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Supplementary information

Pseudo six-component process for the synthesis of tetrahydrodipyrazolo pyridines using Ionic liquid immobilized on $FeNi_3$ nanocatalyst

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Preparation of $FeNi_3$ nanoparticles (method a)
At first $FeNi_3$ nanoparticles were prepared according to method reported in the literature with some modifications [23]. $FeCl_2{\cdot}4H_2O$ and $NiCl_2{\cdot}6H_2O$ (the total amount of Fe^{2+} and Ni^{2+} was 0.04 mol) were dissolved into 200 ml deionized water to form a preliminary reaction solution. Certain amounts of sodium hydroxide (NaOH) solution were added into the former solution with moderate stirring. Adjust the amount of added NaOH solution carefully so that the pH value was in the range $10 \leq pH \leq 13$. At this moment, a dark brown suspension was formed. 0.16 mol aqueous hydrazine ($N_2H_4{\cdot}H_2O$, 80% concentration (Hydrazine solutions are hazardous because of their toxic, corrosive, flammable or explosive properties. Hydrazine solutions should always be handled with great care. Avoid inhaling the vapours from hydrazine solutions at all times and whenever possible use a reliable fume hood. Avoid skin contact with hydrazine at all times)) was then added into the above suspension. This reaction was continued for about 24 h. During this period, the pH value was kept in the range $10 \leq pH \leq 13$ by adding NaOH. Final resulting particles were separated magnetically and washed repeatedly until the pH value was 7. The suspension was repeatedly washed, filtered for several times and dried at 100 ºC in the air.

Preparation of $FeNi_3$ nanoparticles (method b)
At second $FeNi_3$ nanoparticles were prepared according to method reported in the literature with some modifications [20]. $FeCl_2{\cdot}4H_2O$ (1.72 g) and $NiCl_2{\cdot}6H_2O$ (4.72 g) were dissolved in 80 mL of deaerated highly purified water contained in a three neck flask with vigorous stirring (800 rpm) under nitrogen. As the temperature was elevated to 80 °C, 10 mL of ammonium hydroxide was added drop by drop, and the reaction was maintained for 30 min. hydrazine hydrate (20 mL, 80% concentration) was added to the above suspension. The black product was separated by putting the vessel on a permanent magnet and the supernatant was decanted. The black precipitate was washed for six times with highly purified water to remove the unreacted chemicals, then the black product $FeNi_3$ was dried in the vacuum.

General procedure for the preparation of $FeNi_3/SiO_2$nanoparticles

$FeNi_3$-ILs MNPs was prepared according to the procedure reportedin the literature with some modification [20].Firstly, a mixture of ethanol (100 mL) and distilled water (20 mL) was added to magnetic nanoparticles ($FeNi_3$ NPs) (1 g), and the resulting dispersion was sonicated for 15 min. After adding ammonia water (3 mL), tetraethyl orthosilicate (TEOS, 2.2 mL) was added to the reaction solution. The resulting dispersion was under mechanically stirred continuously for 20 h at room temperature. The magnetic $FeNi_3/SiO_2$ nanoparticles were collected by magnetic separation and washed with ethanol and deionized water in sequence.

General procedure for the preparation of $FeNi_3/SiO_2/SO_3H$ nanoparticles

To a round-bottomed flask (100 mL) $FeNi_3/SiO_2$ MNPs (0.40 g) in CH_2Cl_2 (50 mL), was added chlorosulfonic acid (12 mmol) dropwise over a period of 20 min at room temperature (Fig. 1). After vigorous stirring for 24 h, the magnetic $FeNi_3/SiO_2/SO_3H$ nanoparticles were collected by magnetic separation and washed with ethanol and deionized water in sequence.

General procedure for the preparation of $FeNi_3$-ILs nanoparticles

Ethanolamine (5 mmol) was dispersed in dry CH_2Cl_2 (20 mL) and $FeNi_3/SiO_2/SO_3H$ (0.1 g) nanoparticles were added. Then the mixture was heated to 60 °C for 15 h under nitrogen atmosphere. The resulting solid was separated by an external magnet and washed 4 times with CH_2Cl_2, ethanol and H_2O. After drying at room temperature in vacuum, $FeNi_3$-ILs was obtained as reddish-brown powder**.**

General procedure for the preparation of tetrahydrodipyrazolopyridines*:*

A mixture of hydrazine hydrate 80% (2.0 mmol) and ethyl acetoacetate (2.0 mmol) and $FeNi_3$-ILs MNPs (0.002 gr) in EtOH (5 mL) was magnetically stirred at 25 °C followed by addition of aldehyde (1.0 mmol) and ammonium acetate (4.0 mmol). The reaction mixture was heated at reflux for 40-50 min and then cooled to 25 °C. After completion of the reaction monitored by TLC, 10 mL ethanol was added to the reaction mixture and the catalyst $FeNi_3$-ILs MNPs was separated by external magnetic field. The precipitate was washed with EtOH to afford the pure product and then dried well under vacuum pump.

Table S1. The XRD data of $FeNi_3$-ILs MNPs

Pos. [º2Th.]	FWHM [º2 Th.] (method a)	FWHM [º2 Th.] (method b)
44.2790	0.2803	0.1801
51.5361	0.5065	0.4055
61.0906	1.0816	0.8013
75.8084	0.7513	0.8304
Size	30-35	50-55

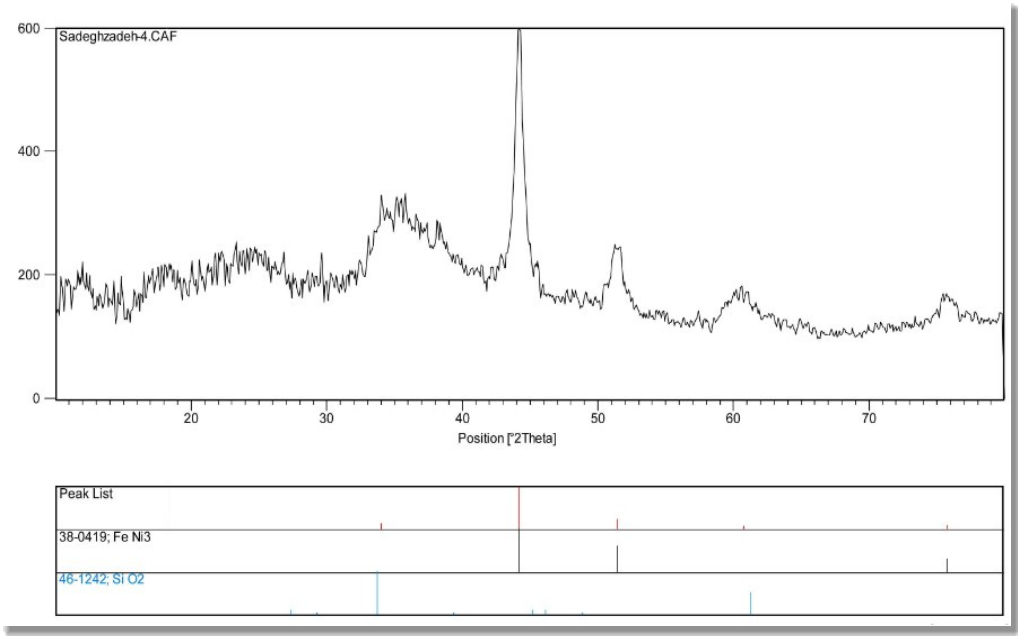

Fig S1.XRD analysis of $FeNi_3$-ILs MNPs (method a)

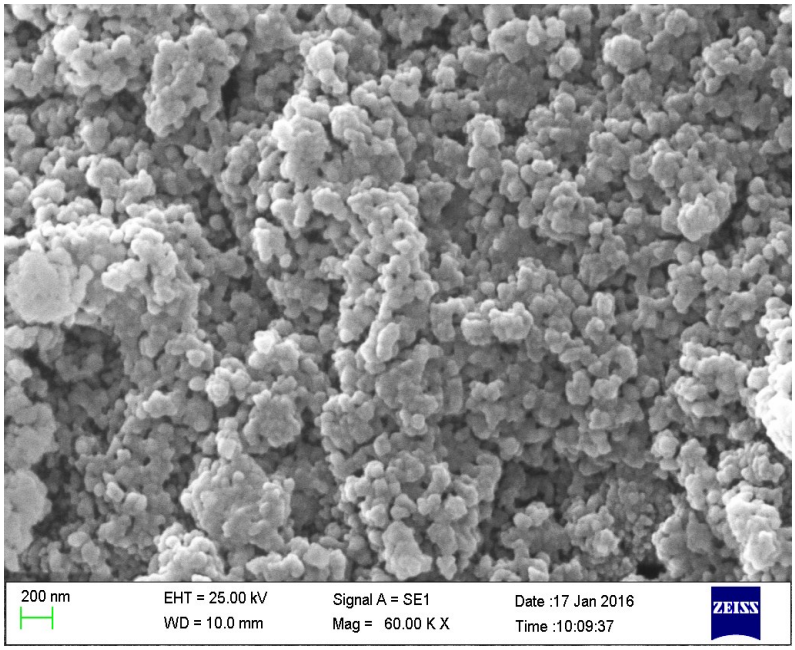

Fig. S2.SEM images of $FeNi_3$-ILs MNPs (method a)

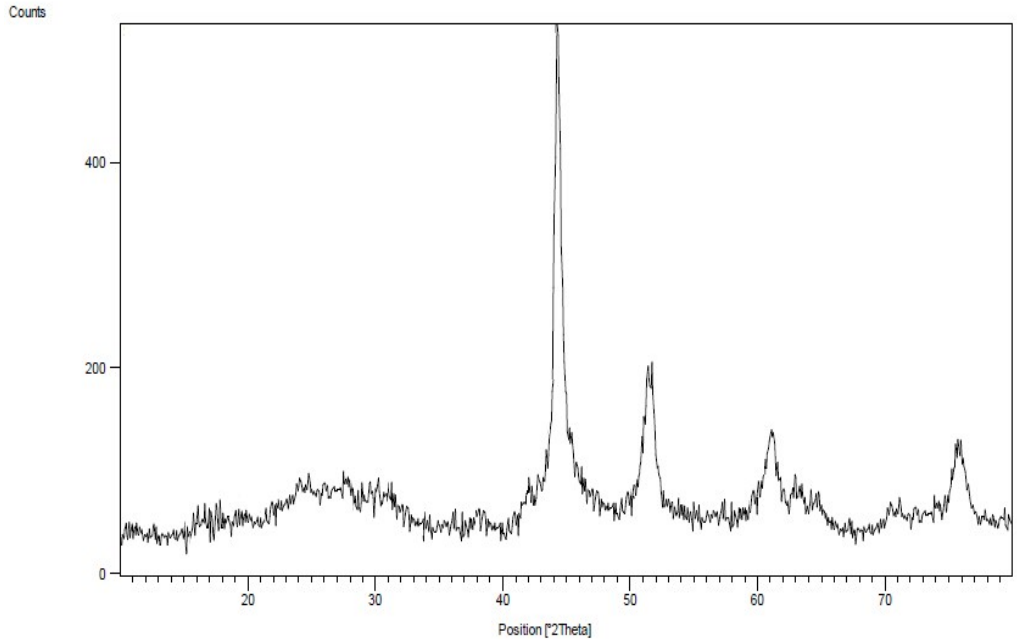

Fig S3.XRD analysis of $FeNi_3$-ILs MNPs (method b)

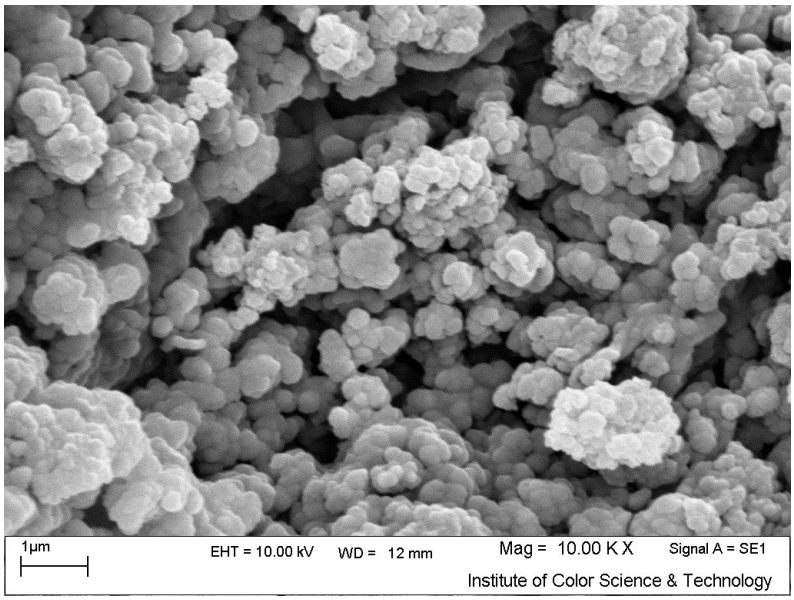

Fig. S4. SEM images of $FeNi_3$-ILs MNPs (method b)

3,5-Dimethyl-4-(4-nitro-phenyl)-1,4,7,8-tetrahydrodipyrazolo[3,4-b;4',3'-e]pyridine (5a)

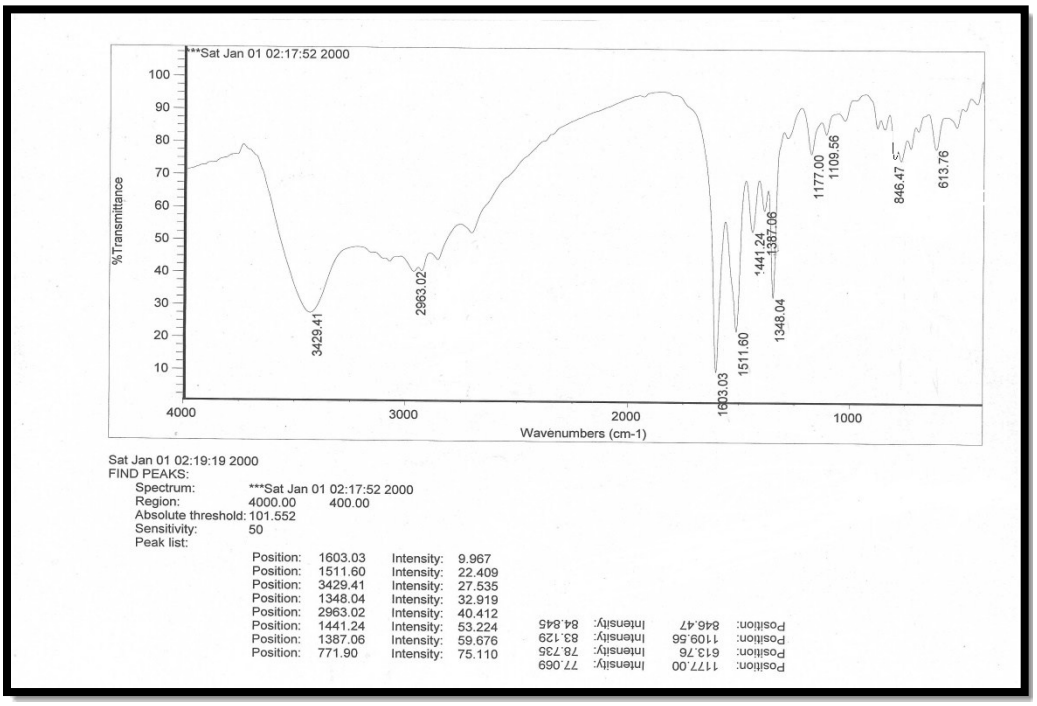

Fig S3: IR of 5a

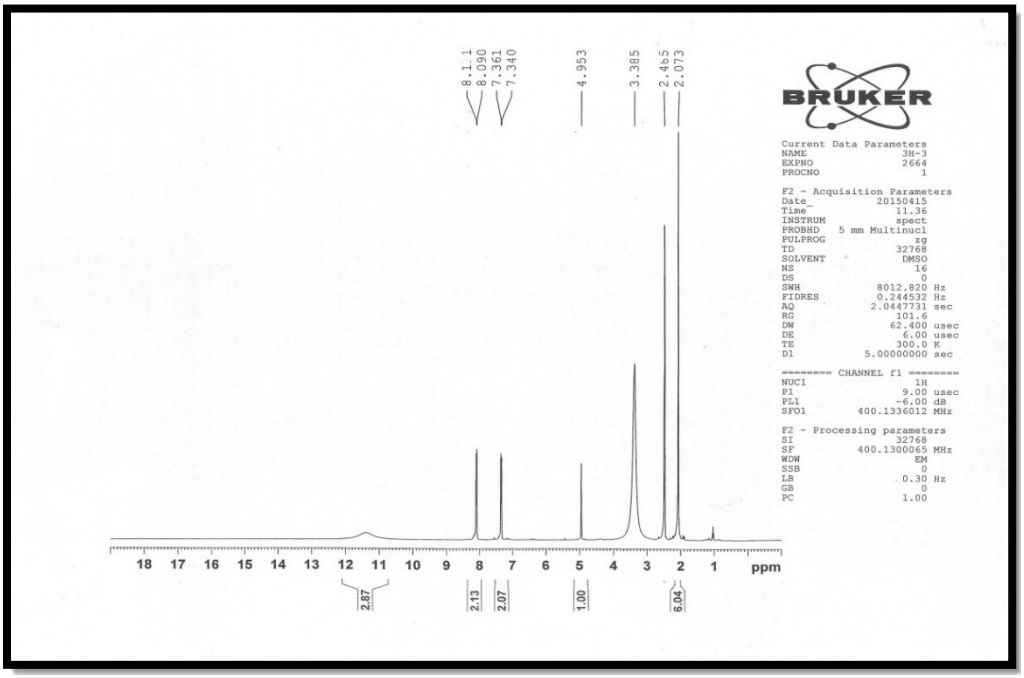

Fig S4: ^{1}H NMR of 5a

3,5-Dimethyl-4-(3-nitro-phenyl)-1,4,7,8-tetrahydrodipyrazolo[3,4-b;4',3'-e]pyridine (5b)

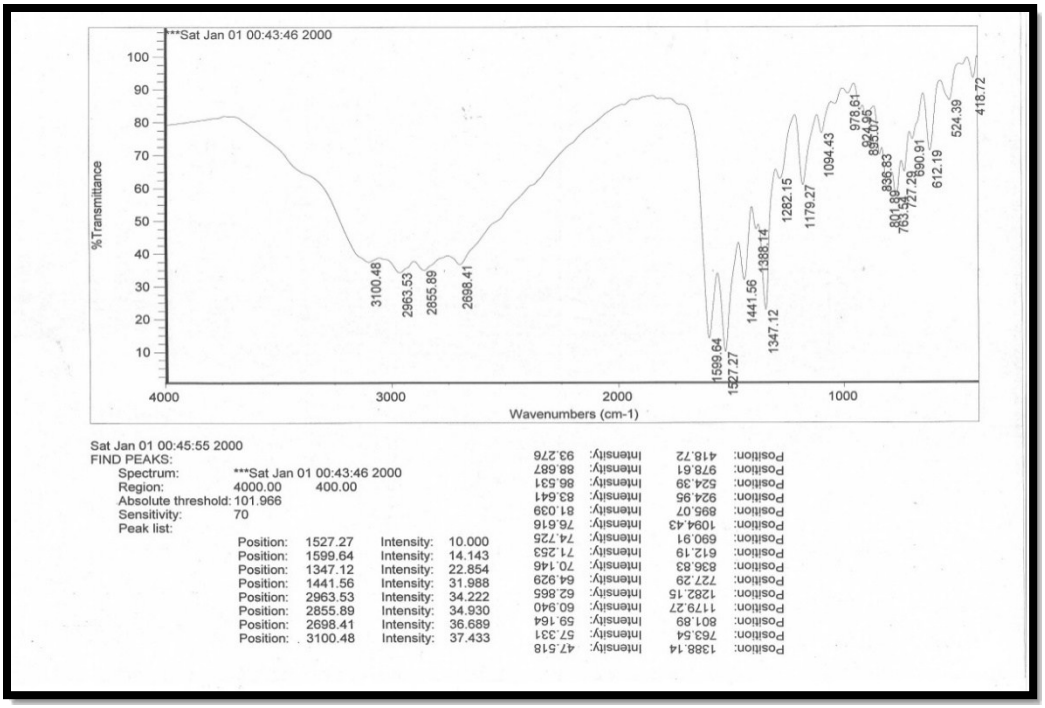

Fig S5: IR of 5b

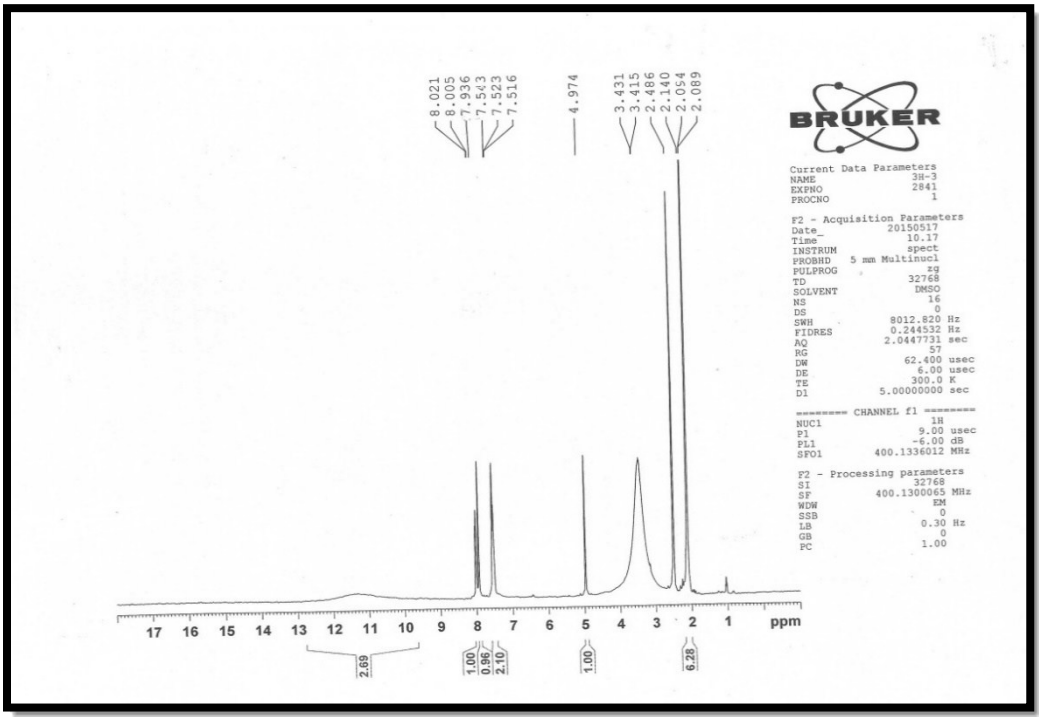

Fig S6: ^{1}H NMR of 5b

3,5-Dimethyl-4-(4-methyl-phenyl)-1,4,7,8-tetrahydro di pyrazolo [3,4-b;4',3'-e]pyridine (5c):

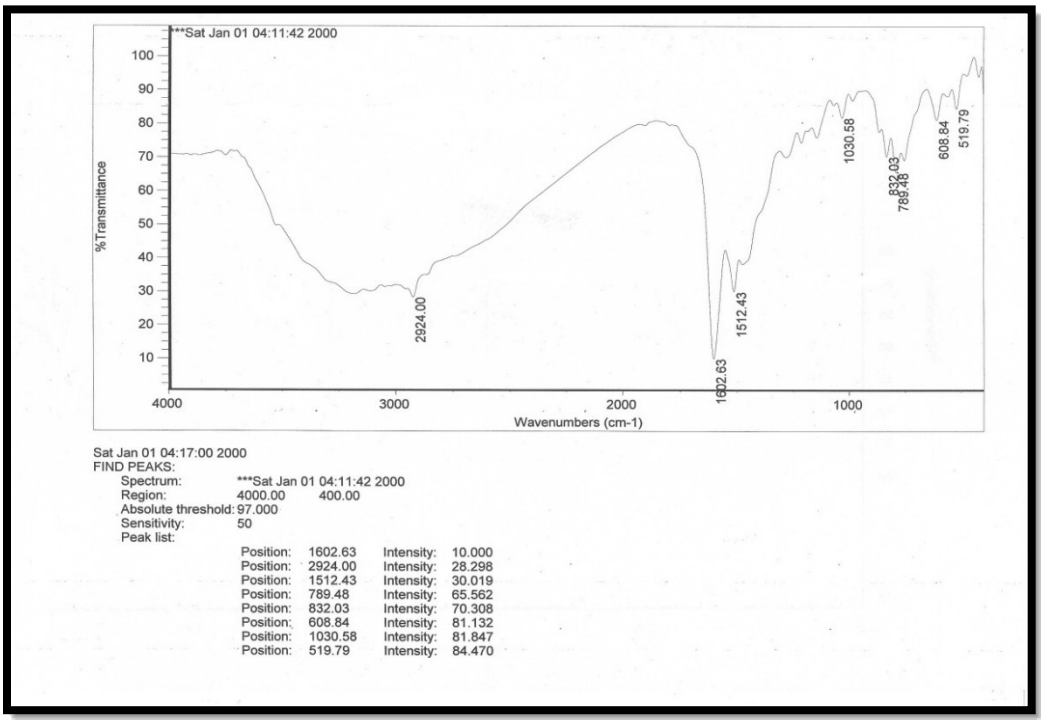

Fig S7: IR of 5c

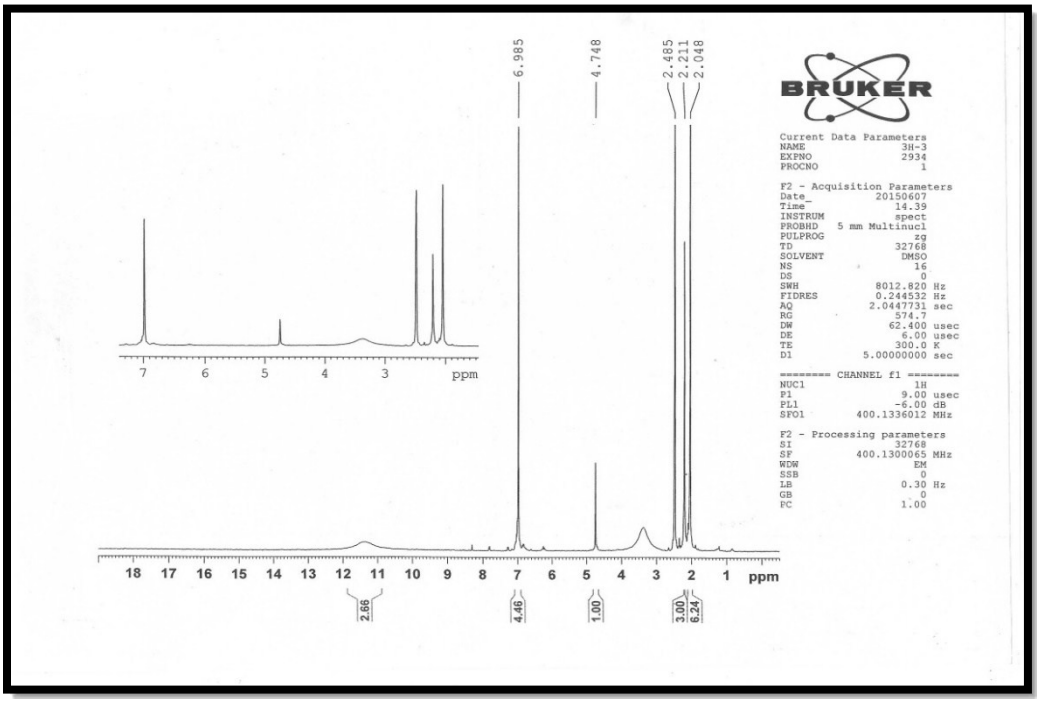

Fig S8: ^{1}H NMR of 5c

3,5-Dimethyl-4-(4-methoxy-phenyl)-1,4,7,8-tetrahydro dipyrazolo [3,4-b;4',3'-e]pyridine (5d):

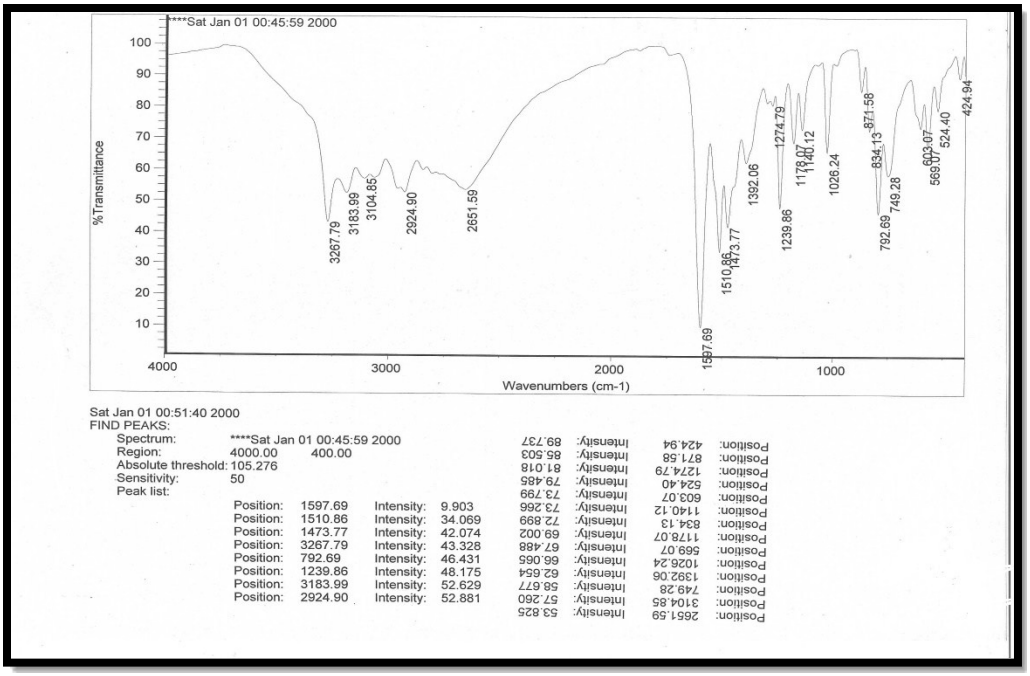

Fig S9: IR of 5d

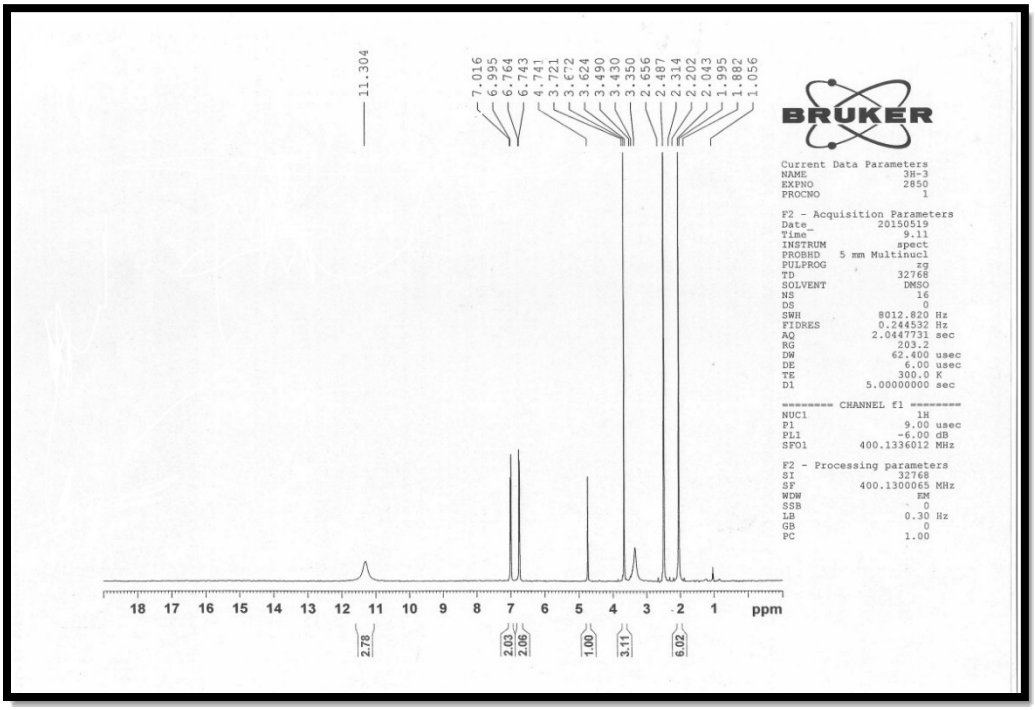

Fig S10: ^{1}H NMR of 5d

1,4,7,8-Tetrahydro-3,5-dimethyl-4-phenyldipyrazolo-[3,4-b:4',3'-e]pyridine (5e):

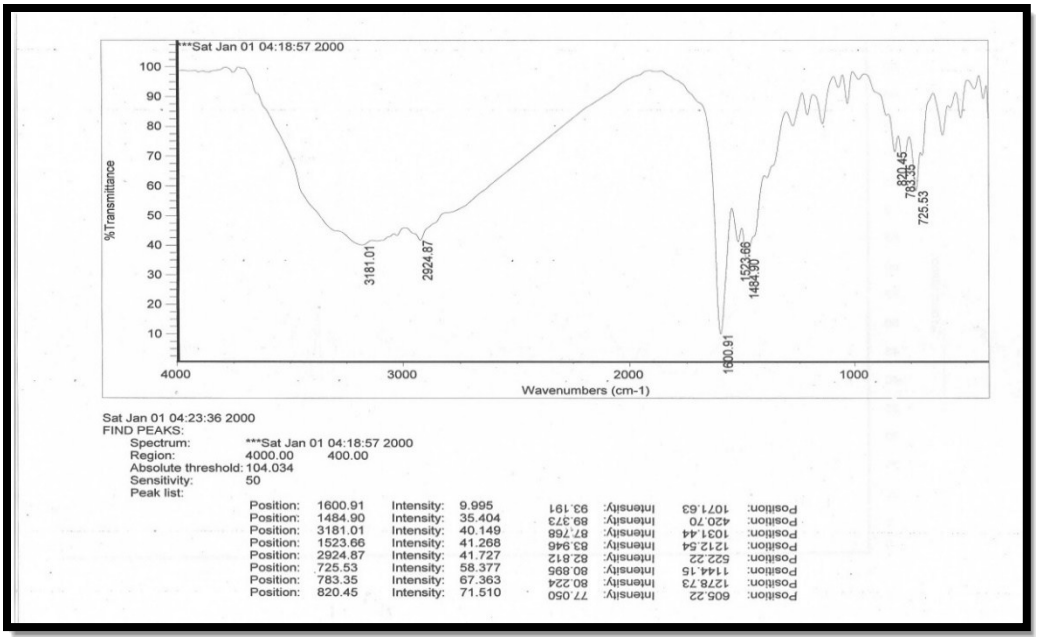

Fig S11: IR of 5e

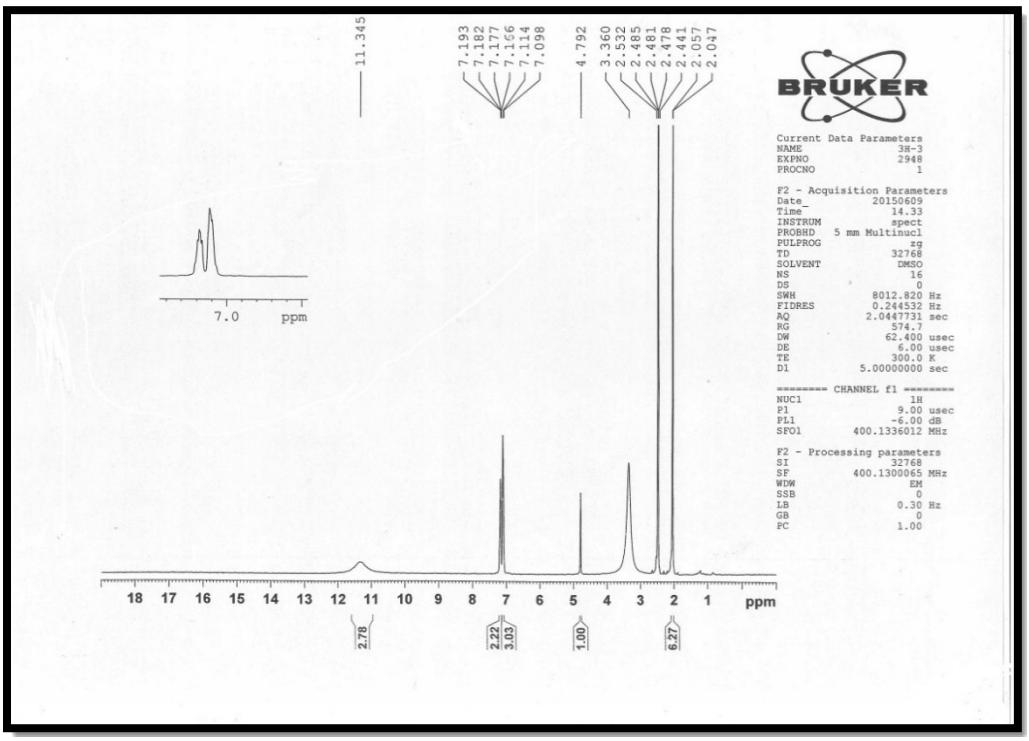

Fig S12: ^{1}H NMR of 5e

3,5-Dimethyl-4-(2-methyl-phenyl)-1,4,7,8-tetrahydro dipyrazolo [3,4-b;4',3'-e]pyridine (5f)

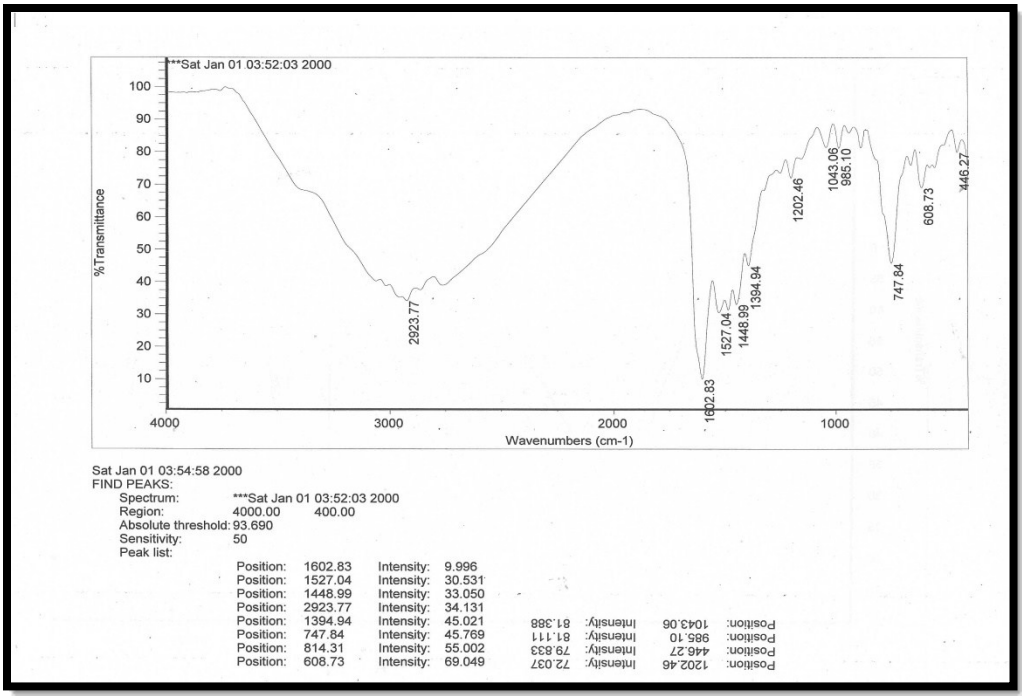

Fig S13: IR of 5f

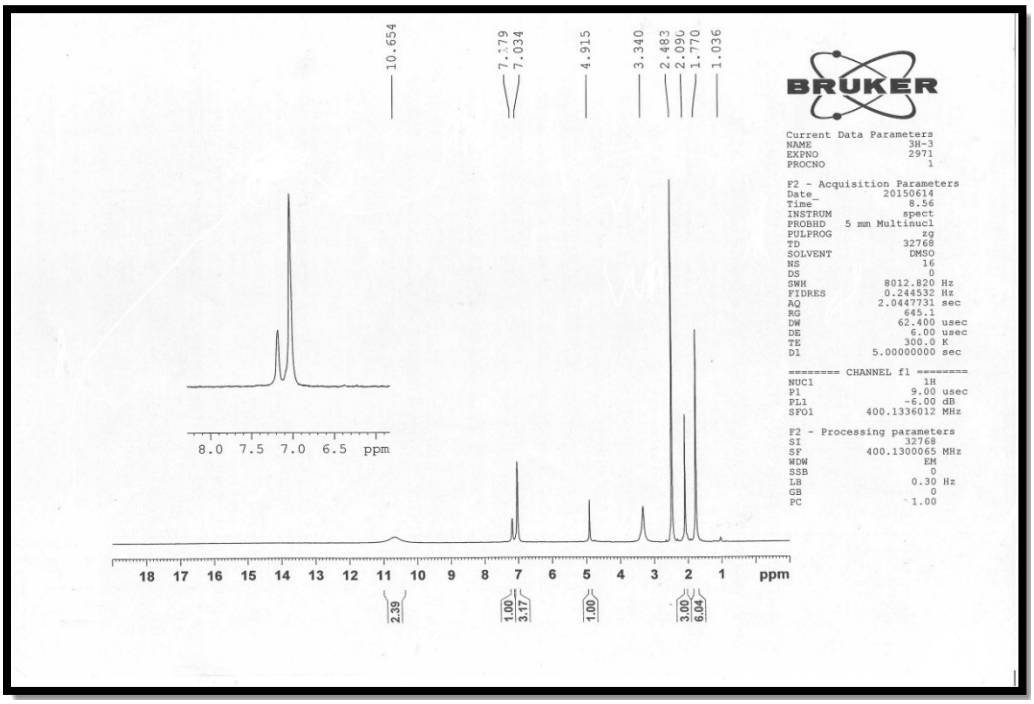

Fig S14: ^{1}H NMR of 5f

3,5-Dimethyl-4-(4-chloro-phenyl)-1,4,7,8-tetrahydro di pyrazolo [3,4-b;4',3'-e]pyridine (5g):

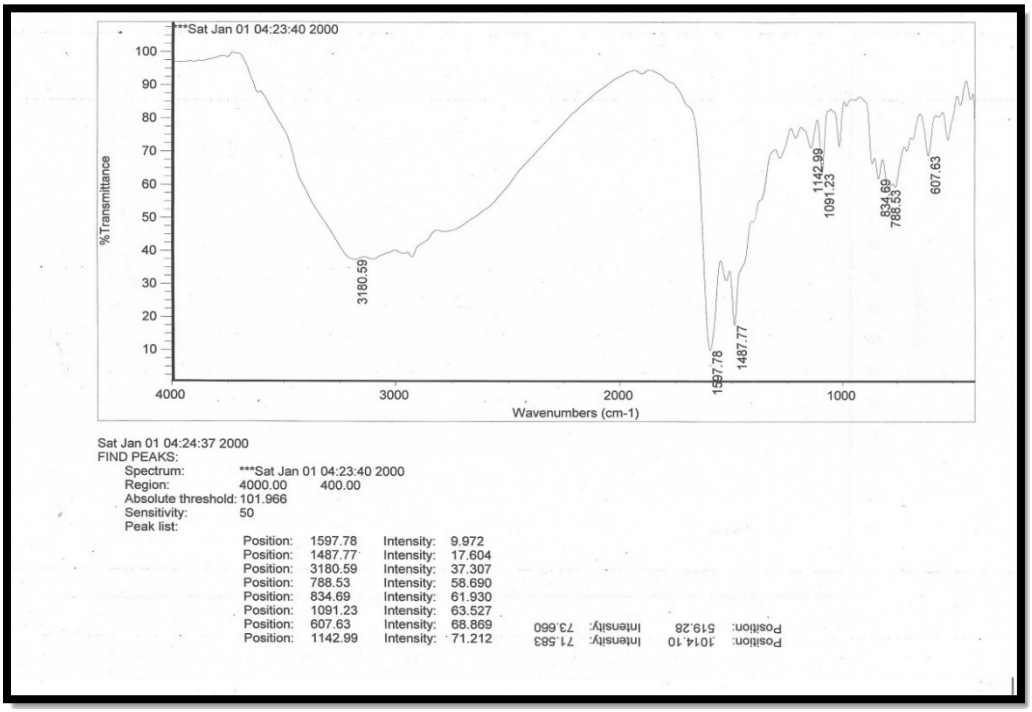

Fig S15: IR of 5g

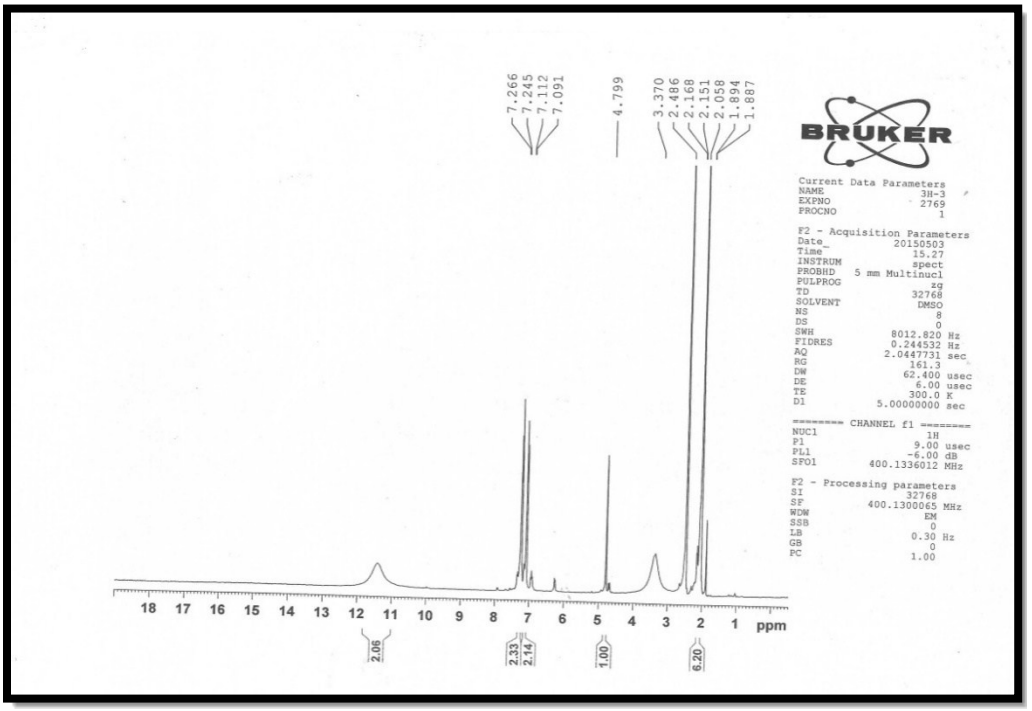

Fig S16: ^{1}H NMR of 5g

3,5-Dimethyl-4-(4-bromo-phenyl)-1,4,7,8-tetrahydro di pyrazolo [3,4-b;4',3'-e]pyridine (5h)

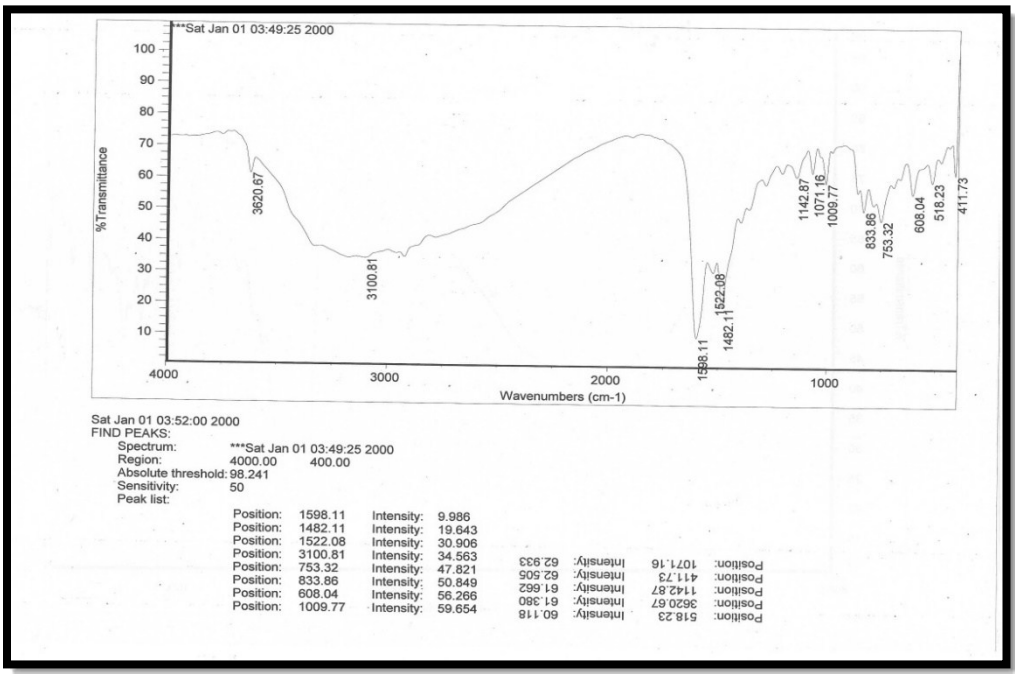

Fig S17: IR of 5h

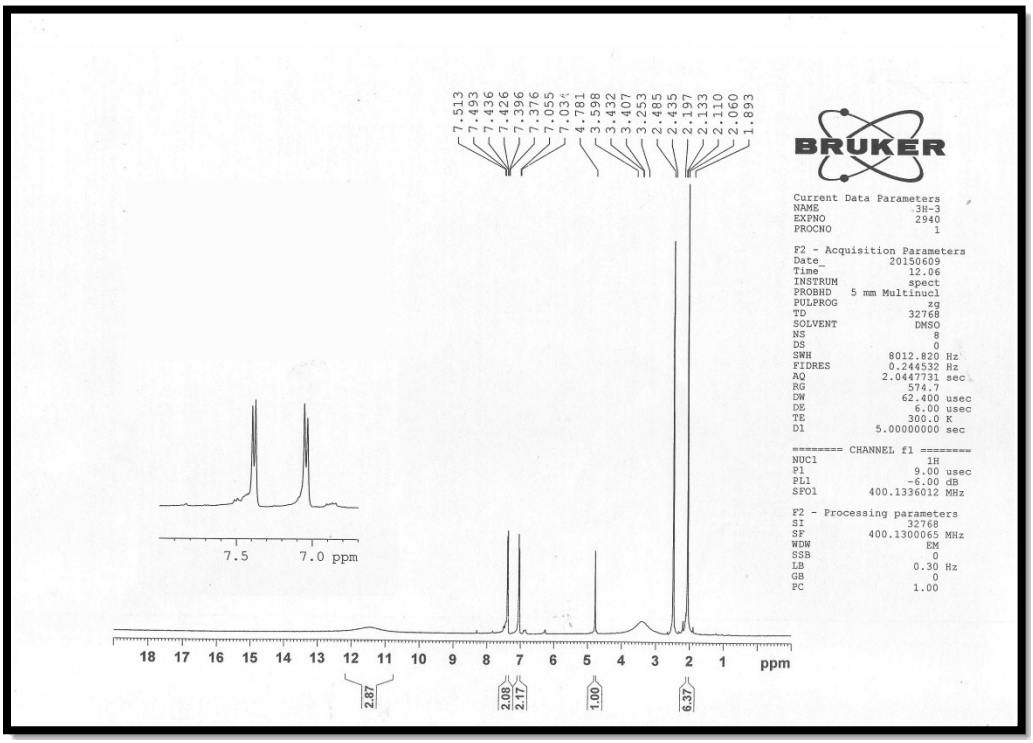

Fig S18: ^{1}H NMR of 5h

4-(1,4,7,8-Tetrahydro-3,5-dimethyldipyrazolo[3,4-b:4',3' e]pyridin-4-yl)-N,N-dimethylaniline (5i):

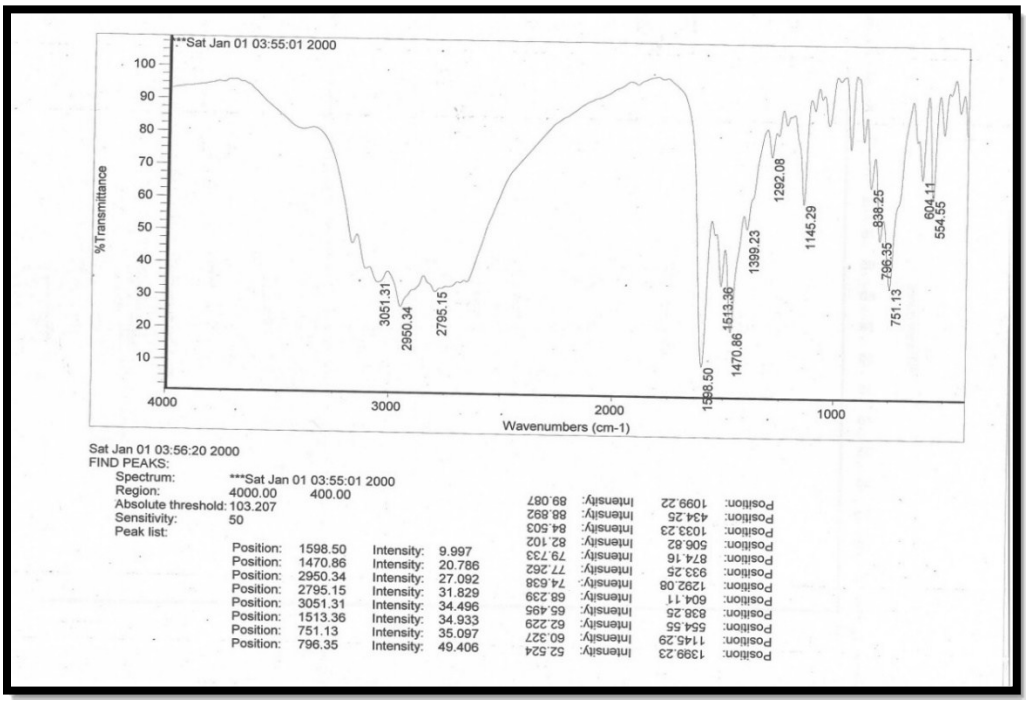

Fig S19: IR of 5i

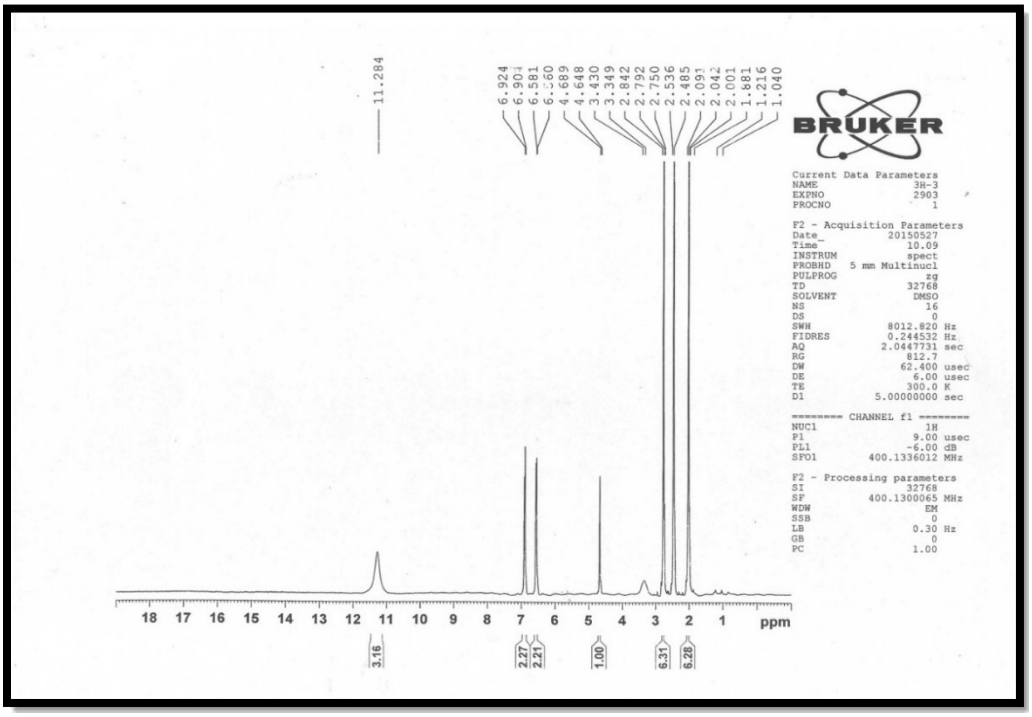

Fig S 20: ^{1}H NMR of 5i

3,5-Dimethyl-4-(4-hydroxy-phenyl)-1,4,7,8-tetrahydro di pyrazolo [3,4-b;4',3'-e]pyridine (5j):

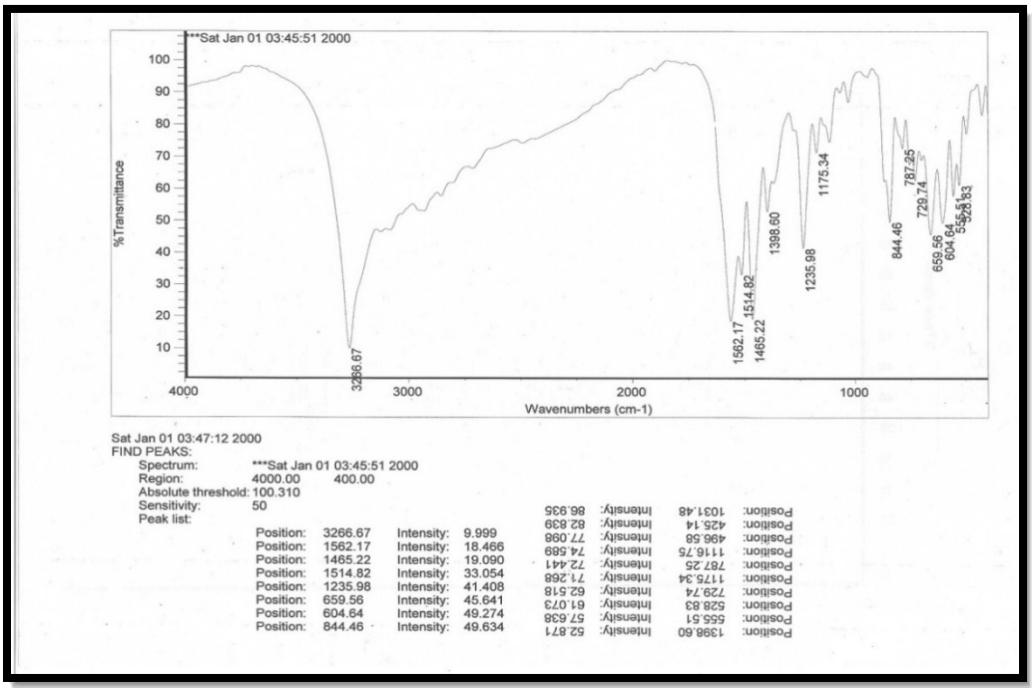

Fig S21: IR of 5j

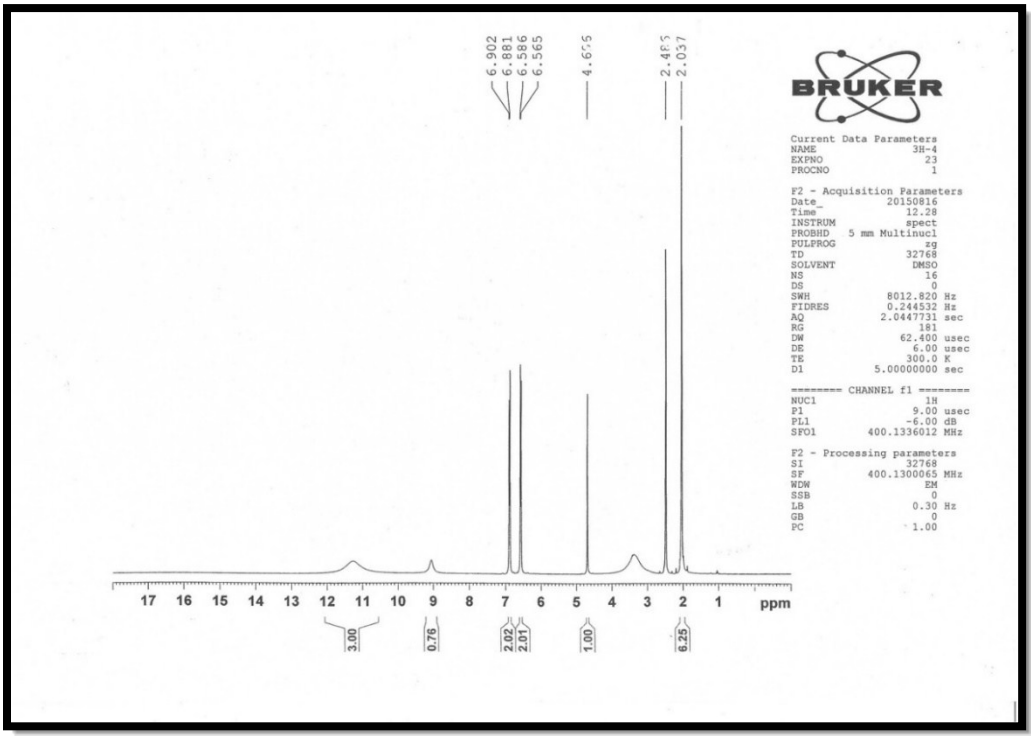

Fig S 22: ^{1}H NMR of 5i

3,5-Dimethyl-4-(2-nitro-phenyl)-1,4,7,8-tetrahydrodipyrazolo[3,4-b;4',3'-e]pyridine (5k):

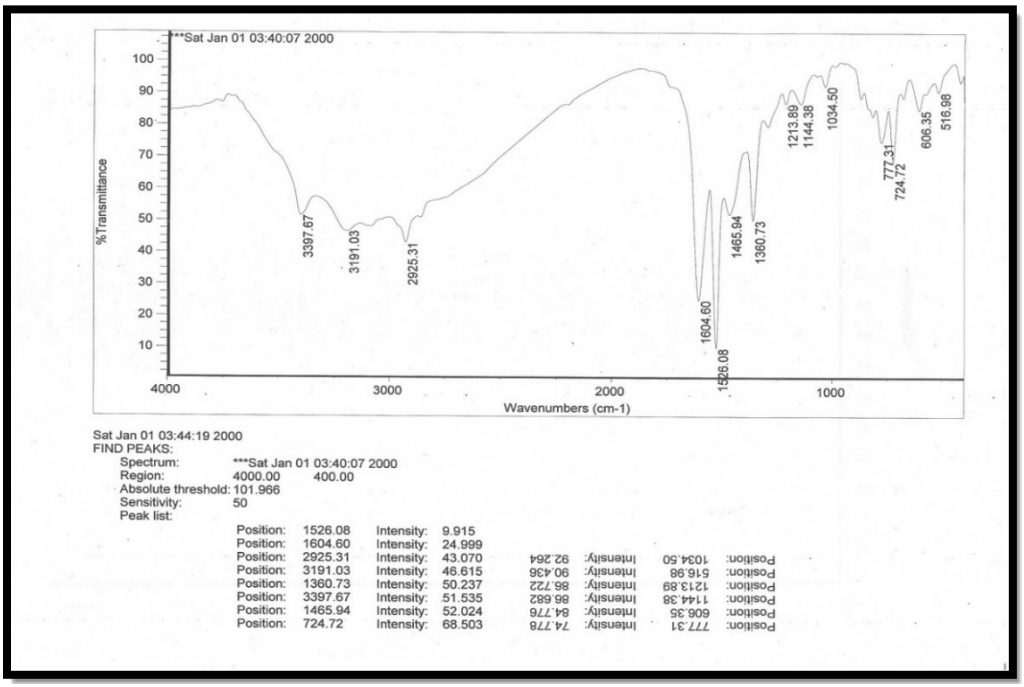

Fig S23: IR of 5k

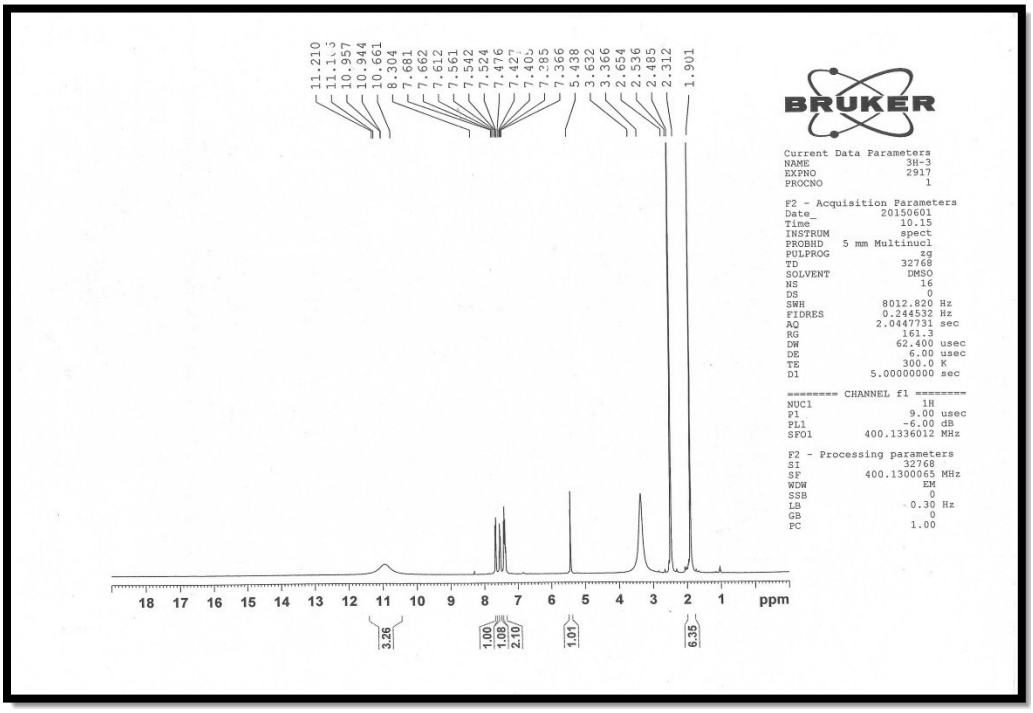

Fig S 24: ^{1}H NMR of 5k

1,4-Bis[(1,4,7,8-Tetrahydro-3,5-dimethyldipyrazolo[3,4-b:4',3'-e]pyridin-4-yl)] benzene (5l):

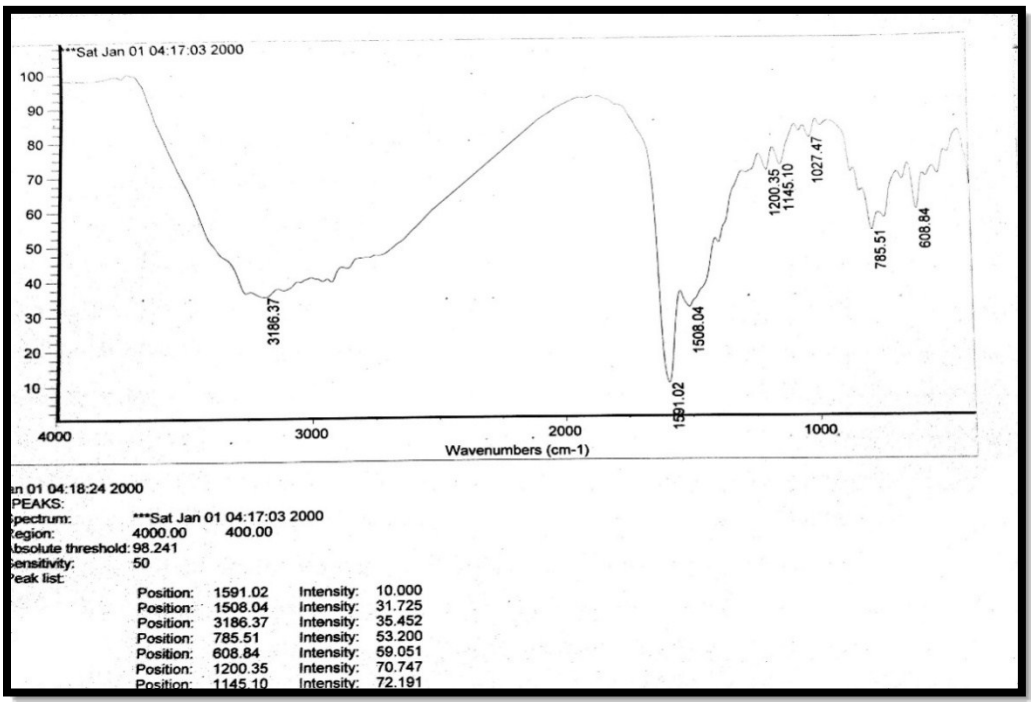

Fig S25: IR of 5l

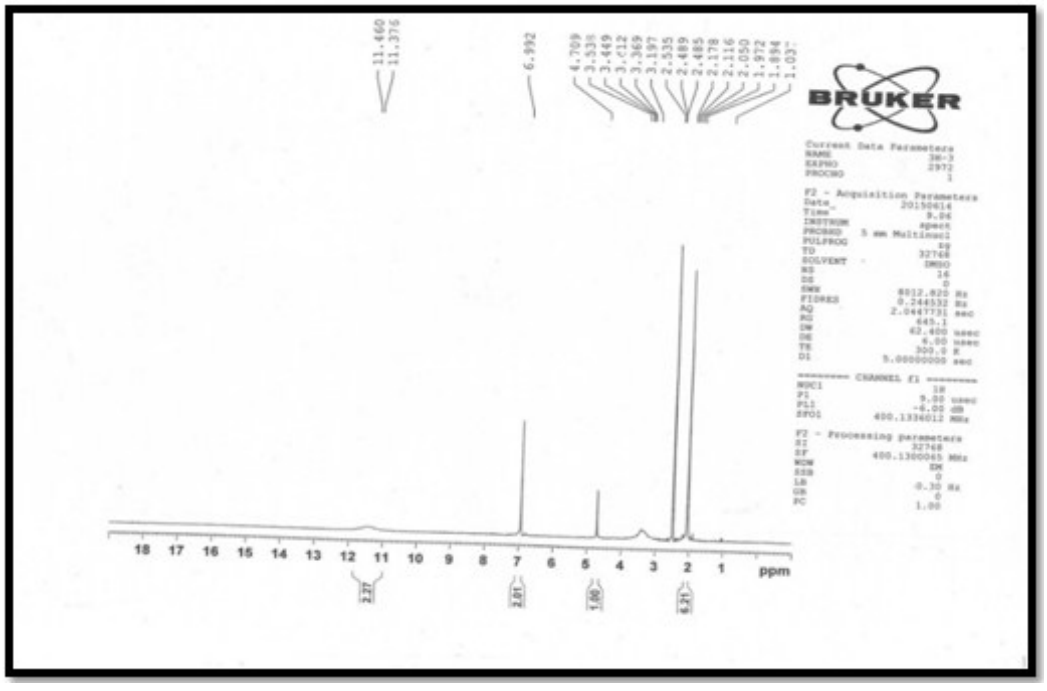

Fig S 26: ^{1}H NMR of 5l

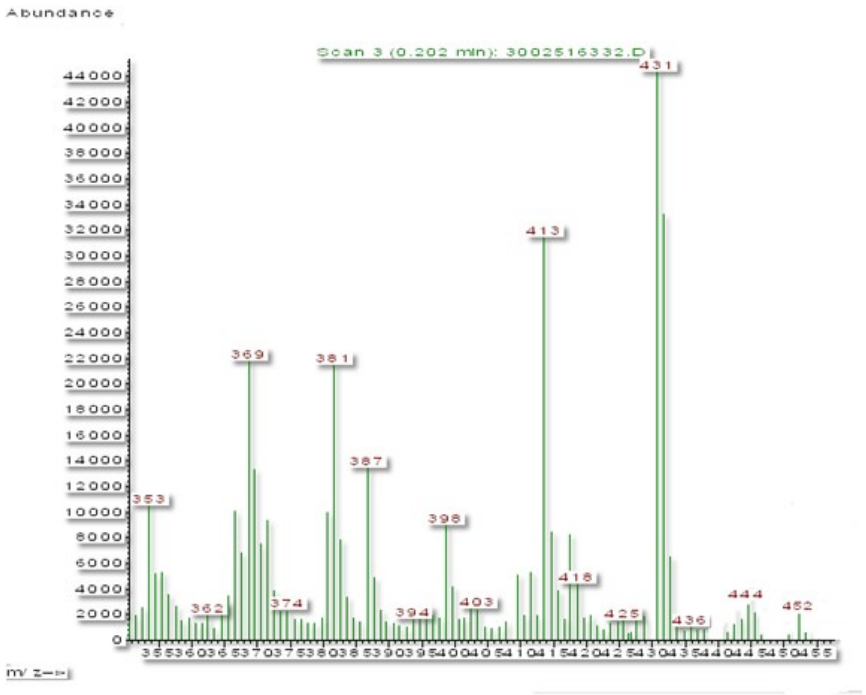

Fig S 27: [1]MS of 5l