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Synthesis and Catalytic Activity of Palladium Mediated Metallodendrimer for the Sonogashira and Heck Coupling Reactions

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Abstract A palladium mediated metallodendrimer was synthesized via the reaction of 2,4,6-Triaminopyrimidine with 4-methyl benzoyl chloride using $(Ph_3P)_2PdCl_2$ in DMF at 70℃ used as an active homogeneous catalyst for the Sonogashira and Heck cross-coupling reactions. The catalyst was characterized by IR, NMR, Mass, and Elemental analysis. This palladium encapsulated metallodendrimer catalyst was also found to be a white crystalline solid air-stable state and highly effective in the phosphine ligand-free conditions for the coupling reactions. The fibril surface morphology and the presence of Palladium chloride of the compound were confirmed by SEM and EDX respectively whereas the good thermal stability of the catalyst was exhibited by TG and DSC techniques.

Keywords Sonogashira Reaction, Heck Reaction, Aroyl chloride, Triaminopyrimidine, Metallodendrimer

1. Introduction

Previous few decades, transition metal mediated cross-coupling reactions have become an essential implementation in organic synthesis. Among the transition metals, palladium is the utmost metal in recent organic synthesis and broadly used for the extensive quantity of synthetic transformations mostly carbon-carbon cross -coupling reactions [1-4]. The enormous significance of C-C bond forming reactions has fortified the chemical community to search for immensely active and strong palladium catalysts, which should be flexible and efficient. In addition, Metallodendrimers are the unique class of synthetic macromolecules having extraordinarily branched, three-dimensional, nano scale-shaped with very low polydispersity and immoderate functionality [5]. The metallodendrimer generally contains three superb areas which show active center in the different catalytic system: (i) metal atom as the dendrimer center, (ii) metal atoms inside the dendrimer branches (iii) metal atoms within the periphery. As for example, metals able to coordinate with the poly(amido)amine(PAMAM) shape encompass amongst others Cu [6, 7], Au [8], Pd [9], Pt [10], Ag [11], Co [12] as well as bimetallic structures such as Pd-Au [13] and Pt-Ru [14]. Lately, metallodendrimers were broadly researched in various fields, which includes molecular light harvesting, catalysts, liquid crystals, molecular encapsulation, and drug delivery [15]. Most of the investigation was succeeded in the arena of catalysis where metals, for example, Cu (II), Rh (III), Ru (II), Pd (II), Fe (I) and Co (III) are utilized in the production of metallodendrimers. Moreover, chemoselective reactions [17], and azide-alkyne reactions are also carried out and catalyzed by metallodendrimer compounds [18, 19].

Despite the fact that the ordinary Pd catalyzed and Cu co-catalyzed Sonogashira reactions has some disadvantages. These include the usage of extremely overpriced Pd catalysts (occasionally essential in high loading), difficulties in convalescing these catalysts, excessive reaction temperatures, air sensitivity of transition metal complexes and the usage of phosphine ligand which is air sensitive. In addition, the formation of homocoupled products due to contact of the alkynes to oxidizing agents, Cu salts or air as for example Glaser coupling [20] or Hay coupling [21] are also weaknesses. However, to minimize these drawbacks we designed as well as synthesized solid crystalline air stable diazine based dendrimer assisted Pd-metallodendrimer catalyst. It has shown efficient catalytic activity under mild and phosphine-free conditions for the heck and Sonogashira reactions. .

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2. Experimental Sections

All procedures of air- and moisture-sensitive compounds were performed by the use of standard Schlenk techniques under an atmosphere of argon or nitrogen. The reagents were bought from Aldrich as high-purity products and usually used as received. Dehydrated DMF, DMSO, CH_3CN, and THF were used as reaction solvent. The IR spectra was taken on a Shimadzu FTIR 8400S Fourier remodel Infrared Spectrophotometer (400-4000 cm^{-1}) with KBr pellets. ^1H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, on a JEOL AL 300/BZ tool in addition to BRUKER DPX-400 MHz & 100 MHz spectrophoto meters respectively. Chemical shifts was taken relative to TMS. Mass spectra (MS) was measured with the aid of the usage of AXIMA-CFR, Shimadzu/Kratos TOF Mass spectrometer. Scanning Electron Microscope (SEM) and power Dispersive X-ray (EDX) was taken on a Hitachi S-4800. Analytical thin layer chromatography (TLC) became silica gel 60 F 254 covered on 25 TCC aluminum sheets (20 × 20 cm). 2, 4, 6-triamino-1, 3, 5-diazine, 4-methyl benzoyl chloride and $(Ph_3P)_2PdCl_2$ were purchased from Sigma Aldrich and had been directly used without further purification. The thermal behavior of metallodendrimer was determined by a thermogravimetric analyzer (NETZSCH STA 449F3) from 26 to 600℃. Elemental analyses were carried out with a Fisons EA 1108 CHNS-O apparatus. All TG and DSC facts had been received under a nitrogen environment by the use of aluminum oxide crucible at the heating rate of 10 °k/min and at a flow rate of 40 and 60 ml/min.

2.1. Synthesis of 2, 4, 6-Tris (di-4-methylbenzamido)-1, 3, 5-Diazine Palladium (II) chloride (3)

4-Methyl benzoyl chloride 2 (1.47 g, 9.54 mmol), $(Ph_3P)_2PdCl_2$ (0.11g, 10% mol) were sequentially added to a solution of 2, 4, 6-triamino-1, 3, 5-diazine 1 (0.2 g, 1.59 mmol) in DMF (10 mL). The solution was degassed and stirred at room temperature under a nitrogen atmosphere for 1 h and the reaction was continued for 5 h at 70℃. The progress of the reaction was monitored by TLC. At the starting of the reaction, the mixture was a clear solution and after sometimes the reactants were turned into white solid precipitated and products was formed checked by TLC. After completion of the reaction, distilled H_2O was added. After the removal of solvent, the product was washed with sodium hydrogen carbonate solution and purified by recrystallization by using ethanol and found the desired product 3. White crystalline solid; yield: 90 %; IR (KBr): δ max 3052.29, 2976.31, 1710.20, 1611.69, 1418.69, 1360.20 cm^{-1}.^1H NMR (300 MHz, CD_3OD): δ 7.80 (m, 12 H), 7.23 (m, 12 H), 4.96 (s, 1H) 2.3 (s, 18 H) ppm.^{13}C NMR (75 MHz, $CDCl_3$): δ 21.63, 129.28, 130.50, 131.28, 144.63 and 172.33 ppm. MALDI-TOF MS: m/z (%) = calcd. for $C_{52}N_5H_{43}O_6$ Pd_3Cl_6 1365.90; found 1369.44 (100) $[M]^+$, Anal. Calcd. (%) for $C_{52}N_5H_{43}O_6Pd_3Cl_6$: C, 45.70; H, 3.17; N, 5.13. Found: C, 45.67; H, 3.10; N, 5.10.

2.2. Catalytic Activity Tests: Palladium Mediated Metallodendrimer 3 in the Sonogasira Reaction

Typical procedure: In a Schlenk tube equipped with a magnetic stirring bar were placed under nitrogen atmosphere with 1.0 mmol of aryl halide, (1.2 mmol) of phenylacetylene, 1 mol % of Pd-metallodendrimer 3, CuI 0.5 mol%, Et_3N (2 mL) as a base and CH_3CN (5 mL) as a solvent. The tube was degassed and the flask was immediately placed in an oil bath. The resulting mixture was stirred at 60℃ temperatures for 3h and the reaction was checked by TLC. Then the solvent was vaporized under reduced pressure and the residue obtained was purified by silica gel chromatography using ethyl acetate and hexane (4:1).

Synthesis of 4-(2-phenylethynyl)phenol 11, [22]

Solid product was obtained, Yield 92%, mp: 124-126℃; ^1H NMR ($CDCl_3$, 400 MHz): δ 5.08 (s, 1 H, OH); 6.75 (d, 2H, *J*=8.8 Hz); 7.29-7.35 (m, 3 H); 7.43 (d, *J*= 8.8, 2H); 7.55 (d, *J*=8.8, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 93.93, 114.13, 115.30, 123.97, 128.47, 129.03, 133.93, 134.43, 159.51.

Synthesis of 1-(2-p-tolylethynyl)benzene 12, [22]

Solid colourless product was obtained, Yield 95%, mp: 70-72℃ (lit. 71℃); ^1H NMR (400 MHz): δ 2.31(s, 3 H); 7.20 (d, 2H, *J*= 8.8 Hz); 7.32 (t, 3H, *J*= 5.6 Hz); 7.33 (d, 2H, *J*=8.4 Hz); 7.54 (d, 2H, *J*= 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 92.51, 93.13, 120.20, 122.23, 128.27, 128.47, 128.97, 132.03, 133.93, 139.13.

Synthesis of 1-(2-(4-methoxyphenyl)ethynyl)benzene 13, [23]

Solid white product was obtained, Yield 96%, mp: 54-56℃ (lit. 57℃); ^1H NMR (400 MHz): δ 3.71 (s, 3H); 6.88 (d, 2H, *J*=8.8 Hz); 7.33 (t, *J*=10.8 Hz, 3H); 7.36 (d, 2 H, *J*=8.8 Hz); 7.44 (d, 2H, *J*=8.0 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.51, 93.23, 113.23, 115.20, 123.37, 128.47, 129.47, 132.03, 133.93, 160.97.

2.3. Catalytic Activity Tests: Palladium Mediated Metallodendrimer 3 in the Heck Reaction

Typical procedure: A combination of 4-iodododophenol (1 mmol) with styrene (1.2 mmol), Pd-metallodendrimer 3 (1.0 mol%) and triethylamine (1.2 mL) was stirred in DMF (5 mL) in an R.B flask under nitrogen environment. The solution was heated at 85℃ for 24 hrs. The advancement of the reaction was observed with the aid of TLC (n-hexane/ethyl acetate 1:1). After the achievement of the desired conversion of the reaction, the reaction mixture was evaporated to dryness under reduced pressure and the residue was turned into extracted with chloroform.

The chloroform extract was washed with distilled water and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Then it was refined by silica gel column chromatography with n-hexane / ethyl acetate (3:1).

Synthesis of trans stilbene, 22 [24]

Colourless Solid was found and melting point was 74-76℃, Yield 94%, 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-o-tolylacrylate 23, [24]

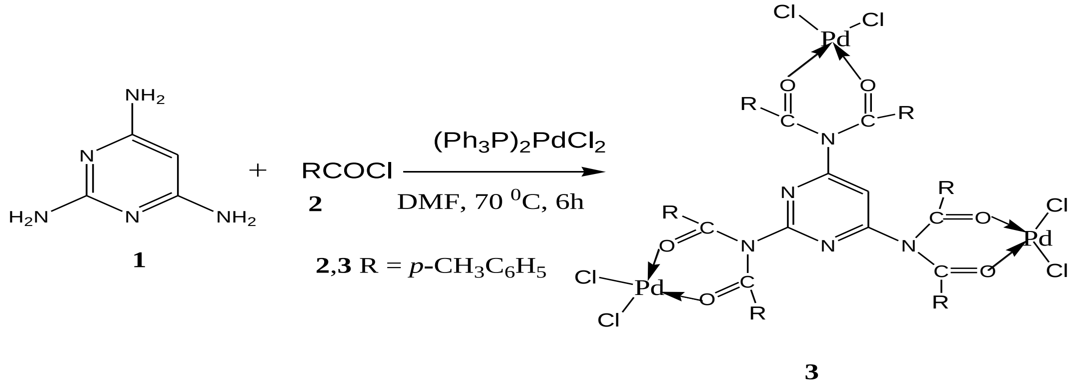
Yield 95%, IR (KBr): δ max 2950.32, 1722.32, 1639.35, 1267.27, 1220.20, 1172.21, 980.30, 764.27. ^1H NMR (400 MHz, $CDCl_3$), δ 2.48 (s, 3H); 3.84 (s, 3H); 6.46 (d, 1H, *J*=16.0 Hz); 7.35-7.68 (m, 3H); 7.83-7.98 (m, 1H); 8.33 (d, *J*=8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.66, 51.56, 118.46, 126.17, 126.61, 130.11, 130.75, 133.56, 137.66, 142.46, 167.36.

Synthesis of 1-Methoxy-4-styrylbenzene 24, [24]

White solid product was found, Yield 96%, mp. 135-137℃, IR (KBr): δ max 2960.74, 1601.35, 1511.24, 1319.35, 1251.27, 1179.75, 1031.15, 966.36, 812.25. ^1H 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

Metallodendrimer **3** was synthesized by the reaction of 2,4,6-Triaminopyrimidine 1(1.59 mmol) with 4-methyl benzoyl chloride **2** (9.54 mmol) in the presence of $(Ph_3P)_2PdCl_2$ (10 mol%) in anhydrous DMF at room temperature to 70℃ for 6 h under a nitrogen atmosphere (Scheme 1). The progress of the reaction was monitored by thin layer chromatography (TLC) and after complete conversion of the reaction, purification of the solid reaction mixture by recrystallization gave the dendrimerized product 3 in 92% yield (Table 1, entry 1). $PdCl_2$ was also effective and provided 3 in 65% (entry 2). Since $(Ph_3P)_2PdCl_2$ was given more yield than $PdCl_2$, we selected $(Ph_3P)_2PdCl_2$ for the later optimization. The use of tetrahydrofuran as the solvent caused in low yields of 3, because of the poor solubility of **3** (entry 3). DMSO also good solvent and gave **3** in 87% (entry 4). Increasing the amount of $(Ph_3P)_2PdCl_2$ from 10 to 20 mol% did not progress the final yield of 3, the yield reduced due to the creation of a complex as a byproduct instead of the desired product (entry 5). The product was found to be soluble in all common organic solvents and was characterized by IR, ^1H NMR, ^{13}C NMR, and mass spectrometry.



Scheme 1

Table 1. Optimization for Preparation of Metallodendrimer 3

Entry	1 (mmol)	2 (mmol)	Pd complex (mol%)	Solvent (mL)	Time h	3 (%)
1	1.59	9.54	$(Ph_3P)_2PdCl_2$ (10)	DMF (10)	6	92
2	1.59	9.54	$PdCl_2$ (10)	DMF (10)	6	65
3	1.59	9.54	$(Ph_3P)_2PdCl_2$ (10)	THF (10)	6	55
4	1.59	9.54	$(Ph_3P)_2PdCl_2$ (10)	DMSO (10)	6	87
5	1.59	9.54	$(Ph_3P)_2PdCl_2$ (20)	DMSO (10)	6	70

The assignments of IR spectral bands most useful in establishing the structural identity of metal complexes. The strong IR peak of 3 confirmed the presence of required groups of the compound. The appearance of the signal in the range of 3000-3100 cm^{-1} and 1680-1760 cm^{-1} represented the C-H, C=O group respectively whereas a strong absorption band at 1580-1620 cm^{-1} displayed C=N. The peak at 1300-1360 and 1250-1335 cm^{-1} confirmed the presence of C=C and C-N group respectively. C-Cl stretching absorption was observed at 761.8 cm^{-1}. Here it's far remarkable that there's no band for N-H in the place approximately 3400–3250 cm^{-1} which turned into indicated that 1° amino group of triaminodiazine is transformed into 3° amido group. In ^{1}H NMR and ^{13}C NMR spectra confirmed the preferred compound 3. Because of the formation of Pd-O coordinated bond, small adjustments within the aromatic area in comparison to starting materials indicated that metallic complexation has been achieved. There's no ^{1}H NMR peak for NH or NH_2 group, which confirmed the shape of compound 3. The self-assembly procedure of the compound 3 was investigated with Pd (II) as the central metal ions, and this led to a well-designated four coordinated complex that was confirmed through MALDI-TOF MS (Figures S 1- S 6 in the Supporting Information).

The images of the compound **3** were taken in a Scanning Electron Microscope (SEM) at an accelerating voltage of 10 KV with magnifications ranging from 100 µm-500 nm. SEM images of the compound 3 revealed that the formation of high component ratio randomly disbursed, entangled nanofibers. The length of the fibers is numerous µM. Coordination between the ligand and Pd (II) shaped branches of a tree without leaves and cylindrical fiber-like shape for compound **3** (Figure 1). Every chain stacked with neighboring chain by way of π-π stacking interaction and fashioned fibril morphology. The fibers are stabilized with the aid of π-stacking of the aromatic core of the ligands.

Metal detection or evaluation of metallodendrimer has been achieved through employing the energy Dispersive X-ray (EDX) method. From EDX assessment, the existence of Palladium was well detected and it was 4.10% of weight and 0.56 % of atomic of the compound and also chlorine was 0.82% of weight and 0.33% of atomic of the compound 3. So it may be stated that palladium was encapsulated as palladium chloride in our preferred produced compound and the reaction was effective for the preparation of the required metallodendrimer **3.**

We have reported new homogeneous palladium containing metallodendrimer **3** based on diazine catalyst which is an air-stable and very much effective catalyst for the Heck, Sonoghasira coupling reactions. In order to evaluate the activities of our catalytic system, the reaction between iodobenzene and phenylacetylene was initially selected for the Sonoghasira coupling reaction in the presence of a catalytic amount of the Pd-metallodendrimer **3** as a homogeneous catalyst (Scheme 2, Table 2). The catalytic systems revealed different reactivity depending not only on the palladium precursor but also on the nature of the base and the solvent and temperature.

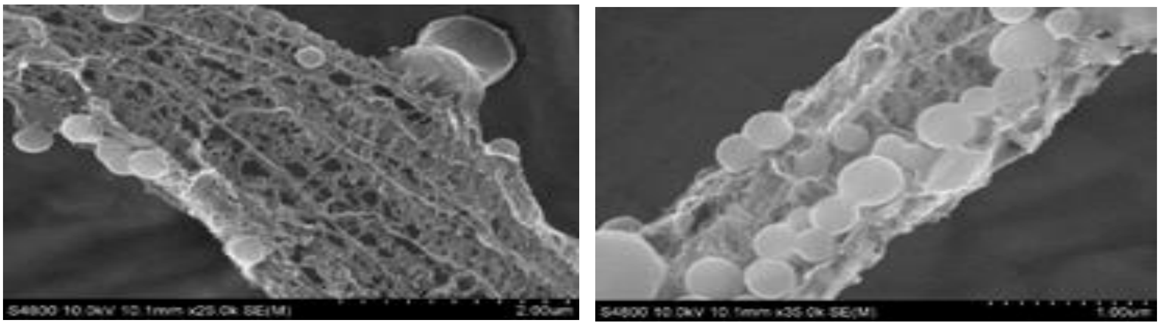
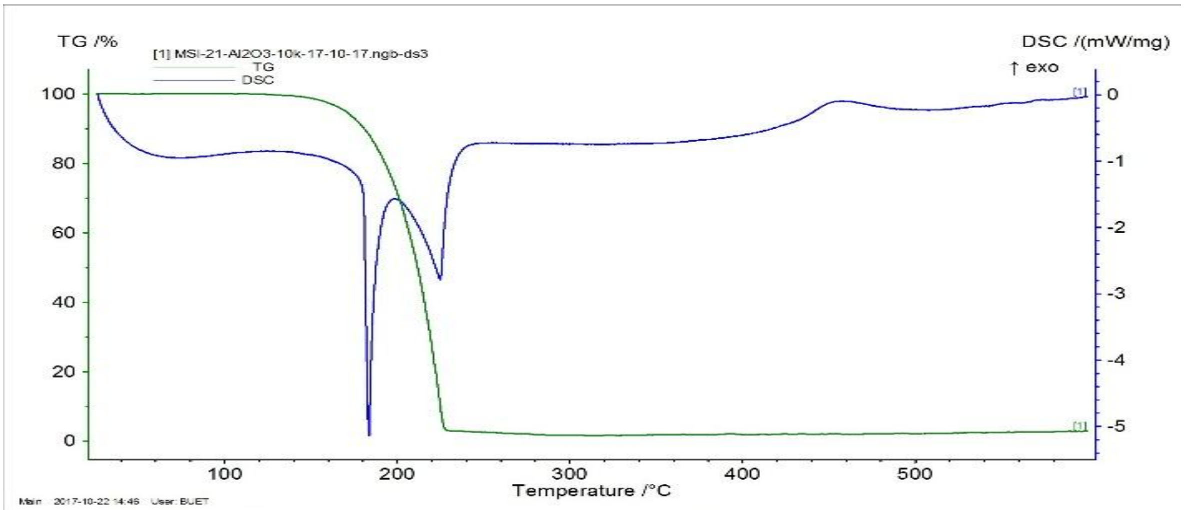


Figure 1. SEM images of the compound 3



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Sample car./TC : DSC/TG Cp S / S
Mode/type of meas. : DSC-TG / sample with correction

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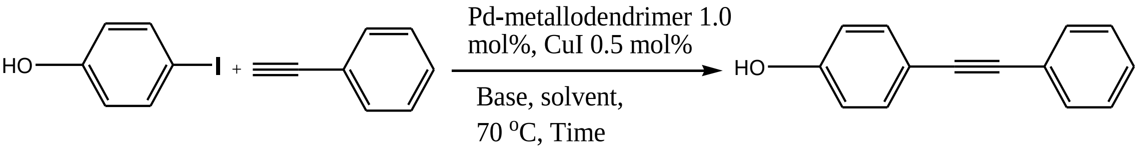
Figure 2. TG and DSC curves of the compound 3



Scheme 2

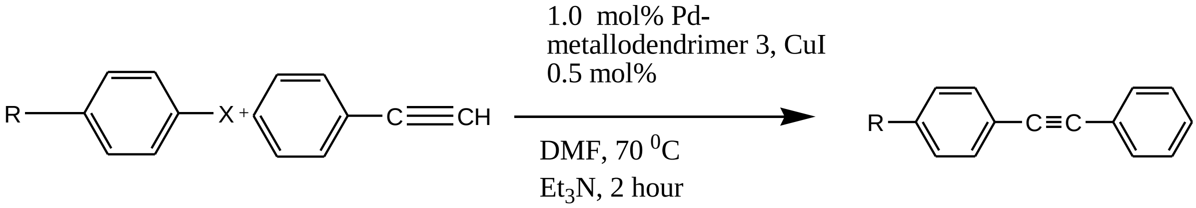
Table 2. Optimization of the Pd-metallodendrimer 3 catalyzed Sonogashira reaction between 4-iodophenol and phenylacetylene

Entry	Base	solvent	Time	Co-Catalyst CuI mol%	Catalyst (3) mol%	Yield%
1	KO^tBu	CH_3CN	3	-	1.0	55
2	Na_2CO_3	CH_3CN	3	-	1.5	51
3	K_2CO_3	DMF	3	-	1.0	50
4	NaOH	CH_3CN	2	0.5	1.0	70
5	NaOH	C_2H_5OH	2	0.5	1.0	75
6	NaOH	CH_3OH	2	0.5	1.0	74
7	KOH	C_2H_5OH	2	0.5	1.0	76
8	KOH	CH_3CN	2	0.5	1.0	79
9	KOH	DMF	2	0.5	1.0	80
10	KOH	CH_3OH	2	0.5	1.0	75
11	KOH	DMF	24	2.0	-	-
12	Et_3N	DMF	2	0.5	1.0	90

t-BuOK, Na_2CO_3, and K_2CO_3 with CH_3CN or DMF as the solvent were appropriate bases to complete the Sonogashira coupling without using CuI at 70℃ for 3h with a yield higher than 50% (Table 2, entries 1–3). Interestingly, when NaOH, KOH with solvent CH_3CN, DMF, C_2H_5OH, CH_3OH as the solvent using CuI 0.5 mol% as co-catalyst and catalyst 1.0 mol% at 70℃ the above Sonogashira reaction was carried out for 2.0 h above upto 80% yield was found (Table 2, entries 4–10).

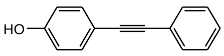
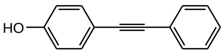
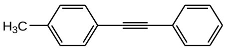
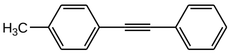
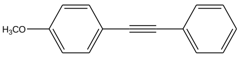
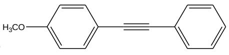
Copper salts are used as co-catalysts within the Sonogashira reaction, even though it makes the Sonogashira method air sensitive. Notwithstanding this drawback, copper salts in the presence of a base have been used notably for the formation of Cu-alkynyl species that transmetallate to palladium within the catalytic cycle. Due to investigate the effect of CuI as a catalyst, a blank experiment was performed in the absence of a palladium-metallodendrimer 3 catalyst revealed that no reaction happened even within the presence of CuI (2 mol%) at 24 hour (Table 2, entry 11). In the presence of Et_3N, DMF, Pd-metallodendrimer 3 (1.0 mol%) as well as CuI (0.5 mol%), the reaction was completed within two hours without any deleterious effects at the conversions with 90% yield (Table 2, entry 12).

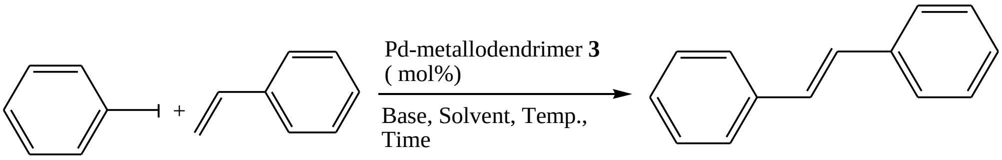
Therefore, the optimized reaction condition was found with 90% yield when 1.0 mol% of Pd-metallodendrimer 3 as a catalyst, 0.5 mol% CuI as a co-catalyst, Et_3N, and DMF were used under the nitrogen atmosphere at 70℃ at 2 hour (Table 2, Entry 12). After optimization, we achieved the catalytic activities with more electron-donating or greater sterically hindered aryl halide substrates. Good to remarkable conversions were acquired with the greater electron-donating or extra sterically hindered methyl and methoxy-substituted aryl halide substrates under the chosen reaction catalyzed by catalyst 3 after 2h (Scheme 3, Table 3, entries 1–6).



4-9 **10** **Scheme 3** **11-13**

Table 3. Sonogashira coupling reaction of different aryl chlorides with phenylacetylene catalyzed by Pd-metallodendrimer 3

Entry	R	X	product	Yield%
1	4, OH	4, I	 11	92
2	5, OH	5, Br	 11	81
3	6, CH_3	6, I	 12	95
4	7, CH_3	7, Br	 12	83
5	8, OCH_3	8, I	 13	96
6	9, OCH_3	9, Br	 13	83



Scheme 4

Table 4. Optimization of the Pd-metallodendrimer **3** catalyzed Heck reaction between 4-iodobenzene and styrene

Entry	**Time (h)**	**Base**	**Temp (°C)**	**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	85	CH_3OH	1.5	60
8	26	KO^tBu	85	$CH_3C_6H_5$	1.5	70
9	24	K_2CO_3	85	DMF	1.5	75
10	24	Et_3N	85	DMF	1.0	90

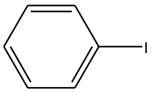
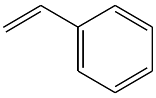
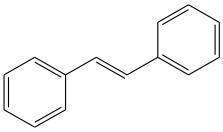
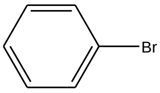
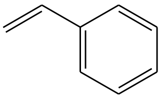
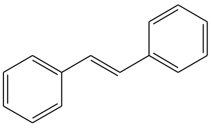
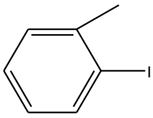
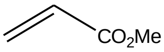
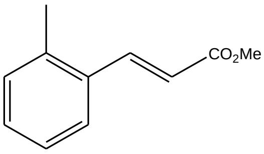
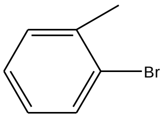
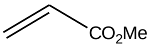
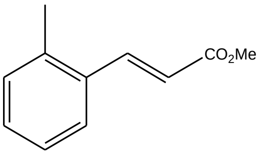
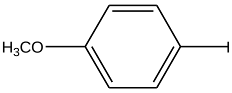
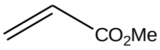
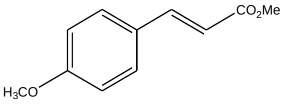
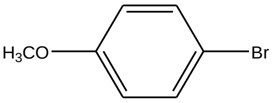
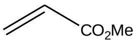
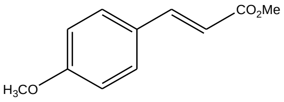
Reaction conditions: Aryl halide (1mmol), phenylacetylene (1.2 mmol), catalyst (1.0 mol%), base (1.2 mmol), solvent (5 mL), 70°C, 2h, under nitrogen atmosphere, Yield% was calculated based on aryl halide.

Likewise, due to optimization the Heck reaction conditions, a series of reactions under various combinations of bases, solvents, and temperatures, using Pd-metallodendrimer 3 as a catalyst, was pursued. Iodobenzene and styrene were designated as the classic substrates in this coupling reaction and the results have been presented in Scheme 4 (Table 4).

Reaction conditions: Iodobenzene (1 mmol), styrene (1.2 mmol), base (1.2 mmol), 24 hour, Temp. 85°C, Yields% was calculated on the basis of iodobenzene.

The coupled product was now not produced, when the coupling reaction was occoured with using 1.5 mol % Pd-metallodendrimer 3 as a catalyst, with styrene (1.2 mmol), and iodobenzene (1 mmol) in CH_3CN, DMF or DMSO (5 mL), and at temperature (Room temp. to 40°C) in the presence of NaOH, Na_2CO_3 or KOH, K_2CO_3 (1.2 equivalent) at 24 h (Table 4, entries 1-5). Fascinatingly, the reaction showed the development of 50% yield with 2.0 mol% of catalyst 3 in the presence of Et_3N and DMF at 60°C at 20 h (Table 4, entry 6). Furthermore, the usage of other bases containing of K_2CO_3, KO^tBu and in the presence of the solvents, methanol, toluene or DMF at 85°C, the coupling products were found above 60% yield (Table 4, entries 7-9). The best result was observed whilst 1.0 mol% of the catalytic system 3 and Et_3N, as a base, and solvent DMF was used under the nitrogen atmosphere at 85°C at 24 h for Heck coupling reaction (Table 4, entry 10).

Table 5. Heck coupling reaction of different aryl chlorides with different olefins catalyzed by Pd-metallodendrimer 3

Entry	Aryl halides	Olefins	products	Yield%
1	 14	 20	 22	94
2	 15	 20	 22	80
3	 16	 21	 23	95
4	 17	 21	 23	81
5	 18	 21	 24	96
6	 19	 21	 25	83

Yield% was calculated based on aryl halide.

A wide variety of olefins and diversely substituted aryl halides were selected for cross-coupling to produce the corresponding 1, 2-disubstituted olefins. The results have been summarized in table 5. Though aryl bromides and aryl iodides performed nicely (Table 5, entries 1-6) under these optimized Heck reaction conditions. However, while compared to the iodo analogues with bromo analogues, a reduced reactivity was discovered in the case of the corresponding bromo derivatives and was found less yield % of the products.

Above all coupling products for Sonogasira and Heck reaction were analyzed by spectroscopic methods and compared with authentic spectra. (Figures S 07-S 12 and S 13-S 21 in the supporting information)

A wide form of olefins and diversely substituted aryl halides were selected for cross-coupling to produce the corresponding 1, 2-disubstituted olefins. The results have been summarized in table 5. Although aryl bromides and aryl iodides completed the conversion properly (Table 5, entries 1-6) under those optimized Heck reaction conditions. But, even as compared to the iodo analogues with bromo analogues, a reduced reactivity was observed in the case of the corresponding bromo derivatives and turned into discovered less yield % of the product.

The coupling products for Sonogasira and Heck reaction were analysed by spectroscopic methods and as compared with proper spectra. (Figures S 07-S 12 and S 13-S 21 in the supporting informations)

4. Conclusions

In precis, a unique palladium mediated metallodendrimer 3 was synthesized through the coordination reaction of 2,4,6-triaminopyrimidine (1) with 4-methyl benzoyl chloride (2). The complexation was virtually determined by IR, ^{1}H NMR, ^{13}C NMR, elemental analysis and mass spectra. The morphological structure of the catalyst like as branches of the tree without leaves or cylindrical fiber was revealed by SEM image and good thermal stability of the compound was observed by TG and DSC investigation. This homogeneous catalytic system showed numerous advantages including low catalyst loading, substrate tolerance, excellent yields, green solvents, short reaction times and a quite simple process for synthesizing Heck and Sonogashira coupling reaction products that are biologically vital in the numerous area in the chemistry world. These special upshots of this catalyst signify a noteworthy improvement in the area of C-C bond formation reactions.

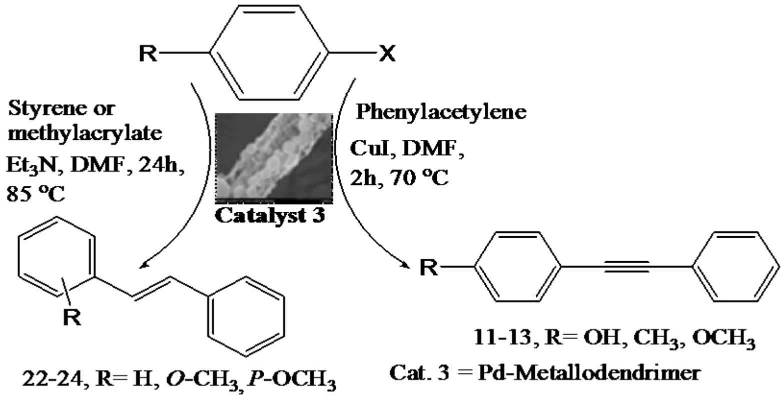
ACKNOWLEDGEMENTS

I would like to express our cordial gratefulness to the Ministry of Science and Technology, Dhaka, Bangladesh (National Science& Technology Ph.D Fellowship program 2018-2019, No- 39.00.0000.012.002.03.18.25, Code no-1260101-120005100-3821117) and Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh for funding the economic support.

Graphical Abstract: Synthesis and

Catalytic Activity of Palladium Mediated Metallodendrimer for the Sonogashira and

Heck Coupling Reaction Md. Sayedul Islam and Md. Wahab Khan



Supporting Information

Md. Sayedul Islam and Md. Wahab Khan

IR spectra of 2, 4, 6-Tris (di-4-methylbenzamido)-1, 3, 5-Diazine palladium (II) chloride 3

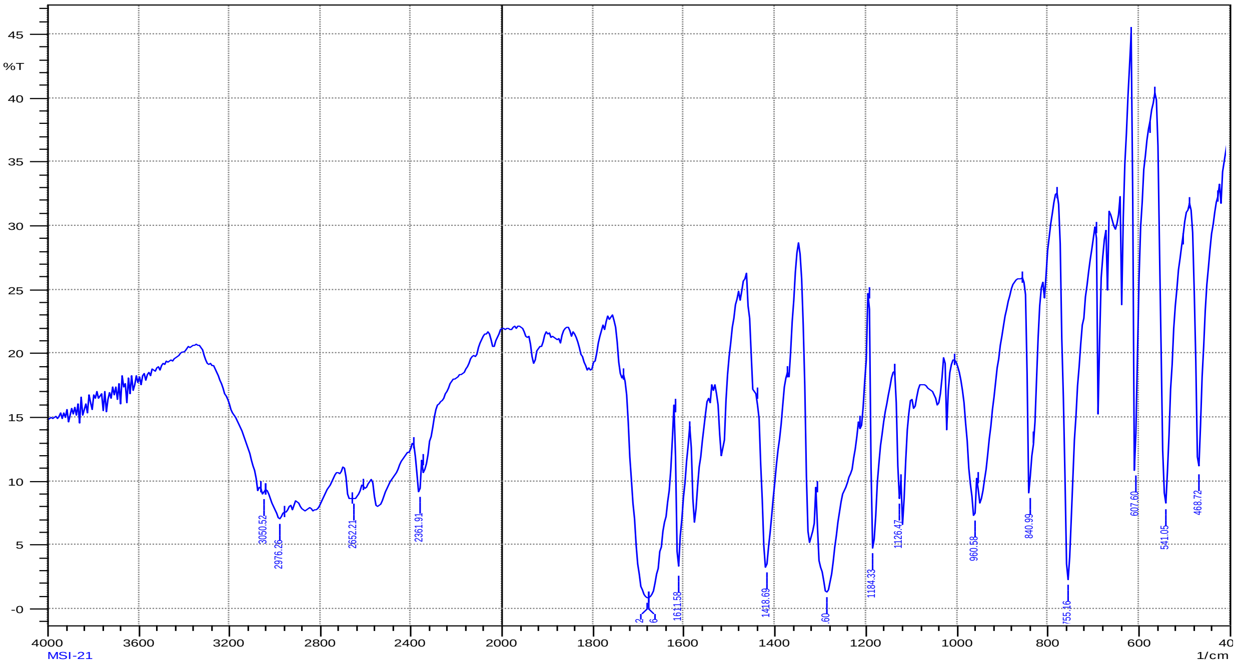
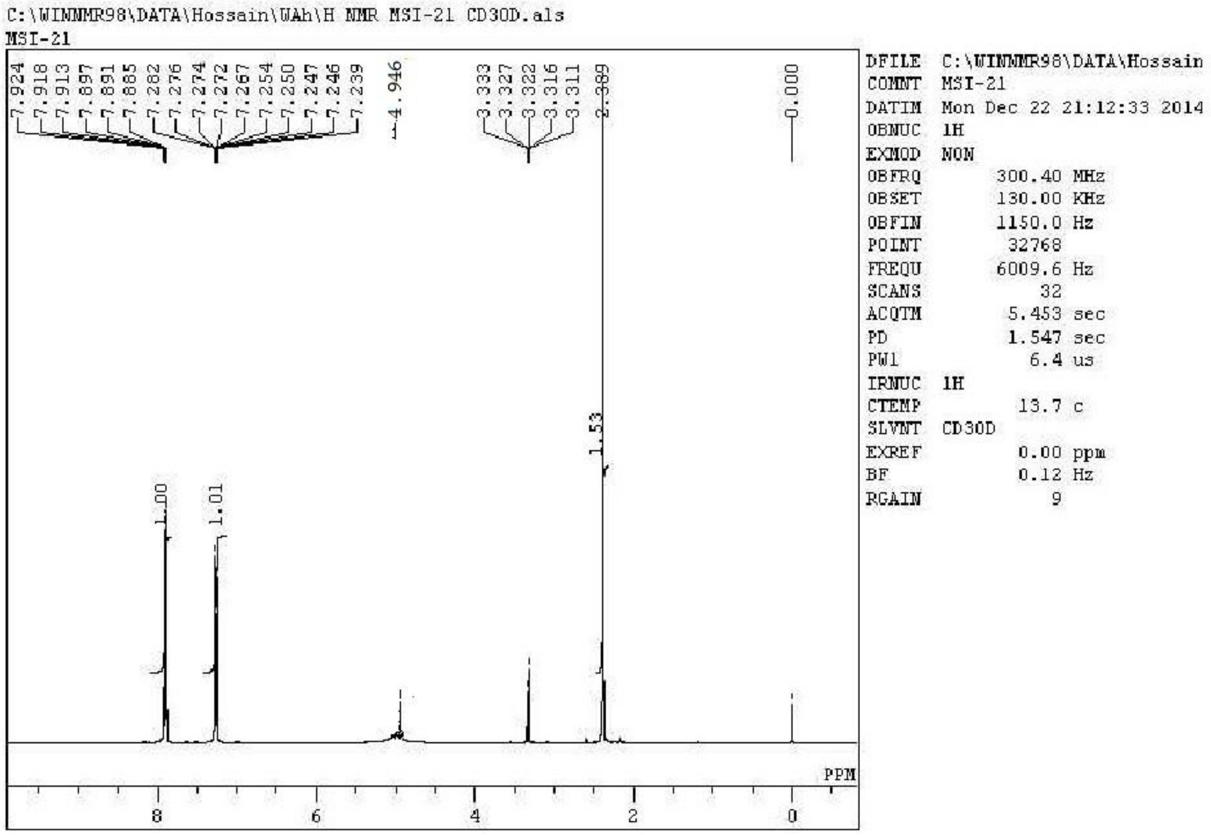


Figure S1

^{1}H NMR spectra of 2, 4, 6-Tris (di-4-methylbenzamido)-1, 3, 5-Diazine palladium (II) chloride 3



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EXMOD   NON
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OBSET        130.00 KHz
OBFIN        1150.0 Hz
POINT         32768
FREQU        6009.6 Hz
SCANS            32
ACQTM         5.453 sec
PD            1.547 sec
PW1             6.4 us
IRNUC   1H
CTEMP          13.7 c
SLVNT   CD3OD
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN             9
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Figure S2

^{13}C NMR spectra of 2, 4, 6-Tris (di-4-methylbenzamido)-1, 3, 5-Diazine palladium (II) chloride 3

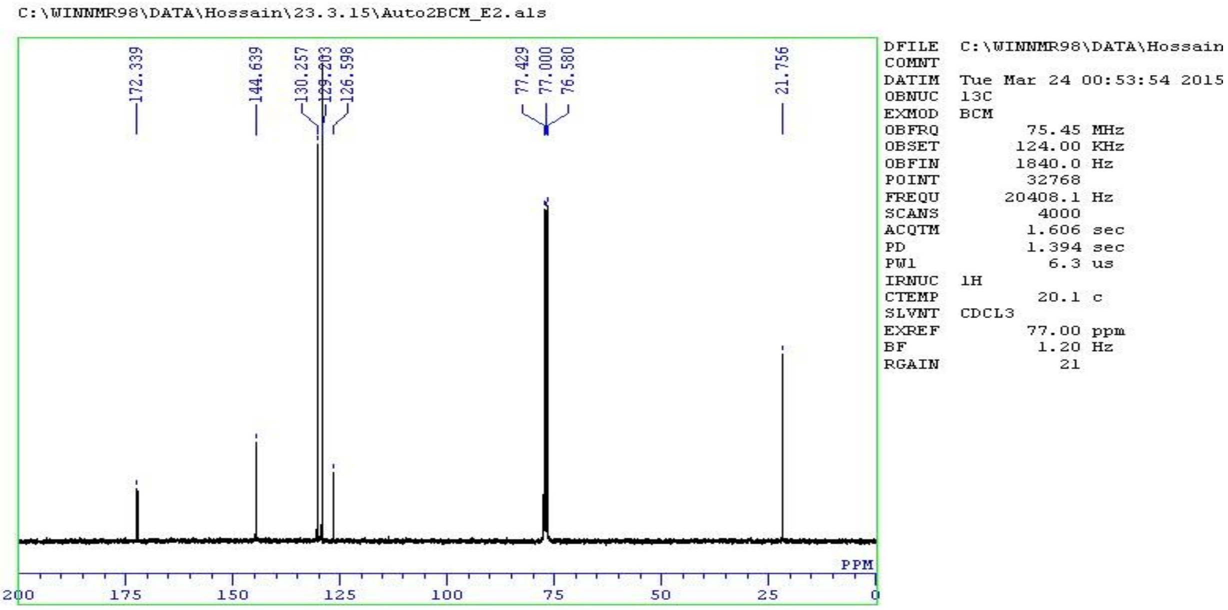


Figure S3

Mass spectra of 2, 4, 6-Tris (di-4-methylbenzamido)-1, 3, 5-Diazine palladium (II) chloride 3

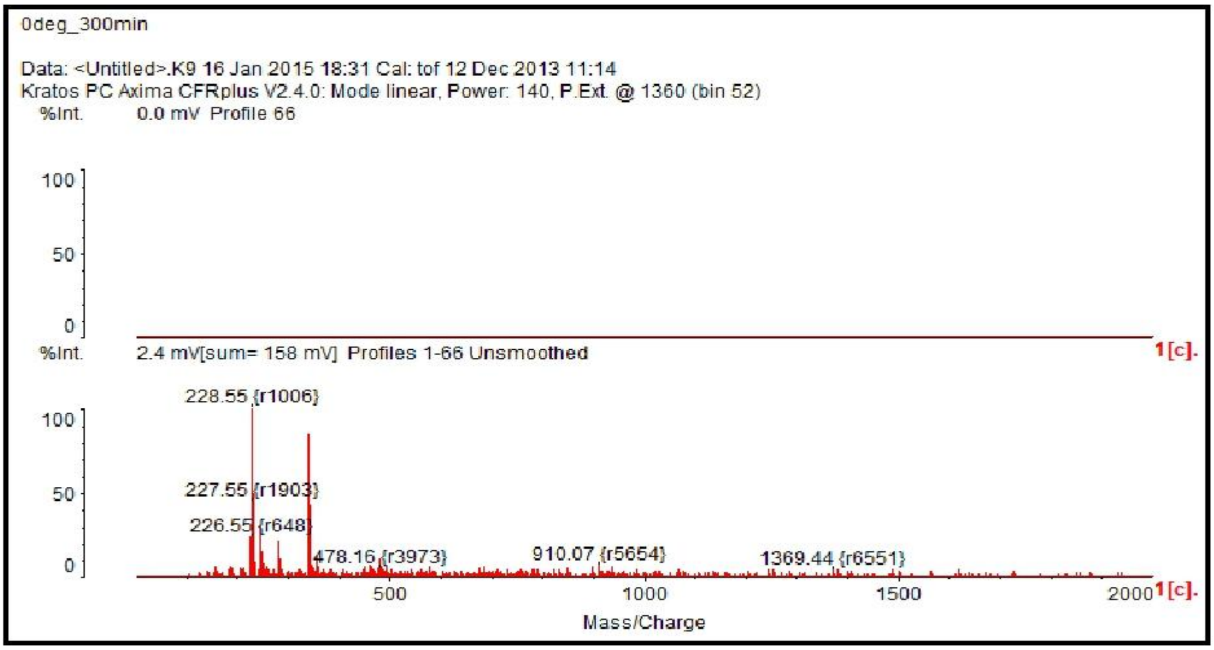
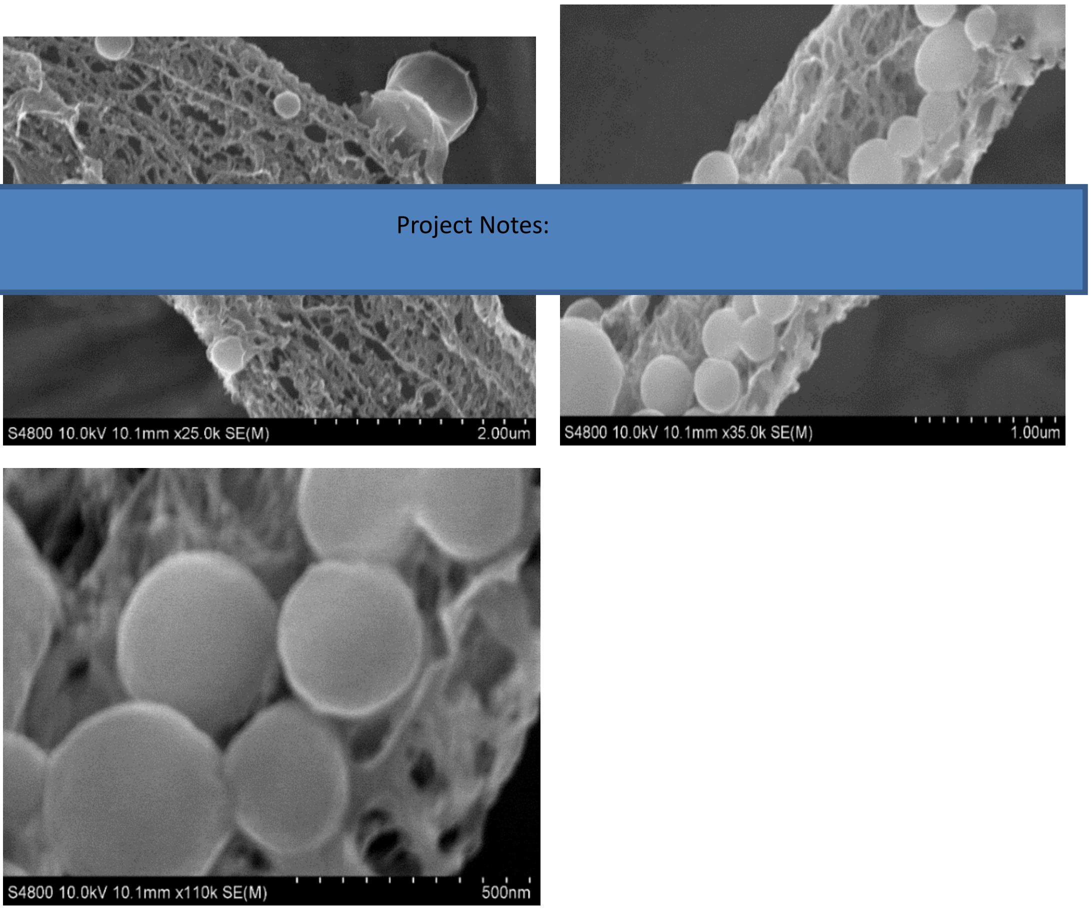


Figure S4

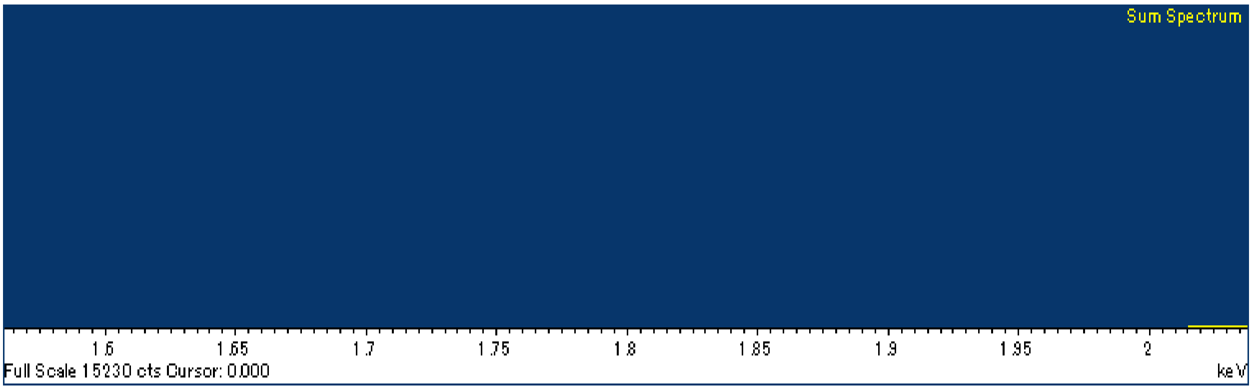
SEM of 2, 4, 6-Tris (di-4-methylbenzamido)-1, 3, 5-Diazine palladium (II) chloride 3



Project Notes:

Figure S5

EDX of 2, 4, 6-Tris (di-4-methylbenzamido)-1, 3, 5-Diazine palladium (II) chloride 3



EDX of compound of 2, 4, 6-Tris(di-4 methylbenzamido)-1, 5-diazine palladium chloride

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	0.82	1.5609	34.51	8.04	41.60
N K	0.09	0.2966	20.88	7.48	21.58
O K	0.55	0.8784	39.70	7.09	35.93
Cl K	0.01	0.8218	**0.82**	2.26	**0.33**
Pd L	0.04	0.6804	**4.10**	6.12	**0.56**
Totals			100.00		

Spectrum processing:

Peaks possibly omitted: 0.800, 0.935, 2.065, 8.047 keV

Processing option: All elements analyzed (Normalised)

Number of iterations = 2

Standard :

C CaCO3 1-Jun-1999 12:00 AM

N Not defined 1-Jun-1999 12:00 AM

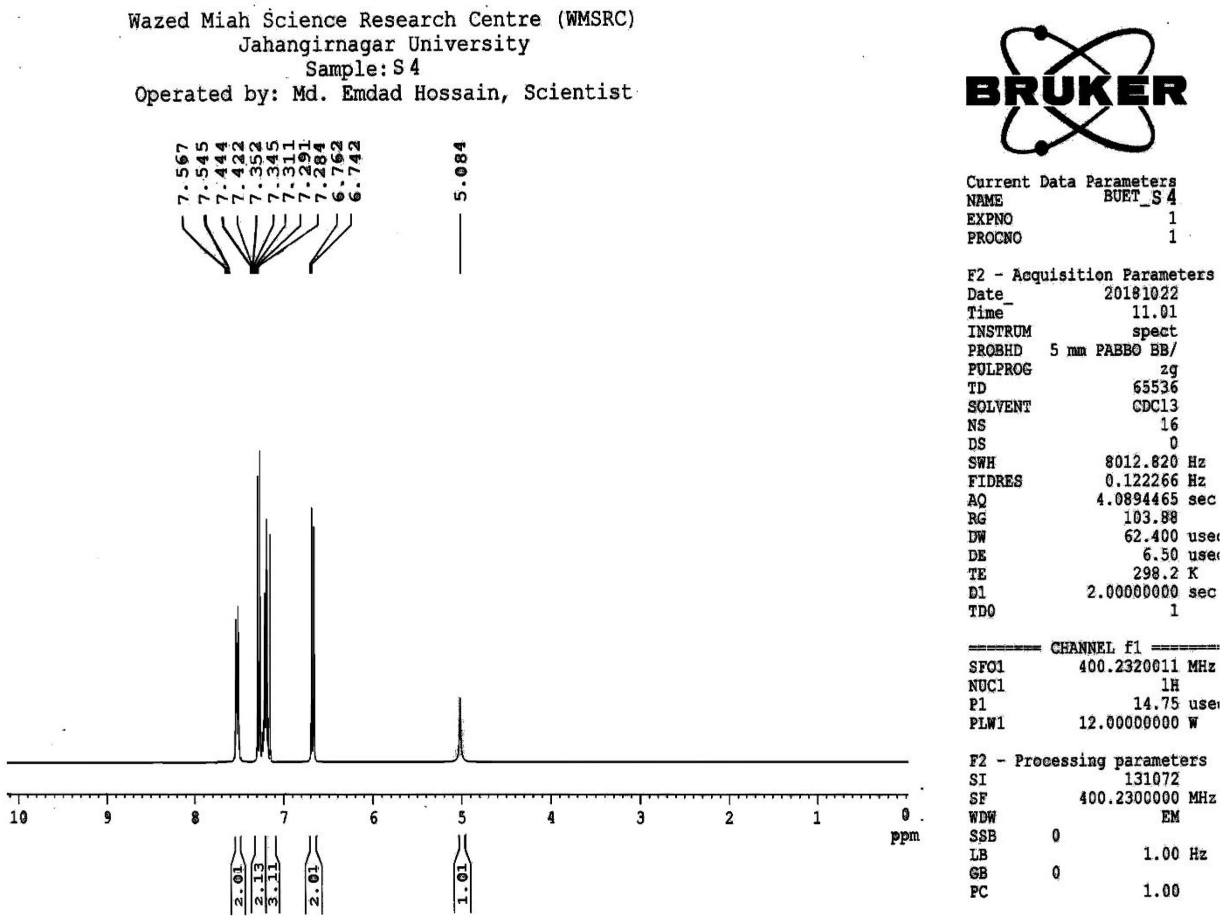
O SiO2 1-Jun-1999 12:00 AM

Cl KCl 1-Jun-1999 12:00 AM

Pd Pd 1-Jun-1999 12:00 AM

Figure S6

^{1}H NMR of 4-(2-phenylethynyl)phenol **11**



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Jahangirnagar University
Sample: S 4
Operated by: Md. Emdad Hossain, Scientist

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PROCNO                  1

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DS                      0
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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

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P1                  14.75 usec
PLW1         12.00000000 W

F2 - Processing parameters
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WDW                    EM
SSB      0
LB                   1.00 Hz
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PC                   1.00
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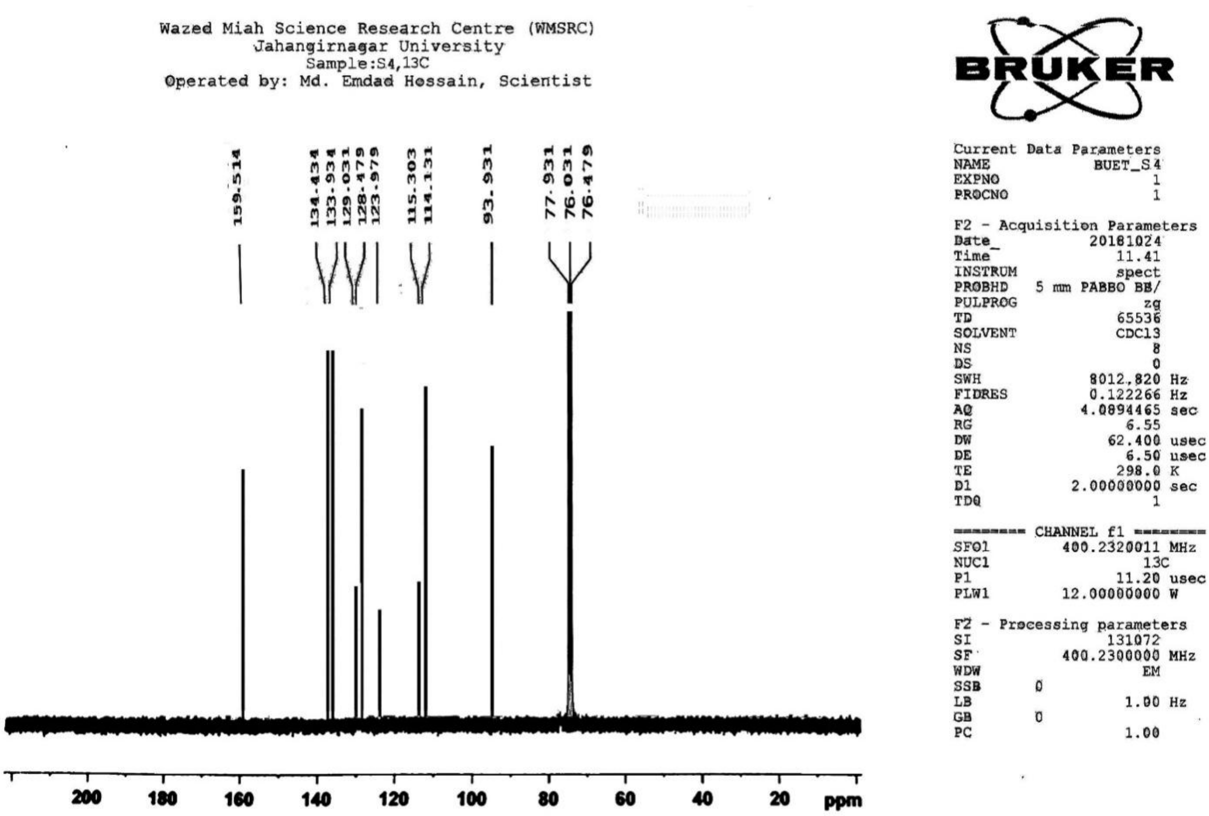
Figure S7

^{13}C NMR of 4-(2-phenylethynyl)phenol, **11**



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

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DS                      0
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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
TDO                     1

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

F2 - Processing parameters
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SF            400.2300000 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.00
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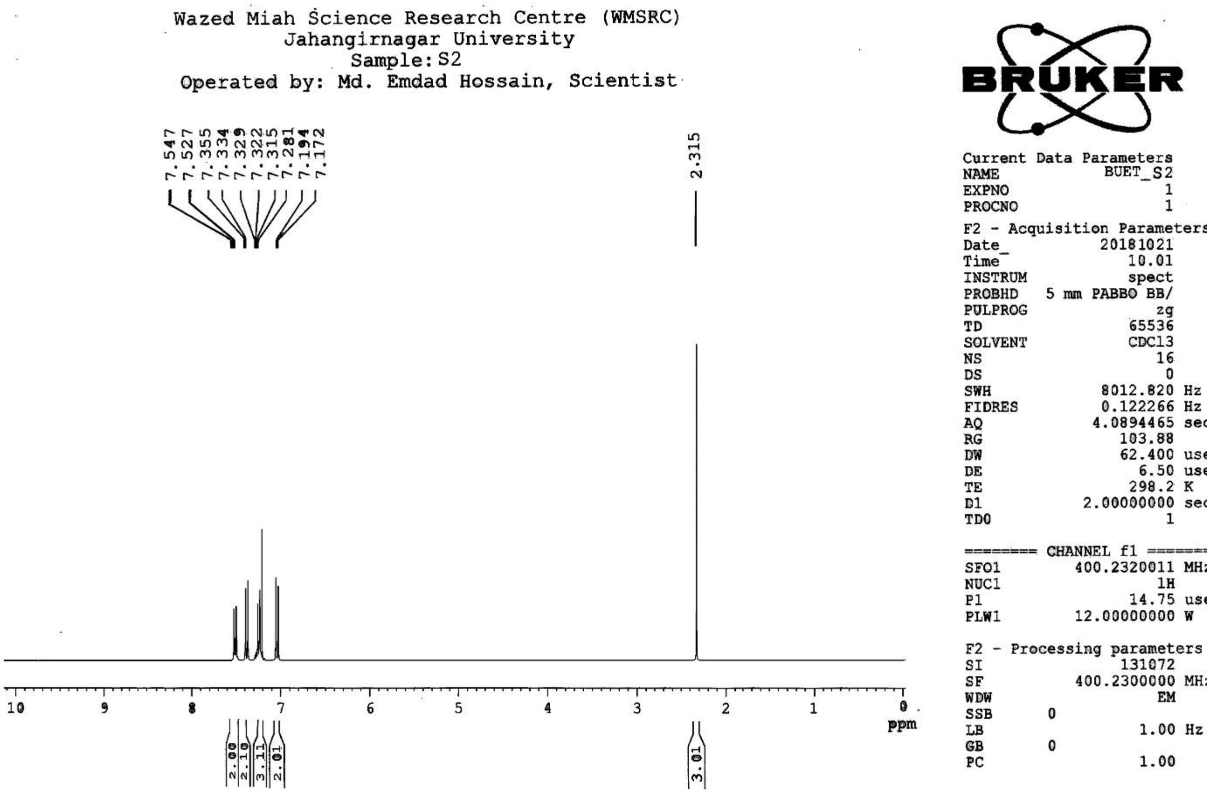
Figure S8

^{1}H NMR of 1-(2-p-tolylethynyl)benzene, **12**



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

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PROCNO                  1

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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

======== CHANNEL f1 ======
SFO1         400.2320011 MH
NUC1                   1H
P1                  14.75 us
PLW1          12.00000000 W

F2 - Processing parameters
SI                 131072
SF            400.2300000 MH
WDW                    EM
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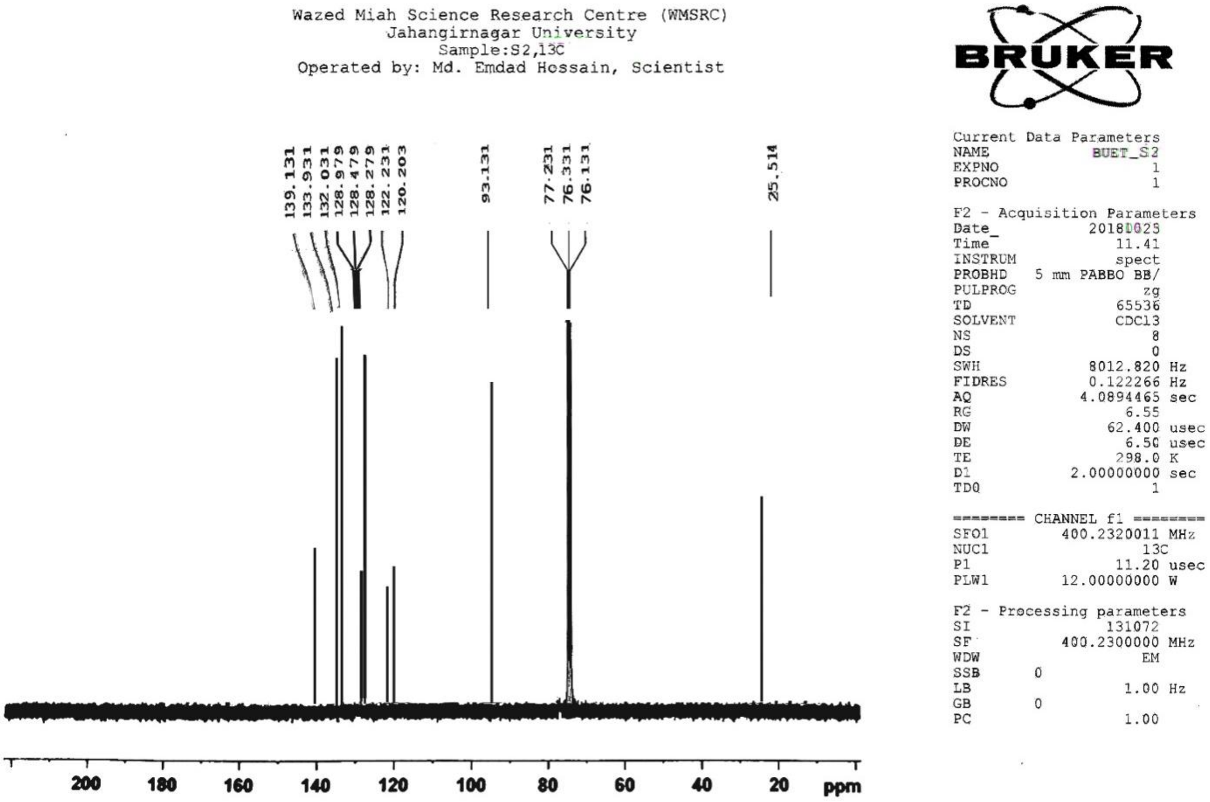
GB       0
PC                   1.00
```

Figure S9

^{13}C NMR of 1-(2-p-tolylethynyl)benzene, **12**



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PROCNO                 1

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FIDRES          0.122266 Hz
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RG                  6.55
DW                62.400 usec
DE                  6.50 usec
TE                 298.0 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
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NUC1                 13C
P1                 11.20 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
```
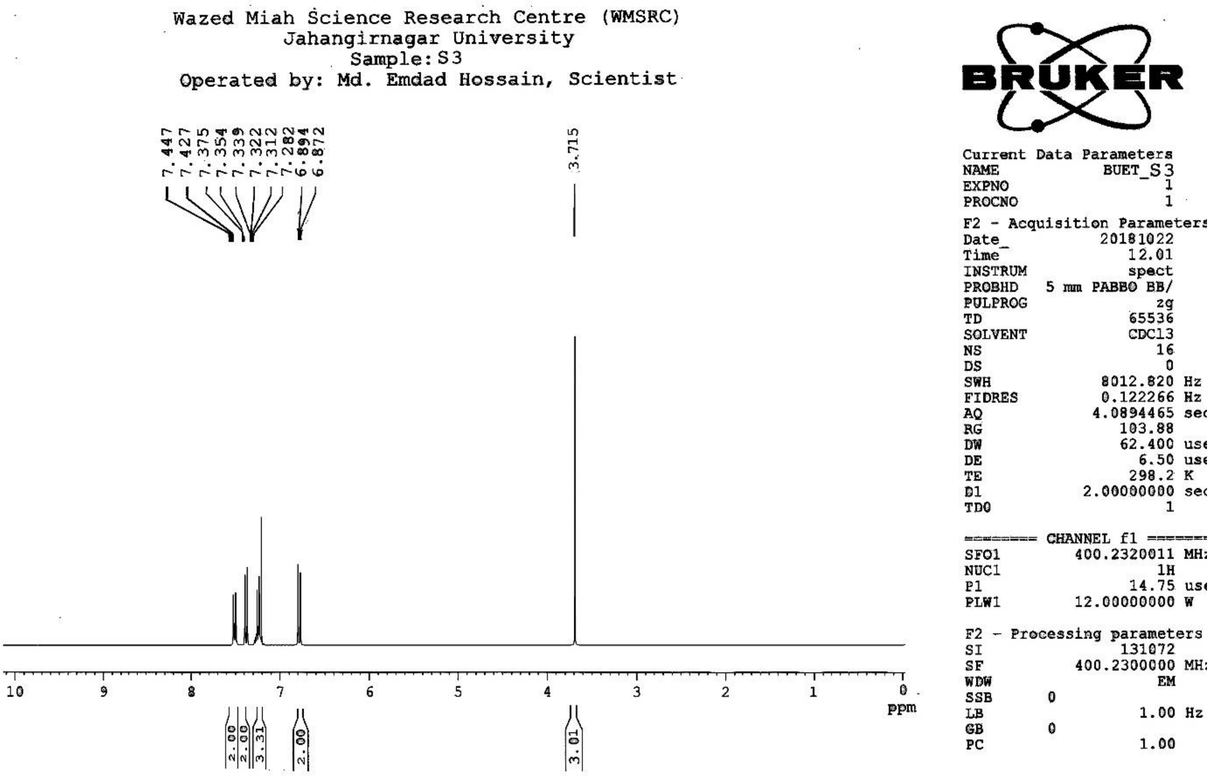

Figure S10

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



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DS                     0
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FIDRES          0.122266 Hz
AQ             4.0894465 se
RG                103.88
DW                62.400 us
DE                  6.50 us
TE                 298.2 K
D1            2.00000000 se
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======== CHANNEL f1 =====
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NUC1                  1H
P1                 14.75 us
PLW1         12.00000000 W

F2 - Processing parameters
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WDW                   EM
SSB      0
LB                  1.00 Hz
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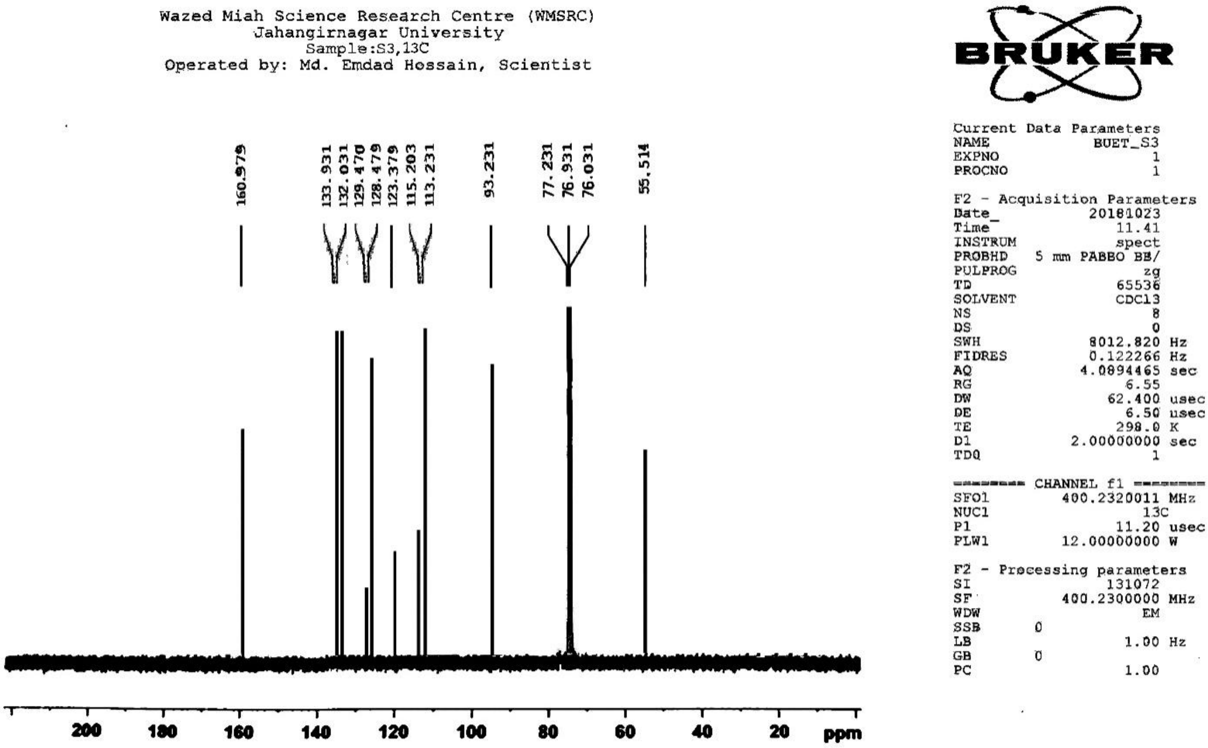
Figure S11

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



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Jahangirnagar University
Sample:S3,13C
Operated by: Md. Emdad Hossain, Scientist

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FIDRES          0.122266 Hz
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RG                  6.55
DW                62.400 usec
DE                  6.50 usec
TE                 298.0 K
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TDQ                    1

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PLW1         12.00000000 W

F2 - Processing parameters
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Figure S12

IR of Transstillbene, **26**

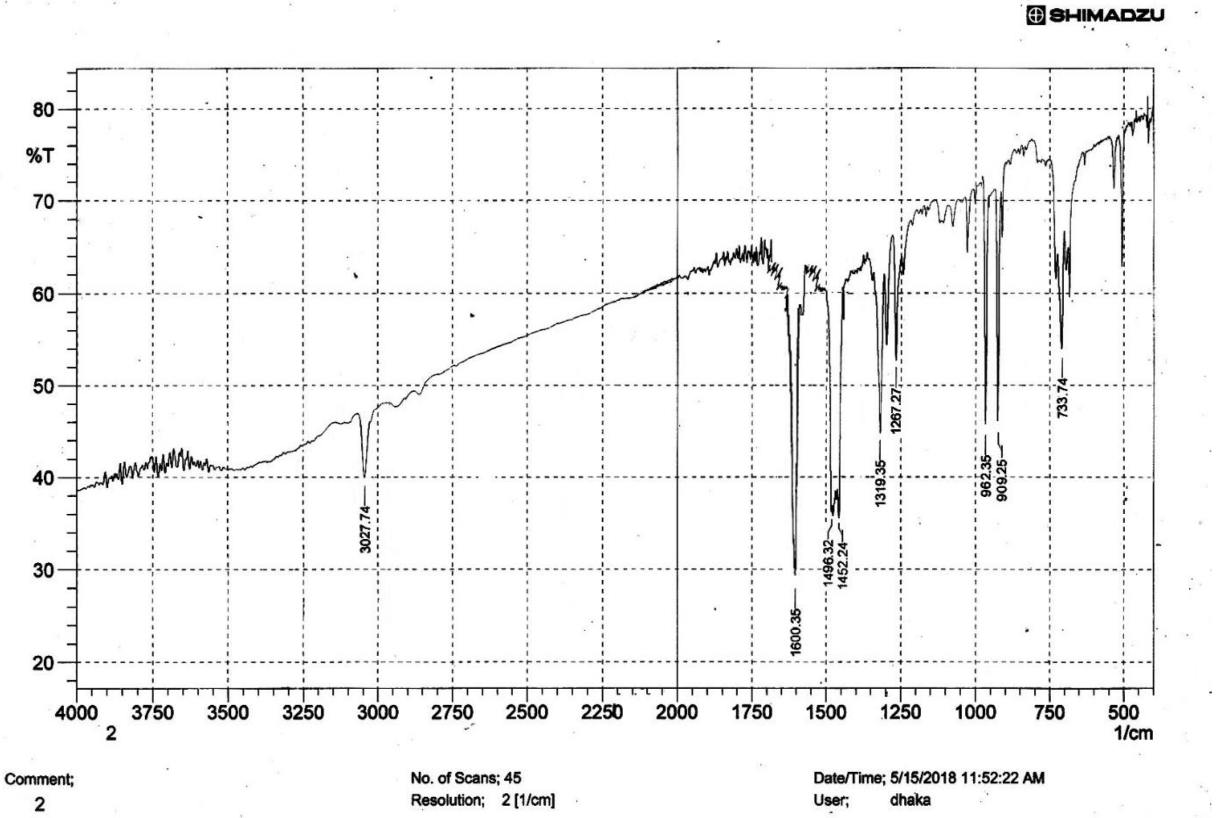

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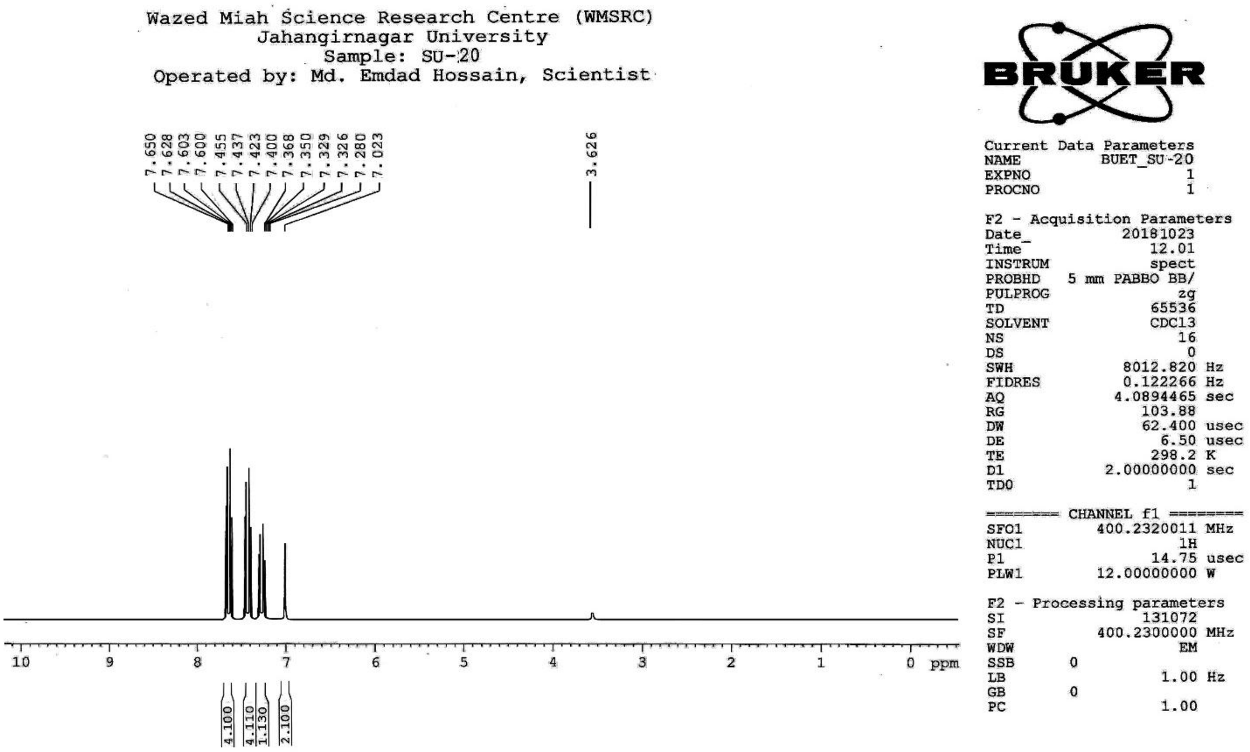
Figure S13

^{1}H nmr of trans stilbene, **26**



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

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PROCNO                    1

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

F2 - Processing parameters
SI                   131072
SF              400.2300000 MHz
WDW                      EM
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LB                     1.00 Hz
GB       0
PC                     1.00
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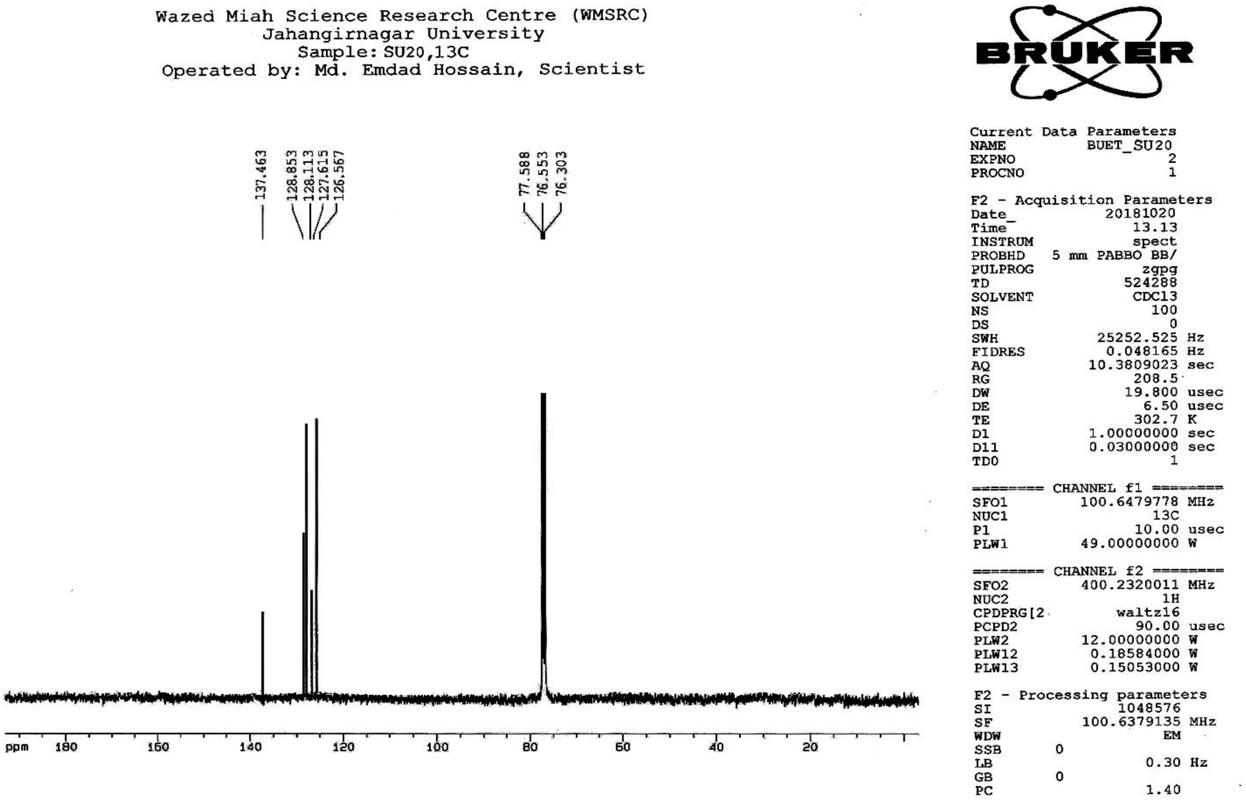
Figure S14

^{13}C nmr of trans stilbene, **26**



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-o-tolylacrylate, **27**

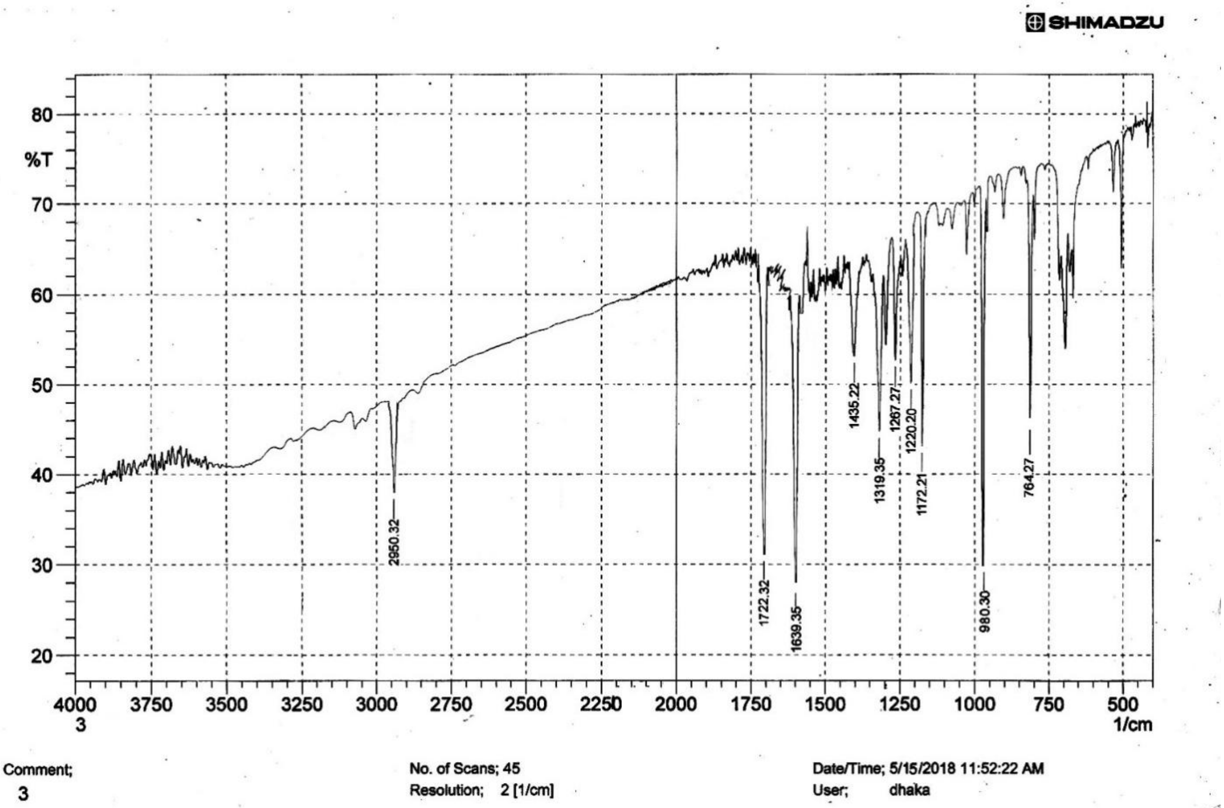


Figure S16

^{1}H nmr of (E)-methyl 3-o-tolylacrylate, **27**

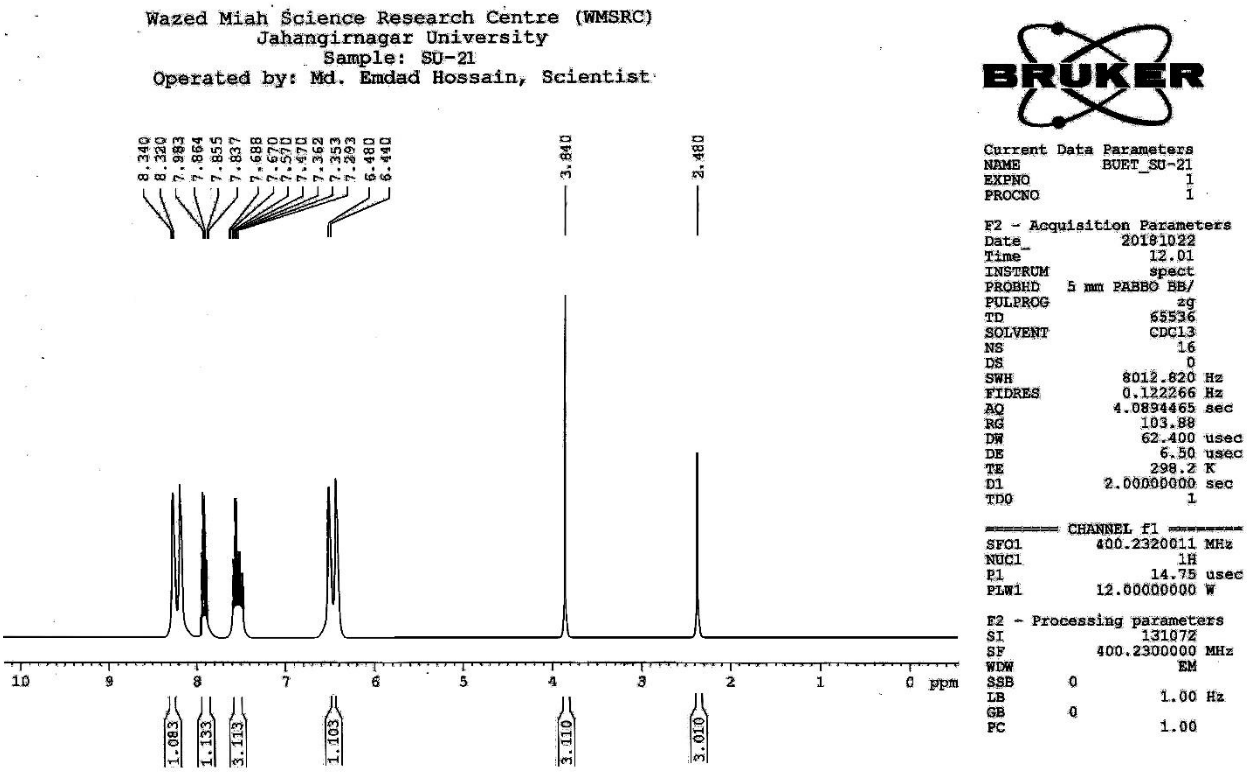
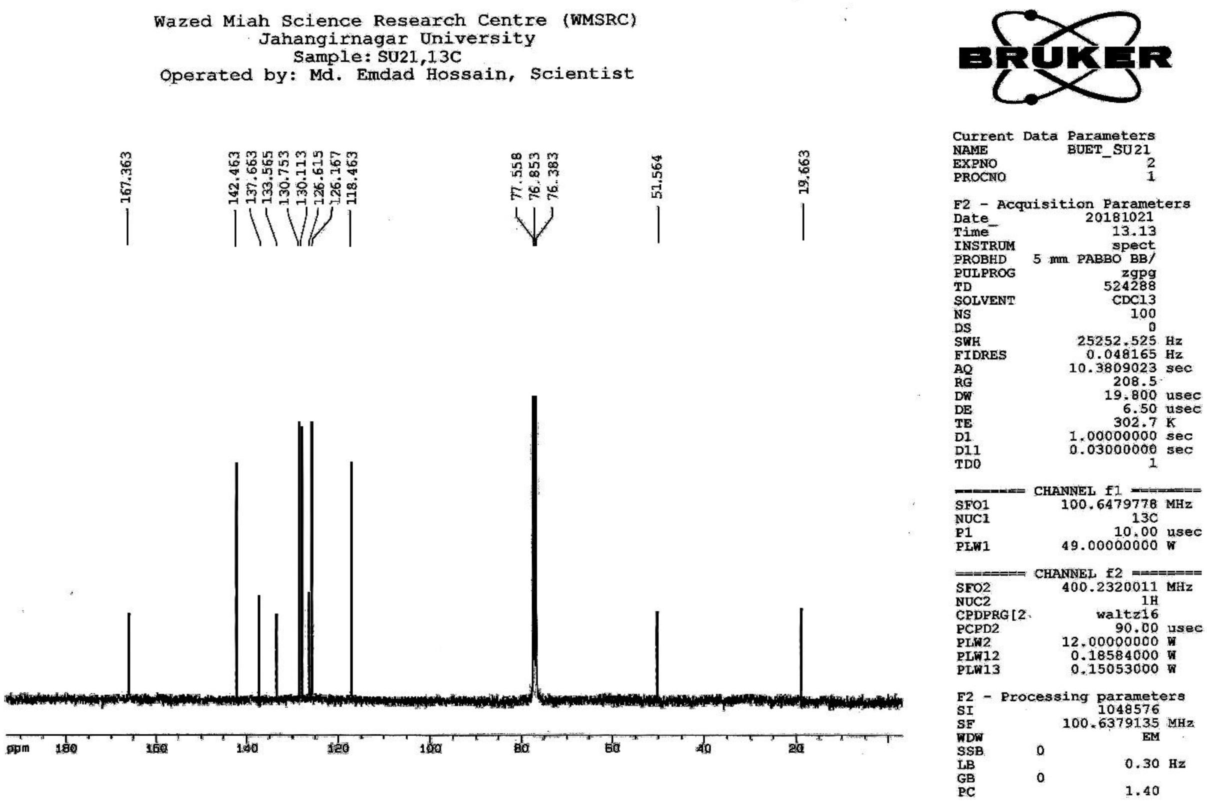


Figure S17

^{13}C nmr of (E)-methyl 3-o-tolylacrylate, **27**

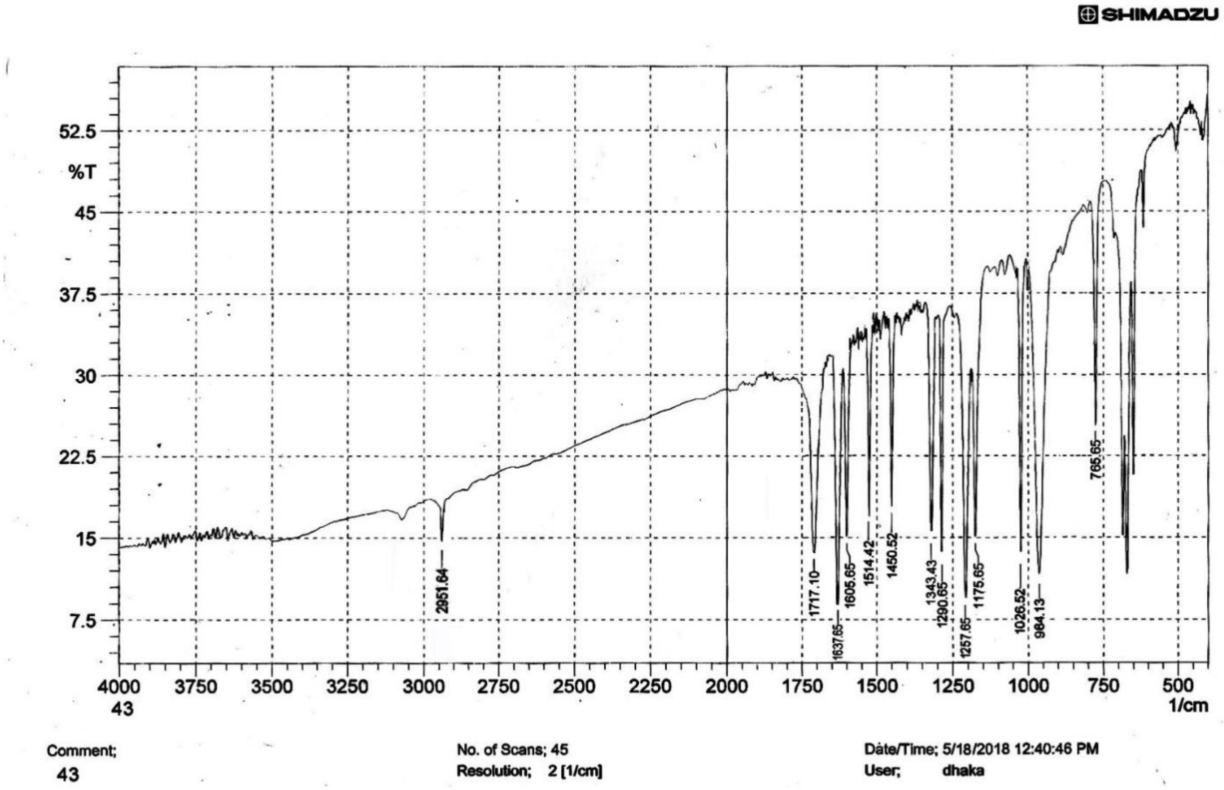


Wazed Miah Science Research Centre (WMSRC)
Jahangirnagar University
Sample: SU21,13C
Operated by: Md. Emdad Hossain, Scientist

```
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

IR of 1-methoxy-4-styrylbenzene, **28**



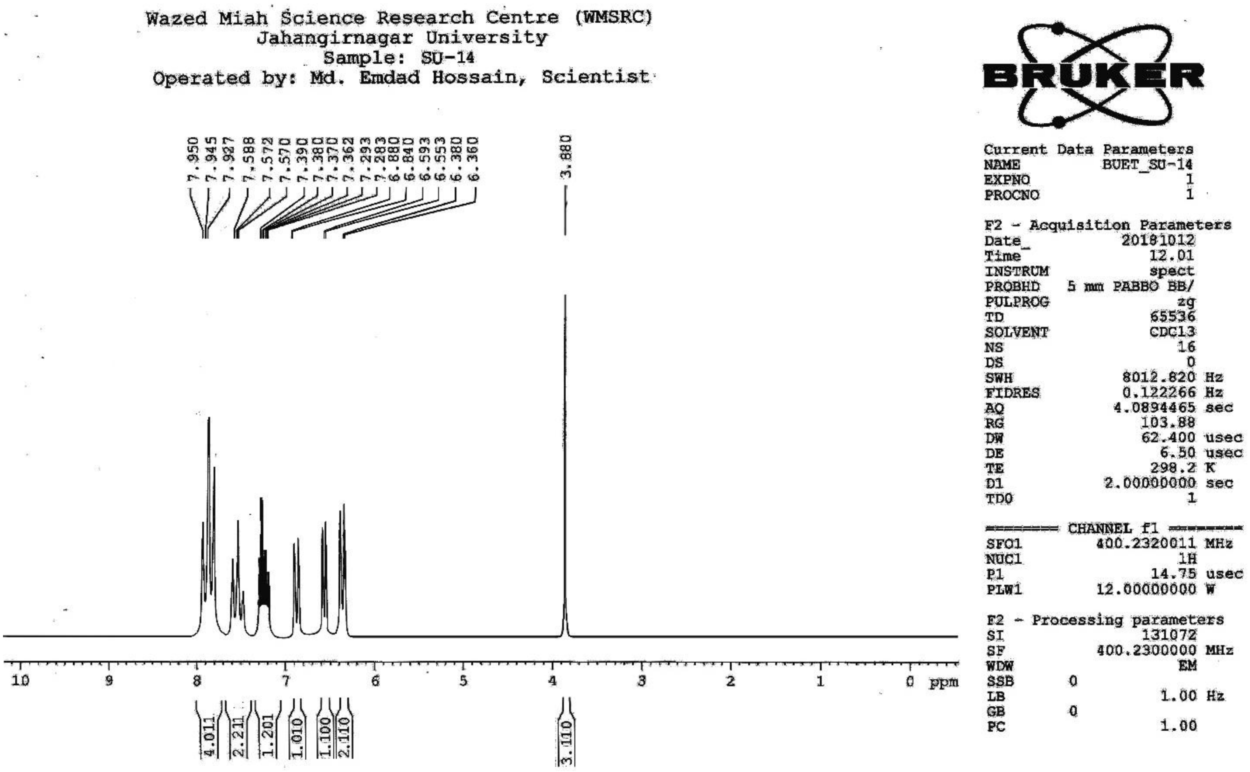
Comment;
43

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

Date/Time; 5/18/2018 12:40:46 PM
User; dhaka

Figure S19

^1H nmr of 1-methoxy-4-styrylbenzene, **28**

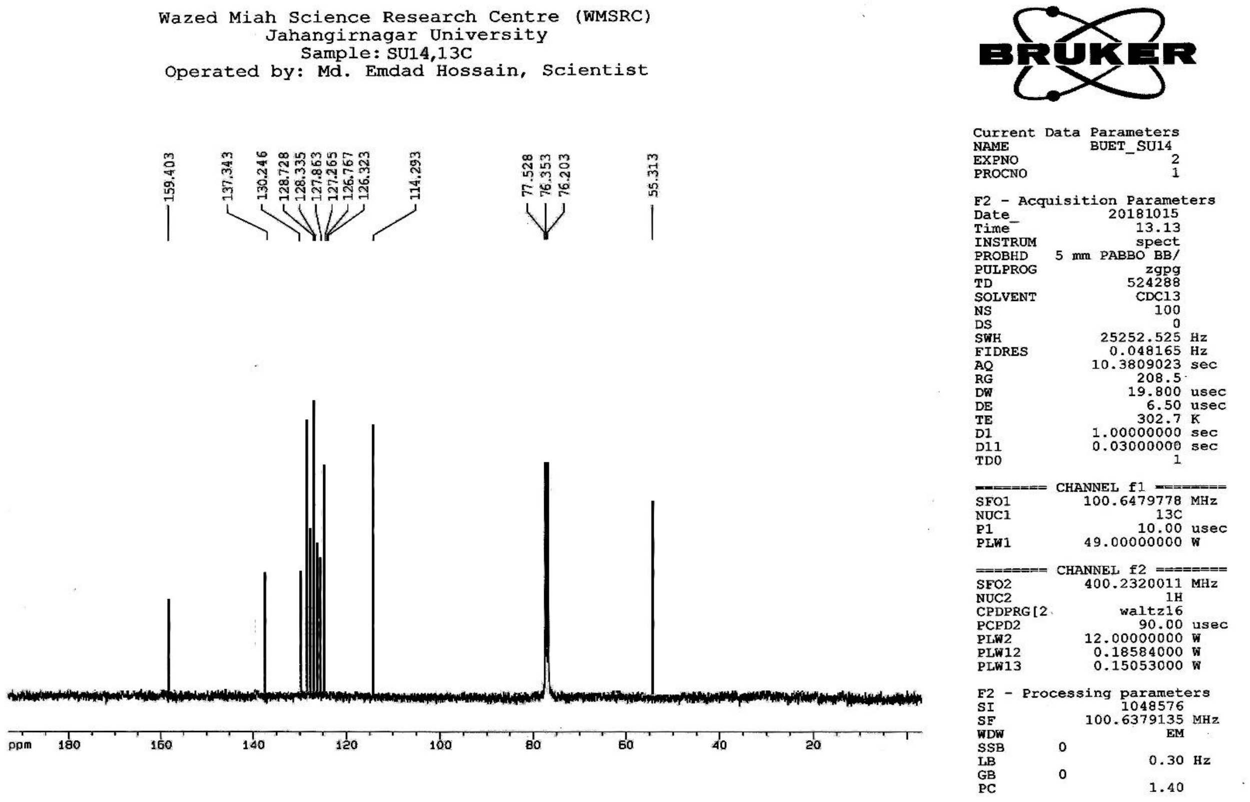


Wazed Miah Science Research Centre (WMSRC)
Jahangirnagar University
Sample: SU-14
Operated by: Md. Emdad Hossain, Scientist

```
Current Data Parameters
NAME          BUET_SU-14
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20181012
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 S20

^{13}C nmr of 1-methoxy-4-styrylbenzene, **28**



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

```
Current Data Parameters
NAME            BUET_SU14
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20181015
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 S21

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