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Synthesis, Characterization and catalytic activity of Palladium-Based Metallodendrimer with Triazine

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ABSTRACT

A novel Pd-based metallodendrimer has been directly prepared by the reaction of substituted triazine with substituted benzoyl chloride in good yields using $(Ph_3P)_2PdCl_2$ and DMF at 70 °C. This procedure avoids the use of high temperature and severe reaction conditions. The surface morphology like as entangled nanofibers from SEM image and the presence of Palladium ions of the compound from EDX analysis were obtained in addition TG and DSC showed the good thermal stability of the compound. This white solid compound was found to be an effective homogeneous catalyst for the synthesis of ynones in where the synthetic route was copper and phosphine ligand-free.

Keywords: Triazine, substituted benzoyl chloride, Ynones, Dendrimers, Metallodendrimers.

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1.Introduction

Dendrimers based on triazine have received an amazing interest attributable to their potential uses and have shown molecular recognition and self-assembly properties [1]. In the beyond two decades, the layout and synthesis of numerous dendrimers have received growing attention [2] not only because of the aesthetically captivating structures of these molecules but also as a result of their various applications in host-guest chemistry [3], material science [4], and membrane chemistry [5]. So far, two complementary methodologies [6, 7] the divergent and the convergent have been applied in the preparation of dendrimers.

On the other hand, Metallodendrimers are the unique magnificence of synthetic macromolecules having enormously branched, three dimensional, nanoscale structure with very low polydispersity and excessive functionality [8]. Active centre in a metallodendrimer can be located in three different regions: (i) metal atom as the dendrimer core, (ii) metal atoms in the dendrimer branches (iii) metal atoms in the periphery. These characteristics have made their utility in nanotechnology, pharmaceutical and medicinal chemistry especially appealing [9].

Recently, metallodendrimers were broadly investigated in unique fields, together with molecular light harvesting, catalysts, liquid crystals, molecular encapsulation, and drug delivery [10]. Metallodendrimer compounds have been prepared via click on chemistry, using Diels-Alder reactions [11], thiolene reactions [12], and azide-alkyne reactions [13-15]. In addition, the facile, copper free, phosphine free and efficient synthetic route of ynones which are very biologically crucial compounds in pharmaceutical science through acylation of terminal alkynes with acid chlorides catalyzed by palladium catalyst is still scarce [16].

However, to the best of our knowledge, there's less report to be had inside the literature for the synthesis of highly stable solid crystalline palladium based metallodendrimers with triazine and the exploration of their homogeneous catalytic interest in coupling reactions. With the intention to generate environmentally benign metallodendrimers, we designed, synthesized, and characterized a novel palladium-based metallodendrimer which was effectively implemented as a homogeneous catalyst in the synthesis of ynones.

2. Experimental Section:

2.1 Materials and Instrumentation:

Unless otherwise cited, all reagents were reagent grade and used without further purification. Dehydrated DMF, DMSO, CH_3CN, and THF had been used as a reaction solvent and sold from Aldrich. De-ionized water was used in the experiment wherein required. The IR spectra was taken on a Shimadzu FTIR 8400S Fourier model 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 instrument as well as BRUKER DPX-400 MHz & 100 MHz spectrophotometer respectively. Chemical shifts was taken relative to TMS. Mass spectra (MS) was measured by using AXIMA-CFR, Shimadzu/Kratos TOF Mass spectrometer. Scanning Electron Microscope (SEM) and Electron Dispersive X-ray (EDX) was taken on a Hitachi S-4800. Analytical thin layer chromatography (TLC) has become silica gel 60 F 254 blanketed on 25 TCC aluminum sheets (20 × 20 cm). 2, 4, 6-triamino-1, 3, 5-diazine, 4-methyl benzoyl chloride and $(Ph_3P)_2PdCl_2$ had been purchased from Aldrich and were used without in addition purification. The thermal behavior of metallodendrimer was determined by a thermogravimetric analyzer (NETZSCH STA 449F3) from 26 to 600 °C. Elemental analyses were done with a Fisons EA 1108 CHNS-O apparatus. All TG and DSC information were obtained under a nitrogen atmosphere by means of using aluminum oxide crucible at a heating rate of 10 ^{0}k/min and at a flow rate of 40 and 60 mL/min.

2.2 Synthesis of compound 2, 4, 6-Tris (di-4-methylbenzamido)-1, 3, 5-triazine palladium (II) chloride (3)

4-methyl benzoylchloride **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-triazine **1** (0.2 g, 1.59 mmol) in DMF (10 mL). The solution was degassed and stirred at 70 °C under a nitrogen atmosphere for 6 h. The progress of the reaction was monitored by TLC. At the starting of the reaction, the mixture was turned into a clear solution and gradually it turned into white solid. 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 alumina column chromatography and finally recrystallized by using ethanol and afforded the desired product **3**.

White crystalline solid; yield: 90%.; IR (KBr): ν_{max} = 3010.43, 1760.21, 1612.52, 1416.23, 1288.46, 1332.46 cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ = 7.92 (m, 12 H), 7.28 (m, 12 H), 2.39 (s, 18 H) ppm. ^{13}C NMR (75 MHz, CDCl3): δ = 170.0, 144.4, 131.3, 130.5, 129.1, 21.6 ppm.

MALDI-TOF MS: *m*/*z* (%) = calcd. for $C_{51}N_6H_{42}O_6$ Pd_3Cl_6 1363.91; found 1363.08 (100) $[M]^+$. Elemental calculation for $C_{51}N_6H_{42}O_6$ Pd_3Cl_6; C, 44.79; H, 3.10; N, 6.15; found C, 44.75; H, 3.09; N, 6.14

2.3. Application of Pd-metallodendrimer 3 as a catalyst in the synthesis of ynones

2.3.a. Synthesis of 1,3-diphenylprop-2-yn-1-one, 11 [17]

A mixture of benzoyl chloride (1.0 mmol) with phenylacetylene (1.2 mmol), Pd-metallodendrimer 3 (3.0 mol %) and triethylamine (1.2 mmol) was stirred in CH_3CN (5 mL) in a round bottom flask under a nitrogen atmosphere at 60 °C for 30 minutes. The progress of the reaction was monitored by TLC (*n*-hexane/chloroform 10:1). At the end of the reaction, the reaction mixture was evaporated to dryness under reduced pressure and the residue was 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 purified by silica gel column chromatography with *n*-hexane / chloroform 10:1.A white solid, mp 47-49 °C (lit. 46-48 °C), IR (KBr): ν_{max} 2915.30, 2226.98, 1636.77.^1H-NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, *J* = 7.6, 2 H); 7.58-7.48 (m, 5 H); 7.20 (d, *J* = 8.0, 3 H). ^{13}C-NMR ($CDCl_3$, 400 MHz): δ 175.782, 140.012, 133.912, 132.313, 131.113, 129.132, 128.131, 122.111, 96.131, 88.312

2.3.b. Synthesis of 1-(4-methoxyphenyl)oct-2-yn-1-one 12 [17]

Light Yellow liquid 10, IR (KBr): ν_{max} 2921.29, 2126.29, 1640.43, ^1H-NMR ($CDCl_3$, 400 MHz): δ 7.35 (d, *J* = 7.2, 2 H); 6.65 (d, *J* = 7.2, 2 H); 3.74 (s, 3 H); 2.13-2.00 (m, 2H); 1.45-1.37 (m, 4H); 0.912 (t, J=8.0, 3H). ^{13}C-NMR ($CDCl_3$, 400 MHz): δ 175.289, 166.479, 130.031, 127.203, 114.231, 94.231, 77.712, 55.51, 114.231, 94.231, 77.712, 55.51, 30.890, 28.572, 21.067, 18.908, 14.746.

2.3.c. Synthesis of 1-(4-methylphenyl)-3-phenylprop-2-yn-1-one 13, [17]

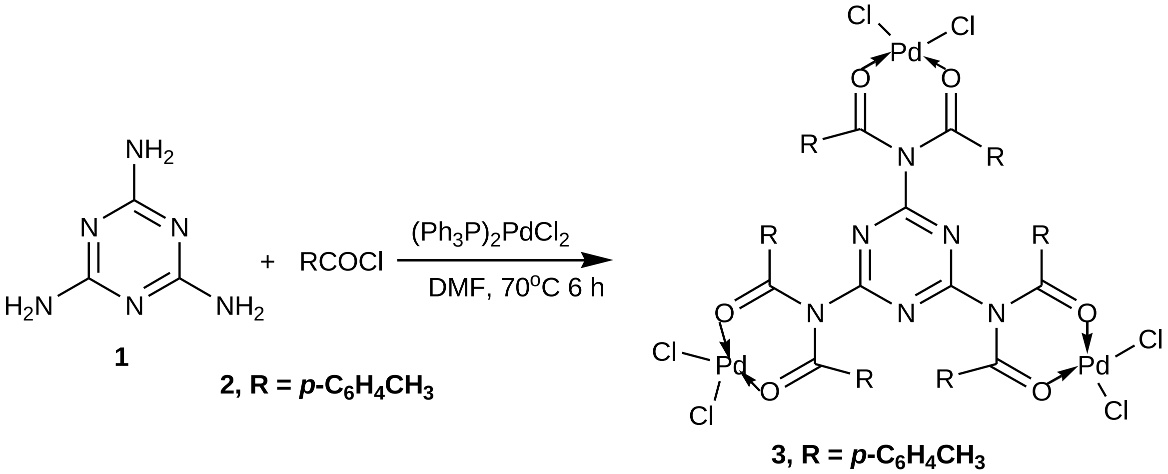
White solid, mp.-89-91 °C (lit. 88-89 °C) IR (KBr): ν_{max} 3047.67, 2171.49, 1600.12. ^1H-NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, *J* = 7.6, 2 H); 7.58-7.49 (m, 4 H); 7.19 (d, *J*=8, 3H); 2.50 (s, 3H); ^{13}C-NMR ($CDCl_3$, 400 MHz): δ 175.789, 166.779, 132.331, 130.331, 129.031, 128.203, 127.303, 122.431, 96.131, 88.131, 55.414.

2. 3.d. Synthesis of 1-(4-nitrophenyl)hept-2-yn-1-one 14, [17]

Yellowish oil. IR (KBr): ν_{max} 3072.71, 2360.95, 1755.30, ^1H-NMR ($CDCl_3$, 400 MHz): δ 7.45 (d, *J* = 8.8, 2 H); 6.67 (d, *J* = 8.0, 2 H); 2.24 (t, *J*=7.2, 2H); 1.83-1.80 (m, 2 H); 1.45-1.37 (m, 2H); 0.91 (t, *J*=7.2, 3 H). ^{13}C-NMR ($CDCl_3$, 400 MHz): δ 175.552, 154.412, 141.202, 131.233, 121.132, 94.441, 30.296, 21.217, 18.210, 13.246.

3. Results and Discussion

2, 4, 6-Tris (di-4-methylbenzamido)-1, 3, 5-triazine palladium (II) chloride (**3**) was obtained by treating 2, 4, 6-triamino-1, 3, 5-triazine (**1**) with 4-Methylbenzoyl chloride (**2**) in the presence of $(Ph_3P)_2PdCl_2$ in anhydrous DMF (Scheme 1). The reaction of **1**(1.59 mmol) with **2** (9.54 mmol) was carried out in the presence of $(Ph_3P)_2PdCl_2$ (10 mol%) in anhydrous DMF at 70°C for 6 h under a nitrogen atmosphere. Purification of the reaction mixture by alumina column chromatography gave the dendrimerized product **3** in 90% yield (Table 1, entry 1). $PdCl_2$ was also effective and gave **3** in 60% (entry 2). Since $(Ph_3P)_2PdCl_2$ was given more yield than $PdCl_2$, we chose $(Ph_3P)_2PdCl_2$ for the later optimization. The use of tetrahydrofuran as the solvent resulted in low yields of **3**, because of the poor solubility of **3** (entry 3). DMSO also good solvent and gave **3** in 85% (entry 4). Increasing the amount of $(Ph_3P)_2PdCl_2$ from 10 to 20 mol% did not improve the final yield of **3**, the yield decreased due to the formation of a complex as a byproduct instead of the desired product (entry 5). The desired product **3** was finally purified by recrystallization. All products were found to be soluble in all common organic solvents and were characterized by IR, ^1H NMR, ^{13}C NMR, Mass Spectroscopy, TG and DSC.



Scheme 1. Synthesis of the **3**

Table 1: Optimization for Preparation of 2, 4, 6-Tris (di-4-methylbenzamido)-1, 3, 5-triazine palladium (II) chloride (3)

Entry	**1 (mmol)**	**2 (mmol)**	**Pd complex (mol%)**	**Solvent (mL)**	**Temp. (°C)**	**Time (h)**	**3 (%)**
1	1.59	9.54	$(Ph_3P)_2PdCl_2$ (10)	DMF (10)	70	6	90
2	1.59	9.54	$PdCl_2$ (10)	DMF (10)	50	6	60
3	1.59	9.54	$(Ph_3P)_2PdCl_2$ (10)	THF (10)	70	6	55
4	1.59	9.54	$(Ph_3P)_2PdCl_2$ (10)	DMSO (10)	70	6	85
5	1.59	9.54	$(Ph_3P)_2PdCl_2$ (20)	DMSO (10)	70	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 (Figure 1). 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 is notable that there is no band for N-H in the region about 3400–3250 cm^{-1} which was indicated that 1˚amino group of triaminotriazine is converted into 3° amido group. ^{1}H NMR (Figure 2) and ^{13}C NMR spectra (Figure 3) showed the desired compound 3. Due to the formation of Pd-O coordinated bond, small changes in the aromatic region compared to starting materials indicated that metal complexation has been achieved. There is no ^{1}H NMR peak for NH or NH_2 group, which was further confirmed the structure of **3** The self-assembly process of the compound **3** was investigated with Pd(II) as the central metal ions, and this resulted in a well-defined four coordinated complex that was confirmed by MALDI-TOF MS (Figure 4).

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

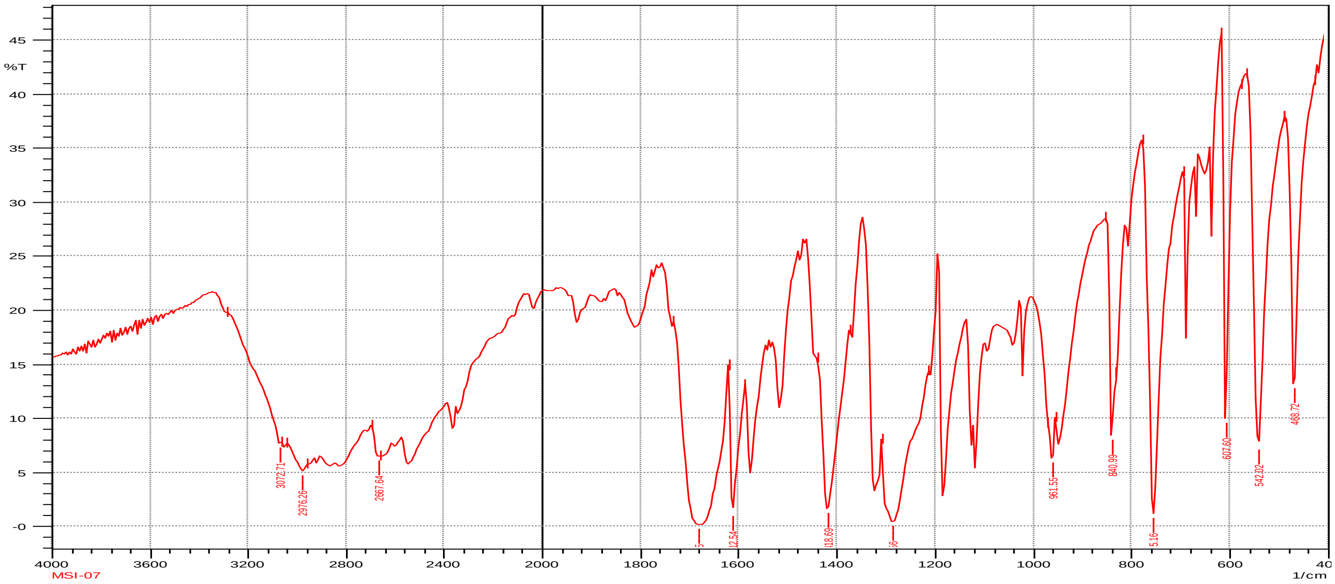


Figure 2. ^{1}H NMR of 2, 4, 6-Tris (di-4-methylbenzamido)-1, 3, 5-triazine palladium (II) chloride, 4

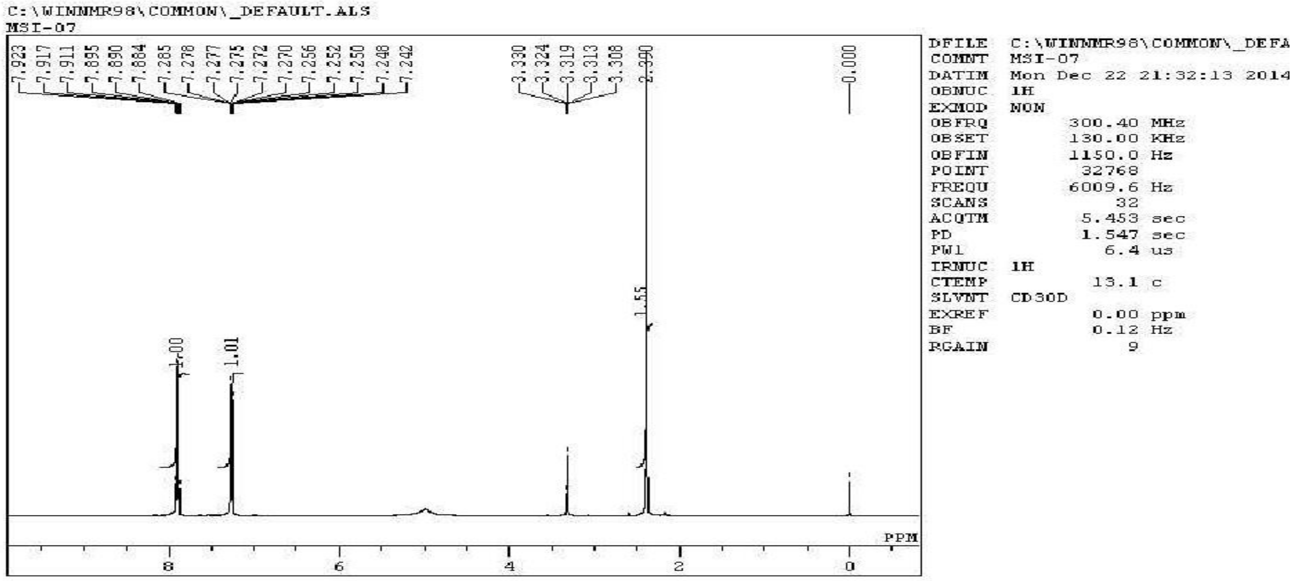
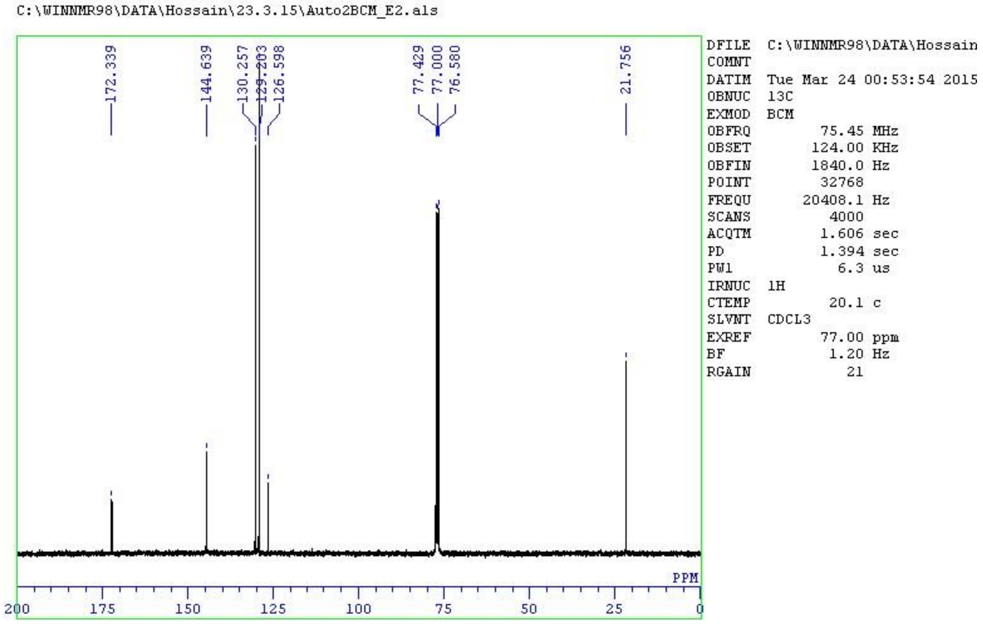


Figure 3. ^{13}**C NMR of 2, 4, 6-Tris (di-4-methylbenzamido)-1, 3, 5-triazine palladium (II) chloride**



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OBFIN        1840.0 Hz
POINT         32768
FREQU       20408.1 Hz
SCANS          4000
ACQTM         1.606 sec
PD            1.394 sec
PW1             6.3 us
IRNUC  1H
CTEMP          20.1 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            21
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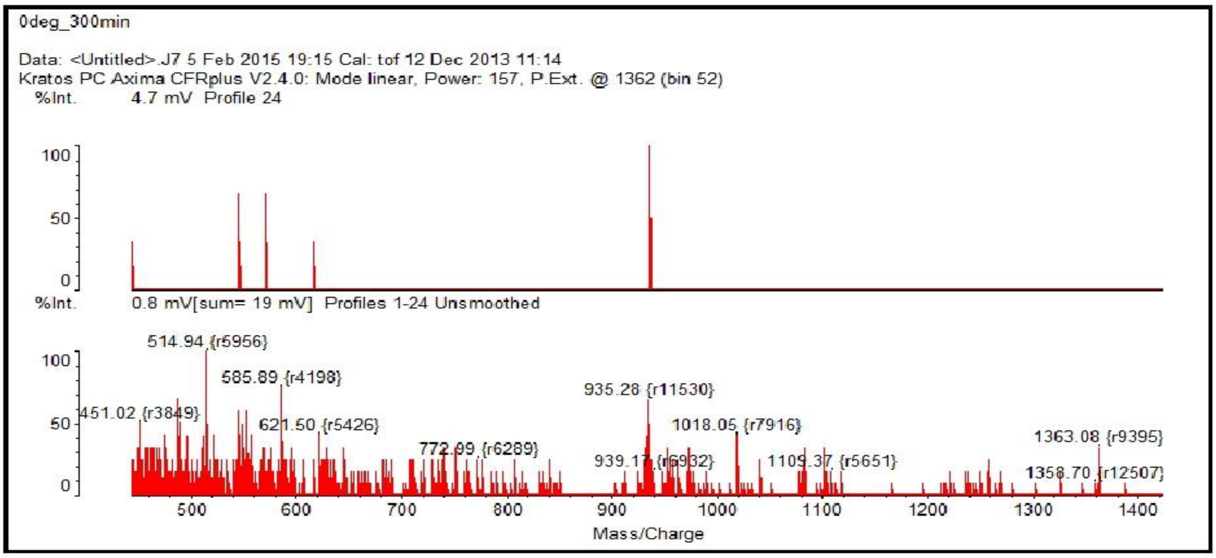
Figure 4. Mass of 2, 4, 6-Tris (di-4-methylbenzamido)-1, 3, 5-triazine palladium (II) chloride



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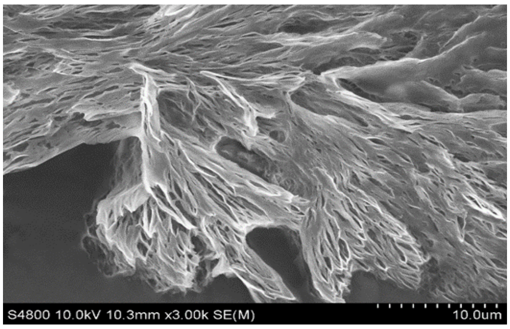


Figure 5. SEM images of compounds 3

SEM images of the compound **3** revealed that formation of high aspect ratio randomly distributed, entangled nanofibers. Coordination between the ligand and Pd(II) formed “blooming flower-like structure for compound **3** (Figure 5). Each chain stacked with neighboring chain by π-π stacking interaction and formed fibril morphology. The fibers are stabilized by π-stacking of the aromatic core of the ligands. Metal detection or investigation of metallodendrimer has been performed by employing Energy Dispersive X-ray (EDX) method (Table 2). From EDX analysis, the presence of Palladium was 1.39% observed of weight for compound **3.**

Table 2. EDX analysis of compound (3)

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	4.81	1.7203	55.35	4.73	61.31
N K	0.25	0.2077	23.93	4.04	22.73
O K	0.68	0.7187	18.69	3.16	15.55
Cl K	0.03	0.8090	0.64	0.56	0.24
Pd L	0.05	0.6701	1.39	1.38	0.17
Totals			100.00		

The thermal properties of the metallodendrimer **3** was investigated by TG and DSC at temperatures of 26 to 600 °C under nitrogen atmosphere (Figure 6).

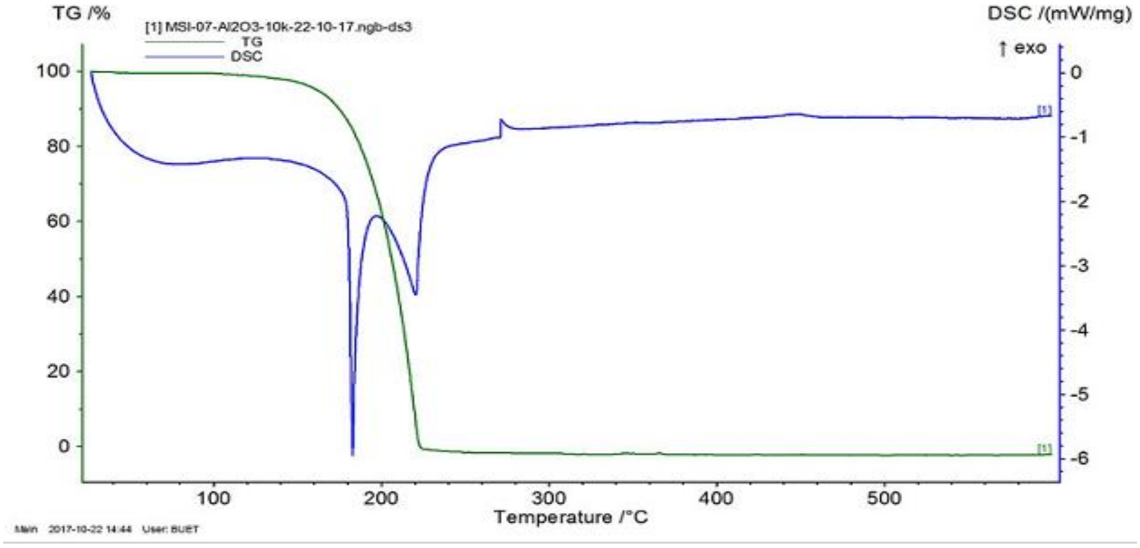
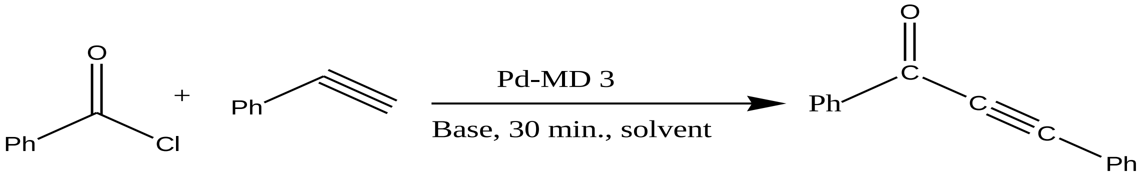


Figure 6. TG & DSC analysis of compound (3)

The content of a particular component of metallodendrimer changes with its composition & structure and determined on the basis of the weight loss of these components in the thermogravimetric graph. It was observed from the TG curve that effective weight loss of the compounds **3** from 178 °C to 225 °C. The thermogram of TG for compound 3 showed two different stages of decomposition at 178 °C, 240 °C and the DSC values of these compounds are almost the same as that of TG values of the compounds. In the DSC curve of **3** show the sharp endothermic curve above 180 °C indicating the melting point. The first decomposition step showed 74-76% for the loss of mass for compounds **3**.

The catalytic activity of synthesized homogeneous palladium-based metallodendrimer (Pd-MD **3)** which is air-stable and very much effective catalyst for the synthesis of ynones through cross-coupling reaction of acyl chlorides with terminal alkynes. The reaction between benzoyl chloride and phenylacetylene was selected for the optimization of the synthesis of ynones by using Pd-MD-**3** (Scheme 2). The cross-coupling reaction was carried out the presence of KOH as base and DMF as solvent at 80 °C to obtain 25% yield for catalyst Pd-MD 3 (entry 1). We selected another three bases KO^{t}Bu, K_2CO_3, and Et_3N (Table 3, entries 2-5) and Et_3N was found to be the good base for this reaction. The effect of the solvent was also studied and by using H_2O, DMF, toluene and CH_3CN and acetonitrile was found to be the good solvent. Therefore, the optimized reaction condition was found when 3.0 mol% of Pd-MD 3 and Et_3N and CH_3CN were used under the nitrogen atmosphere at 60°C (Table 3, Entry 5).



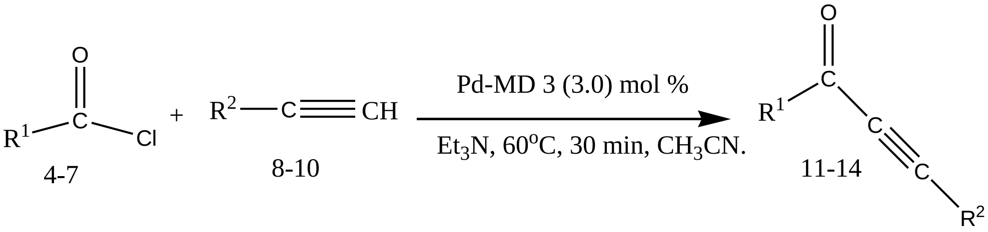
Scheme 2.

Table 3. Reaction condition optimization for the Sonogashira coupling reaction of benzoyl chloride with phenylacetylene catalyzed by Pd-MD **3**

Entry	Base	Temp (°C)	solvent	Compound, 3 (%)	Yield (%)
1	KOH	80	DMF	2.5	25
2	KO^{t}Bu	80	DMF	2.0	10
3	KO^{t}Bu	R.T.	CH_3CN	3.0	N. R
4	K_2CO_3	80	H_2O	2.5	40
5	Et_3N	60	CH_3CN	3.0	80

Reaction conditions: benzoyl chloride (1 mmol), phenylacetylene (1.2 mmol), base (1.2 mmol), Time-30 min, Solvent (2 mL), b) Yield % of products is based on benzoyl chloride.

Different ynones 11-14 were synthesized (Scheme 3, Table 4) by using optimized condition.



Scheme 3.

Table-4. List of various ynones catalyzed by Pd-MD **3**

Entry	Acyl chloride, R^1	Alkyne, R^2	Product	Yield (%) for compound 3
1	4. C_6H_5	8. C_6H_5	11	90
2	5. $C_6H_4OCH_3$(p)	10. C_5H_{11}	12	88
3	6. $C_6H_4CH_3$(p)	8. C_6H_5	13	95
4	7. $C_6H_4NO_2$(p)	9. C_4H_9	14	92

Yield % based on acylchloride; Acylchloride: Alkyne: Triethylamine (1:1.2:1.2).

All Ynone products were characterized by spectroscopic methods and compared with authentic spectra of literature [17].

Conclusions

Novel palladium based metallodendrimers 3 was prepared by coordination reaction of substituted triazine with substituted benzoyl chloride. The complexation was clearly observed in ^{1}H NMR, ^{13}C NMR, elemental analysis and mass spectra. SEM images of 3 revealed blooming flower, and leaves of tree-like structures respectively. Thermal stability of the metallodendrimers 3 was determined by TG and DSC analysis which showed a good stability of the compounds. The synthesized compound 3 was found active homogeneous catalysts for the synthesis of ynone compounds and the synthetic route was green, copper, phosphine ligand-free. Details on catalytic properties for various c-c cross-coupling reactions of the metallodendrimer are now under investigation.

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

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