CHAPTER 2

SYNTHESIS OF POLYANILINE ANCHORED METAL CATALYST AND ITS APPLICATIONS

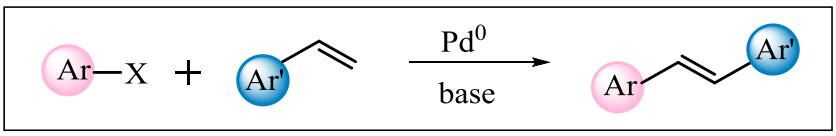
Contents

Section-I

Synthesis, characterization and applications of polyaniline anchored palladium for C-C coupling and one-pot reactions

2.1.1 Introduction

Metal mediated cross-coupling reactions have grown into an extremely powerful and general strategy for forming C-C, and C-heteroatom bond formation. The Chemistry Nobel Prize of 2010 was awarded jointly to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki "for palladium-catalyzed cross couplings in organic synthesis". Coupling of aryl, benzyl or vinyl halide with an alkene in the presence of palladium catalyst and a base, known as Mizoroki-Heck reaction[1] is one of the most widely explored methods to access derivatives of stilbene or cinnamic acid with predominantly formed *trans* olefins. Many researchers have extensively utilized this reaction for synthesis of useful natural products, drugs or materials with specific properties.[2]



Scheme 1: Mizoroki-Heck reaction

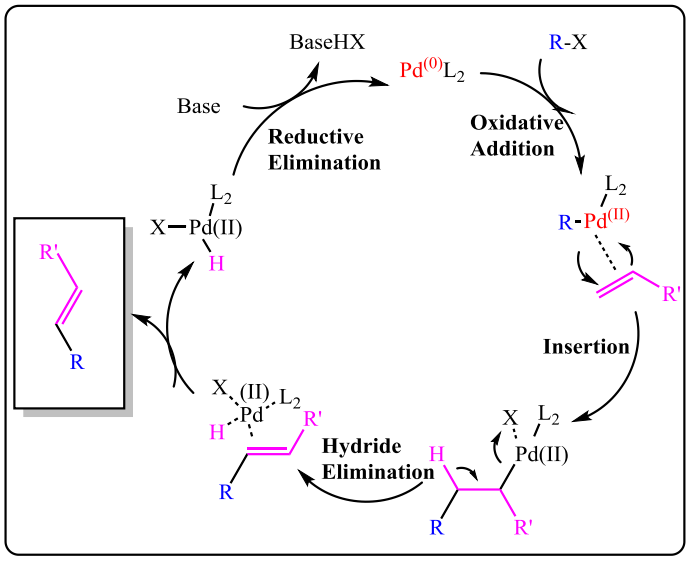
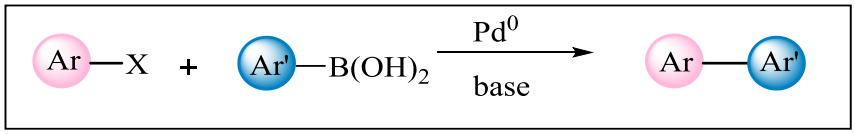


Figure 1: Mechanism of Mizoroki-Heck reaction

The catalyst in the standard Heck reaction is a Pd(0) species stabilized by suitable ligands. The catalytic cycle involves four step mechanism as shown in (Figure 1) which includes oxidative addition, insertion, β-hydride elimination and reductive elimination.

Similarly, coupling of aryl halides with aryl boronic acids in the presence of palladium catalyst and suitable base furnishes biaryls by Suzuki-Miyaura reaction.[3]



Scheme 2: Suzuki-Miyaura reaction

The mechanism of the Suzuki reaction involves oxidative addition of Pd to the halide to form the organopalladium species. Second step is reeaction with base *via* transmetalation with the boron-ate complex to forms the organopalladium species followed by reductive elimination (Figure 2).

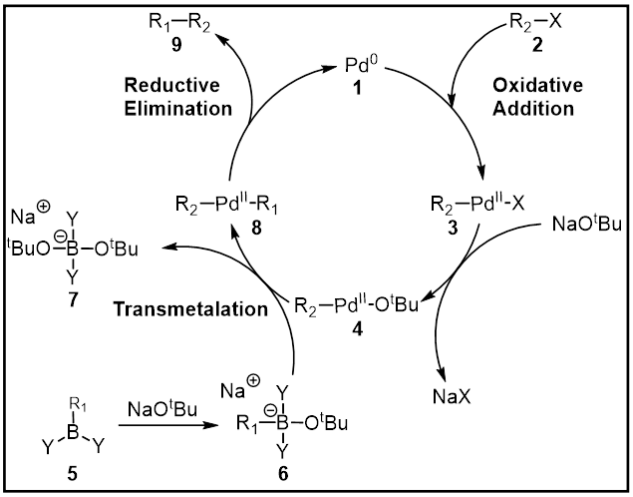


Figure 2: Mechanism of Suzuki reaction

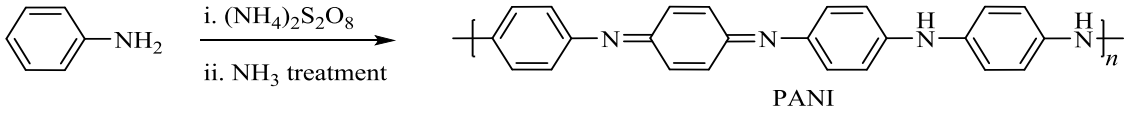
Both these reactions are of great importance and are much investigated in recent times. However, due to the high cost of palladium, some environmental and toxicological concerns, there is a growing need to develop heterogeneous catalytic reactions by means of immobilization on solid supports.[4] Although, some success has been achieved, there is further requirement to search different support materials for easy and practical preparation of the heterogeneous palladium catalysts. These materials need to have strong binding interactions with the metal ions as well as to offer effective access to the reagents for smooth chemical transformations.

2.1.2 Results and discussion

In this chapter we present our findings for the immobilization of palladium salts on polyaniline support, its preliminary characterization and applications in Heck, Suzuki and one pot Wittig-Heck and Wittig-Suzuki reactions.

2.1.2.1 Synthesis and characterization of polyaniline and palladium anchored polyaniline

The synthesis of polyaniline (PANI) was done by chemical oxidation protocol using ammonium persulfate from aniline hydrochloride salt followed by neutralization with aqueous ammonia.[5] (Scheme 3).



PANI

Scheme 3: Synthesis of PANI

The sample of PANI free from oligomers was then exposed to a solution of $PdCl_2$ in acetonitrile to immobilize the metal ions on the support. The PANI-Pd catalyst was separated dried and characterized by usual spectral and analytical techniques.

The most important bands in the FTIR spectrum of PANI are located at 1584, 1494, 1376 cm^{-1}due to the stretching vibrations of quinoid (C=N & C=C) and benzenoid (C=C), 1307 due to C-N stretching frequency in aromatic amine and 3271 cm^{-1} due to N-H stretching of aromatic amine. Upon incorporation of Pd^{2+} ions into PANI no shifts in the quinoid or benzenoid ring band positions have been observed, which is in accordance with earlier studies.[6] (Figure 3)

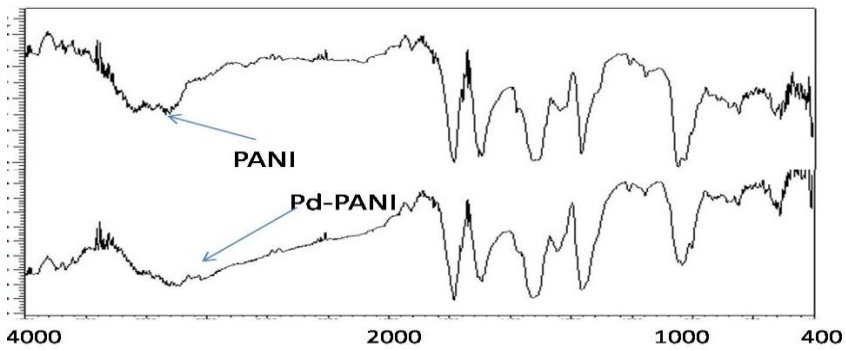


Figure 3: IR of PANI and PANI-Pd

The X-ray Powder Diffraction XRD analysis of the purified PANI and its complex with palladium salt was investigated. From XRD analysis shows two signals corresponding to 2 *theta* values at 40 and 46 (Figure 4), which are characteristic of elemental Palladium.[6] Thermogravimetric Analysis (TGA) for PANI-Pd shows that the sample is stable up to ~300^{o}C, which shows its suitability for the use as heterogeneous catalyst in standard reaction parameters, Figure 4.The samples of PANI were also subjected to Brunauer-Emmett-Teller (BET) surface area analysis surface analysis to determine its surface properties. The BET measurement of PANI showed the surface area to be 36.205 m^2/g, while the same for PANI-Pd increased to 43.086 m^2/g. The ICP-AES analysis of the sample of catalyst indicated 3.86 % loading of palladium metal.

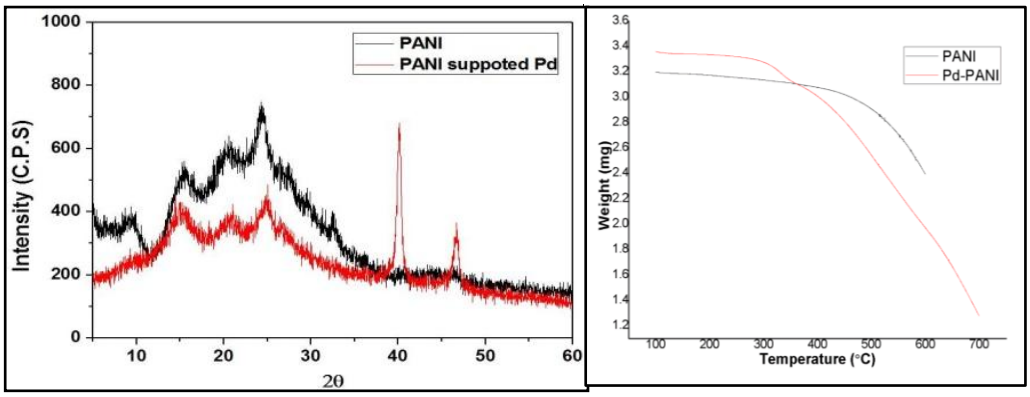


Figure 4: (a) XRD (left) and (b) TGA (right) Of PANI and PANI-Pd

The morphology and composition of PANI and palladium loaded PANI catalysts was examined by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) using Jeol5610LV. Some changes were observed after loading of metal on PANI (Figure 5). The SEM images of PANI-Pd clearly indicate successful loading of palladium as the change was seen in the brightness of images. The white shining particles which can be clearly seen are attributed to palladium. They appear bright as they are heavier than C, O, N etc. in back scattered mode of SEM micrographs. Furthermore EDX spectrum also confirms the presence of other ions attributing to PANI and PANI-Pd, establishing its composition, Figure 5.

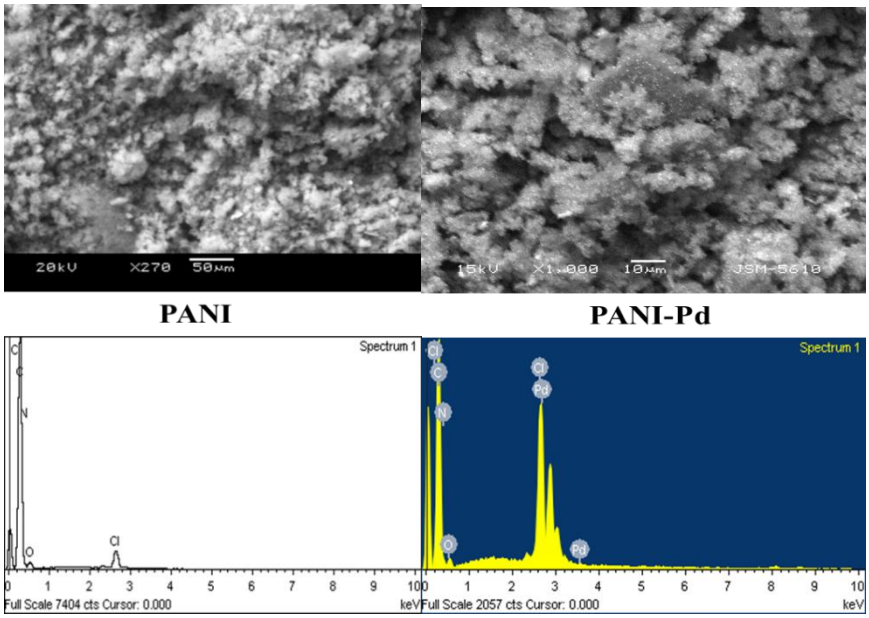
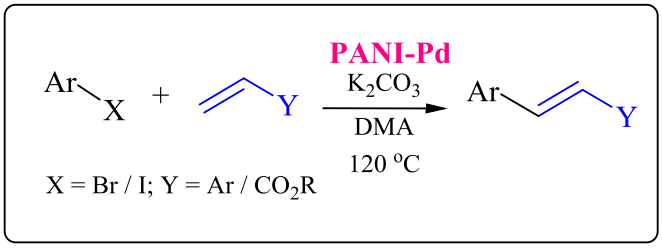


Figure 5: SEM and EDX Of PANI and PANI-Pd

2.1.2.2 Applications of supported catalyst for Mizoriki-Heck and Suzuki reactions

The synthesized PANI-Pd catalyst was examined for the standard Mizoroki-Heck coupling reaction of aryl halides and styrene derivatives in the presence of a suitable base (Scheme 4). Preliminary experiment suggested that K_2CO_3 was an effective mild base and dimethylacetamide (DMA) was found to be a suitable solvent.



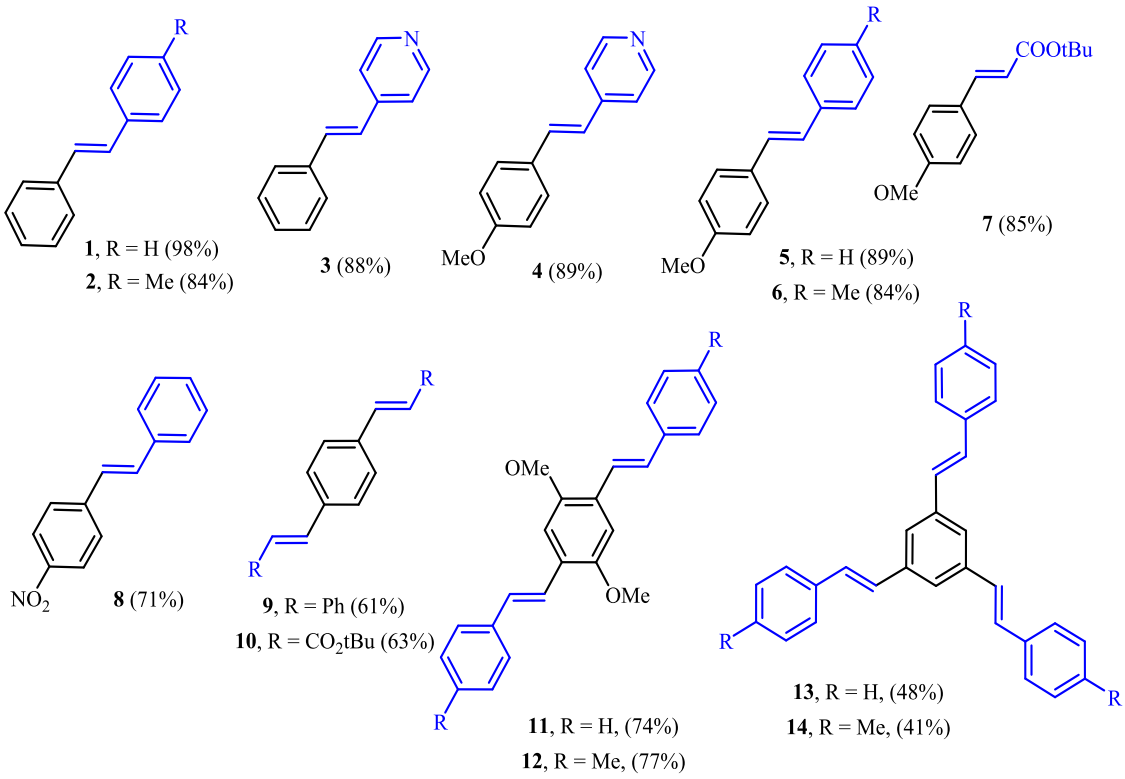
Scheme 4: PANI-Pd catalyzed Mizoroki-Heck reaction

Aryl chlorides remain unreactive under the above conditions for the Mizoroki–Heck reaction, while aryl bromides and aryl iodides furnish the stilbene derivatives in good to excellent yields. All the synthesized stillbene derivatives were isolated generally as the *E*-isomer. A comparison study for reactivity of bromobenzene and iodobezene were done which reveals the latter one being significantly more reactive as shown in Table 1.

Table 1: Comparison of Mizoroki–Heck reaction of PhBr and PhI

Entry	Temperature(^{o}C) [Time (h)]	PhX	% yield of E- stilbene
1	80 [8]	PhBr	4
2	80 [8]	PhI	28
3	120 [8]	PhBr	14
4	120 [8]	PhI	86
5	80 [40]	PhBr	45
6	120 [40]	PhI	98

To search the scope of the reaction a series of aryl bromides and aryl iodides were subjected to Mizoroki-Heck reaction with different alkenes. A series of compounds were prepared as shown in scheme 5. For the products**8**, **9**, **10**, **13** and **14** aryl bromides were used while for remaining aryl iodides were used. Similarly for products **1**, **5**, **8**, **9**, **11**, **13** (styrene), **2**, **6**, **12**, **14** (4-methyl styrene), **3**, **4** (4-vinyl pyridine) and **7**, **10** (*tert*-butyl acrylate) were obtained. Disubstituted alkenes were obtained from corresponding aryl halides in excellent yields, while the dihalogenated arenes (for **9**, **10**, **11** and **12**) or trisubstituted arenes (for **13** and **14**) gave the alkene products in slightly lower yields (Scheme 5). Reactions were carried out at 120 ^{o}C for 40h in presence of mild base, potassium carbonate. All the synthesized stillbene derivatives were characterized by the usual spectroscopic techniques and by comparing the physical properties. Thus, series of compounds were prepared by this catalytic system which clearly indicates the efficiency of PANI-Pd catalyst.



Scheme 5: Molecules synthesized by Mizoroki-Heck reaction with PANI-Pd catalyst

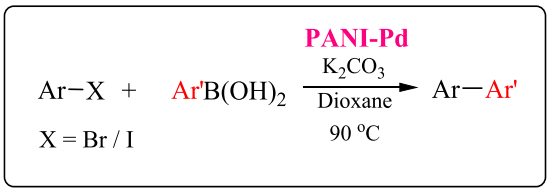
However, the success of a heterogeneous catalyst is measures by its ability to be recycled and reused for subsequent reactions. The recycle study was conducted by performing a reaction of PhI with styrene in the presence of PANI-Pd at the standard condition. As can be seen from Table 2, the catalyst could be easily separated by filtration and reused for two more cycles without losing much catalytic activity, fulfilling the primary requirement of a heterogeneous catalyst.

Table 2: Recyclability study of PANI-Pd for Mizoroki-Heck reaction for reaction of PhI and styrene

Cycle	Isolated yield (%)
1	98
2	95
3	90

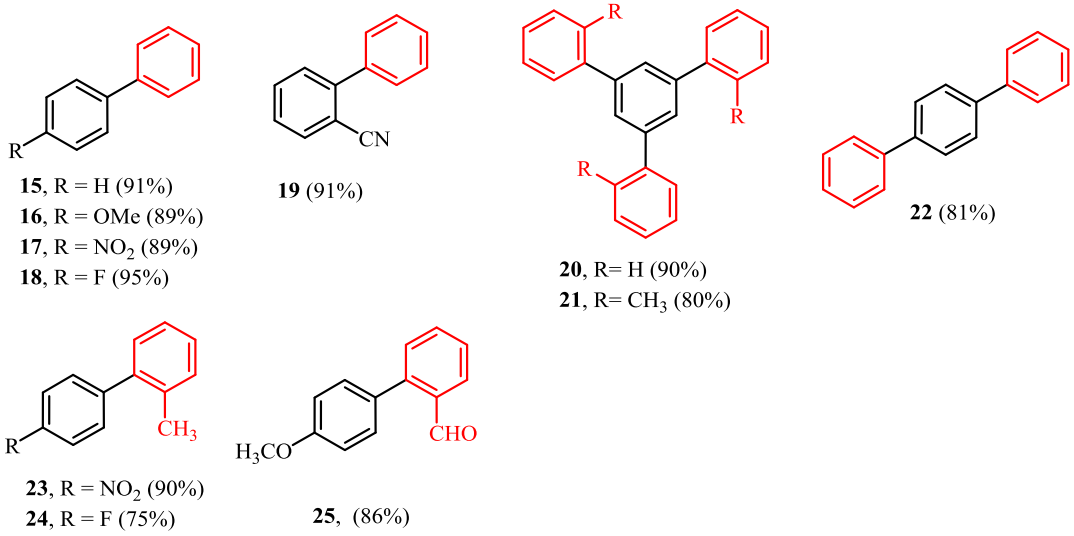
The catalyst system was then applied for Suzuki-Miyaura coupling reaction. The standard reaction condition is shown in Scheme 6, where an aryl bromide or aryl iodide was treated with aryl boronic acid in the presence of PANI-Pd catalyst and the suitable base, potassium carbonate for 4-10 h in dioxane:water(1:1) as solvent. Dioxane:water (1:1) was

used as solvent except for di and tri substituted aryl halides in case of products **21, 22** and **23** (Scheme 7). The biaryls, product of this coupling reaction, were isolated in high yields and characterized by the usual spectroscopic techniques and comparison of the physical properties with the known data.



Scheme 6: PANI-Pd catalyzed Suzuki-Miyaura reaction

A series of aryl halides were subjected to the above Suzuki-Miyaura reaction. From this series compounds **15, 16** and **25** were synthesized from aryl iodide while rest of others from corresponding aryl bromides. Aryl halides were subjected to phenyl boronic acid for **15**, **16**, **17**, **18**, **19**, **20** and **22** with *o*-tolylboronic acid for **21**, **23** and **24** and with (2-formylphenyl)boronic acid for **25.** Reaction time with aryl iodides was 4 h while that with aryl bromides was 6 h. Compound **20-22** were synthesized in 10 h. All the products were isolated by column chromatography in excellent yields (Scheme 7).



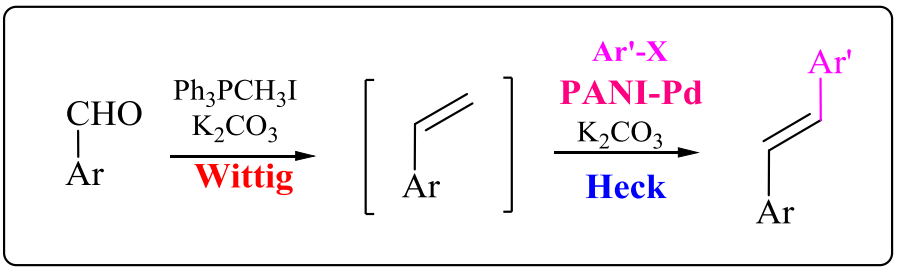
Scheme 7: Molecules prepared by Suzuki-Miyaura reaction with PANI-Pd catalyst

2.1.2.3 Applications of PANI-Pd catalysts in One-Pot reactions

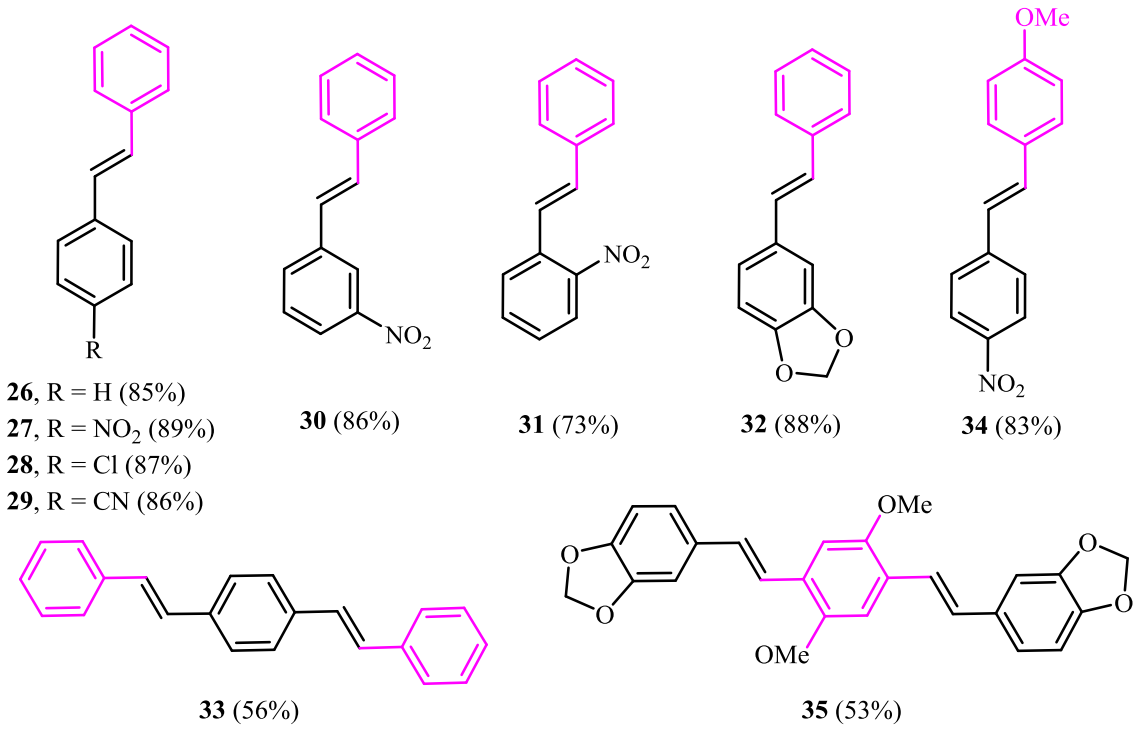
One-pot synthesis is a strategy to improve the efficiency of a chemical reaction whereby performing several chemical operations simultaneously in a single vessel, also referred as domino or tandem reactions. It offers several advantages including the

combination of operations resulting in the lowering the overall consumption of reagents required for reaction/work-up, can reduce the purifications of the intermediate compounds, particularly important with unstable intermediates, reduction in the total reaction time, and often fulfill some of the requirements of the alternative greener synthesis. In recent decades several procedures have been developed for making useful molecules and intermediates by adopting one-pot or domino or tandem synthetic schemes.[8] Our group is actively involved in the research on applications of one-pot methods to build interesting, useful conjugate compounds. The one-pot procedures may involve different types, but compatible set of reactions. In this section such one-pot procedures which will involve the palladium catalysts prepared earlier will be involved to bring about coupling reactions.[9]

One of the key components of the Mizoroki-Heck reaction is a alkene, usually a styrene derivative. Some of the styrene derivatives are not readily available, or are costly or are unstable in nature. With an objective to overcome these drawbacks of Heck reaction, we have recently developed[9a] a one-pot procedure where the styrene was prepared *in situ* by Wittig reaction of an aromatic aldehyde and Ph_3PCH_3X, and then subjected to Mizoroki-Heck reaction. In this work we have screened the PANI-Pd catalyst for this approach presented in Scheme 8. Wider commercial availability of aromatic aldehydes as compared to the styrenes also favors such an approach for the construction of stilbene derivatives. Sample of *p*-substituted benzaldehydes (ArCHO) was subjected to a one carbon homologation reaction with appropriate phosphonium salt (Ph_3PCH_3X) under the base mediated condition to *insitu* generate styrene derivative ($ArCH=CH_2$). As soon as this styrene is formed, it is exposed to a suitable aryl halide in presence of catalyst PANI-Pd and an appropriate base, to readily undergo Mizoroki-Heck reaction. A number of stilbene derivatives were synthesized and the results are summarized in Scheme 9. Although Witting gives an alkene, the stereochemistry of stillbene is actually determined in the second step, which favors the *E*-isomer, as expected from a Heck reaction.



Scheme 8: One-pot Wittig-Heck reaction catalyzed by PANI-Pd



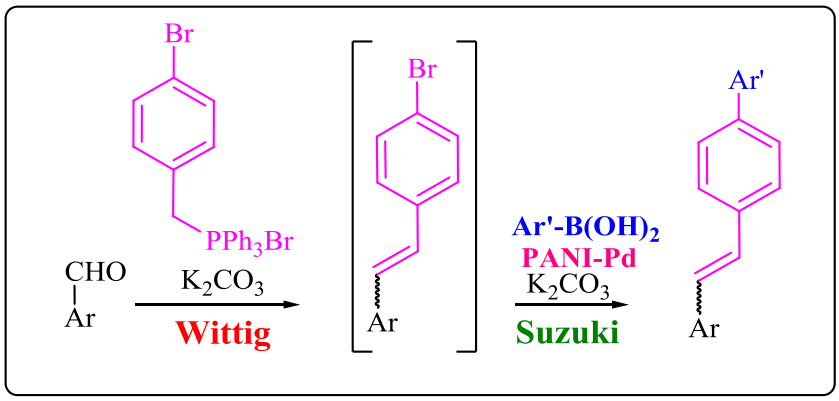
26, R = H (85%)
27, R = NO_2 (89%)
28, R = Cl (87%)
29, R = CN (86%)

30 (86%) **31** (73%) **32** (88%) **34** (83%)

33 (56%) **35** (53%)

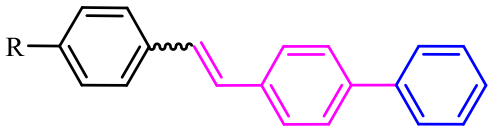
Scheme 9: Molecules prepared by one-pot Wittig-Heck reaction with PANI-Pd catalyst

Another component was added in this sequence. The one-pot reaction was performed with aromatic aldehyde and the Wittig salt prepared from 4-bromobenzyl bromide ($BrPh_3PCH_2C_6H_4Br$), where by the styrene is formed with a substitution of bromo group on one of the aromatic rings. This bromo was subjected to the *in situ* Suzuki-Miyaura reaction as the second component of one-pot reaction sequence.[10] The olefin is efficiently synthesized by Wittig reaction of aromatic aldehyde and the Wittig phosphonium salt in presence of K_2CO_3. The *insitu* Suzuki-Miyaura reaction of the initially formed bromostilbene proceeds smoothly in presence of PANI-Pd as catalyst, K_2CO_3 as base in DMF for 24h (Scheme 10).

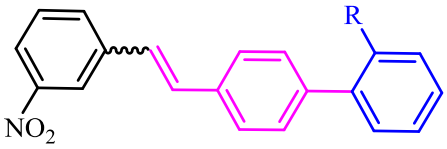


Scheme 10: One-pot Wittig-Suzuki reaction catalyzed by PANI-Pd

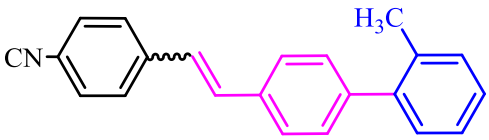
A series of aldehydes was subjected to this one-pot Wittig-Suzuki reaction to efficiently construct conjugated compounds. Since the stereochemistry is determined at the formation of stilbene by Wittig reaction, which as expected gives considerable *Z*-isomer of the product.[11] Typically we have detected the ratio of 31 to 59 in favor of *Z*-isomer for the products reported in Scheme 11, with the PANI-Pd catalyst. This ratio was determined by ^{1}H-NMR analysis of the purified product and its comparison with the known physical data.



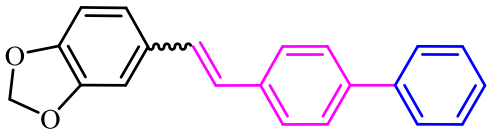
36, R = H (60%)
37, R = Cl (62%)
38, R = NO_2 (65)
39, R = CN (70%)



40, R = H (68%)
41, R = CH_3 (72%)



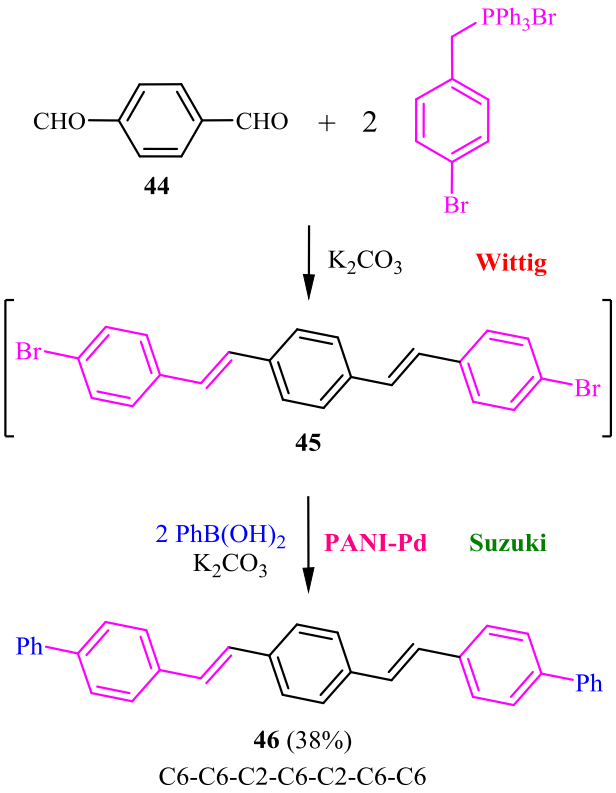
42, (55%)



43, (65%)

Scheme 11: C6-C6-C2-C6 Type compounds prepared by one-pot Wittig-Suzuki reaction

This one-pot protocol was then extended for the synthesis of styryl stilbenes, important class of highly conjugated systems.[12] We designed the synthesis by starting with terephthalaldehyde **44** as the aldehyde component and condensed it with two molecules of the phosphonium salt prepared from 4-bromobenzyl bromide to initially form the Wittig product **45**. This intermediate dibromo compound was subjected to the *in situ* Suzuki-Miyaura reaction to finally furnish **46**. Such molecules have been known to show many interesting electrical and optical properties. In this one-pot process we have offered a very simple and practical alternative to access this or its other derivatives.



Scheme 12: Preparation of a highly conjugated system by sequential Wittig-Suzuki reaction

2.1.3 Conclusion

In conclusion we wish to report the preparation and applications of polyaniline supported palladium catalysts for some useful coupling reactions of aryl halides. The catalyst was found suitable for aryl iodides and bromides while it is not effective for aryl chlorides, at the same time the system can tolerate a number of functional groups during these one-pot reactions. The catalyst is easy to prepare and works efficiently for an important application of one-pot Mizoroki-Heck and Suzuki-Miyaura reactions.

2.1.4 Experimental Section

All reactions were carried out in oven-dried glassware with magnetic stirring. Thin Layer Chromatography was performed on silica gel plates coated on aluminium sheets. The spots were visualized under UV light and/or with iodine vapor. All the compounds were purified by column chromatography on silica gel (60-120 mesh). All the reactions were carried out under inert atmosphere (nitrogen) unless other conditions are specified. The NMR spectra were recorded on Bruker Avance 400 Spectrometer with $CDCl_3$ as solvent and TMS as internal standard. Mass spectra were recorded on Thermo-Fischer DSQ II GCMS

instrument, while the IR spectra were recorded on a Perkin-Elmer FTIR RXI spectrometer (KBr pallets). Melting points (M.p.) were recorded in Thiele's tube in paraffin oil and are uncorrected.

2.1.4.1 Preparation of catalyst

Procedure for Preparation of Polyaniline

Sample of PANI was prepared as per the reported method.[5a] Freshly distilled aniline (10 mL, 109.5 mmol) was dissolved in aqueous HCl (1.5 M, 125 mL), and a solution of ammoniumpersulfate (12.5 g, 54.8 mmol) in HCl (1.5 M, 125 mL) at 0°C. Since aniline polymerization is strongly exothermic, the oxidant must be added slowly over a period of 1 h. After the addition of the oxidant, the reaction was stirred (4 h). The precipitated polyaniline hydrochloride which is dark green in color was separated by filtration and washed successively with water (3x30 mL), methanol (2x25 mL) and diethyl ether (2x15 mL) to remove the oligomers and the reaction side products. The polymer was then vacuum-dried until constant weight. Deprotonation of polyaniline hydrochloride was achieved with aqueous ammonia (3 wt %) to give dark blue color polymer. Deprotonated polymer was again washed with water, methanol and diethyl ether and dried until constant weight (4.26 g).

Procedure for Preparationof Pd loaded polyaniline:

PANI (0.5 g) was charged into a round-bottomed flask containing solution of palladium chloride (0.1 g, 0.56 mmol) in acetonitrile solution (25 mL) and stirred under nitrogen atmosphere (48 h). The resultant catalyst was filtered off and washed with acetonitrile followed by acetone. The residue was dried in air (24 h) to afford the black colored powder of PANI-Pd. The amount of palladium was measured by ICP-AES (3.865 % w/w).

2.1.4.2 Screening of supported catalysts for standard Mizoroki-Heck reaction

General procedure for the Mizoroki-Heck reaction (Scheme 5):

Synthesis of *trans*-stilbene (1)

A two neck round bottom flask was charged with iodobenzene (0.2 g, 0.98 mmol), PANI-Pd catalyst (0.06 g, 0.022 mmol), dry potassium carbonate (0.27 g, 70.48 mmol) and dry DMA (6 mL) under nitrogen atmosphere. This mixture was slowly heated, till the temperature reaches 65 ^{o}C, a solution of styrene (0.153 g, 1.47 mmol) in DMA (2 mL) was introduced. The

reaction mixture was then heated to 140 ^{o}C for 40 h. The reaction mixture was quenched with water and extracted with ethyl acetate (3x25 mL).The combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed in vacuum and crude product was purified by column chromatography on silica gel to afford *trans* stilbene (**1**) as white solid.(0.17g, 98 %). M.p 120-122 ^{o}C [Lit.[13] 121 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.15 (s, 2H), 7.28-7.31 (m, 2H), 7.38-7.41 (m, 4H), 7.54-7.56 (m, 4H).

IR[KBr]: υ 1651, 1497, 1552, 1572, 762, 688 cm^{-1}.

Similarly prepared the other derivatives:

(*E*)-1-Methyl-4-styrylbenzene (**2**)

Yield: 84% (White solid)

M.p. 117-119 ^{o}C [Lit.[14]117-118 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.38 (s, 3H), 7.05-7.14 (Two d, *J* = 16.4 Hz, 2H), 7.18-7.20 (d, *J* = 8.0 Hz, 2H), 7.27-7.28 (m, 1H), 7.35-7.39 (m, 2H), 7.43-7.45 (d, *J* = 8.0 Hz, 2H), 7.52-7.54 (m, 2H).

IR[KBr]: υ 3024, 1729, 1594, 1513, 1448, 808, 748, 690 cm^{-1}.

(*E*)-4-Styrylpyridine **(3)**

Yield: 88% (Off white solid)

M.p. 121 ^{o}C [Lit.[15] 122-123 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.02-7.06 (d, *J* = 16.4 Hz, 1H), 7.28-7.56 (m, 5H), 8.59-8.60 (m, 2H), 8.59-8.60 (m, 2H).

IR[KBr]: υ 3026, 1708, 1634, 1588, 1493, 1455, 1410, 759, 691 cm^{-1}.

(*E*)-4-(4-Methoxystyryl) pyridine **(4)**

Yield: 89% (Off white solid)

M.p. 139-140 ^{o}C [Lit.[16]139-141 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 3.86 (s, 3H), 6.88-6.92 (d, *J* = 16.0 Hz, 1H), 6.93-6.96 (m, 2H), 7.26-7.30 (m, 2H), 7.35-7.37 (dd, *J* = 6.0, 1.2 Hz, 2H), 7.50-7.52 (m, 2H).

IR[KBr]: υ 3020, 2967, 2840, 1688, 1632, 1588, 1550, 1459, 1415, 1175, 971, 835, 761 cm^{-1}.

(*E*)-1-Methoxy-4-styrylbenzene **(5)**

Yield: 89% (White solid)

M.p. 134-138 ^{o}C [Lit. [17]135-136 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 3.86 (s, 3H), 6.91-6.94 (d, *J* = 8.8 Hz, 2H), 7.13-7.02 (Two d, *J* = 16.4 Hz, 2H), 7.23 (m, 1H), 7.35-7.39 (t, *J* = 7.6 Hz, 2H), 7.48-7.51 (m, 4H).

IR[KBr]: υ 2935, 2836, 1672, 1601, 1511, 1447, 1249, 1179, 812, 750, 689 cm^{-1}.

(*E*)-1-Methoxy-4-(4-methylstyryl)benzene **(6)**.

Yield: 84% (White solid)

M.p. 166-167 ^{o}C [Lit. [18] 164 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.37 (s, 3H), 3.85 (s, 3H), 6.90-6.93 (m, 2H), 6.95-7.06 (Two d, *J* = 16.4 Hz, 2H), 7.17-7.19 (d, *J* = 8.0 Hz, 2H), 7.40-7.42 (d, *J* = 8.0 Hz, 2H), 7.45-7.48 (m, 2H).

IR[KBr]: υ 3030, 2913, 2839, 1669, 1652, 1643, 1566, 1516, 1456, 1252, 1176, 826 cm^{-1}.

(*E*)-*tert*-Butyl 3-(4-methoxyphenyl)acrylate (**7**)

Yield: 85% (Thick oil) [Lit. [19]]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.54 (s, 9H), 3.84 (s, 3H), 6.24-6.28 (d, *J* = 16.0 Hz, 2H), 6.90-6.92 (m, 2H), 7.46-7.49 (m, 2H), 7.54-7.58 (d, *J* = 16.0 Hz, 2H).

IR[KBr]: υ 3007, 2975, 2930, 2360, 1705, 1634, 1514, 1451, 1419, 1392, 1368, 1256, 1151, 996, 830 cm^{-1}.

(*E*)-1-Nitro-4-styrylbenzene (**8**)

Yield: 71% (Yellow solid)

M.p. 155 ^{o}C [Lit.[17] 154-156 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.15-7.19 (d, *J* = 16.4 Hz, 1H), 7.28-7.45 (m, 4H), 7.57-7.59 (m, 2H), 7.65-7.67 (m, 2H), 8.24-8.26 (m, 2H).

IR[KBr]: υ 3024, 2920, 1631, 1591, 1447, 1510, 1324, 833, 767, 695 cm^{-1}.

(*E*)-1,4-(di-styryl)benzene (**9**)

Yield: 61% (Off white solid)

M.p.: 262-265 ^{o}C [Lit.[20]264-266 ^{o}C]

^{1}HNMR ($CDCl_3$, 400 MHz): δ 7.10-7.19 (Two d, *J* = 16.4 Hz, 4H), 7.27-7.31 (m, 2H), 7.37-7.41 (m, 4H), 7.54-7.56 (m, 8H).

IR[KBr]: υ 3055, 3024, 1592, 1511, 1487, 1446, 1416, 966, 814, 745, 690 cm^{-1}.

(*E*,*E*)-Di-*tert*-butyl benzene-1,4-dipropenoate (**10**)

Yield: 63% (White solid)

M.p. 148 ^oC [Lit.[21]]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.55 (s, 18 H), 6.39-6.43 (d, *J* = 16.0 Hz, 2H), 7.53-7.60 (m, 6H).

IR[KBr]: υ 3007, 2975, 2930, 1705, 1634, 1514, 1452, 1368, 1256, 1213, 1151, 830 cm^{-1}.

(*E*,*E*)-(2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl)dibenzene (**11**)

Yield: 74% (Yellow solid)

M.p. 178-179 ^oC [Lit.[22] 177-178 ^oC]

^{1}HNMR ($CDCl_3$, 400 MHz): δ 3.95 (s, 6H), 7.27-7.29 (m, 4H), 7.367.40 (t, *J* = 7.6 Hz, 4H), 7.49-7.53 (d, *J* = 16.4 Hz, 2H), 7.57-7.59 (m, 4H)

IR[KBr]: υ 305, 2992, 2933, 2826, 1688, 1680, 1593, 1554, 1461, 1243, 1259, 1178, 960, 842, 871, 749, 694 cm^{-1}.

4,4'-((1*E*,1'*E*)-(2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl))bis(methylbenzene) (**12**)

Yield: 77 % (Yellow solid)

M.p. 177 ^oC [Lit.[22]176-178 ^oC]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.38 (s, 6H), 3.94 (s, 6H), 7.09-7.20 (m, 8H), 7.43-7.48 (m, 6H).

IR[KBr]: υ 2999, 2828, 1495, 1460, 1406, 1256, 1208, 962, 846, 803 cm^{-1}.

1,3,5-tri[(*E*)-Styryl]benzene**(13)**

Yield : 0.115 g, 48% (White solid)

M. p.: 188-190 ^oC [Lit.[23]196 ^oC]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.16-7.27 (Two d, *J* = 16.4 Hz, 6H), 7.30-7.34 (m, 3H), 7.40-7.43 (m, 6H), 7.58-7.60 (m, 9H).

IR[KBr]: υ 3023, 1679, 1594, 1493, 882, 749, 692 cm^{-1}.

1,3,5-tris((*E*)-4-Methylstyryl)benzene (**14**)

Yield: 41% (White solid)

M. p.: 215-217 ^{o}C [Lit.[23]215 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ- 2.40 (s, 9H), 6.99-7.16 (Two d, *J* = 16.4 Hz, 6H), 7.20-7.22 (d, *J* = 8.0 Hz, 6H), 7.43-7.45 (d, *J* = 8.0 Hz, 6H), 7.54-7.55 (m, 3H).

IR[KBr]: υ 3020, 2917, 1679, 1586, 1555, 1511, 1428, 1409, 1377, 965, 954, 838 cm^{-1}.

2.1.4.3 Screening of supported catalysts for standard Suzuki-Miyaura reaction

General procedure for the Suzuki-Miyaura reaction (Scheme 7):

Synthesis of biphenyl (15)

To an oven-dried two neck round bottom flask equipped with a stirrer bar was charged iodobenzene (0.2 g, 0.98 mmol), potassium carbonate (0.27 g, 1.96 mmol), PANI-Pd catalyst (0.06 g, 0.022 mmol of Pd) in dioxane:water (1:1).To the reaction mixture phenylboronic acid (0.14 g, 1.17 mmol, 1.2 eq.) was added and the reaction mixture was at 95 ^{o}C (4 h). The reaction mixture was quenched with water and extracted with ethyl acetate (3x25 mL).The combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed in vacuum and crude product was purified by column chromatography on silica gel to afford biphenyl (**15**) as white solid**.** (0.136 g, 91 %). M.p. 71 ^{o}C [Lit.[24] 71 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz) δ7.36-7.38 (m, 2H), 7.46-7.47 (m, 4H), 7.60-7.62 (m,4H).

IR[KBr]: υ3059, 3032, 1596, 1568, 1477, 1427, 1375, 730, 695 cm.$^{-1}$

The other derivatives were prepared by the similar procedure:

4-Methoxy-1,1'-biphenyl (**16**)

Yield: 89% (Off white solid)

M.p. 89 ^{o}C [Lit.[25] 88-89 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 3.88 (s, 3H), 6.99-7.01(m, 2H), 7.28-7.32 (m, 1H), 7.42-7.46 (m, 2H), 7.54-7.56 (m, 4H).

IR[KBr]: υ 3000, 2961, 2835, 1606, 1522, 1487, 1439, 1250, 1184, 834, 760, 688 cm^{-1}.

4-Nitro-1,1'-biphenyl (**17**)

Yield: 89% (Pale Yellow solid).

M.p. 114-116 ^{o}C [Lit.[26]113-115 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.47-7.52 (m, 2H), 7.62-7.66 (m, 1H), 7.73-7.78 (m, 1H), 8.30-8.34 (m, 1H).

IR[KBr]: υ1598, 1574, 1518, 1478, 1448, 1346, 853, 740, 698 cm^{-1}.

4-Fluoro-1,1'-biphenyl (**18**)

Yield: 95% (White solid)

M.p. 70-71 ^oC [Lit.[27] 72-73 ^oC]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.15-7.17 (m, 2H), 7.46 (m, 1H), 7.50-7.59 (m, 4H).

IR[KBr]: υ 3061, 1598, 1520, 1486, 1165, 1075, 837, 760, 687, 632 cm^{-1}.

[1,1'-Biphenyl]-2-carbonitrile (**19**)

Yield: 91% (Brown solid)

M.p. 46 ^oC [Lit.[28] 41 ^oC]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.45-7.56 (m, 5H), 7.58-7.60 (m, 2H), 7.65-7.70 (m, 1H), 7.78-7.80 (m, 1H).

IR[KBr]: υ 3033, 3064, 2225, 1596, 1564, 1477, 1451, 1434, 760, 735, 699 cm^{-1}.

5'-Phenyl-1,1':3',1''-terphenyl (**20**)

Yield: 90% (Off white solid)

M.p. 175 ^oC [Lit.[29]173 ^oC].

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.40-7.44 (m, 1H), 7.47-7.53 (m, 2H), 7.72-7.75 (m, 2H), 7.82 (s, 1H).

IR[KBr]: υ 3057, 3032, 1644, 1595, 1560, 1496, 872, 764 cm^{-1}.

2,2''-Dimethyl-5'-(o-tolyl)-1,1':3',1''-terphenyl (**21**)

Yield: 80% (Off white solid).

M.p. 137-140 ^oC [Lit.[30] 138-140 ^oC]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.41 (s, 3H), 7.29-7.33 (m, 4H), 7.36-7.39 (m, 1H).

IR[KBr]: υ 3061, 3018, 2922, 2859, 1591, 1488, 1455, 1377, 892, 754 cm^{-1}.

1,1',4',1''-Terphenyl (**22**)

Yield: 81% (White solid).

M.p. 214 ^oC [Lit.[31]211-212 ^oC]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.49 (m, 2H), 7.66-7.68 (m, 4H), 7.71 (s, 2H).
IR[KBr]: υ 3059, 1668, 1550, 1532, 1479, 1455, 839, 746, 688 cm^{-1}.

2-Methyl-4'-nitro-1,1'-biphenyl (**23**)
Yield: 90% (Off white solid).
M.p. 102 ^oC [Lit.[32a] 100-102 ^oC]
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.23-7.25 (m, 1H), 7.28-7.39 (m, 3H), 7.50-7.56 (m, 2H), 8.29-8.32 (m, 2H).
IR[KBr]: υ 3072, 2955, 1596, 1514, 1479, 1383, 1346, 857, 752, 775, 699 cm^{-1}.

4'-Fluoro-2-methyl-1,1'-biphenyl (**24**)
Yield: 75% (Gummy liquid) [Lit.[32b]]
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.88 (s, 3H), 7.11-7.15 (m, 2H), 7.24-7.33 (m, 7H).
IR[KBr]: υ3474, 3061, 3036, 1597, 1517, 1484, 1003, 836, 758, 686, 553, 483 cm^{-1}.

4'-Methoxy-[1,1'-biphenyl]-2-carbaldehyde (**25**)
Yield: 86% (Light orange solid).
M.p. 54 ^oC [Lit.[33]52-53 ^oC]
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 3.89 (s, 3H), 7.02 (m, 2H), 7.28-7.65 (m, 5H), 8.02 (m, 1H), 10.10 (s, 1H).
IR[KBr]: υ 3064, 2960, 2934, 2840, 1692, 1607, 1594, 1560, 1513, 1464, 1390, 1244, 1181, 842, 772 cm^{-1}.

2.1.4.4 Screening of supported catalysts for standard Wittig-Heck reaction

General procedure for Wittig-Heck reaction (Scheme 9):

Synthesis of (E)-1-chloro-4-styrylbenzene (28):

In a dry, N_2 flushed two neck round bottom flask, a mixture of 4-chlorobenzaldehyde (0.165 g, 1.176 mmol), Wittig salt, methyl triphenylphosphonium iodide (0.553 g; 1.37 mmol) and dry potassium carbonate (0.405 g, 2.93 mmol) in dry DMA (6 mL) was stirred at 60 ^oC. At this temperature iodobenzene (0.20 g, 0.98 mmol) and catalyst PANI-Pd (0.06 g, 0.0218 mmol of Pd) were added. The reaction mixture was then heated to 140 ^oC (40 h). The reaction mixture was quenched with water (2x20 mL) and extracted with ethyl acetate (3x25 mL). The

combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel to afford 1-chloro-4-styrylbenzene (**28**) (0.183 g, 87.1%) as white solid. M.p. 129-130^{o}C [Lit.[34]129^{o}C].

^{1}H-NMR ($CDCl_3$, 400 MHz) υ 7.05-7.13 (two d, *J* = 16.4 Hz, 2H), 7.28-7.40 (m, 5H), 7.45-7.48 (m, 2H), 7.52-7.54 (m, 2H).

IR[KBr]: υ 3430, 3019, 1679, 1554, 1492, 1448, 1405, 1376, 967, 818, 752, 690, 529 cm^{-1}.

Mass (EI): 214 (M^+ 52), 213 (88), 179 (78), 178 (100), 76 (43), 151 (18).

Other derivatives were prepared by the similar procedure:

(*E*)-1,2-Diphenylethene (**26**)

Yield: 85% (White solid)

M.p. 120-122 ^{o}C [Lit.[13]121 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.15 (s, 2H), 7.28-7.31 (m, 2H), 7.38-7.42 (t, *J* = 7.6 Hz, 4H), 7.54-7.56 (d, *J* = 7.6 Hz, 4H).

IR[KBr]: υ 1651, 1497, 1552, 1573, 762, 688 cm^{-1}.

Mass (EI): 180 (M^+ 70), 179(100), 178 (24), 152(9).

(*E*)-1-Nitro-4-styrylbenzene (**27**)

Yield: 89% (Yellow solid)

M.p. 155 ^{o}C [Lit.[17]154-156 ^{o}C]

^{1}H-NMR($CDCl_3$, 400 MHz): δ 7.15-7.19 (d, *J* = 16.4 Hz, 1H), 7.28-7.45 (m, 4H), 7.570-7.591 (m, 2H), 7.65-7.67 (m, 2H), 8.24-8.26 (m, 2H).

IR[KBr]: υ 3024, 2920, 1631, 1591, 1447, 1510, 1324, 833, 767, 695 cm^{-1}.

Mass (EI): 225 (M^+ 70), 178 (100), 179(17), 151(8).

(*E*)-4-Styrylbenzonitrile (**29**)

Yield: 86% (White solid)

M.p. 118 ^{o}C [Lit.[35]117-119 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.09-7.13 (d, *J* = 16.4 Hz, 1H), 7.22-7.26 (d, *J* = 16.0 Hz, 1H), 7.34-7.36 (m, 1H), 7.41-7.43 (m, 2H), 7.55-7.57 (m, 2H), 7.59-7.62 (m, 2H), 7.63-7.67 (m, 2H).

IR[KBr]: υ 3024, 2225, 1684, 1600, 1503, 1450, 1412, 824, 759, 692 cm^{-1}.

Mass (EI): 205 (M^+72), 204(M-1100), 203 (75), 176(9).

(*E*)-1-Nitro-3-styrylbenzene (**30**)

Yield: 86% (Pale yellow solid).

M.p. 109-111 ^oC [Lit.[36]108-110 ^oC]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.14-7.18 (d, *J* = 16.0 Hz, 1H), 7.25-7.56 (m, 7H), 7.82-7.84 (d, *J* = 8.0 Hz, 1H), 8.11-8.14 (m, 1H).

IR[KBr]: υ 3424, 3081, 3026, 1680, 1570, 1560, 1449, 1522, 1350, 967, 898, 755, 694 cm^{-1}.

Mass (EI): 225 (M^+ 35), 224 (72), 178(100), 177 (45), 149(5).

(*E*)-1-Nitro-2-styrylbenzene (**31**)

Yield: 73% (Yellow solid)

M.p. 73-74 ^oC [Lit.[37]72-73 ^oC]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.10-7.14 (d, *J* = 16.0 Hz, 1H), 7.32-7.45 (m, 4H), 7.55-7.65 (m, 4H), 7.79-7.81 (m, 1H), 7.98-8.00 (dd, *J* = 7.2, 1.2 Hz, 1H).

IR[KBr]: υ 3435, 3081, 3026, 1679, 1570, 1521, 1449, 1350, 967, 755, 694 cm^{-1}.

Mass (EI): 225 (M^+), 179 (73), 178 (81), 69 (100).

(*E*)-5-Styrylbenzo[*d*][1,3]dioxole (**32**)

Yield: 88% (Light brown solid)

M.p. 91 ^oC [Lit.[17] 88-91 ^oC]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 6.00 (s, 2H), 6.81-6.86 (m, 1H), 6.94-6.98 (m, 2H), 7.04-7.01 (m, 2H), 7.25-7.28 (m, 1H), 7.35-7.39 (m, 2H), 7.50-7.52 (m, 2H).

IR[KBr]: υ 3026, 2933, 2909, 2837, 1604, 1573, 1513, 1502, 1447, 1364, 1263, 1177, 1030, 963, 856, 825, 792, 755 cm^{-1}.

Mass (EI): 225 (M+1, 15), 224 (M^+ 100), 223 (80), 209(6), 165 (54).

(*E*,*E*) 1,4-di(Styryl)benzene (**33**)

Yield: 56% (Off white solid)

M.p. 107-109 ^oC [Lit.[36] 108-110 ^oC]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.10-7.19 (Two d, *J* = 16.4 Hz, 4H), 7.27-7.31 (m, 2H), 7.37-7.41 (m, 4H), 7.54-7.56 (m, 8H).

IR[KBr]: υ 3055, 3025, 1592, 1511, 1487, 1446, 1416, 966, 815, 746, 689 cm^{-1}.

Mass (EI): 282 (M^+100), 281 (57), 202 (22), 132(8).

(E)-1-methoxy-4-(4-nitrostyryl)benzene (**34**)

Yield: 86% (Yellow solid)

M.p. 161-163 ^oC [Lit.[38]162 ^oC]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 3.87 (s, 3H), 6.94-6.96 (m, 2H), 7.01-7.05 (d, *J* = 16.0 Hz, 1H), 7.23-7.27 (d, *J* = 16.0 Hz, 1H), 7.51-7.53 (m, 2H), 7.61-7.63 (m, 2H), 8.22-8.24 (m, 2H).

IR[KBr]: υ 3439, 2899, 2835, 1679, 1690, 1587, 1376,1461, 1250, 1173, 970, 821 cm^{-1}.

Mass (EI): 255 (M^+ 100), 254 (37), 208(7), 165(72), 164 (26).

5,5'-((1*E*,1'*E*)-(2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl))bis(benzo[d][1,3]dioxole)(**35**)

Yield: 52% (Brown solid)

M.p. 238 ^oC [Lit.[39] 237-239 ^oC]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 3.93 (s, 3H), 6.00 (s, 2H), 6.81-6.83 (m, 1H), 6.98-7.07 (m, 2H), 7.11-7.14 (m, 2H), 7.31-7.35 (m, 1H).

IR[KBr]: υ 3007, 2894, 2835, 2778, 1684, 1627, 1601, 1554, 1503, 1444, 1407, 1367, 1256, 1209, 1039, 971, 860, 805, 754, 692 cm^{-1}.

2.1.4.5 Screening of supported catalysts for standard Wittig Suzuki reaction

General procedure for Wittig-Suzuki reaction (Scheme 11):

Synthesis of 4-(2-([1,1'-biphenyl]-4-yl)vinyl)benzonitrile (39):

In a dry, N_2 flushed round bottom flask a mixture of 4-cyanobenzaldehyde (0.20 g; 1.53 mmol), Wittig salt, 4-bromobenzyltriphenylphoshphonium bromide (0.783 g, 1.53 mmol) and dry potassium carbonate (0.57 g, 4.13 mmol) in dry DMF (6 mL) was kept. The reaction was heated to 130 ^oC for 6 h and then phenylboronic acid (0.223 g, 1.83 mmol), potassium carbonate (0.485 g, 3.52 mmol), catalysts PANI-Pd (0.06 g, 0.022 mmol of Pd) were added and continued heating at the same temperature for 24 h. The reaction mixture was added to water (20 mL) and extracted with ethyl acetate (3x25 mL). The combined organic layer was washed with water (2x20 mL), dried with anhydrous sodium sulfate and concentrated under vacuum. The residue was purified by column chromatography on silica gel to get desired

product 4-(2-([1,1'-biphenyl]-4-yl)vinyl)benzonitrile (**39**) (0.301 g, 70.1%) *Z*:*E* ratio 58:42 (determined by ^{1}H-NMR).

^{1}H-NMR of *Z*-**39**: ($CDCl_3$, 400 MHz) δ 6.60-6.64 (d, *J* = 12.4 Hz, 1H), 6.79-6.82 (d, *J* = 12.4, 1H), 7.28-7.30 (m, 2H), 7.37-7.40 (m, 1H), 7.40-7.44 (m, 2H), 7.45-7.48 (m, 2H), 7.51-7.56 (m, 2H), 7.60-7.62 (m, 2H). M.p. = 152-5 ^{o}C.

^{1}H-NMR of *E*-**39**: ($CDCl_3$, 400 MHz) δ 7.13-7.18 (d, *J* = 16.4 Hz, 1H), 7.26-7.30 (d, *J* = 16.4 Hz, 1H), 7.37-7.42 (m, 1H), 7.46-7.50 (m, 2H), 7.61-7.68 (m, 10H). M.p. = 195-7 ^{o}C.

IR[KBr]: υ 3468, 3063, 2227, 1630, 1603, 1553, 1484, 1448, 1413, 972, 840 cm^{-1}.

Mass (EI): 281 (M^+ 100), 279 (11), 252 (7)

4-Styryl-1,1'-biphenyl (**36**)

Yield: 60% (White solid); {*Z*:*E* = 63:37}

M.p. 215-216 ^{o}C [Lit.[10]]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 6.65 and 7.18 (Two s, 2H, for olefinic H of *Z* and *E* isomer), 7.23-7.26 (m, 1H), 7.27-7.38 (m, 8H), 7.40-7.50 (m, 5H), 7.55-7.66 (m, 6H).

IR[KBr]: υ 3048, 2924, 2852, 1671, 1580, 1572, 1555, 1485, 968, 764, 695 cm^{-1}.

Mass (EI): 256 (M^+ 100), 255 (88), 178(24).

4-(4-Chlorostyryl)-1,1'-biphenyl (**37**)

Yield: 62% (White solid); {*Z*:*E* = 35:65}

M.p. 242-244 ^{o}C [Lit.[10]]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 6.56-6.68 (Two d, *J* = 12.4 Hz, 2H olefinic H of *Z* isomer), 7.12-7.13 (m, 2H), 7.24-7.28 (m with a d, *J* = 16.0 Hz of olefinic H of *E* isomer, 6H), 7.31-7.38 (m, 6H), 7.44-7.51 (m, 8H), 7.60-7.64 (m, 8H).

IR[KBr]: υ 3051, 2926, 2854, 1674, 1560, 1487, 1415, 1342, 967, 837, 685 cm^{-1}.

Mass (EI): 289 (M^{-1}100), 252(34), 178 (21).

4-(4-Nitrostyryl)-1,1'-biphenyl (**38**)

Yield: 65% (Yellow solid); {*Z*:*E*= 35:65}

M.p. 212-225 ^{o}C [Lit.[10]216-218 ^{o}C]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 6.65-6.87 (Two d, *J* = 12.4 Hz, 2H olefinic for *Z* isomer), 7.02-7.09 (m, 1H), 7.13-7.71 (d, *J* = 16.0 Hz, 2H olefinic for *E* isomer), 7.19-7.23 (m, 3H), 7.30-7.66 (m, 18H), 8.10-8.14 (m, 2H), 8.23-8.26 (m, 2H).

IR[KBr]: υ3434, 1630, 1589, 1509, 1449, 1413, 1345, 972, 846, 718, 692 cm^{-1}.

Mass (EI): 301 (M^+100), 300(88), 254(14), 177(19), 57.

(*E*) 4-(3-Nitrostyryl)-1,1'-biphenyl (**40**)

Yield: 68% (Yellow solid)

M.p. 155-165 ^oC {*E* isomer}

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.18-7.23 (d, *J* = 16.0 Hz, 1H olefinic H of *E* isomer), 7.28-7.41 (m, 3H, with the other H), 7.46-7.59 (m, 3H), 7.63-7.68 (m, 6H), 7.83-7.85 (m, 1H), 8.12-8.15 (m, 1H), 8.41-8.42 (m, 1H).

IR[KBr]: υ 3369, 3077, 1573, 1522, 1347, 1485, 1347, 968, 833, 775, 856, 687 $cm.^{-1}$

Mass (EI): 301 (M^+100), 254(14), 252 (47), 226 (5), 151(3).

2-Methyl-4'-(3-nitrostyryl)-1,1'-biphenyl (**41**)

Yield: 72% (Yellow semi-solid) {Z:E = 63:37}

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.31 and 2.35 (Two s, for *Z*/*E* isomer, 6H), 6.65-6.87 (two d, *J* = 12.4 Hz, olefinicproton of *Z* isomer, 2H), 7.23-7.32 (m, 1H), 7.34-7.64 (m, 17H, including 2 olefinicproton of *E* isomer), 7.85 (m, 1H), 8.07-8.17 (m, 6H), 8.42 (m, 1H).

IR[KBr]: υ3072, 3023, 2861, 1608, 1574, 1529, 1350, 1482, 1398, 964, 861, 821, 769, 677 $cm.^{-1}$

Mass (EI): (m/z)315 (M^+100), 314 (47), 266 (40), 178 (45), 165 (54).

4-(2-(2'-Methyl-[1,1'-biphenyl]-4-yl)vinyl)benzonitrile (**42**)

Yield: 55% (Pale yellow semi-solid) {Z:E= 51:49}

^{1}H-NMR($CDCl_3$, 400 MHz): δ 2.30 and 2.33 (Two s, of Z/E isomers, 3H), 6.61-6.83 (Two d, *J* = 12.0 Hz, olefinic H of *Z* isomer, 2H), 7.14-7.18 (d, *J* = 16.4 Hz, olefinic H of *E* isomer, 1H),7.14-7.31 (m, including the second olefin H of *E* isomer, 13H),7.38-7.43 (m, 4H), 7.54-7.55 (m, 2H), 7.54-7.67 (m, 5H).

IR[KBr]: υ 3021, 2917, 2851, 2223, 1684, 1599, 1550, 1481, 1412, 1174, 973, 835, 736 $cm.^{-1}$

Mass (EI): 295 (M^+100), 203(2).

5-(2-([1,1'-Biphenyl]-4-yl)vinyl)benzo[*d*][1,3]dioxole (**43**)

Yield: 0.261 g, 65% (Pale yellow solid) (Mostly *E* isomer)

M.p. 178-180 ^oC [Lit.[38] 175-176 ^oC]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 6.01 (s, 2H), 6.82-6.84 (d, *J* = 8.0 Hz, 2H), 6.97-7.02 (m, including one d, *J* = 16.0 Hz for the olefinic H, total 2H), 7.08-7.12 (m, including one d, *J* = 16.0 Hz for the olefinic H, total 2H), 7.33-7.90 (m, 1H), 7.45-7.49 (m, 2H), 7.56-7.58 (m, 6H).

IR[KBr]: υ 3030, 2906, 1671, 1661, 1499, 1446, 1362, 1260, 1045, 965, 831, 760 cm.$^{-1}$

Mass (EI): 300 (M^+100), 302(3), 299(70), 209(4).

General procedure for preparation of compound 46 (Scheme 12):

Synthesis of 1,4-bis((*E*)-2-([1,1'-Biphenyl]-4-yl)vinyl)benzene (**46**):

In a dry N_2 flushed round bottom flask a mixture of terphthaldehye **44** (0.20 g; 1.48 mmol), Wittig salt, 4-bromobenzyltriphenylphoshphonium bromide (1.53 g, 2.98 mmol) and dry potassium carbonate (1.11 g, 8.05 mmol) in dry DMF (6 mL) was charged. The reaction was heated to 130 ^{o}C for 6 h and then phenylboronic acid (0.435 g, 3.57 mmol), potassium carbonate (0.945 g, 6.85 mmol), catalysts PANI-Pd (0.15 g, 0.055 mmol of Pd) were added and continued heating at the same temperature for 24 h. The reaction mixture was added to water (20 mL) and extracted with ethyl acetate (3 X 25 mL). The combined organic layer was washed with water (2 X 20 mL), dried with anhydrous sodium sulfate and concentrated under vacuum. The residue was purified by column chromatography on silica gel to get desired product.0.25gm (38%) [yellow solid].[40]

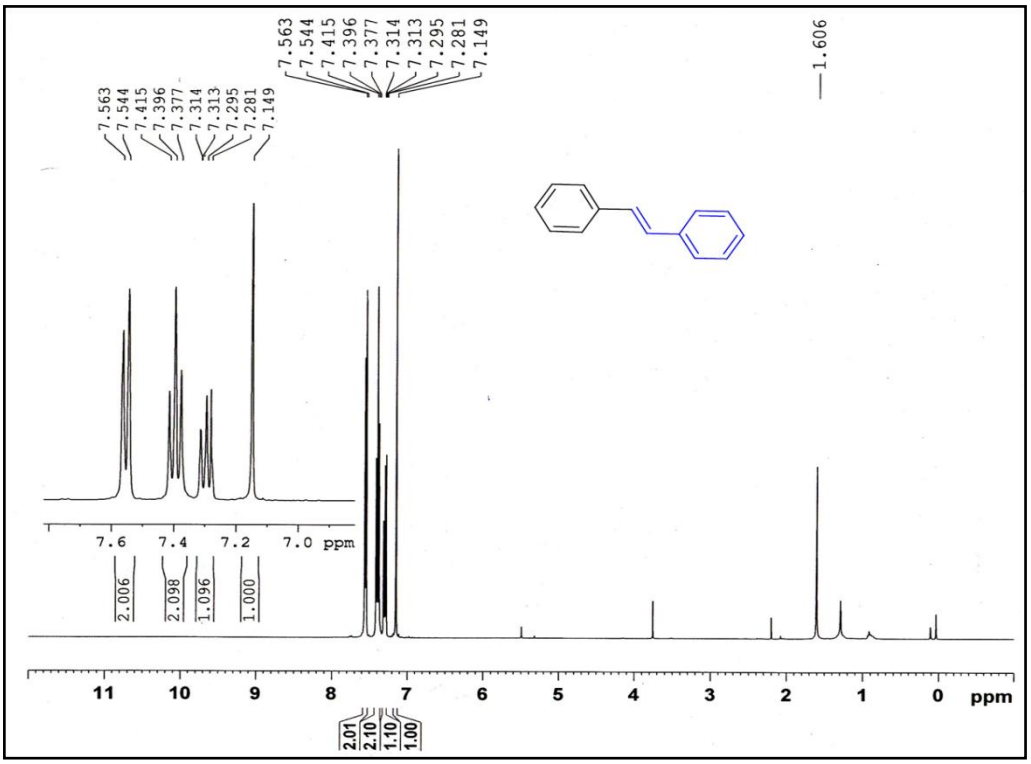
M.p: > 250 ^{o}C,

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 6.61-6.64 (m, 2H), 7.14-7.63 (m, 11H).

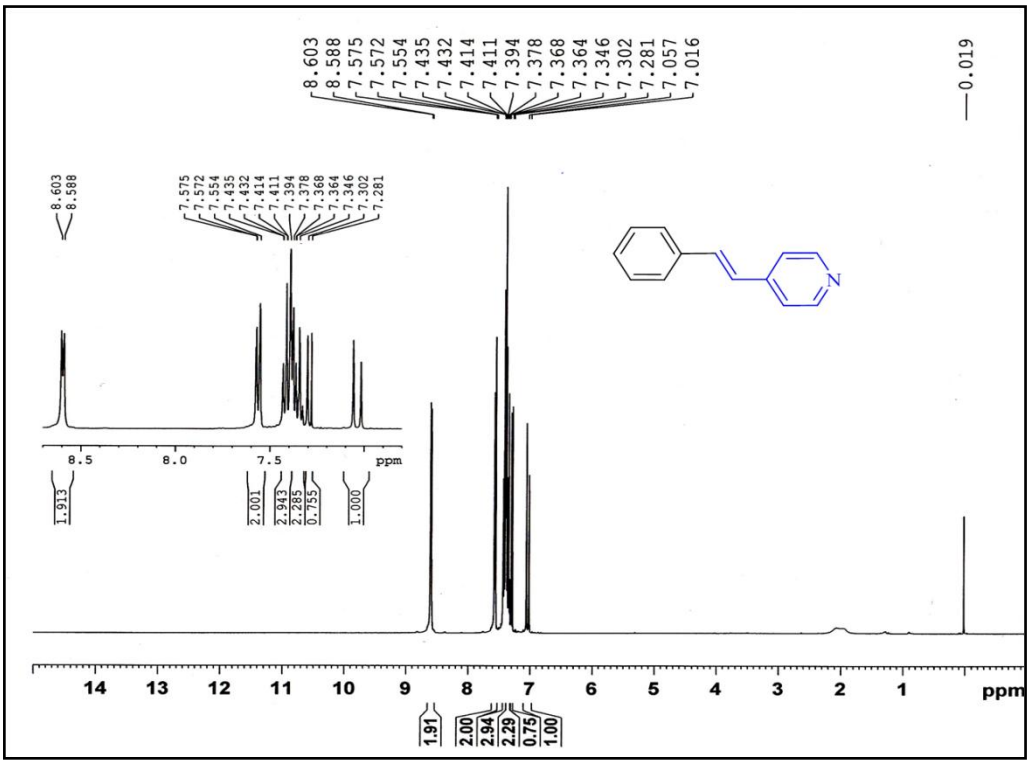
IR[KBr]: υ 3057, 1599, 1510, 1484, 1419, 1380, 837 cm.$^{-1}$

Mass (EI): 434.1(M^+)

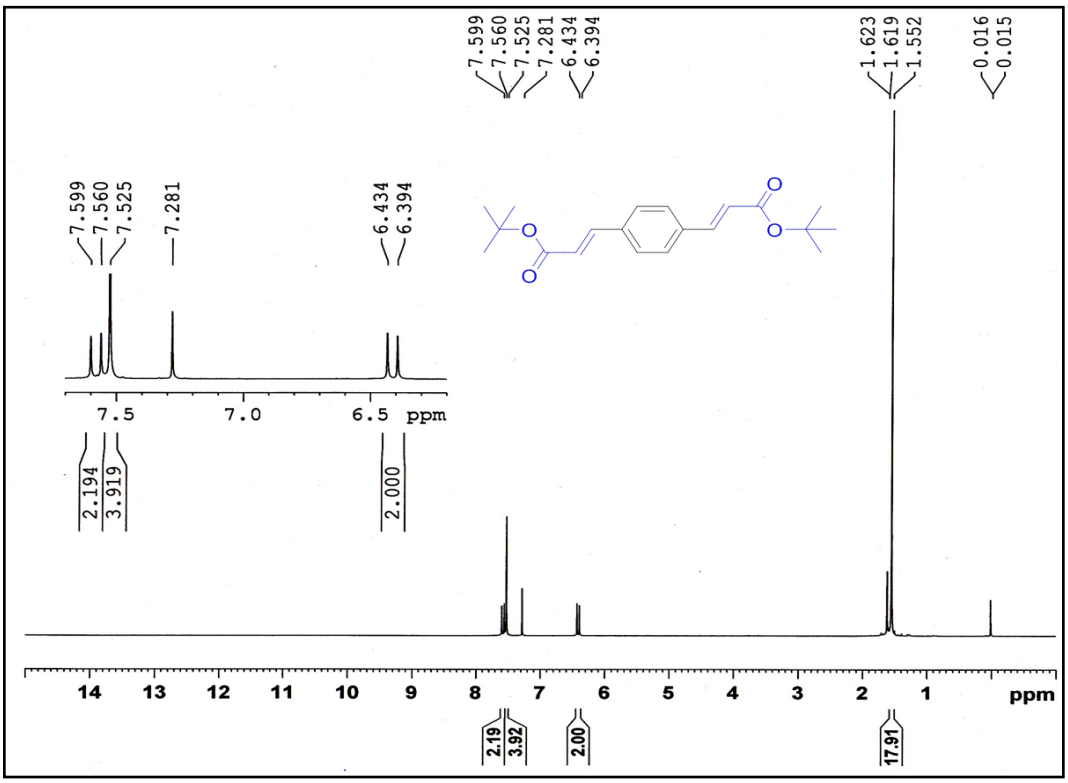
Spectral Data:



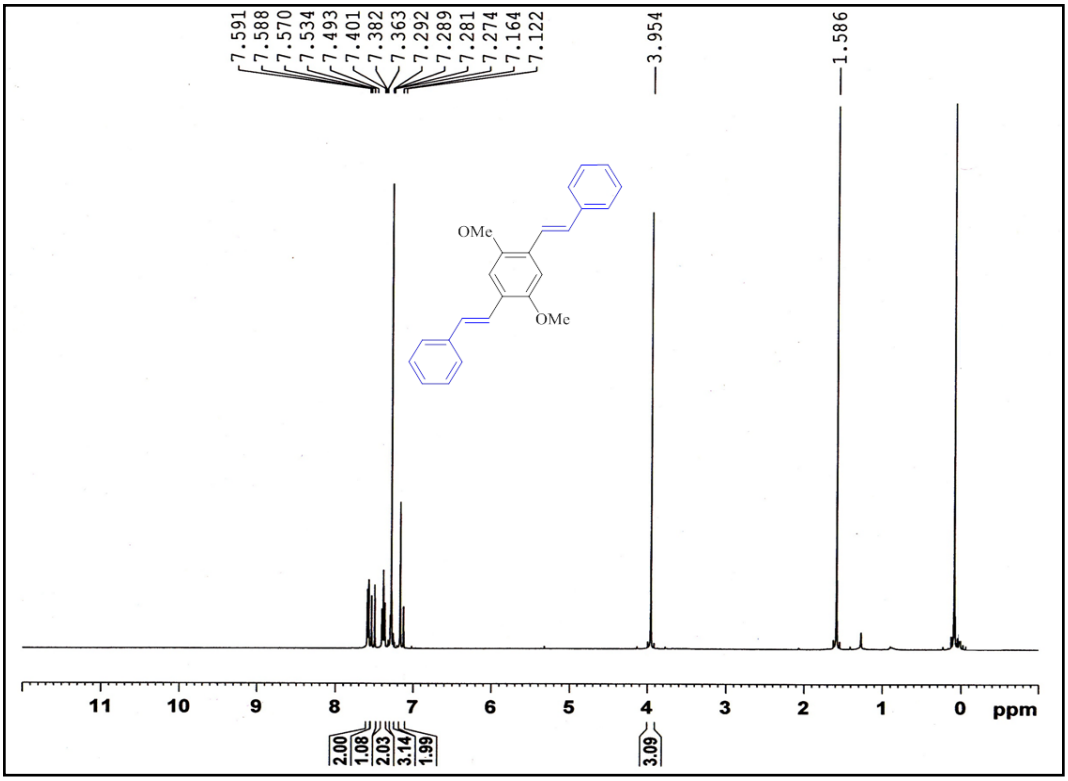
^{1}H NMR of Compound **1**



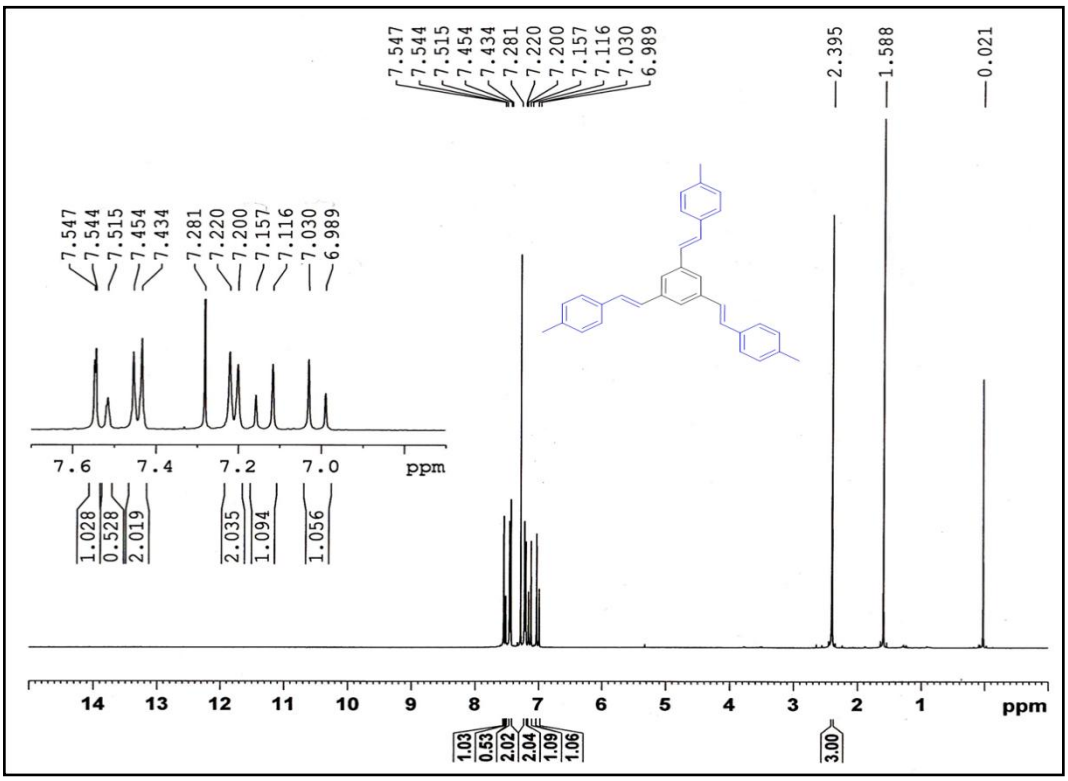
^{1}H NMR of Compound **3**



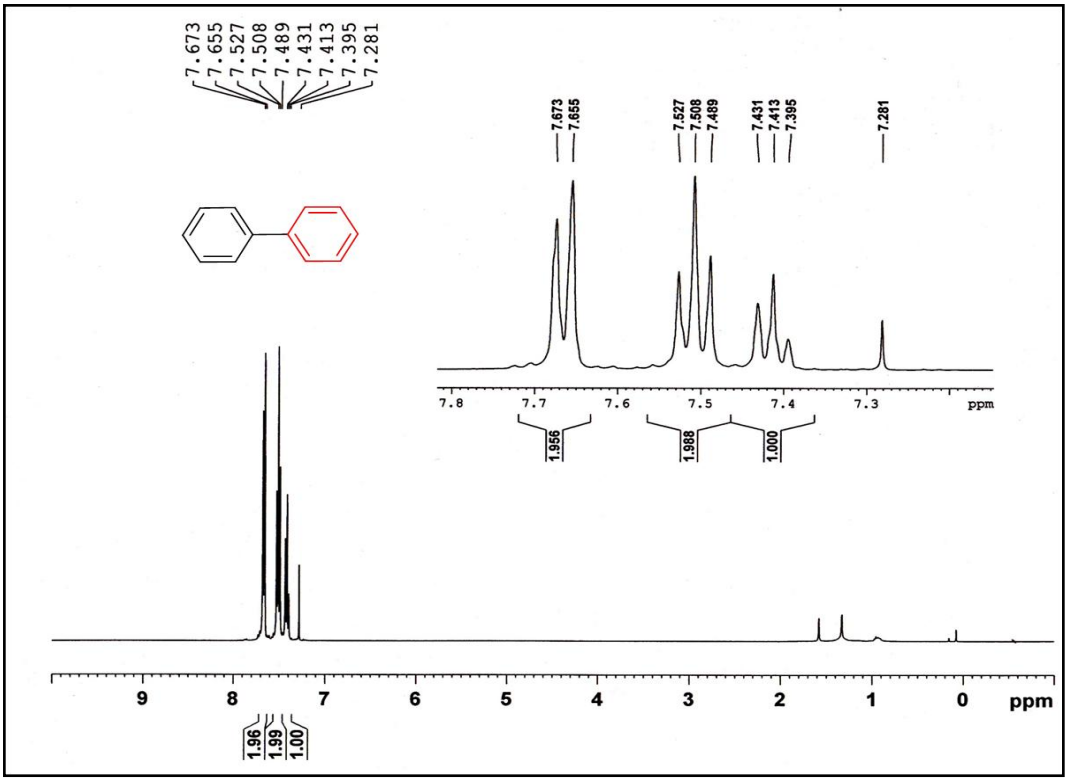
^{1}H NMR of Compound **10**



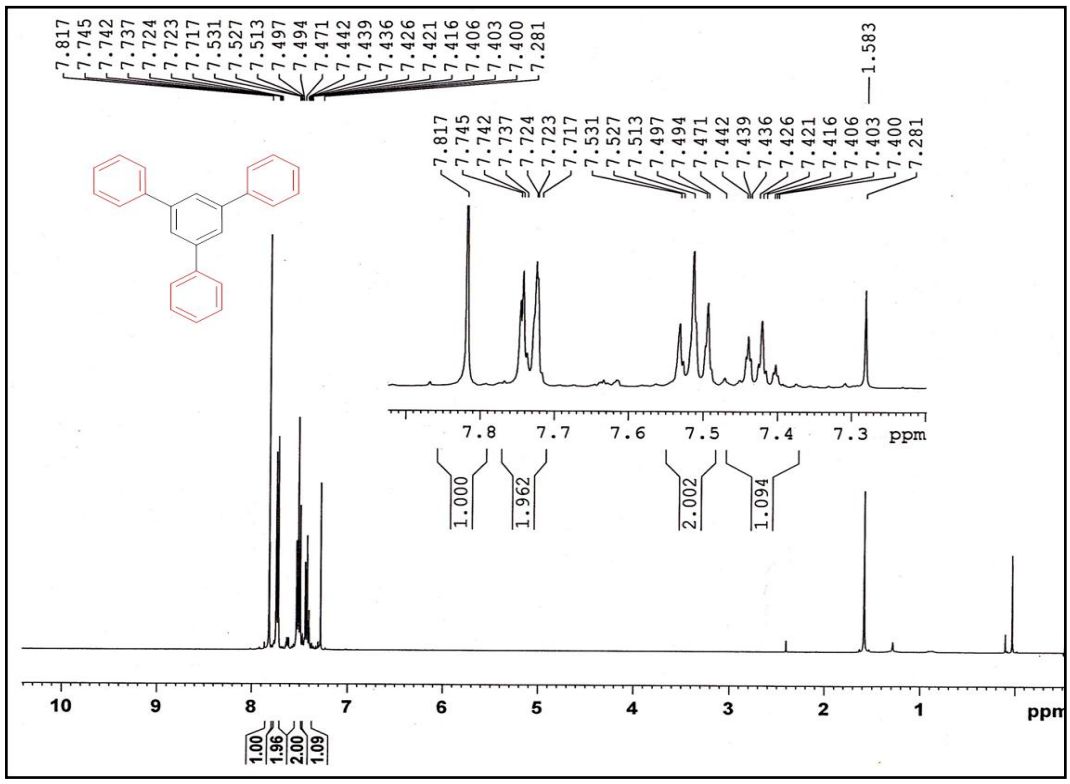
^{1}H NMR of Compound **11**



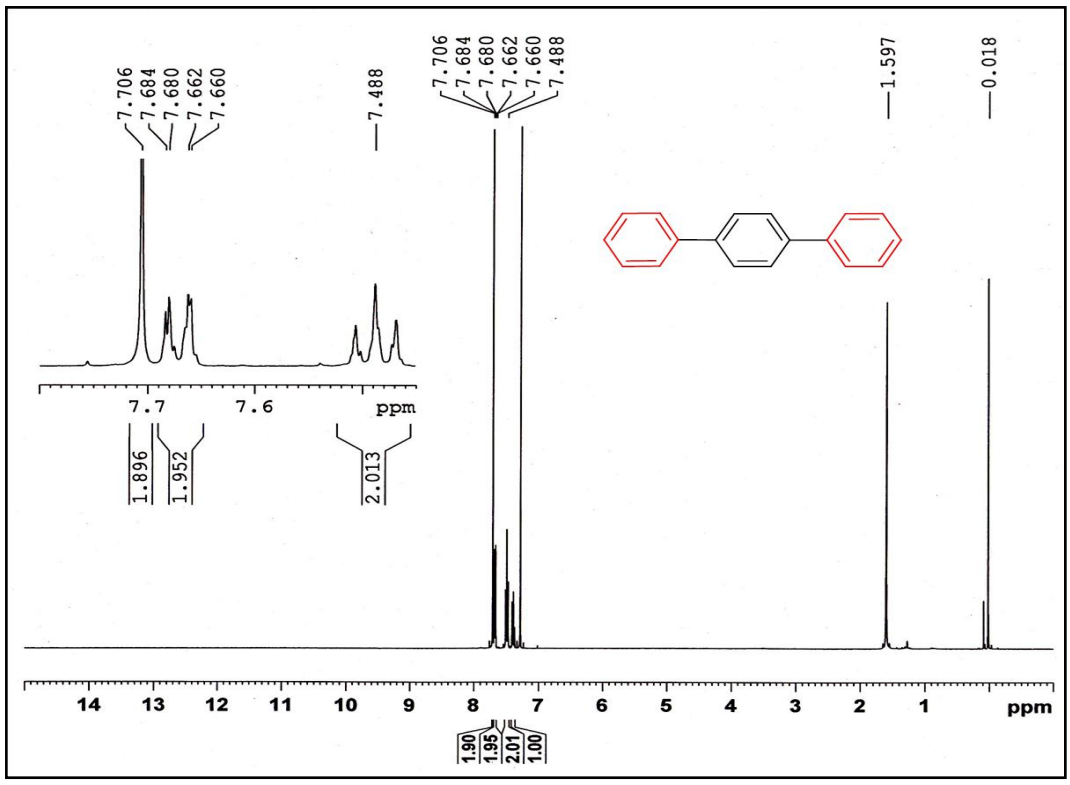
^{1}H NMR of Compound **14**



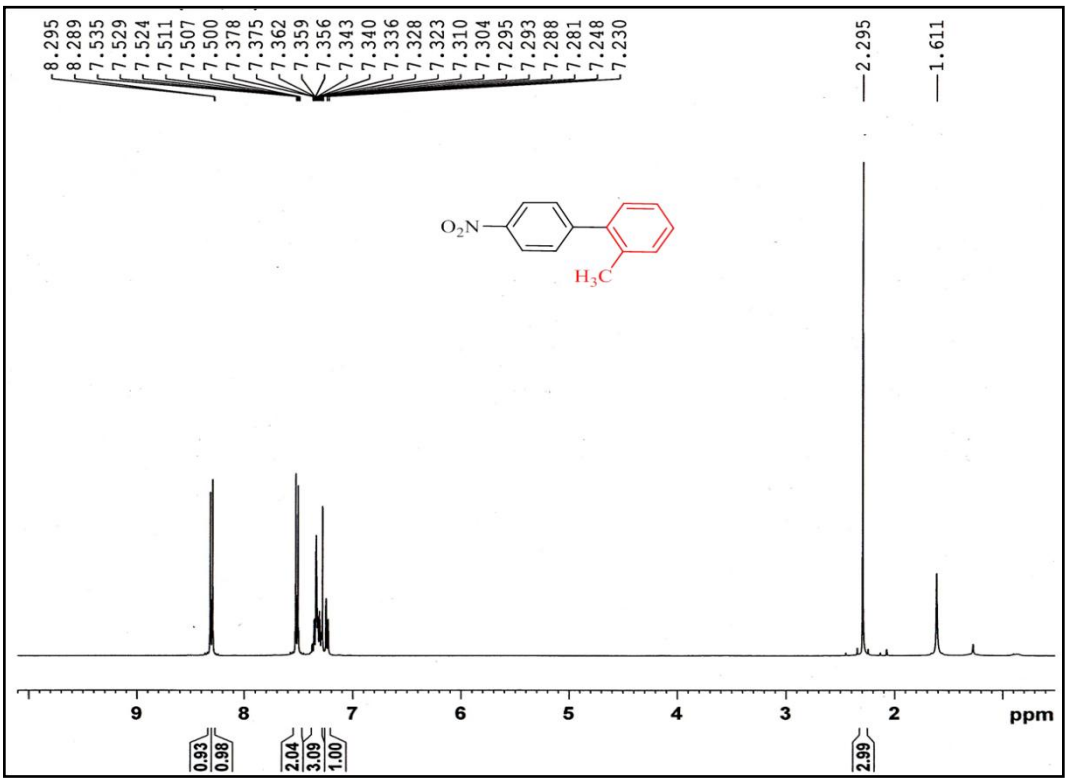
^{1}H NMR of Compound **15**



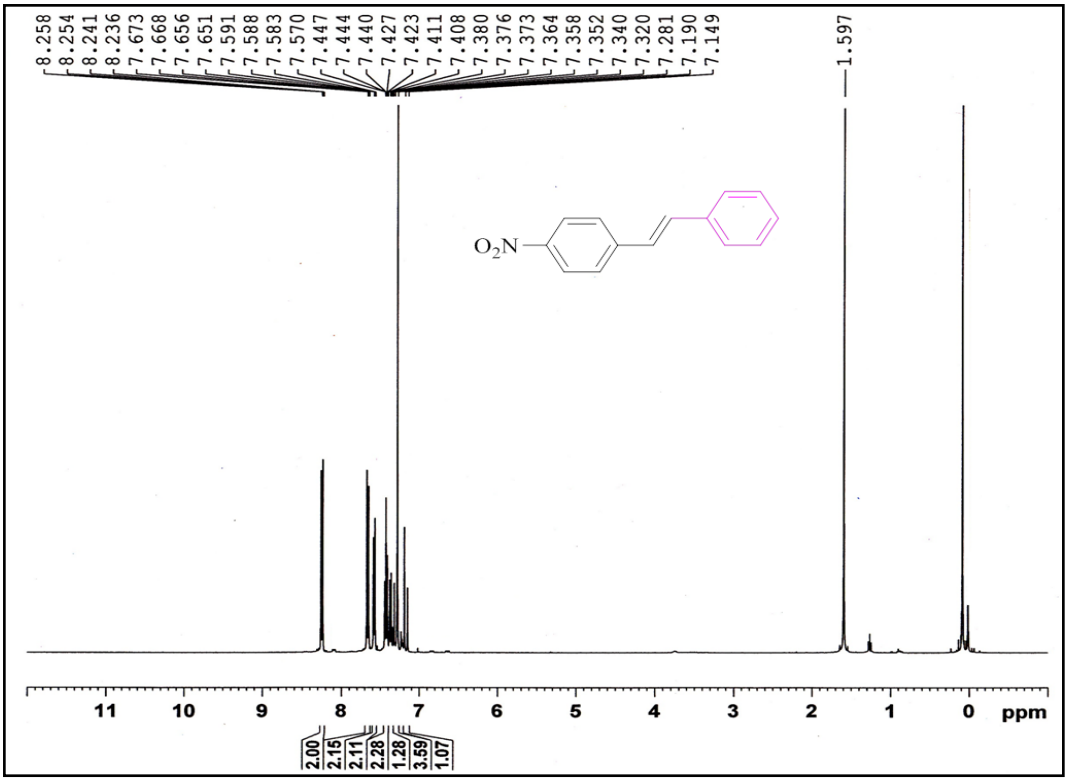
^{1}H NMR of Compound **20**



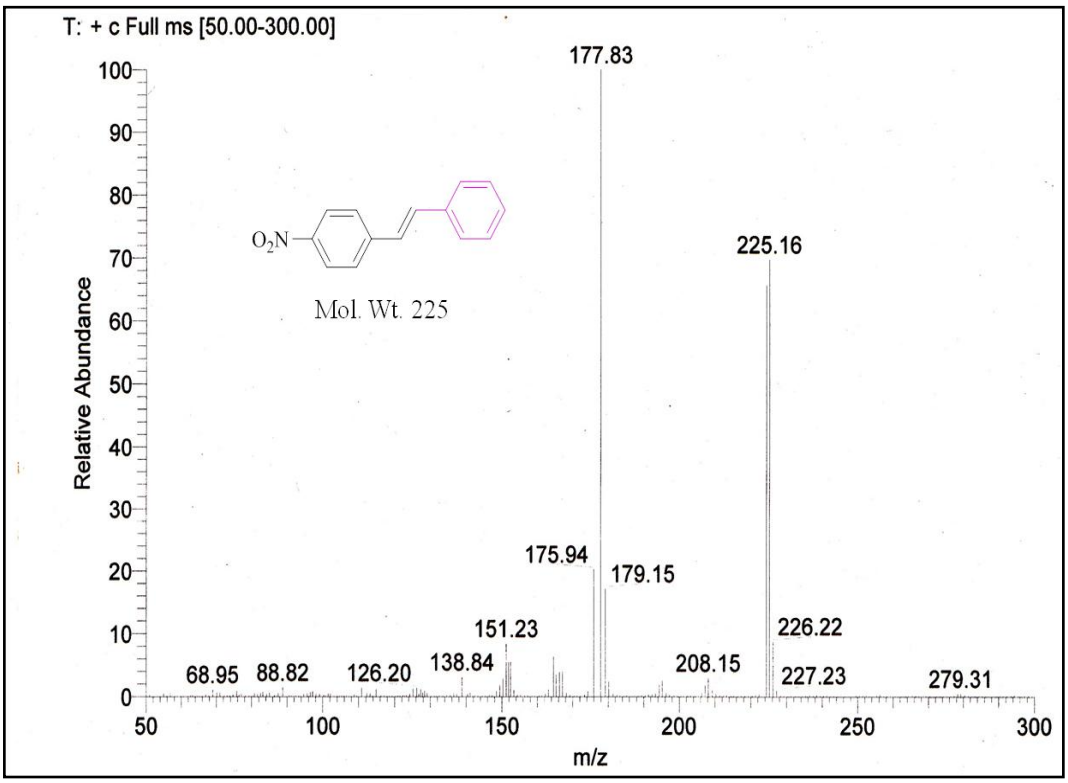
^{1}H NMR of Compound **22**



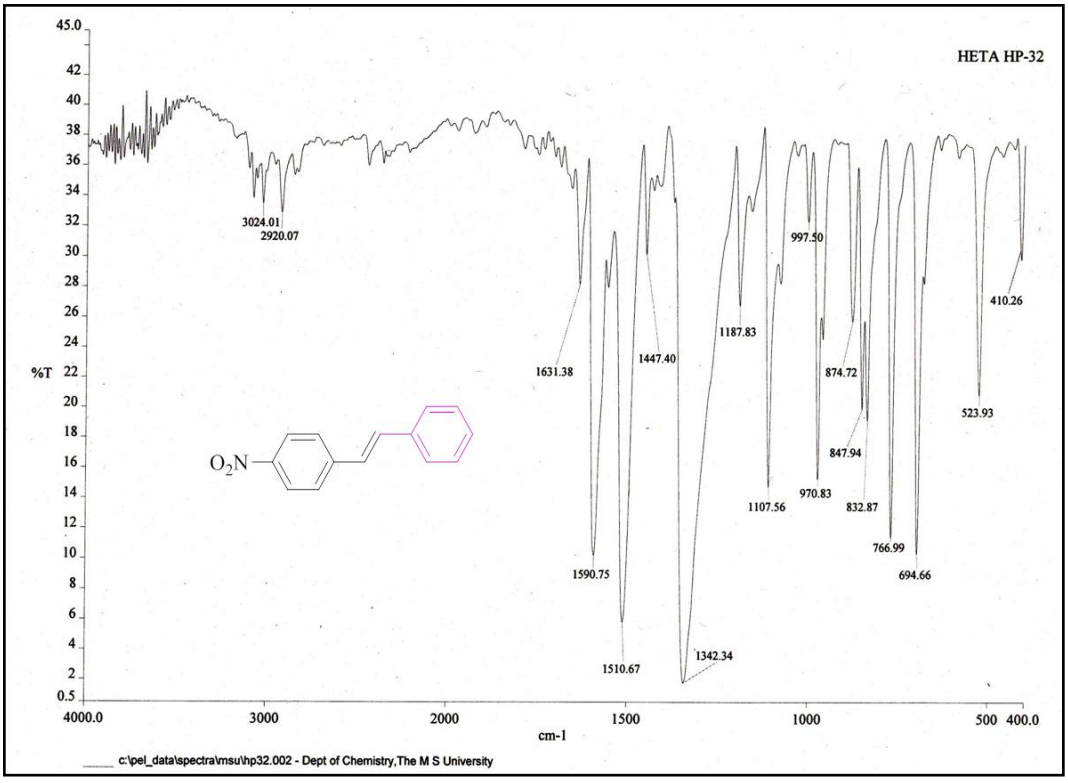
^{1}H NMR of Compound **23**



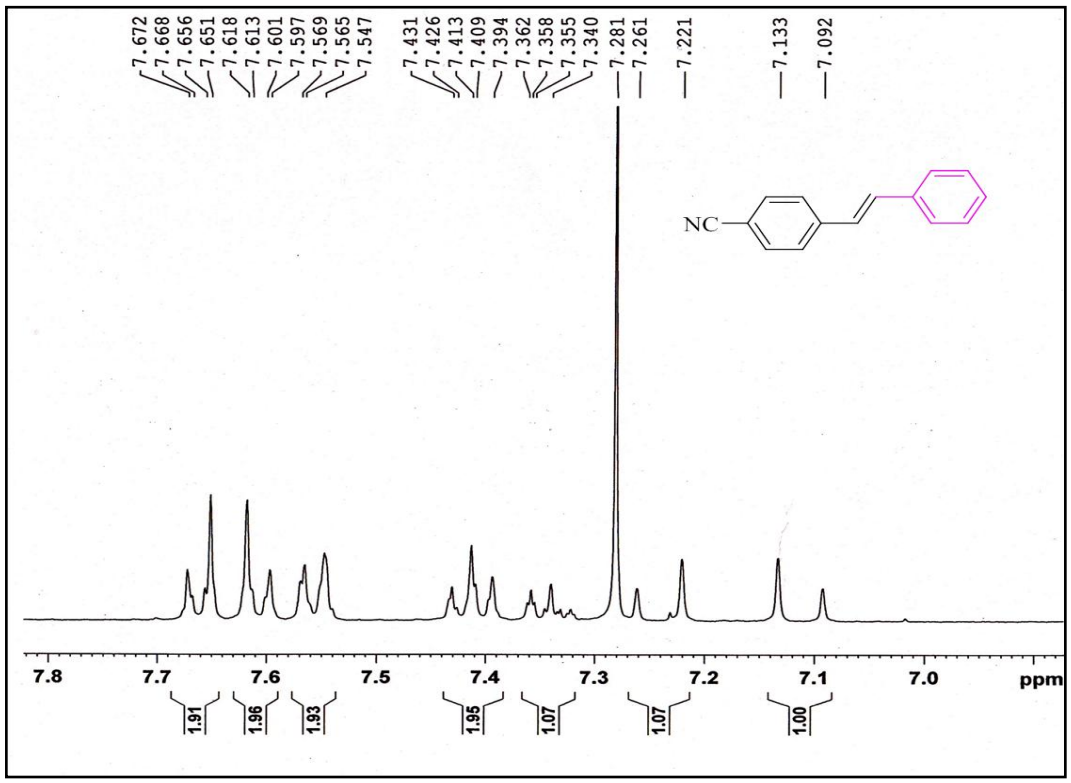
^{1}H NMR of Compound **27**



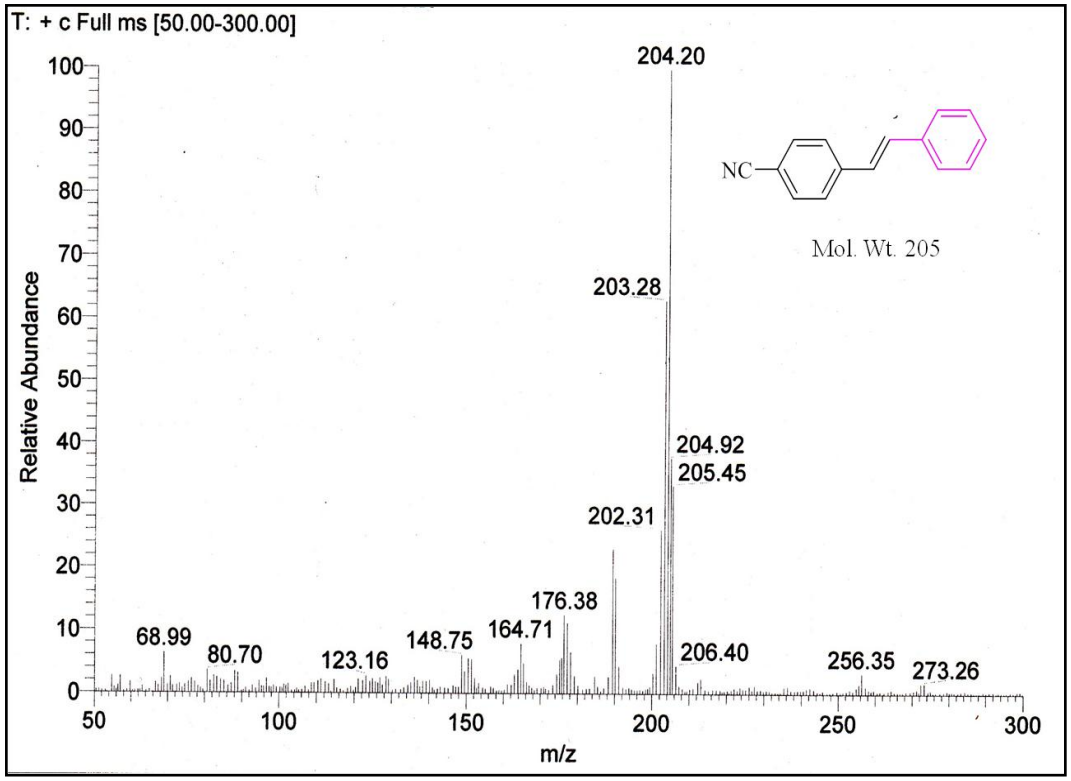
Mass Spectra of Compound **27**



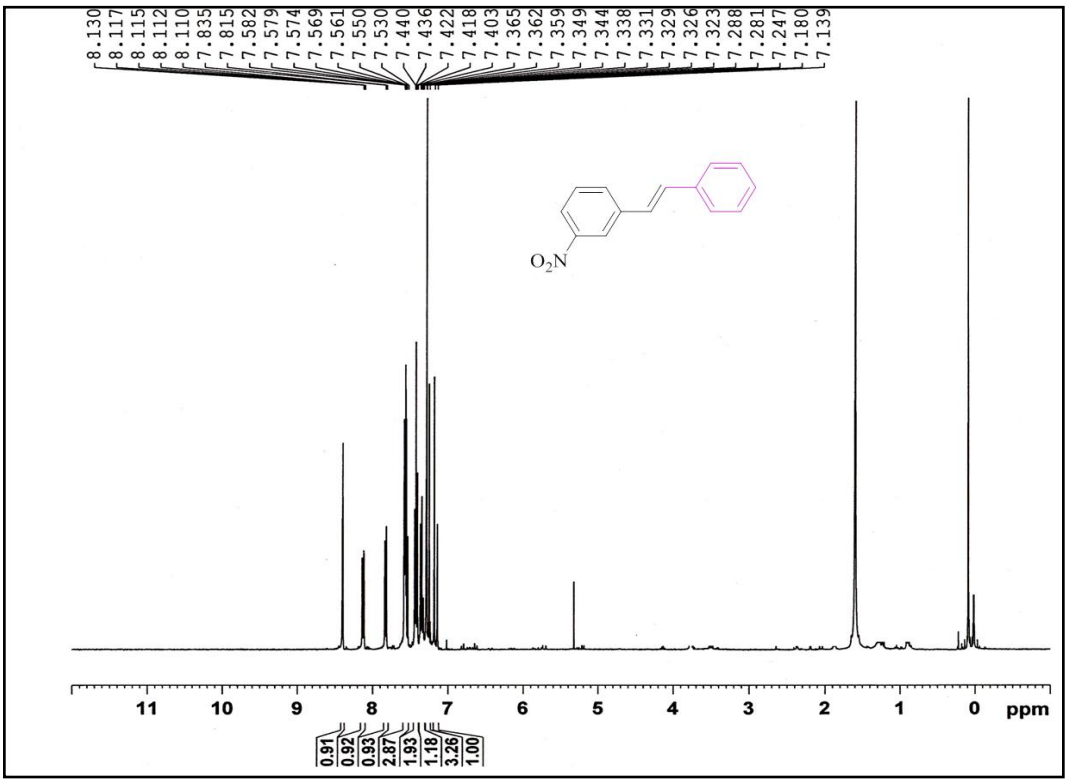
IR of Compound **27**



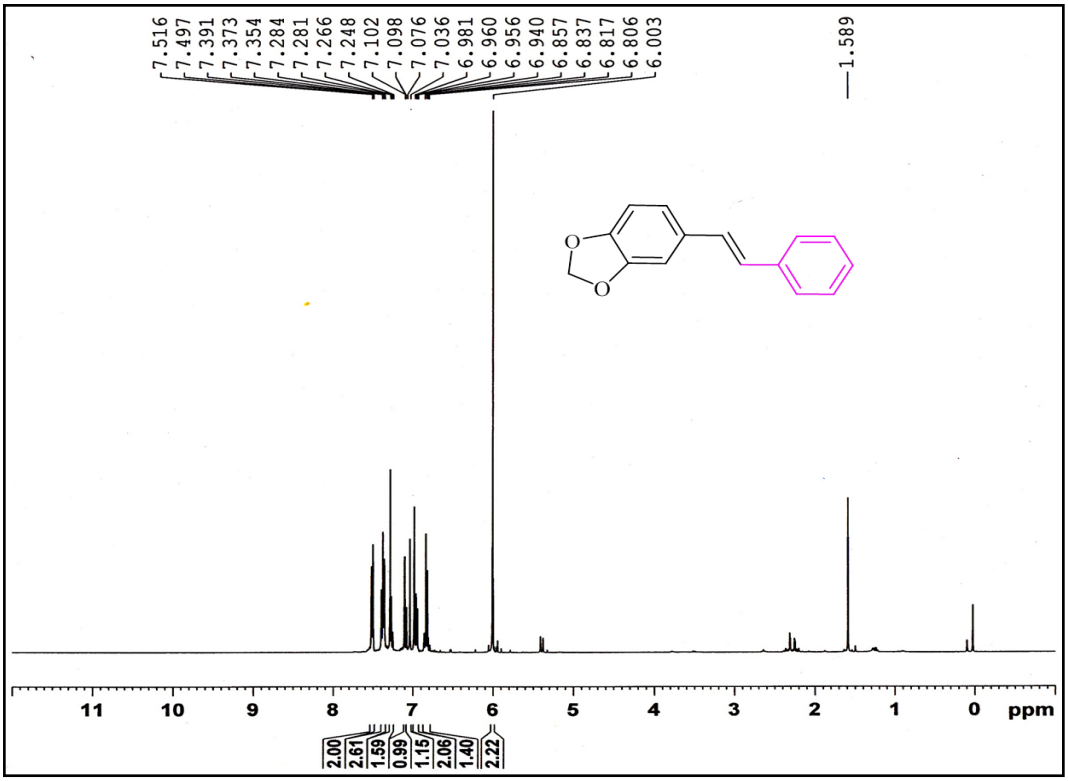
^{1}H NMR of Compound **29**



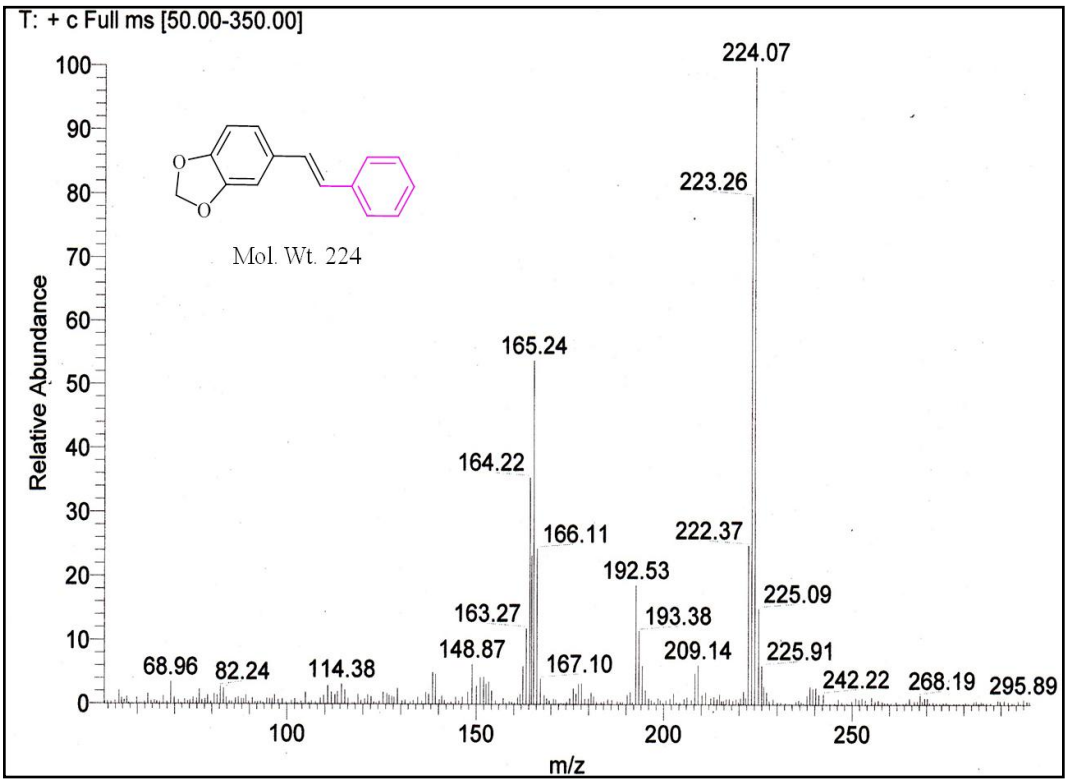
Mass Spectra of Compound **29**



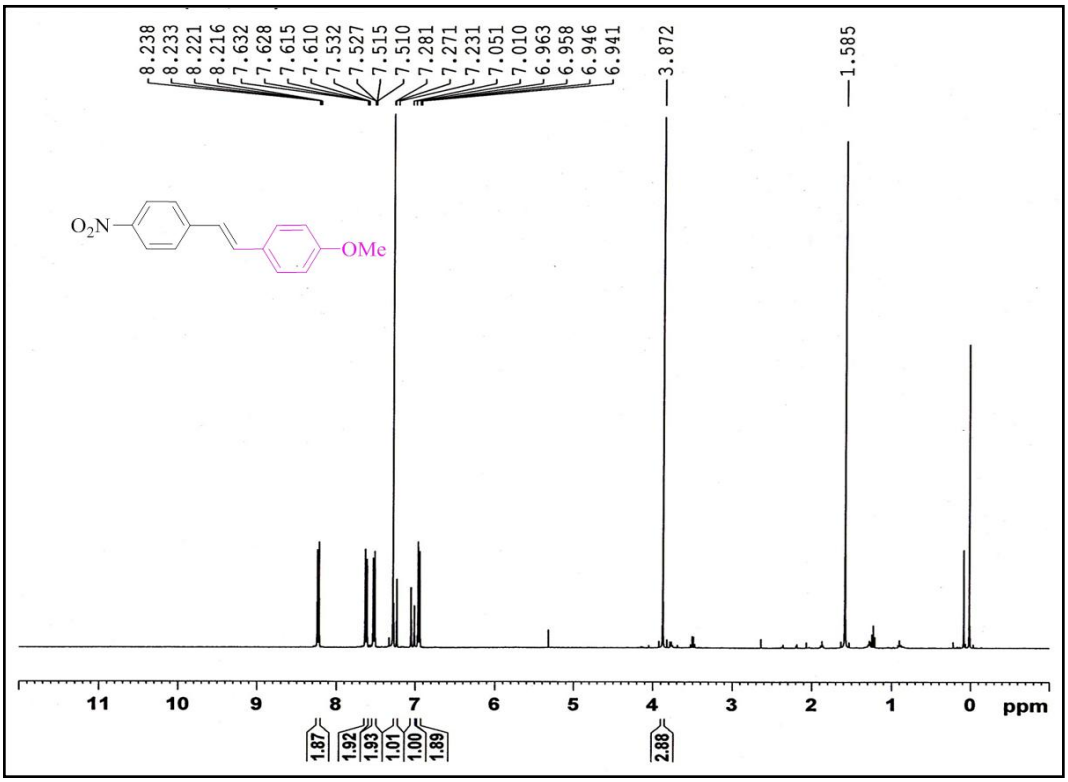
^{1}H NMR of Compound **31**



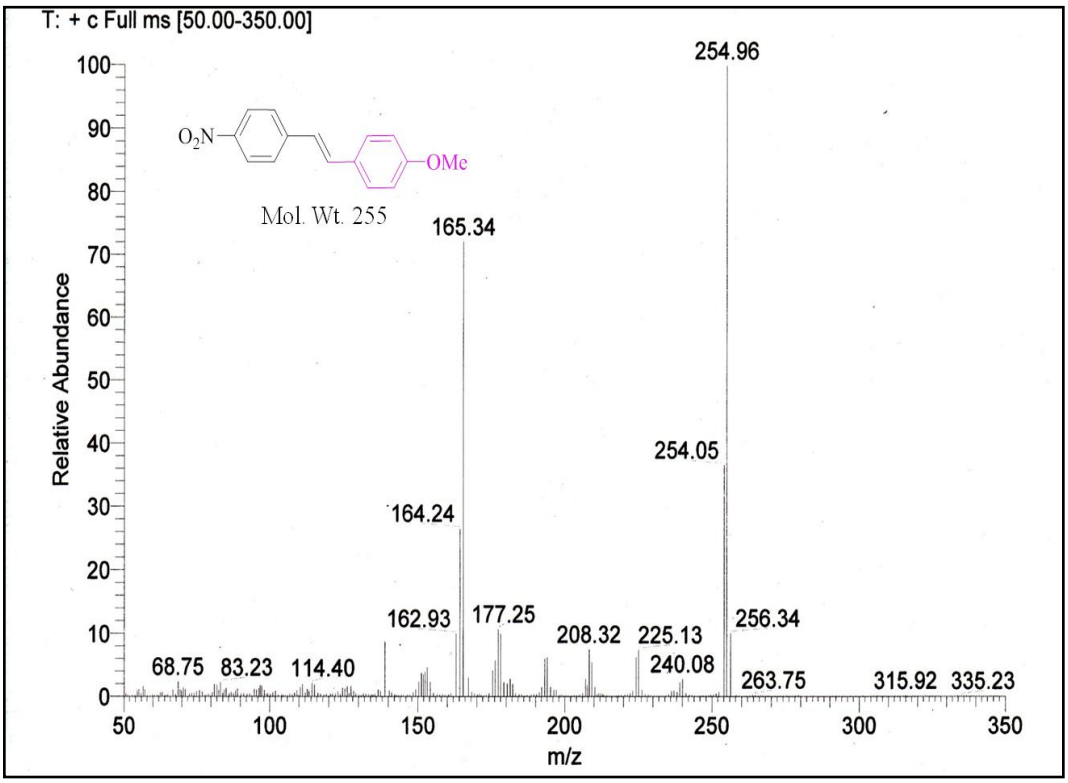
^{1}H NMR of Compound **32**



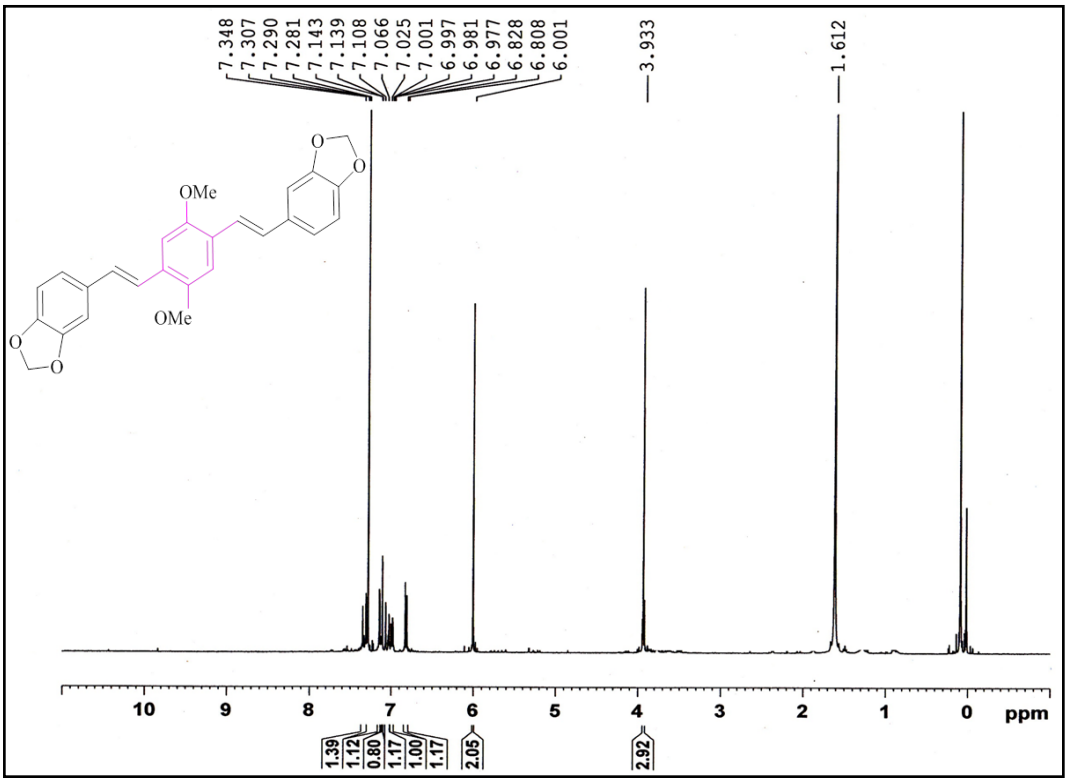
Mass Specta of Compound **32**



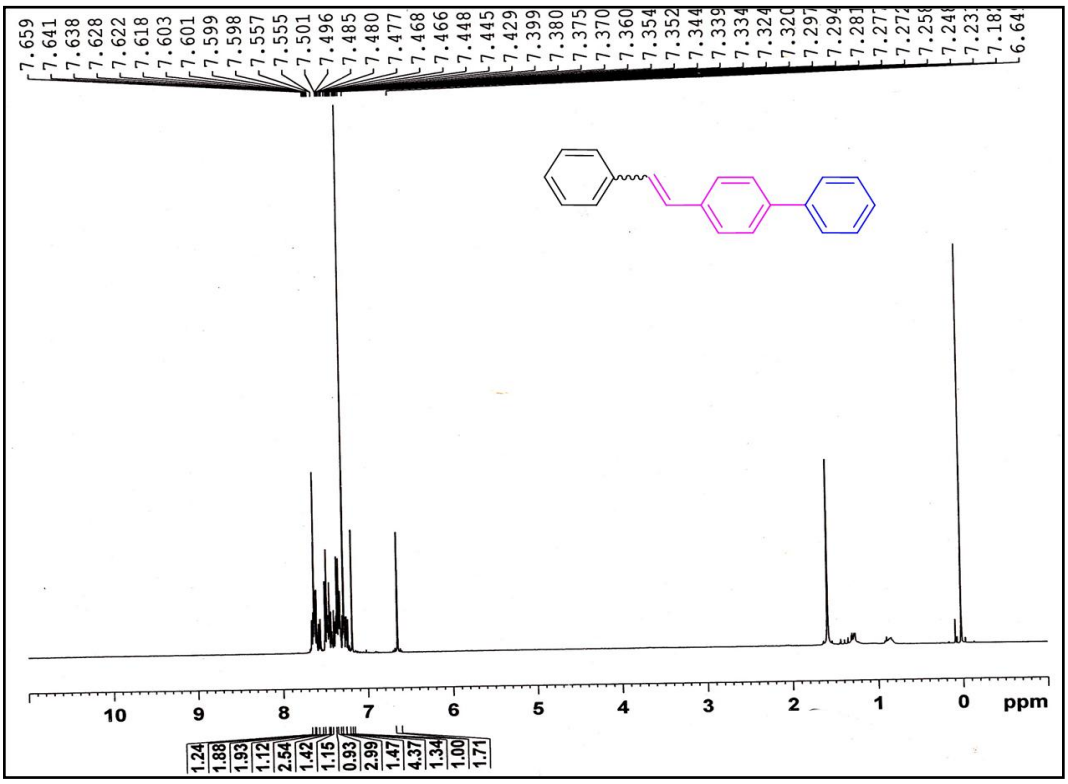
^{1}H NMR of Compound **34**



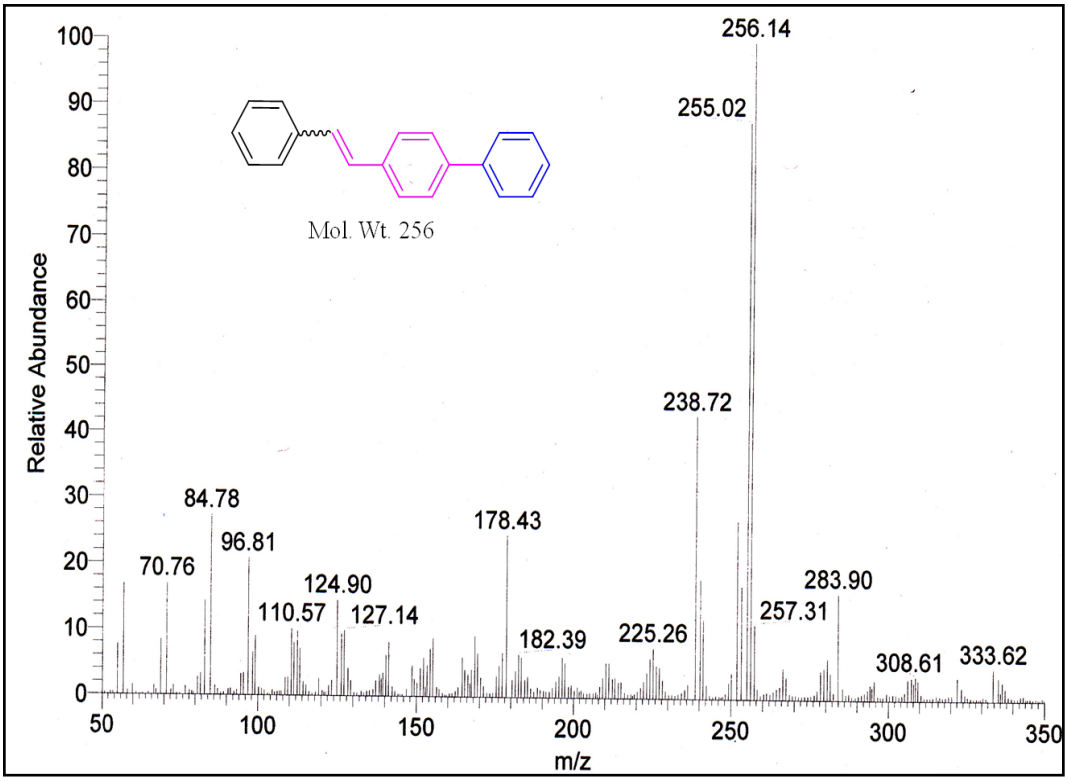
Mass Spectra of Compound **34**



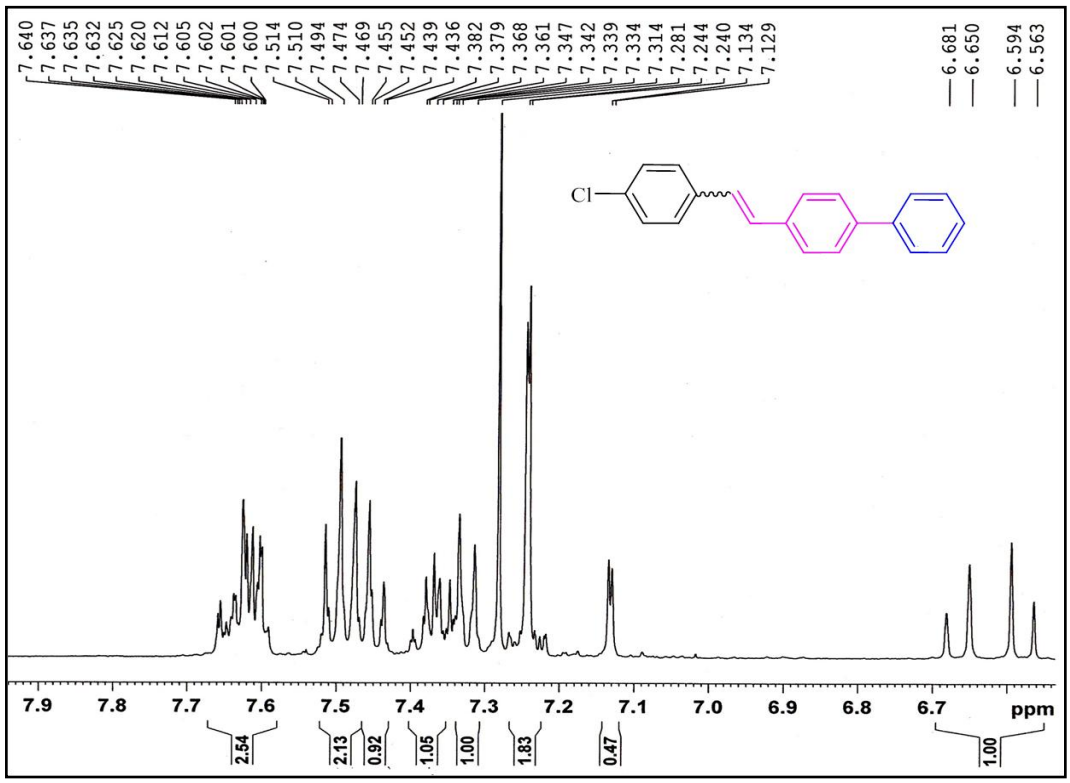
^{1}H NMR Of Compound **35**



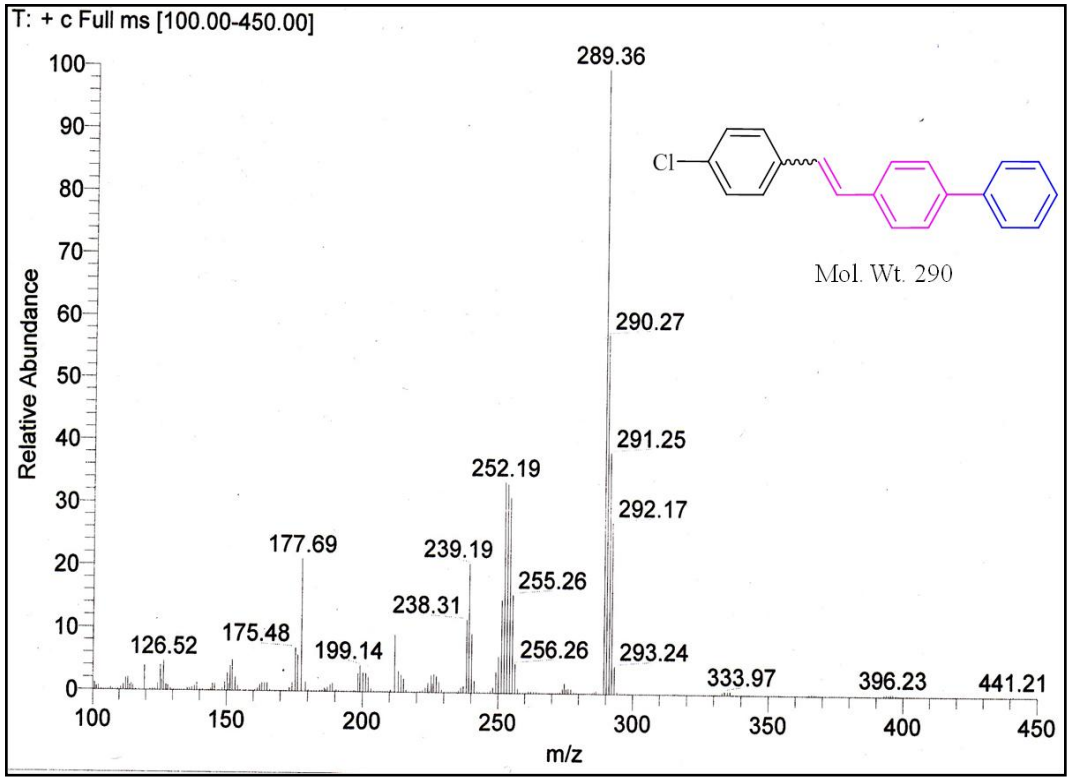
^{1}H NMR of Compound **36**



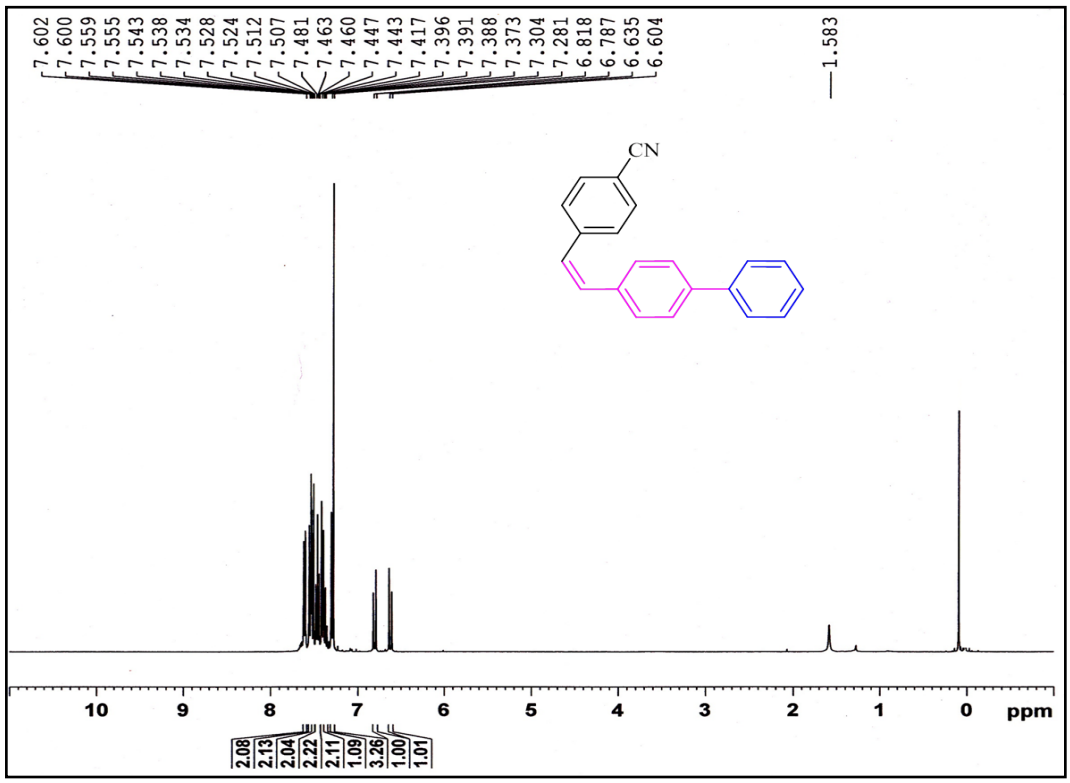
Mass Spectra of Compound **36**



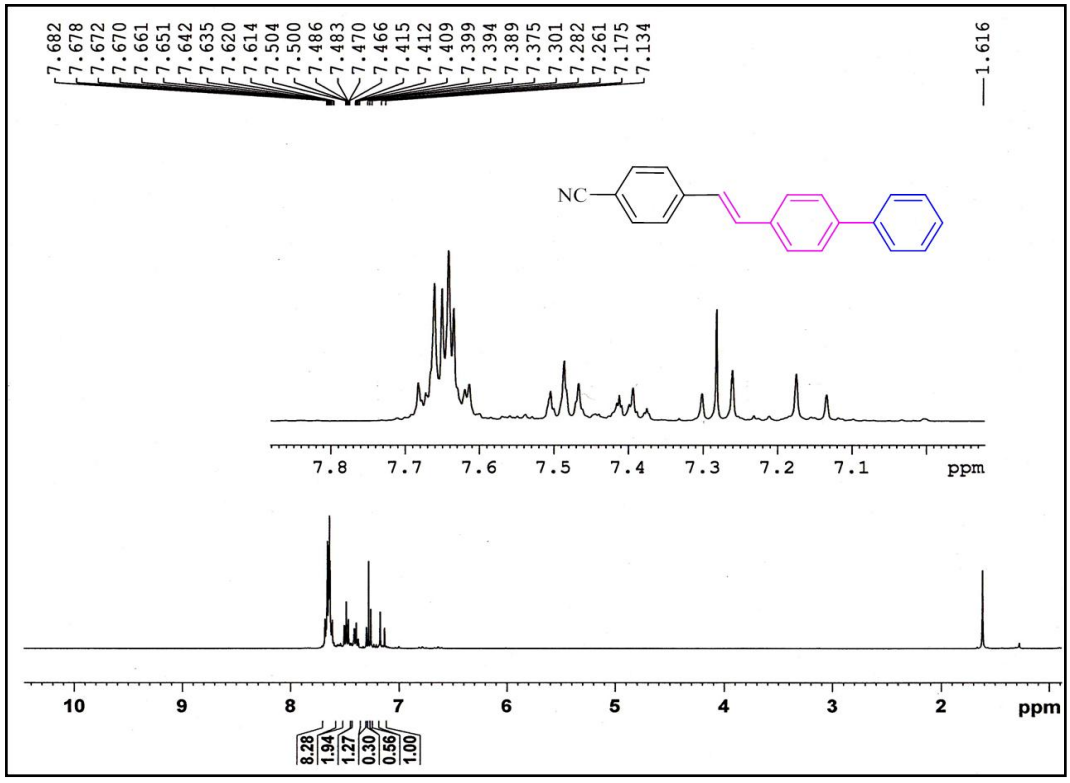
^{1}H NMR of Compound **37**



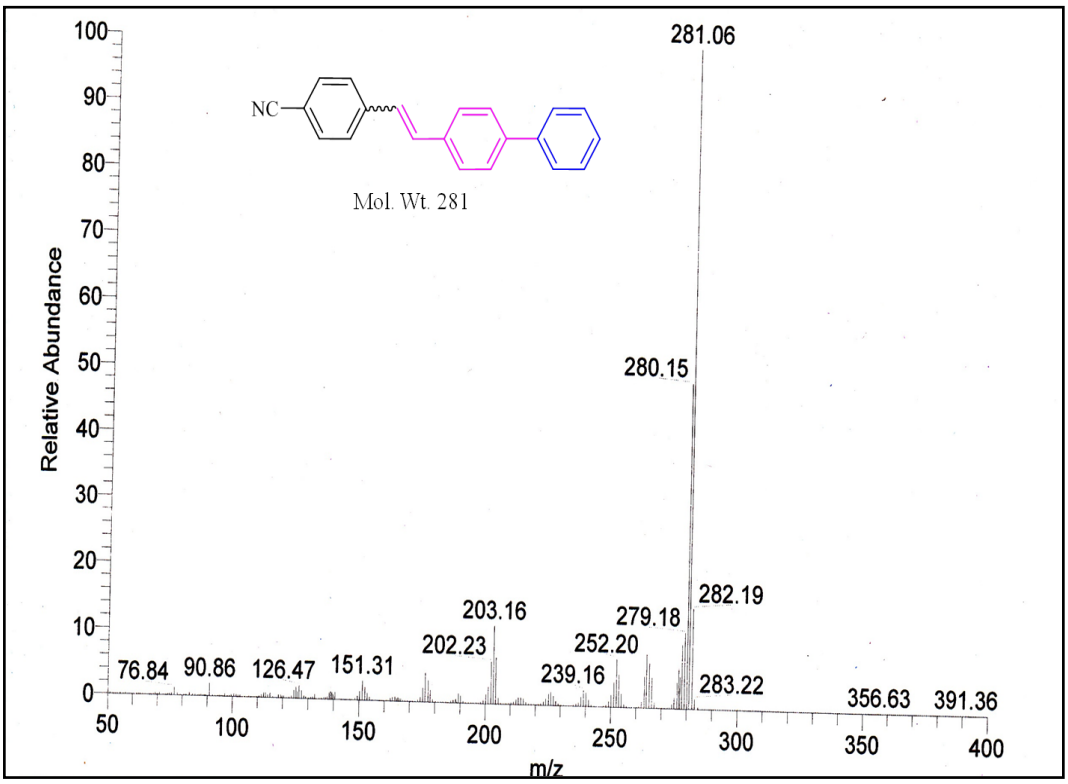
Mass Spectra of Compound **37**



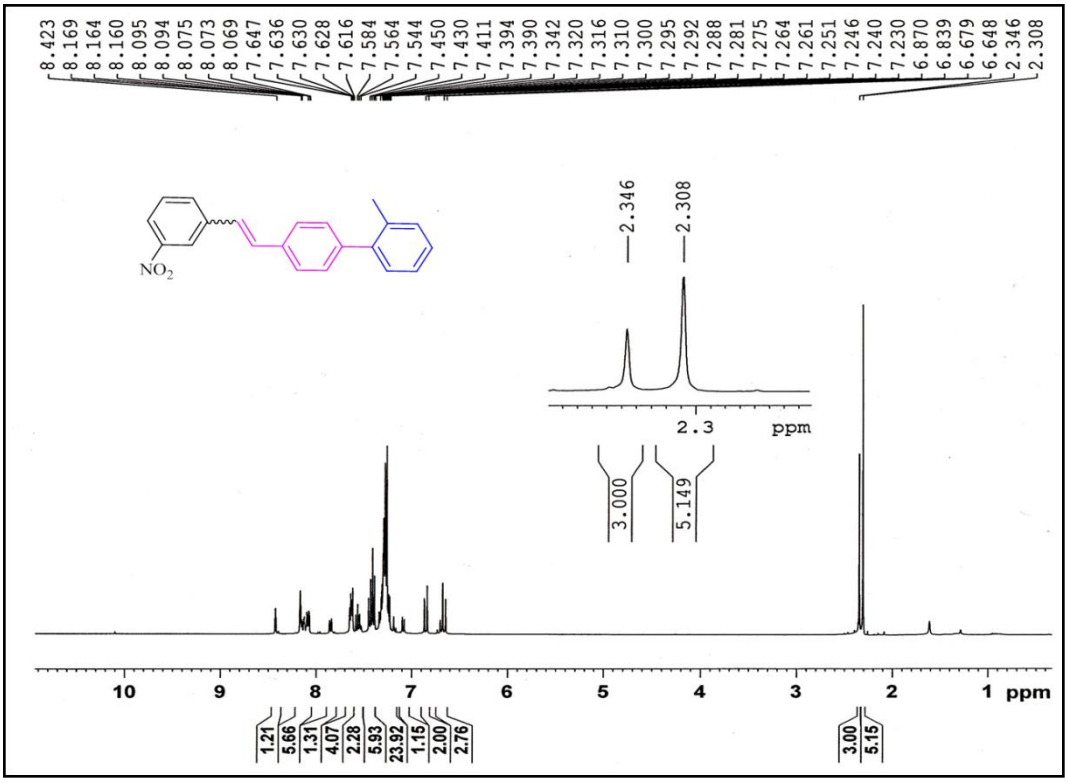
^{1}H NMR of cis isomer Compound **39**



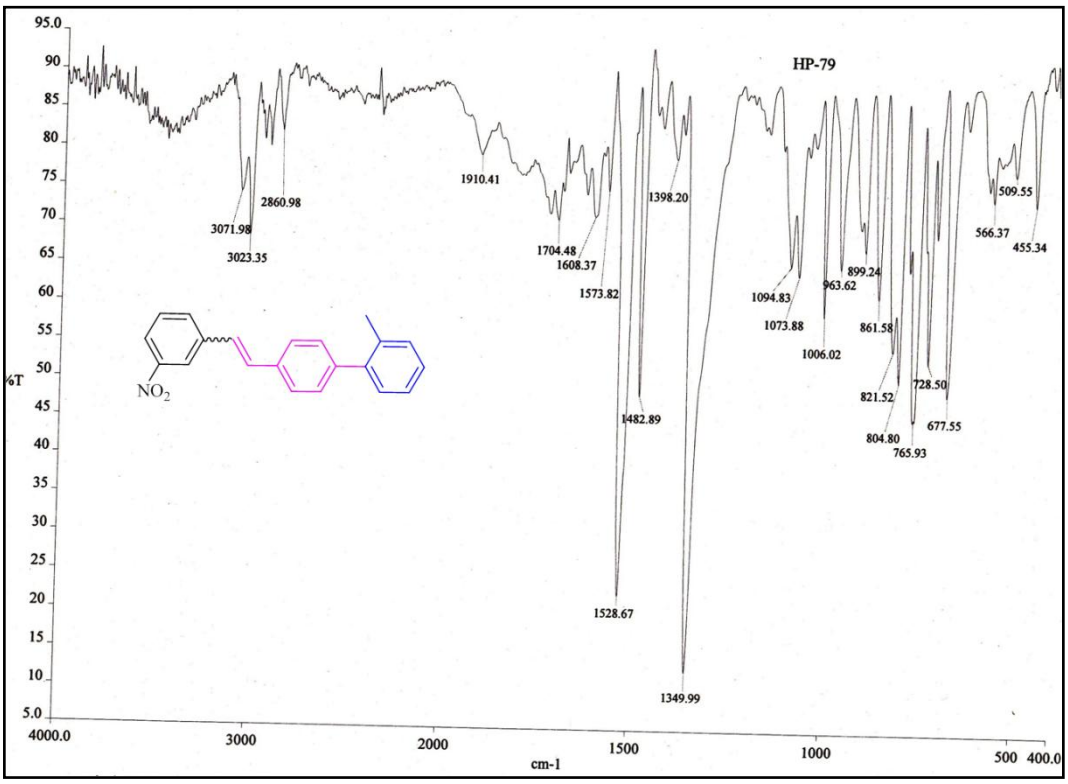
^{1}H NMR of trans isomer Compound **39**



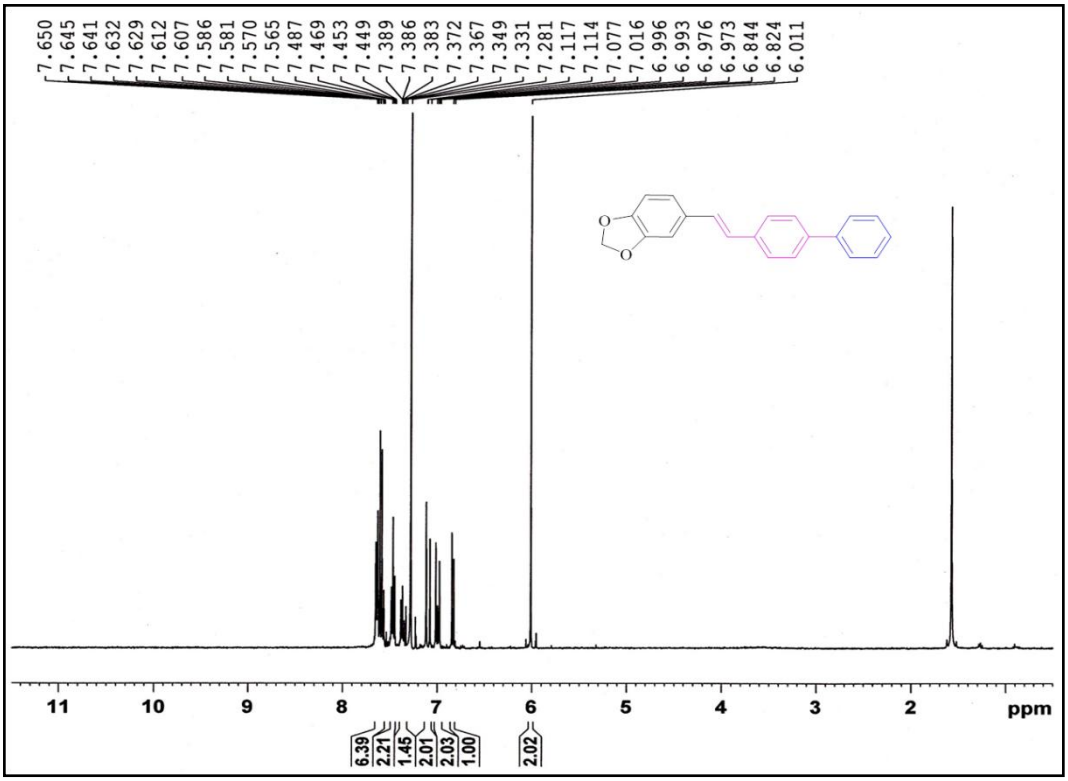
Mass Spectra of Compound **39**



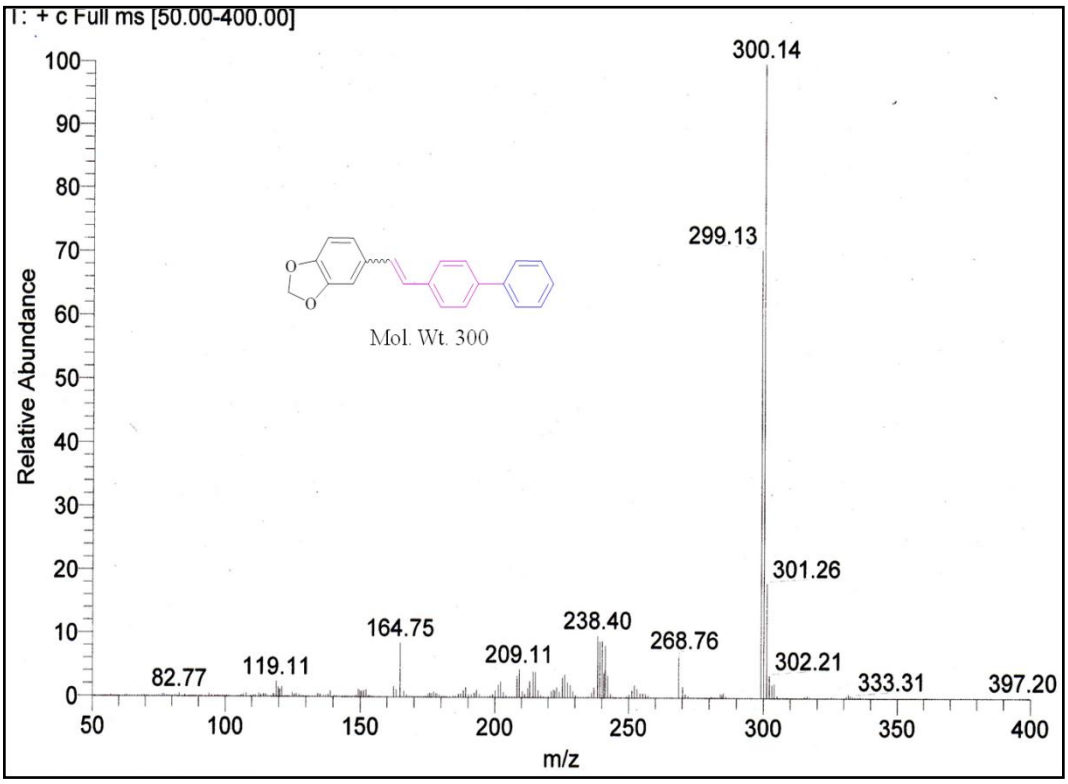
^{1}H NMR of Compound **41**



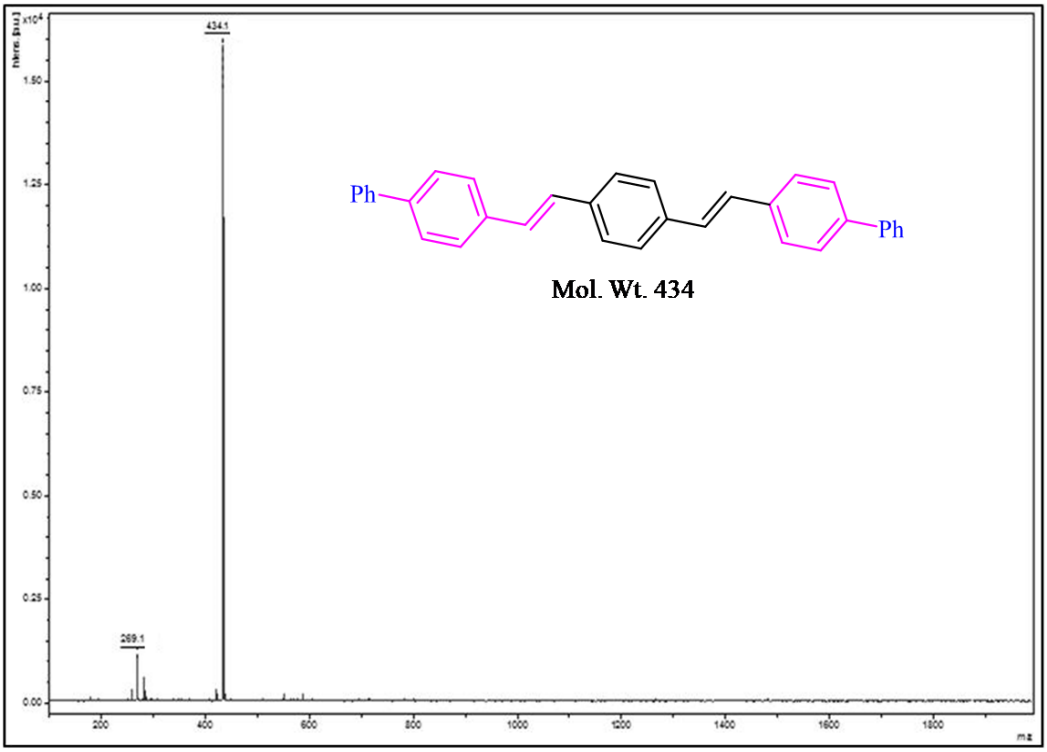
IR of Compound **41**



[1]H NMR of trans isomer Compound **43**



Mass Spectra of Compound **43**



Mass Spectra of Compound **46**

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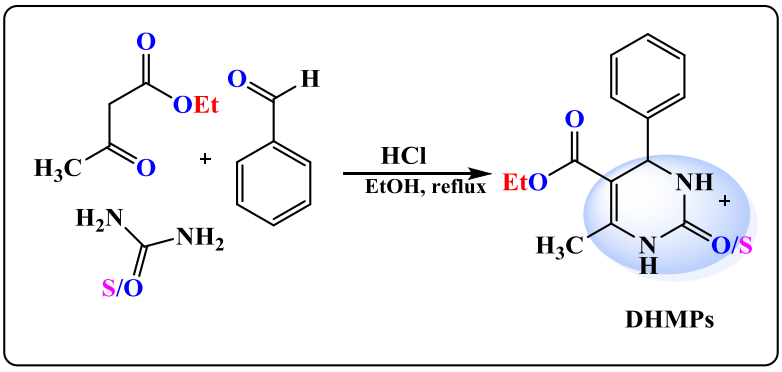
Section-II

Synthesis, characterization and application of polyaniline supported $FeCl_3$ for one-pot Biginelli reaction

2.2.1 Introduction

One of the most important examples of one-pot multicomponent reactions is Biginelli reaction, where 3,4-dihydropyrimidine-2(1*H*)-one (DHPMs) is synthesized efficiently. This is a condensation reaction between three components named aldehyde, urea and active methylene compound like β-keto ester. An Italian chemist named Pietro Biginelli reported this reaction in late 19th century[1] as shown in scheme 1.

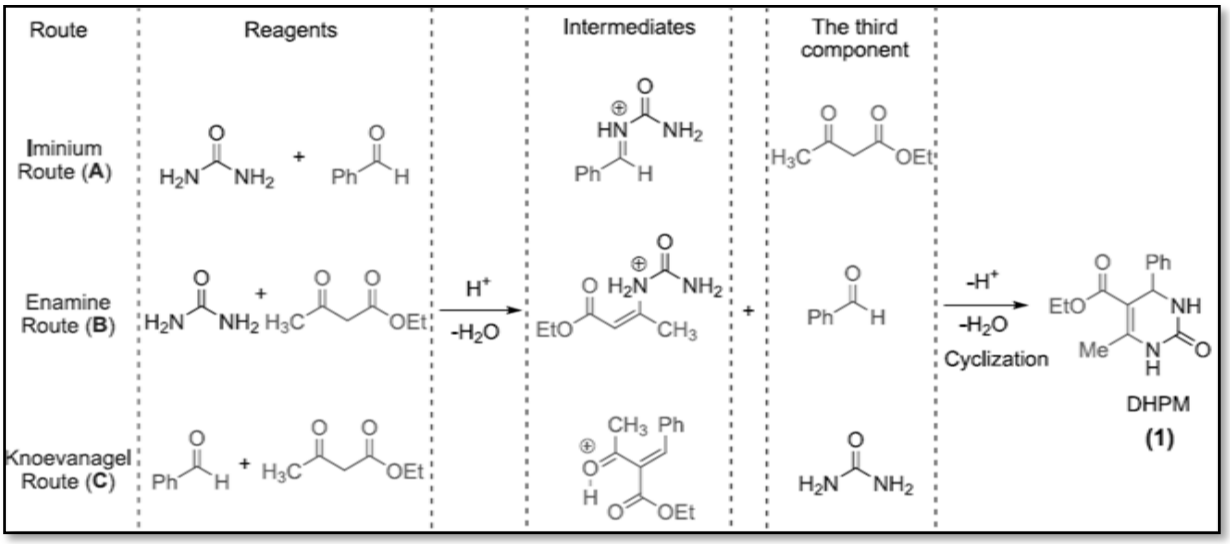


Scheme 1: Biginelli reaction

However, after about hundred years in 1990s its real potential was realized when several new methods of this reaction were explored and novel applications of DHPMs were found. Many Lewis acid based homogeneous catalysts have been successfully employed for this reaction, while other basic and organic molecules have also been known for this purpose,[2] though originally hydrochloric acid or other protic acids were used for the reaction. The DHPM unit is present in few biologically active molecules of natural and artificial origin, and due to such significant properties and applications in asymmetric multicomponent reactions have been reported for synthesis of optically pure DHPMs.[3] The reaction is also widely investigated to recognize its mechanism and further prospects.[4]

Three possible mechanisms involving protonated intermediates have been proposed by researchers which are shown below:

- First case comprises of condensation between aldehyde and urea to further escalate to an iminium intermediate, which endures a nucleophilic addition with a β-keto ester to give DHPM.
- 'Enamine route'; the second mechanism which involves condensation between urea and β-keto ester leading to a protonated enamine intermediate, which then reacts with aldehyde to give rise to the DHPM.
- The third case includes reaction between aldehyde and β-keto ester which results in the formation of a carbenium ion intermediate, which then reacts with urea to afford the DHPM which is called Knovenagel type mechanism.



Scheme 2: Proposed mechanism for Biginelli reaction

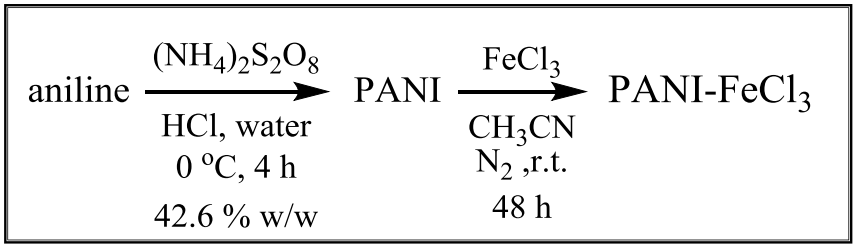
Even though several catalysts are available to carry out this reaction with variable degree of success, there are quite a few heterogeneous mild catalysts reported for the reaction. At the same time there is growing interest to use iron based economically viable, environmentally suitable and chemically mild catalyst system for organic transformations,[5] few of them are also reported for Biginelli reaction[2,6]. In previous section we have outlined our research on the use of Polyaniline-metal salt (PANI-M) for organic transformations,[7] the concept occasionally investigated for other of organic reactions.[8]In this section we shall discuss our efforts to use PANI-Lewis acid catalyst for Biginelli reaction.

2.2.2 Results and discussion

Our current study includes preparation of few complexes of metal salts and PANI and to scan them as catalysts for this important Biginelli reaction. As per our observation, PANI anchored ferric chloride seems to be a good catalyst for the reaction where the desired 3,4-dihydropyrimidine-2(1*H*)-ones were isolated in virtuous to excellent yields.

2.2.2.1 Synthesis and characterization of Palladium anchored polyaniline

Metal chloride and polyaniline were added to a solution of acetonitrile or 1:1 solution of acetonitrile and acetic acid and stirred at ambient temperature (48 h) under nitrogen atmosphere. The above process was employed for $FeCl_3$, $CoCl_2$, $CuCl_2$, $MnCl_2$ and $PdCl_2$. The entire procedure for the preparation of catalyst can be summarized in Scheme 2.



Scheme 3: Synthesis of PANI-$FeCl_3$.

The prepared catalysts were characterized by usual analytical and spectral methods. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) on Jeol5610LV to examine the morphology and composition of PANI and metal loaded PANI catalysts. Few changes are observed after loading of metal on PANI (Figure 1).For SEM analysis images were obtained by coating the material on carbon tape.

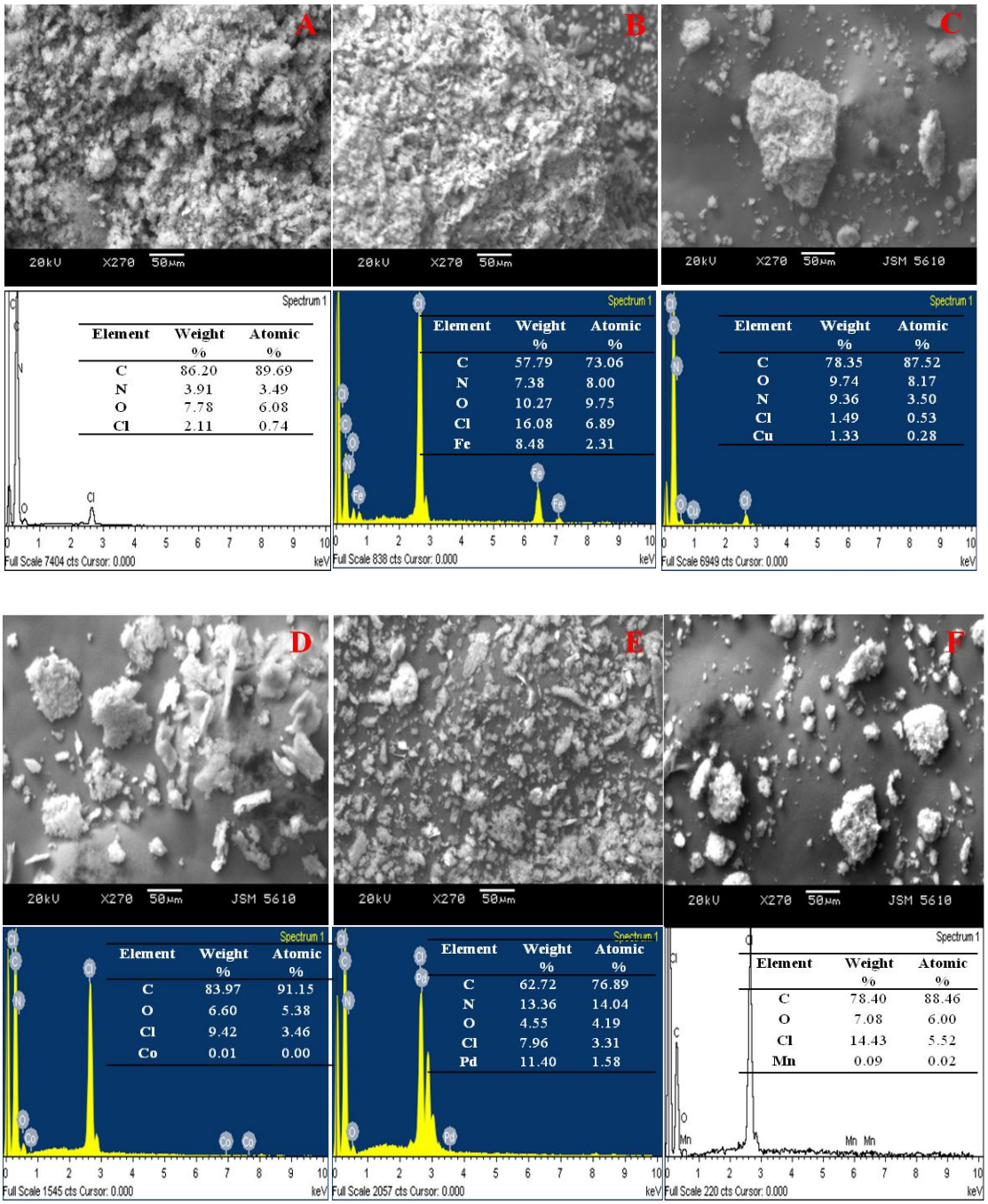


Figure 1: SEM with EDX images of A) PANI (top left), B) PANI-Fe (top middle), C) PANI-Cu (top right), D) PANI-Co (bottom left), E) PANI-Pd (bottom middle), F) PANI-Mn (bottom right)

Incorporation metal salts like $FeCl_3$, $MnCl_2$, $CuCl_2$, $CoCl_2$, $PdCl_2$ etc. can be confirmed by changes in brightness of images. Since they are heavier then C, O, N etc. hence they look brighter in back dispersed mode of SEM micrographs. The heavier elements have a tendency to show brighter images in the analysis. The doping of $FeCl_3$, $MnCl_2$, $CuCl_2$, $CoCl_2$ and $PdCl_2$ respectively is established by Back-scattered electrons (BSE) images as shown in Figure 1, where PANI-Mn and PANI-Cu shows more agglomeration. In case of PANI-Co, flattened

surface appeared among all samples. In PANI-Pd, sample accumulation is quite less but close appearance of particles is observed. PANI-Fe sample shows more and uniform porous appearance on the surface. Loading of metal chlorides on PANI is confirmed by EDX analysis. The results of presence of $FeCl_3$, $MnCl_2$, $CuCl_2$, $CoCl_2$, $PdCl_2$ are presented in Figure 1.

Thermal stability of PANI-Fe sample has been performed by thermogravimetric analysis (TGA) with a heating rate of 10.0 °C/min using SII TG/DT A6300 EXSTAR. Further it was found 95% non-degradable up to ~350^{o}C, (Figure 2) which illustrates its suitability for the use as heterogeneous catalyst in standard reaction parameters.

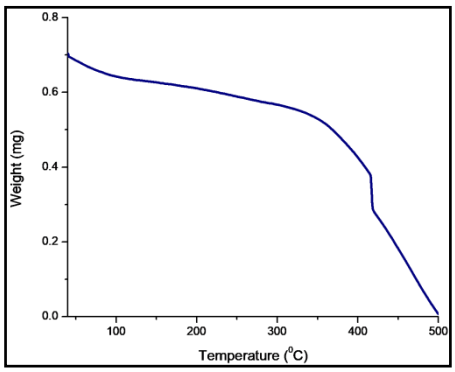
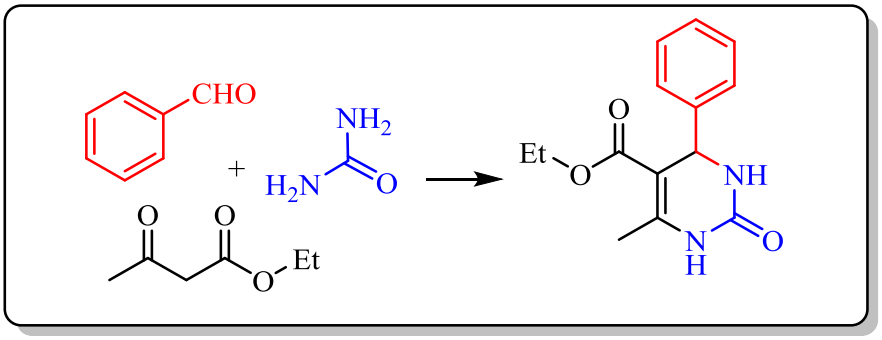


Figure 2: TGA of PANI-Fe

The ICP-AES analysis of the PANI-Fe catalyst indicates 6.47 % of Fe loading on PANI.

2.2.2.2 Catalytic activity of metal loaded catalysts for Biginelli reaction

After characterization of the prepared catalysts the synthesized PANI supported catalysts were scanned for standard Biginelli reaction of benzaldehyde **1a**, urea **2** and ethyl acetoacetate **3a** (or acetyl acetone **3b**). All the catalysts were systematically screened for standard Biginelli reaction for the search of best condition and the results are summarized in Table 1. Here we have studied the effect of variation in solvent and the amount of catalyst. Initially a combination of slightly lower amount of catalyst (PANI-Fe 25 and 50 % w/w) were used to assess the efficiency. The encouraging results were seen with 83 % yield of corresponding DHPM using 100% w/w PANI-Fe catalyst. With PANI-Cu and PANI-Mn catalysts the reaction did not proceed with good yields while in presence PANI-Co and PANI-Pd no product was detected. Solvent study indicated acetonitrile (ACN) to be best solvent. To confirm the activity of metal for this reaction we performed the reaction with only PANI and without any catalyst but no product was observed in either cases, as seen by TLC.



Scheme 4

Table 1: Screening of PANI-M catalyst

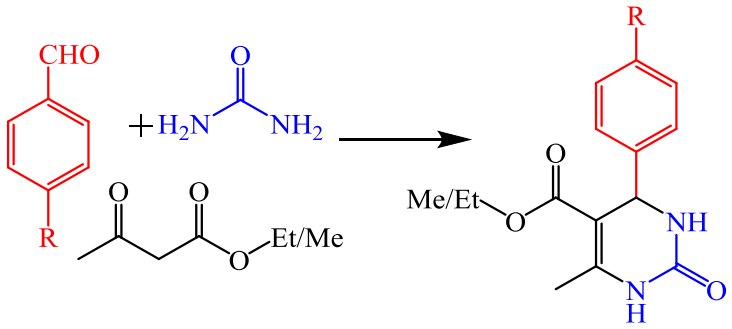
Sr. No.	Catalyst	Amount of Catalyst used (g)	Solvent	Yield[a] (%)
1	PANI-Fe	0.05	ACN	39 %
2	PANI-Fe	0.1	ACN	49 %
3	**PANI-Fe**	**0.2**	**ACN**	**83 %**
4	PANI-Fe	0.2	EtOH	62 %
5	PANI-Fe	0.2	Toluene	36 %
6	PANI-Fe	0.2	DCE	11 %
7	PANI-Fe	0.2	1,4 Dioxane	49 %
8	PANI-Fe	0.2	THF	75 %
9	PANI-Cu	0.1	EtOH	38 %
10	PANI-Cu	0.2	EtOH	50 %
11	PANI-Cu	0.2	ACN	52 %
12	PANI-Mn	0.2	ACN	37 %
13	PANI-Co	0.2	ACN	NR
14	PANI-Pd	0.2	ACN	NR
15	PANI	0.2	ACN	NR
16	--[b]	--	ACN	NR

Conditions: PhCHO (0.2 g, 1.8 mmol), ethyl acetoacetate (1.8 mmol), urea (2.3 mmol), reflux, 24 h, [a]Isolated, [b]No catalyst, NR = no reaction

After the optimization of reaction condition, with benzaldehyde, urea and ethylaceto acetate; the catalytic activity of the PANI-Fe sample was further investigated in the synthesis of different derivatives of 3,4-dihydropyrimidin-2(1*H*)-ones as shown in Scheme 5.

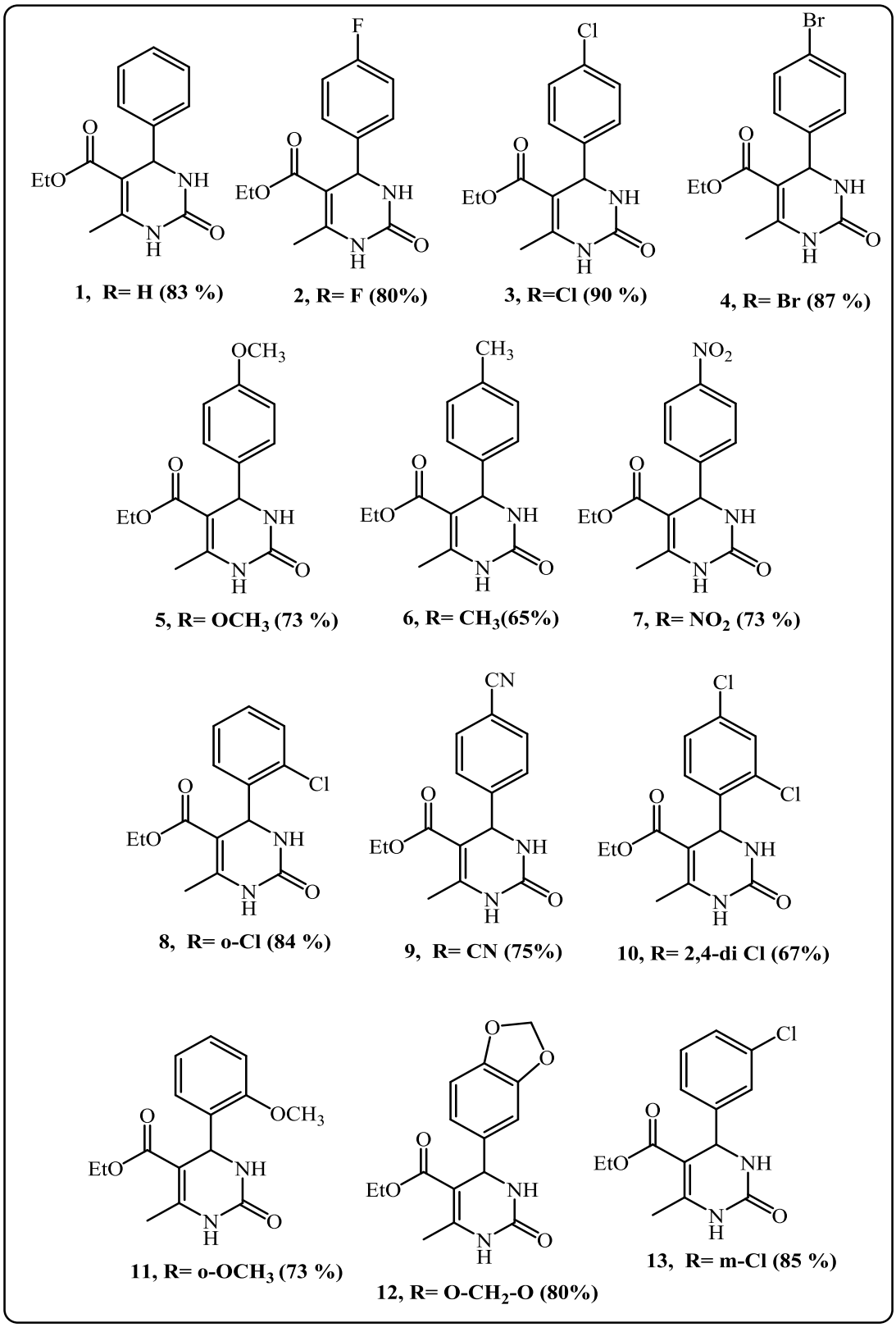
The benzaldehyde derivatives with various substitutions on the aromatic ring were used and reacted with ethyl acetoacetate and urea. Series of products were synthesized in good yield as shown in Scheme 6.Aromatic aldehydes with different substituent like electron releasing or withdrawing groups were scanned. The substituent on the ring of the aromatic aldehyde did not show any strong effects in terms of reaction yields and reaction time under selected conditions, while the steric effects showed a slight influence on observed yield.

The reaction was further investigated with acetyl acetone as the source of active methylene along with derivative of aromatic aldehyde and urea in presence of PANI-Fe catalyst as shown in scheme 5. Products were obtained in good yields as shown in scheme 7.

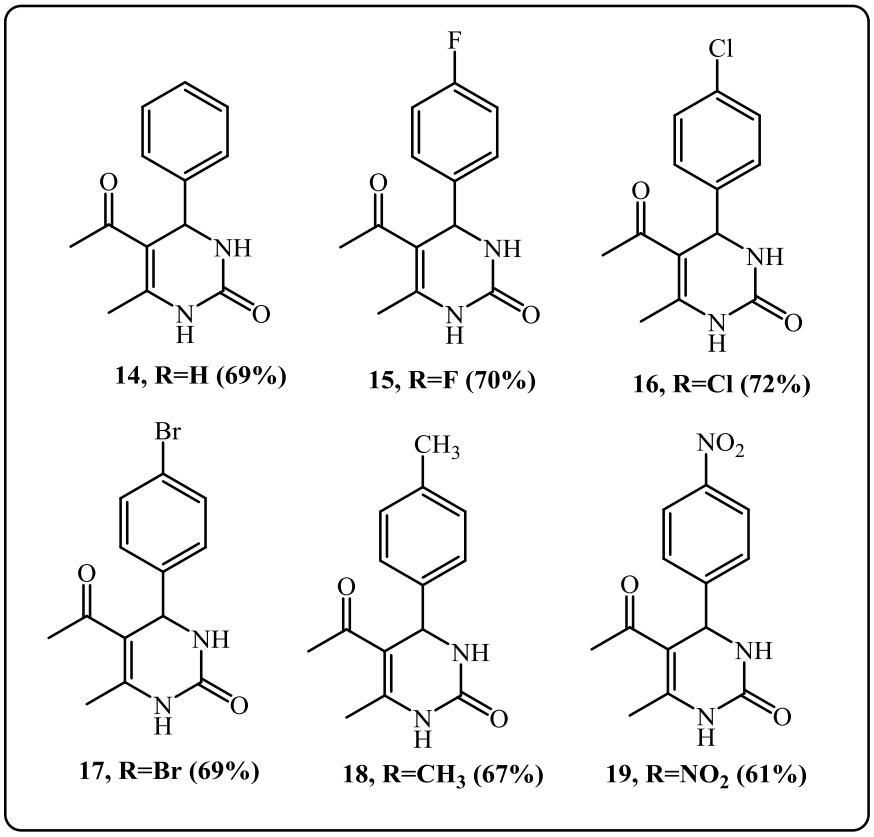


Scheme 5: PANI-$FeCl_3$ catalyzed Biginille reaction

All the products were isolated by column chromatography and characterized by comparison with known analytical and spectroscopic data.

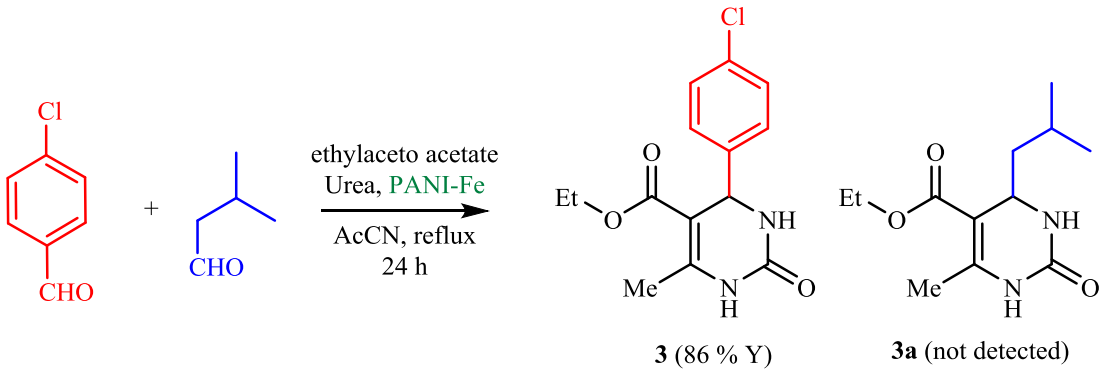


Scheme 6: Molecules synthesized by Fe-PANI using ethylacetoacetae, urea and substituted aldehyde



Scheme 7: Molecules synthesized by Fe-PANI using acetyl acetone, urea and substituted aldehyde

The selectivity of the present catalyst system towards reaction with aromatic aldehyde in comparison with aliphatic aldehydes was established by performing a controlled experiment. A mixture of 4-chlorobenzaldehyde and isobutyraldehyde in equal ratio was subjected to the Biginelli reaction with ethylaceto acetate, urea and PANI-Fe catalyst under the previous condition as discussed for Table 2 and the products were carefully analyzed (Scheme 8). As expected the only product isolated was **3** in good yield, while the DHPM **3a** resulting from aliphatic aldehyde was not detected.



Scheme 8: Selectivity for ArCHO

Thus the catalyst system of PANI-Fe was effectively screened as catalyst for a number of variations of Biginelli reaction.

Heterogeneity test: The true nature of heterogeneity of the catalyst in effective reaction was further established. For the purpose the hot filtration method was used to study the leaching of iron ions during the reaction.[9] For this experiment, a standard Biginelli reaction with benzaldehyde (1.8 mmol), ethyl acetoacetate (1.8 mmol), urea (2.3 mmol), PANI-Fe, in acetonitrile at reflux was selected. Two sets of the reaction were carried out under the optimized identical conditions.

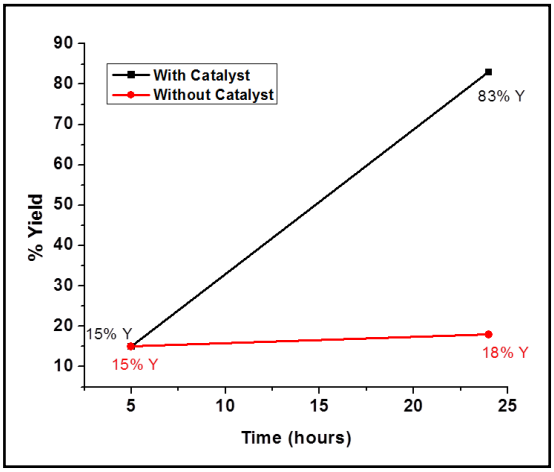


Figure 3: Hot filtration test to study leaching of iron ions

First set of reaction was quenched after five hour and product was isolated (15% yield). In the other set, the catalyst was separated after five hour by hot filtration and the reaction was allowed to continue for 24 hours, which resulted in only marginal increase in conversion (18% yield, Figure 2). The experimental results showed no significant change in the yield when run after separation of the catalyst, which suggests very low leaching of the metal ions during the reaction. This indicates a satisfactory heterogenization of $FeCl_3$ on PANI and potential for further applications as heterogeneous catalyst for more reactions in future study and widening of the scope.

Comparison of the catalyst: A comparison ofour results with few of the previously reported catalysts for Biginelli reaction suggests an encouraging information. The result of coupling of 4-chlorobezaldehyde with urea and ethylaceto acetate with previously reported procedures from literature is presented for this purpose (Table 4).The catalyst showed comparable yield

as compared to other catalyst. As can be seen from the entry 9, PANI-FeCl3 shows slightly improved conversion as compared to homogeneous $FeCl_3$.

Table 4: Catalytic performance of some catalysts for the synthesis of ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate with other catalyst

Sr.No.	Catalyst	Temperature (°C)	Solvent	Time (h)	Yield (%)	Refrence
1	D-Xylonic acid	100	D-Xylonic acid	5	89	Ma et al. *Green Chem.***2016**, *18*, 1738.
2	Partially Fluorinated, Water-Stable Cu(II)−MOF	60	Soivent free	2	89	Pal et al. *Inorg. Chem.***2016**, *55*, 7835.
3	Fe3O4@SiO2-imid-PMAb	80	Solvent-free	0.75	90	Javidi*RSC Adv.***2015**, *5*, 308.
4	Silicagel-L-pyrrolidine-2-carboxylic acid-4-hydrogen sulfate	reflux	Ethanol	6	90	Choghamarani et al. *Chem. Lett.* **2013**, *24*,804.
5	PPF-SO3H(sulfonic acid functionalized polypropylene fiber)	Reflux	Ethanol	8	74	Shi et al. *RSC Adv.* **2013**, *3*, 3939.
6	Fe3O4@mesoporous SBA-15	90	Ethanol	6	80	Mondal at al. *Dalton Trans.*, **2012**, *41*,6173.
7	Imidazole-1-yl-acetic acid	100	Solvent free	0.7	90	Kargar et al. *Catal. Commun.***2011**, *15*, 123.
8	12-Tungstophosphoric acid	Reflux	AcOH	6-7	70	Heravi et al. *J. Mol. Catal. A* **2005**, *242*,173.
9	$FeCl_3.6H_20$	Reflux	ACN	12	88	Wang et al. *Tetrahedron Lett.* **2004**, *45*, 7951.
10	Fe-PANI	Reflux	ACN	24	90	**This work**

2.2.3 Conclusion

In this section we have disclosed our results on the study of the applications of PANI-Fe as an efficient heterogeneous catalyst for three component Biginelli reaction. The reaction was selective for aromatic aldehydes for urea and ethyl acetoacetate or acetyl acetone. The low leaching was established by a control experiment indicating potential use as heterogeneous catalyst in such, and similar reactions.

2.2.4 Experimental Section

Preparation of metal loaded PANI:

Metal chloride (500 mg) and polyaniline (500 mg) were added to a solution acetonitrile (50 mL) or 1:1 solution of acetonitrile (25 ml) and acetic acid (25 ml) and stirred at ambient temperature (48 h) under nitrogen atmosphere. The resultant catalyst was filtered and washed with acetic acid and then thoroughly with acetonitrile and acetone until the filtrate was colorless. The resulting residue was dried in an air oven (100 °C; 2 h) to afford the catalyst as black powder. The above process was employed for $FeCl_3$, $CoCl_2$, $CuCl_2$, $MnCl_2$ and slightly modified for $PdCl_2$ (100 mg for 500 mg PANI).

General procedure for Biginelli reaction*:*

The present set of catalysts of PANI supported metal ions were screened for the three component classical one-pot Biginelli reaction. The reactions were run with aromatic aldehyde (1.8 mmol, 0.2 g), ethyl acetoacetate (or acetyl acetone) (1.8 mmol), urea (2.3 mmol), and PANI-Fe (0.2 g, 0.24 mmol) in acetonitrile and reflux for 24 h. Generally, the reactions were monitored by thin layer chromatography, catalyst was separated by filtration and the product was purified by column chromatography over silica gel. The yields mentioned refer to the isolated yield and the products have been characterized by comparison of their melting point and NMR Spectroscopy performed on Bruker Avance 400 Spectrometer (400 MHz for ^{1}H-NMR).

NMR Data:

Ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(1)**

M.p. 206°C [Lit[10] 200-204°C]

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17-1.21 (t, *J* = 7.2 Hz, 3H), 2.35 (s, 3H), 4.05-4.13 (m, 2H,), 5.38-5.39 (d, *J* = 2.8Hz,1H), 6.11 (br s),7.25-7.31(m, 5H), 8.43 (br s).

Ethyl 4-(4-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(2)**

M.p. 180°C [Lit[11] 180-182°C]

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16-1.20 (t, *J* = 8 Hz, 3H), 2.36 (s, 3 H), 4.05-4.13 (m, 2H), 5.40 (d, 1H), 5.75 (br s), 6.99-7.03 (m, 2H), 7.28-7.32 (m, 2H), 8.03 (br s).

Ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate**(3)**

M.p. 210°C-212°C [Lit[10] 211-215°C]

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16-1.20 (t, *J* = 7.2 Hz, 3H), 2.36 (s, 3H), 4.05-4.13 (m, 2H), 5.42-5.42 (d, *J*= 2Hz, 1H), 5.74 (br s), 7.33-7.34 (m, 4H), 8.11 (br s).

Ethyl 4-(4-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate**(4)**

M.p. 221°C [Lit[12] 225-226°C]

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17-1.21 (t, *J* = 7.2 Hz), 2.35 (s, 3H), 4.07-4.12 (m, 2H), 5.37-5.38 (d, *J* = 2.8 Hz, 1H), 5.87 (br s), 7.20-7.22 (m, 2H), 7.44-7.45 (m, 2H), 8.12 (br s).

^{1}H NMR (400 MHz, DMSO-d_6): δ 1.08-1.11 (t, *J* = 7.2Hz, 3H), 2.24 (s, 3H), 3.95-4.01 (q, *J* = 7.2 Hz, 2H), 5.11-5.12 (d, *J*=3.2 Hz, 1H), 7.17-7.19 (m, 2H), 7.51-7.54 (m, 2H), 7.78-7.80 (br s), 9.26-9.27 (br s).

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(5)**

M.p. 200-202°C [Lit[10] 208-211°C]

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17-1.21 (t, *J* = 7.2 Hz, 3H), 2.36 (s, 3H), 3.80 (s, 3H), 4.05-4.13 (m, 2H), 5.36-5.37 (d, *J* = 4 Hz, 1H), 5.48 (br s), 6.83-6.87 (m, 2H), 7.24-7.28 (m, 2H), 7.47 (br s).

Ethyl 6-methyl-2-oxo-4-(p-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(6)**

M.p. 208 °C [Lit[13] 205-206°C]

^{1}H NMR (400 MHz, $CDCl_3$): δ1.17-1.21 (t, *J* = 8 Hz, 3H), 2.33-2.35 (s, 6 H), 4.06-4.11(q, *J* = 8Hz, 2H), 5.37-5.38 (d, *J* = 4 Hz, 1H), 5.62(br s), 7.12-7.14 (m, 2H), 7.21-7.23(m, 2H), 7.90 (br s).

Ethyl 6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(7)**

M.p. 206°C [Lit[10] 208°C]

^{1}H NMR (400 MHz, DMSO- d_6): δ 1.10-1.11 (t, *J*= 7.2 Hz, 3H), 2.26 (s, 3H), 3.95-4.00 (q, *J*= 7.2 Hz, 2H), 5.26-5.27 (d, *J* = 3.6 Hz, 1H), 7.49-7.52 (m, 2H), 7.90-7.91(br d, *J*= 2 Hz), 8.21-8.31(m, 2H), 9.37(br s).

Ethyl 4-(2-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(8)**
M.p. 218°C [Lit[14] 216-217°C]
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06-1.09 (t, *J* = 4Hz, 3H), 2.46 (s, 3H), 4.00-4.06 (q, *J* = 8 Hz, 2H), 5.66 (br s), 5.89-5.90 (q, *J*= 4 Hz, 1H), 7.22-7.25 (m, 3H), 7.37-7.41 (m, 1H), 7.95(br s).

Ethyl 4-(4-cyanophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(9)**
M.p. 179-182°C [Lit[15]180-182°C]
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18-1.22(t, *J* = 8 Hz, 3H), 2.38 (s, 3H), 4.08-4.15 (m, 2H), 5.48-5.49 (d, *J*= 4 Hz, 1H), 5.55 (br s), 7.18 (br s), 7.46-7.48 (m, 2H), 7.63-7.66 (m, 2H).

Ethyl-4-(2,4-dichlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(10)**
M.p. 247°C [Lit[16] 247-249°C]
^{1}H NMR (400 MHz, DMSO- d_6): δ 0.98-1.01 (t, *J* = 8 Hz, 3H), 2.28 (s, 3H), 3.86-3.91(q, *J* = 8 Hz, 2H), 5.58-5.59 (d, *J* = 4 Hz, 1H), 7.30-7.32 (m, 1H), 7.40-7.43 (m, 1H), 7.56-7.57 (m, 1H), 7.77(br s, 9.33 (br s).

Ethyl 4-(2-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(11)**
M.p. 256°C [Lit[17] 257-258°C]
^{1}H NMR (400 MHz, DMSO- d_6): δ1.00-1.03 (t, *J* = 8 Hz, 3H), 2.27(s, 3H), 3.78 (s, 3H), 3.86-3.94 (m, 2H), 5.47-5.48(d, *J* = 4 Hz, 1H), 6.85-6.88(m, 1H), 6.97-6.98 (m, 1H), 7.01-7.05(m, 1H), 7.20-7.25(m, 1H), 7.30 (br s), 9.13 (br s).

Ethyl4-(benzo[d][1,3]dioxol-5-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5 carboxylate **(12)**
M.p. 182°C [Lit[13] 188-190°C]
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18-1.21 (t, *J* = 8 Hz, 3H), 2.34 (s, 3H), 4.07-4.13 (m, 2H), 5.31-5.32 (d, *J* = 4 Hz, 1H), 5.85-5.90 (br s), 5.95 (s, 2H), 6.72-6.82 (m, 3H), 8.32 (br s).

Ethyl 4-(3-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate**(13)**

M.p. 185-187°C [Lit[14]190-192°C]

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18-1.21 (t, *J* = 8 Hz, 3H), 2.37 (s, 3H), 4.08-4.12 (m, 2H), 5.38-5.39 (d, *J* = 4 Hz, 1H), 5.88 (br s), 7.22- 7.23 (m, 1H), 7.25-7.27 (m, 2H), 7.28-7.31 (m, 1H), 8.17 (br s).

5-Acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one **(14)**

M.p.212 °C [Lit[18]212-214°C]

^{1}H NMR (400 MHz, DMSO-d_6): δ 2.10 (s, 3H), 2.28 (s, 3H), 5.24-5.25 (d, *J* = 4 Hz, 1H), 7.23-7.26 (m, 3H), 7.30-7.34 (m, 2H), 7.84 (br s), 9.20 (br s).

5-Acetyl-4-(4-fluorophenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one**(15)**

M.p.258 °C [Lit[19] 260-261°C]

^{1}H NMR (400 MHz, DMSO-d_6): δ 2.11 (s, 3H), 2.28 (s, 3H), 5.24-5.25 (d, *J* = 4 Hz, 1H), 7.13-7.17 (m, 2H), 7.24-7.28 (m, 2H), 7.86 (br s), 9.24 (br s).

5-Acetyl-4-(4-chlorophenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one**(16)**

M.p. 248°C [Lit[20]249-251°C]

^{1}H NMR (400 MHz, DMSO- d^6): δ 2.12(s, 3H), 2.28 (s, 3H), 5.24-5.25(d, *J* = 4 Hz, 1H), 7.23-7.26 (m, 2H), 7.37-7.40 (m, 2H), 7.88 (br s), 9.25 (br s).

5-Acetyl-4-(4-bromophenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one **(17)**

M.p. 233 °C [Lit[20]232-233°C]

^{1}H NMR (400 MHz, DMSO- d_6): δ 2.12(s, 3H), 2.28 (s, 3H), 5.23 (s, 1H), 7.18-7.20 (m, 2H), 7.51-7.53 (m, 2H), 7.83 (br s), 9.20 (br s).

5-Acetyl-6-methyl-4-(p-tolyl)-3,4-dihydropyrimidin-2(1H)-one **(18)**

M.p. 256 °C [Lit[19]256-257°C]

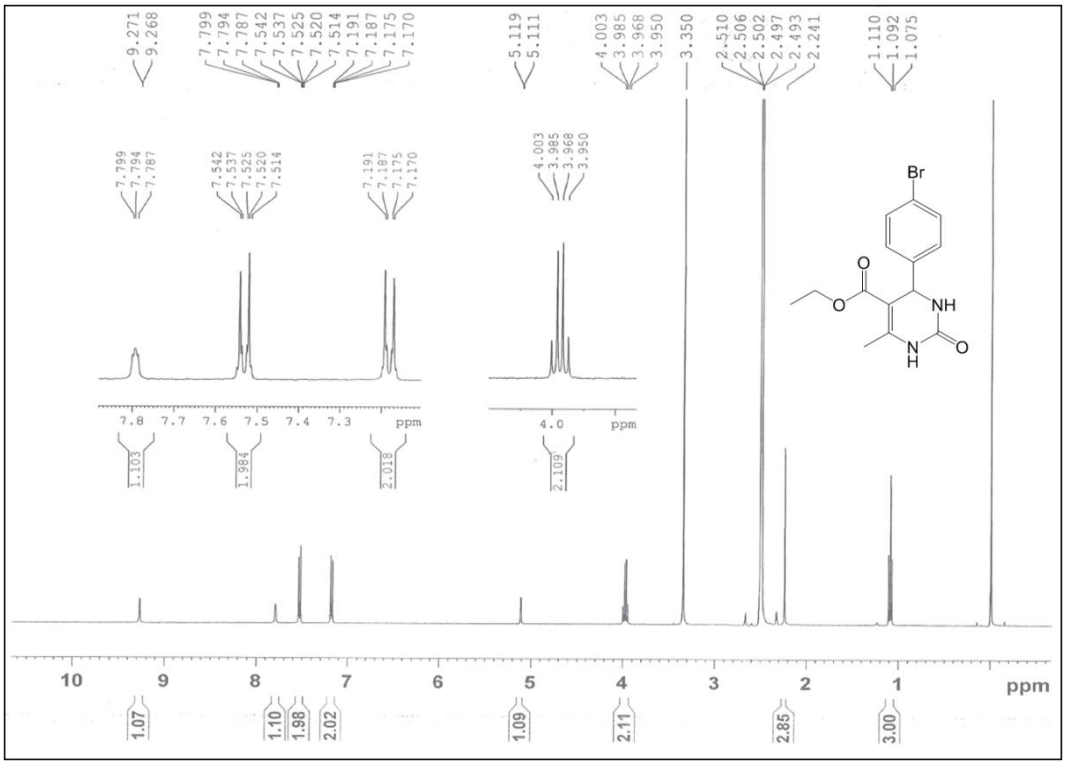
^{1}H NMR (400 MHz, DMSO- d_6): δ 2.08(s, 3H), 2.25-2.27 (two s merged, 6H), 5.20-5.21 (d, *J* = 2.8 Hz, 1H), 7.12 (m, 4H), 7.79 (br s), 9.17 (br s).

5-Acetyl-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-one **(19)**

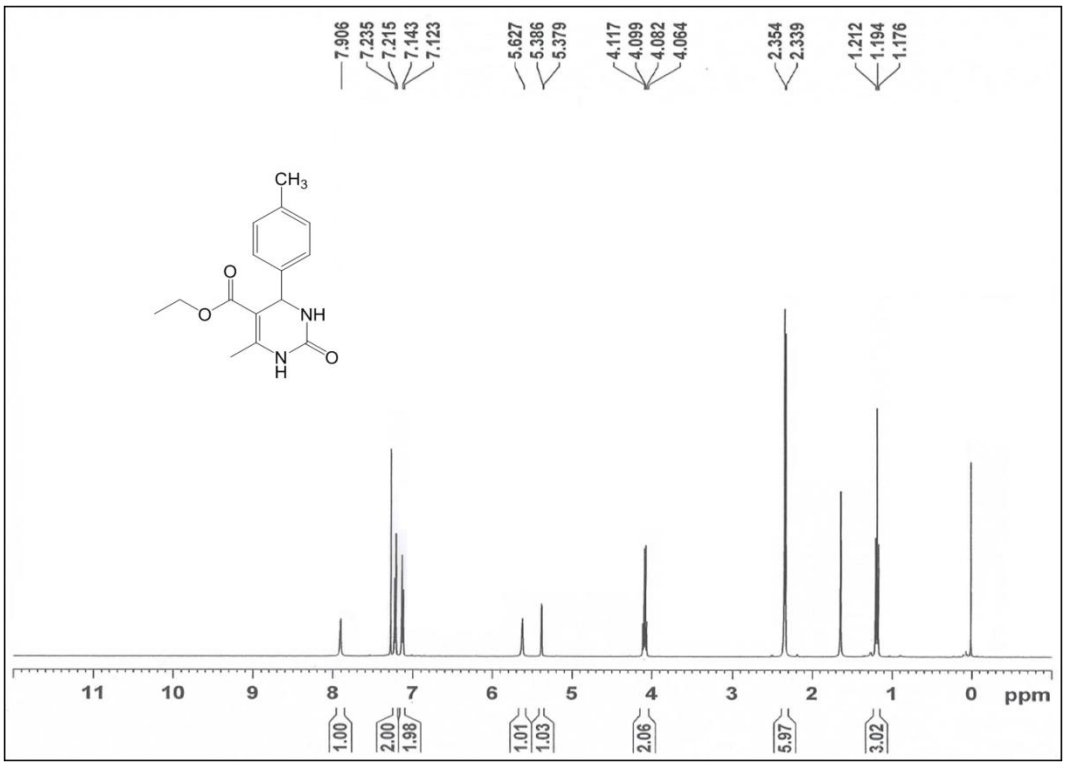
M.p. 252-254 °C [Lit[21]254-256°C]

^{1}H NMR (400 MHz, DMSO- d_6): δ 2.18 (s, 3H), 2.30 (s, 3H), 5.37-5.38 (d, J = 3.6 Hz, 1H), 7.48-7.52 (m, 2H), 8.00 (br s), 8.18-8.22 (m, 2H), 9.35 (br s).

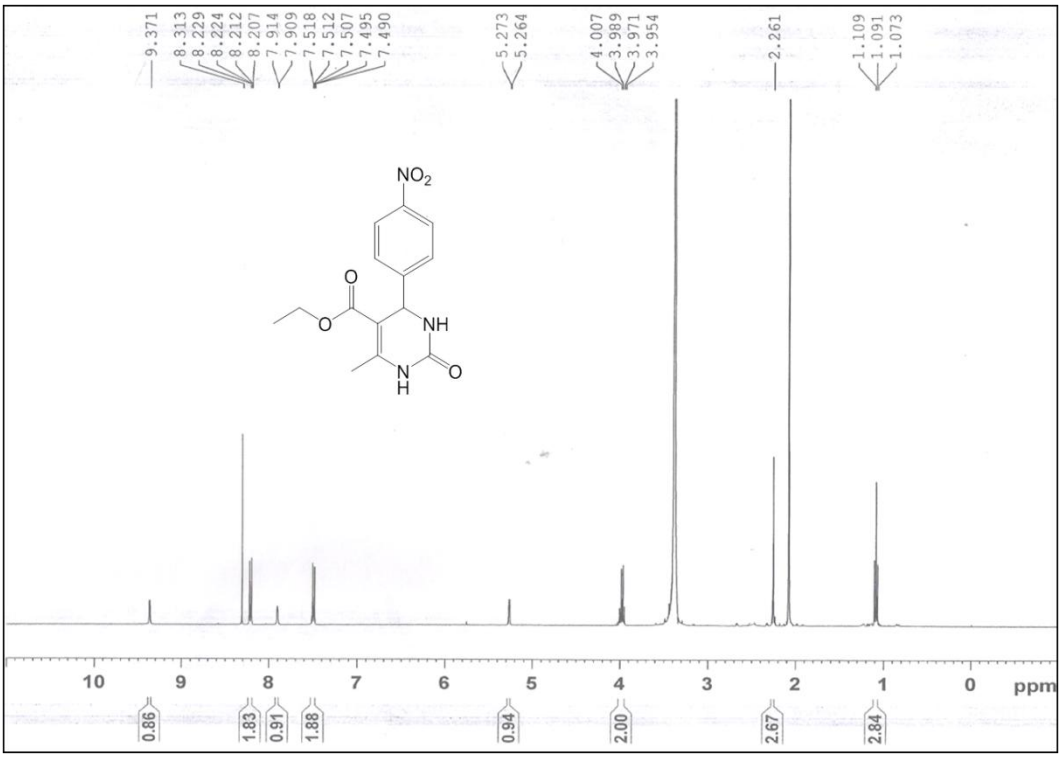
Spectral data:



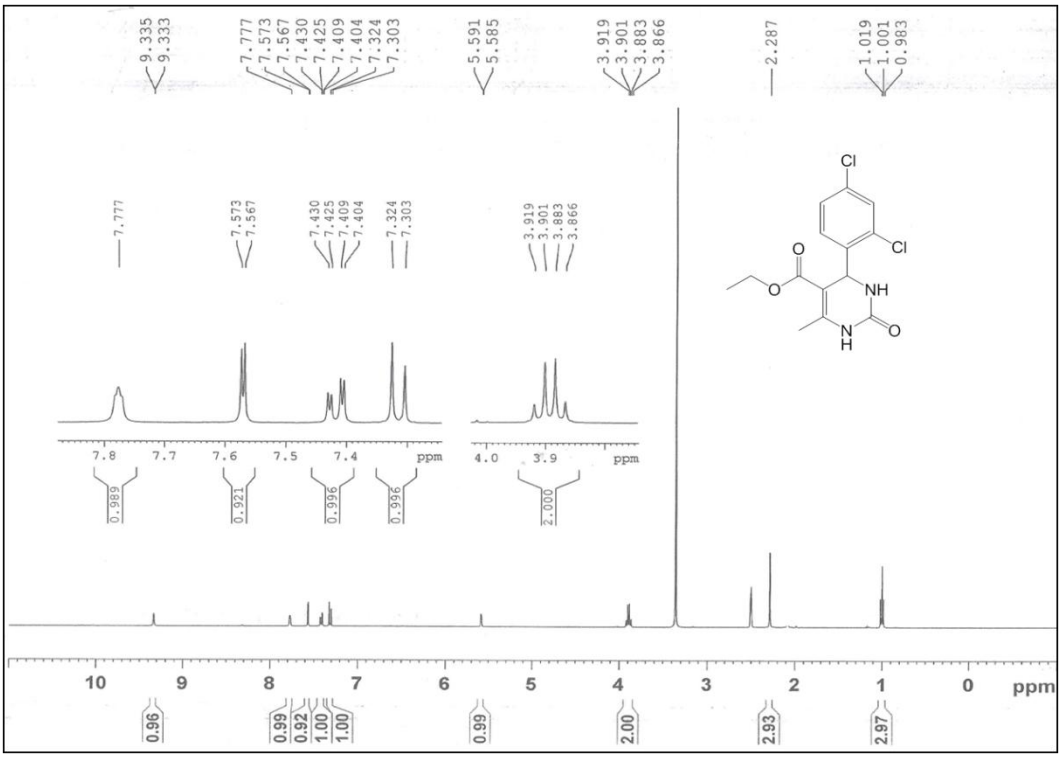
^{1}NMR of Compound **4**



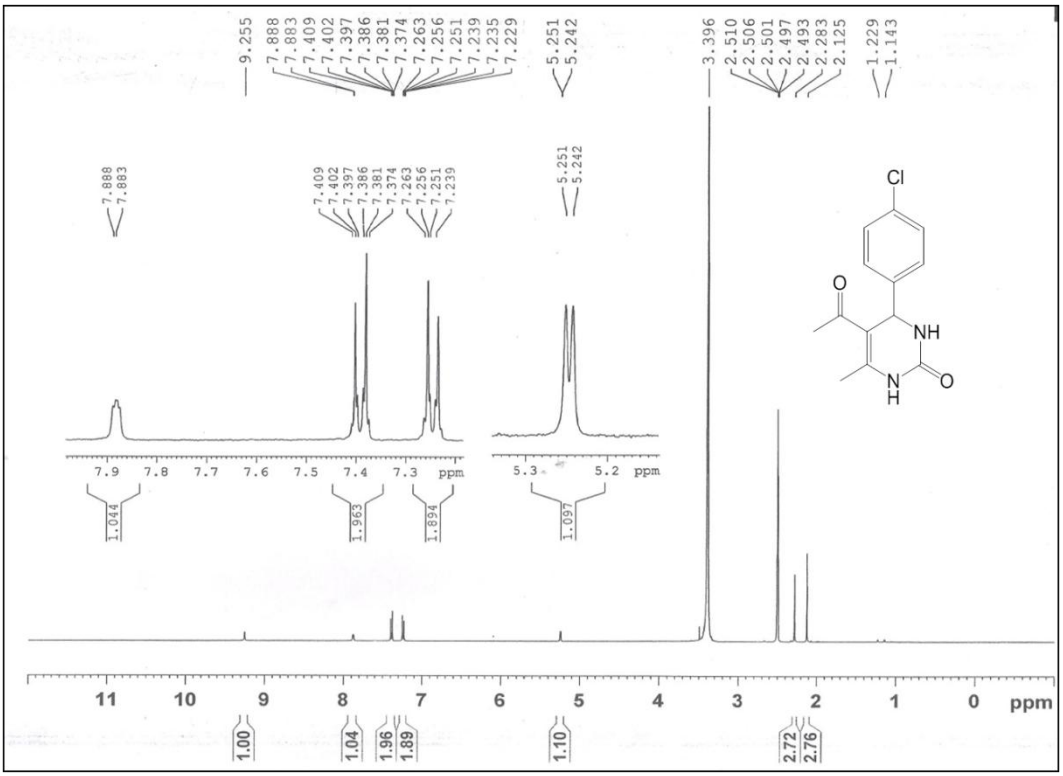
^{1}NMR of Compound **6**



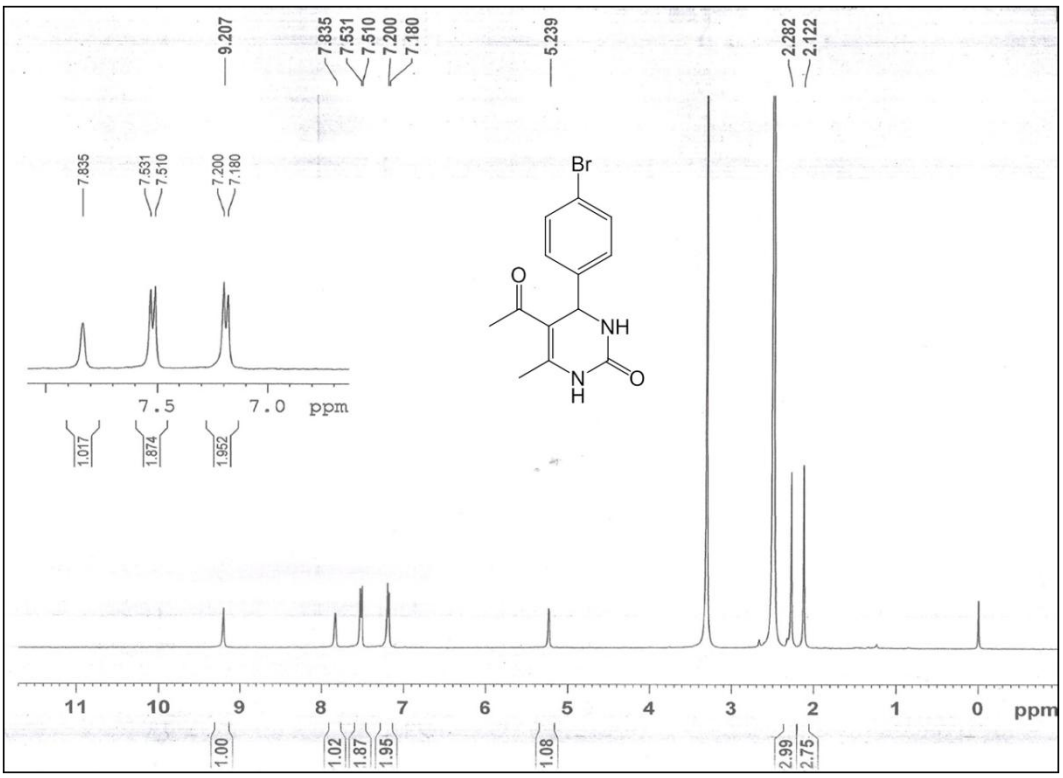
^{1}NMR of Compound **7**



^{1}NMR of Compound **10**



[1]NMR of Compound **16**



[1]NMR of Compound **17**

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