Supporting information

Transfer Hydrogenation of Carbonyl Compounds and Carbon-Carbon Multiple Bonds by Zeolite Supported Cu Nanoparticles

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S1. Materials

Na Y zeolite, Copper (II) nitrate and other starting materials were purchased from Sigma-Aldrich. Hydrazine hydrate (A.R.) and 2-propanol was obtained from Merck. All the organic solvents used in our experiments were analytically pure and were used with further purification.

S2. Characterization of materials

UV-Vis. DRS were recorded using the JASCO-Spectra Manager (V-550). The XRD pattern of the catalyst samples was measured with a PW3050/60 (XPERT-PRO Diffractometer system) instrument using a Cu Kα radiation at room temperature. The XPS spectrum was taken by ESCA model VG 3000 system. High resolution transmission electron microscopy (HRTEM) images were obtained using a Philips CM12 TEM operating at 200 kV. The electron diffraction pattern was also recorded for the selected area. The percentage conversion and relative yield of the final products were calculated using gas chromatography (Shimadzu GC-17A model, ZB-5 (10%) capillary column with FID detector using high purity nitrogen as carrier gas). NMR spectra were registered on Bruker DRX spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C NMR. All ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ with TMS as the internal standard.

S3. Preparation and Characterization of Copper-exchanged zeolite (Cu^{II}-Y zeolite)[1a]

Copper exchanged zeolite (Cu^{II}-Y zeolite) were obtained by an ion-exchange method, NaY zeolite (10 g) was stirred with $Cu(NO_3)_2 \cdot 3H_2O$ (100 ml, 10%) solution at 90 ^{o}C for about 12 hrs. The exchange was repeated at least four times. Each time, after exchange, the zeolite powder was repeatedly washed with distilled water and then dried. All these cation-exchanged zeolites were activated at 450 ^{o}C for about 6 hrs. We have obtained 10.56 percentage of copper loading as evident from EDX (Fig. 1).

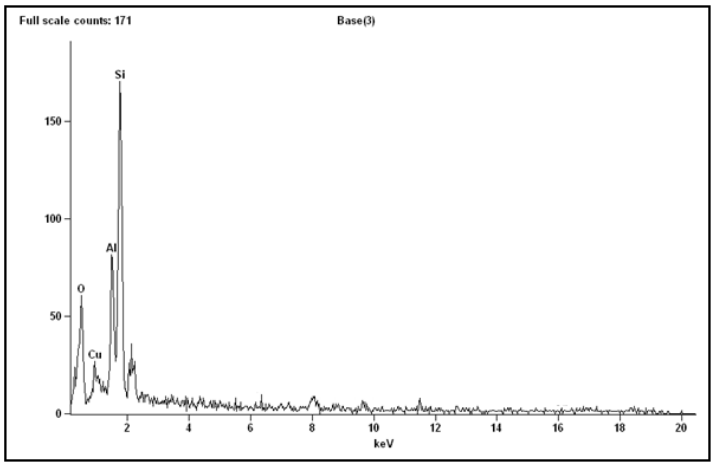


Fig. 1. EDX for Copper cation exchanged zeolite

Element Line	Net Counts	Weight %	Atom %	Formula
O K	416	36.05	51.91	O
Al K	724	13.73	11.72	Al
Si K	1973	39.66	32.54	Si
Cu K	102	10.56	3.83	Cu
Cu L	97	---	---	
Total		100.00	100.00	

Table 1. Percentage of elements present in Cu exchanged zeolite

S4. Synthesis of zeolite supported copper nanoparticles

After activation one gm of copper exchanged zeolite (Cu^{II}-Y zeolite) was treated with one ml of hydrazine hydrate in ethanolic solution. The solution was stirred at 50 ^{o}C for about 15-30 min. The color of the sample changed from light green to dark brown during the treatment with hydrazine hydrate, indicating the formation of copper nanoparticles within the zeolite. After the reduction, the solid powders were recovered by filtration and washed with ethanol to remove the excess of hydrazine hydrate. The recovered samples were dried in vacuum. The synthesized copper nanoparticles in zeolite Y were characterized by UV-Vis. DRS, powder-XRD, XPS and HRTEM (Fig. 2-5).

S5.Characterization of zeolite supported copper nanoparticles (CuNPs/zeolite)

a) UV-Vis. DRS

The UV-DR Spectrum (Fig. 2a) of Cu nanoparticle shows a peak observed at 590 nm which was attributed to the surface plasmon resonance band of Cu nanoparticles which provide an evidence for generation of Cu nanoparticles. UV-Vis. DRS of first to sixth run of the catalyst was recorded and shown in (Fig. 2b). Up to fourth run, the structural charactericstic peak of copper nanoparticles (590 nm) was not altered. Only after 5th run, a peak at ~650 nm which corresponds to CuO is seen.

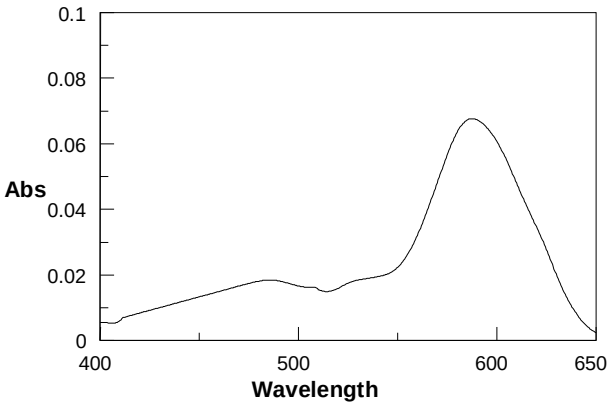


Fig. 2a. UV-Vis DRS recorded for freshly prepared catalyst

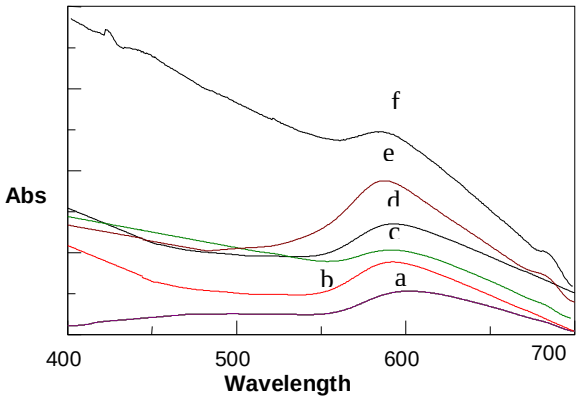


Fig. 2b) UV-Vis. DRS of catalyst a) after first b) second, c) third, d) fourth, e) fifth and f) sixth run.

S6. Powder XRD pattern of zeolite supported copper nanoparticles

X-ray powder diffraction patterns of Cu exchanged zeolite and zeolite supported Cu nanoparticles are shown in Figs. 3a and 3b. The peak positions at 2θ values 43.1°, 50.3° and 73.9° indicated by astericks corresponding to [111], [200] and [220] (Fig. 3b) are consistent with Cu nanoparticles.

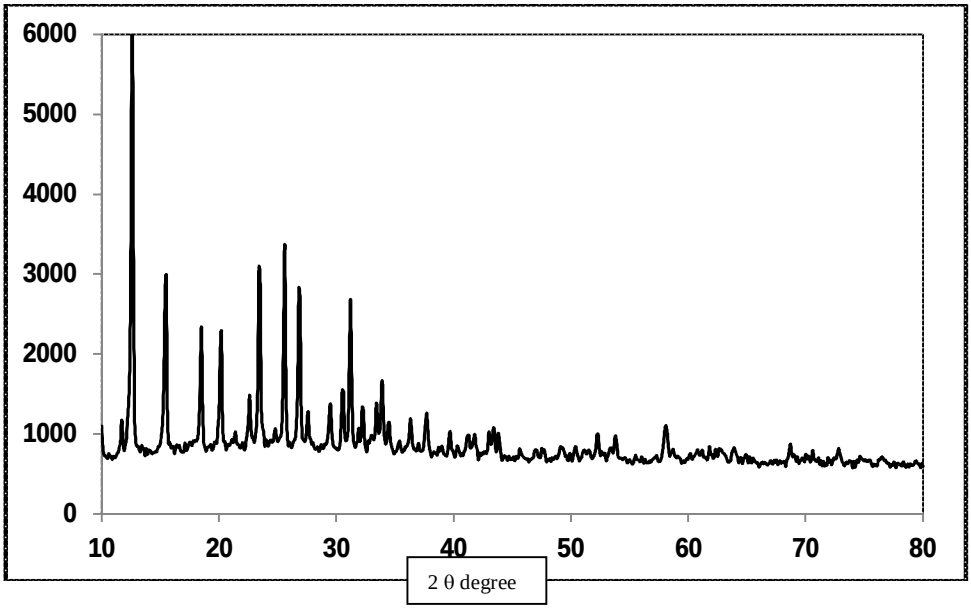


Fig. 3a. Powder XRD patterns of copper exchanged zeolite Y (Cu^{II}-Y zeolite)

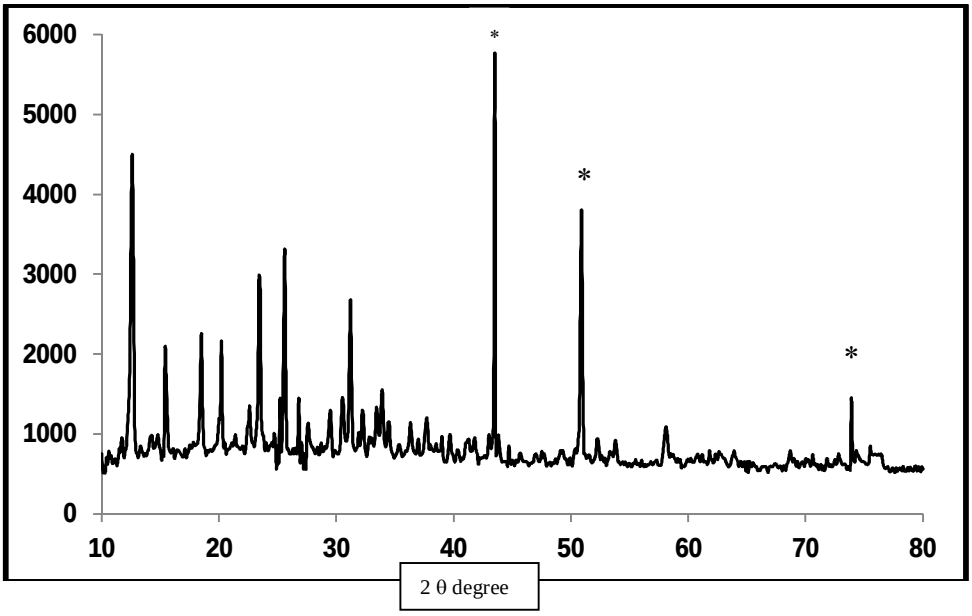


Fig. 3b. Powder XRD patterns of zeolite supported Cu nanoparticles

S7. X-Ray photoelectron spectra (XPS) of zeolite supported copper nanoparticles

The oxidation states of Cu in the as-prepared zeolite supported copper nanoparticles were examined by X-ray photoelectron spectroscopy (XPS) and the obtained results are shown in Fig. 4. In the Cu 2p core level XPS spectra, the peaks corresponding to the Cu 2p3/2 is observed at around 932.4 ± 0.2 eV.[1b]

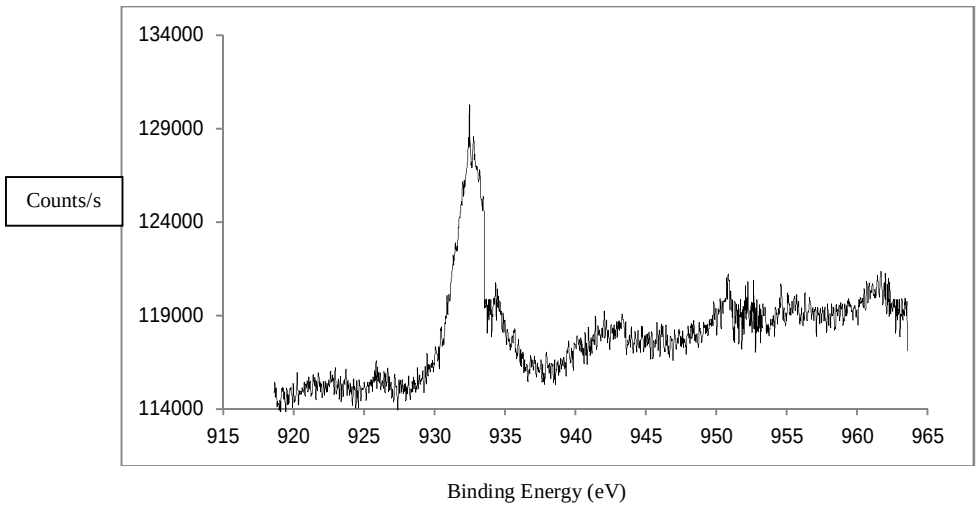


Fig. 4. X-Ray photoelectron spectra of zeolite supported Cu nanoparticles

S8. TEM image of zeolite supported Cu nanoparticles

The morphology and composition of copper nanoparticles in zeolite were investigated by HR-TEM. A typical high-resolution transmission electron micrograph (HRTEM) and the size distribution of the copper nanoparticles obtained in zeolite are shown in Fig. 5a. The size distribution of the nanoparticles was determined by measuring the sizes of individual particles in the TEM images (more than 100 particles) (Fig. 5b). It was found that the average diameter was 8 nm.

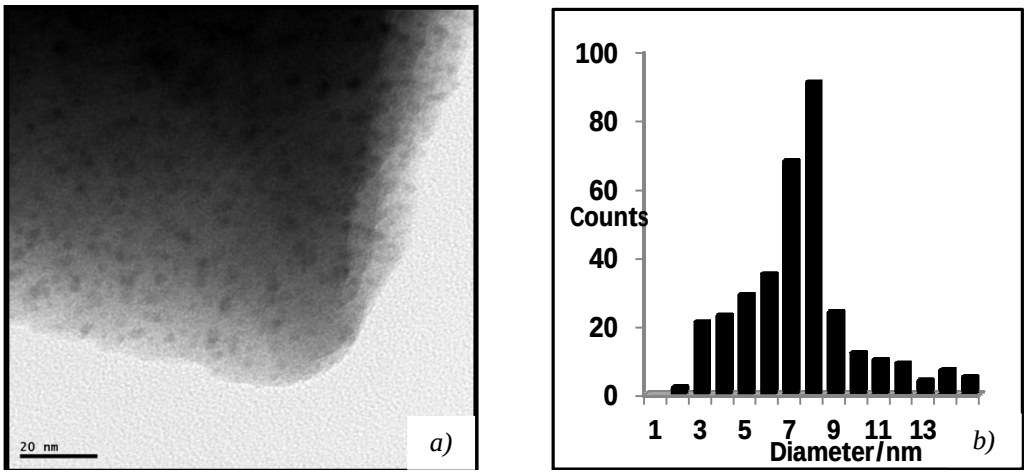


Fig. 5 a) HRTEM image and 5b) size distribution of zeolite supported Cu nanoparticles

S9. General procedure for the reduction of carbonyl compounds and olefin hydrogenation

The catalyst (30 mg) was suspended in 2 mL of 2-propanol followed by the addition of substrate (1mmol). This heterogeneous solution was heated at 70 ^{o}C in an autoclave bomb for 1h. After the completion of reaction, the products were quantitatively recovered by simple extraction with ethyl acetate. The reaction mixture was analyzed in GC and products were confirmed by ^{1}H and ^{13}C-NMR.

S10. Sheldon Test carried out with CuNPs/zeolite catalyzed reduction of carbonyl compounds

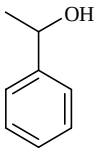
The catalyst (30 mg) was suspended in 2 mL of 2-propanol followed by the addition of acetophenone (1mmol). This heterogeneous solution was heated at 70 ^{o}C in an autoclave bomb for 30 min. The reaction mixture was filtered and the filtrate was further stirred for additional 2 hrs. The obtained results indicate that there is no appreciable leaching of metal ions during the present reaction conditions. To the recovered solid catalyst, reactants (acetophenone + 2-propanol) were added and the mixture was heated at 70 ^{o}C in autoclave for 1hr.

Catalyst	Yield % [a]		
CuNPs/zeolite	30 min	30 min+2hrs	Reused catalyst
	49	51	97

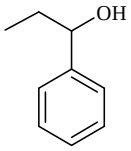
[a] yield was determined by GC.

S11. NMR spectroscopic data for reduced products

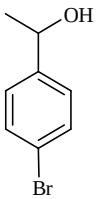
1-Phenylethanol (1a).[2] Boiling point 203 ^{o}C. Eluent: petroleum ether/ethyl acetate 10:1. Yield 92%. Colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.5-7.25 (m, 5H), 4.90-4.87 (m, 1H), 1.95 (bs, 1H), 1.50-1.48 (d, 3H).



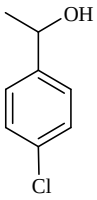
1-Phenylpropan-1-ol (1b):[3] Boiling point 218 ^{o}C. Eluent: petroleum ether/ethylacetate 10:1. Colourless liquid. Yield 89%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.44-7.24 (m, 5H), 4.54-4.50 (t, 1H), 2.30 (bs, 1H), 1.83-1.65 (m, 2H), 0.90-0.855 (m, 3H).



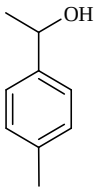
1-(4-Bromophenyl)ethanol (1c):[2] Boiling point 119 ^{o}C. Eluent: petroleum ether/ethyl acetate 10:1. Colourless liquid. Yield 91%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.41-7.38 (d, 2H), 7.15-7.12 (m, 2H), 4.73-4.68 (m, 1H), 3.21 (bs, 1H), 1.46-1.35 (m, 3H).



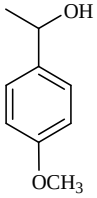
1-(4-Chlorophenyl)ethanol (1d):[4] Boiling point 120 ^{o}C. Eluent: petroleum ether/ethyl acetate 10:1. Colourless liquid. Yield 90%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.48-7.12 (m, 4H), 4.79-4.70 (m, 1H), 3.26 (bs, 1H), 1.44-1.35 (m, 3H).



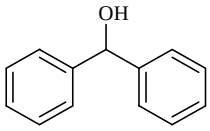
1-*p*-Tolylethanol (1e):[4] Boiling point 222 ^{o}C. Eluent: petroleum ether/ethyl acetate 10:1. Colourless liquid. Yield 86%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 4.37 (s, 2H), 7.26 (s, 2H), 4.9-4.911 (m, 1H), 4.69 (bs, 1H), 2.33 (s, 3H), 1.37 (m, 3H).



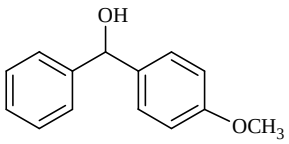
1-(4-Methoxyphenyl)ethanol (1f):[2] Boiling point 97 ^{o}C. Eluent: petroleum ether/ethyl acetate 10:1. Colourless liquid. Yield 79%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.27-7.24 (d, 2H), 6.86-6.84 (d, 2H), 4.83-4.77 (m, 1H), 3.77 (s, 3H), 2.28 (bs, 1H), 1.5-1.25 (d, 3H).



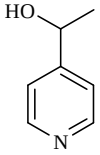
Benzhydrol (1g)[4]: Melting point 68 ^{o}C. Eluent: petroleum ether/ethyl acetate 10:1. White crystals. Yield 94%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.36-7.23 (m, 11H), 5.83-5.82 (s, 1H), 2.29 (s, 1H).



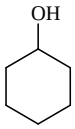
(4-Methoxyphenyl)(phenyl)ethanol (1h)[3]: Melting point 98 ^{o}C. Eluent: petroleum ether/ethyl acetate 10:1.White crystals. Yield 86%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.23-7.13 (m, 9H), 5.56 (s, 1H), 3.20 (s, 3H), 2.02 (bs, 1H).



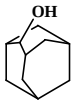
1-(4-Pyridin-4-yl)ethanol (1i):[3] Boiling point 242 ^{o}C. Eluent: petroleum ether/ethyl acetate 10:1. Yellow color liquid. Yield 87%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 8.41 (bs, 2H), 7.30 (s, 2H), 4.80 (bs, 2H), 1.48-1.46 (d, 3H).



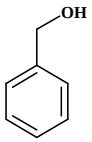
Cyclohexanol (1j):[3] Boiling point 162 ^{o}C. Eluent: petroleum ether/ethyl acetate 10:1. Colourless liquid. Yield 87%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.59 (s, 1H), 3.21 (s, 1H), 1.89-1.26 (m, 10H).



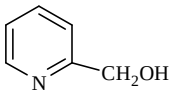
2-Adamantanol (1k):[3] Melting point 262 ^{o}C. Eluent: petroleum ether/ethyl acetate 10:1. White crystals. Yield 76%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 3.8 (s, 1H), 2.02 (d, 2H), 1.85 (d, 7H), 1.65 (s, 6H), 1.52-1.48 (m, 2H).



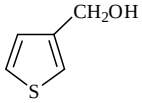
Benzyl alcohol (1l):[2] Boiling point 204 ^{o}C. Eluent: petroleum ether/ethyl acetate 10:1.colourless liquid. Yield 74%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): 7.51-7.21 (m, 4H), 4.62-4.56 (m, 1H), 3.70 (bs, 1H).



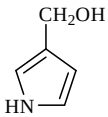
(Pyridin-2-yl)methanol (1m):[3] Boiling point 227 ^{o}C. Eluent: petroleum ether/ethyl acetate 10:1.Yellow color liquid. Yield 91%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 8.41-8.40 (d, 1H), 7.66-7.63 (m, 1H), 7.61-7.60 (m, 1H), 7.13-7.09 (m, 1H), 5.92 (bs, 1H), 4.82-4.75 (d, 2H).



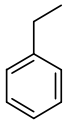
1-(Thiophen-3-yl)methanol (1n):[3] Boiling point 206 ^{o}C. Eluent: petroleum ether/ethyl acetate 10:1.colourless liquid. Yield 87%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.20-7.14 (d, 1H), 6.88-6.86 (d, 2H), 4.57 (s, 2H), 4.16 (bs, 1H).



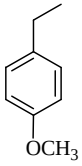
1-(1*H*-Pyrrol-3-yl)ethanol (1o):[3] Eluent: petroleum ether/ethyl acetate 10:1. Brown color solid. Yield 91%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 6.99-6.72 (d, 2H), 6.68 (s, 1H), 4.74 (bs, 1H), 4.46 (s, 2H)



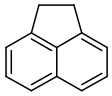
1-Ethylbenezene (2a):[3] Boiling point 137 ^{o}C. Eluent: petroleum ether/ethyl acetate 10.5:0.5.colourless liquid. Yield 95%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.65-7.49 (m, 4H), 3.03-2.95 (m, 2H), 1.61-1.56 (m, 3H).



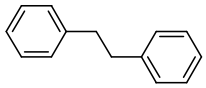
1-Ethyl-4-methoxybenezene (2b):[5] Boiling point 192 ^{o}C. Eluent: petroleum ether/ethyl acetate 10.5:0.5.colourless liquid. Yield 77%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.18-7.10 (d, 2H), 6.95-6.81 (d, 2H), 3.78 (s, 3H), 2.57-2.55 (m, 1H), 1.49-1.29 (m, 3H)



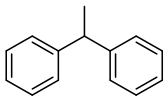
1,2-Dihydroacenaphthylene (2c):[6] Melting point 95 ^{o}C. Eluent: petroleum ether/ethyl acetate 10.5:0.5.White solid. Yield 88%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.54-7.51 (d, 2H), 7.40-7.35 (m, 2H), 7.21-7.19 (d, 2H), 3.328 (s, 4H).



1, 2-Diphenylethane (2d):[7] Boiling point 281 ^{o}C. Eluent: petroleum ether/ethyl acetate 10.5:0.5.White solid. Yield 88%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.93 (s, 4H), 7.21 (s, 10H).

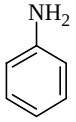


1,1-Diphenylethane (2e):[3] Boiling point 270 ^{o}C. Eluent: petroleum ether/ethyl acetate 10.5:0.5.colourless liquid. Yield 84%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.89-7.13 (m, 10H), 4.16-4.09 (m, 1H), 1.77 (d, 3H).



Cyclohexane (2f): Boiling point 80 ^{o}C. Eluent: petroleum ether/ethyl acetate 10.5:0.5.White solid. Yield 88%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS):

Aniline (2l):[3] Boiling point 184 ^{o}C. Eluent: petroleum ether/ethyl acetate 10:1. Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 6.62-6.78 (m, 3H), 7.10-7.27 (m, 2H), 3.58 (bs, 2H).



S11. References

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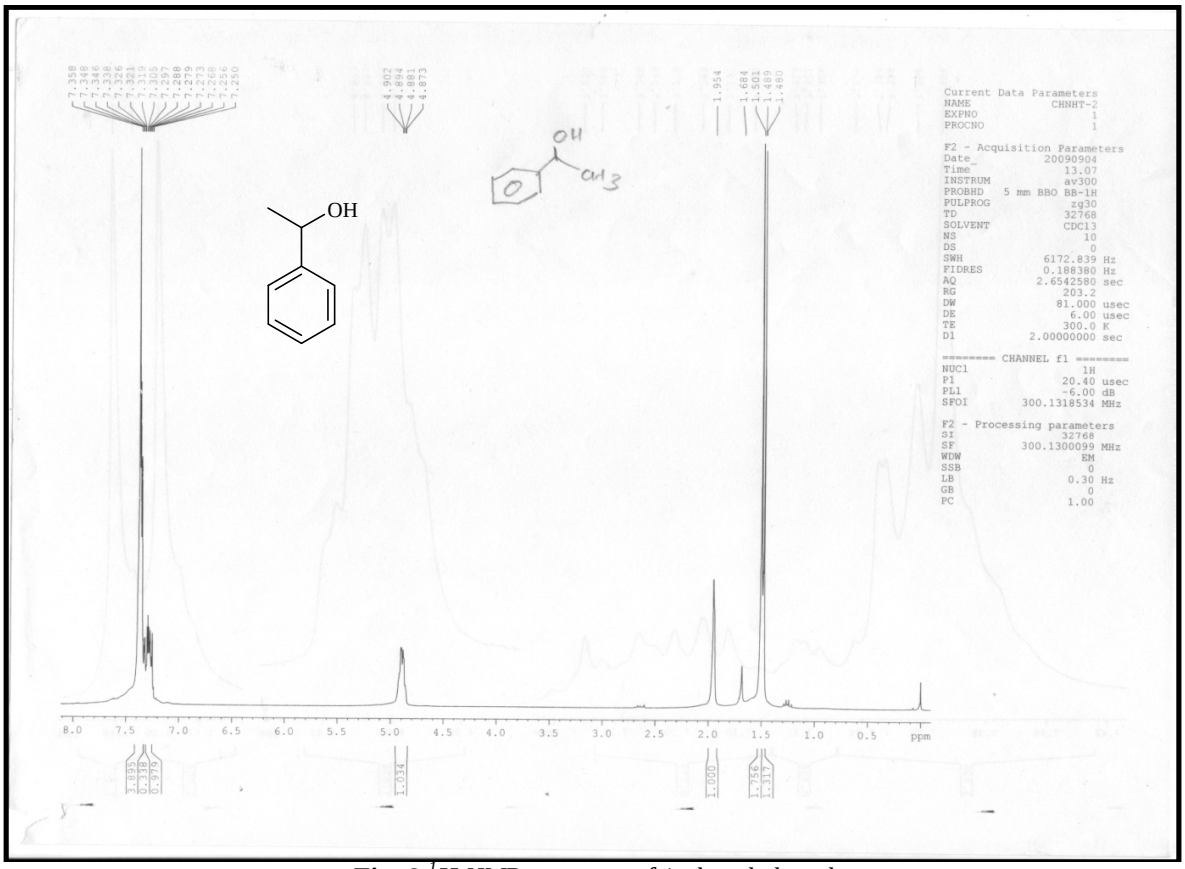

Fig. 6. *^{1}H-NMR specturm of 1-phenylethanol*

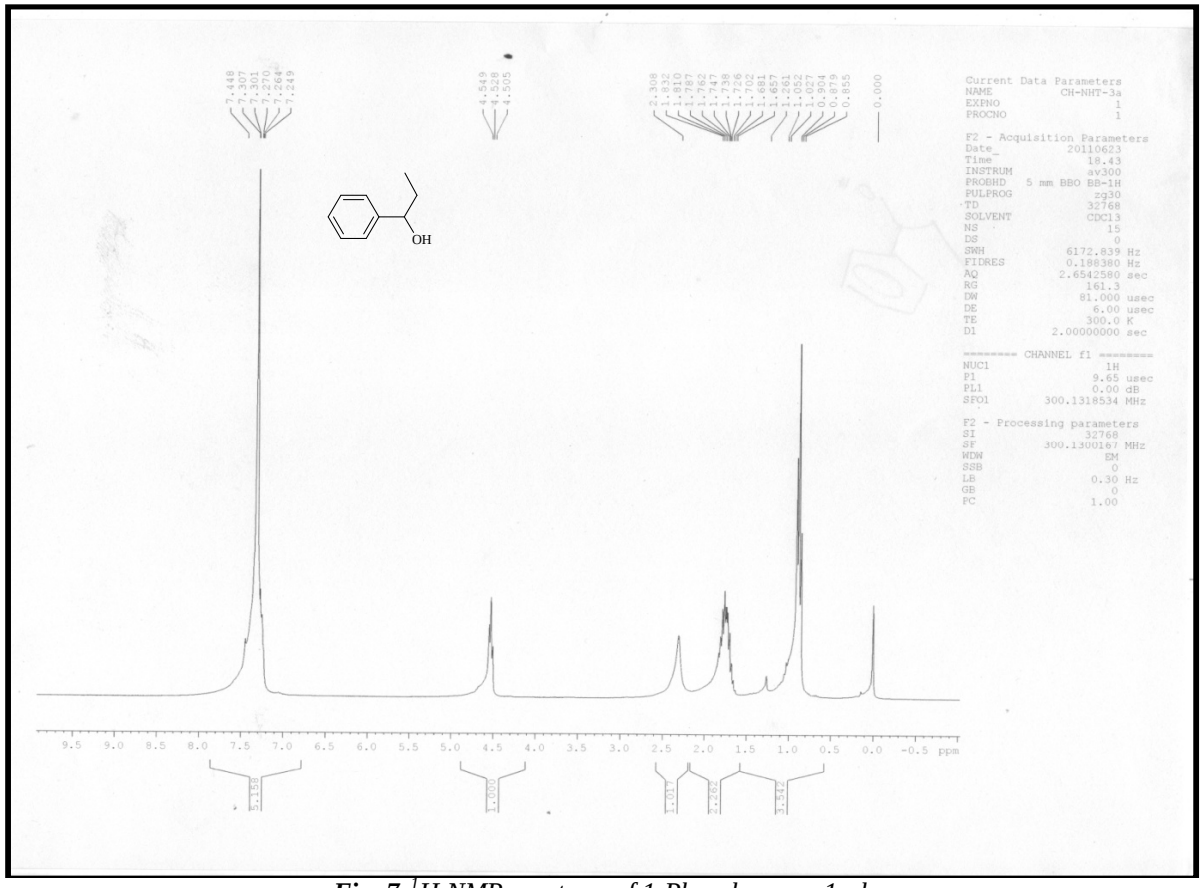

Fig. 7. *^{1}H-NMR specturm of 1-Phenylpropan-1-ol*

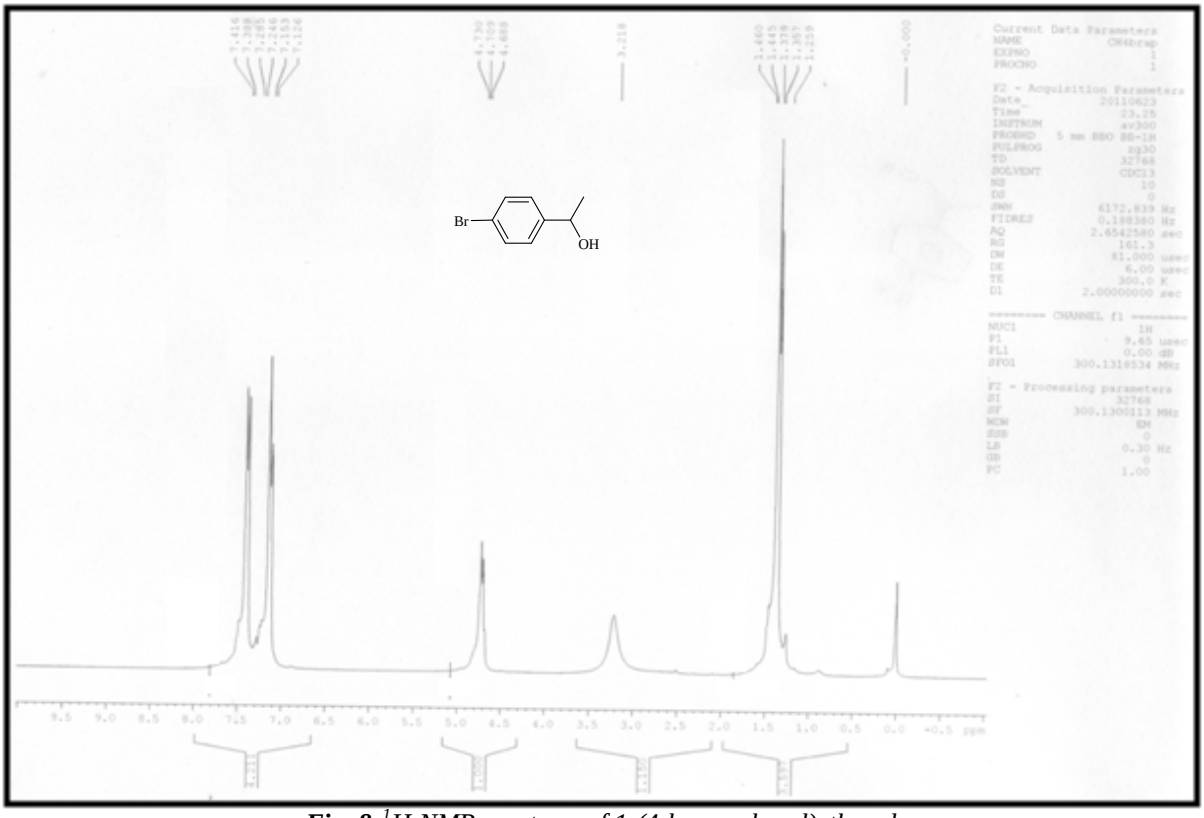

Fig. 8. *^{1}H-NMR specturm of 1-(4-bromophenyl)ethanol*

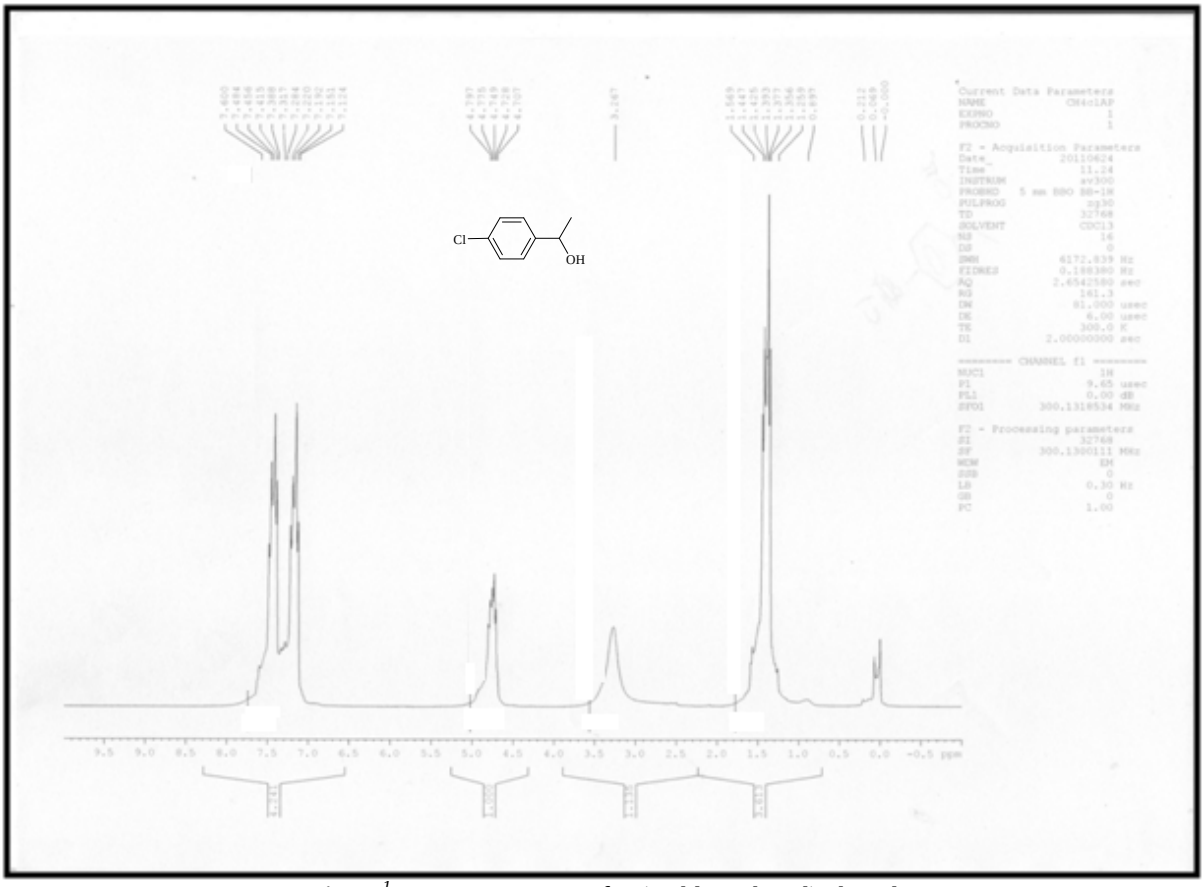

Fig. 9. *^{1}H-NMR specturm of 1-(4-chlorophenyl)ethanol*

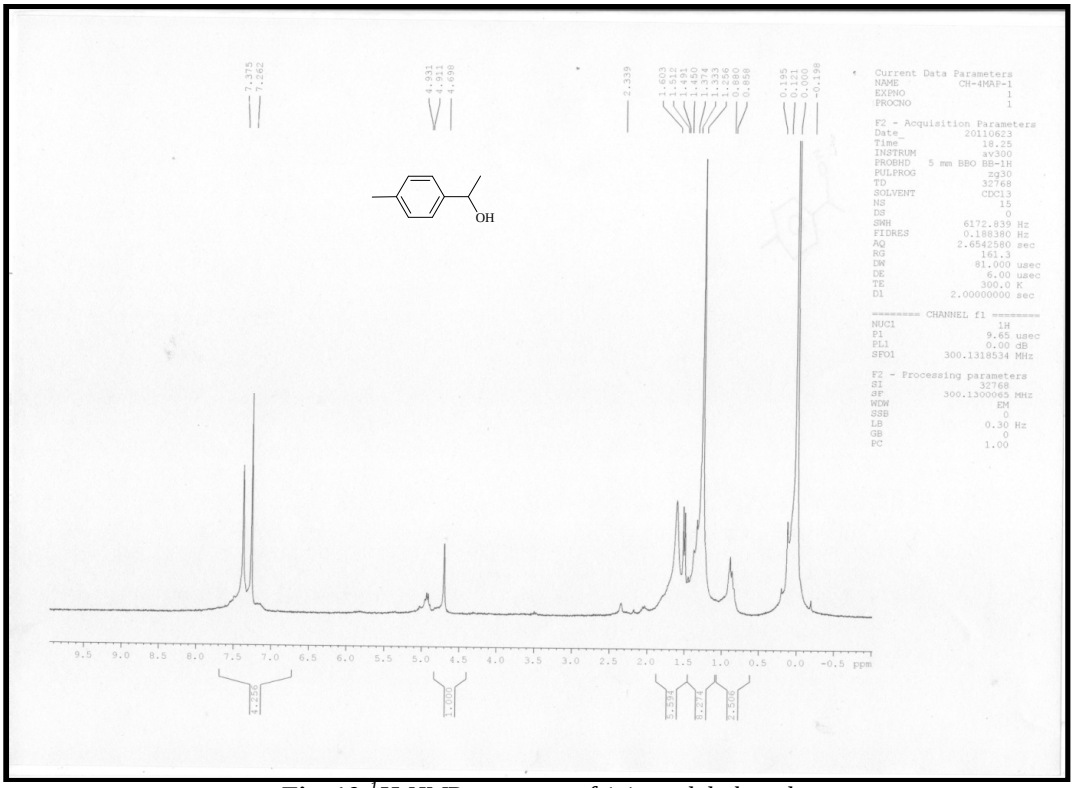

Fig. 10. *^{1}H-NMR specturm of 1 1-p-tolylethanol*

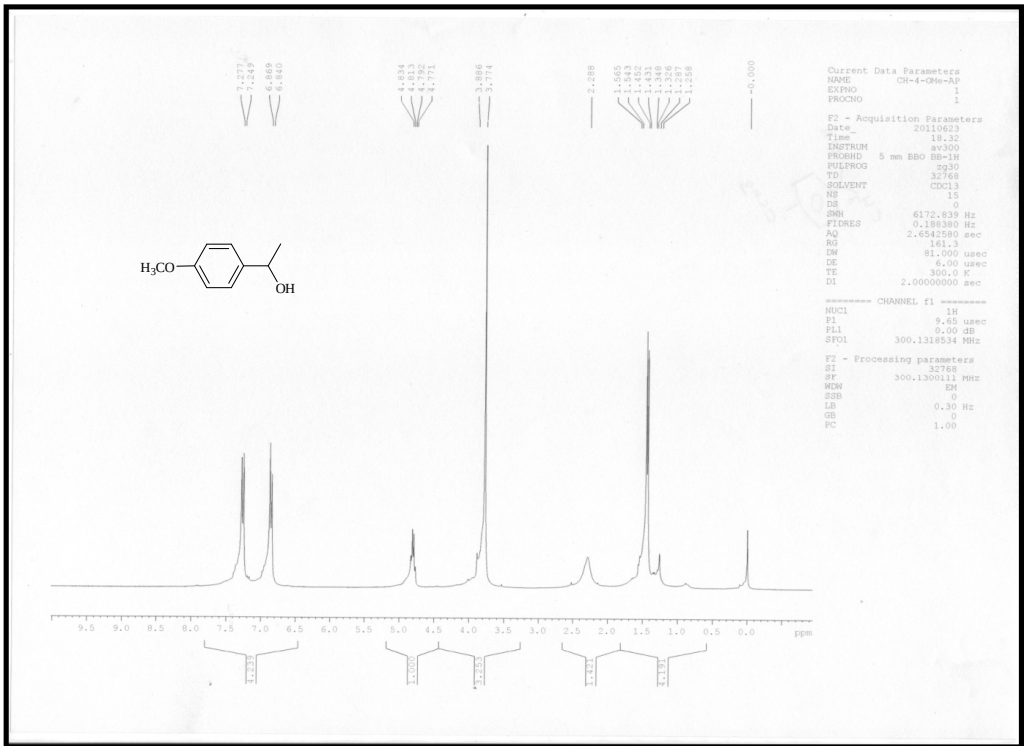

Fig. 11. *^{1}H-NMR specturm of 1-(4-methoxyphenyl)ethanol*

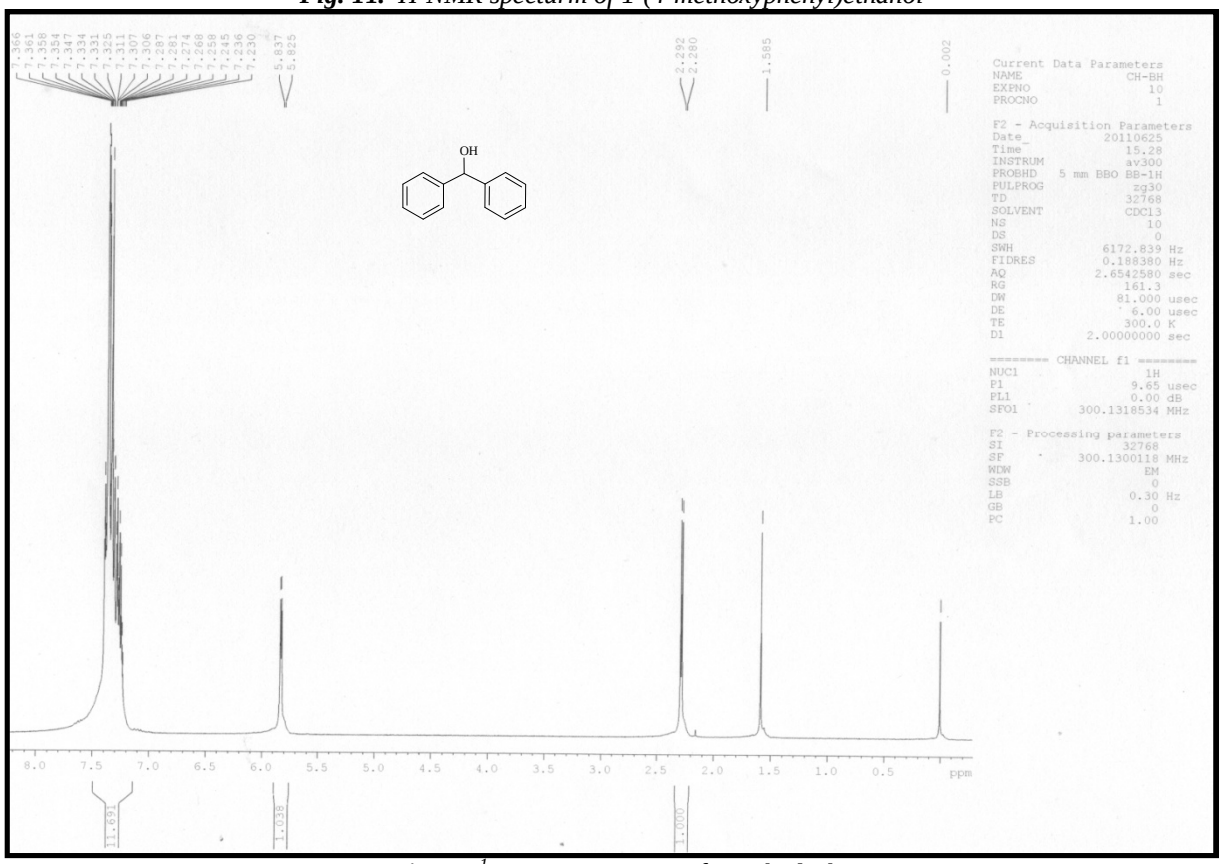

Fig. 12. *^{1}H-NMR specturm of Benzhydrol*

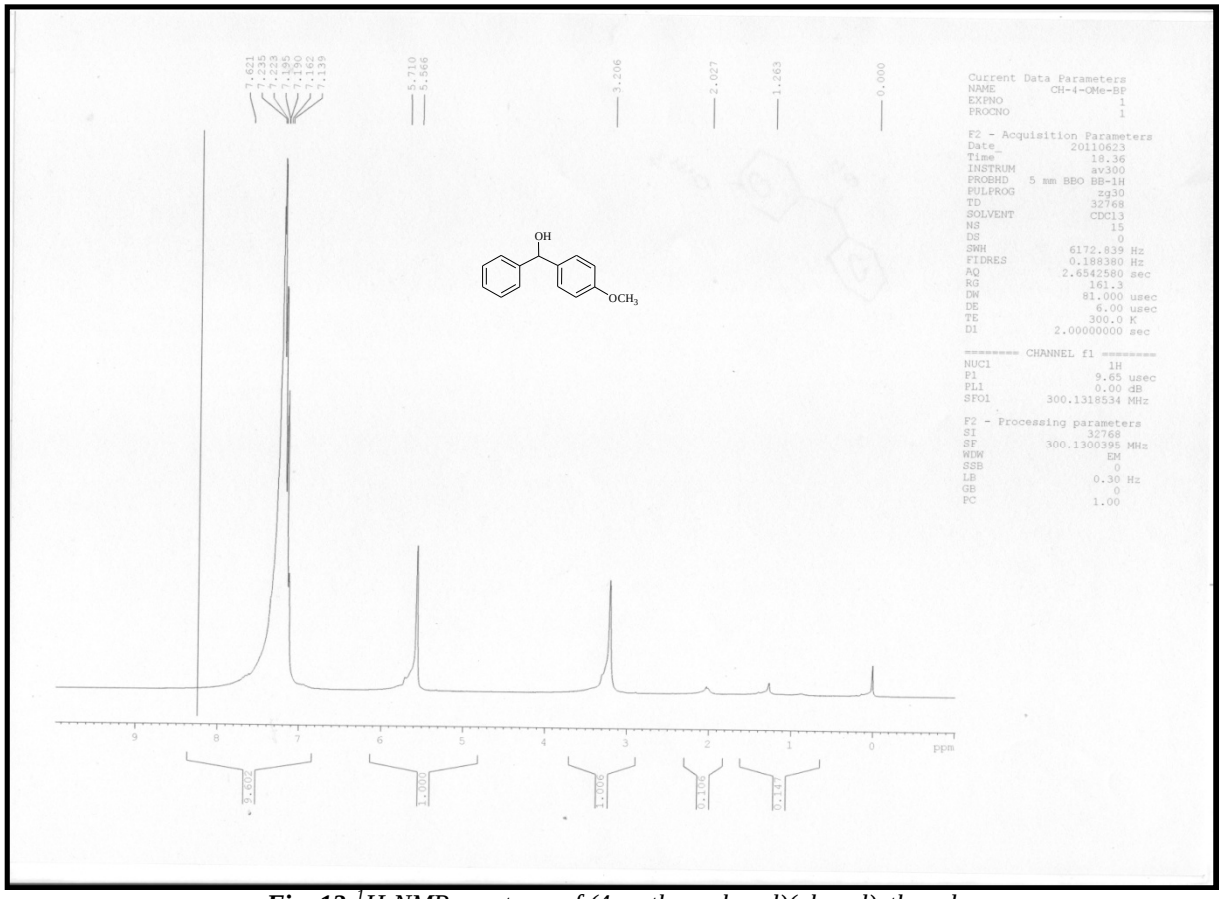

Fig. 13. *^{1}H-NMR specturm of (4-methoxyphenyl)(phenyl)ethanol*

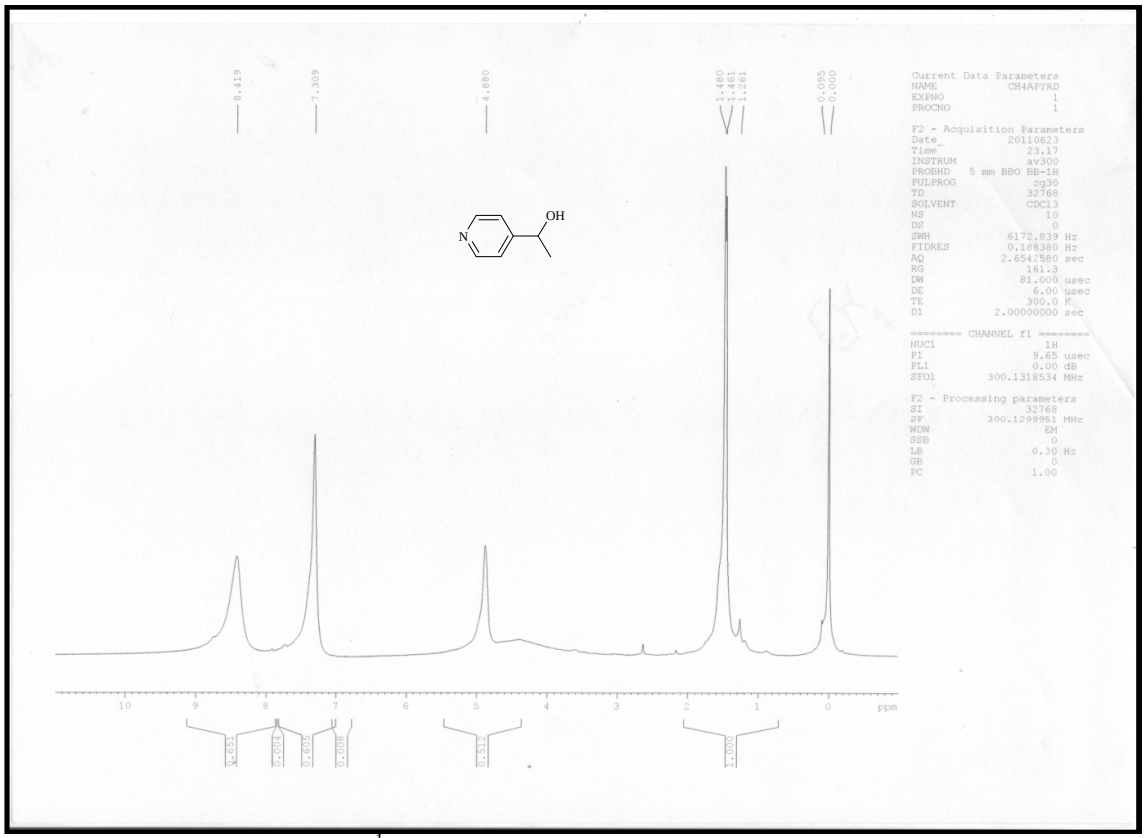

Fig. 14. *^{1}H-NMR specturm of -(4-pyridin-4-yl)ethanol*

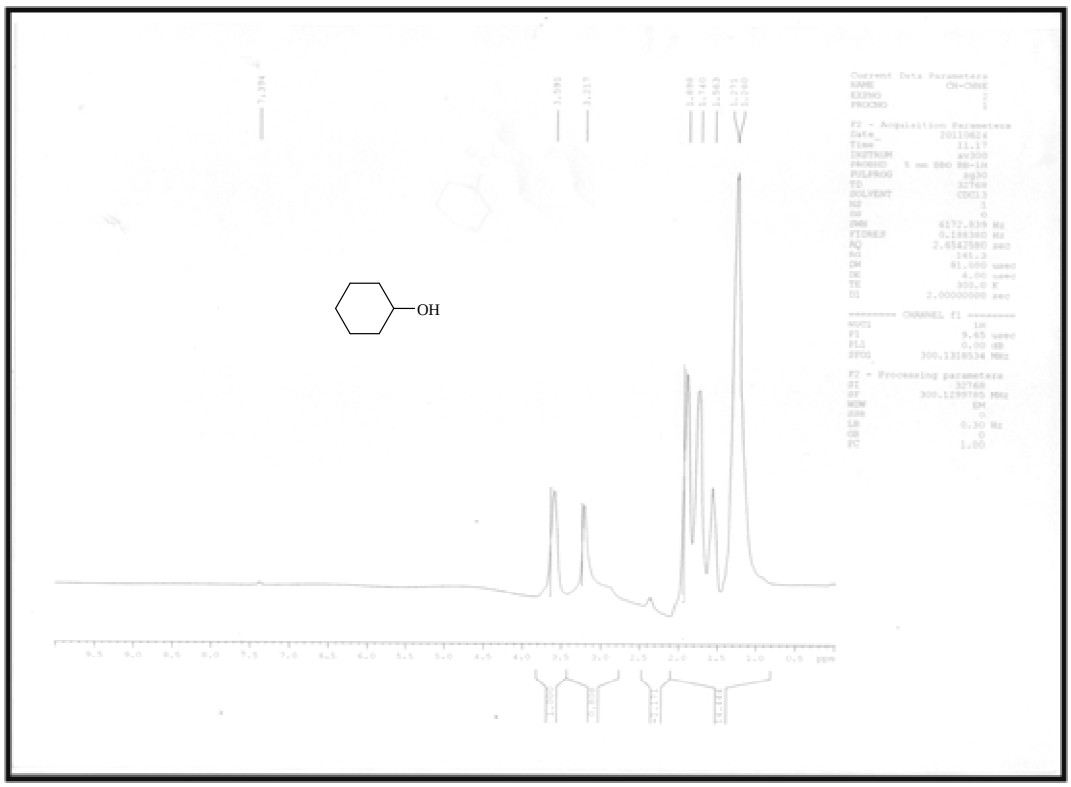

Fig. 15. *^{1}H-NMR specturm of Cyclohexanol*

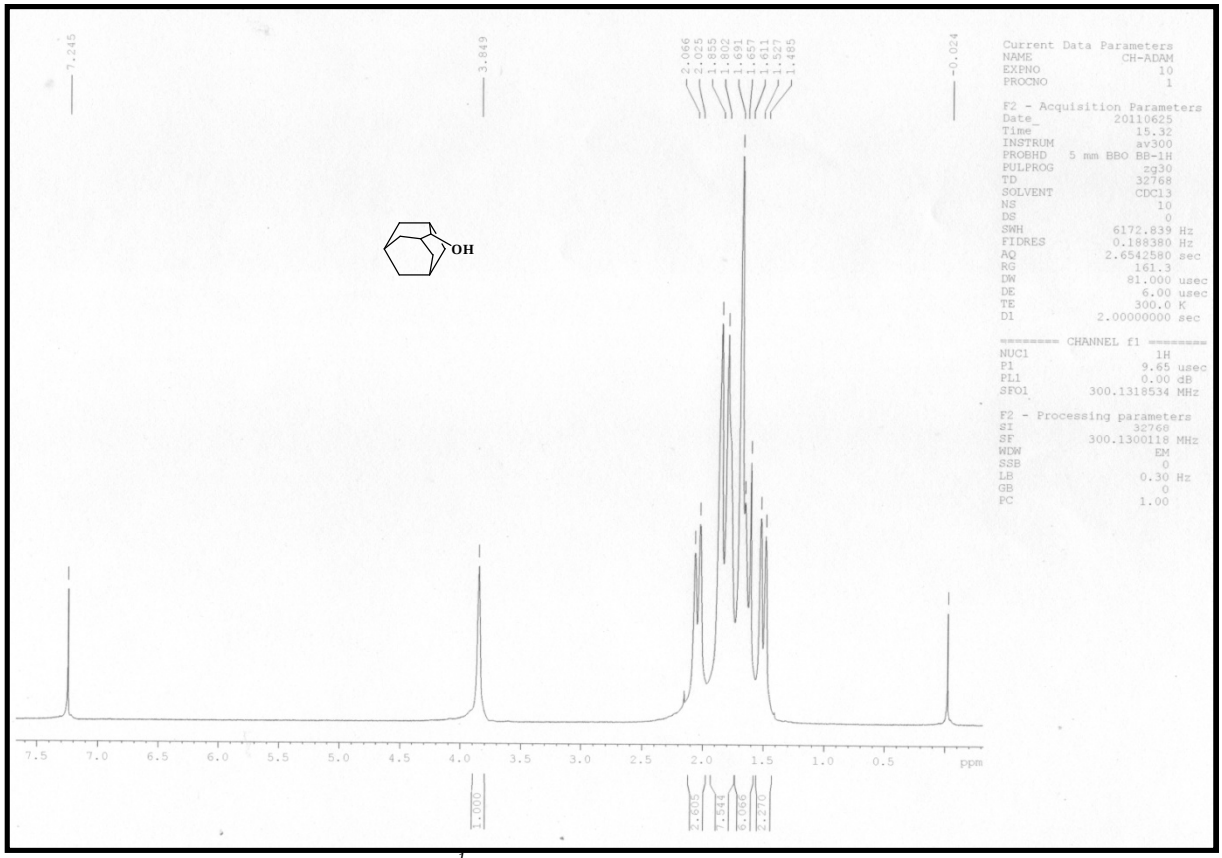

Fig. 16. *^{1}H-NMR specturm of 2-Adamantanol*

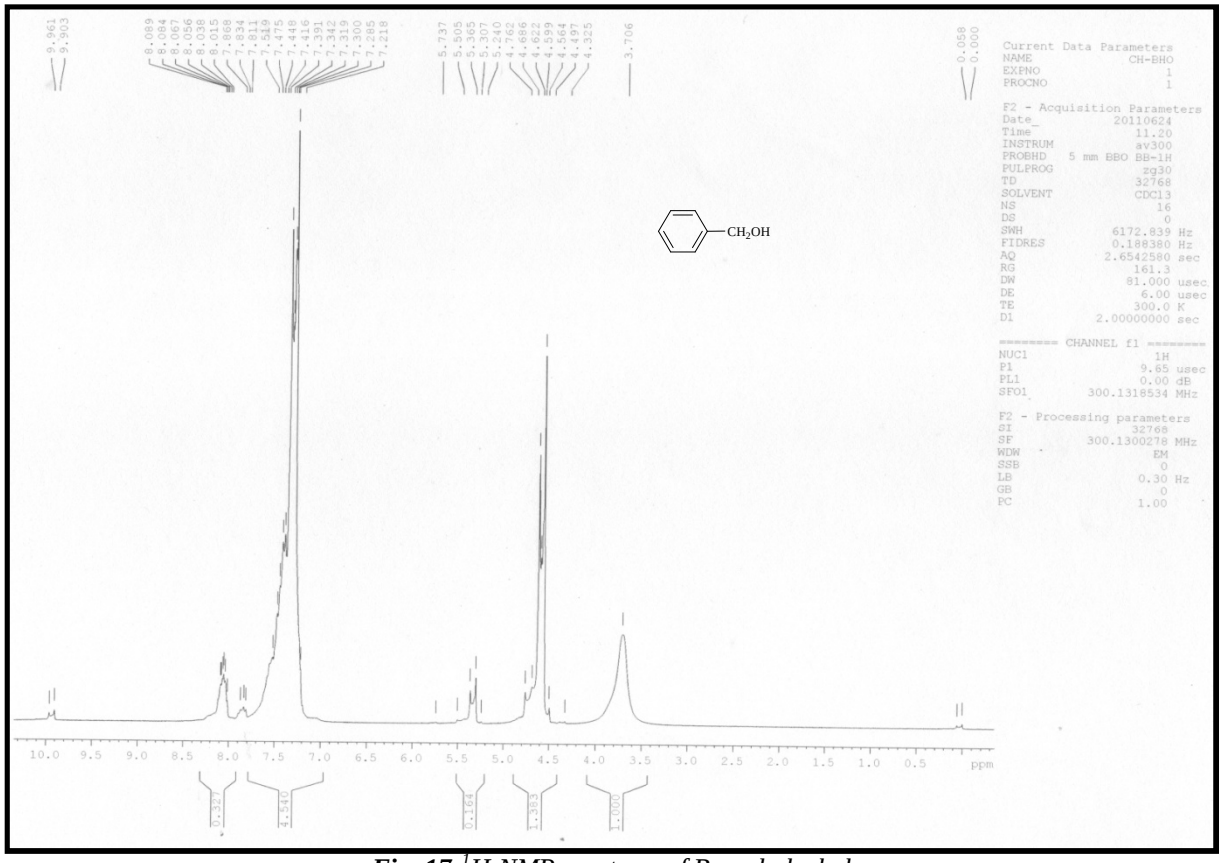

Fig. 17. *^{1}H-NMR specturm of Benzyl alcohol*

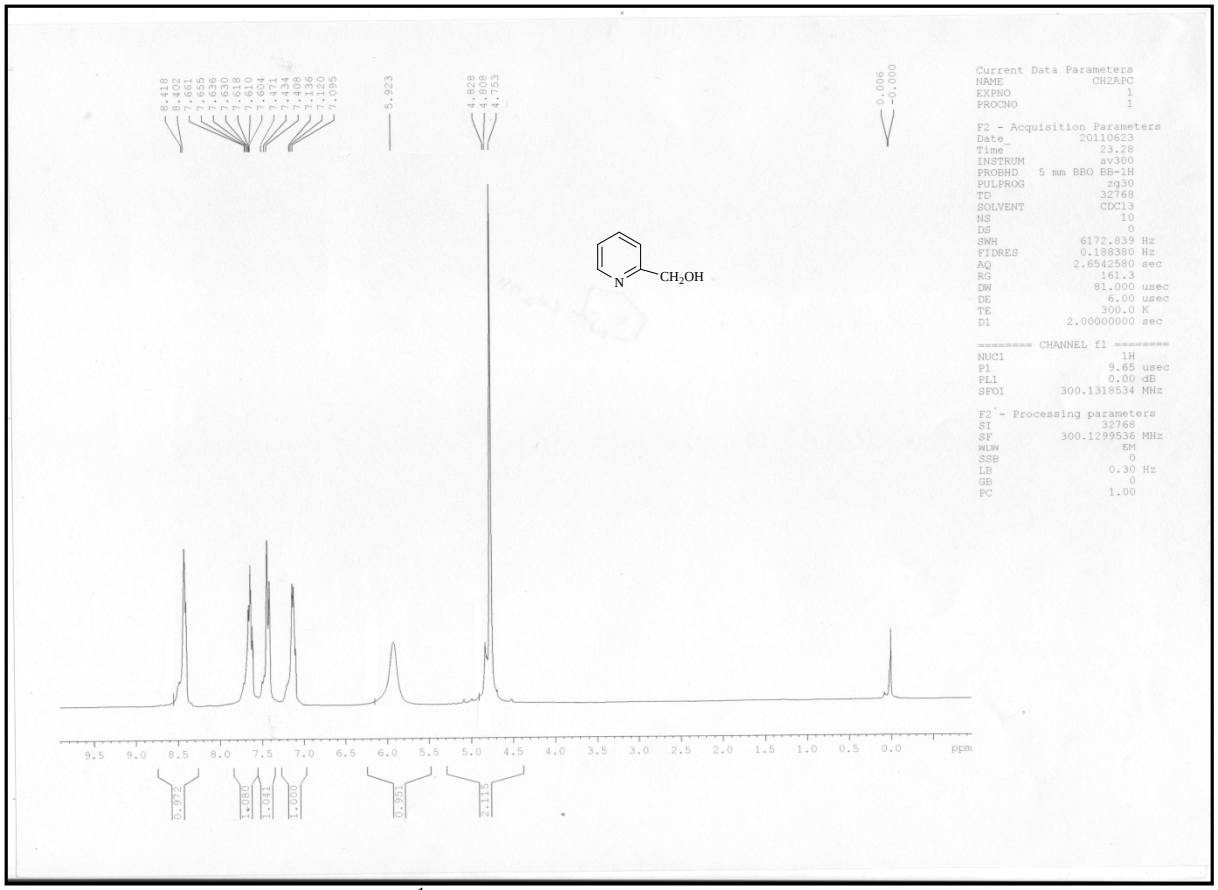

Fig. 18. *^{1}H-NMR specturm of (pyridin-2-yl)methanol*

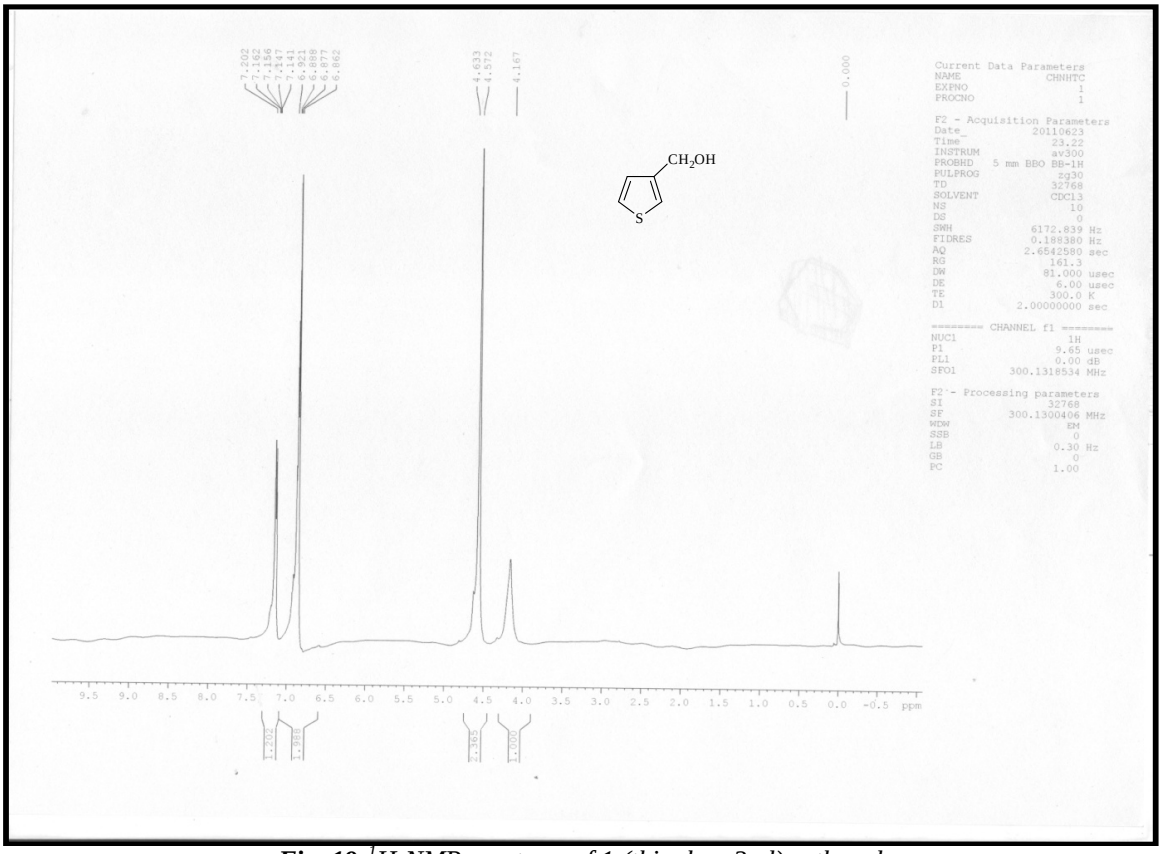

Fig. 19. *^{1}H-NMR specturm of 1-(thiophen-3-yl)methanol*

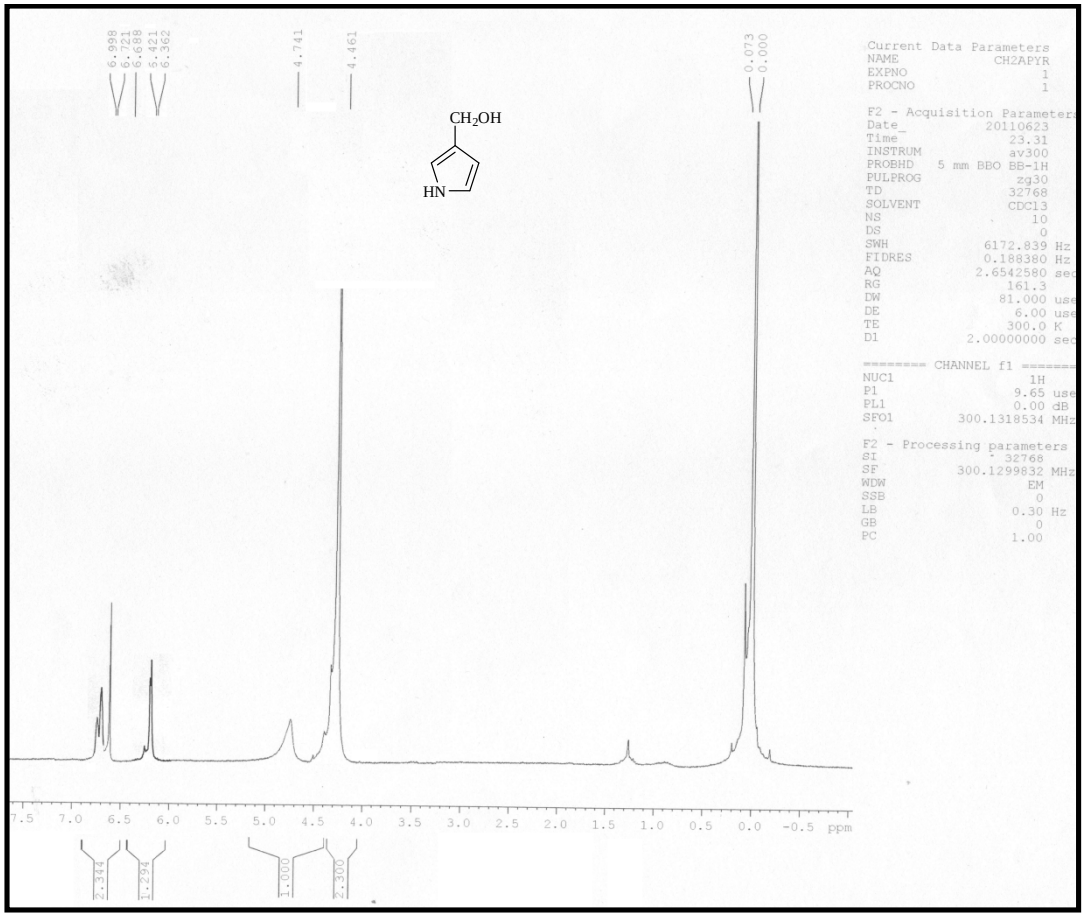

Fig. 20. *^{1}H-NMR specturm of -(1H-pyrrol-3-yl)ethanol*

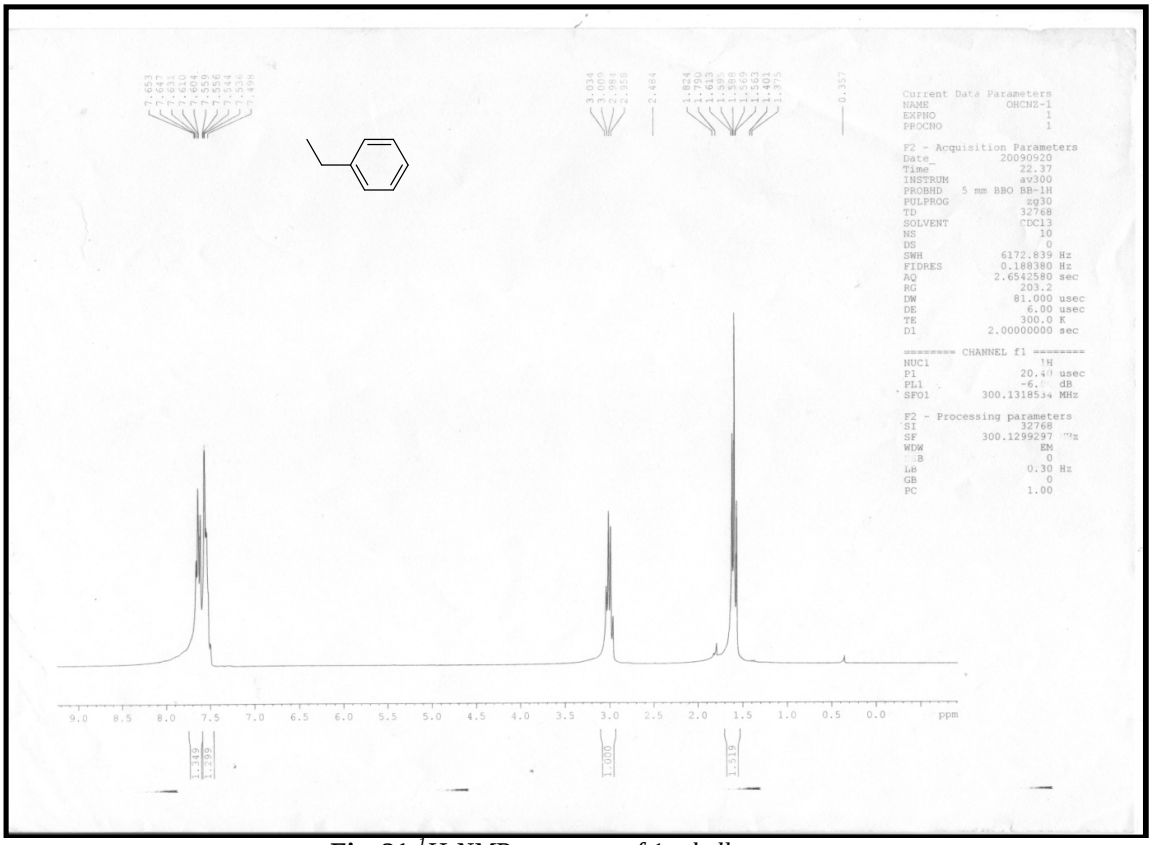

Fig. 21. *^{1}H-NMR specturm of 1-ethylbenezene*

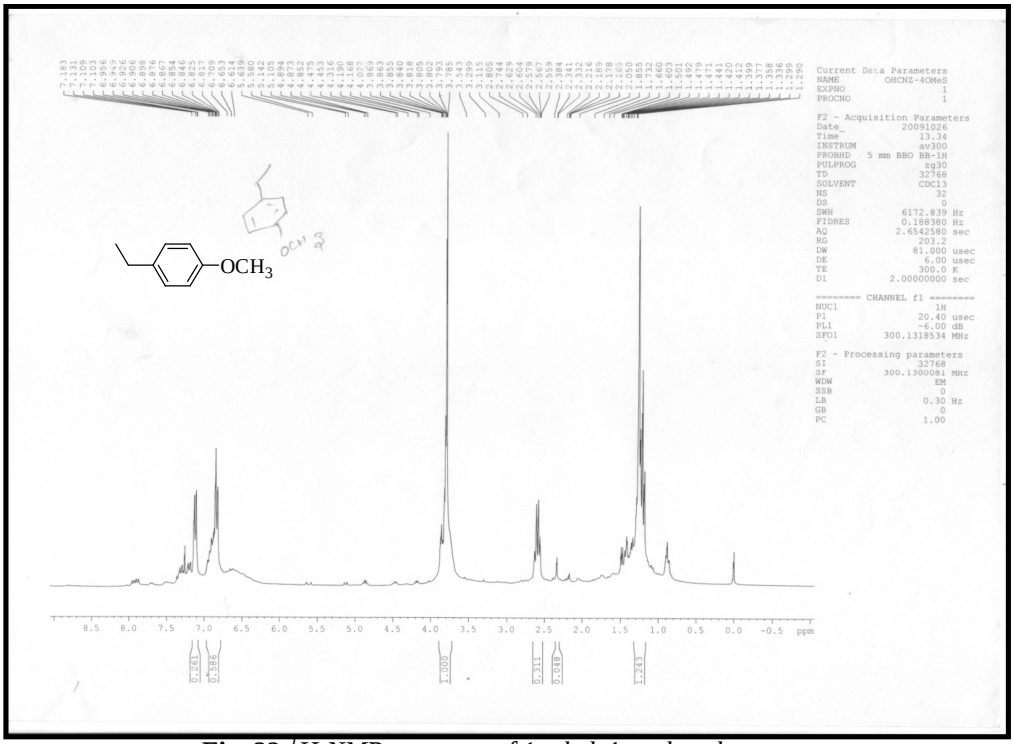

Fig. 22. *^{1}H-NMR specturm of 1-ethyl-4-methoxybenezene*

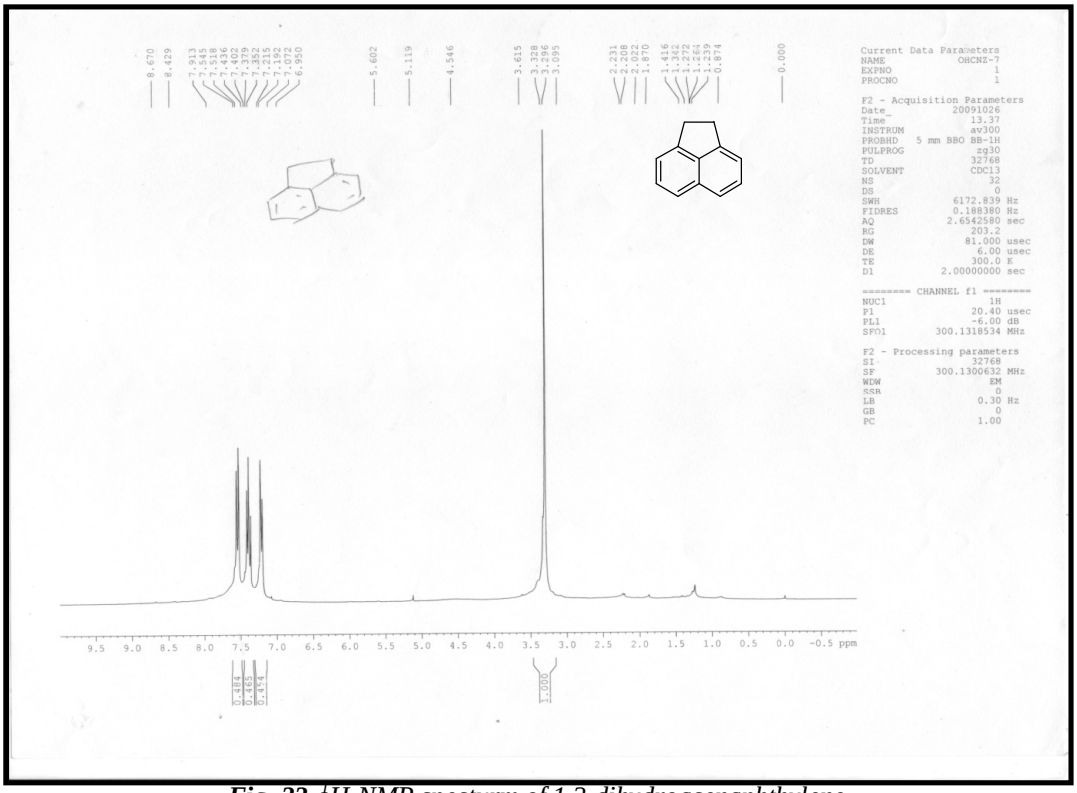

Fig. 23. *^{1}H-NMR specturm of 1,2-dihydroacenaphthylene*

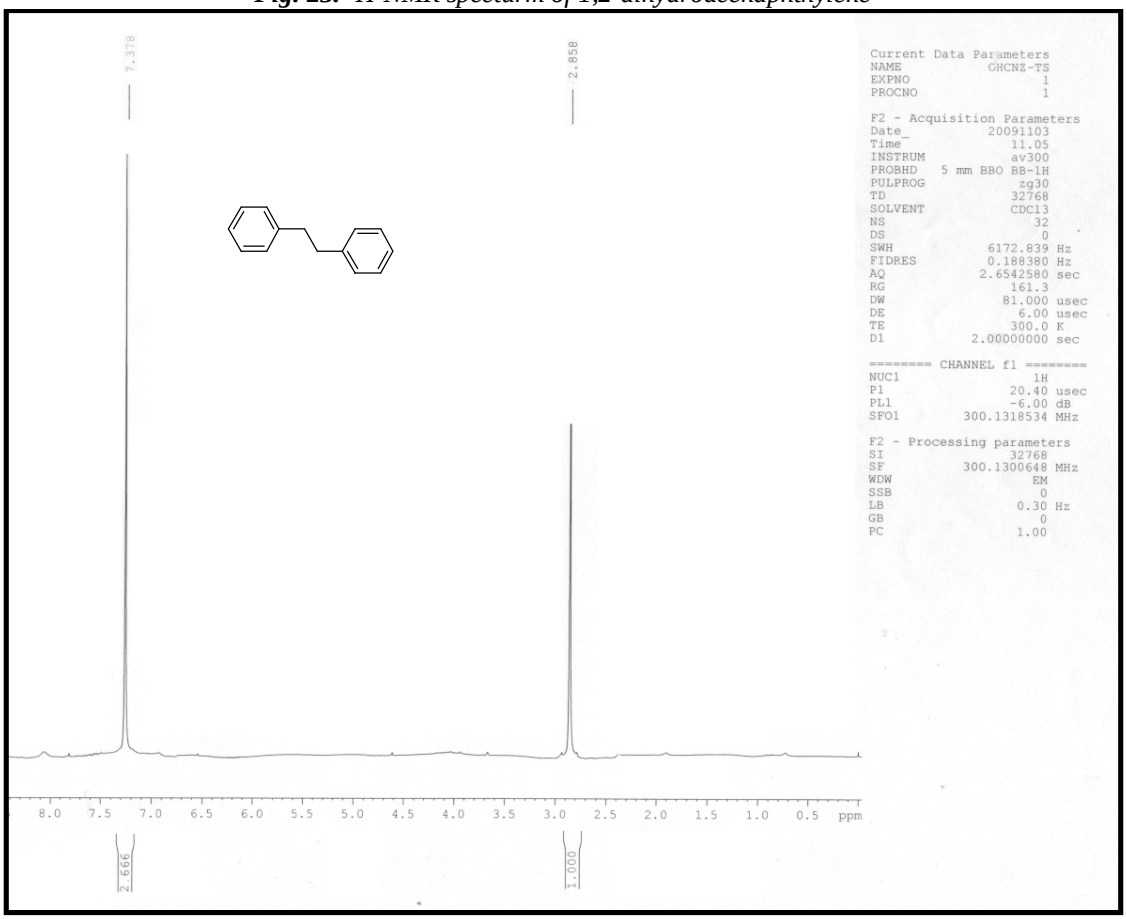

Fig. 24. *^{1}H-NMR specturm of 2-diphenylethane*

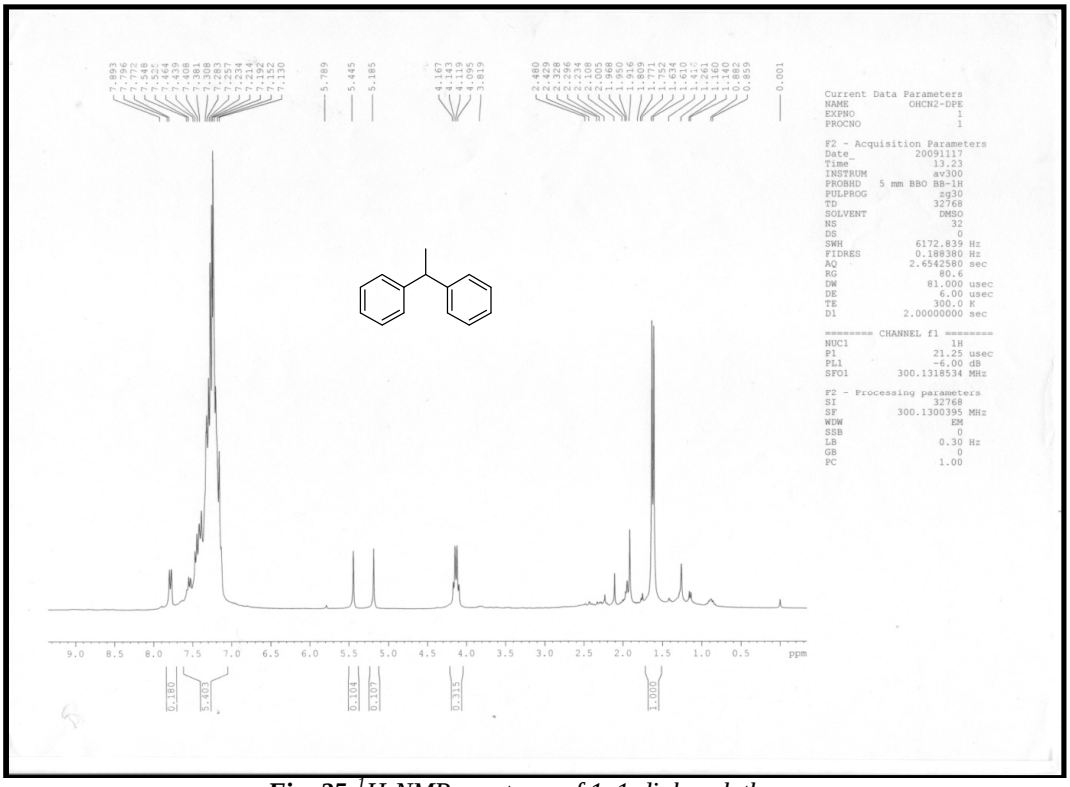

Fig. 25. *^{1}H-NMR specturm of 1, 1-diphenylethane*

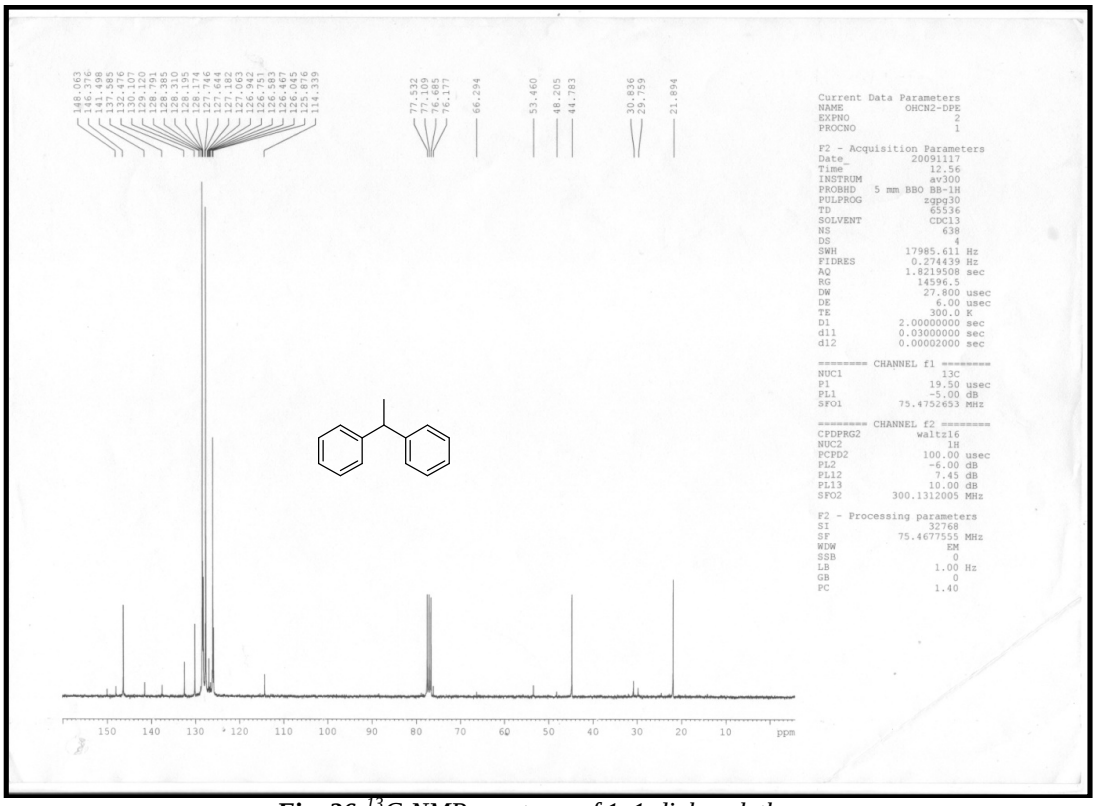

Fig. 26. *^{13}C-NMR specturm of 1, 1-diphenylethane*

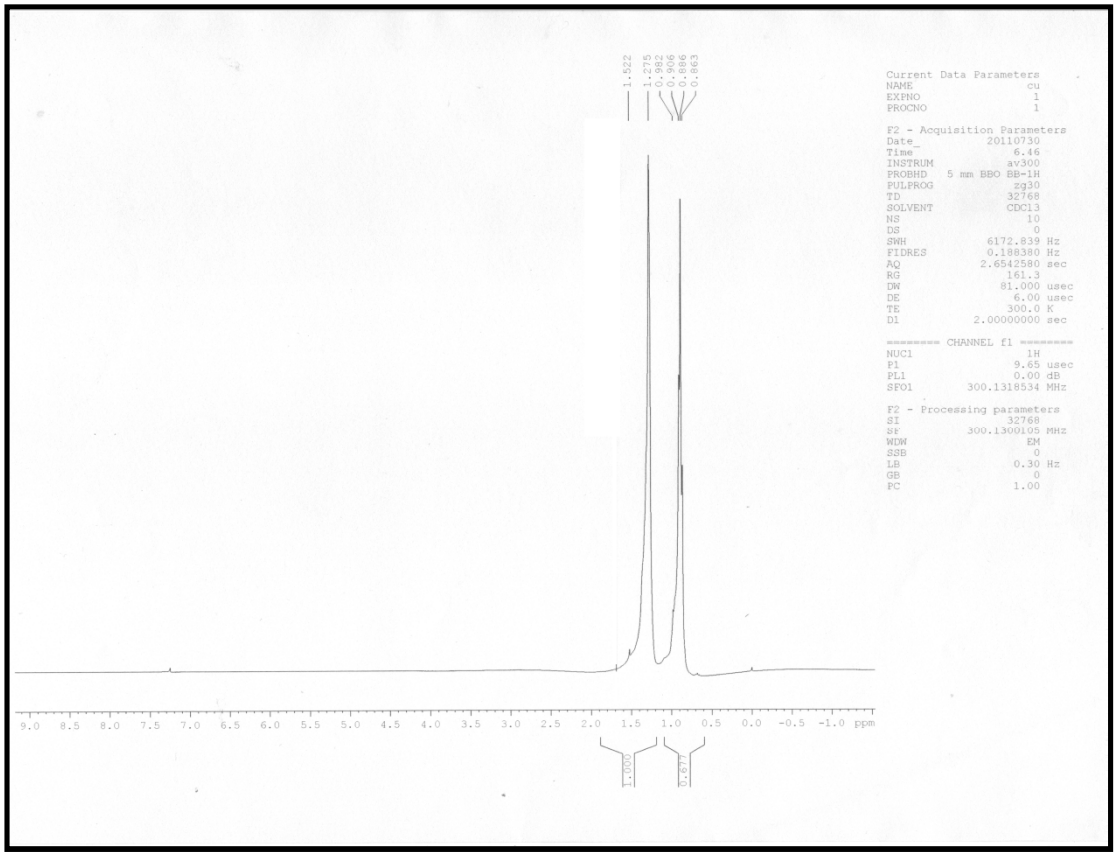

Fig. 27. *^{1}H-NMR specturm of hexane*

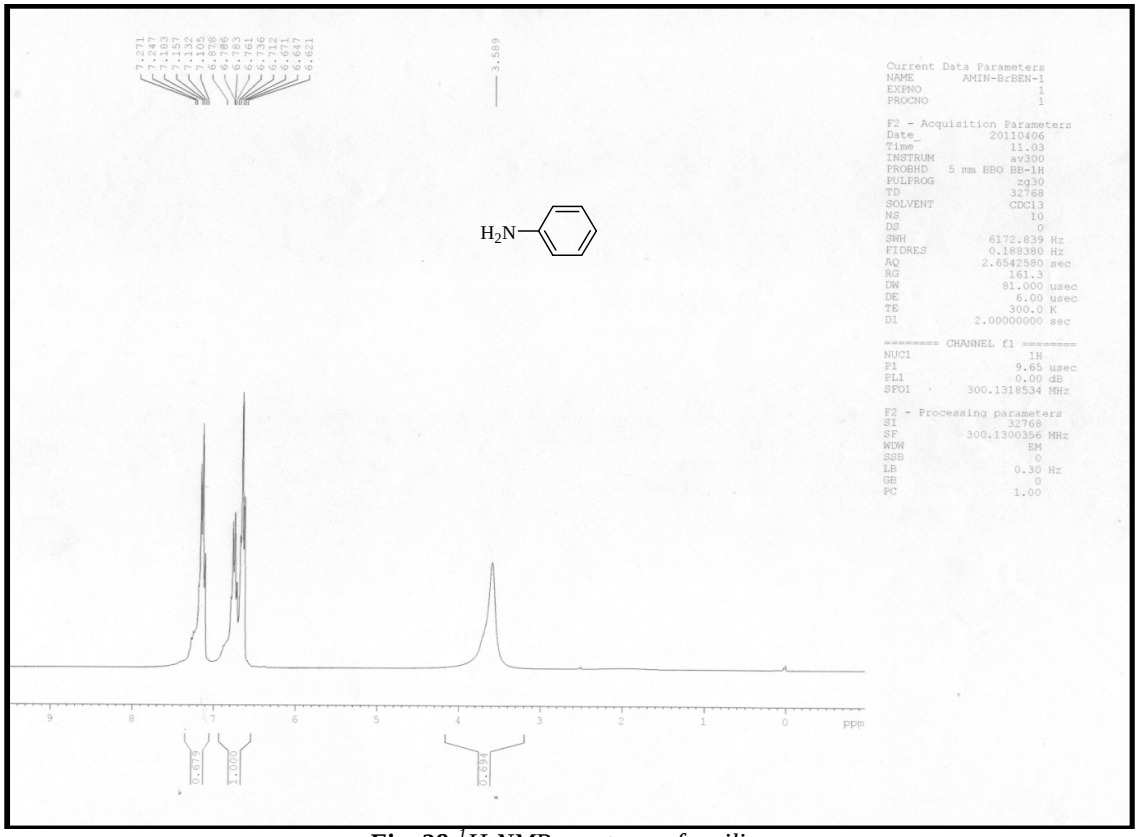

Fig. 28. *^{1}H-NMR specturm of aniline*