Chapter I

Section C

Graphene oxide (GO): a metal-free catalyst for one-pot three-component synthesis of triarylpyridines

I.C.1. Introduction

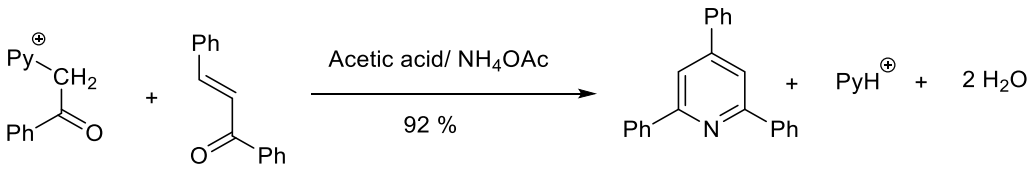
Pyridine ring systems are of great interest because of the occurrence of their derivatives in natural products and biologically active compounds such as pyridoxal (vitamin B_6), NAD nucleotides, and pyridine alkaloids [1]. These compounds have a unique position in synthetic organic chemistry because of their wide range of activities in pharmaceuticals such as antimalarial, anesthetics, vasodilators, anticonvulsants, antiepileptics, and agrochemicals such as pesticides and herbicides [2-4]. In addition, pyridines have received a growing interest as monomeric building blocks in thin films and organometallic polymers [5]. Among the pyridine derivatives, 2,4,6-triarylpyridines are frequently used as a synthon in supramolecular chemistry owing to their π-stacking ability along with directional hydrogen-bonding capacity [6].

I.C.2. Background and objectives

During the last two decades, multicomponent reactions (MCRs) have been widely used as an attractive strategy in organic synthesis due to their efficiency to generate heterocyclic compounds in a single synthetic step [7]. In MCRs, complex organic molecules are formed after a cascade of bond-forming individual steps without the isolation of intermediates using three or more reactants. MCRs are an environmentally friendly process that reduces the number of synthetic steps, waste production, and energy consumption. Thus, the improvement of known MCRs and the discovery of new MCRs are of significant interest. In view of the different chemical and biological applications of substituted pyridines, the evolution of suitable synthetic pathways for their preparation has been a great topic of interest. The general method for 2,4,6-triarylpyridine (Kr hnke pyridine) synthesis involves the reaction between α,β-unsaturated ketones, and N-phenacylpyridinium salts using ammonium acetate

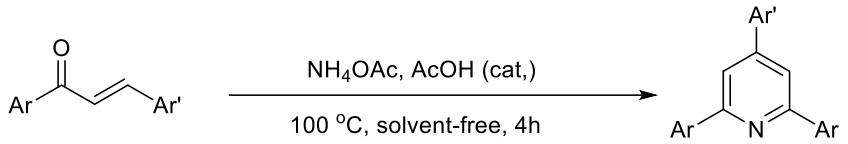
[8]. In recent years, many efforts have been given to develop 2,4,6-triarylpyridines using benzaldehydes, acetophenones, and ammonium acetate in presence of different acid catalysts such as pentafluorophenylammonium triflate [9], heteropolyacid [10], $HClO_4$–SiO_2 [11], Brønsted-acidic ionic liquid [12], and nano-metal catalyst [13, 14]. Synthesis of 2,4,6-triarylpyridines using various synthons is given below.

Kr hnke *et al*. synthesized 2,4,6-triphenylpyridines using *N*-phenacylpyridinium bromide and benzalacetophenone in a mixture of glacial acetic acid and ammonium acetate (Scheme I.C.1) in one step in about 90 % yield [8]. This mixture promotes Michael's addition and does not cause any acid cleavage of the adduct formed using phenacylpyridinium bromide and unsaturated ketone.



Scheme I.C.1. Kr hnke pyridine synthesis.

Adib *et al.* focused their study to introduce a new facile and efficient method for pyridine synthesis. Therefore, a certain range of symmetrical 2,4,6-triarylpyridines was synthesized using 1,3-diaryl-2-propen-1-ones with NH_4OAc [15] in presence of a catalytic amount of AcOH at 100 °C under solvent-free condition for 4 h with 93-98 % yield (Scheme I.C.2). Here, the formation of the pyridine ring system involves the formation of three bonds from [3+2+1] atom fragments. The structures of the isolated products were analyzed with element analysis and spectral data (mass, IR, ^1H, and ^{13}C NMR).

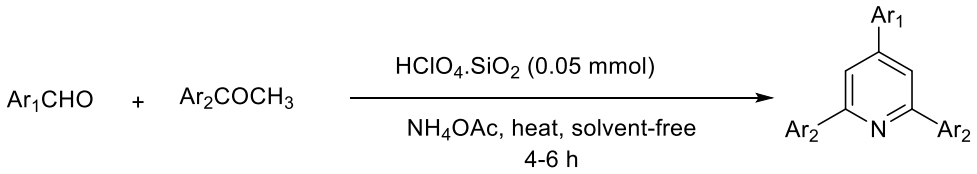


Yield 93-98 %

Ar= C_6H_5, *p*-$CH_3C_6H_5$, *p*-$OCH_3C_6H_5$, 2,4-$Cl_2C_6H_3$
Ar'= C_6H_5, *p*-$CH_3C_6H_5$, *o*-$CH_3C_6H_5$, *p*-$OCH_3C_6H_5$
p-$N(CH_3)_2C_6H_5$, *p*-ClC_6H_5, *o*-$CH_3C_6H_5$, 4-$NO_2C_6H_5$
pyridyl, furyl, thienyl

Scheme I.C.2. *The synthesis of triarylpyridine from* 1,3-diaryl-2-propen-1-ones.

Nagarapu *et al*. reported the synthesis of 2,4,6-triarylpyridines by a one-pot reaction of substituted acetophenones, aldehydes, and NH_4OAc at 120 °C temperature using $HClO_4$–SiO_2 as a powerful heterogeneous catalyst (Scheme I.C.3) [11]. This solid-supported perchloric acid ($HClO_4$–SiO_2) offers excellent yield, shorter reaction time (4-8 h), simple reaction procedure and the catalyst showed remarkable reusability. The effect of the nature of substituents present on the aromatic ring of the aldehyde and acetophenone showed no obvious effect on the yield of the reaction.



Yield 68-88 %

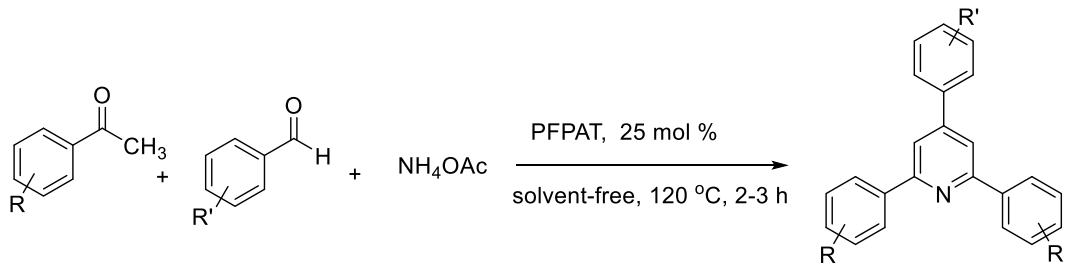
Ar_1= C_6H_5, *p*-ClC_6H_4, *p*-BrC_6H_4,
p-$CH_3C_6H_4$, *p*-OHC_6H_4
Ar_2= *p*-ClC_6H_4, 2,4-$Cl_2ClC_6H_4$, *p*-BrC_6H_4, *p*-OHC_6H_4
p-$OCH_3C_6H_4$, *p*-$N(CH_3)_2C_6H_4$, furyl, napthyl

Scheme I.C.3. *Synthesis of* 2,4,6-triarylpyridines using $HClO_4$–SiO_2.

Pentafluorophenylammonium triflate (PFPAT) was found to be a novel organocatalyst in organic transformations such as Mukaiyama aldol and Mannich reactions [16], esterification of carboxylic acids with alcohols [17],

synthesis of coumarins via von pechmann condensation [18]. Montazeri *et al.* developed a one-pot three-component synthesis of 2,4,6-triarylpyridines using aryl aldehydes, acetophenone, and ammonium acetate at 120 ^{o}C temperature under neat reaction conditions (Scheme I.C.4). The presence of electron-withdrawing groups at aromatic aldehyde favored the product formation; however, the electron-donating group containing aldehydes lowered the yield of the reaction. Moreover, reactions with substituted acetophenones proceeded very well and no undesirable side product was observed.

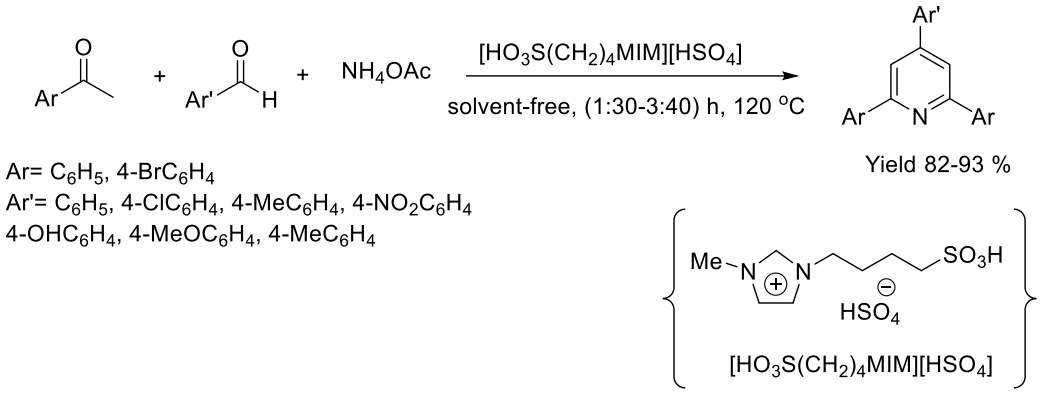
Ionic liquids (ILs) are generally salt-type compounds that exist as a liquid at room temperature (rt) and have a very low vapor pressure. Due to the lack of evaporation, they are considered promising green solvents for replacing harmful conventional solvents. Davoodnia *et al*. described the synthesis of 2,4,6-triarylpyridines in presence of a Brønsted acidic ionic liquid, 3-methyl-1-(4-sulfonylbutyl)imidazolium hydrogen sulfate [$HO_3S(CH_2)_4MIM][HSO_4$], as an effective and reusable catalyst (Scheme I.C.5) [12]. The catalyst was recycled upto three times with a slight reduction in its catalytic activity.



R= H, 4-Br, 4-Me, 4-NO_2, 4-OMe
R'= H, 4-NO_2, 4-Me, 2-Me, 4-OH, 4-OMe, 4-Cl, 2-Cl

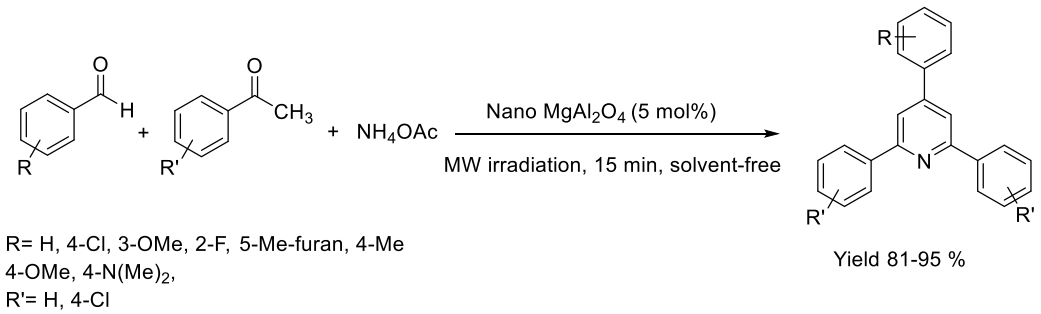
Yield 86-94 %

Scheme I.C.4. (PFPAT) catalyzed pyridine synthesis.



Scheme I.C.5. *Ionic liquid catalyzed synthesis of triarylpyridines.*

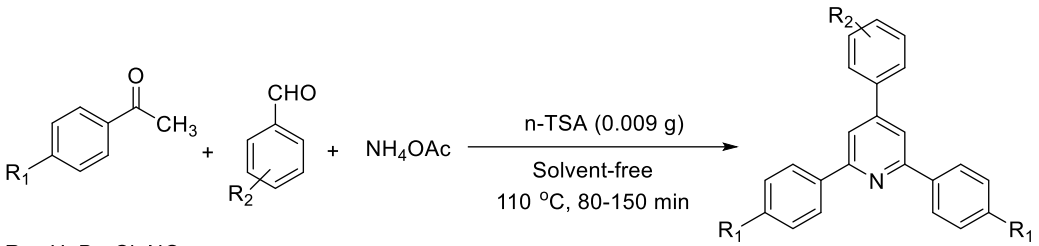
The nanosized spinel particles have found much application as catalyst support [19], humidity sensors [20], ceramic pigments [21] because of their good physical and chemical properties [22]. Magnesium aluminate ($MgAl_2O_4$) is one of the widely used and best-known spinel materials. Safari *et al.* designed nanocrystalline $MgAl_2O_4$ as a powerful heterogeneous catalyst for the synthesis of 2,4,6-triarylpyridines under microwave irradiation (Scheme I.C.6) [14]. The catalyst can be recycled upto 5 successive runs without a significant decrease in its catalytic activity.



Scheme I.C.6. *Synthesis of triarylpyridine catalyzed by magnesium aluminate.*

Tabrizian *et al*. reported a highly efficient, eco-friendly, and recyclable heterogeneous catalyst nano titania-supported sulfonic acid (n-TSA) for the one-

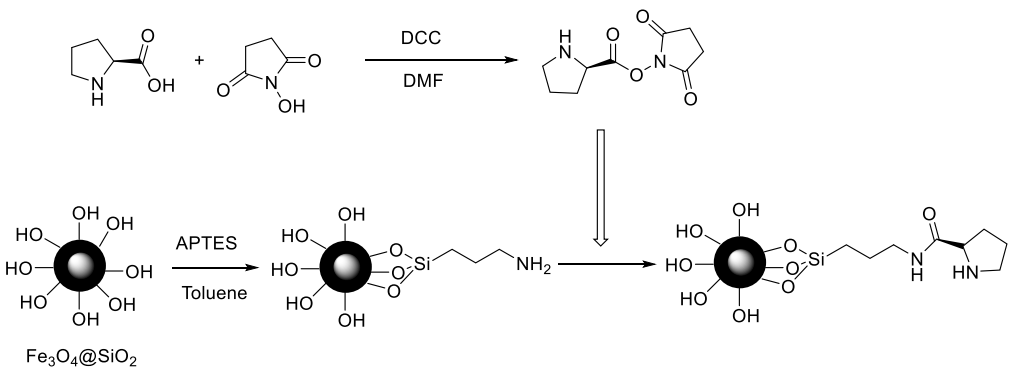
pot solvent-free synthesis of 2,4,6-triarylpyridines through the reaction of acetophenones, aryl aldehydes, and ammonium acetate at 110 °C temperature (Scheme I.C.7) [23]. Aromatic aldehydes with electron-donating and electron-withdrawing substituents reacted successfully and afforded the product in good yield. The simple work-up process without tedious column chromatographic purification, operational simplicity, short reaction time, and solvent-free condition are the main advantages of the reported protocol.



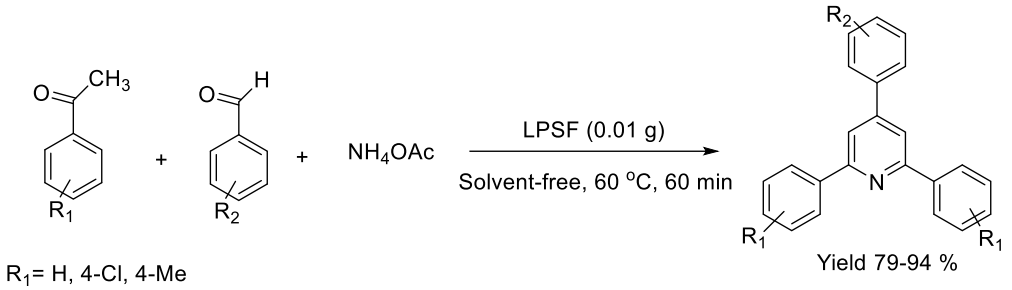
R_1= H, Br, Cl, NO_2
R_2= 4-H, 4-Cl, 4-Br, 4-CH_3, 4-OCH_3, 4-$N(CH_3)_2$, 4-NO_2

Scheme I.C.7. Nano titania-supported sulfonic acid as efficient catalyst for the synthesis of triarylpyridines.

Maleki *et al.* synthesized nanomagnetic catalyst Fe_3O_4\SiO_2\propyltriethoxysilane\L-proline (LPSF) (Scheme I.C.8) and applied for the one-pot synthesis of 2,4,6-triarylpyridines under solvent-free mild reaction condition (Scheme I.C.9) [13]. Recently, magnetic nanoparticles (MNPs) have been considered as a new type of catalytic support for organocatalysts owing to their price, good stability, high dispersion, easy synthesis and functionalization method, high surface area, and easy separation with the help of an external magnetic field [24-27]. The structure of the prepared nanoparticles was characterized by FT-IR, FE-SEM, TGA, EDX analysis.



Scheme I.C.8. *Preparation of LPSF magnetic nanocatalyst.*

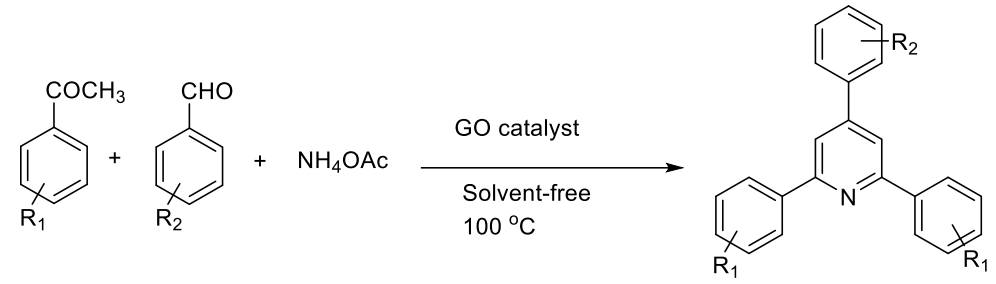


Scheme I.C.9. *LPSF nanocatalyst used for the synthesis of triarylpyridine*.

I.C.3. Present work

Nevertheless, most of the traditional synthetic method requires harsh reaction condition, prolonged heating, and use of toxic transition metal catalyst as well as only a few protocols have shown greener context and high atom economy. Recently, GO has been emerged as an efficient carbocatalyst for various organic transformations. Our present study (Scheme I.C.10) explores the role of GO as an acid catalyst using the surface-bound oxygen-containing functional groups. The versatility and sustainability of GO as a catalyst leads us to employ GO as a metal-free catalyst for the synthesis of 2,4,6-triarylpyridines

to overcome the drawbacks of the reported protocols and reduce environmental hazards



R_1= 4-H, 4-Me,4-Br
R_2= 4-H, 4-Me, 4-Cl, 4-NO_2, 4-OMe, Furan-2-carbaldehyde, 4-Cl

Yield 78-93 %

Scheme I.C.10. *Graphene oxide (GO) catalyzed one-pot synthesis of triarylpyridines.*

I.C.3.1. Result and disscussion

In connection to our previous work, the catalytic activity of synthesized GO was investigated in the case of 2,4,6-triarylpyridine synthesis. To find out the optimized condition of the reaction, acetophenone (2 mmol), benzaldehyde (1 mmol), and ammonium acetate (2 mmol) were selected as model substrates and the results were summarized in Table I.C.1. As can be seen from Table I.C.1 that neither polar nor non-polar solvents were found suitable for the reaction. The best result was obtained under neat or solvent-free conditions (Table I.C.1, entry11). The effect of temperature and the amount of catalyst was also examined to find out the optimized condition. Studies reveal that the yield increases with increasing temperature. Room-temperature reaction afforded only 20% of the product which strongly indicates the vital role of temperature in governing the reaction (Table I.C.1, entry 16). However, after 120 ^{o}C the yield decreases with a further increase in temperature (Table I.C.1, entry 10). To

ascertain the catalytic function of GO, the reaction was performed in absence of catalyst and only a trace amount of product was obtained. The amount of the catalyst was also altered and optimum condition offered a neat reaction with 30 mg of GO at 100 ºC temperature (Table I.C.1, entry 11). Ammonia sources other than ammonium acetate produced the corresponding product with a low yield (Table I.C.1, entries 14-15).

Table I.C.1. Optimization of reaction condition for the reaction of 2,4,6-triarylpyridine[a]

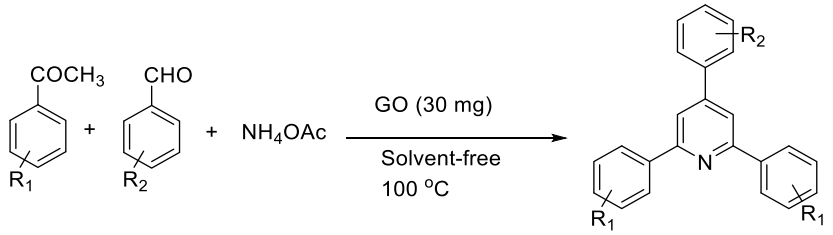
Entry	Temp (ºC)	Solvent	Catalyst (mg)	Ammonia source	Yield (%)[b]
1	100	H_2O	15	NH_4OAc	65
2	80	Ethanol	15	NH_4OAc	55
3	100	DMF	15	NH_4OAc	53
4	100	DMSO	15	NH_4OAc	45
5	100	Toluene	15	NH_4OAc	50
6	80	CH_3CN	15	NH_4OAc	30
7	100	Ethylene glycol	15	NH_4OAc	60
8	100	Neat	15	NH_4OAc	83
9	120	Neat	30	NH_4OAc	90
10	150	Neat	30	NH_4OAc	86
11	**100**	**Neat**	**30**	**NH_4OAc**	**92**
12	80	Neat	30	NH_4OAc	80
13	100	Neat	-	NH_4OAc	Trace
14	100	Neat	30	$(NH_4)_2CO_3$	48
15	100	Neat	30	$(NH_4)_2SO_4$	Trace
16	rt	Neat	30	NH_4OAc	<20[c]

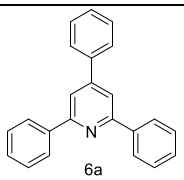
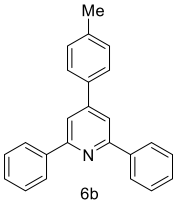
[a]Reaction condition: Acetophenone (2 mmol), benzaldehyde (1 mmol), ammonium acetate (2 mmol), reaction time: 2h.
[b]Isolated yields.
[c]Room temperature reaction.

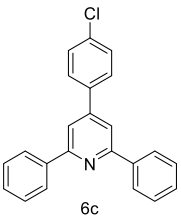
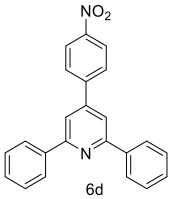
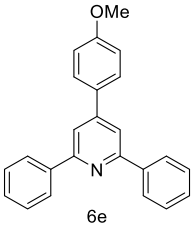
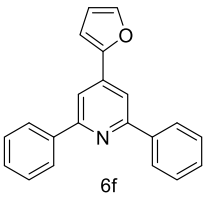
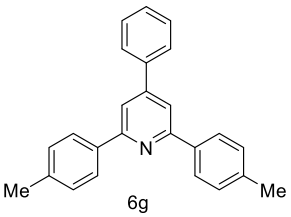
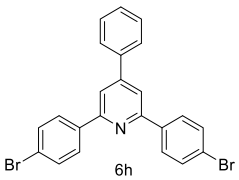
To explore the catalytic activity of GO, a wide variety of aromatic aldehydes and substituted acetophenones were subjected to synthesize 2,4,6-triarylpyridines. Based on the above-optimized results, GO catalyzed reaction was carried out at 100 ºC temperature under solvent-free condition and the

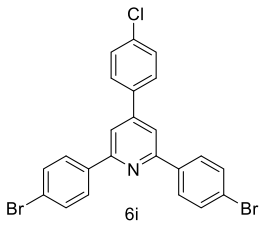
results are summarized in Table I.C.2. First, the compatibility of the substituents in the phenyl ring of acetophenone and benzaldehyde was examined. All the electron-donating and electron-withdrawing substituents on the aromatic ring are equally capable of producing the corresponding product with a good yield. However, aldehydes with electron-withdrawing groups (Table I.C.2, entries 3-4, 8-9) exerted excellent yield and reacted faster than the aromatic aldehydes with electron-donating groups (Table I.C.2, entries 2, 5, 7). In the case of heterocyclic aldehydes, the reaction has smoothly proceeded as can be seen from Table I.C.2, entry 6.

Table I.C.2. Synthesis of 2,4,6-triarylpyridine derivatives in presence of GO[a]



Entry	R_1	R_2	Product	Time (h)	Yield (%)[b]
1	4-H	4-H	 6a	2h	92
2	4-H	4-Me	 6b	2h	86

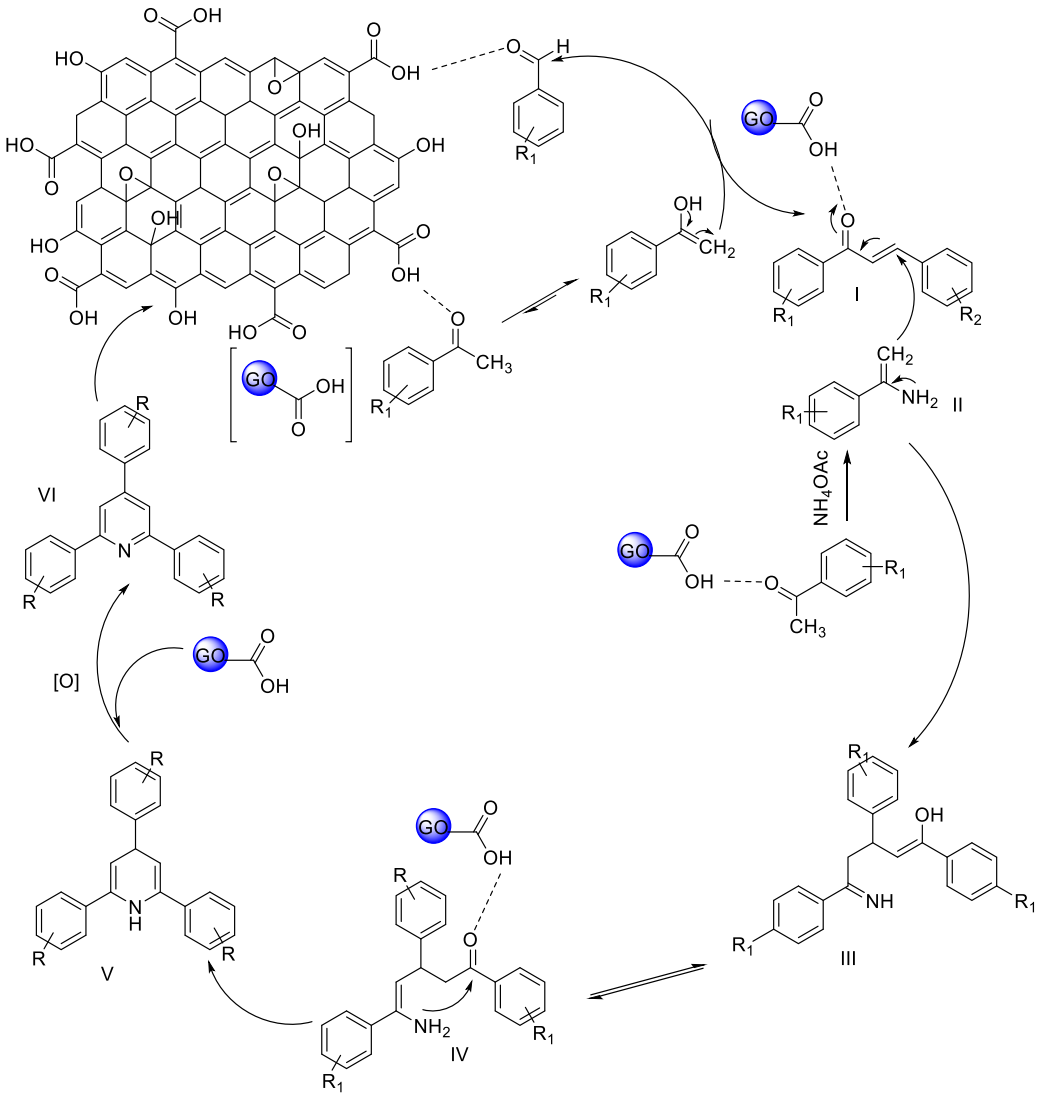
3	4-H	4-Cl	 6c	1h	93
4	4-H	4-NO_2	 6d	1h	88
5	4-H	4-OMe	 6e	2h	83
6	4-H	Furan-2-carbaldehyde	 6f	2h	78
7	4-Me	4-H	 6g	2h	87
8	4-Br	4-H	 6h	1h	90

9	4-Br	4-Cl	 6i	1h	94

[a]Reaction condition: Acetophenone (2 mmol), benzaldehyde (1 mmol), ammonium acetate (2 mmol) and GO (30 mg).
[b]Isolated yields after purification through column chromatography on silica gel.

I.C.3.2. Mechanism

The probable mechanism for the synthesis of 2,4,6-triarypyridines using GO is described in Scheme I.C.11. At the very first step, aldol condensation occurs between acetophenone and aromatic aldehyde. Acetophenone is activated by the acidic group of GO and the nucleophilic attack occurs at the carbonyl carbon of aromatic aldehyde. After that, an acetophenone molecule is reacted with an ammonia source to form enamine (II). In the third stage, Michael's addition between enamine (II) and the aldol condensation product (I) occurs. GO protonates the condensation product (I), thereby facilitating the Michael addition by enamine (II). The intermediate (III) is formed by Michael's addition and undergoes cyclization to form dihydropyridine (V). At the last step, oxidation to dihydropyridine occurs and gives the ultimate product 2,4,6-triarylpyridine (VI).



Scheme I.C.11. *A possible route of GO catalyzed synthesis of 2,4,6-triarylpyridine.*

The main advantage of heterogeneous catalysts is their reusability in organic transformation. For this purpose, acetophenone, benzaldehyde, and ammonium acetate were taken in a reaction vial in presence of 120 mg of GO.

The model reaction was carried out for an adequate time and after completion of the reaction, ethyl acetate (30 mL) was added into the reaction vial and centrifuged for four times. The supernatant liquid after centrifugation was decanted off and the residual catalyst was washed repeatedly with water and acetone. The dry GO was then collected and reused for the 2nd run. It was observed that GO could easily retain its acidic property without significant loss in its catalytic activity even after 5 successive runs (Figure I.C.1). Although there may be loss of some oxygenated groups due to subsequent runs, the recovered catalyst shows almost equal efficiency with the fresh GO.

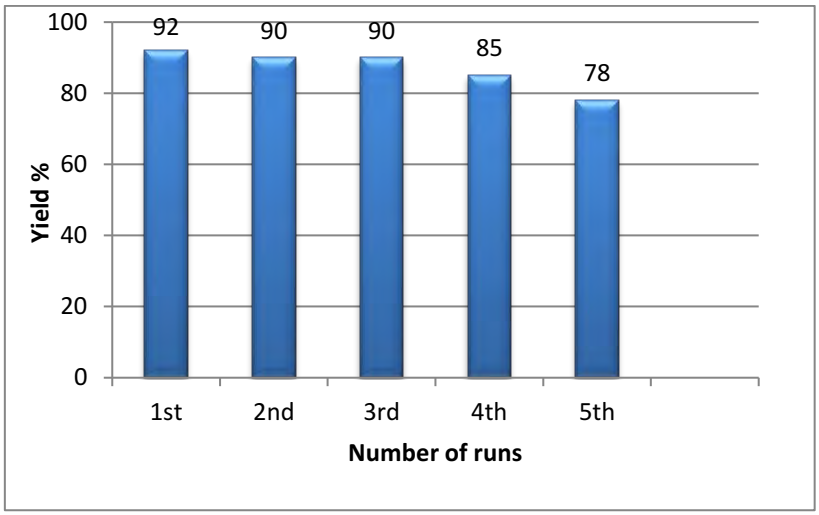


Figure I.C.1. *Recyclability experiment of catalyst GO for the synthesis of 2,4,6-triarylpyridines.*

I.C.4. Conclusion

In conclusion, GO has been proved to be efficient carbocatalyst for the synthesis of 2,4,6-triarylpyridines. Replacement of metal-free and toxic catalysts by inexpensive carbocatalyst is the main advantage of this protocol. The solid

acid catalyst, GO exerts the the desired triarylpyridines with good yield under neat reaction. Easy recovery and reusability of the catalyst provides a clean strategy to form a wide variety of trisubstituted pyridines.

I.C.5. Experimental section

I.C.5.1. General experimental procedure

All the chemicals and reagents were purchased from Sigma–Aldrich, Spectrochem, TCI and were used without further purification. The solvents were purchased from commercial suppliers and were used after proper distillation.The progress of the reaction was monitored by Merck TLC plates which are coated with silica gel (60 F_{254}) and UV light was used as visualizing agent. NMR spectra of all the synthesized compounds were carried out in $CDCl_3$/DMSO-d_6 solvent and TMS was used as an internal standard. All the NMR spectroscopic data are recorded in BrukerAvance FT-NMR operating for ^1H at 300/400 MHz. The ^1H NMR data are represented by chemical shift δ (ppm), multiplicity (s = singlet, d= doublet, t = triplet, m = multiplet), integration, coupling constants (J values) in Hertz (Hz). The ^{13}C NMR spectroscopic data are also reported in ppm as ^1H NMR spectra.

I.C.5.2. General procedure for the preparation of (GO) catalyst

There are several methods for the preparation of graphene oxide (GO). Herein, Graphene oxide (GO) was synthesized by the Tours method using graphite powder as starting material. At first, 9:1 volume ratio of (180 mL) sulfuric acid (H_2SO_4) and (20 mL) phosphoric acid (H_3PO_4) were taken in a 500 ml conical flask, and then 1.5 g of graphite powder was added to it under stirring condition. The temperature of the whole mixture was kept below 10 ^oC using an ice bath and 9g of potassium permanganate ($KMnO_4$) was added very slowly

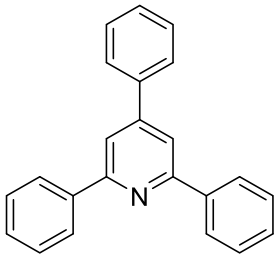
into it as the addition of $KMnO_4$ evolves heat. Then the reaction mixture was stirred for 12 hrs and after that hydrogen peroxide (H_2O_2) was added drops wise to eliminate excess $KMnO_4$. After that, 30-40 mL hydrochloric acid (HCl) (strength 30%) was added to this mixture followed by the addition of 200 mL of deionized water. Then the mixture was centrifuged at 5000 rpm for 20 minutes. After that, the supernatant liquid was decanted away and the residual was dried at 90 ^oC rotary evaporator to get dry graphene oxide (GO) with pH (4.2 at 0.1 mg/mL).

I.C.5.3. General procedure for the synthesis of 2,4,6-triarylpyridines

A mixture of acetophenone (1 mmol), aromatic aldehyde (1 mmol), ammonium acetate (1.5 mmol), and 30 mg of GO was stirred for 2h at 100 ^oC temperature. The reaction was monitored by TLC and after completion of the reaction; the reaction mixture was extracted with ethyl acetate. The catalyst was recovered by centrifugation and washed with acetone and water and then dried. The ethyl acetate extractswere further purified by column chromatography using silica gel of 60-120 mesh and the desired product is obtained.

I.C.5.4. ^1H and ^{13}C NMR of various synthesized compounds

2,4,6-triphenylpyridine (Table I.C.2, entry 1) [26]



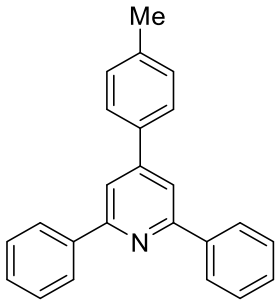
White solid;

MP 132-133 ^oC;

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.42-7.48 (m, 9H), 7.77 (d, 2H, *J* = 7.2 Hz), 8.14 (s, 2H), 8.28 (d, 4H, *J* =7.8Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 117.16, 127.20, 127.23, 128.08, 128.76, 129.02, 129.10, 129.16, 139.11, 139.65, 150.23, 157.55.

2,6-diphenyl-4-(*p*-tolyl)pyridine (Table I.C.2, entry 2) [27]



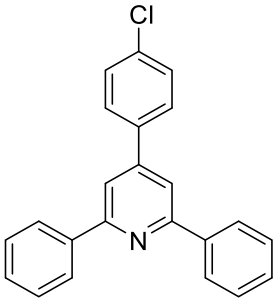
Light yellow solid;

MP 118-119 ºC;

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.49 (s, 3H), 7.45-7.56 (m, 8H), 7.90 (d, 2H, *J* = 7.2Hz), 8.11 (s, 2H), 8.23 (d, 4H, *J* = 7.8Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.01, 116.36, 126.65, 127.98, 128.08, 128.47, 129.21, 137.92, 139.22, 140.56, 150.42, 157.37.

4-(4-chlorophenyl)-2,6-diphenylpyridine (Table I.C.2, entry 3) [26]



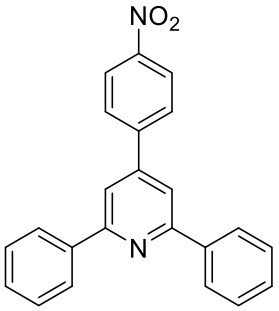
White solid;

MP 121-123 ^{o}C;

^{1}H NMR (300 MHz, CDCl^{3}) δ (ppm) 7.39-7.48 (m, 8H), 7.80 (d, 2H, *J* = 7.2 Hz), 8.13 (s, 2H), 8.30 (d, 4H, *J* = 7.8Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 116.59, 127.15, 128.07, 128.41, 128.67, 129.04, 129.42, 138.91, 139.77, 148.77, 157.45.

4-(4-nitrophenyl)-2,6-diphenylpyridine (Table I.C.2, entry 4) [26]



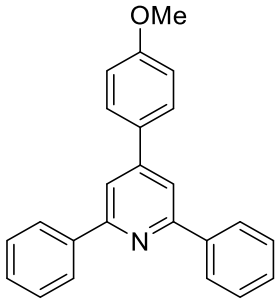
Off white solid;

MP 192-193 ^{o}C;

^{1}H NMR (300 MHz, $CDCl_3$)δ (ppm) 7.46-7.56 (m, 8H), 7.89 (d, 2H, *J* =8.1Hz), 8.21 (s, 2H), 8.40 (d, 4H, *J* = 7.8Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 116.42, 123.85, 126.64, 127.67, 128.31, 128.93, 133.11, 133.65, 143.53, 147.37, 157.52.

4-(4-methoxyphenyl)-2,6-diphenylpyridine (Table I.C.2, entry 5) [26]



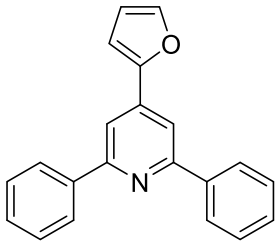
White solid;

MP 100-102 ^{o}C;

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 3.74 (s, 3H), 7.10 (d, 2H, *J* = 7.8 Hz), 7.29-7.51 (m, 8H), 7.72 (s,2H), 7.92 (d, 4H, *J* = 6.9 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 54.90, 119.35, 127.16, 127.92, 128.06, 129.73, 132.04, 138.05, 140.37, 144.18, 151.72, 161.22.

4-(furan-2-yl)-2,6-diphenylpyridine (Table I.C.2, entry 6) [26]



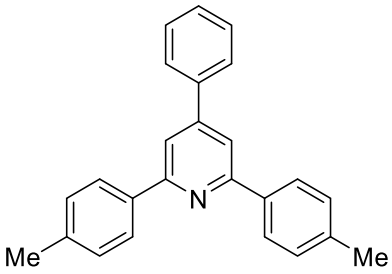
Light brown solid;

MP 112-13 ^{o}C;

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.56 (d, 1H, *J* =1.5Hz), 6.96 (d, 1H, *J* = 3Hz), 7.44-7.58 (m, 7H), 7.92 (s, 2H), 8.19 (d, 4H, *J* = 8.1 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 107.96, 111.61, 112.51, 126.58, 128.18, 128.59, 138.57, 138.99, 143.12, 151.51, 157.03.

4-phenyl-2,6-di-p-tolylpyridine (Table I.C.2, entry 7)



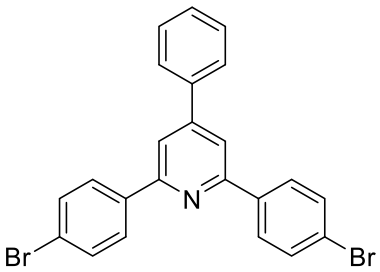
White solid;

MP 152-154 ^{o}C;

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.37 (s, 6H), 7.21 (d, 4H, *J* =7.2Hz), 7.38-7.43 (m, 3H), 7.61-7.72 (m, 2H), 7.74 (s, 2H), 7.99 (d, 4H, *J* =8.1Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.40, 116.56, 127.05, 127.23, 128.54, 128.92, 129.12, 136.94, 139.00, 139.30, 150.04, 157.43.

2,6-bis(4-bromophenyl)-4-phenylpyridine (Table I.C.2, entry 8) [27]



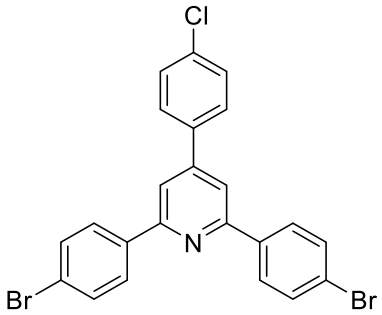
White solid;

MP 105-106 ºC;

^{1}H NMR (300 MHz, $CDCl_3$)δ (ppm) 7.09-7.36 (m, 5H), 7.49 (s, 2H), 7.76 (d, 4H, *J* = 7.8 Hz), 8.10 (d, 4H, *J* =8.1 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 116.46, 123.05, 127.05, 128.40, 128.94, 129.49, 132.94, 135.19, 139.60, 149.07, 154.16.

2,6-bis(4-bromophenyl)-4-(4-chlorophenyl)pyridine (Table I.C.2, entry 9) [28]



White solid;

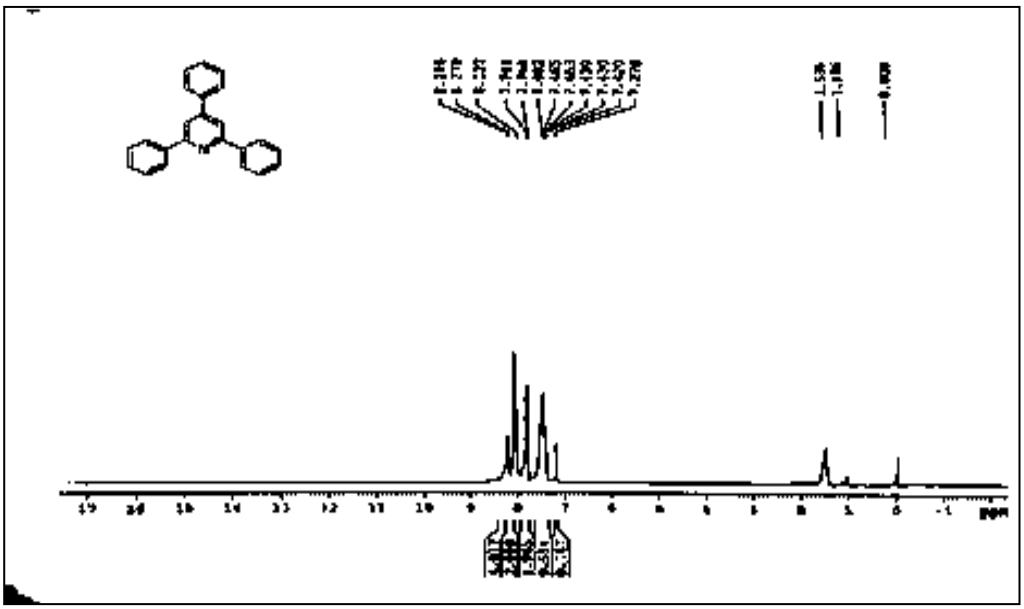
MP> 250 ºC;

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.02-7.06 (m, 4H), 7.34 (d, 2H. *J* = 7.2 Hz), 7.73 (d, 2H, *J* = 7.5 Hz), 7.87 (s, 2H), 8.13 (d, 4H, *J* = 8.4 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 116.32, 122.89, 128.68, 128.87, 129.10, 130.59, 137.58, 138.07, 149.38, 156.62.

I.C.5.5. Scanned copies of ^{1}H and ^{13}C NMR spectra of synthesized compounds

Figure I.C.2. *Scanned copy of ^{1}H and ^{13}C NMR spectra of 2,4,6-triphenylpyridine*



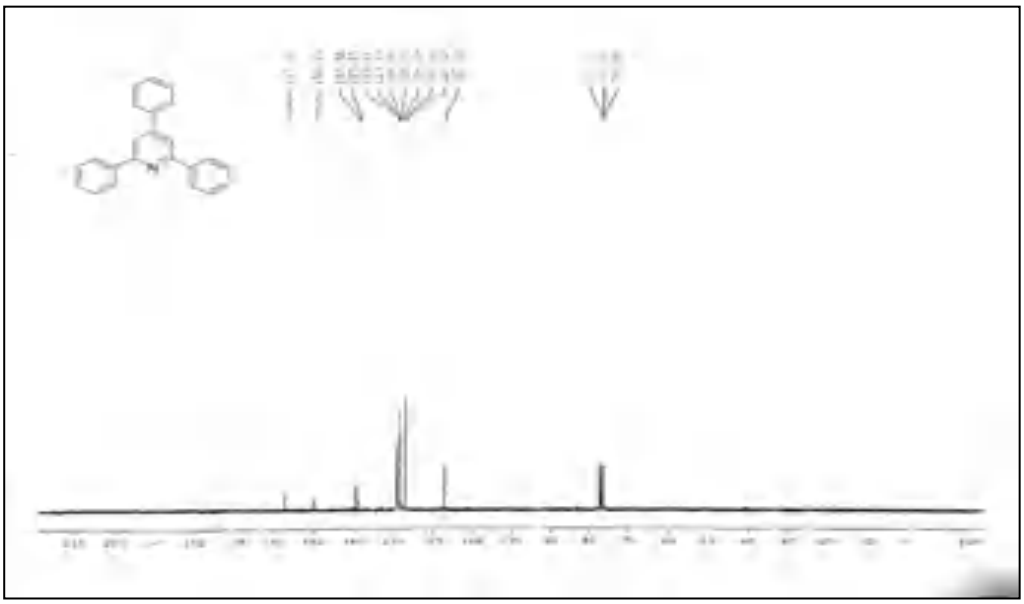


Figure I.C.3. *Scanned copy of ^{1}H and ^{13}C NMR spectra of 2,6-diphenyl-4-(p-tolyl)pyridine*

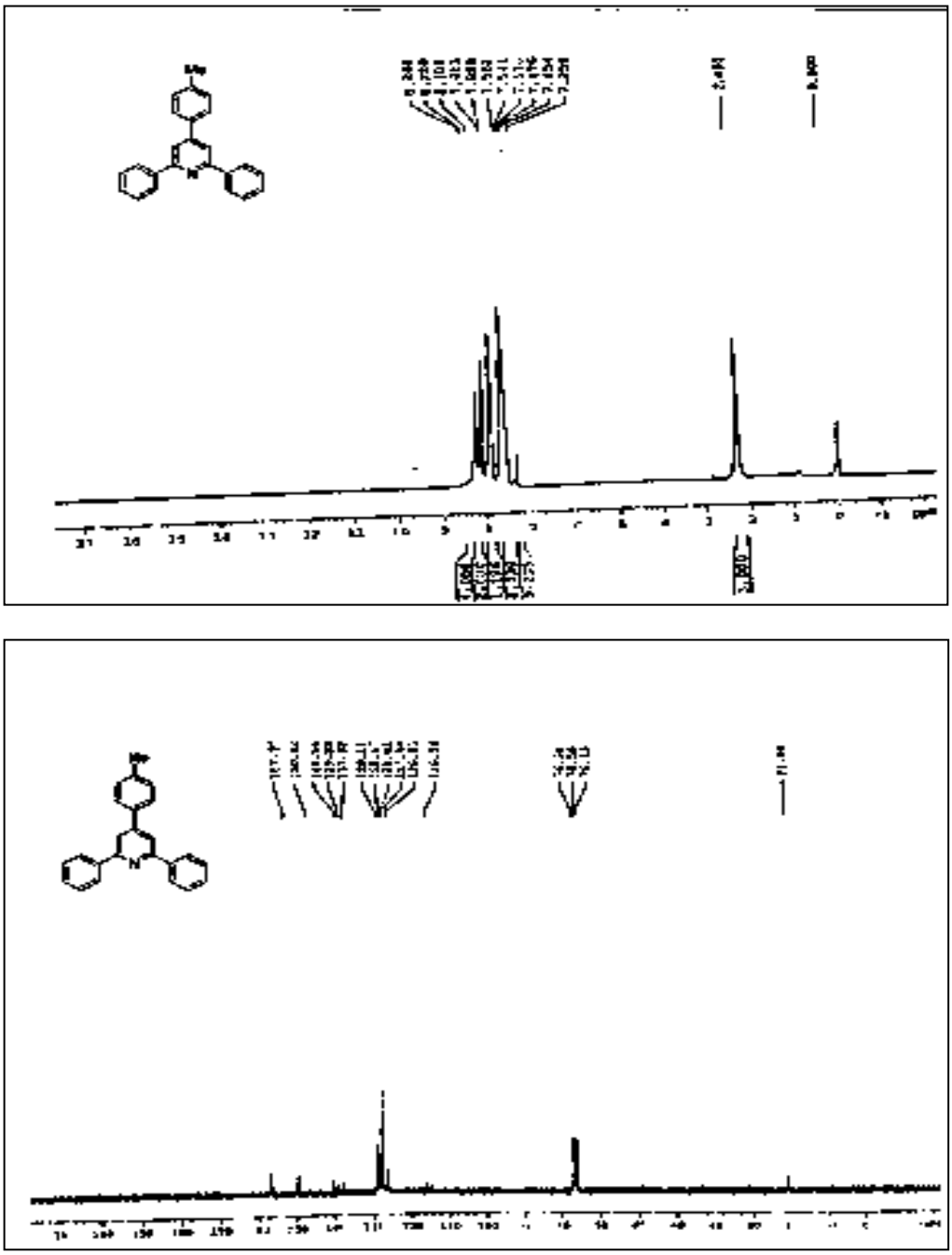
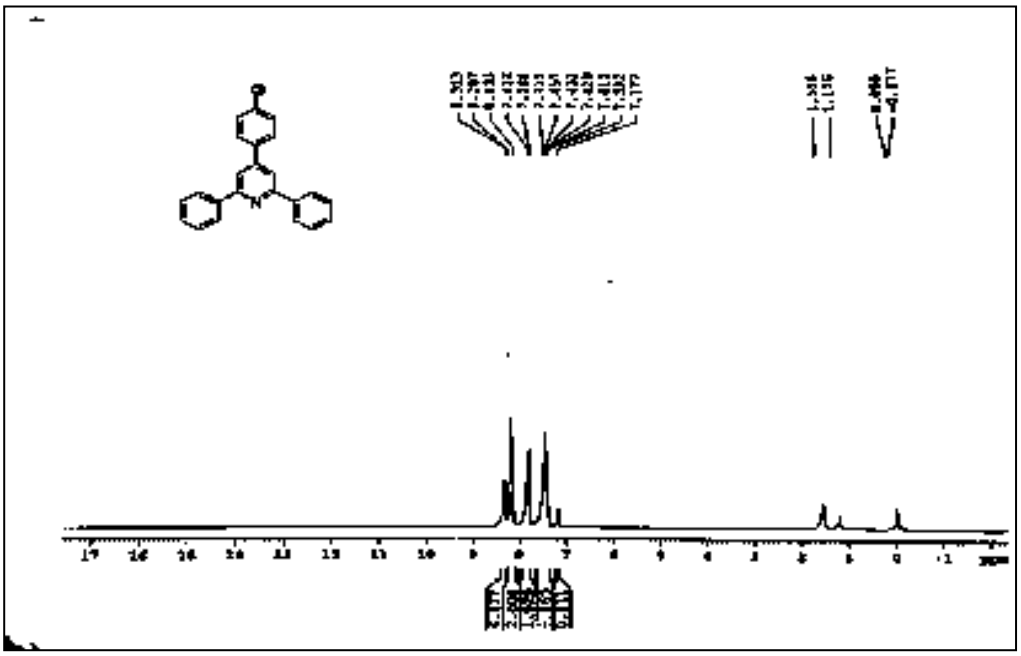


Figure I.C.4. *Scanned copy of ^{1}H and ^{13}C NMR spectra of 4-(4-chlorophenyl)-2,6-diphenylpyridine*



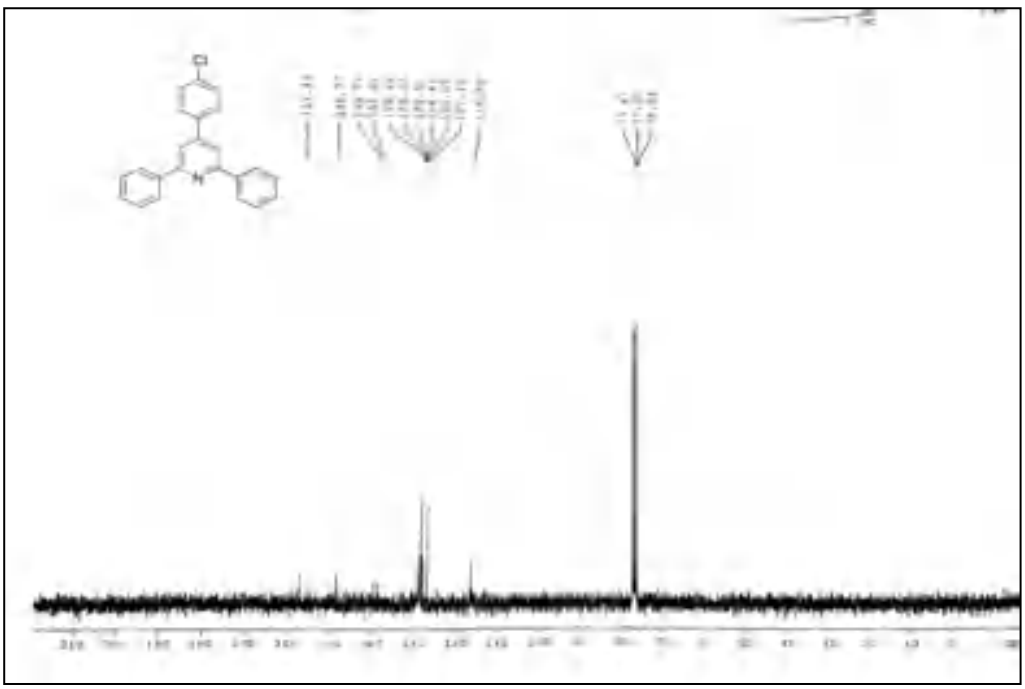
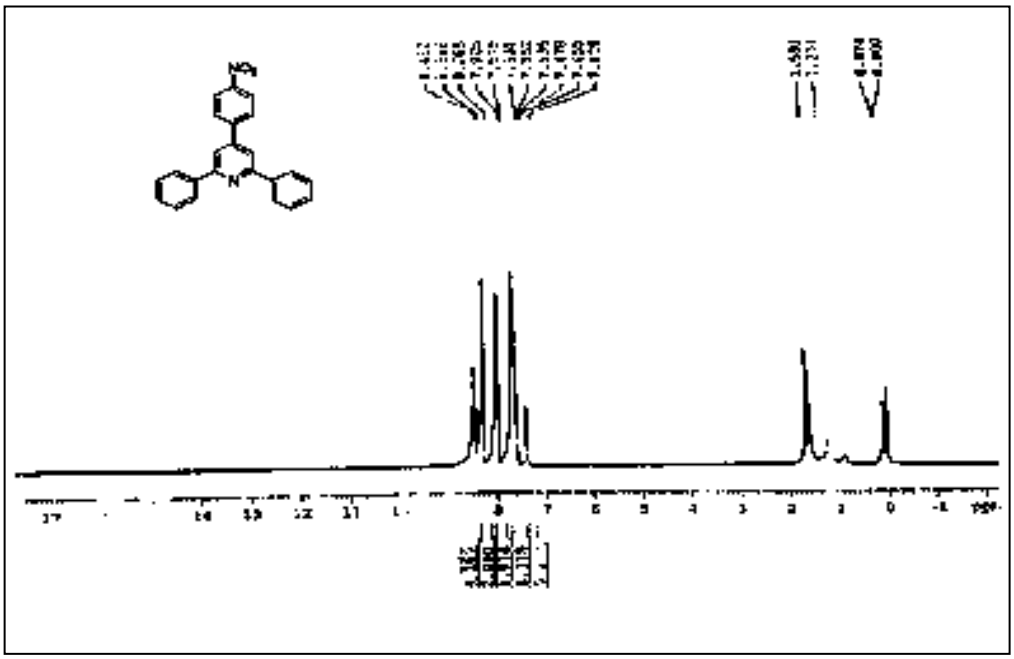


Figure I.C.5. *Scanned copy of ^{1}H and ^{13}C NMR spectra of 4-(4-nitrophenyl)-2,6-diphenylpyridine*



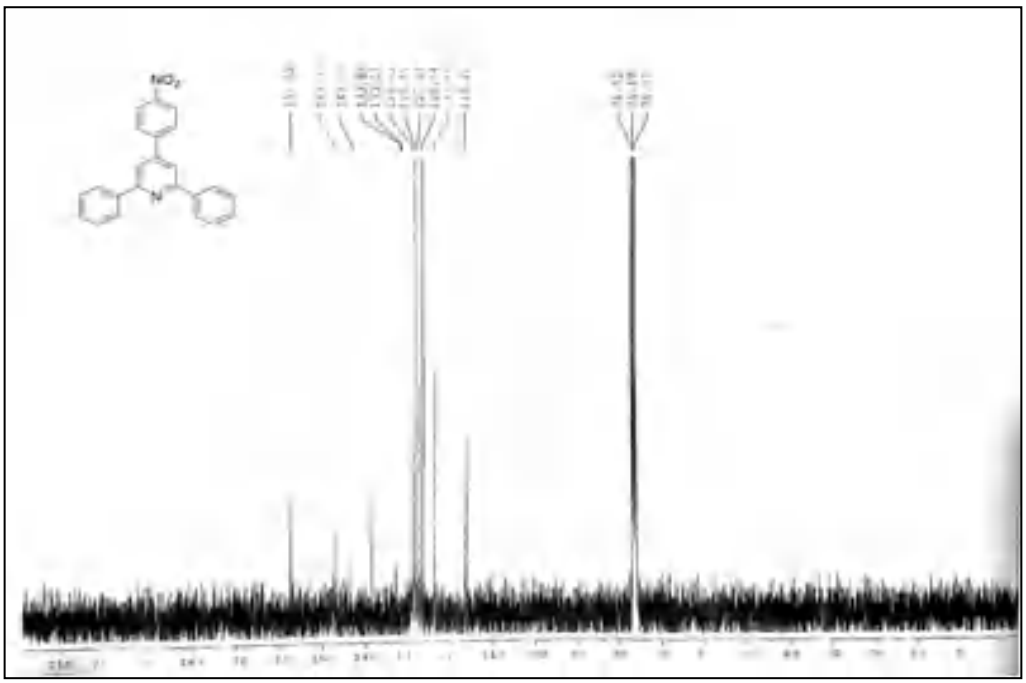
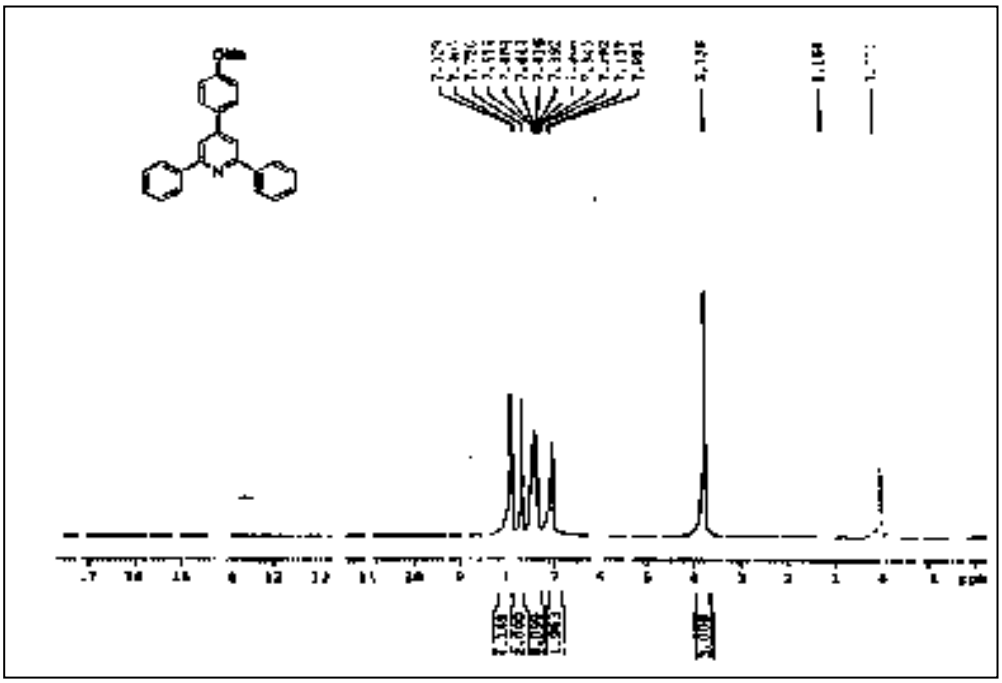


Figure I.C.6. *Scanned copy of ^{1}H and ^{13}C NMR spectra of 4-(4-methoxyphenyl)-2,6-diphenylpyridine*



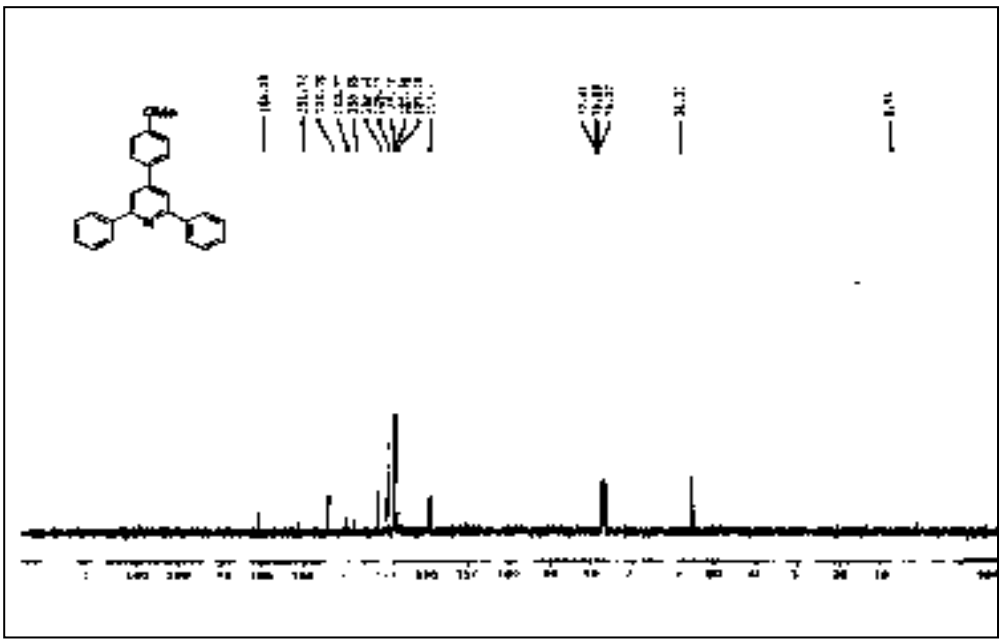
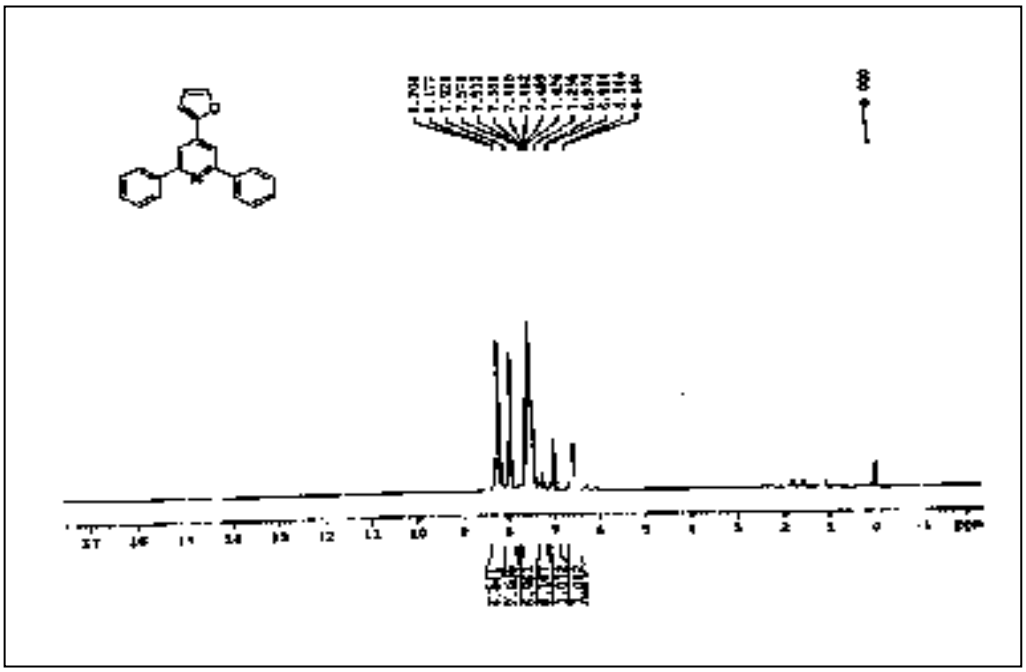


Figure I.C.7. *Scanned copy of ^{1}H and ^{13}C NMR spectra of 4-(furan-2-yl)-2,6-diphenylpyridine*



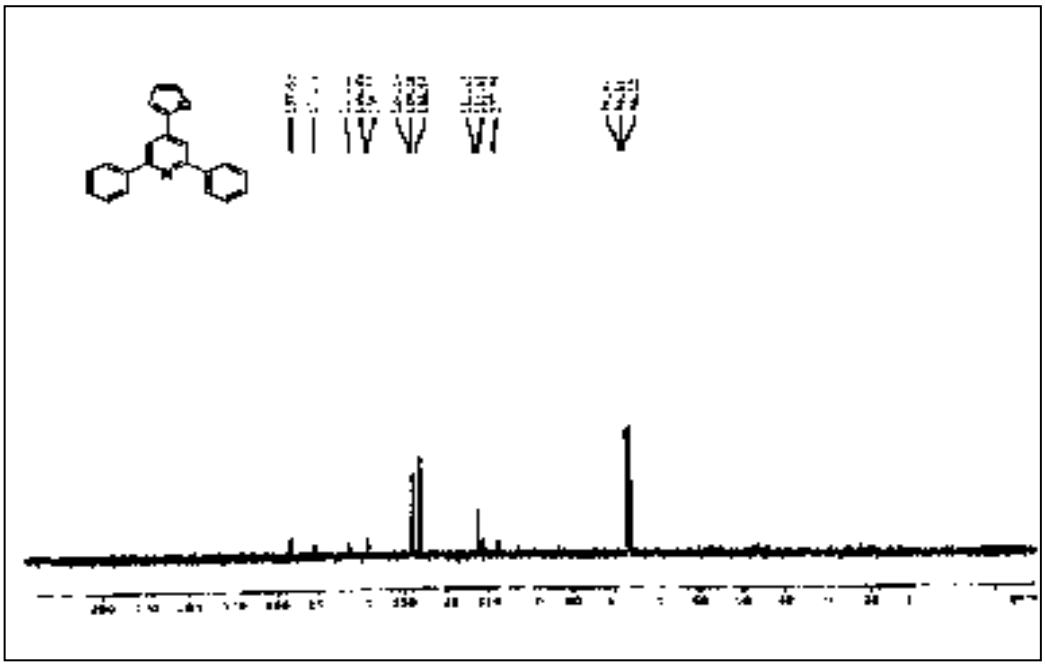
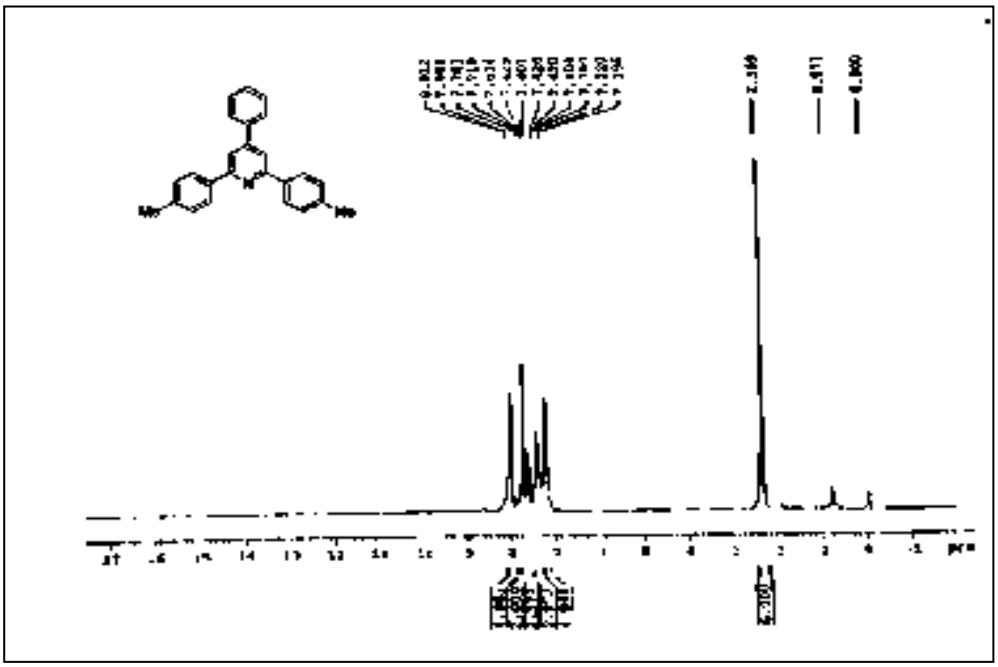


Figure I.C.8. *Scanned copy of ^{1}H and ^{13}C NMR spectra of 4-phenyl-2,6-di-p-tolylpyridine*



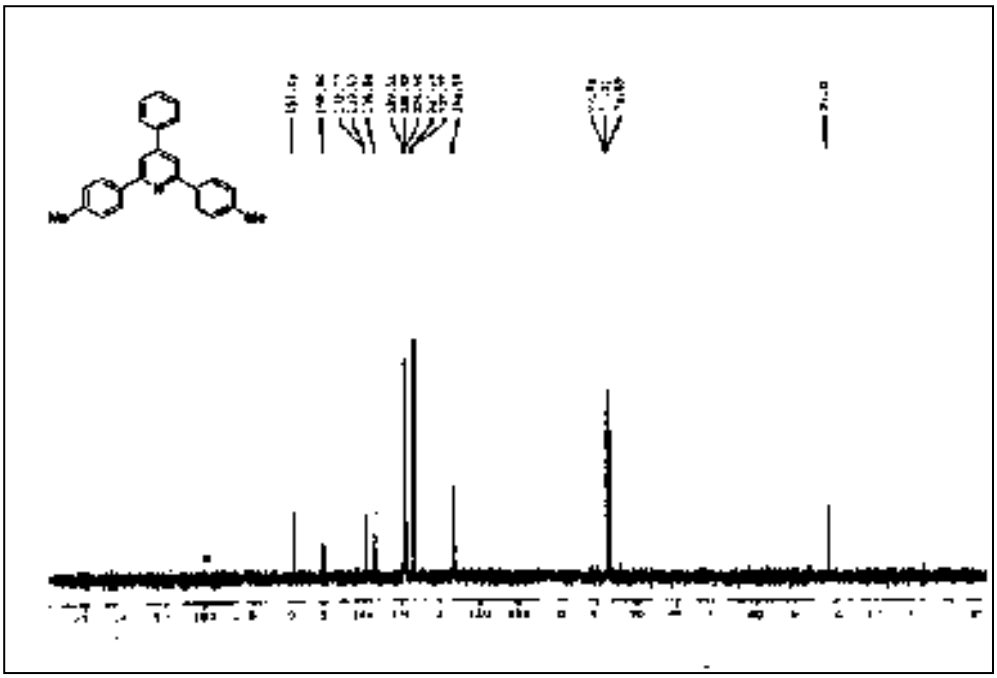
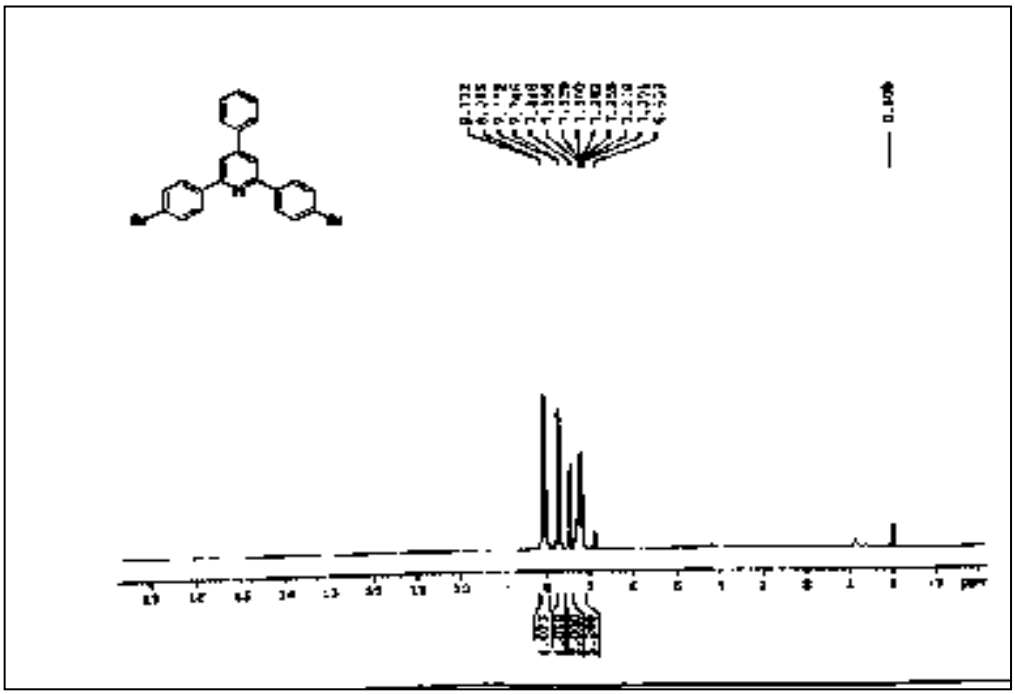


Figure I.C.9. *Scanned copy of ^{1}H and ^{13}C NMR spectra of 2,6-bis(4-bromophenyl)-4-phenylpyridine*



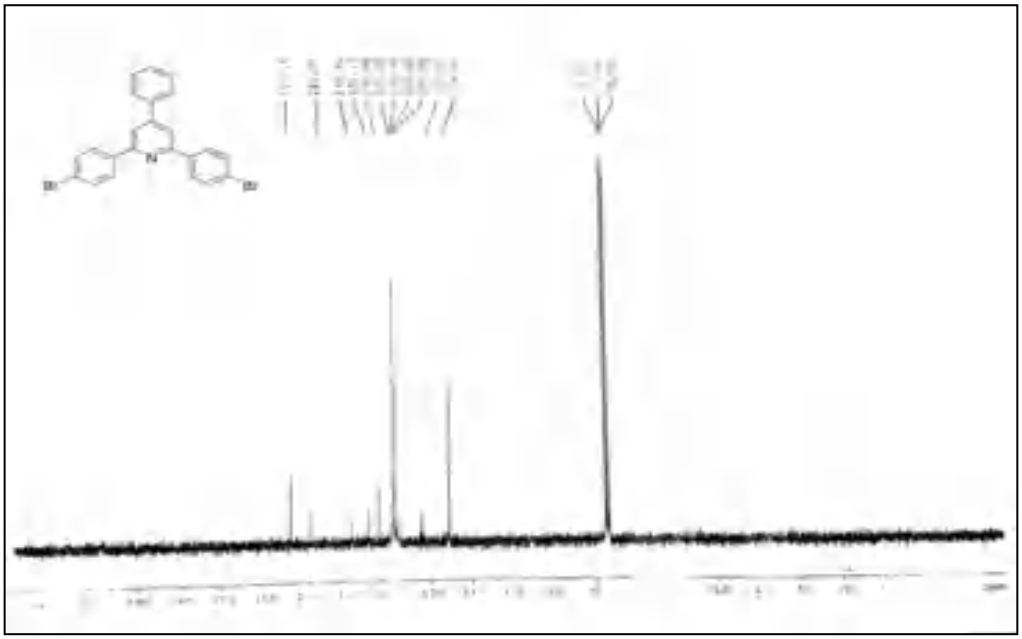
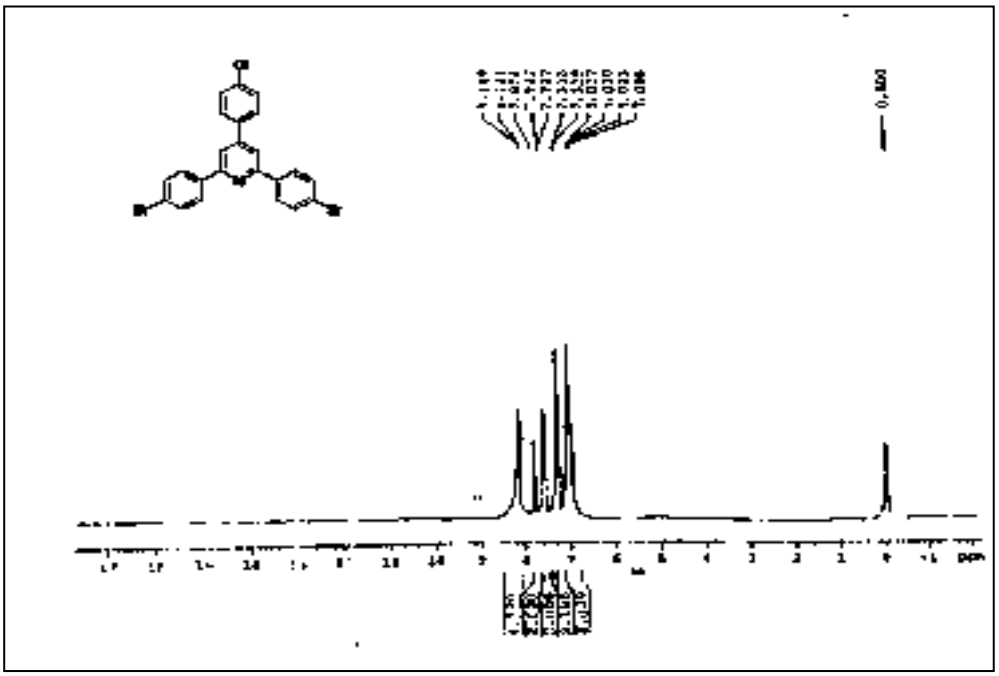
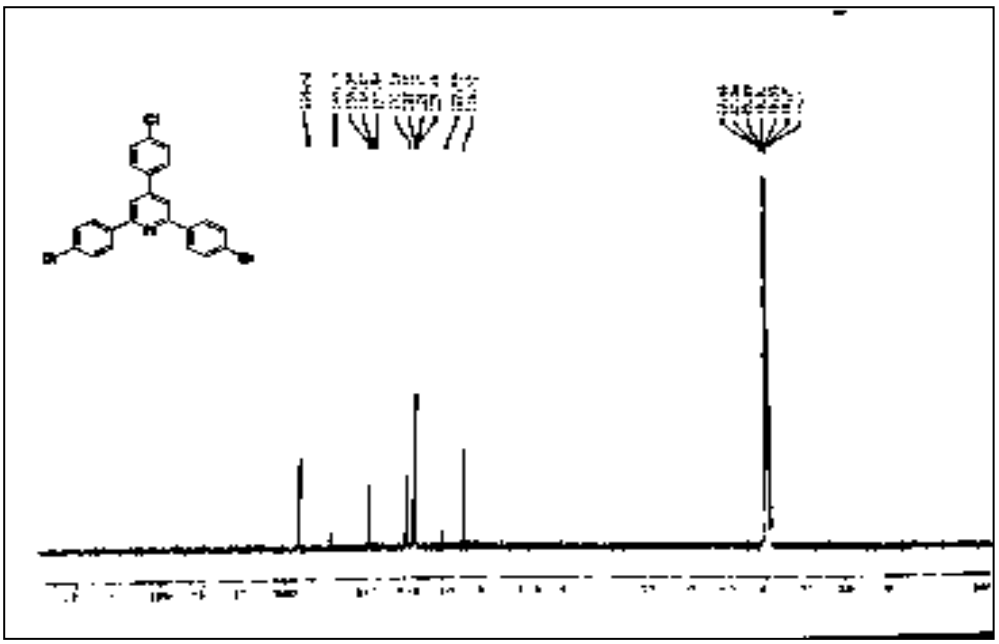


Figure I.C.10. *Scanned copy of ^{1}H and ^{13}C NMR spectra of 2,6-bis(4-bromophenyl)-4-(4-chlorophenyl)pyridine*





I.C.6. References

References are given in Bibliography under Chapter I, Section C