CHAPTER – 2

SYNTHESIS AND CHARACTERIZATION OF SOME TETRADENTATE SCHIFF BASES DERIVED FROM 4-BENZOYL-3-METHYL -1-[4′-NITROPHENYL]-2-PYRAZOLIN-5-ONE WITH SOME DIAMINES AND THEIR METAL CHELATES

2. A. PRESENT WORK:

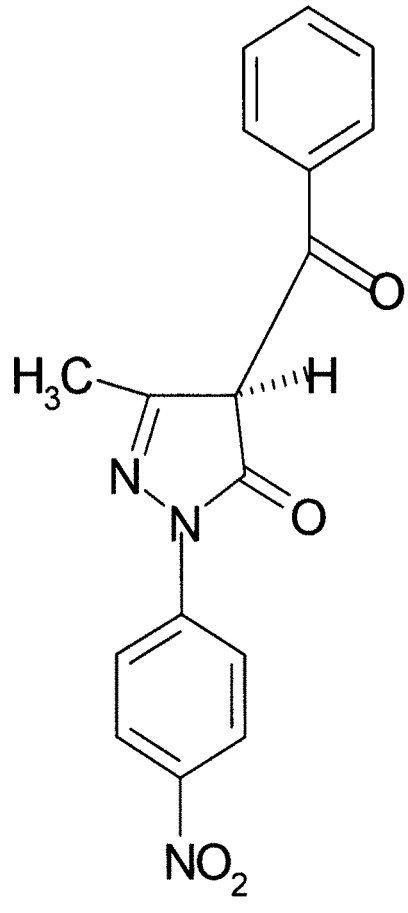
This chapter describes the experimental methods used for the synthesis of 4-Benzoyl-3-methyl-1-[4'-nitrophenyl]-2-pyrazolin-5-one and its tetradentate Schiff bases with ethylenediamine ,m-phenylenediamine,p-phenylenediamine and benzidine, The present chapter also describes the general procedure used for the synthesis of VO(II), Cr(III), Mn(II), Fe(II) ,Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) chelates of above tetradentate Schiff bases.

2. A.1 The 4-Benzoyl-3-methyl-1-[4'-nitrophenyl]-2-pyrazolin- 5-one has been used in the preparation of the tetradentate Schiff bases:

Molecular formula: $C_{17}H_{13}N_3O_4$

Molecular weight: 323.31 gm/mol

Structural formula:



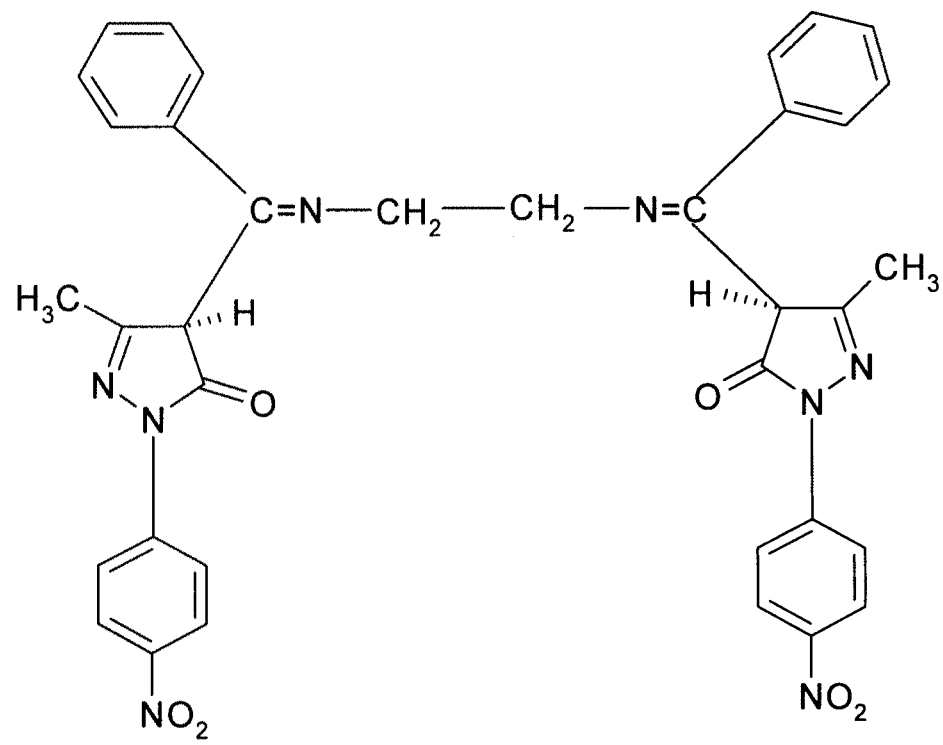
2. A.2. The following tetradentate Schiff bases were prepared for the preparation of metal chelates:

[I] Tetradentate Schiff base of 4-Benzoyl-3-methyl-1-[4'-nitrophenyl]-2-pyrazolin-5-one with ethylenediamine **[H_2BPP_z-en]**

Molecular formula: $C_{36}H_{30}N_8O_6$

Molecular weight: 670.68 gm/mol

Structural formula:



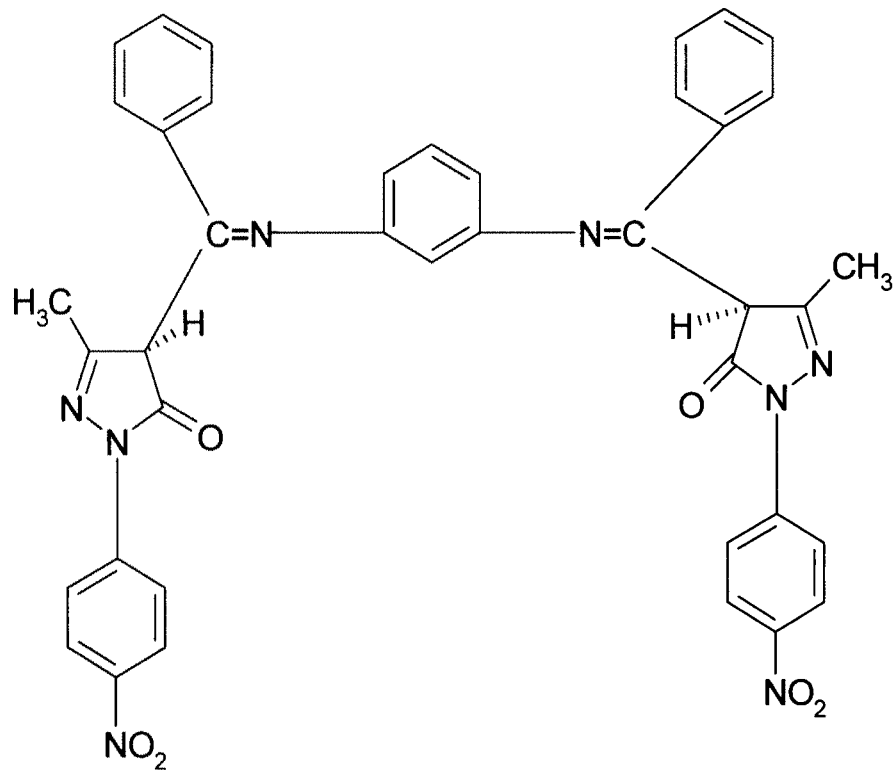
[II] Tetradentate Schiff base of 4-Benzoyl-3-methyl-1-[4'-nitrophenyl]-2-pyrazolin-5-one with m-phenylenediamine

[H_2BPP_z-mph]

Molecular formula: $C_{40}H_{30}N_8O_6$

Molecular weight: 718.73 gm/mol

Structural formula:



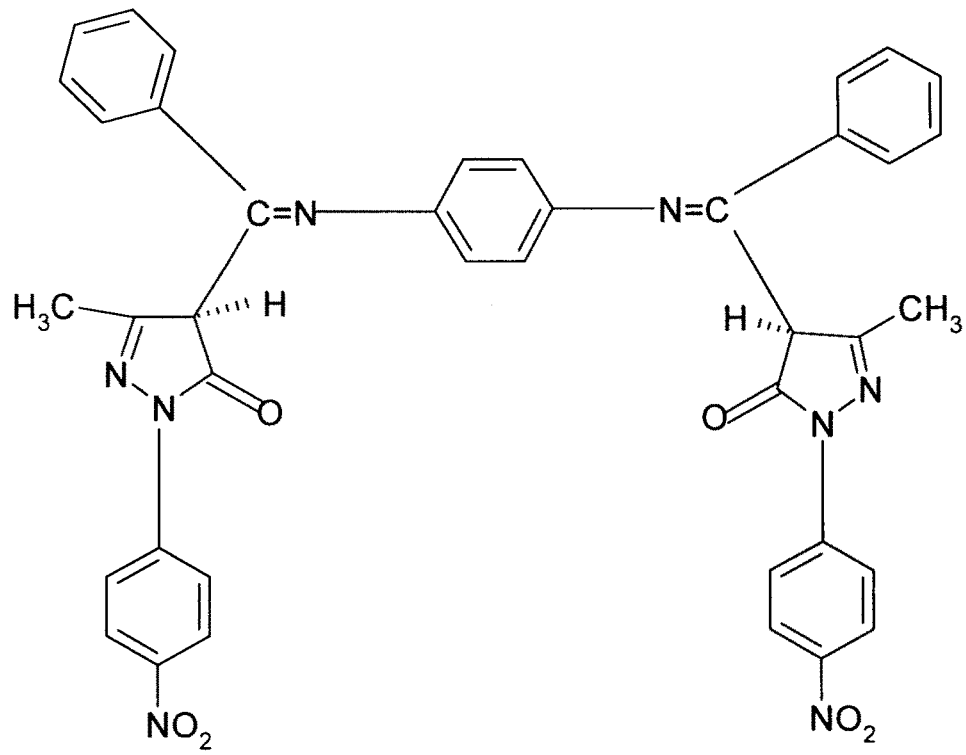
[III] Tetradentate Schiff base of 4-Benzoyl-3-methyl-1-[4'-nitrophenyl]-2-pyrazolin-5-one with p-phenylenediamine

[H_2BPP_z-pph]

Molecular formula: $C_{40}H_{30}N_8O_6$

Molecular weight: 718.73 gm/mol

Structural formula:

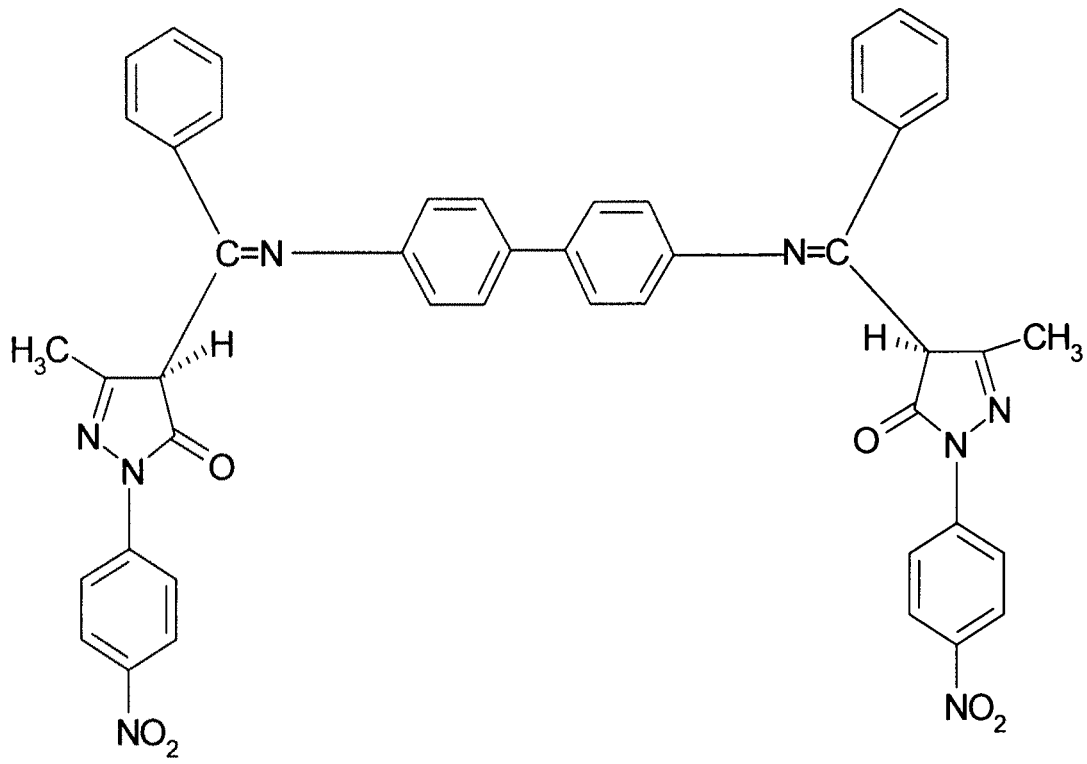


[IV] Tetradentate Schiff base of 4-Benzoyl-3-methyl-1-[4'-nitrophenyl]-2-pyrazolin-5-one with benzidine **[H_2BPP_z-benz]**

Molecular formula: $C_{46}H_{34}N_8O_6$

Molecular weight: 792.84 gm/mol

Structural formula:



2. B. MATERIALS:

All chemicals used in this present study were of A.R.grade. Ethylacetoacetate, p-nitrophenylhydrazine, calcium hydroxide, benzoylchloride [SD's fine chemicals Ltd., British Drug House, Qualigens-Glaxo, Mumbai] were used.Dioxane and N, N' – dimethylformamide (DMF) [Qualigens –Glaxo, Mumbai] were used after purification. Absolute ethanol from Alembic Chemical works Co. Ltd., Baroda, was used after distillation .All diamines were obtained from [SD's fine chemical Ltd., British Drug house, Qualigens –Glaxo, Mumbai] and were used without further purification. Cr(III), Mn(II), Co(II), Ni(II),Cu(II) and Zn(II) metal acetates [SD's fine chemicals Ltd., British Drug house ,Qualigens –Glaxo,Mumbai] were used .Vanadylsulphate, ferrous sulphate and anhydrous ferric chloride [SD's fine chemicals Ltd., British Drug House, Qualigens-Glaxo, Mumbai]were used in the preparation of VO(II), Fe(II) and Fe(III) chelates respectively.

2. C. EXPERIMENTAL:

All tetradentate Schiff base ligands prepared in the present study are characterized by colour ,m.p.,elemental analyses,FT-IR,^{1}H-NMR,^{13}C-NMR and mass spectral studies, Melting points were taken in one side open capillaries. Carbon ,hydrogen and nitrogen were estimated on Perkin Elmer, Series II,2400 C , H, N, analyzer (Central Salt and Marine Chemical Research Institute,Bhavnager, India).The infrared spectra of the ligands studied in the present work were recorded on a Shimadzu 8201 PC FT-IR model in KBr (Gujarat Laboratory, Ahmedabad, India). The ^{1}H-NMR, ^{13}C-NMR spectra in DMSO of all ligands were recorded on a Bruker DRX-400 FT-NMR spectrophotometer using TMS

[$(CH_3)_4Si$] as internal standard (Zydus Research Centre, Ahmedabad, India).The mass spectra in a matrix of neat glycerol of all ligands studied in the present work were recorded on a Jeol SX-102 FAB mass spectrophotometer (Zydus Research Centre, Ahmedabad, India).

2.D. SYNTHESIS AND CHARACTERIZATION OF TETRADENTATE SCHIFF BASE LIGANDS:

The ligands H_2BPP_z-en, H_2BPP_z-mph, H_2BPP_z-pph and H_2BPP_z-benz used in the present study were prepared in three steps using literature method [1-5].

(a) Preparation of 3-methyl-1-[4'-nitrophenyl]-2-pyrazolin-5-one

(b) Preparation of 4-Benzoyl-3-methyl-1-[4'-nitrophenyl]-2-pyrazolin- 5-one

(c) Preparation of the tetradentate Schiff bases

2. D.1. PREPARATION OF 3-METHYL-1-[4'-NITROPHENYL]- 2-PYRAZOLIN-5-ONE:

It was obtained by condensing the equimolar quantities of ethyl acetoacetate with 4-Nitro phenyl hydrazine in ethanol, containing few drops of concentrated sulphuric acid.

4-Nitrophenyl hydrazine (25g, 0.16 mol) was stirred in glacial acetic acid (50mL) and warmed at 40°C until a complete solution is resulted. The stirred mixture was cooled to room temperature and ethyl acetoacetate (21.25g, 0.16 mol) was added rapidly, After 10 minutes, at room temperature the flask was placed in an oil bath and heating was commenced to 85°C for 30 minutes. At this temperature a dense yellow precipitate formed .The reaction was left at 80° to 85°C for 4 hours and

then the reaction mass was cooled to room temperature .The crystals were collected by filtration, washed with several small portions of acetic acid until the filtrate was colorless, then washed with water and air dried to give 21.5g, 60% yield, m.p.219°C-220°C.

2. D.2.PREPARATION OF 4-BENZOYL-3-METHYL-1-[4'-NITROPHENYL]-2-PYRAZOLIN-5-ONE:

The following literature procedure was used to prepare the 4-Benzoyl-3-methyl-1-[4'-nitrophenyl]-2-pyrazolin-5-one [1-4].

The 3-methyl-1-[4'-nitrophenyl]-2-pyrazolin-5-one (20g,0.091mol) was placed in a three neck flask equipped with stirrer, separating funnel and reflux condensor .It was then dissolved in dioxane (120mL) by application of heat .To the reaction mixture ,calcium hydroxide (13.68g, 0.18mol) was added ,followed by the drop wise addition of benzoyl chloride (12.80g ,0.091 mol) .At this stage ,the mixture became a thick paste and its temperature also increased as this being a exothermic reaction .The reaction mixture was then refluxed in oil bath for an hour, The resulting calcium chelates were then decomposed by pouring it into dilute hydrochloric acid (180 mL, 2 M), The resulting coloured compounds were collected by filtration ,washed several times with water.

4-Benzoyl-3-methyl-1-[4'-nitrophenyl]-2-pyrazolin-5-one:

Light: yellow; m.p. found: 222°C; Yield: 86%,

Analyses calculated for $C_{17}H_{13}N_3O_4$ (Molecular Wt. = 323.31):

C, 63.16; H, 4.05; N, 13.00 %. Found: C, 62.99; H, 3.98; N, 13.15 %

FT-IR (KBr pellet, cm^{-1}) ν_{max} :3455-3200 br (ν_{OH}, 5-OH group of pyrazole ring), 1645 s ($\nu_{C=O}$, 4-benzoyl group), 1615 s ($\nu_{C=N}$, pyrazole ring), 1323 s (ν_{NO2}, 4-nitrophenyl ring), 1421 ($\nu_{C=O}$ pyrazole ring).

2. D.3. PREPARATION OF THE TETRADENTATE SCHIFF BASES :

The tetradentate Schiff bases were prepared by literature method [6, 7] as described below.

The tetradentate Schiff –bases were prepared by refluxing 2:1 mole of 4-Benzoyl-3-methyl-1-[4'-nitrophenyl]-2-pyrazolin-5-one [0.01 mol,7.18 gm] and diamines [ethylenediamine; 0.005mol, 0.35 gm, m-phenylenediamine; 0.005 mol,0.54 gm, p- phenylenediamine; 0.005 mol, 0.54gm and benzidine 0.005 mol, 0.85gm] in ethanol for 2 hours on water bath .The resulting mixture was allowed to stand overnight ,The Solid product obtained was collected by filtration ,washed with water and air dried .All the tetradentate Schiff bases are recrystalized in ethanol.

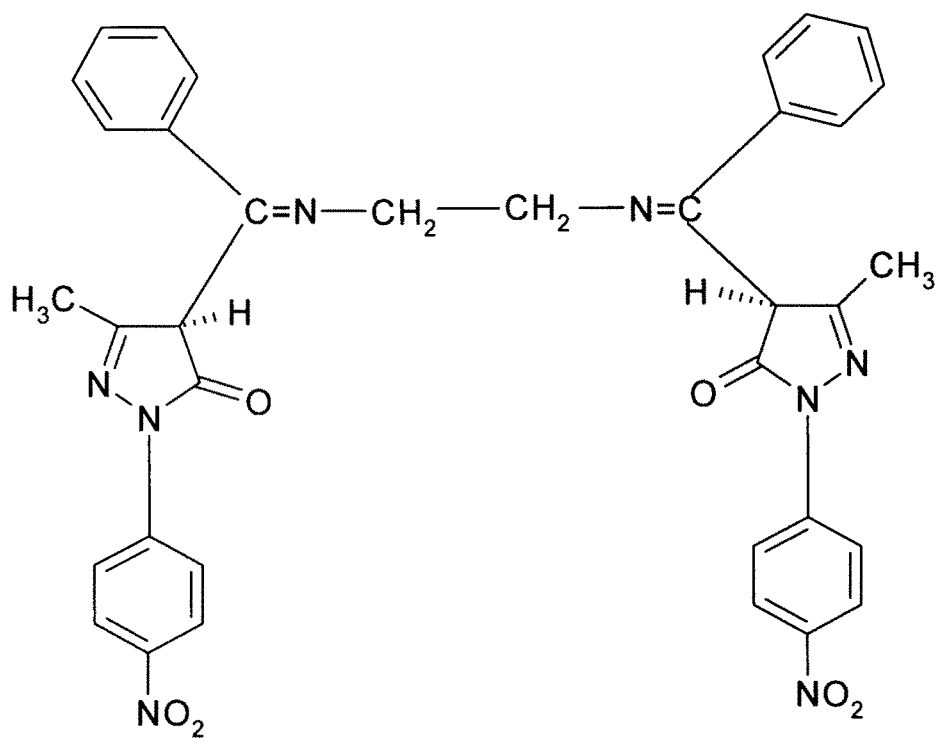
2. E. CHARACTERIZATION OF TETRADENTATE SCHIFF BASES DERIVED FROM 4-BENZOYL-3- METHYL-1-[4'-NITROPHENYL]-2-PYRAZOLIN-5-ONE WITH DIAMINES:

An attempt has been made to characterize all the tetradentate Schiff -base ligands [I-IV] by m.p., colour, elemental analyses, IR, ^{13}C NMR and mass spectral studies, The ^{13}C NMR and mass spectra of all ligands (I-IV) are shown in Figs.2.1-2.8.

The detailed assignments of infrared bands of all ligands used in the present study is given in chapter IV. The present chapter describes only important infrared bands [10-13] of all tetradentate Schiff base ligands used. The ^{1}H and ^{13}C chemical shifts have been assigned using reported values for the 2-pyrazolin-5-one derivatives [14-18].

The following ligands [I-IV] were used in the present investigation to prepare the metal chelates.

[I]. H_2BPPz-en 4-Benzoyl-3-methyl-1-[4'-nitrophenyl]-2-pyrazolin-5-one with ethylenediamine.



Light Brown; m.p. found: 210-212°C; yield: ~68 %

Analyses calculated for $C_{36}H_{30}N_8O_6$: C,64.47 ; H,4.51 ; N,16.71 %. Found: C,64.40; H,4.45; N,16.59 %,

FT-IR (KBr pellet, cm^{-1}) ν_{max}: 3396-2923 (m,vb); ($\upsilon_{O-H,}$ 5-OH group of pyrazolin ring), 1616(s,br) $\nu_{C=N}$(pyrazolin ring), 1637(s,s)$\nu_{C=N}$ (azomethine), 1394(s,s) ($\upsilon_{c-o(enolic)}$), 1330(s,s) ($\nu_{NO2,}$ nitrophenyl ring)

^{1}H– Chemical Shift (Fig. 2.1, DMSO,δ_{PPm}): 8.1 -8.5 [-$C_6H_4NO_2$,(4H)],7.5-7.9[C_6H_5,(5H)],2.47[-CH_3 Pz ring ,(3H)],11.53[-OH,(1H)],5.23[-CH_2,(2H)]

^{13}C- Chemical Shift (Fig. 2.2, DMSO,δ_{PPm}):

14.8(C-1),149.2(C-2),114.6(C-3),159.3(C-4),118.4(C-5&C-9),124.5(C-6&C-8),415.4(C-7),143.6(C-10),169.2(C-11),139.0(C-12),129.2(C-13&C-17),128.8(C-14&C-16),131.0(C-15),62.5(C-18)

Massspectral data,m/z: 671[M^+],653, 598, 500, 449, 407, 364, 322, 276, 255, 218, 179

Fig: 2.1 ^{1}H NMR of H_2BPPz-en

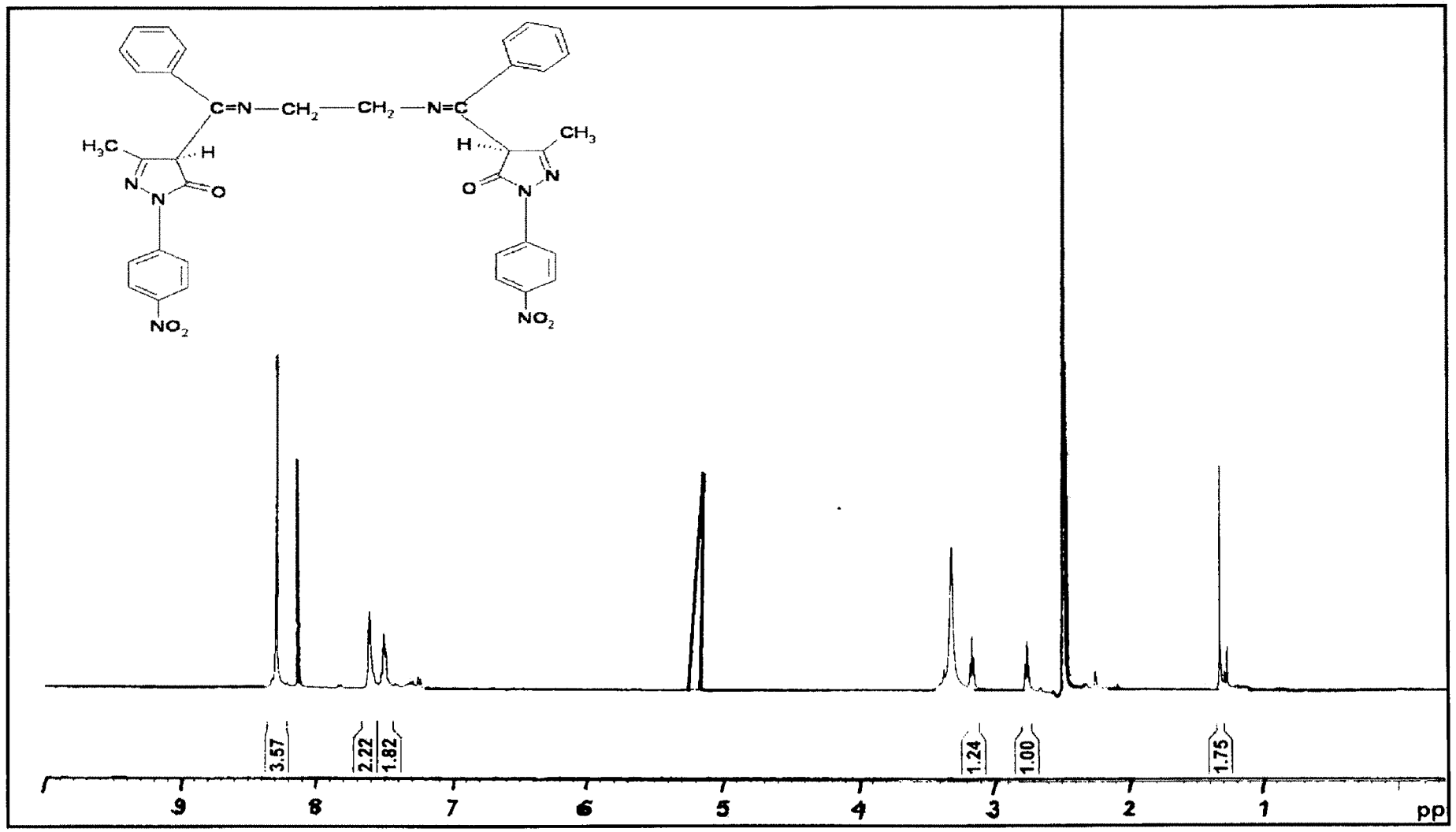


Fig: 2.2 ^{13}C NMR Spectra of H_2BBPz-en

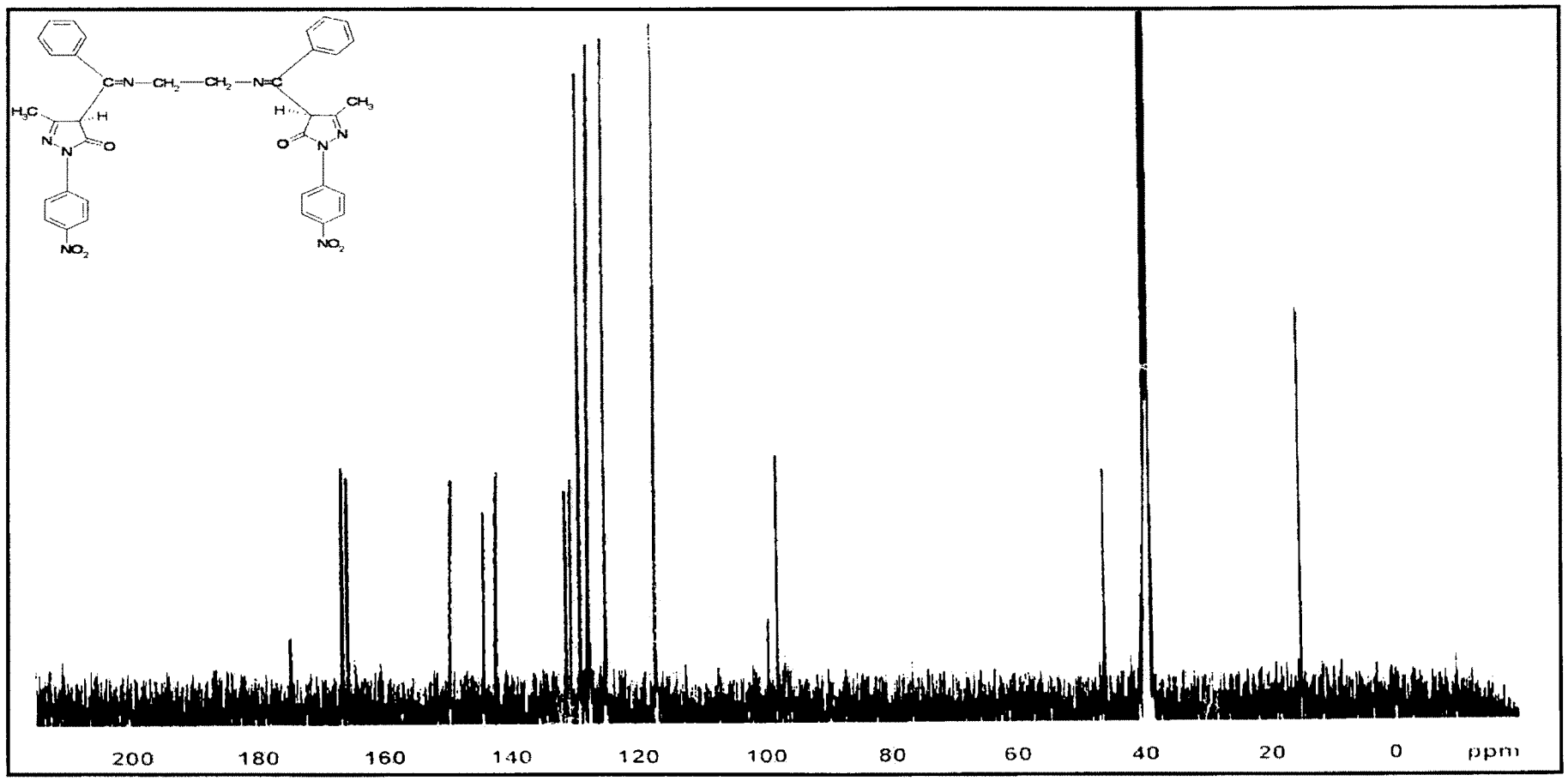
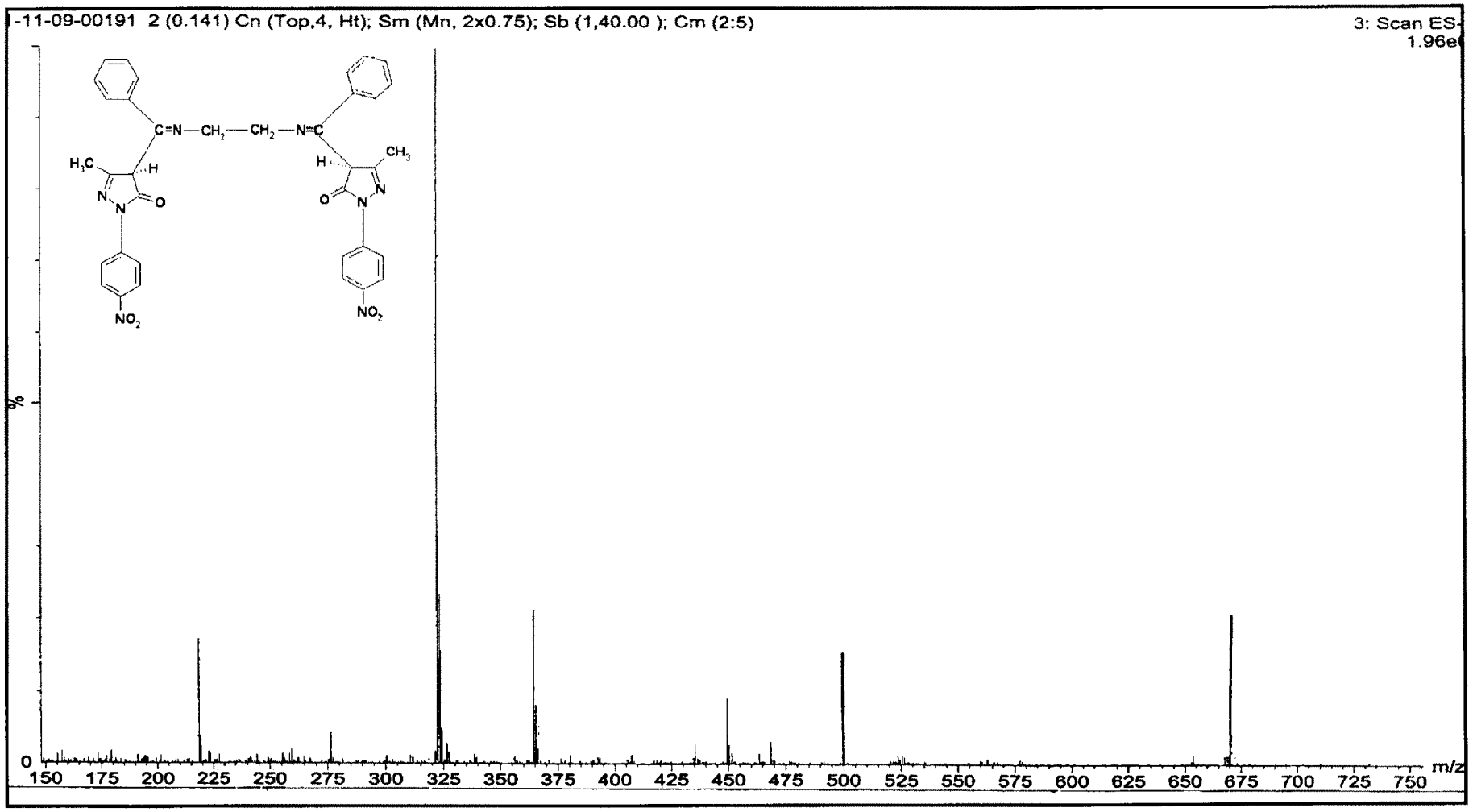
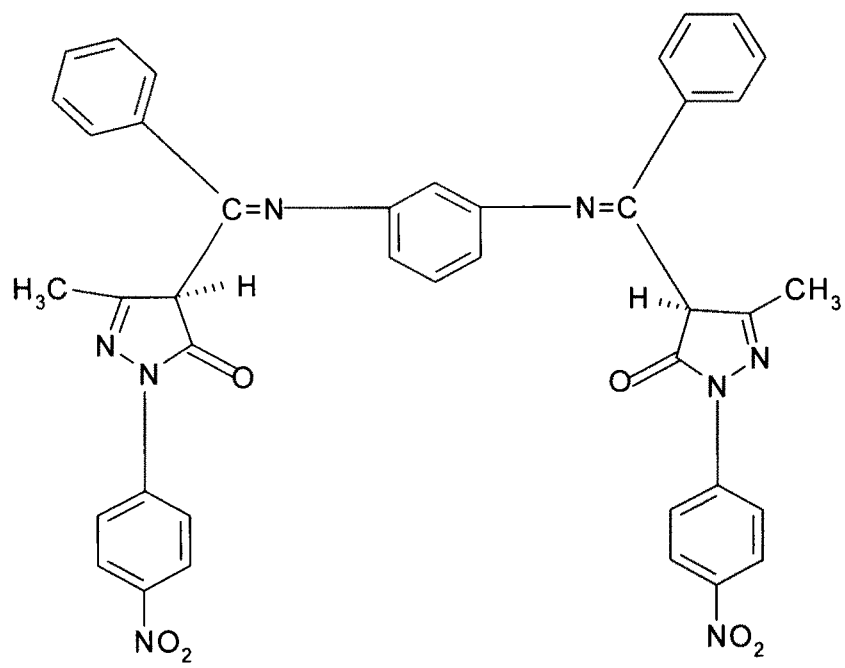


Fig: 2.3 Mass Spectra of H_2BPPz-en



[II] [H_2BPP_z-mph] 4-Benzoyl-3-methyl-1-[4'-nitrophenyl]-2-pyrazolin-5-one with m-phenylenediamine



Light Brown; m.p. found: 206-208°C; yield: ~53 %

Analyses calculated for $C_{40}H_{30}N_8O_6$: C,66.85 ; H,4.21 ; N,15.59 %.

Found: C,66.71; H,4.19; N,15.45 %,

FT-IR (KBr pellet, cm^{-1}) ν_{max}: 3476-2924 (m,vb); ($\upsilon_{O-H,}$ 5-OH group of pyrazolin ring), 1587(s,br) $\nu_{C=N}$(pyrazolin ring), 1633(s,s)$\nu_{C=N}$ (azomethine), 1374(s,s) ($\upsilon_{c-o(enolic)}$), 1327(s,s) ($\nu_{NO2,}$ nitrophenyl ring)

1H – Chemical Shift (Fig. 2.4, DMSO,δ_{PPm}):

8.1 -8.5[-$C_6H_4NO_2$,(4H)],7.5-7.9[-C_6H_5,(5H)],2.47[-CH_3 Pz ring ,(3H)], 11.53[-OH,(1H)],6.9-7.9[-C_6H_4,(4H)]

^{13}C- Chemical Shift (Fig. 2.5, DMS**O,δ_{PPm}):**

14.8(C-1),149.2(C-2),114.6(C-3),159.3(C-4),118.4(C-5&C-9),124.5(C-6&C-8),415.4(C-7),143.6(C-10),169.2(C-11),139.0(C-12),129.2(C-13&C-17)128.8(C-14&C-16)131.0(C-15),154.5(C-18&C-22), 120.8(C-19&C-21), 132.9(C-20),116.8(C-23)

Mass spectral data,m/z:

719[M^+],719,635,570,540,468,437,414,374,352,324,297,235,220,175

Fig: 2.4 ^{1}H NMR of H_2BPPz-mph

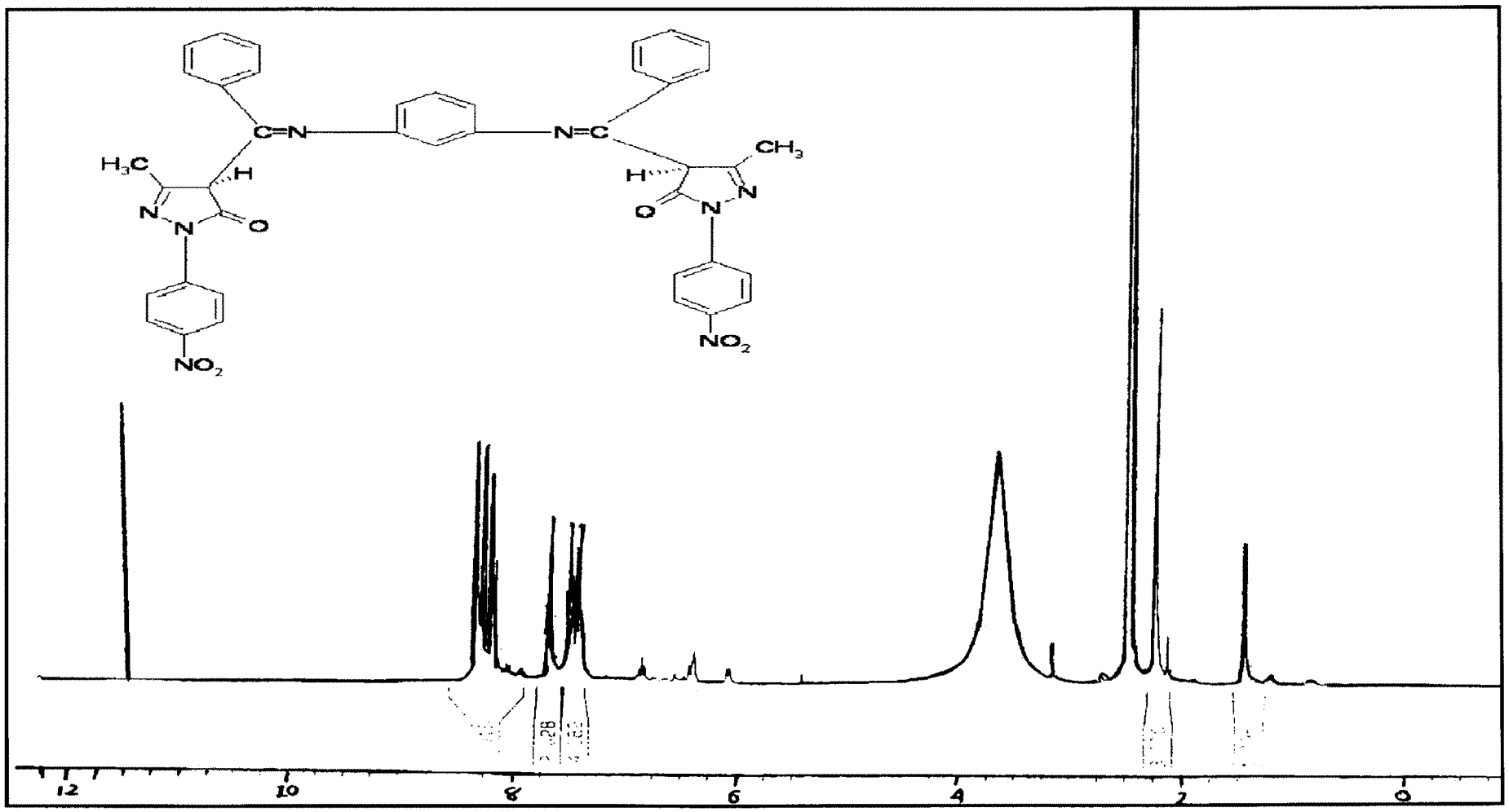


Fig: 2.5 ^{13}C NMR Spectra of H_2BPPz-mph

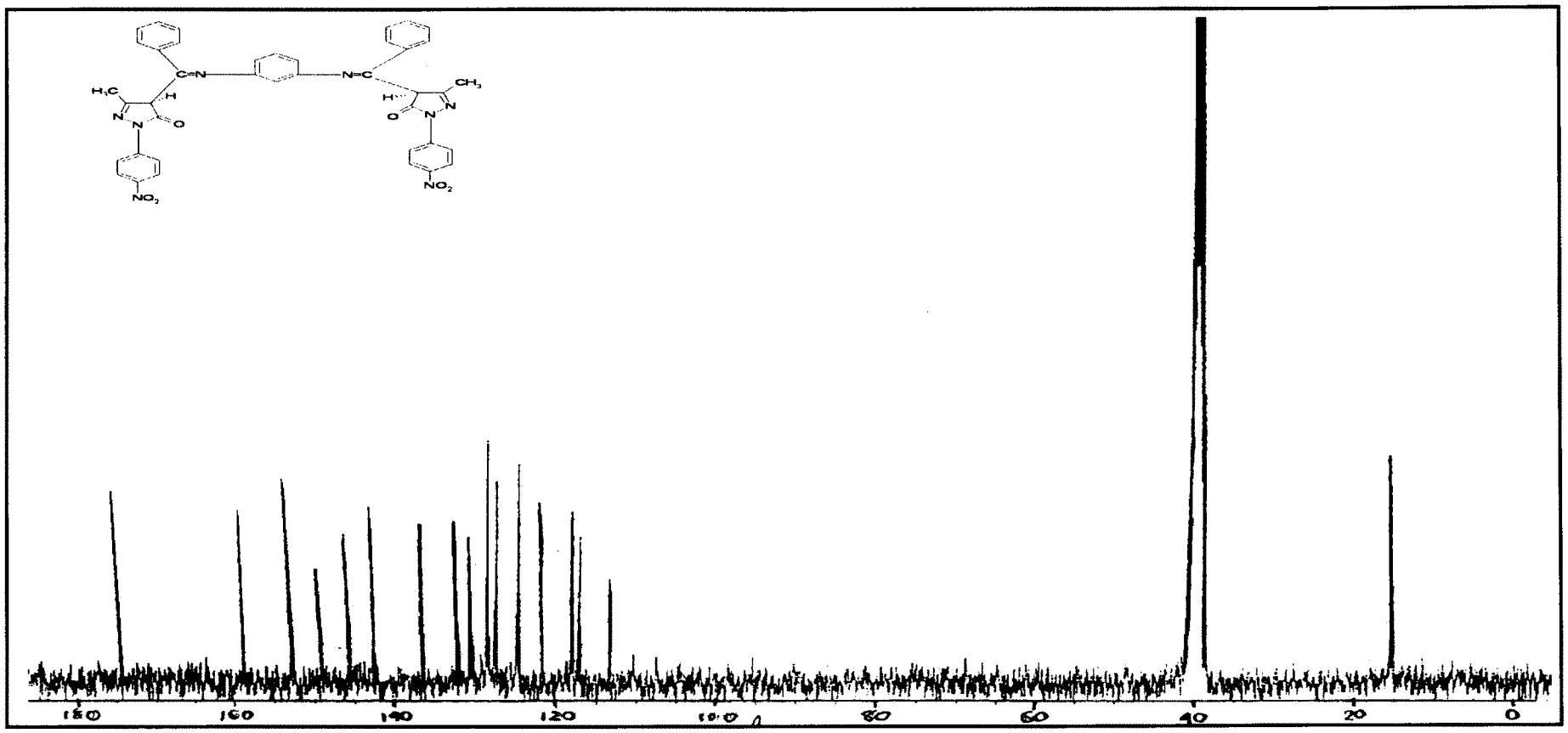
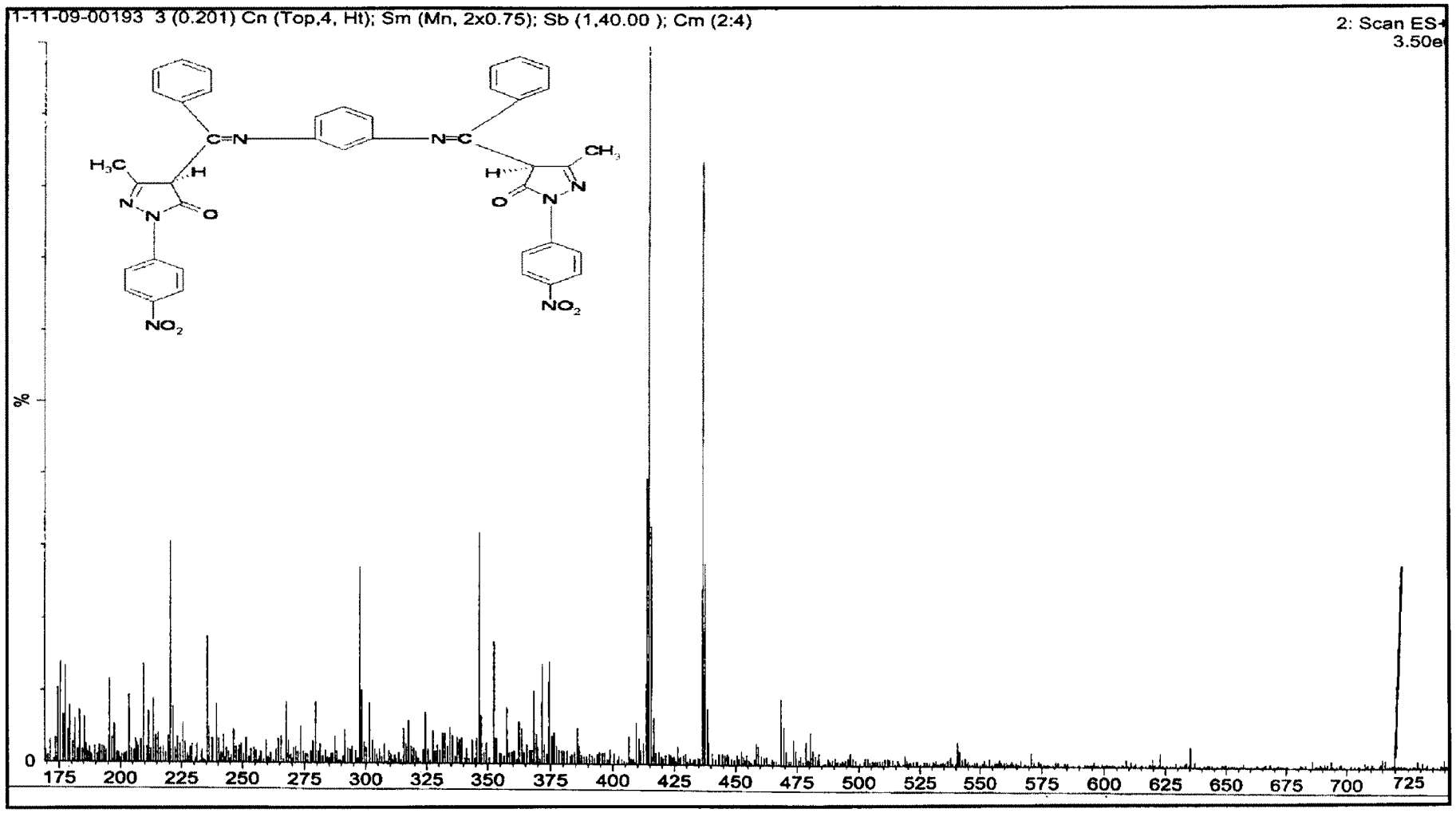
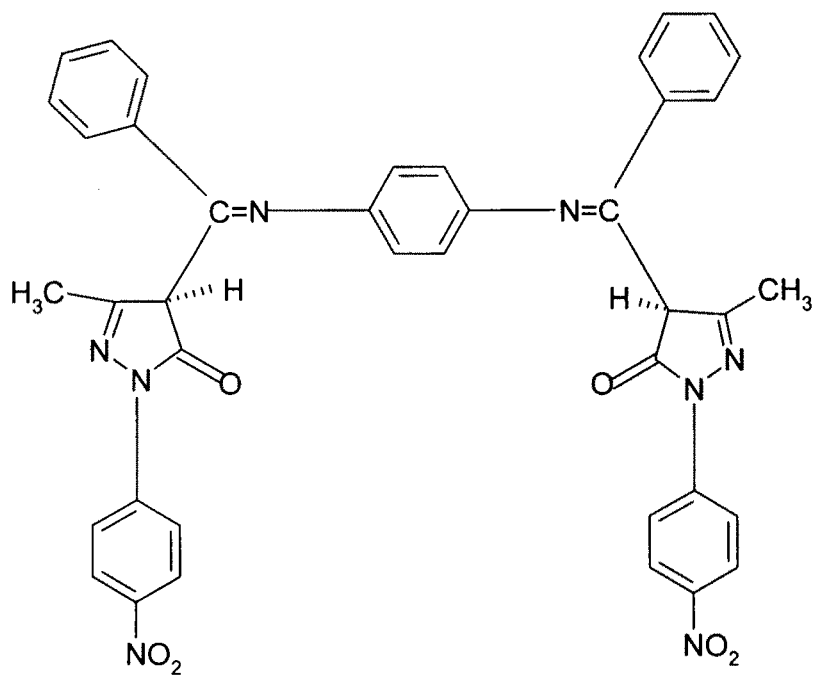


Fig: 2.6 Mass Spectra of H_2BPPz-mph



[III][H_2BPP_z-pph] 4-Benzoyl-3-methyl-1-[4'-nitrophenyl]-2-pyrazolin-5-one with p-phenylenediamine



Parrot Green; m.p. found: 182-183°C; yield: ~64 %

Analyses calculated for $C_{40}H_{30}N_8O_6$: C,66.85 ; H,4.21 ; N,15.59 %. Found: C,66.70; H,4.15; N,15.46 %,

FT-IR (KBr pellet, cm^{-1}) ν_{max}: 3464-2922 (m,vb); ($\upsilon_{O-H,}$ 5-OH group of pyrazolin ring), 1585(s,br) $\nu_{C=N}$(pyrazolin ring), 1628(s,s)$\nu_{C=N}$ (azomethine), 1400(s,s) ($\upsilon_{c-o(enolic)}$), 1325(s,s) ($\nu_{NO2,}$ nitrophenyl ring)

1H – Chemical Shift [Fig. 2.7, DMSO,δ_{PPm}

7.9 -8.4[- $C_6H_4NO_2$,(4H)],7.3-79[C_6H_5,(5H)],2.45[-CH_3 Pz ring ,(3H)] , 11.53[-OH,(1H)],6.6-6.7[-C_6H_4,(4H)]

^{13}C- Chemical Shift (Fig. 2.8, DMS**O,δ_{PPm}):**

14.8(C-1),149.2(C-2),114.6(C-3),159.3(C-4),118.4(C-5&C-9),124.5(C-6&C-8),415.4(C-7),143.6(C-10),169.2(C-11),139.0(C-12),129.2(C-13&C-17)128.8(C-14&C-16)131.0(C-15), 149.5(C-18&C-21), 123.6(C-19,C-20,C-22&C-23)

Mass spectral data,m/z:

719[M^+],719,646,611,541,518,474,468,458,437,416,414,393,374,346,327

Fig: 2.7 ^{1}H NMR of H_2BPPz-pph

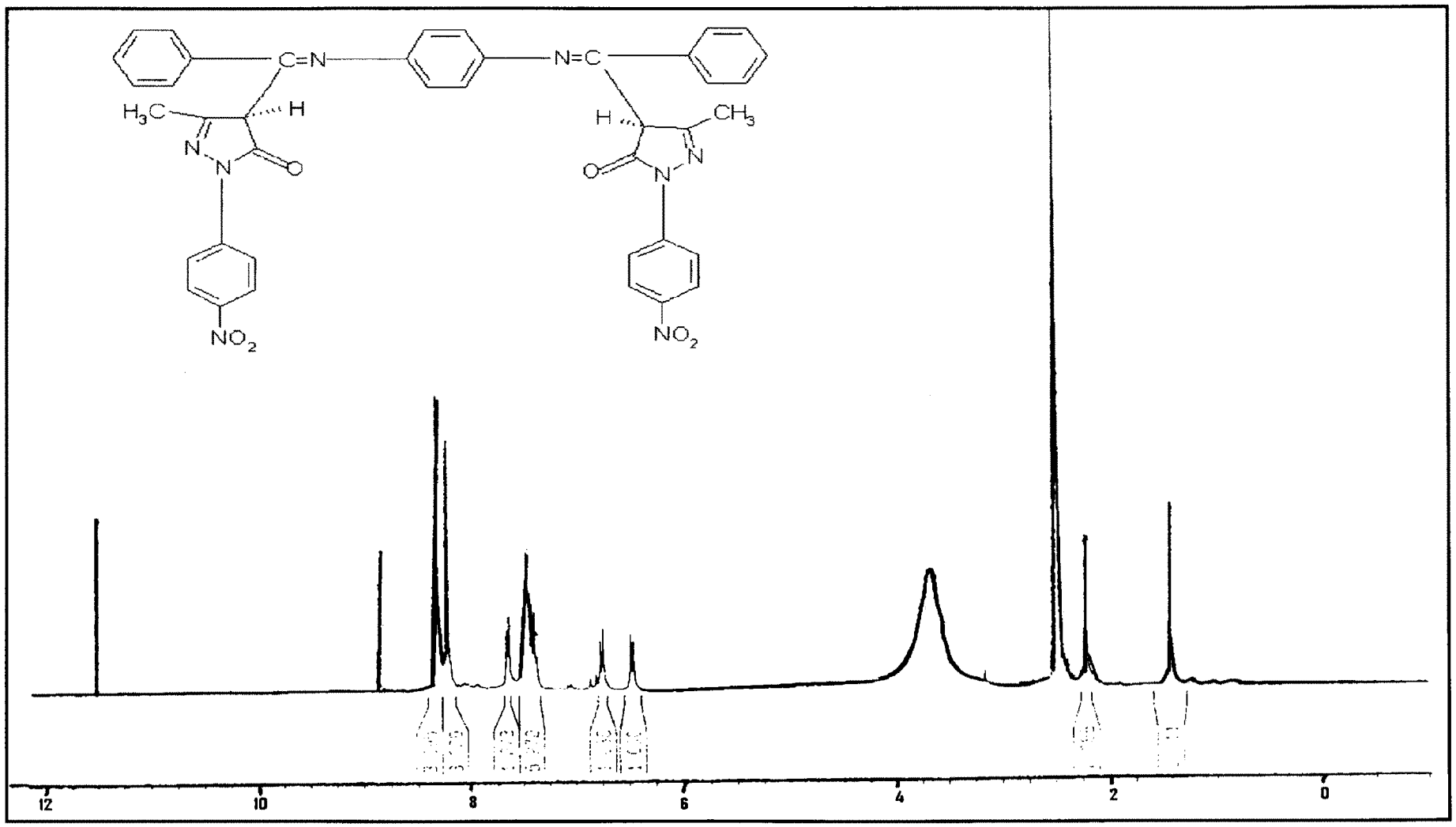


Fig: 2.8 ^{13}C NMR Spectra of H_2BPPz-pph

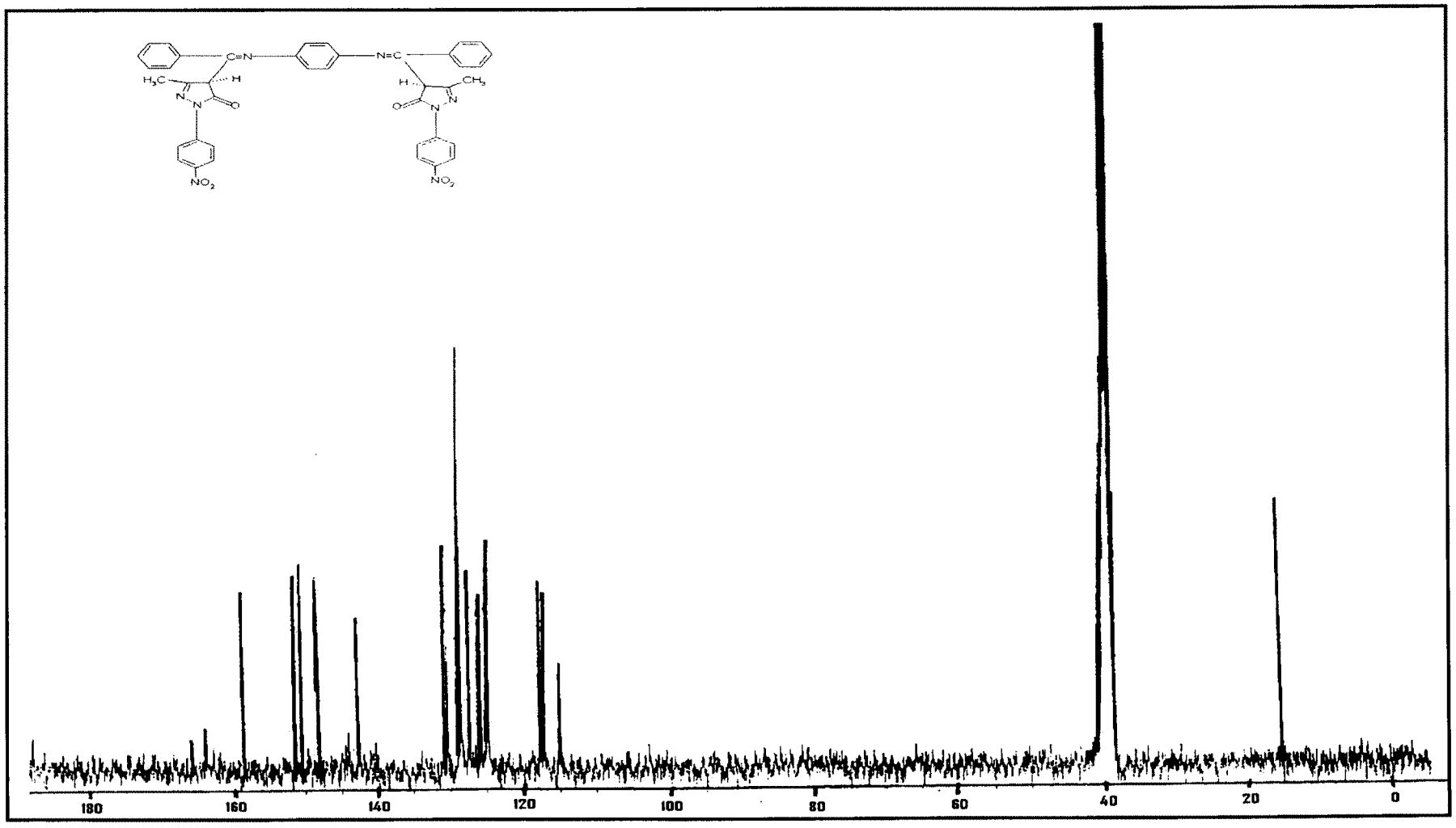
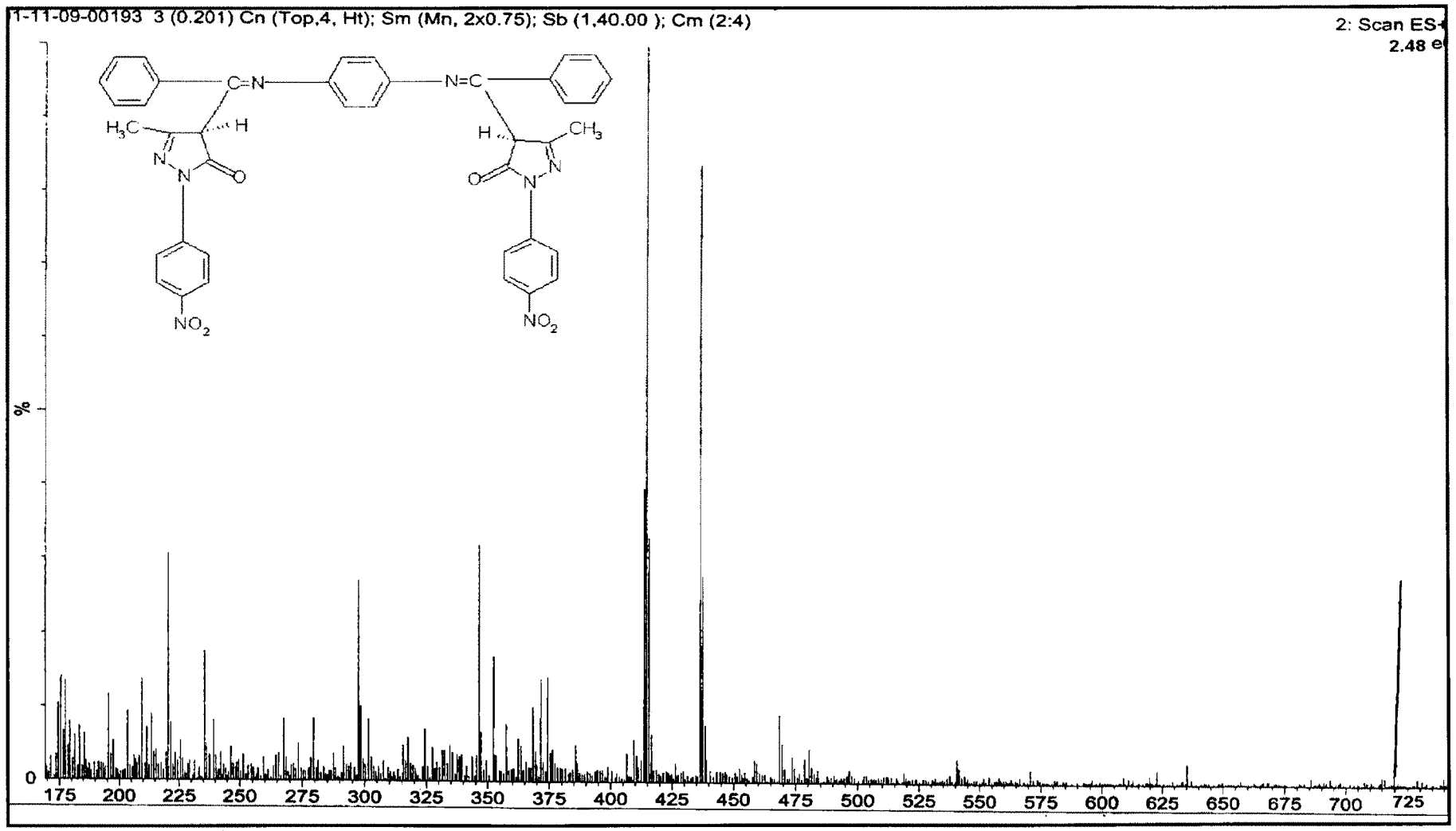
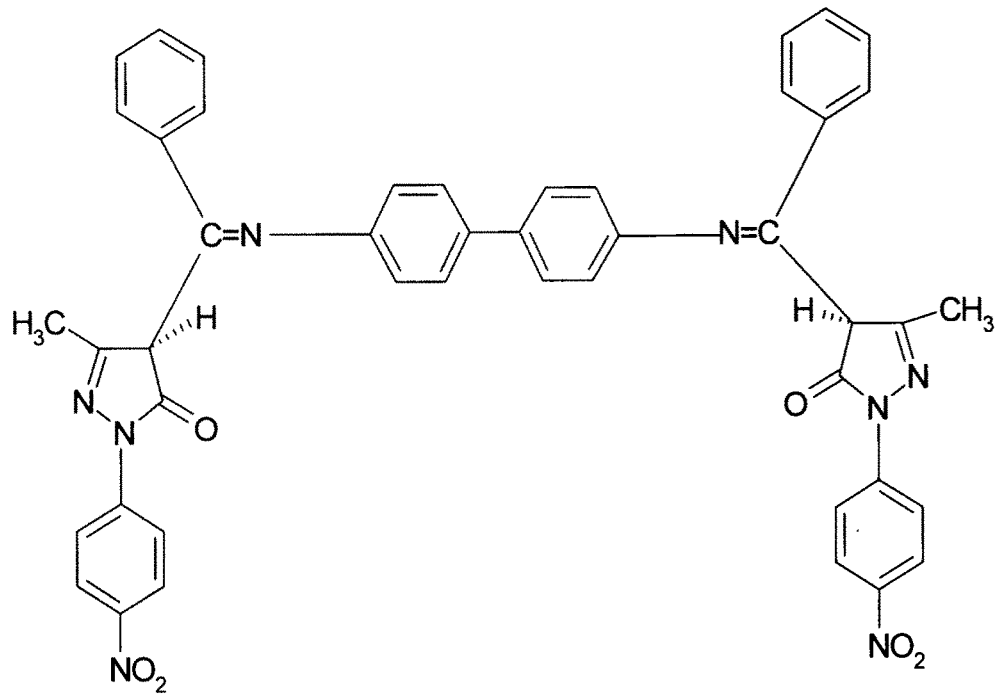


Fig: 2.9 Mass Spectra of H_2BPPz-pph



[IV] [H_2BPP_z-benz] 4-Benzoyl-3-methyl-1-[4'-nitrophenyl]-2-pyrazolin-5-one with benzidine



Brown; m.p. found: 207-208°C; yield: ~59 %

Analyses calculated for: $C_{46}H_{34}N_8O_6$: C,69.51 ; H,4.31 ; N,14.10 %.

Found: C,69.45; H,4.29; N,13.99 %,

FT-IR (KBr pellet, cm^{-1}) ν_{max}: 3457-2918 (m,vb); ($\upsilon_{O-H,}$ 5-OH group of pyrazolin ring), 1504(s,br) $\nu_{C=N}$(pyrazolin ring), 1599(s,s)$\nu_{C=N}$ (azomethine), 1315(s,s) ($\upsilon_{c-o(enolic)}$), 1325(s,s) ($\nu_{NO2,}$ nitrophenyl ring)

1H – Chemical Shift (Fig. 2.10, DMSO,δ_{PPm}):

8.1 -8.4[-$C_6H_4NO_2$,(4H)],7.5-7.9[C_6H_5,(5H)],2.47[-CH_3 Pz ring ,(3H)], 11.53[-OH,(1H)],7.5-7.7[-C_6H_4,(4H)]

^{13}C- Chemical Shift (Fig. 2.11, DMSO,δ_{PPm}):

14.8(C-1),149.2(C-2),114.6(C-3),159.3(C-4),118.4(C-5&C-9),124.5(C-6&C-8),415.4(C-7),143.6(C-10),169.2(C-11),139.0(C-12),129.2(C-13&C-17)128.8(C-14&C-16)131.0(C-15),149.5(C-18),139.3(C-21), 122.8(C-19&C-23),129.2(C-20&C-22)

Mass spectraldata,m/z:

792[M^+],792,702,658,601,502,371,346,311,289,267,220,186,177,168,149 ,137

Fig: 2.10 ^{1}H NMR of H_2BPPz-benz

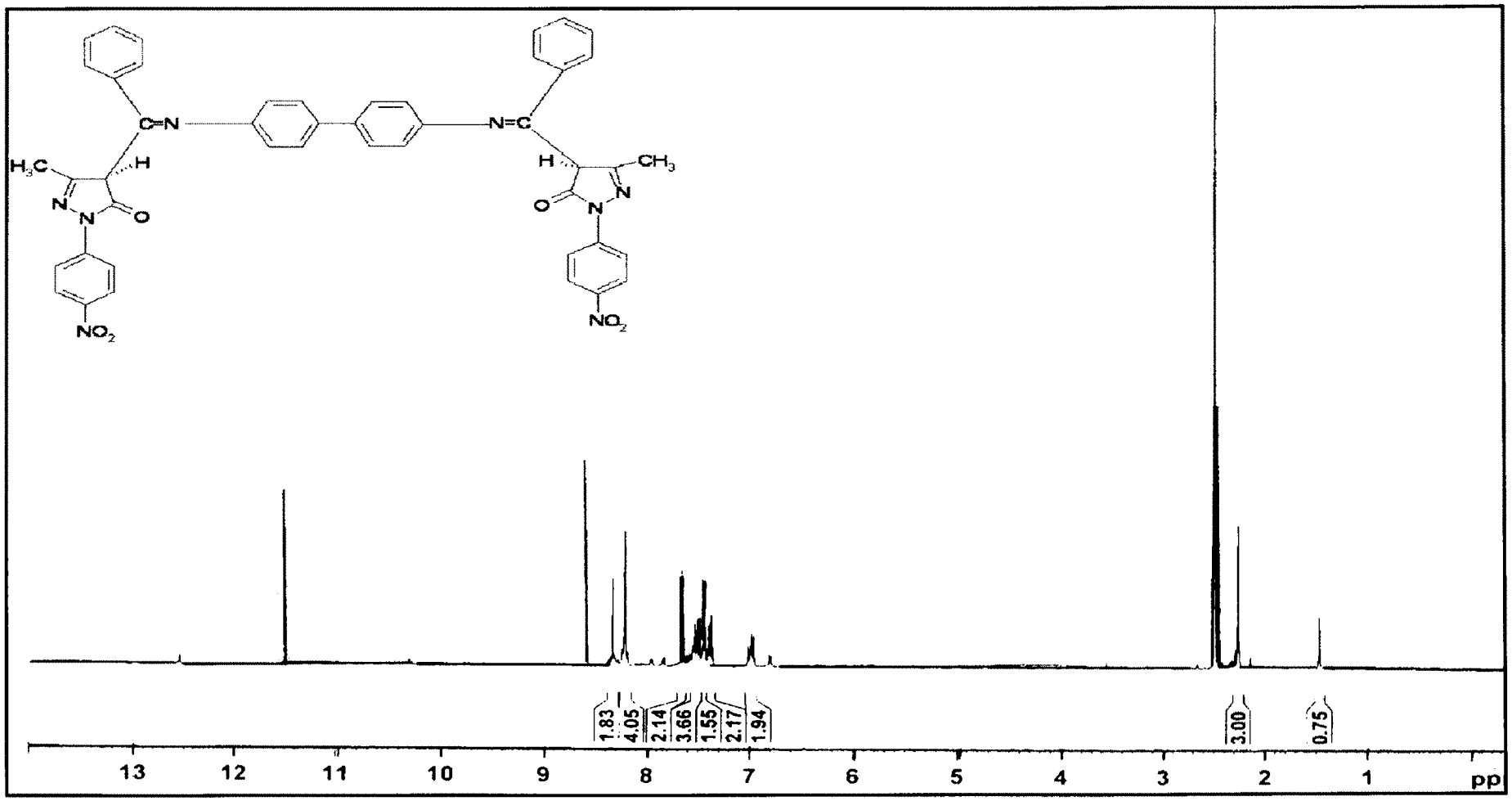


Fig: 2.11 ^{13}C NMR Spectra of H_2BPPz-benz

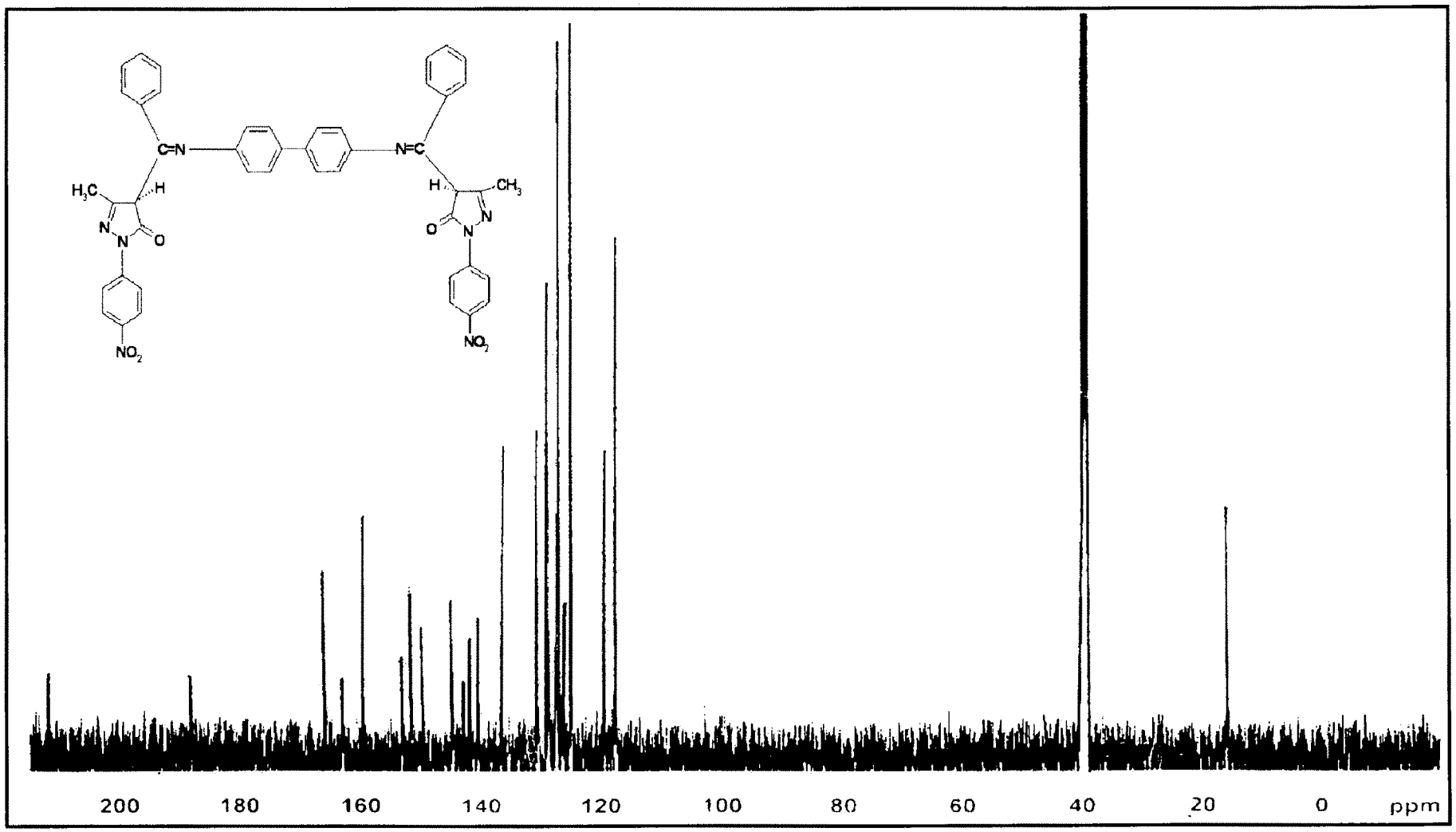
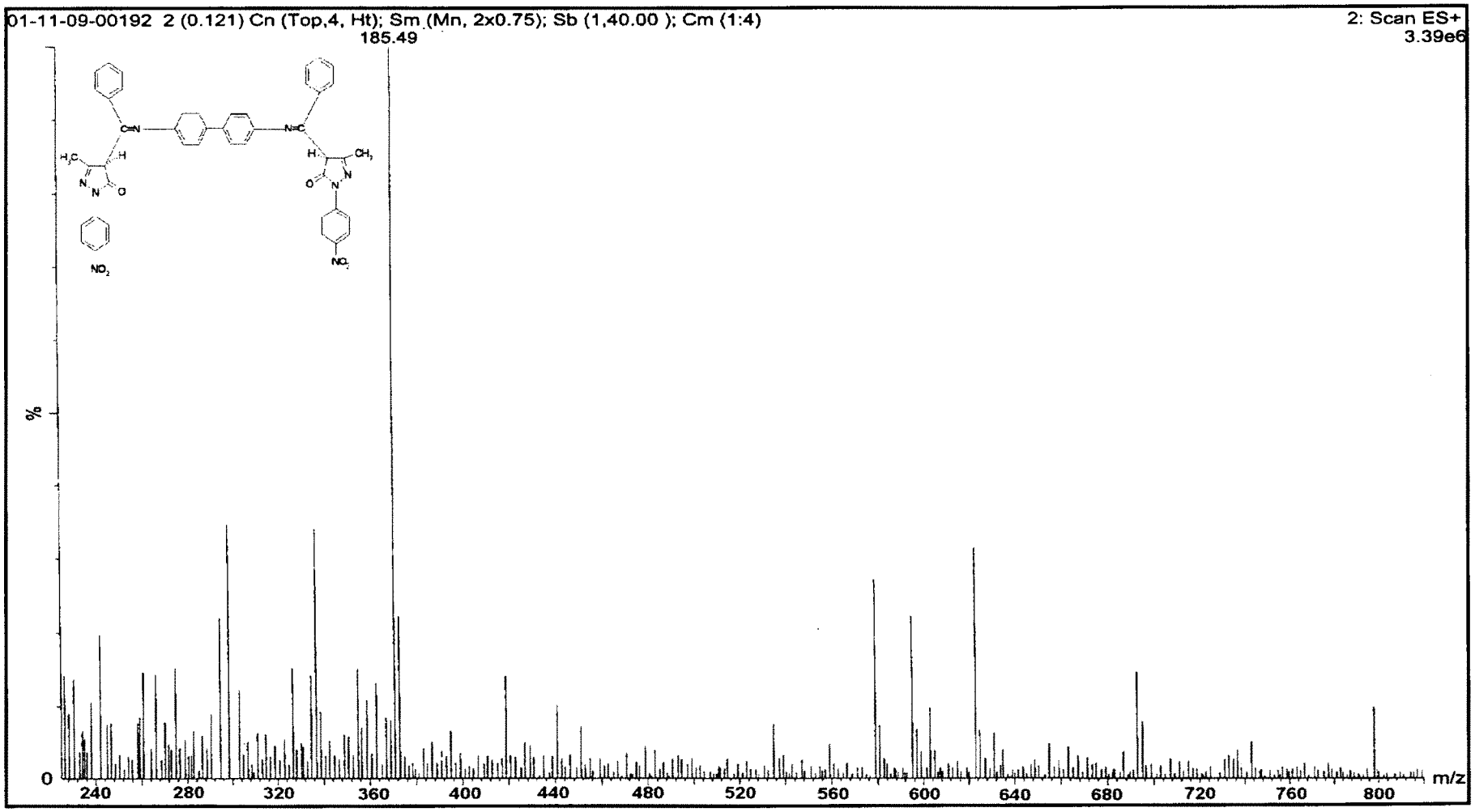


Fig: 2.12 Mass Spectra of H_2BPPz-benz



2. F. SYNTHESIS OF THE CHELATES:

The following general procedure was used in the synthesis of all the metal chelates.

Metal salt was dissolved in a minimum amount of hot ethanol. The hot ethanolic ligand solution in slight excess over the metal: ligand ratio 1:1 (for all chelates), was added drop wise with constant stirring. To the resulting mixture 2 grams of sodium acetate was added and then the mixture was refluxed for 2 hrs. The resulting mixture thus obtained was then concentrated of half of its original volume. The metal chelates were filtered and washed several times with hot water and finally with hot ethanol. The metal chelates were air dried. The yields of the chelates were almost quantitative.

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