NAME              BUET_SU20
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20181020
Time                  13.13
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zgpg
TD                   524288
SOLVENT               CDCl3
NS                      100
DS                        0
SWH               25252.525 Hz
FIDRES             0.048165 Hz
AQ               10.3809023 sec
RG                    208.5
DW                   19.800 usec
DE                     6.50 usec
TE                    302.7 K
D1               1.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            100.6479778 MHz
NUC1                    13C
P1                    10.00 usec
PLW1            49.00000000 W

======== CHANNEL f2 ========
SFO2            400.2320011 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 90.00 usec
PLW2            12.00000000 W
PLW12            0.18584000 W
PLW13            0.15053000 W

F2 - Processing parameters
SI                  1048576
SF              100.6379135 MHz
WDW                      EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.40
```

Figure S15

IR of (E)-methyl 3-(4-methoxyphenyl)acrylate **18**



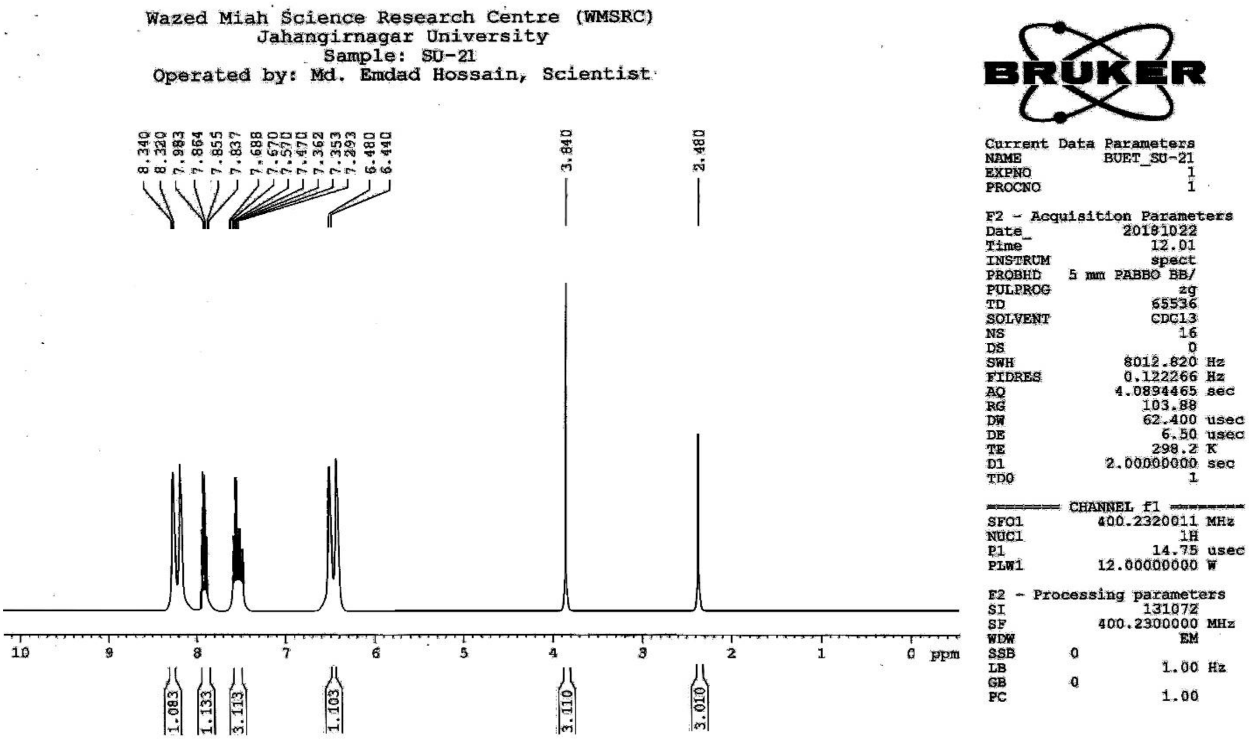
Comment;
3

No. of Scans; 45
Resolution; 2 [1/cm]

Date/Time; 5/15/2018 11:52:22 AM
User; dhaka

Figure S16

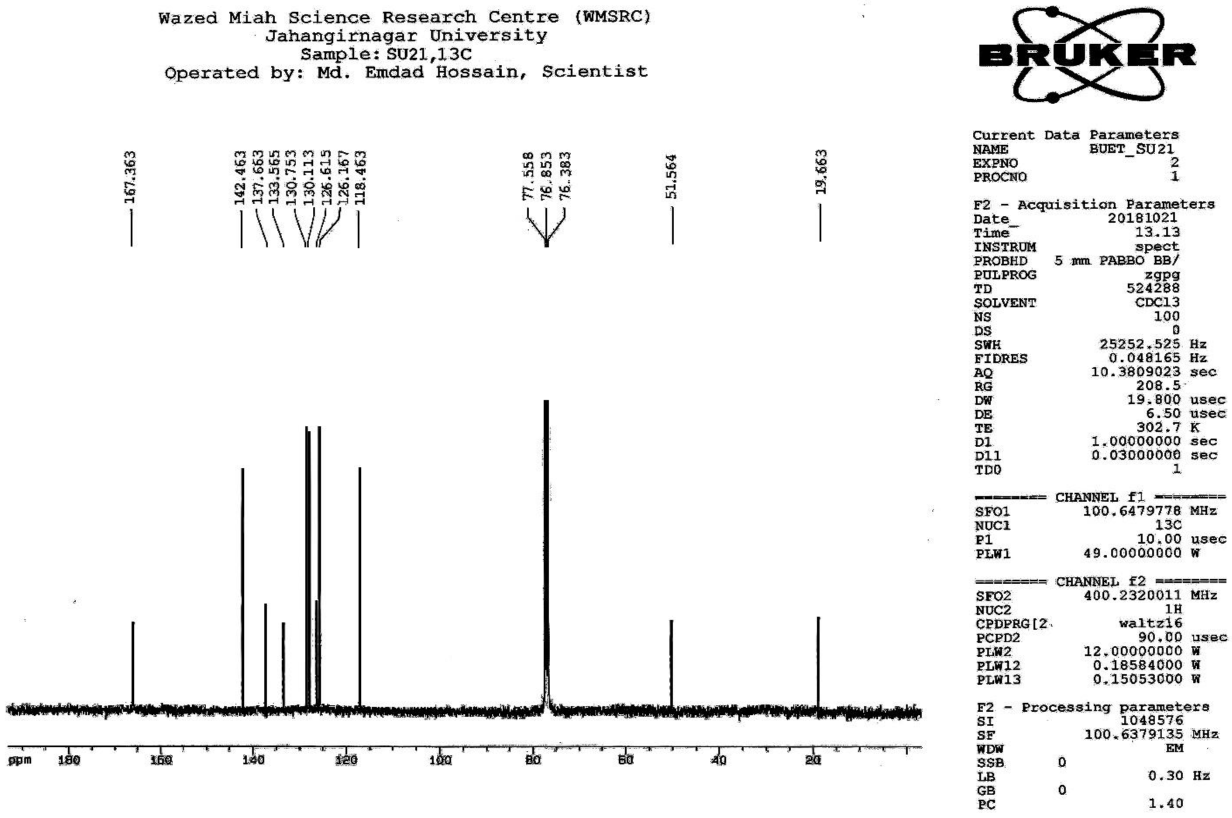
^{1}H nmr of (E)-methyl 3-(4-methoxyphenyl)acrylate **18**


Wazed Miah Science Research Centre (WMSRC)
Jahangirnagar University
Sample: SU-21
Operated by: Md. Emdad Hossain, Scientist

```
Current Data Parameters
NAME           BUET_SU-21
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20181022
Time                12.01
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894465 sec
RG                 103.88
DW                 62.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.2320011 MHz
NUC1                   1H
P1                  14.75 usec
PLW1          12.00000000 W

F2 - Processing parameters
SI                 131072
SF            400.2300000 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.00
```

Figure S17

^{13}C nmr of (E)-methyl 3-(4-methoxyphenyl)acrylate **18**


Wazed Miah Science Research Centre (WMSRC)
Jahangirnagar University
Sample: SU21,13C
Operated by: Md. Emdad Hossain, Scientist

```
Current Data Parameters
NAME             BUET_SU21
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20181021
Time                 13.13
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG               zgpg
TD                  524288
SOLVENT              CDCl3
NS                     100
DS                       0
SWH              25252.525 Hz
FIDRES            0.048165 Hz
AQ              10.3809023 sec
RG                   208.5
DW                  19.800 usec
DE                    6.50 usec
TE                   302.7 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           100.6479778 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           49.00000000 W

======== CHANNEL f2 ========
SFO2           400.2320011 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2           12.00000000 W
PLW12           0.18584000 W
PLW13           0.15053000 W

F2 - Processing parameters
SI                 1048576
SF             100.6379135 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.40
```

Figure S18

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