

Supplementary Information

Sulfonated nanohydroxyapatite functionalized with 2-aminoethyl dihydrogen phosphate (HAP@AEPH₂-SO₃H) as a new recyclable and eco-friendly catalyst for rapid one-pot synthesis of 4,4'-(aryl methylene)bis(3-methyl-1H-pyrazol-5-ol)s

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Experimental

General

The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FTIR spectra were recorded on pressed KBr pellets using a AVATAR 370 FT-IR spectrometer (Therma Nicolet spectrometer, USA) at room temperature in the range between 4000 and 400 cm⁻¹ with a resolution of 4 cm⁻¹, and each spectrum was the average of 32 scans. NMR spectra were recorded on a NMR Bruker Avance spectrometer at 400 and 300 MHz in DMSO-d₆ as solvent in the presence of tetramethylsilane as internal standard. Mass spectra were recorded with a CH7A Varianmat Bremem instrument at 70

eV electron impact ionization; in m/z (rel %). All of the products were known compounds and characterized by the FT-IR and comparison of their melting points with known compounds. The structure of selected products was further confirmed by ^1H NMR, ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.

4,4'-(Phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)(3a)

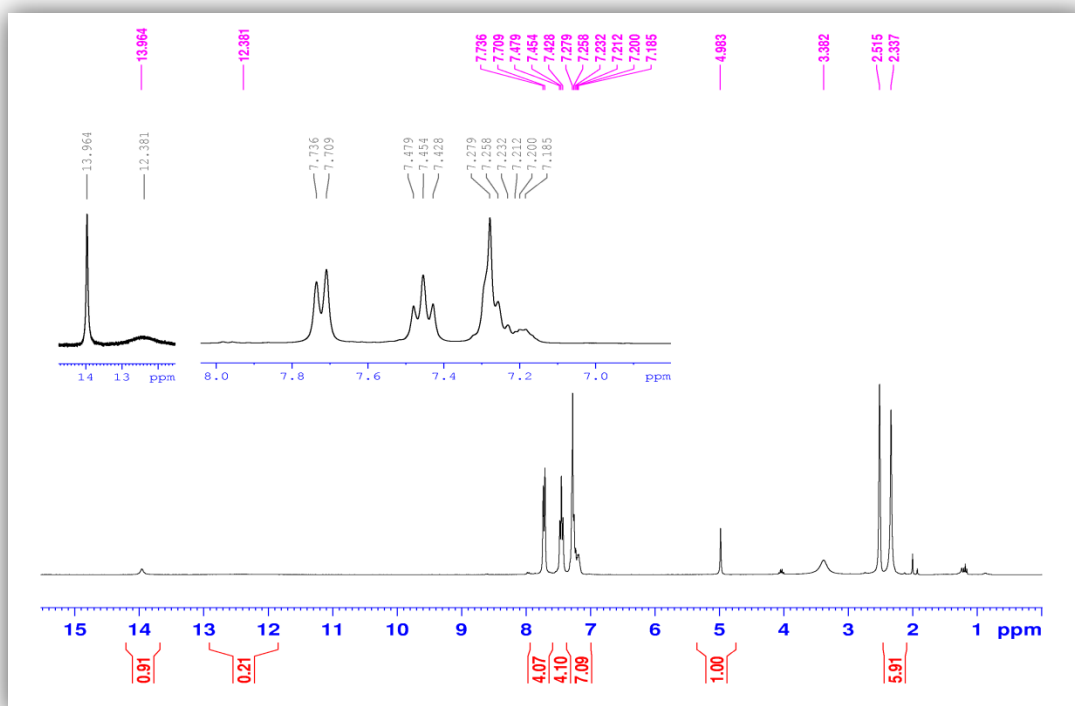
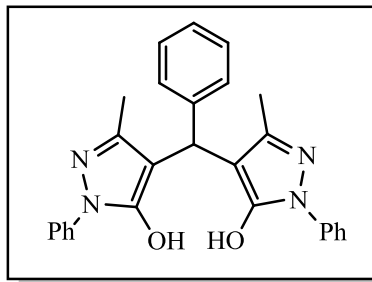


Figure 1a: ^1H NMR (300 MHz, $\text{DMSO}-d_6$) of 4,4'-(Phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

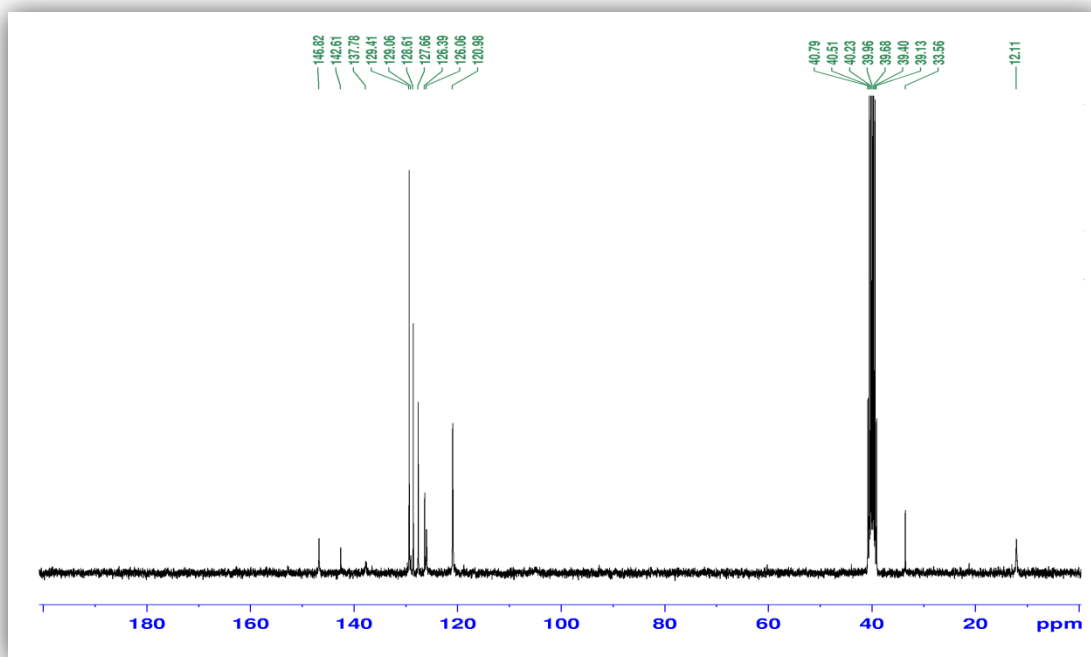


Figure 1b: ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) of 4,4'-(Phenylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)

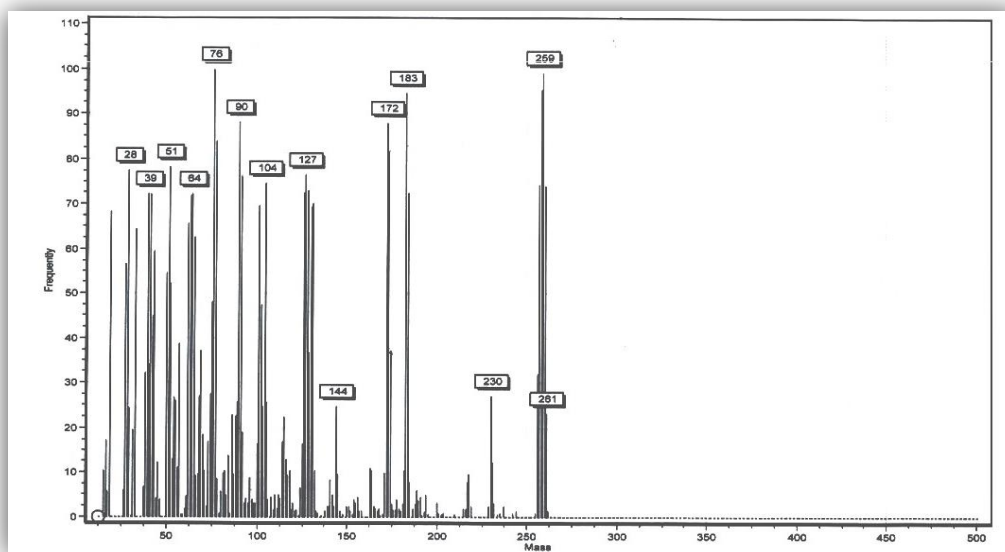
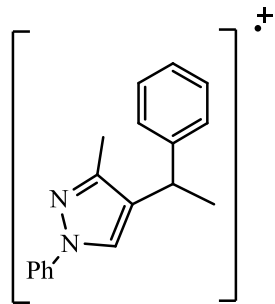
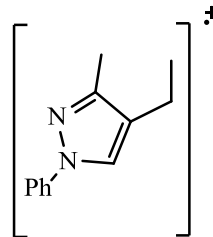


Figure 1c: Mass spectrum of 4,4'-(Phenylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).



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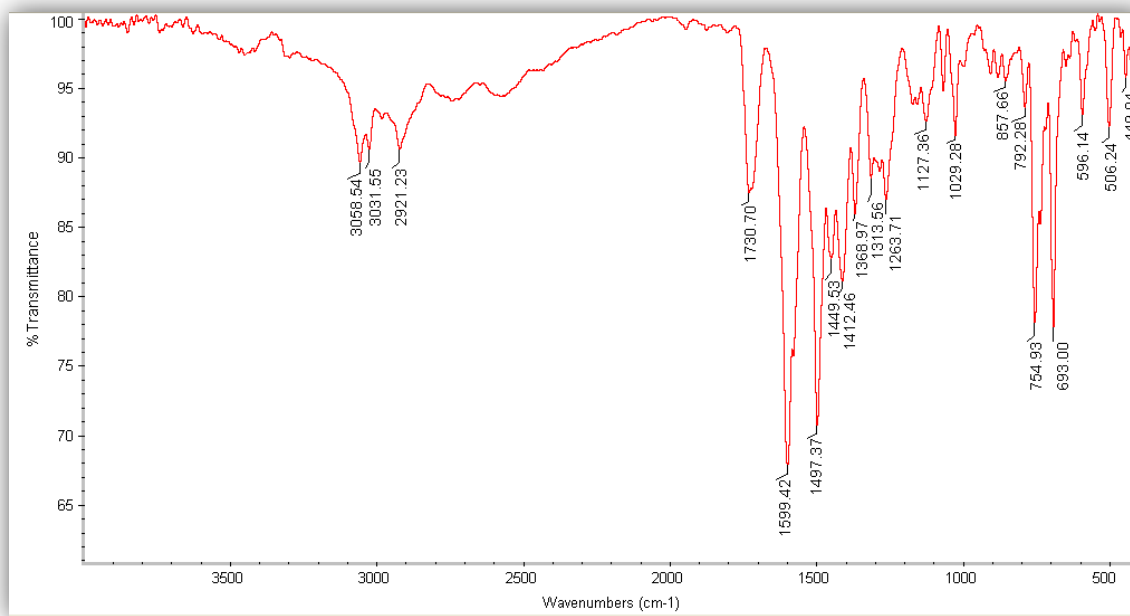


Figure 1d: FT-IR (KBr) spectrum of 4,4'-(Phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

4,4'-((4-Hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3b)

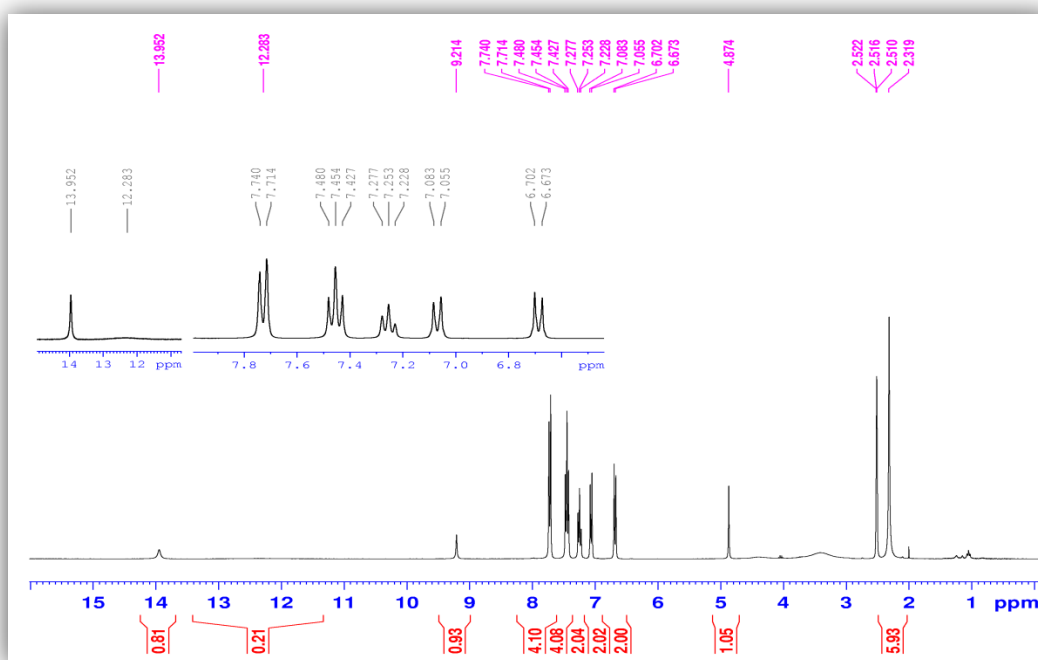
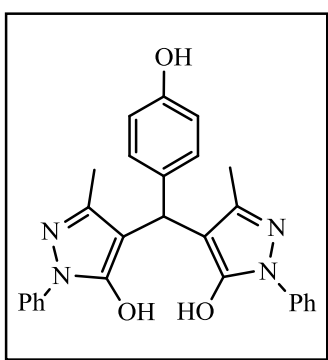


Figure 2a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of 4,4'-((4-Hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)

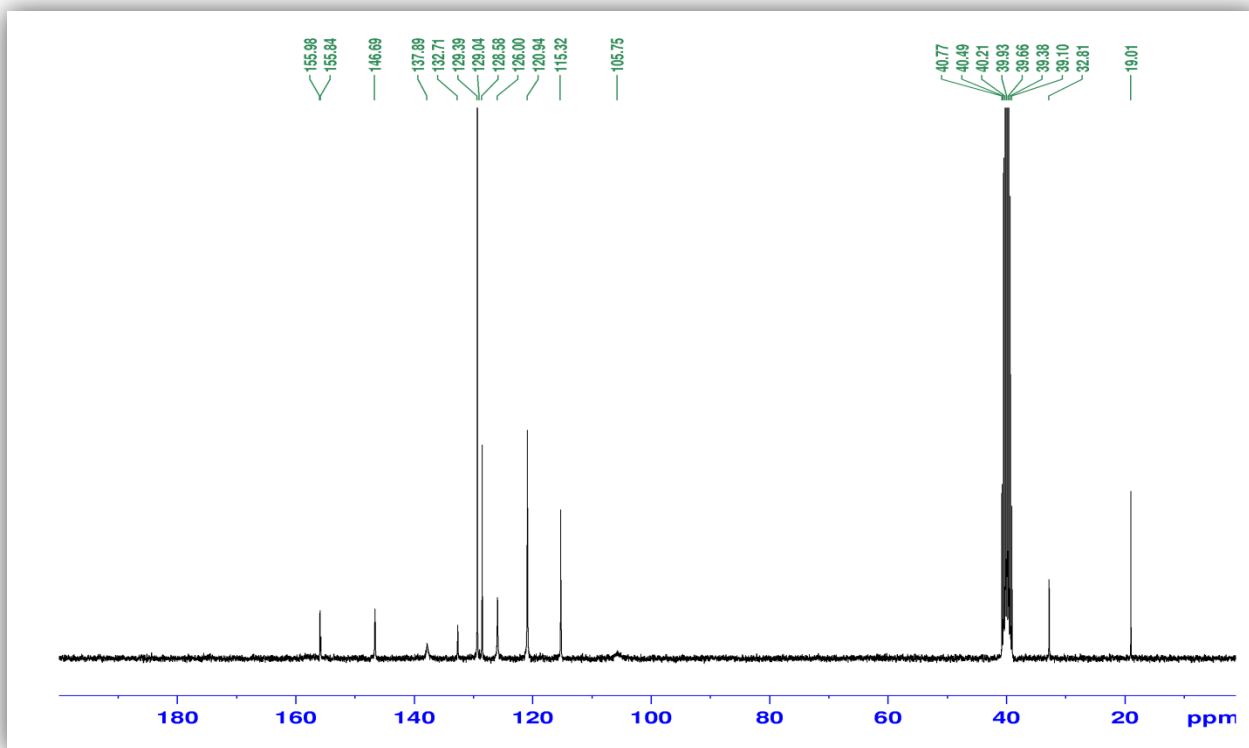


Figure 2b: ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) of 4,4'-((4-Hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)

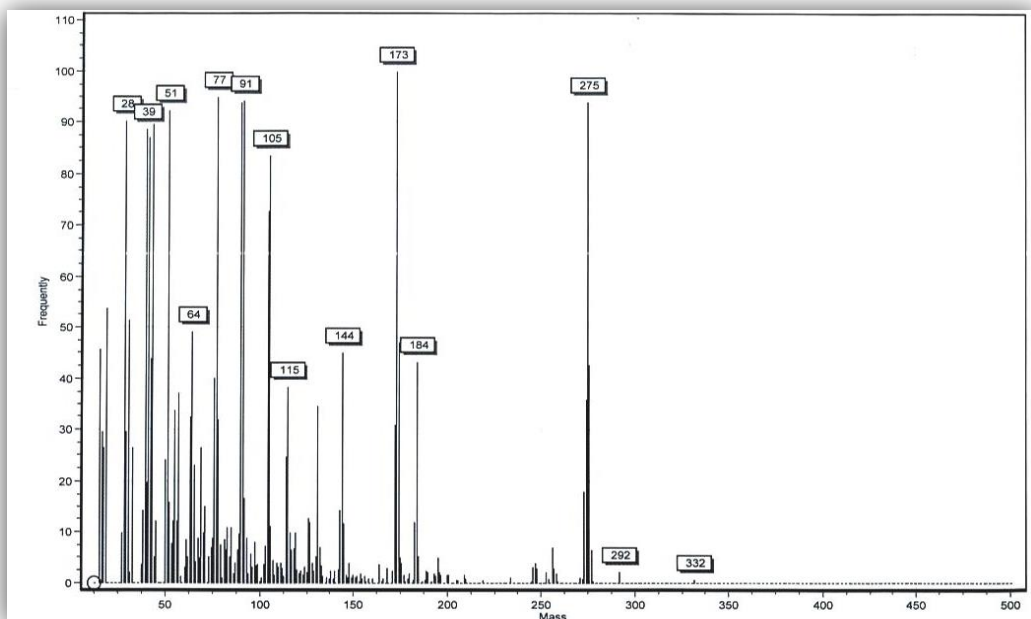


Figure 2c: Mass spectrum of 4,4'-((4-Hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)

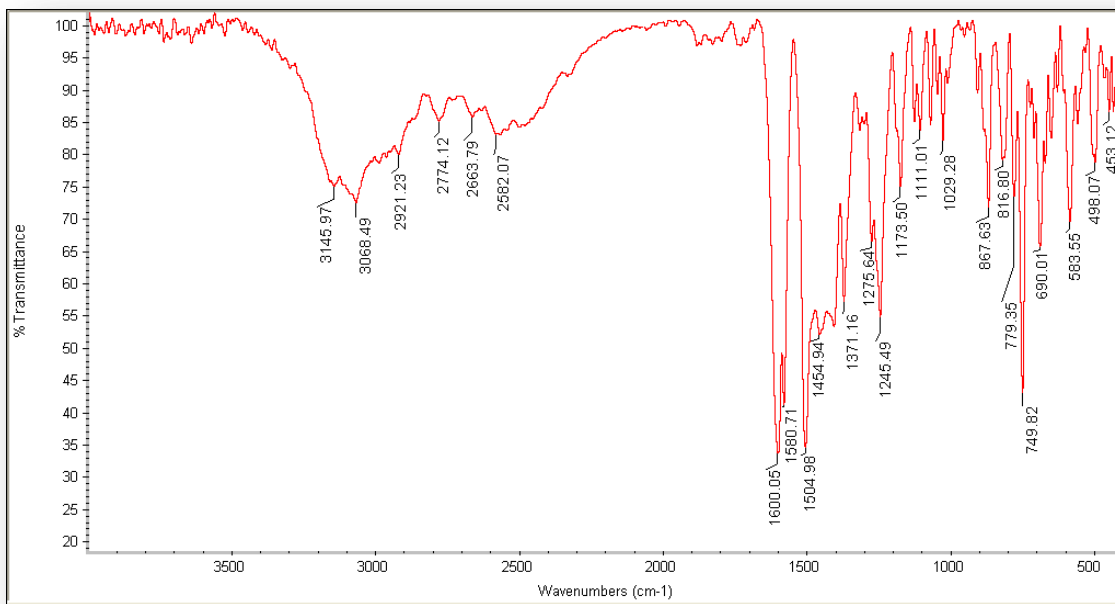


Figure 2d: FT-IR (KBr) spectrum of 4,4'-((4-Hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

4,4'-((3-Hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3c)

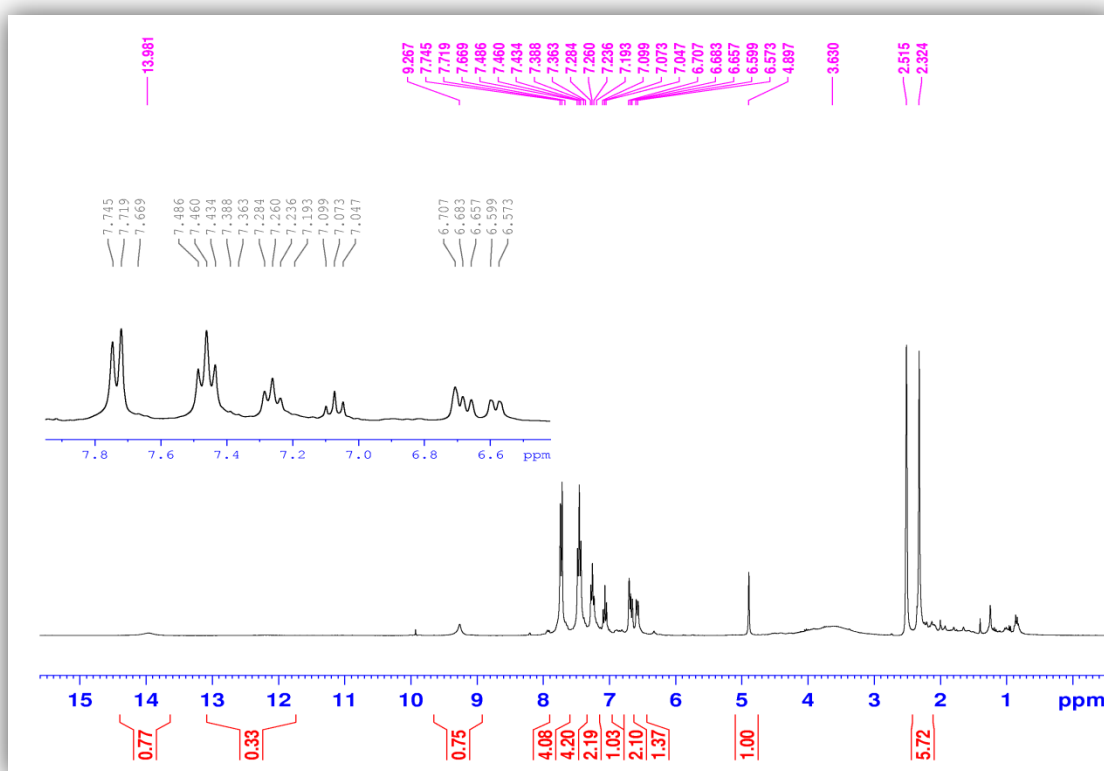
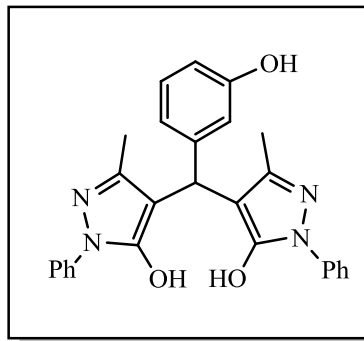


Figure 3a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of 4,4'-((3-Hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

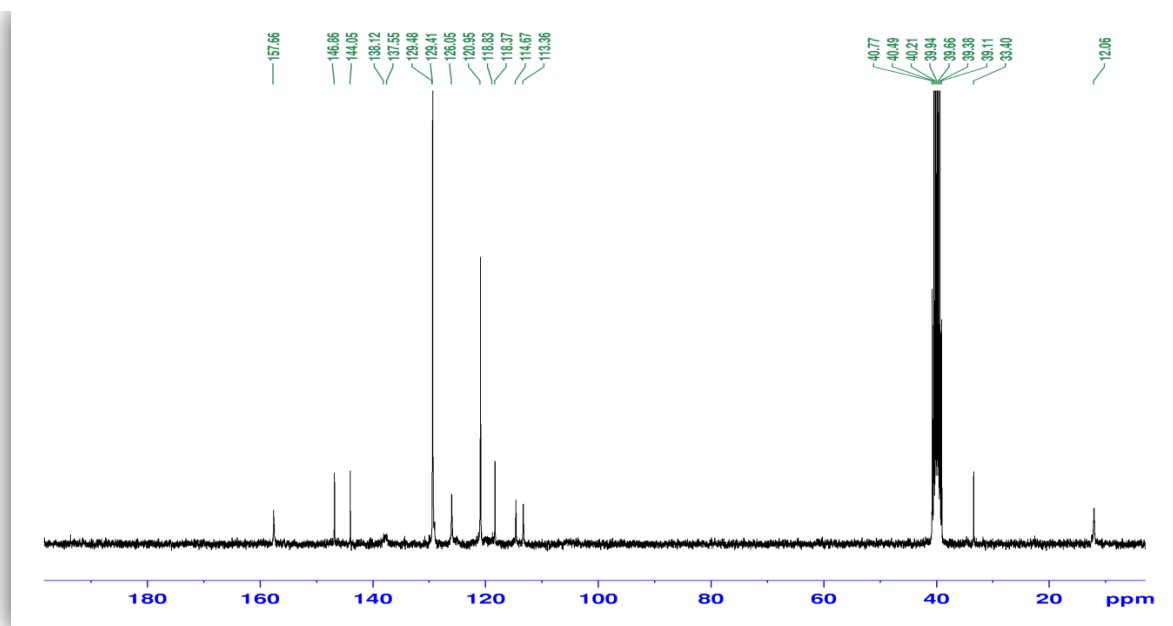


Figure 3b: ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) of 4,4'-((3-Hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

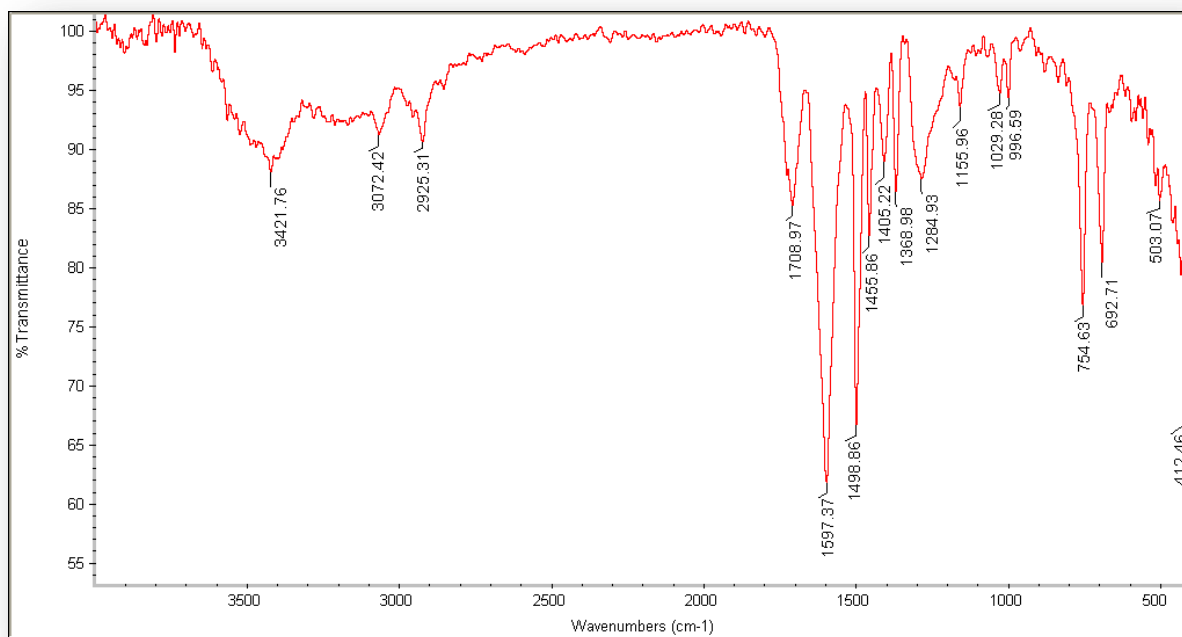


Figure 3c: FT-IR (KBr) spectrum of 4,4'-((3-Hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

4,4'-((2-Hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3d)

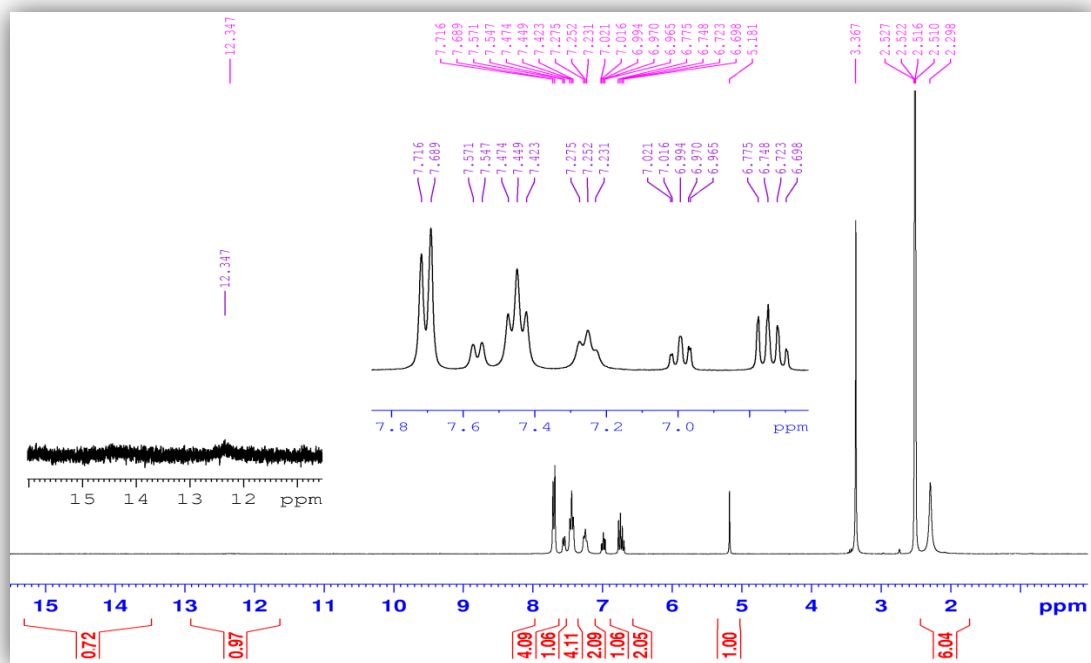
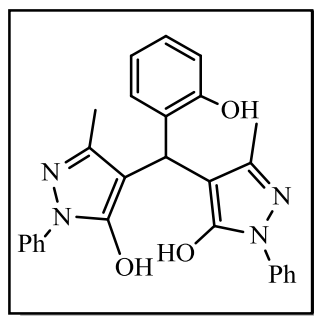


Figure 4a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of 4,4'-((2-Hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

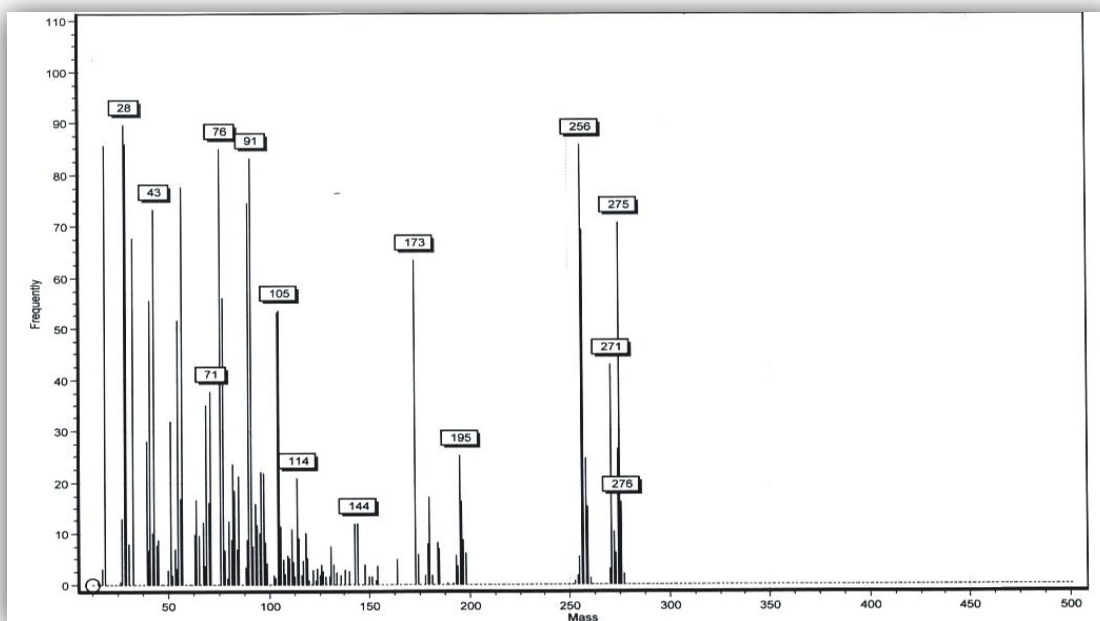


Figure 4b: Mass spectrum of 4,4'-((2-Hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

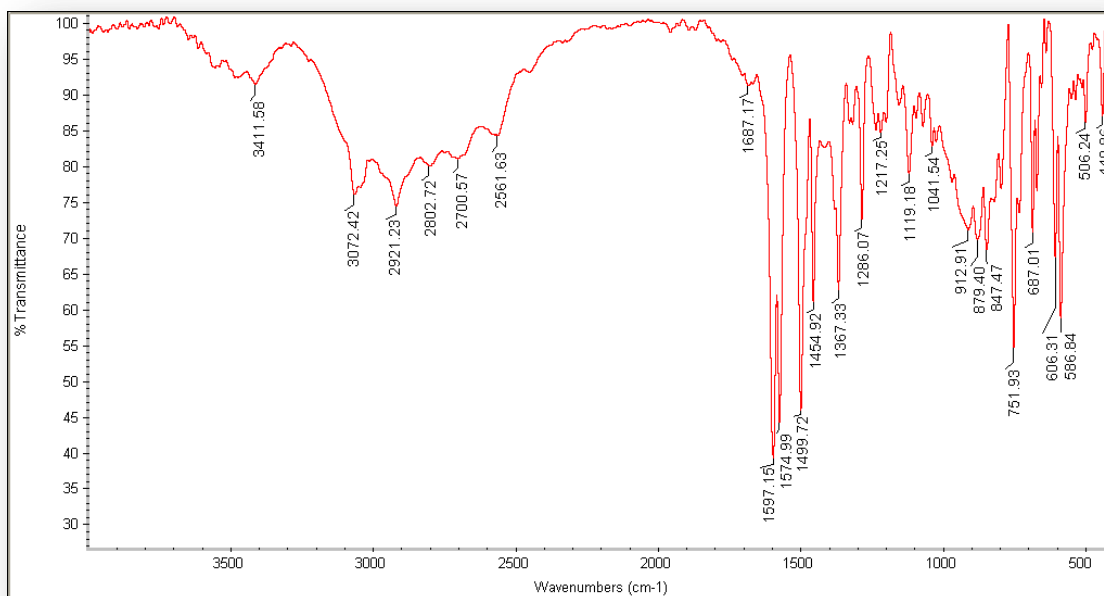


Figure 4c: FT-IR (KBr) spectrum of 4,4'-((2-Hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

4,4'-((4-Methoxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3e)

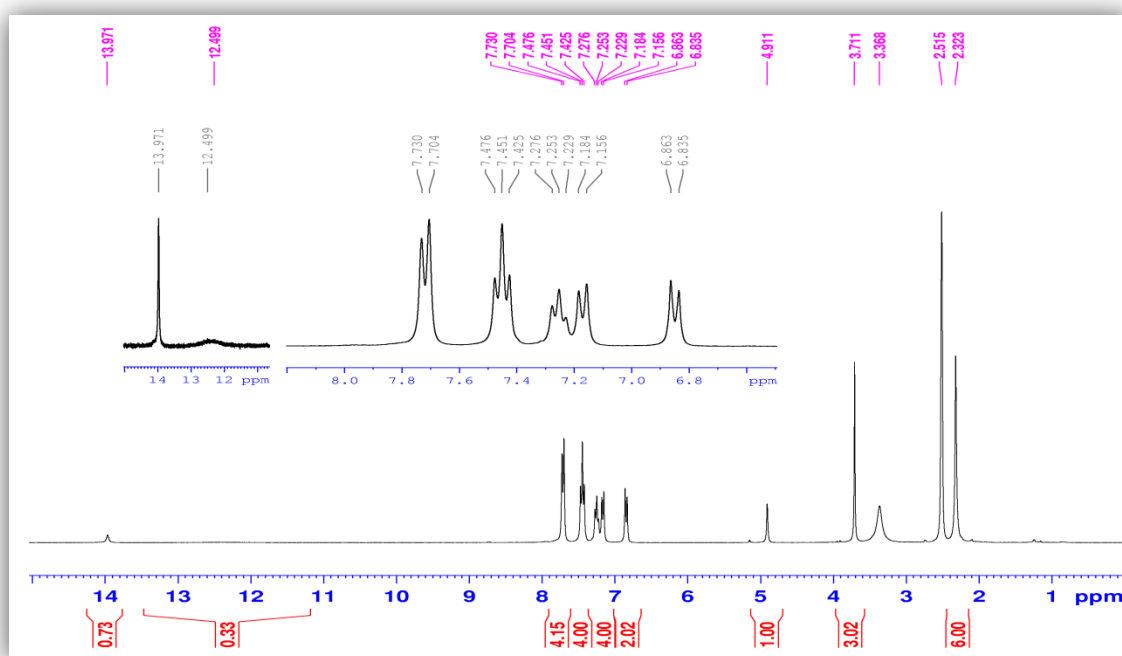
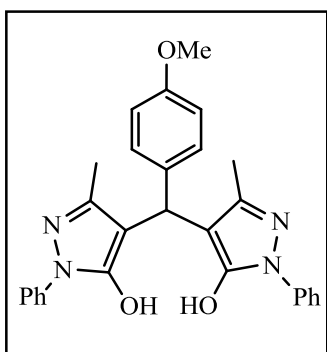


Figure 5a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of 4,4'-((4-Methoxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

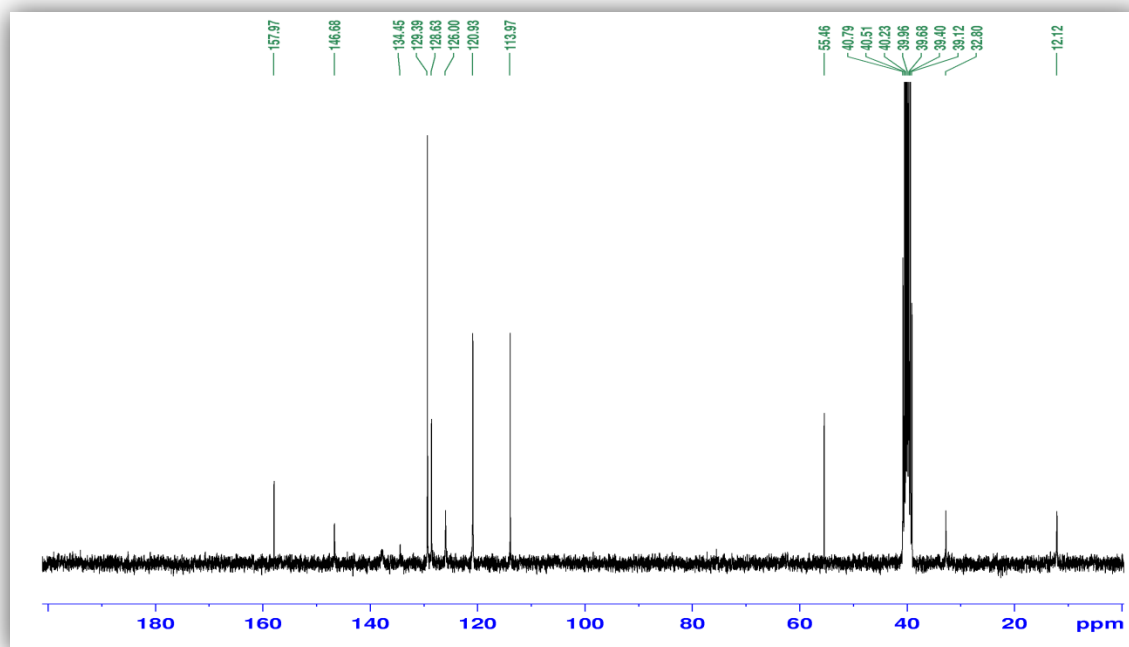


Figure 5b: ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) of 4,4'-((4-Methoxyphenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)

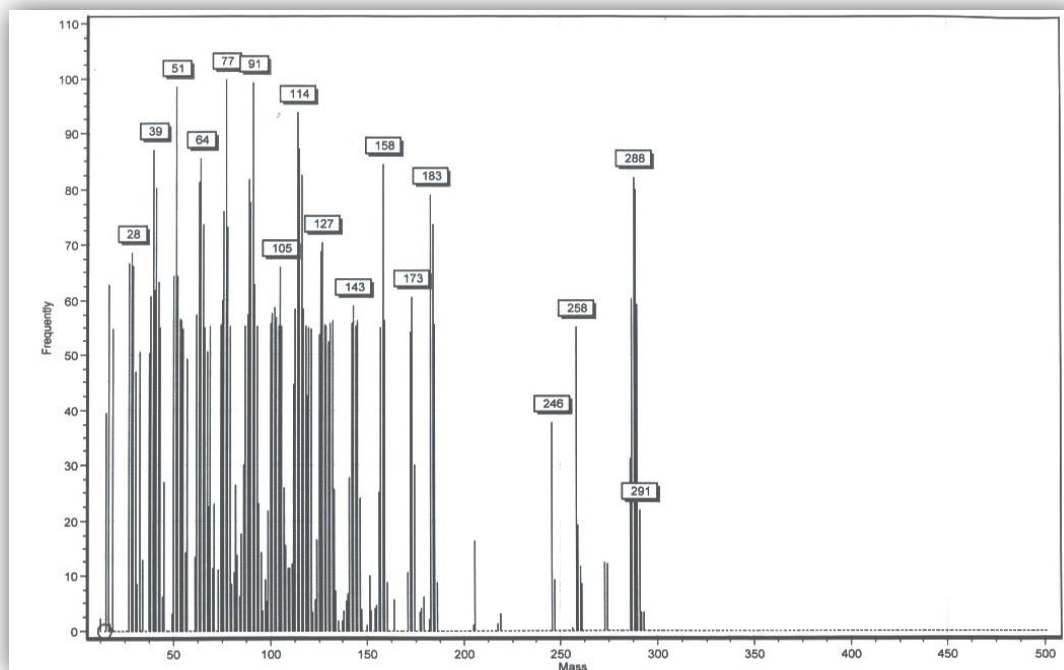


Figure 5c: Mass spectrum of 4,4'-((4-Methoxyphenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

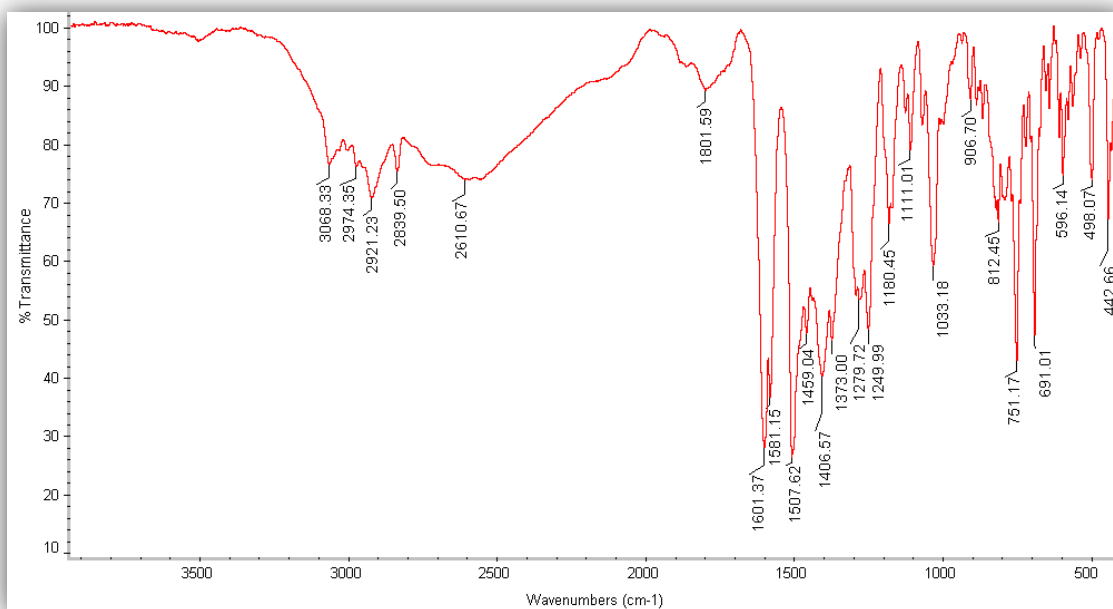


Figure 5d: FT-IR (KBr) spectrum of 4,4'-((4-Methoxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol))

4,4'-((3-Methoxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3f)

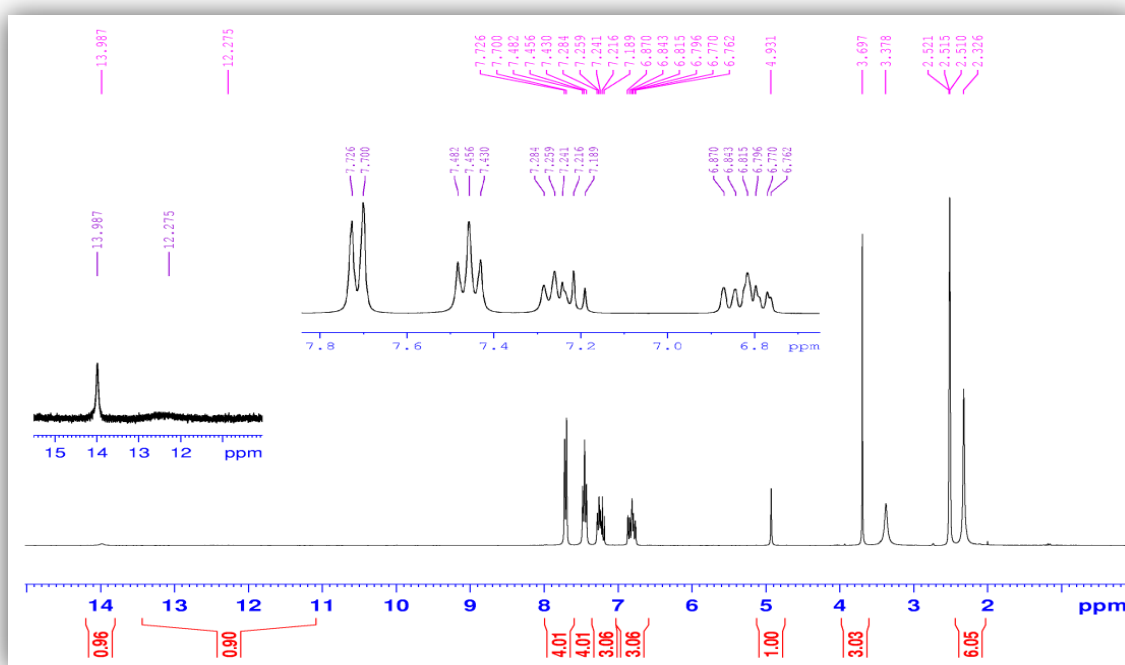
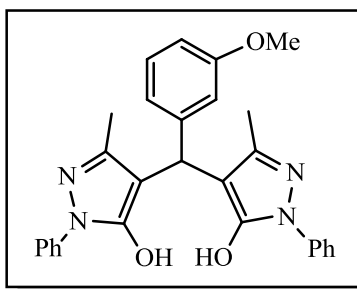


Figure 6a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of 4,4'-((3-Methoxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

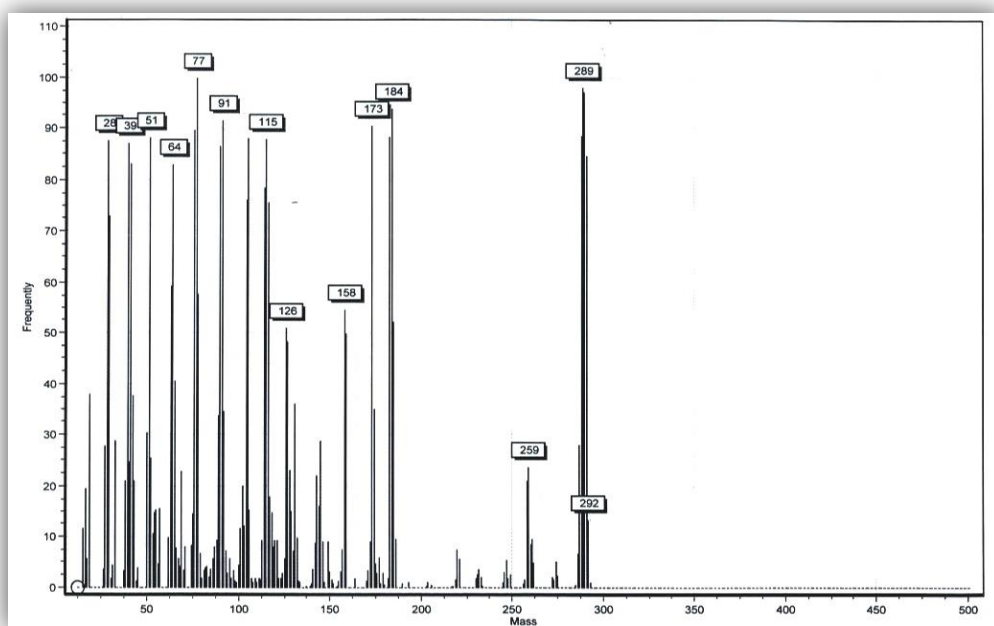


Figure 6b: Mass spectrum of 4,4'-((3-Methoxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

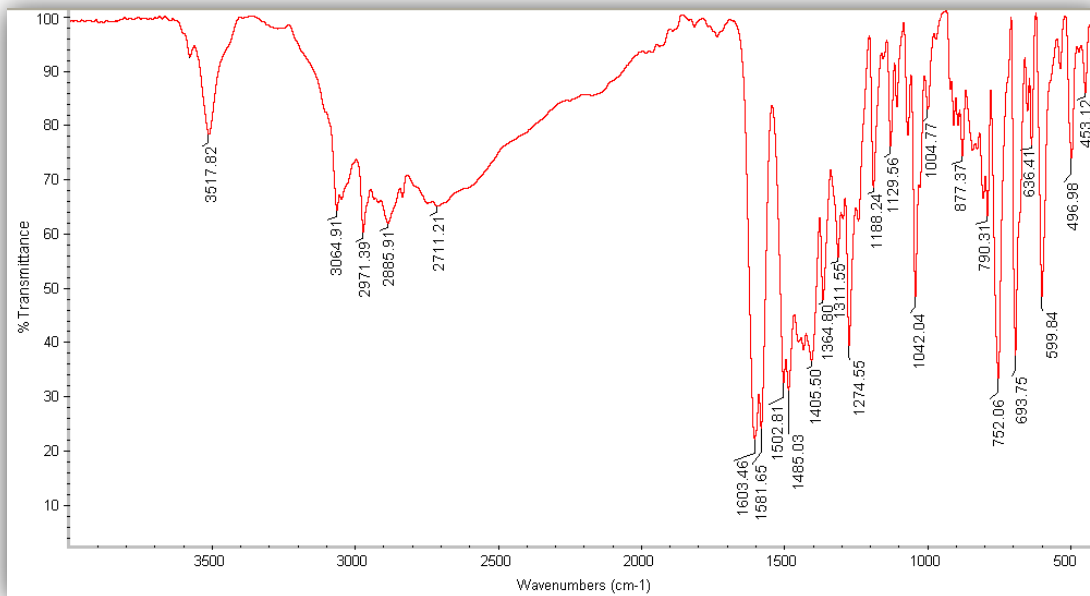


Figure 6c: FT-IR (KBr) spectrum of 4,4'-((3-Methoxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

4,4'-(*p*-Tolylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)(3g)

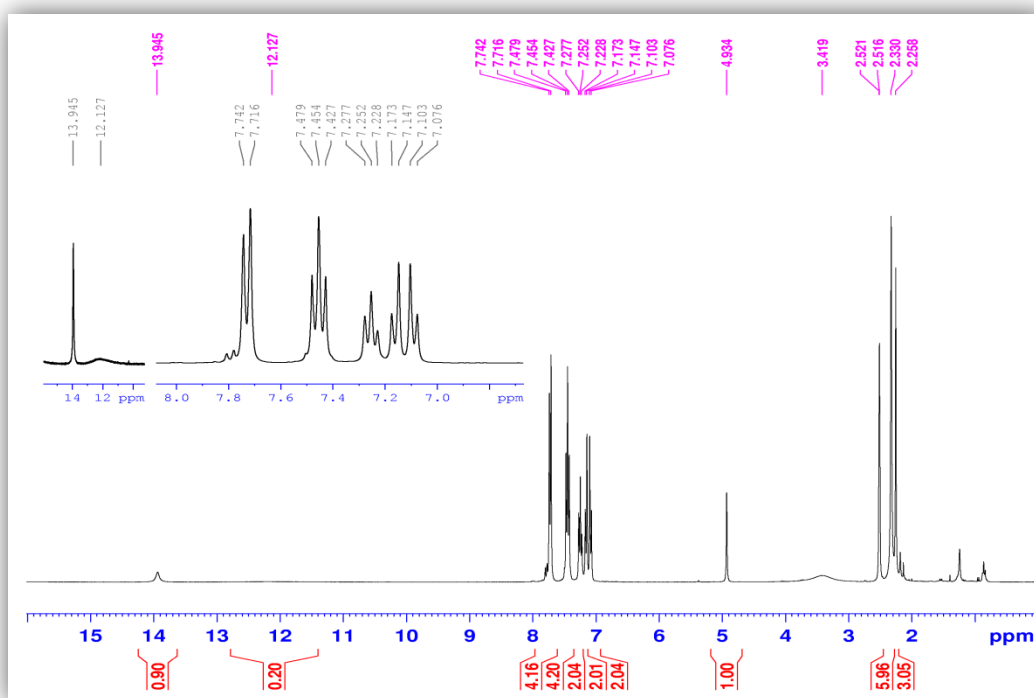
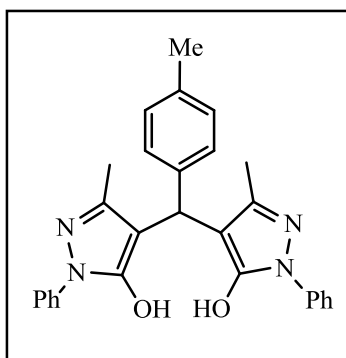


Figure 7a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of 4,4'-(*p*-Tolylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)

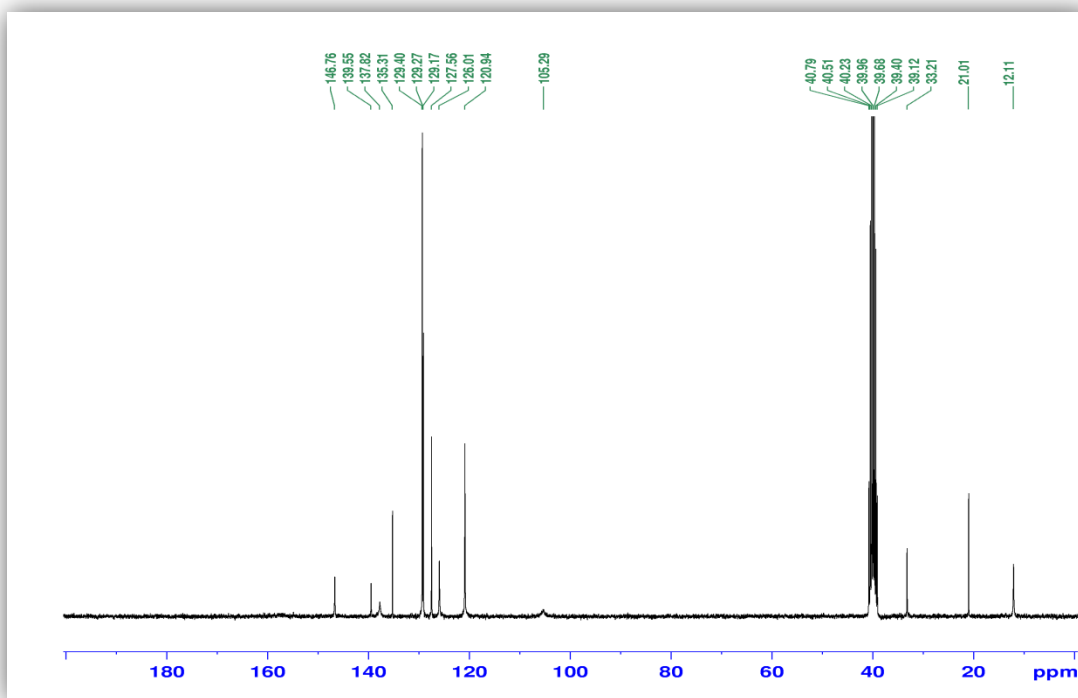


Figure 7b: ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) of 4,4'-(*p*-Tolylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)

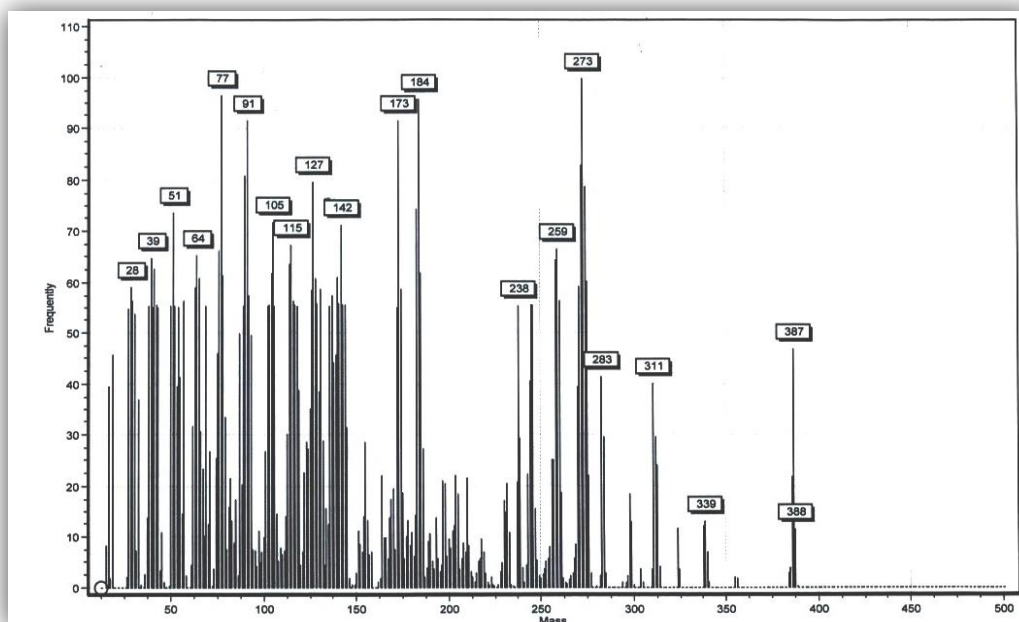


Figure 7c: Mass spectrum of 4,4'-(*p*-Tolylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

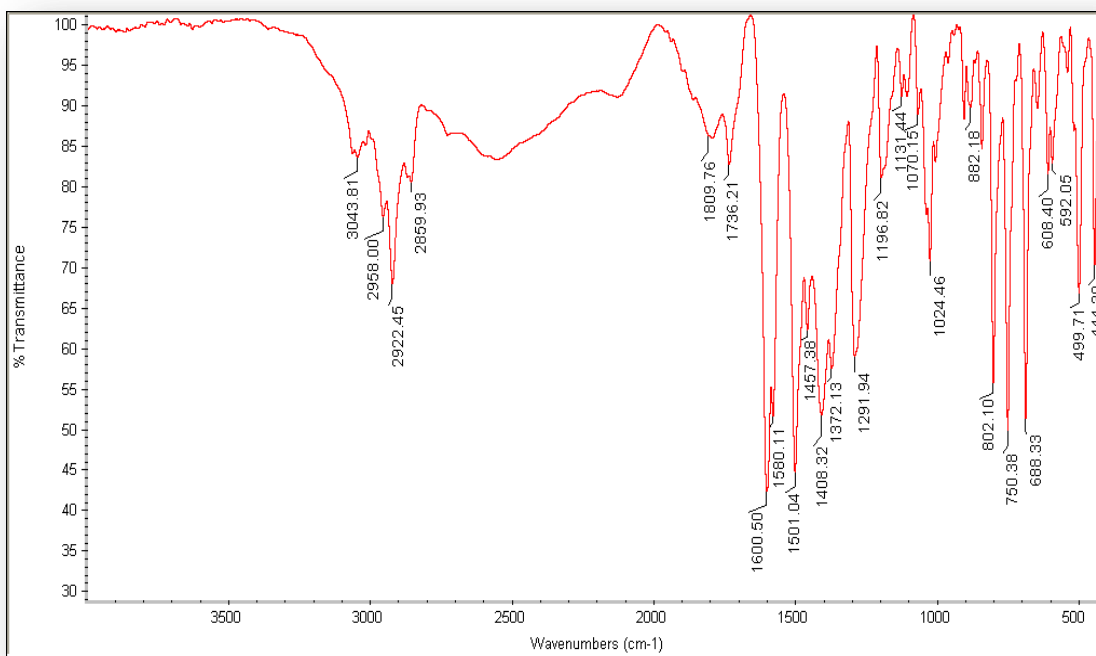


Figure 7d: FT-IR (KBr) spectrum of 4,4'-(*p*-Tolylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

4,4'-(*m*-Tolylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol) (3h)

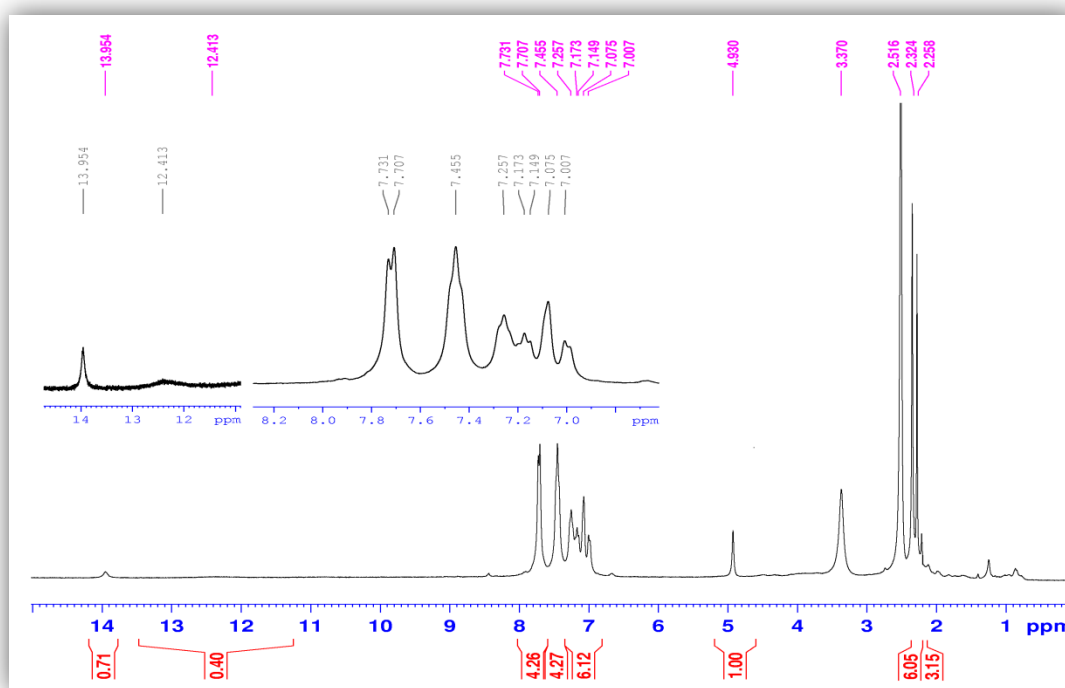
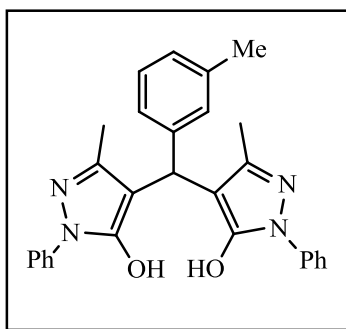


Figure 8a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of 4,4'-(*m*-Tolylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

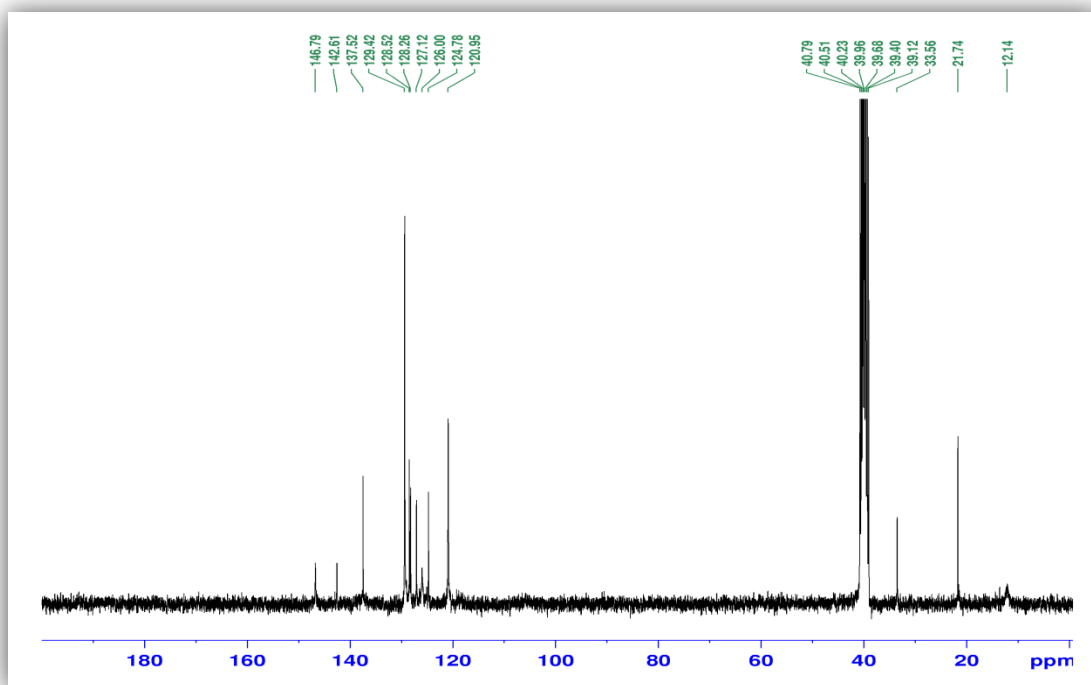


Figure 8b: ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) of 4,4'-(*m*-Tolylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

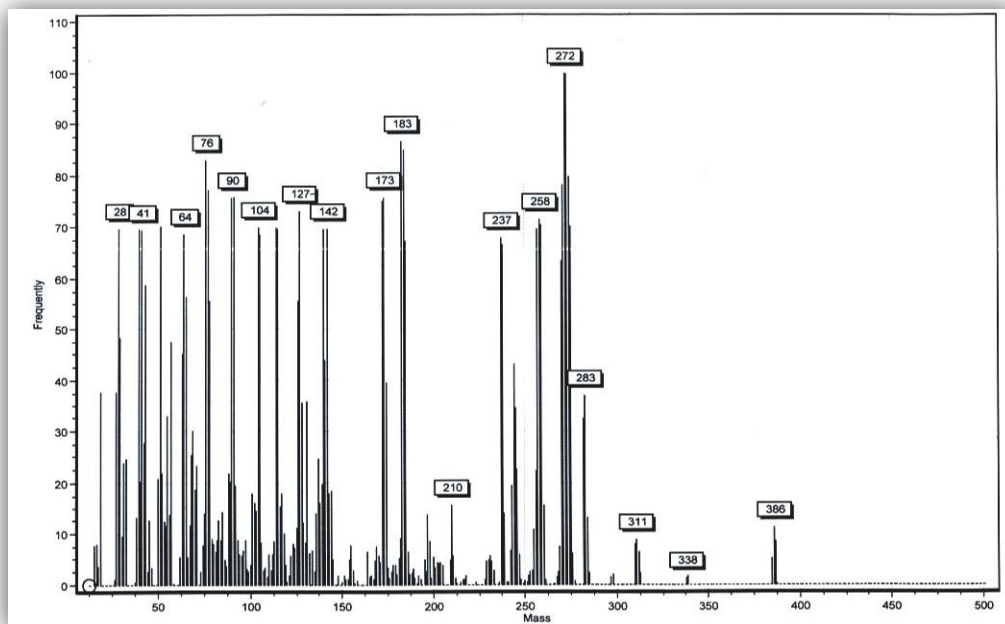


Figure 8c: Mass spectrum of 4,4'-(*m*-Tolylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

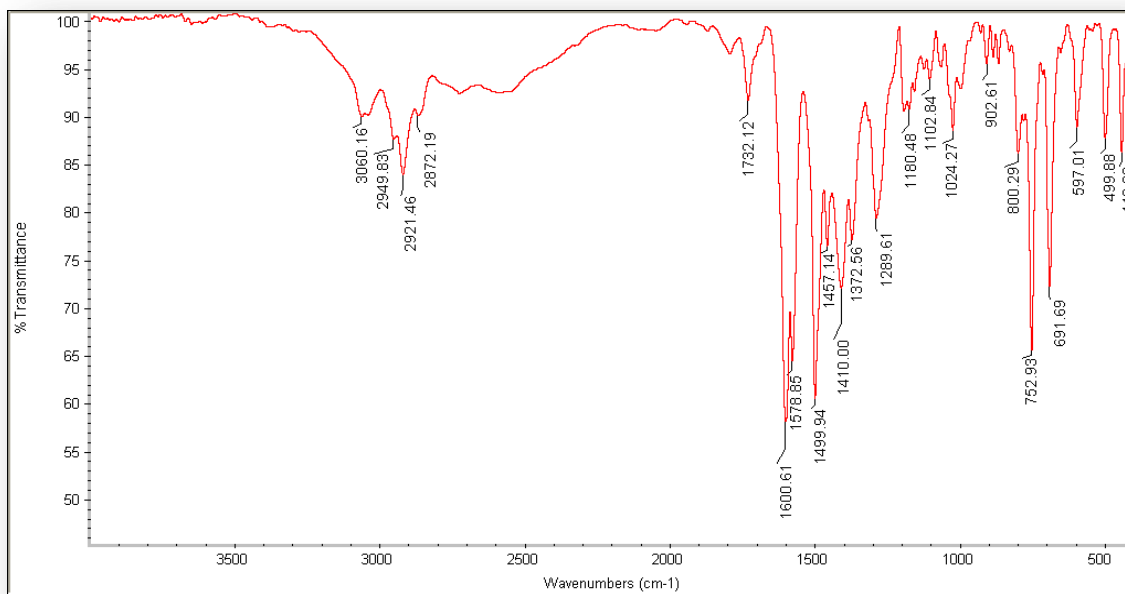


Figure 8d: FT-IR (KBr) spectrum of 4,4'-(*m*-Tolylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

4,4'-((5-Bromo-2-hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3i)

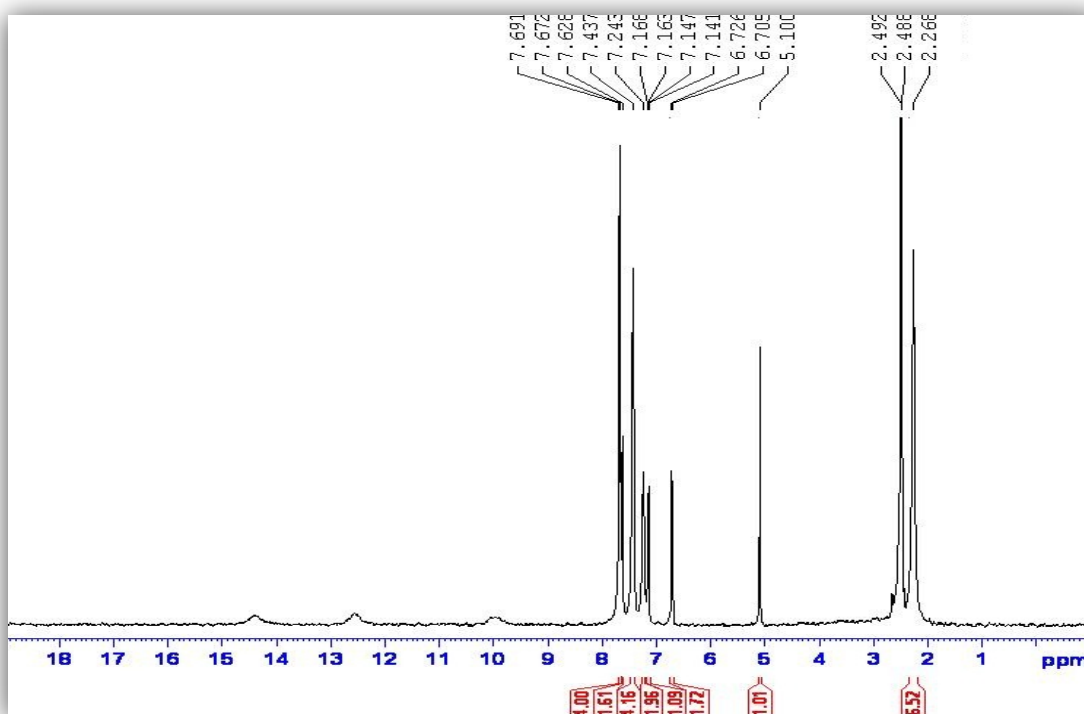
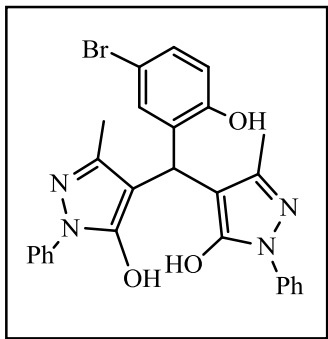


Figure 9a: ^1H NMR (400 MHz, $\text{DMSO}-d_6$) of 4,4'-((5-Bromo-2-hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

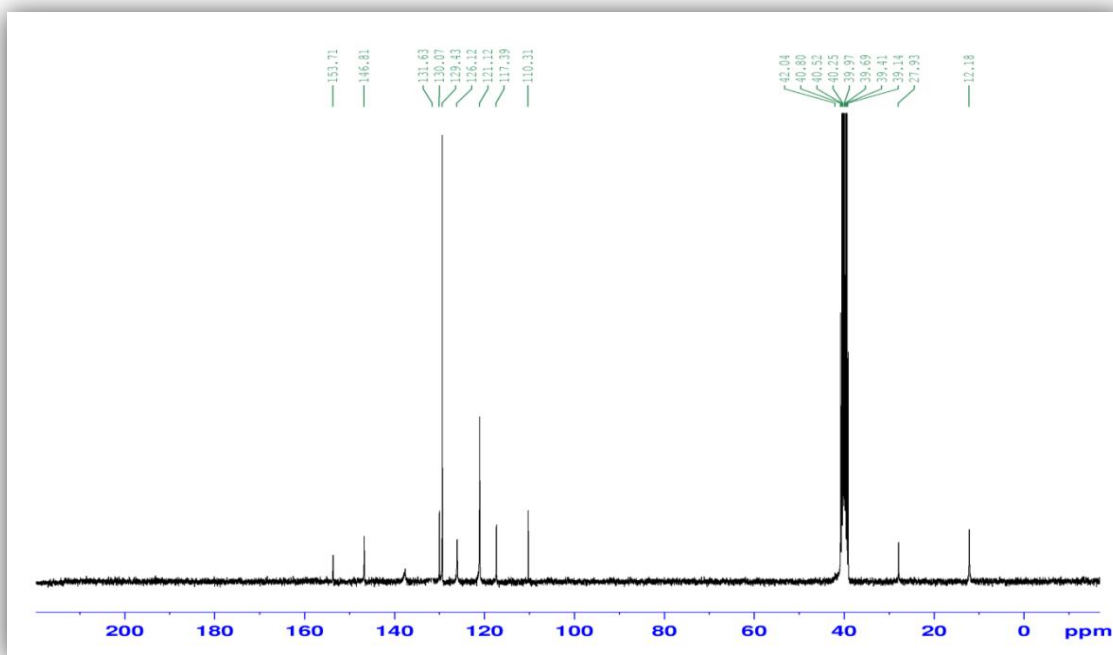


Figure 9b: ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) of 4,4'-((5-Bromo-2-hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

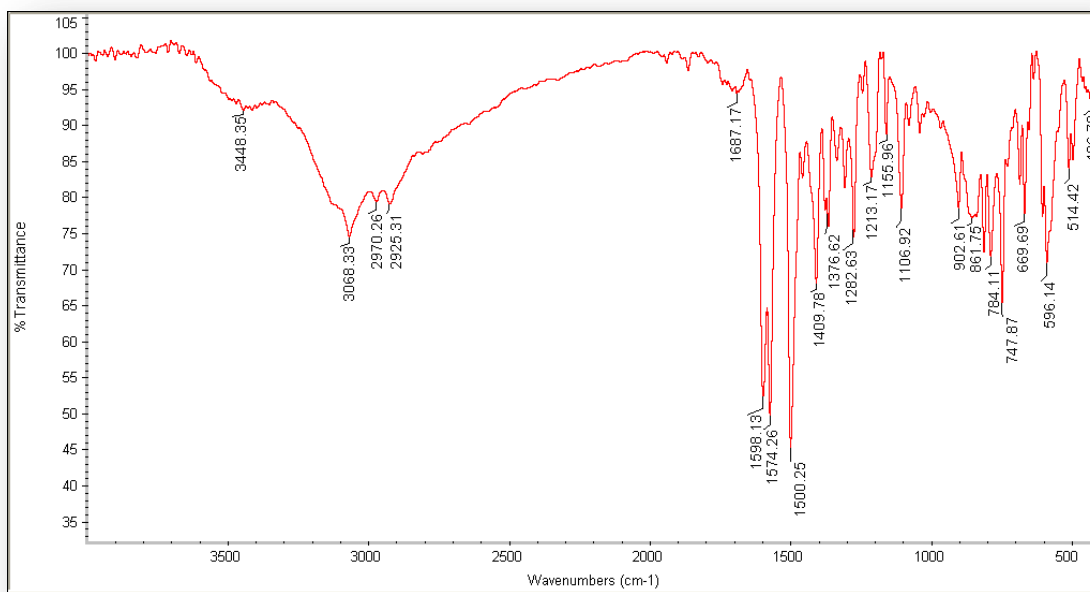


Figure 9c: FT-IR (KBr) spectrum of 4,4'-((5-Bromo-2-hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

4,4'-((4-Isopropylphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3j)

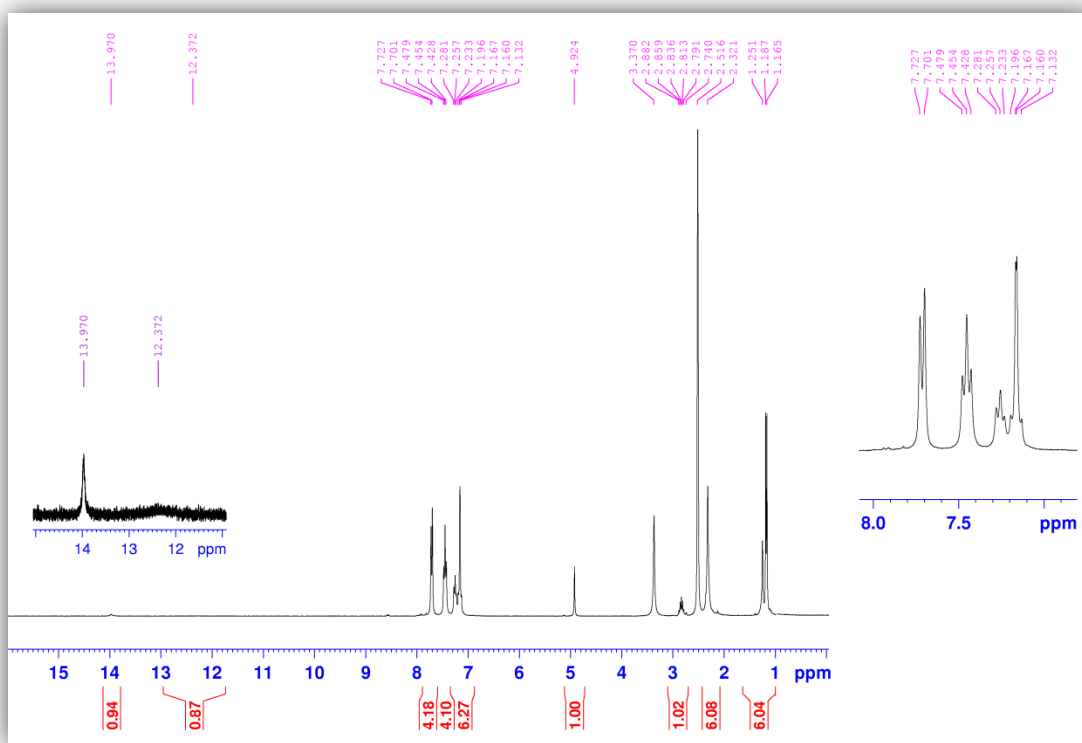
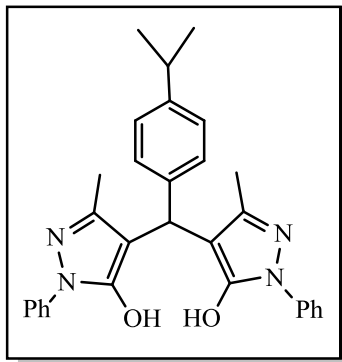


Figure 10a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of 4,4'-((4-Isopropylphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

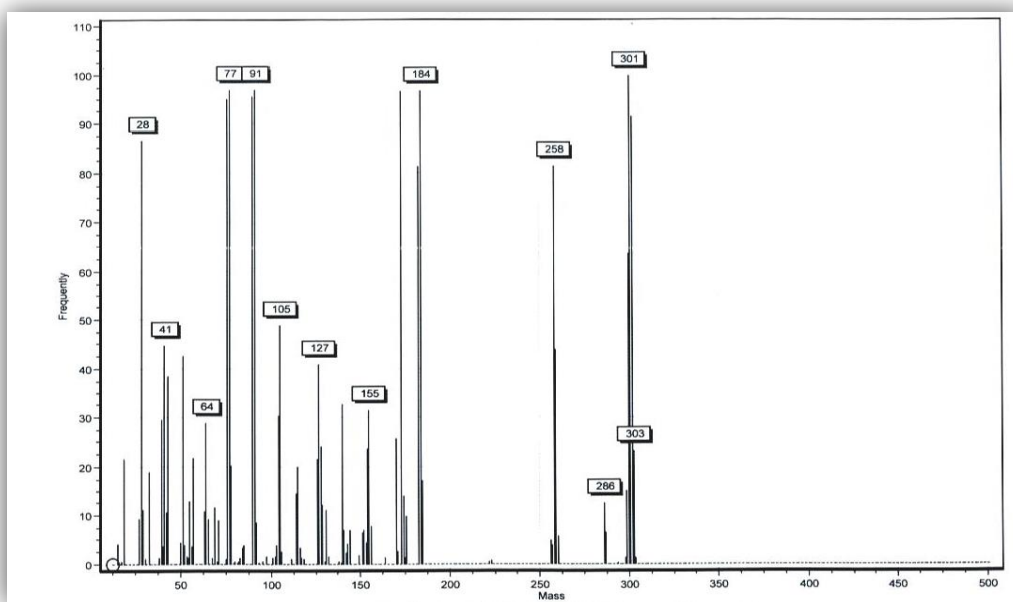


Figure 10b: Mass spectrum of 4,4'-((4-Isopropylphenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

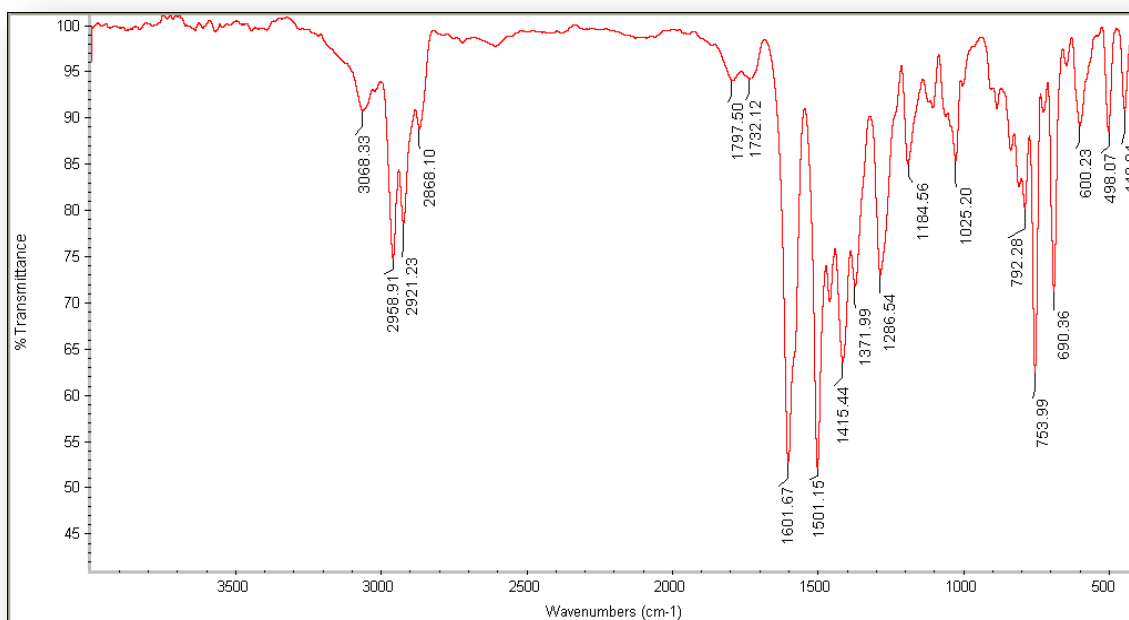


Figure 10c: FT-IR (KBr) spectrum of 4,4'-((4-Isopropylphenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

4,4'-((2-Chlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3k)

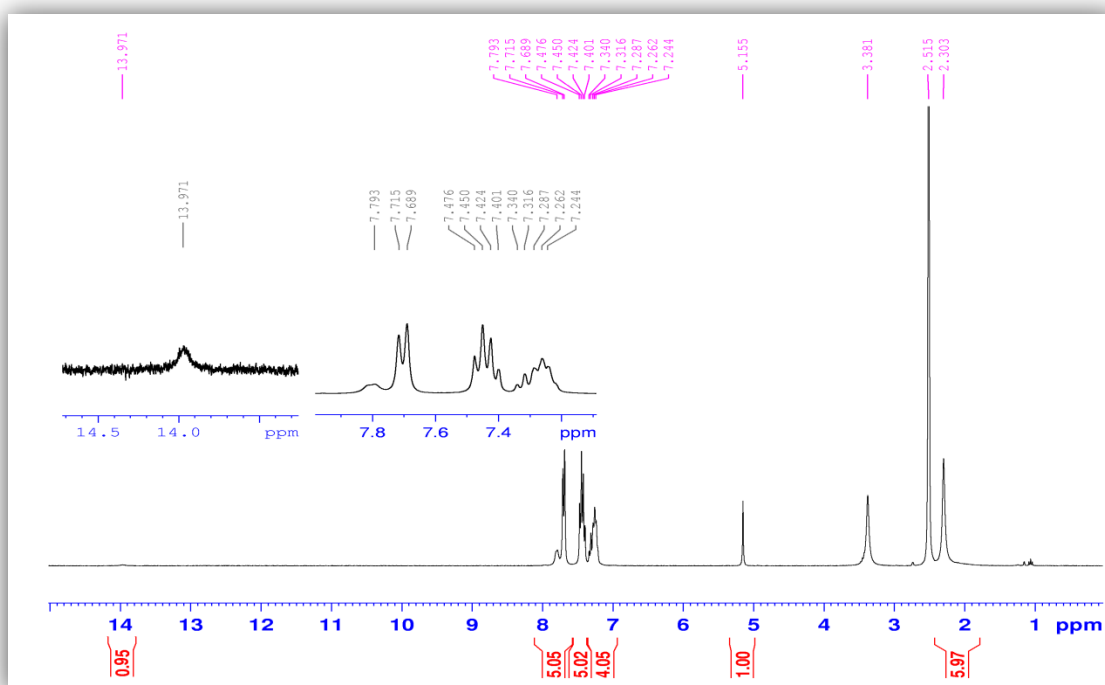
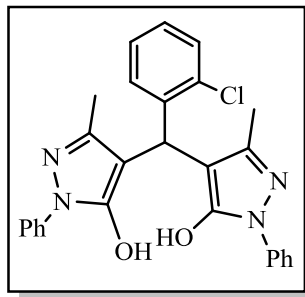


Figure 11a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of 4,4'-((2-Chlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

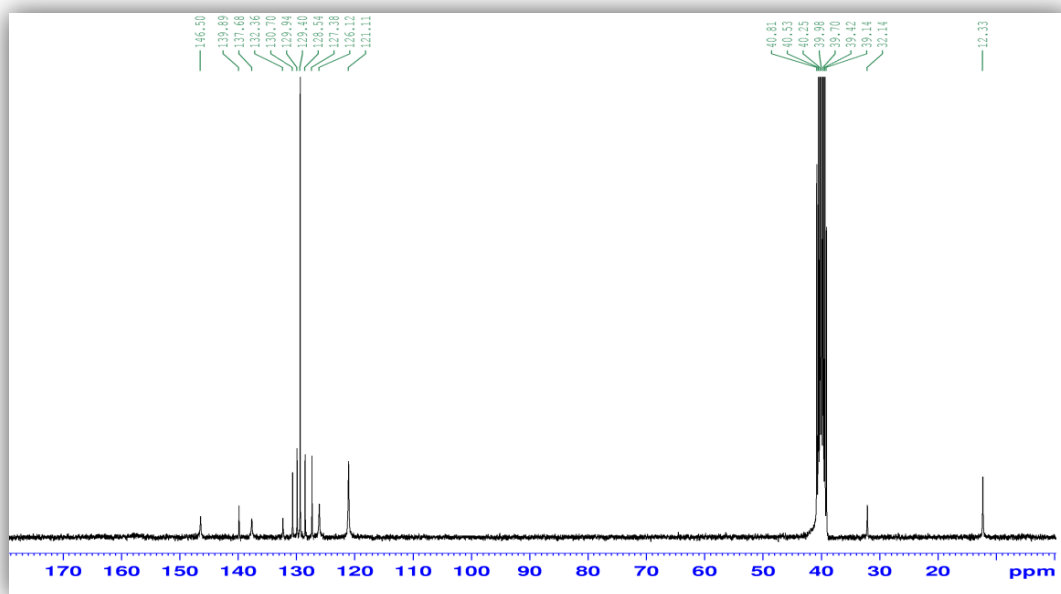


Figure 11b: ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) of 4,4'-((2-Chlorophenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

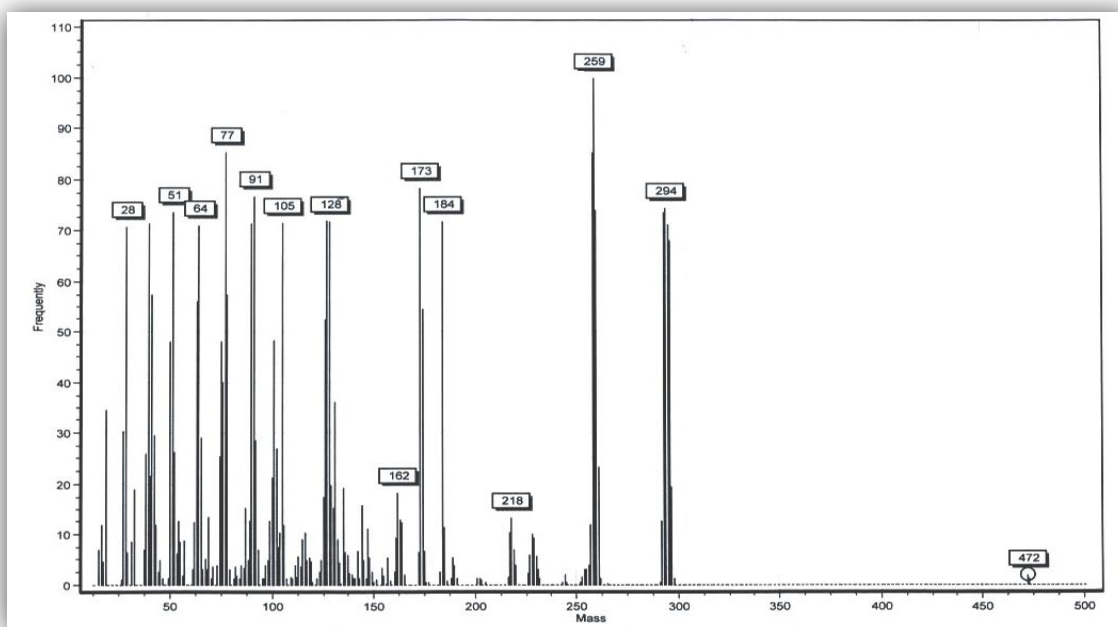


Figure 11c: Mass spectrum of 4,4'-((2-Chlorophenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

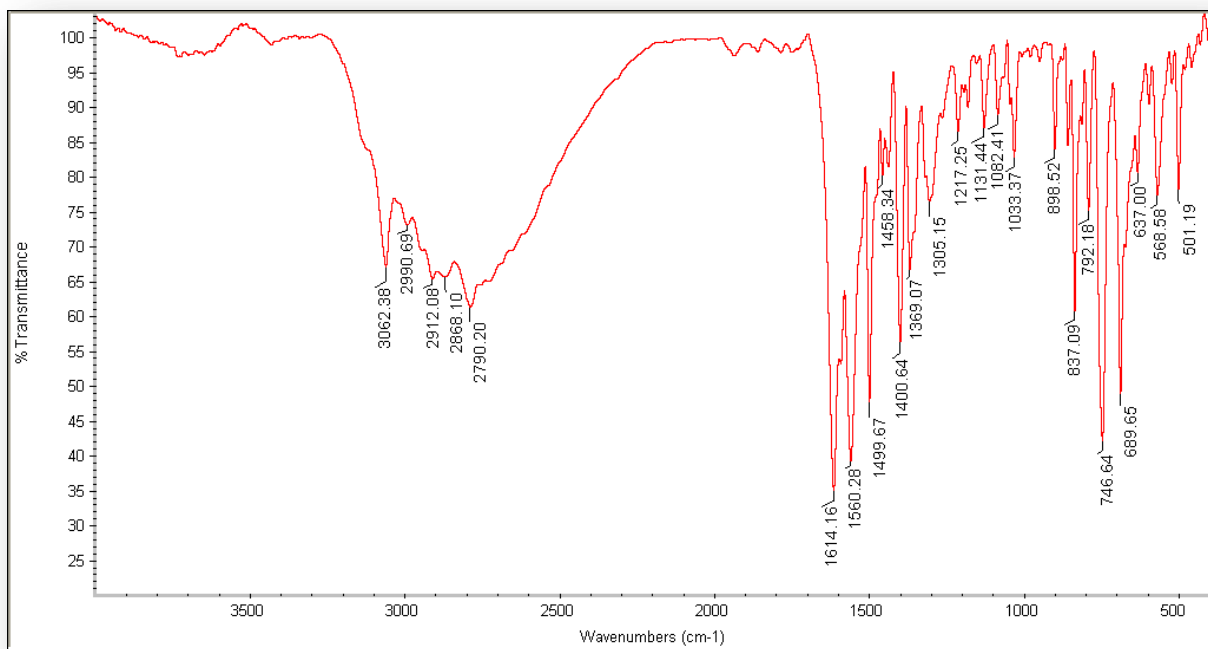


Figure 11d: FT-IR (KBr) spectrum of 4,4'-((2-Chlorophenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

4,4'-((4-Chlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3l)

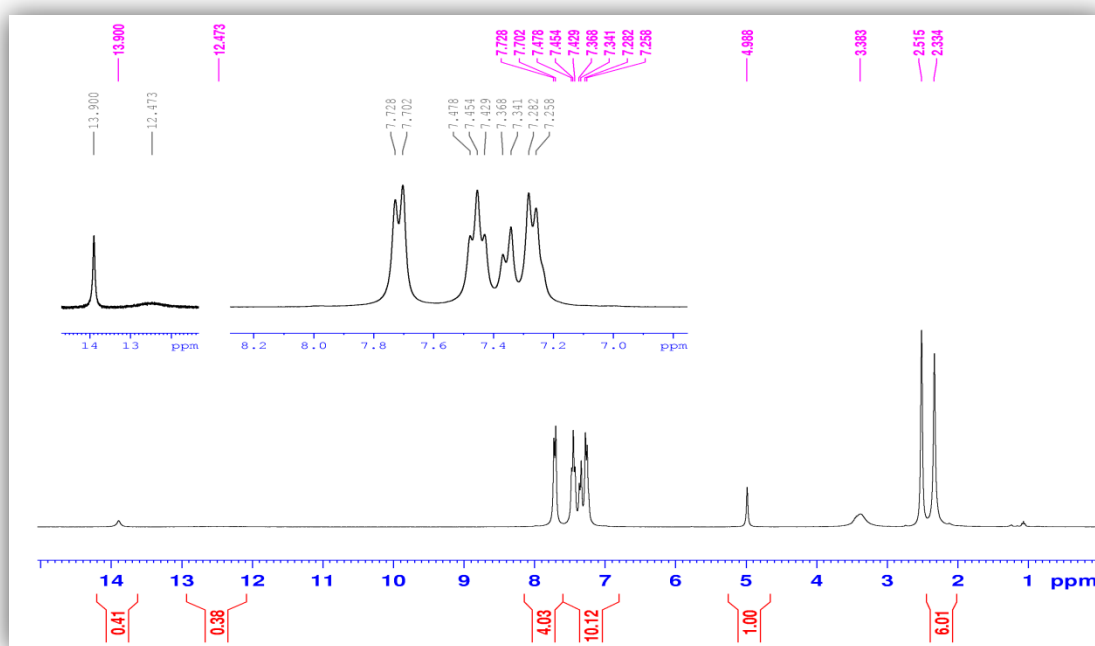
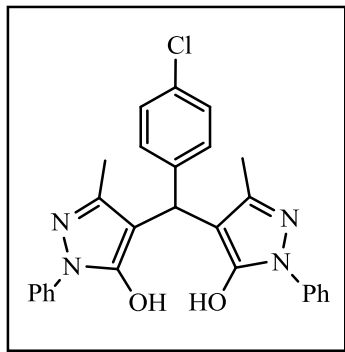


Figure 12a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of 4,4'-((4-Chlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

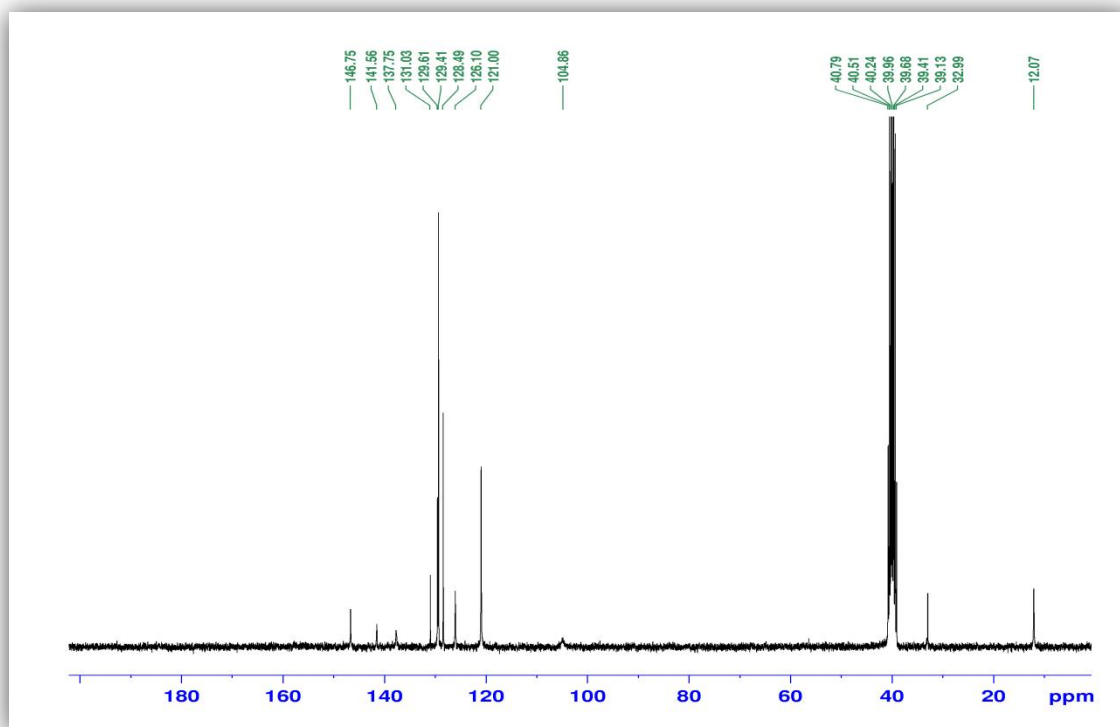


Figure 12b: ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) of 4,4'-((4-chlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

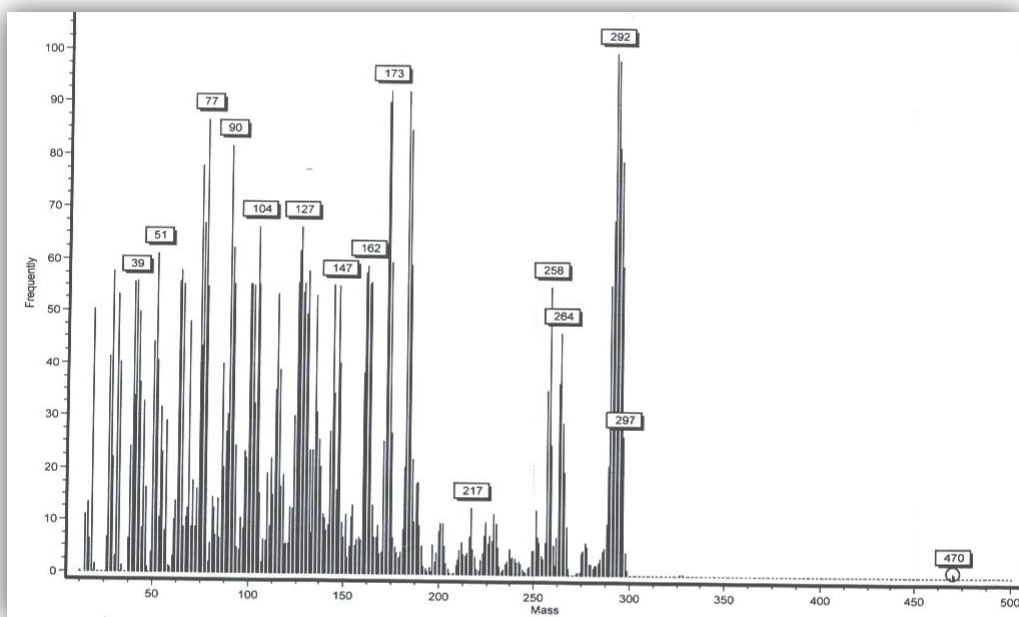
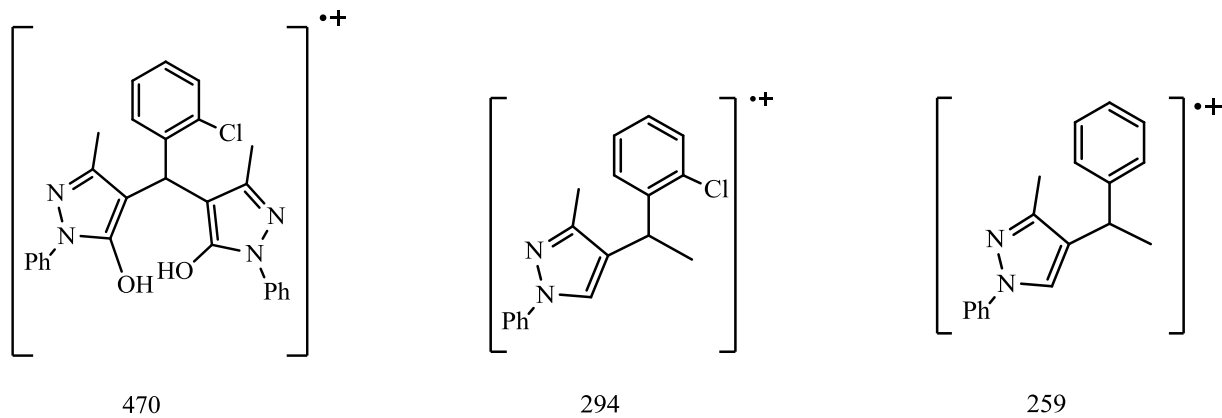


Figure 12c: Mass spectrum of 4,4'-((4-chlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).



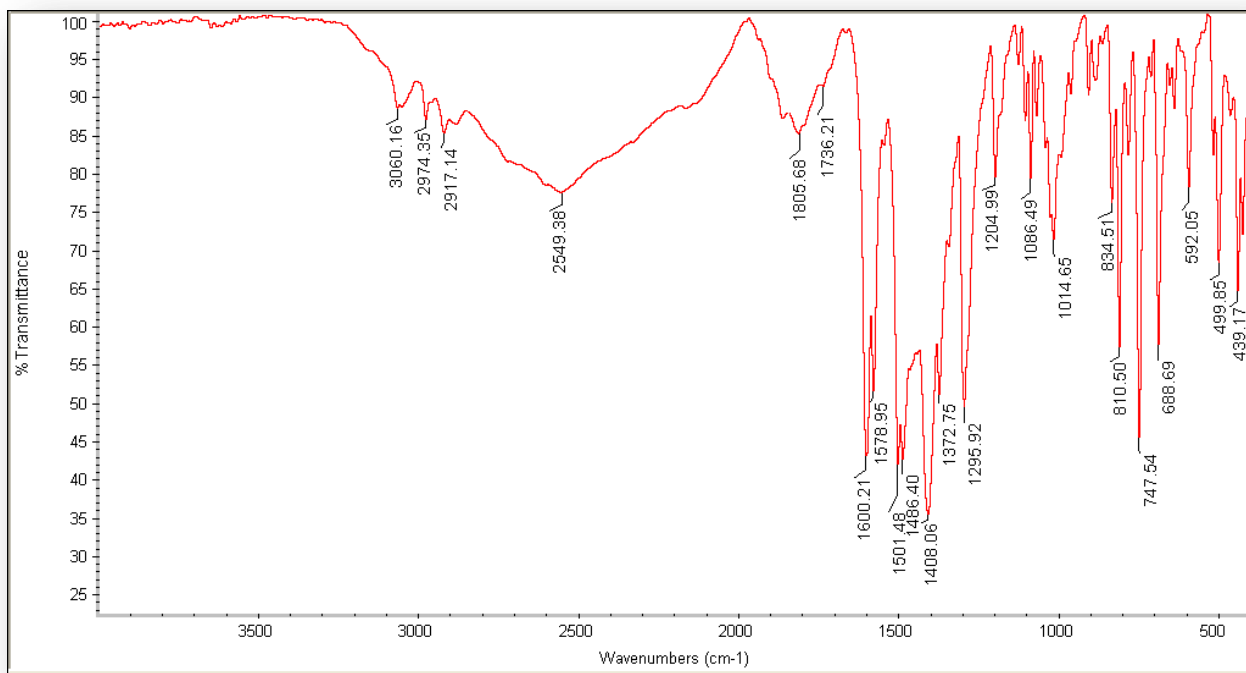


Figure 12d: FT-IR (KBr) spectrum of 4,4'-((4-Chlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

4,4'-((2,4-Dichlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3m)

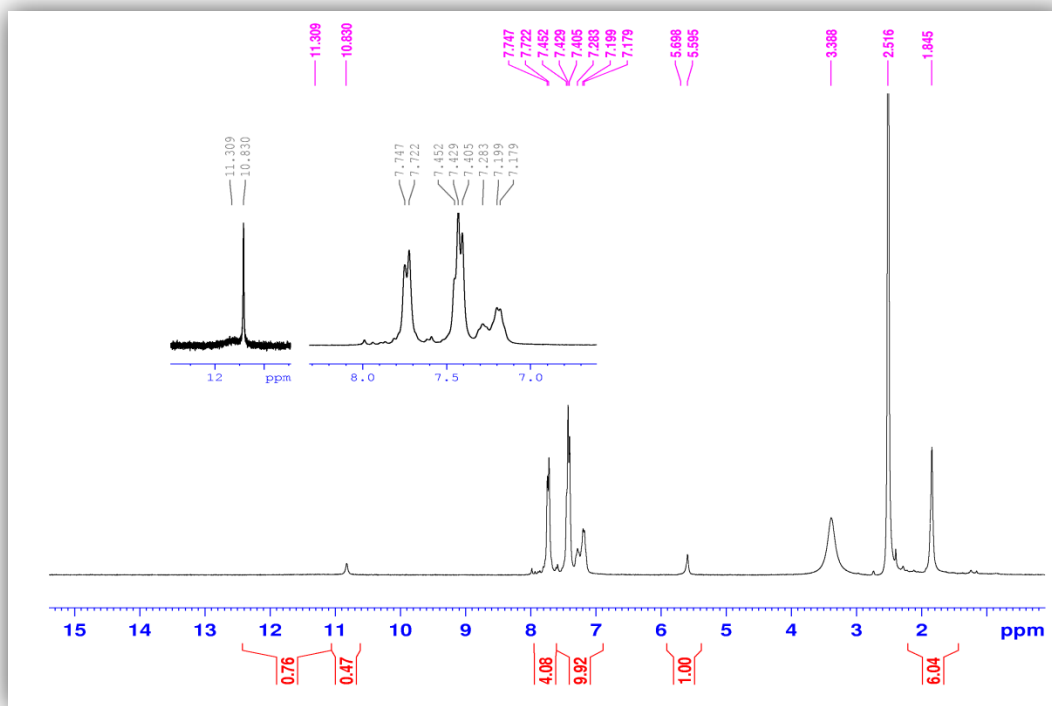
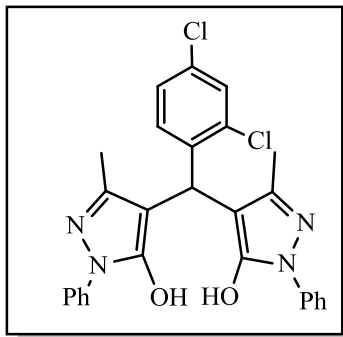


Figure 13a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of 4,4'-((2,4-Dichlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

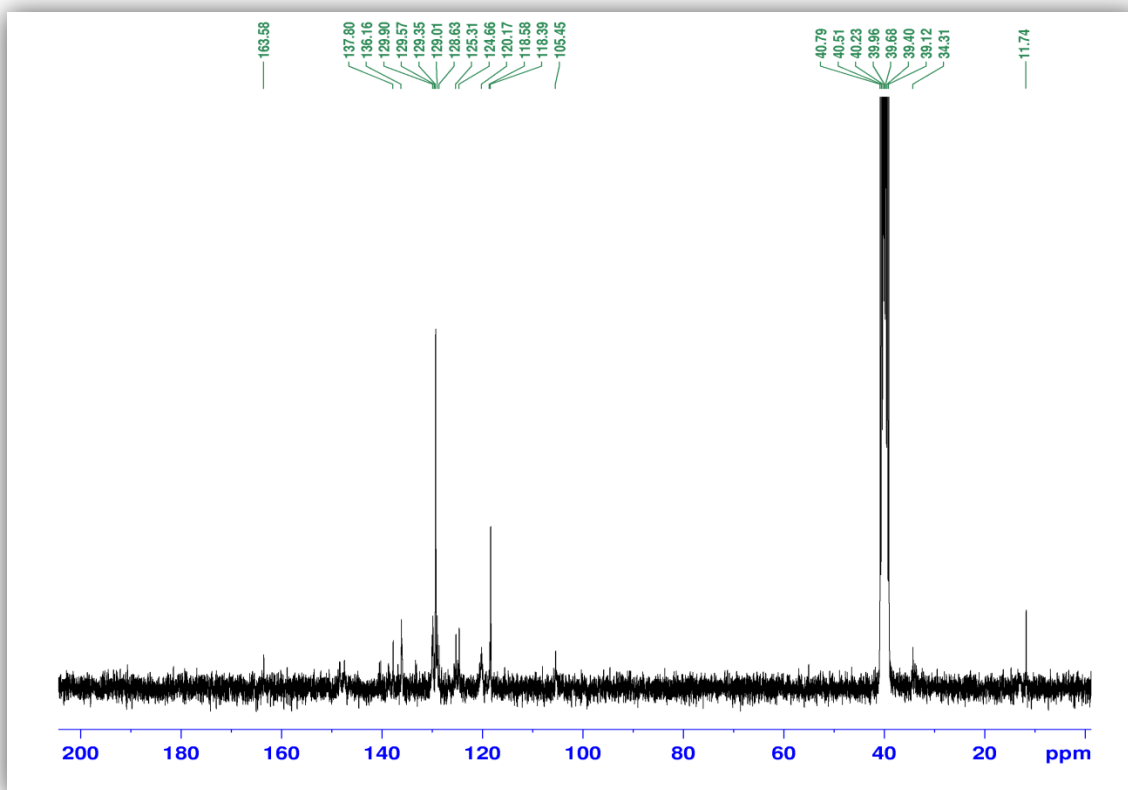


Figure 13b: ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) of 4,4'-((2,4-Dichlorophenyl)methylene)bis(3-methyl-1H-pyrazol-5-ol).

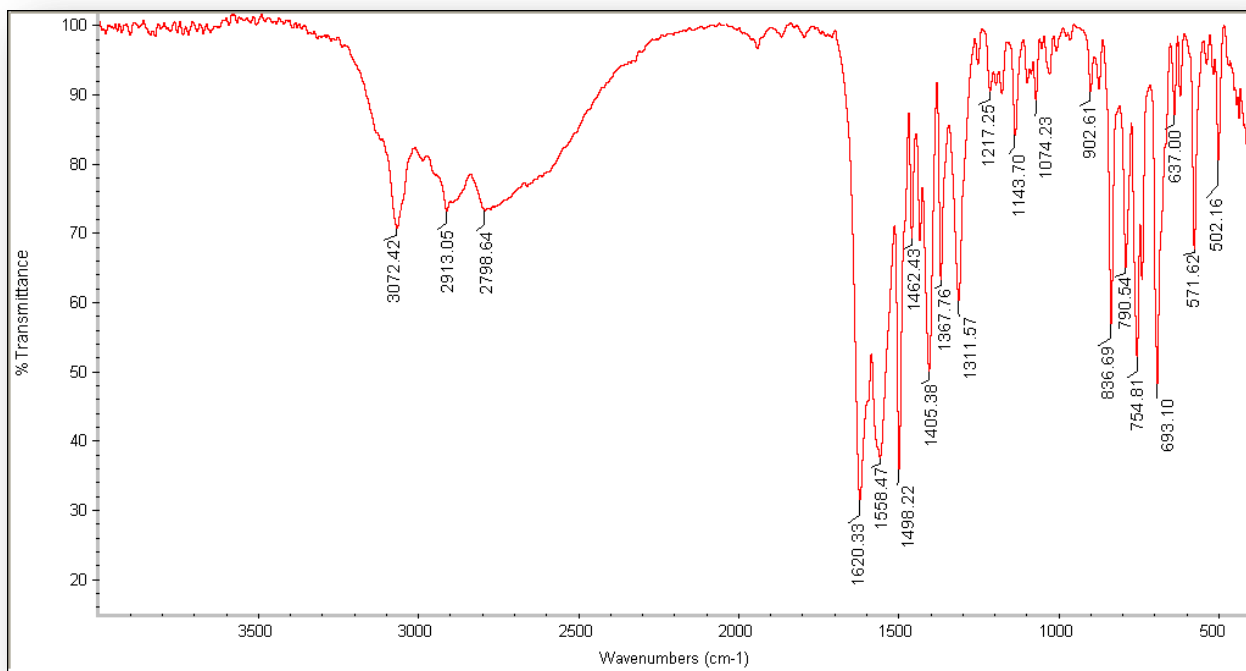


Figure 13c: FT-IR (KBr) spectrum of 4,4'-((2,4-Dichlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

4,4'-((4-Bromophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3n)

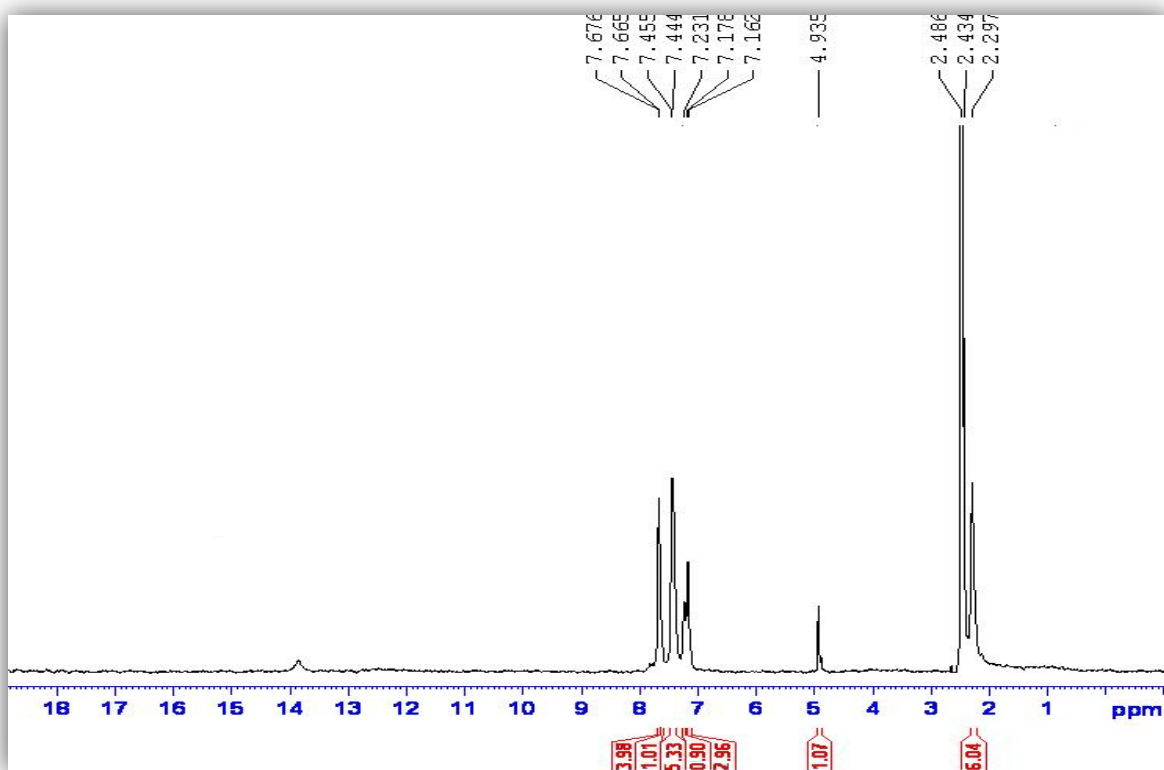
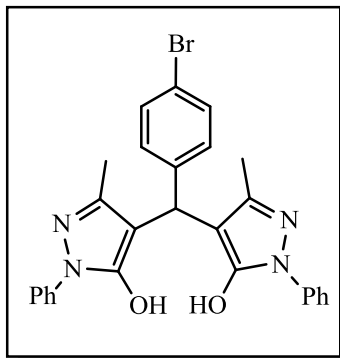


Figure 14a: ^1H NMR (400 MHz, $\text{DMSO-}d_6$) of 4,4'-((4-Bromophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

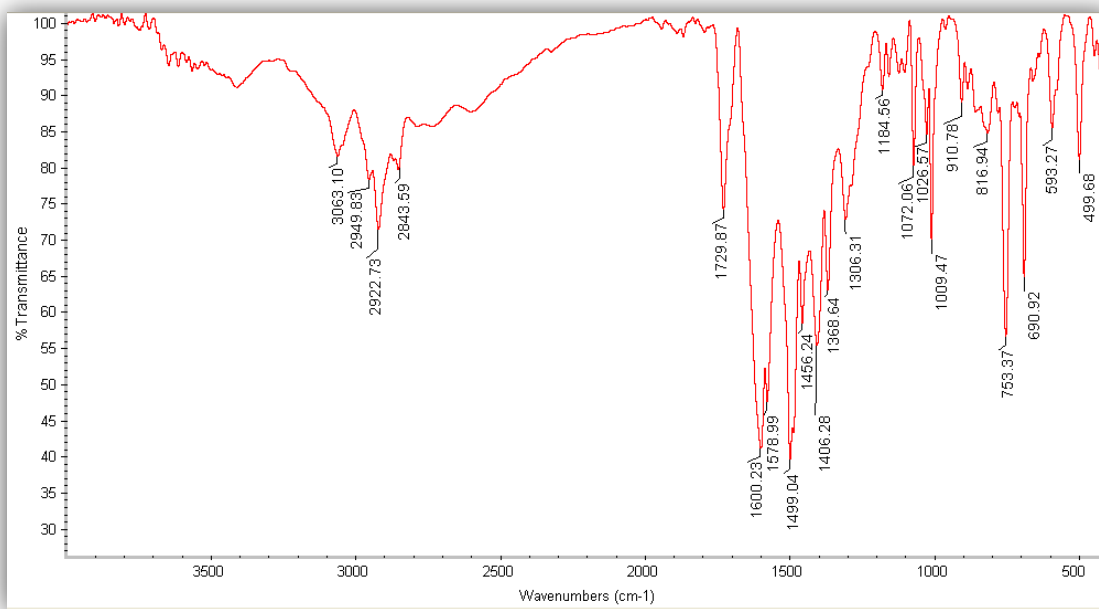


Figure 14b: FT-IR (KBr) spectrum of 4,4'-((4-Bromophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

4,4'-((3-Nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3o)

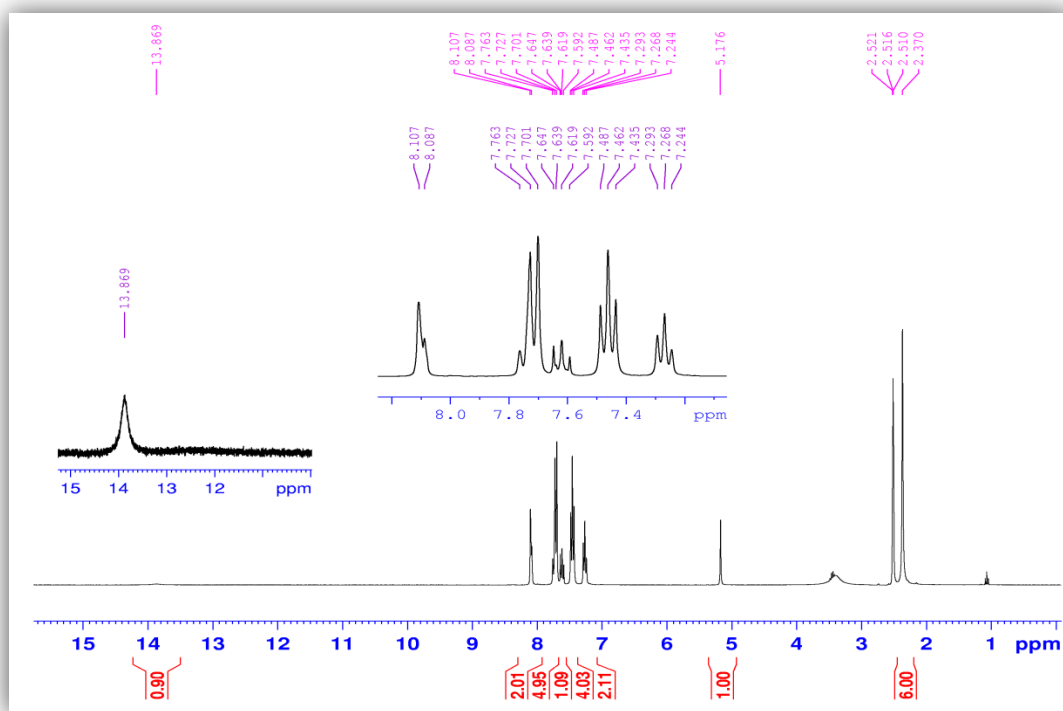
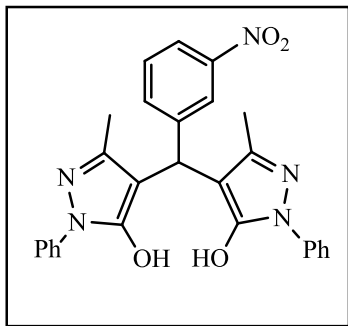


Figure 15a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of 4, 4'-((3-Nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

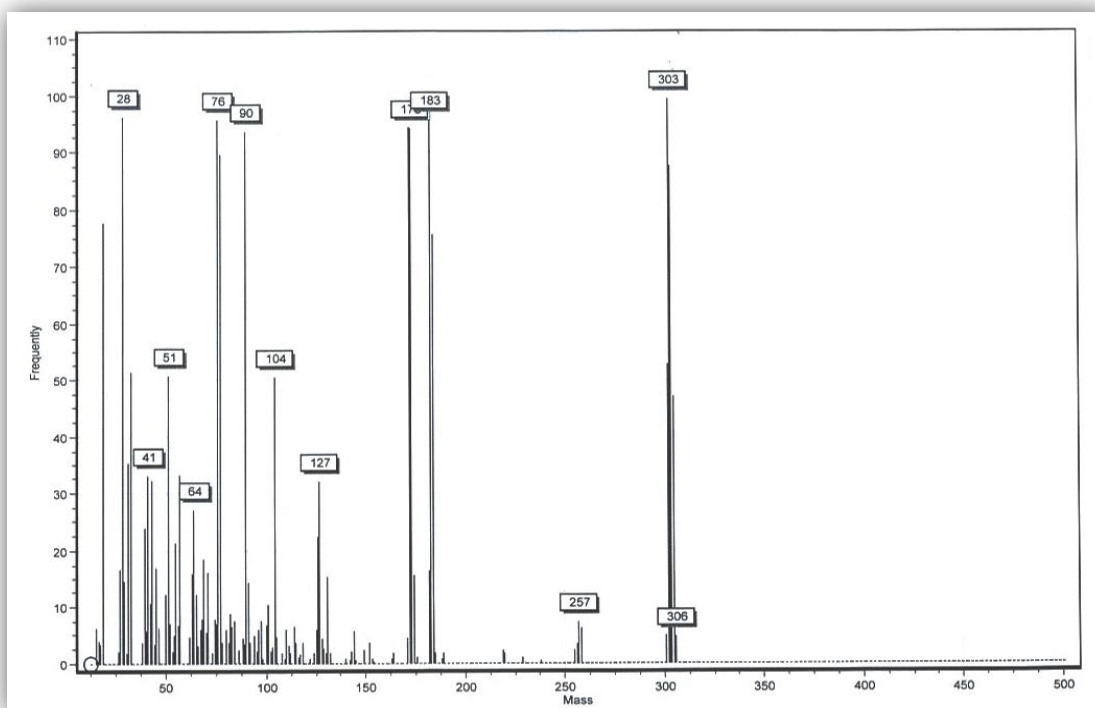
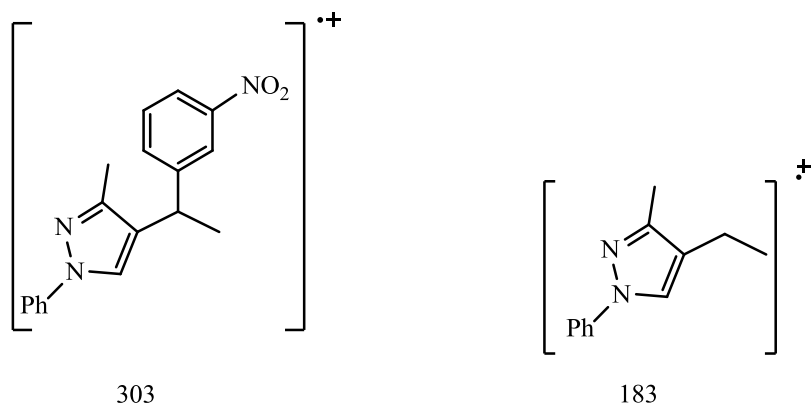


Figure 15b: Mass spectrum of 4, 4'-((3-Nitrophenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).



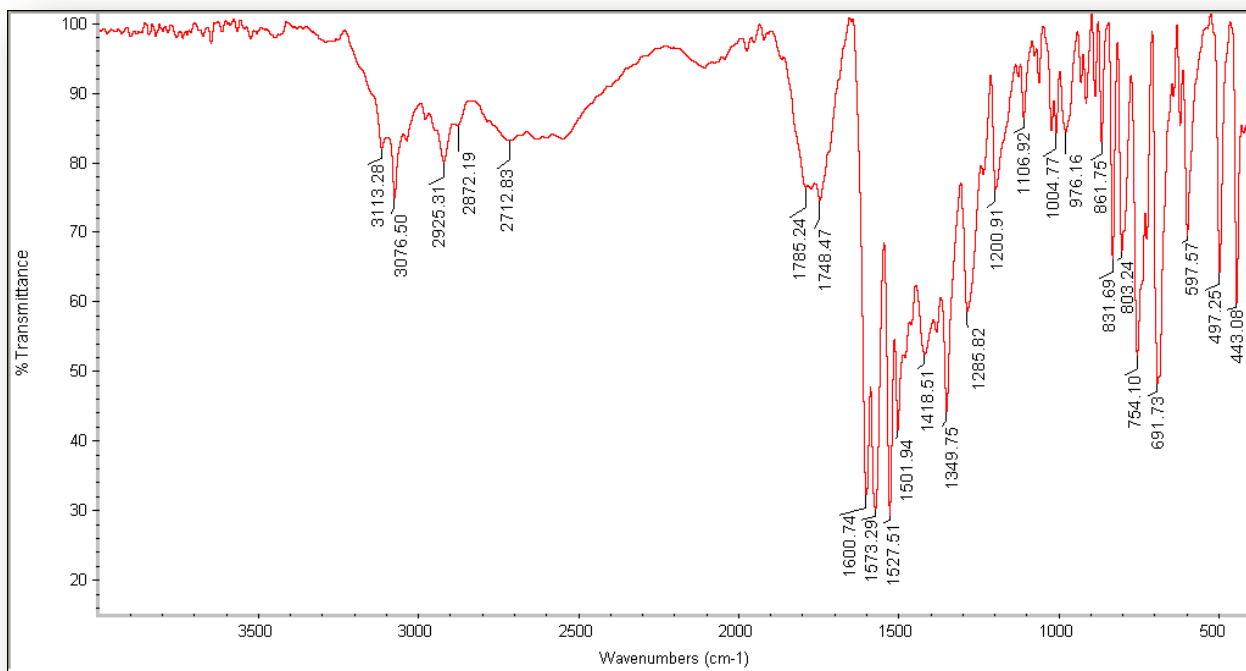


Figure 15c: FT-IR (KBr) spectrum of 4,4'-((3-Nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

4,4'-((2-Nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3p)

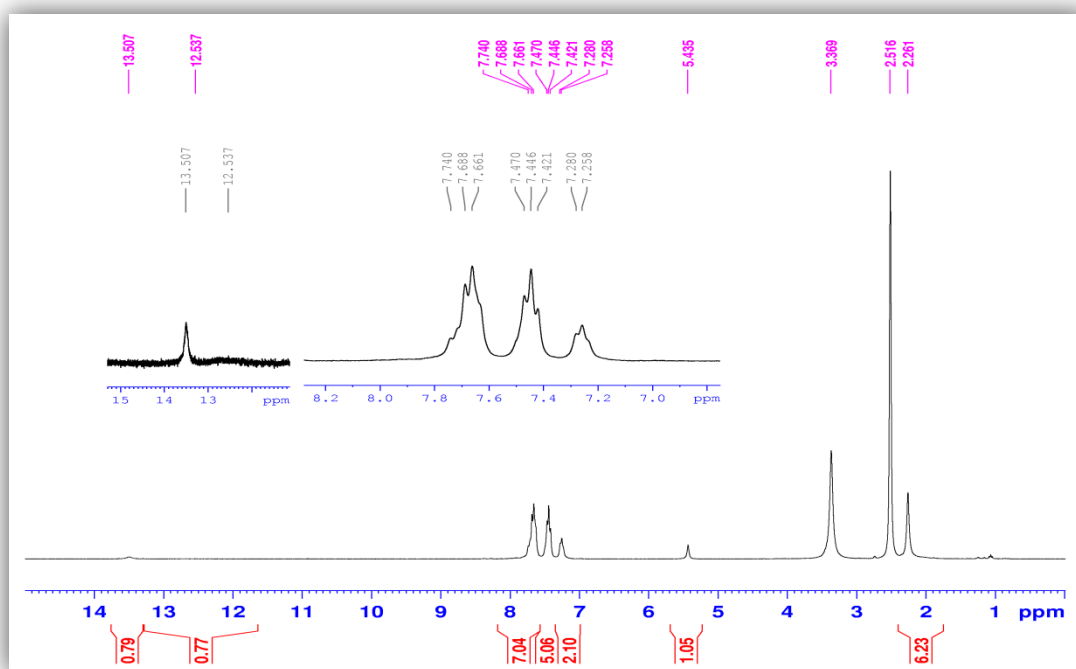
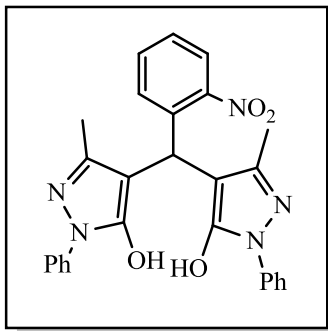


Figure 16a: ^1H NMR (300 MHz, $\text{DMSO}-d_6$) of 4, 4'-((2-Nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

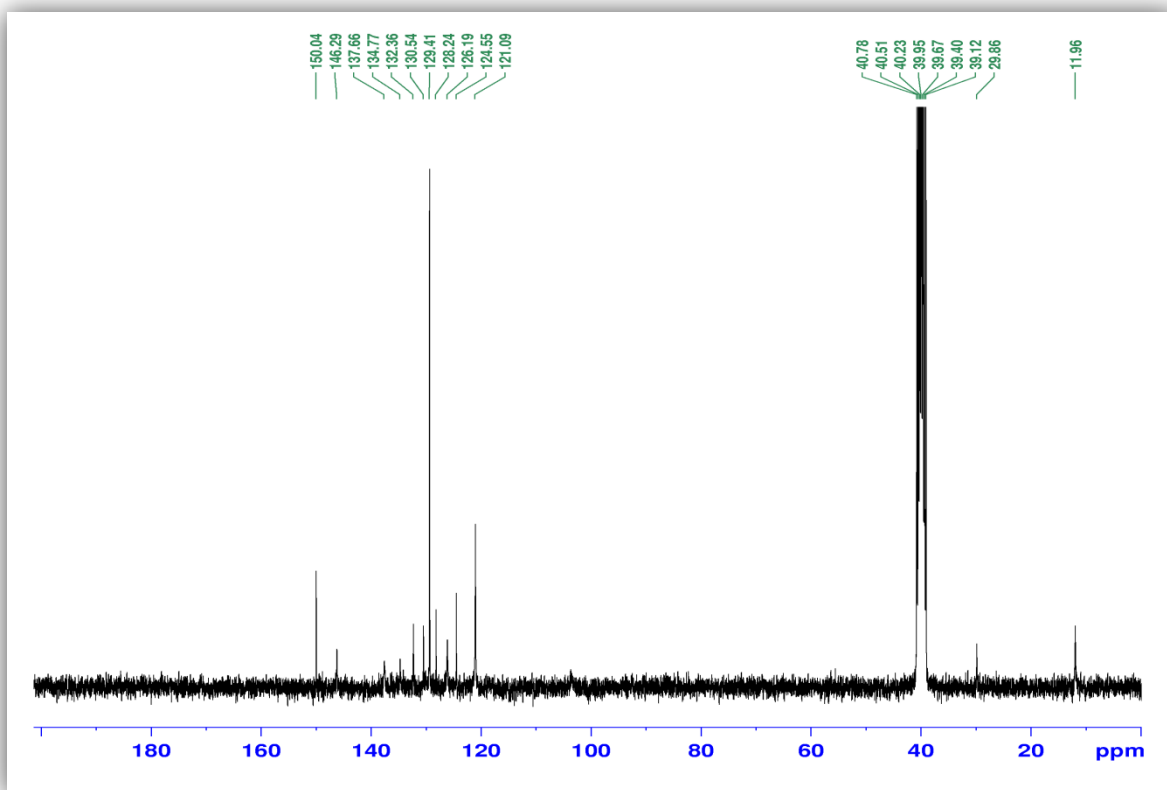


Figure 16b: ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) of 4, 4'-((2-Nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

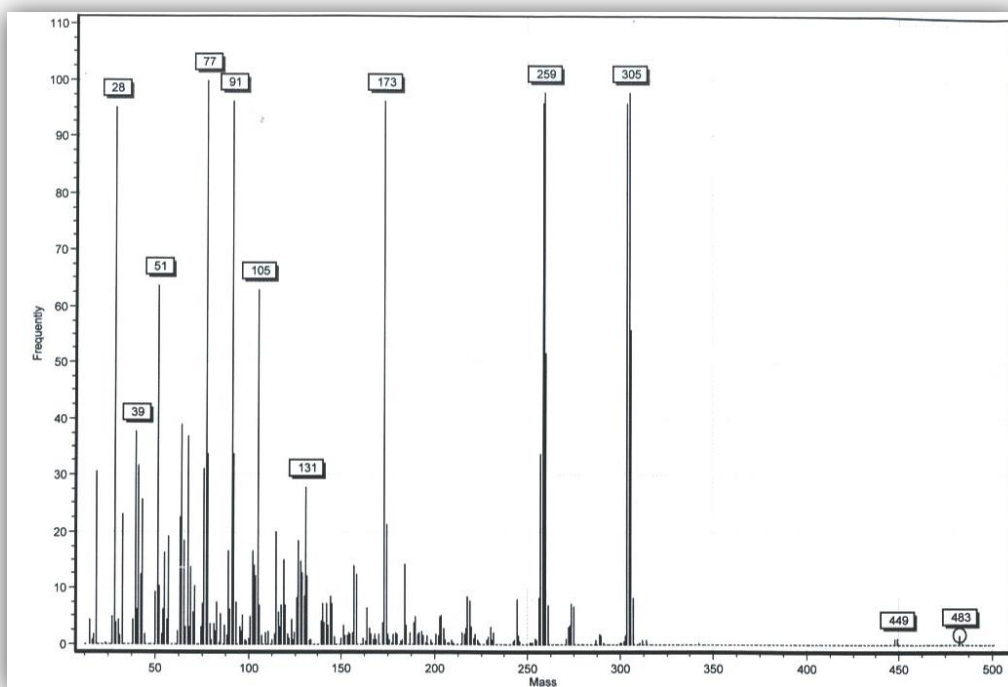


Figure 16c: Mass spectrum of 4,4'-((2-Nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

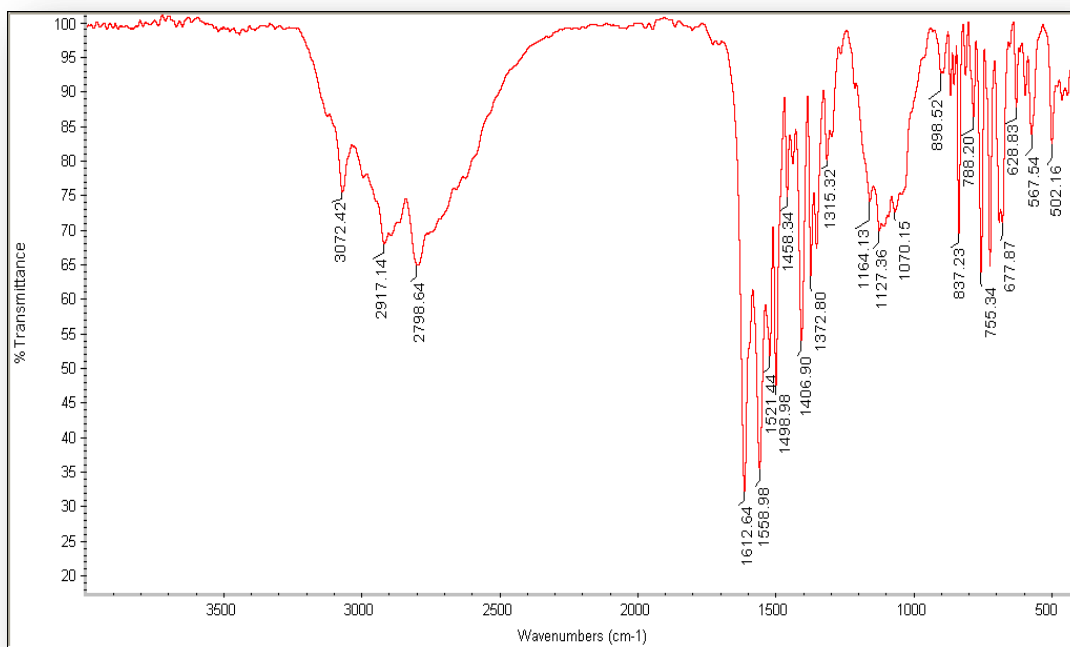


Figure 16d: FT-IR (KBr) spectrum of 4,4'-((2-Nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

4,4'-(Naphthalen-1-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3q)

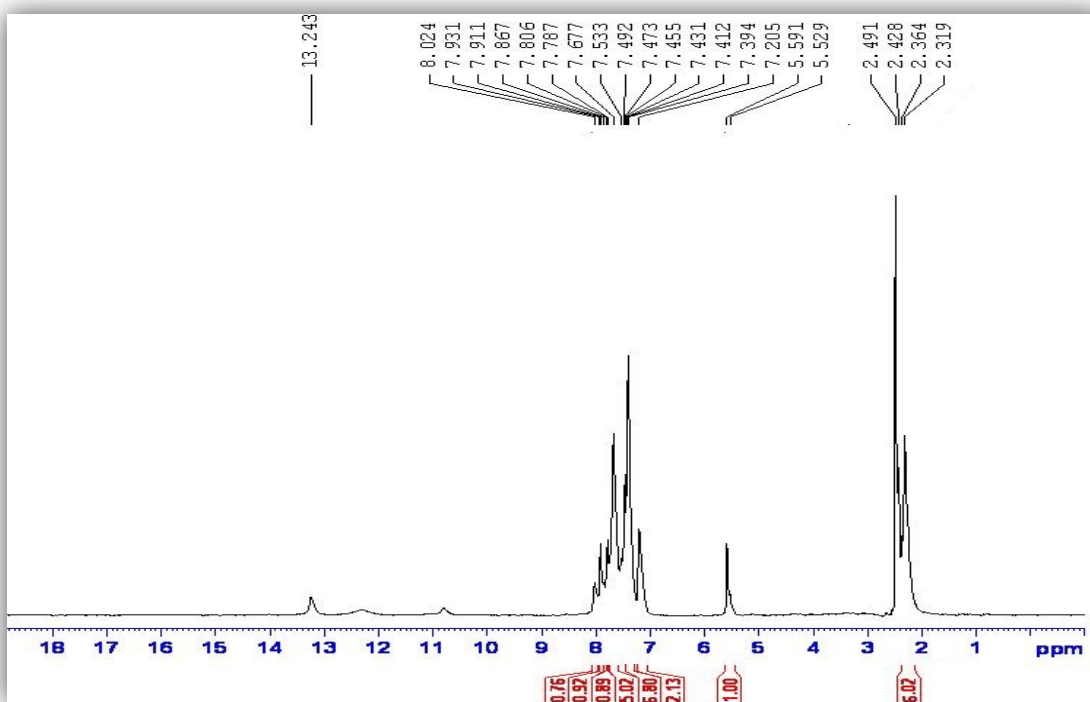
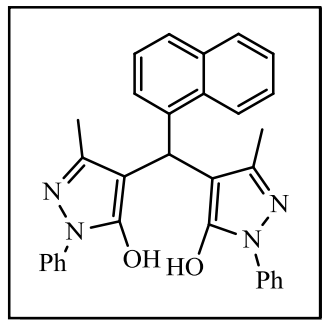


Figure 17a: ^1H NMR (400 MHz, $\text{DMSO-}d_6$) of 4,4'-(Naphthalen-1-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

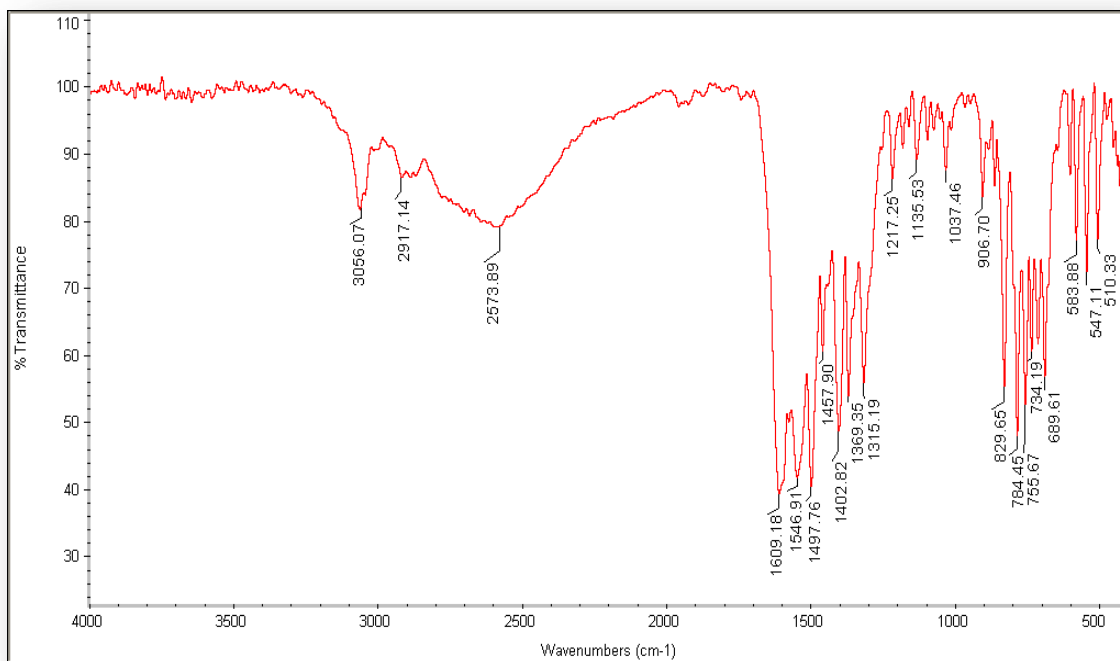


Figure 17b: FT-IR (KBr) spectrum of 4,4'-(Naphthalen-1-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

4,4'-(Pyridin-2-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3r)

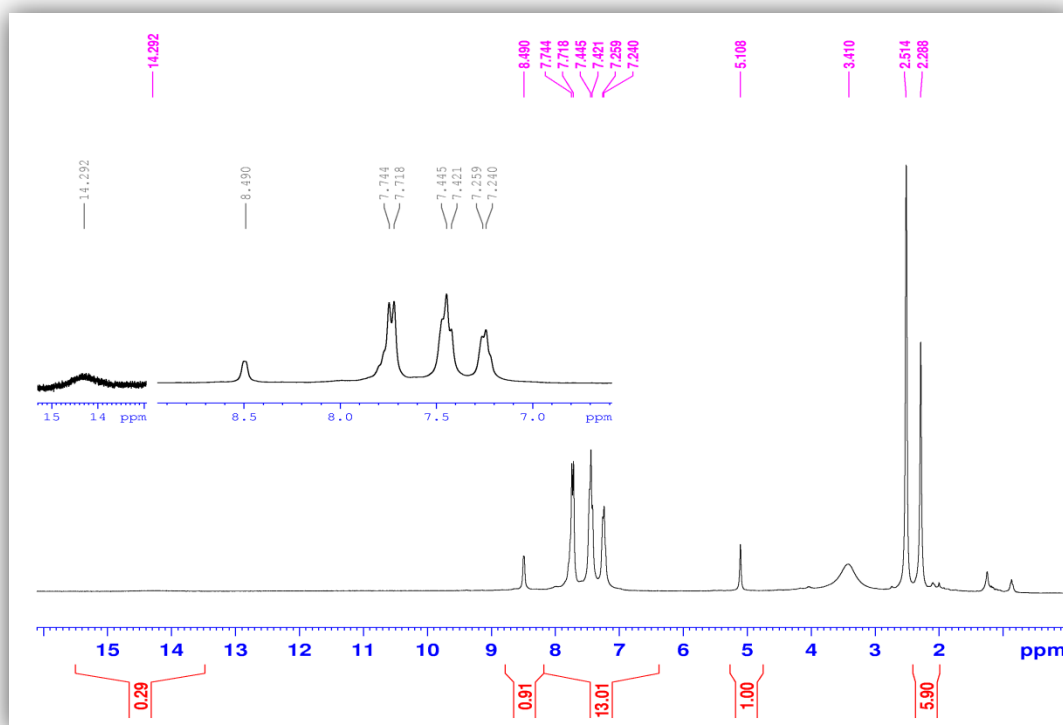
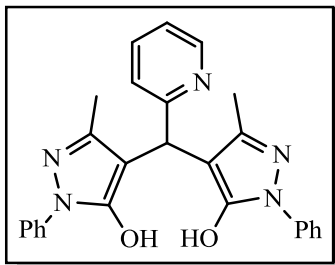


Figure 18a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of 4,4'-(Pyridin-2-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

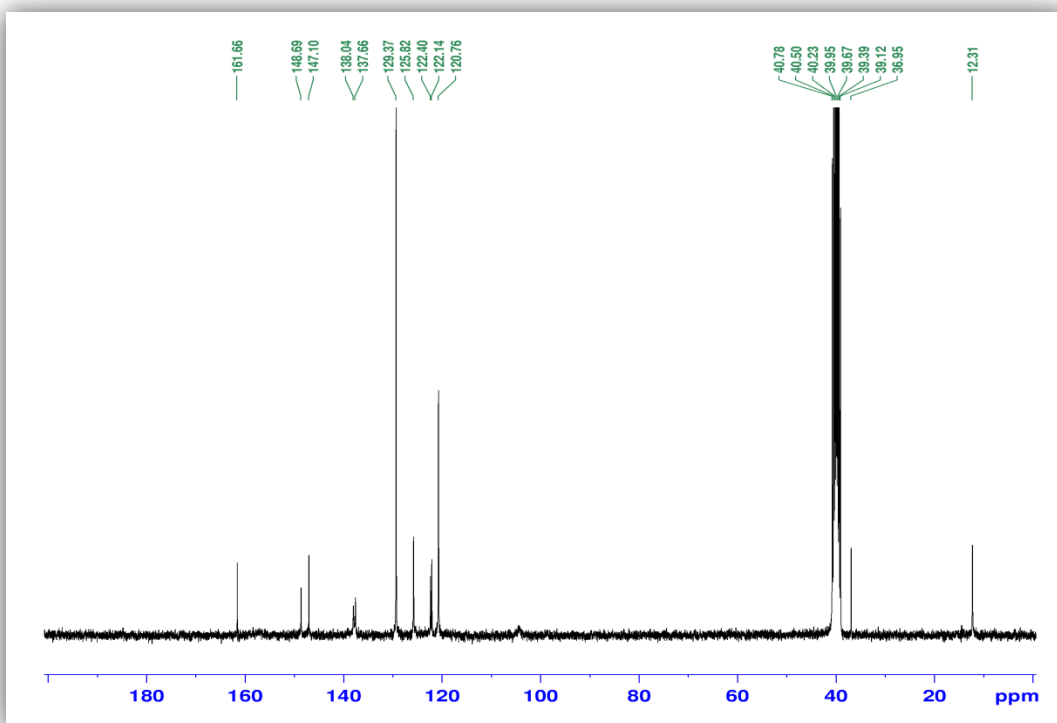


Figure 18b: ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) of 4,4'-(Pyridin-2-ylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)

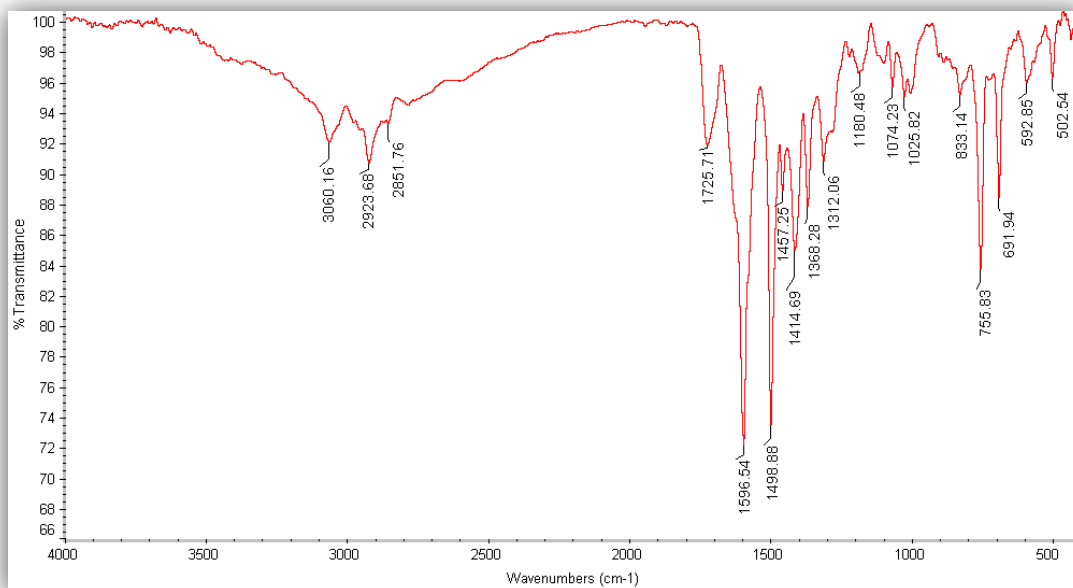


Figure 18c: FT-IR (KBr) spectrum of 4,4'-(Pyridin-2-ylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)

4,4'-(Pyridin-3-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3s)

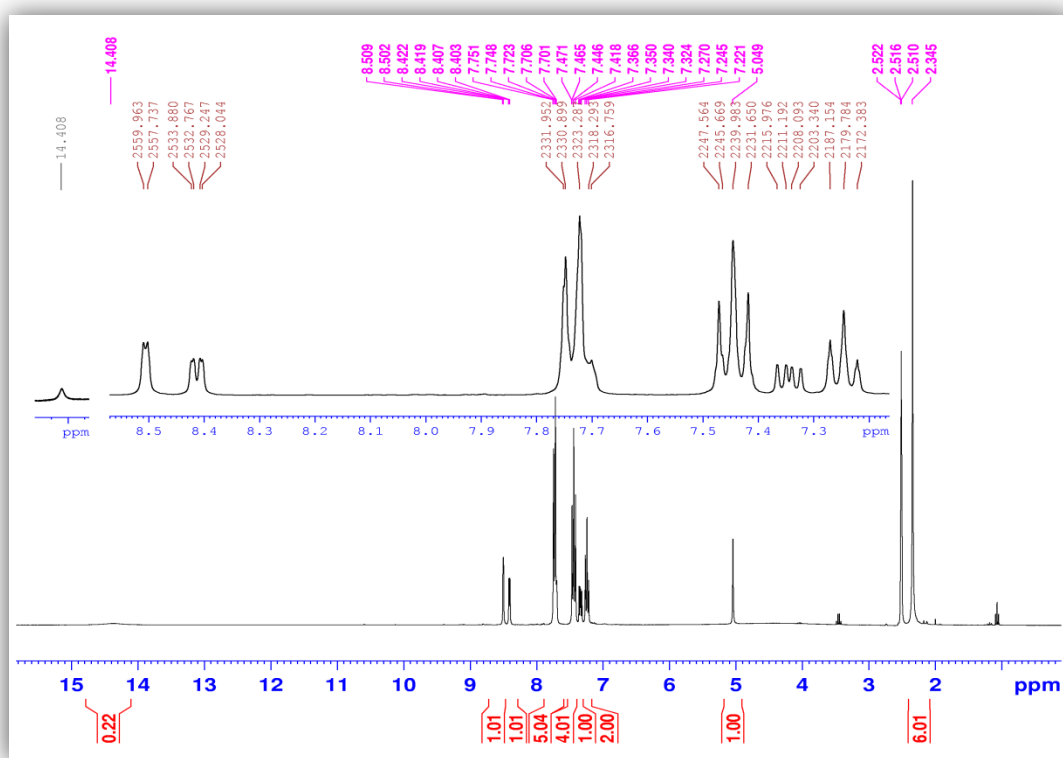
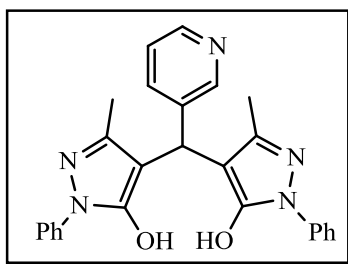


Figure 19a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of 4,4'-(Pyridin-3-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

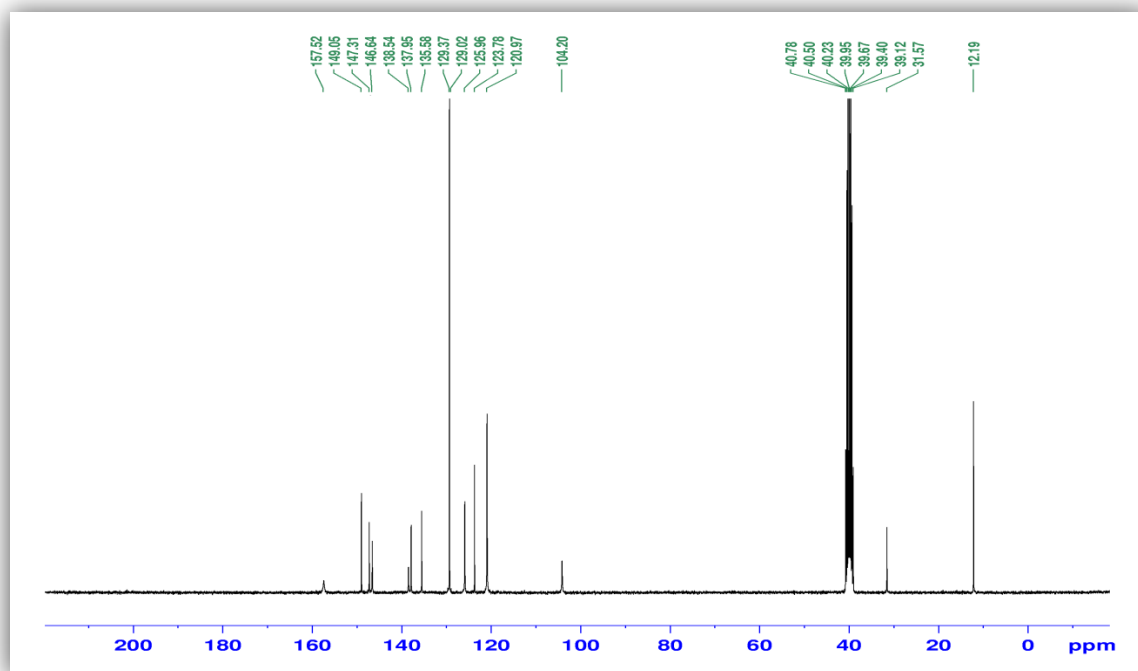


Figure 19b: ^{13}C NMR (75MHz, $\text{DMSO-}d_6$) of 4,4'-(Pyridin-3-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).

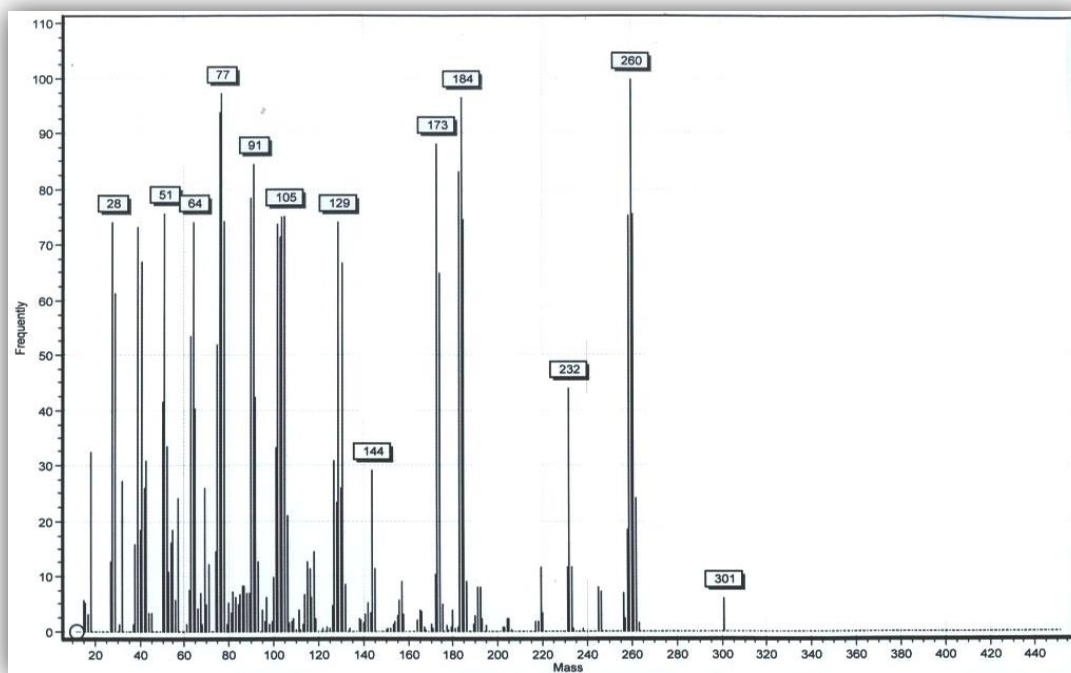
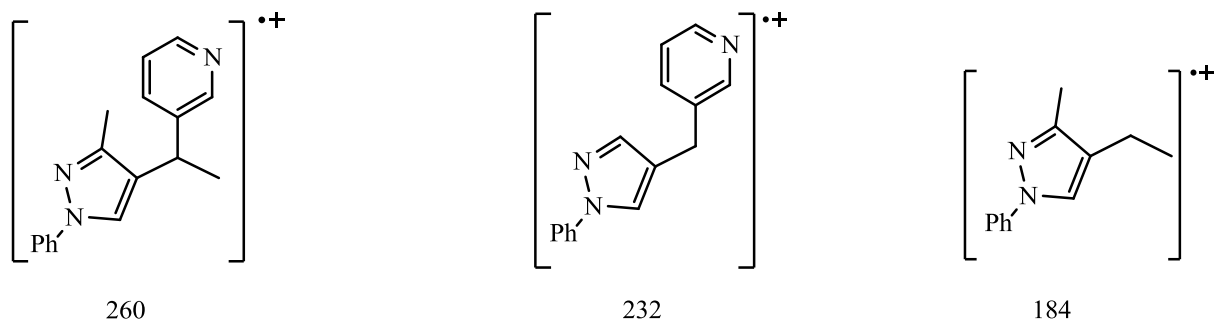


Figure 19c: Mass spectrum of 4,4'-(Pyridin-3-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)



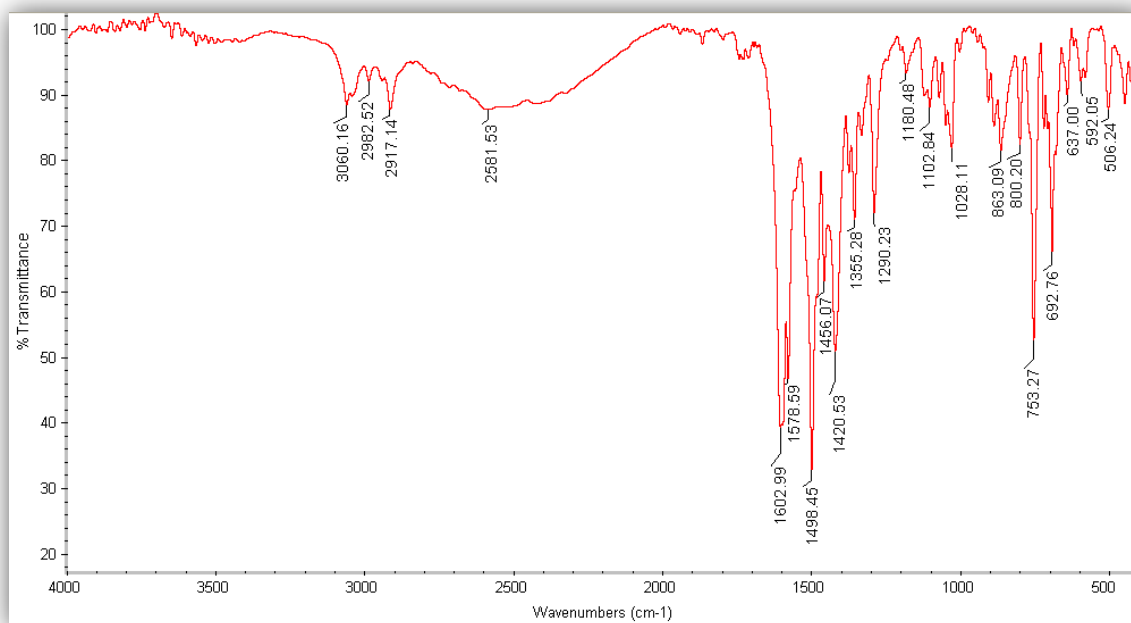


Figure 19d: FT-IR (KBr) spectrum of 4,4'-(Pyridin-3-ylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

(E)-4,4'-(3-Phenylprop-2-ene-1,1-diyl)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3t)

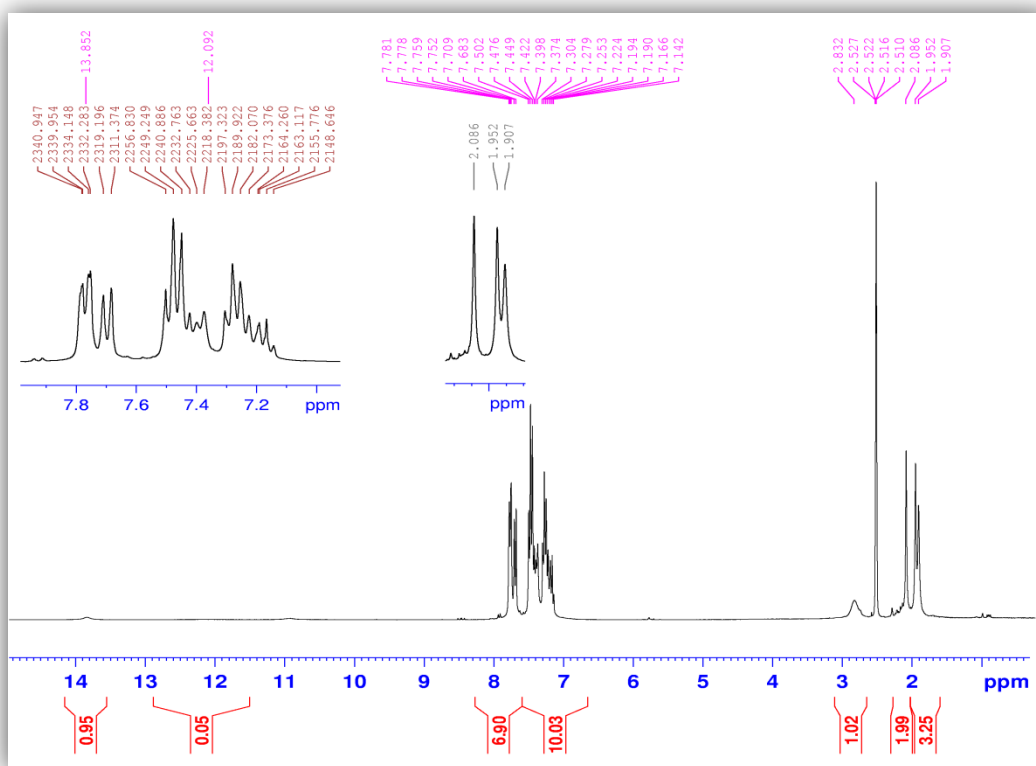
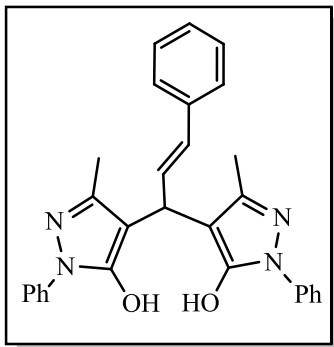


Figure 20a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of (E)-4,4'-(3-Phenylprop-2-ene-1,1-diyl)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

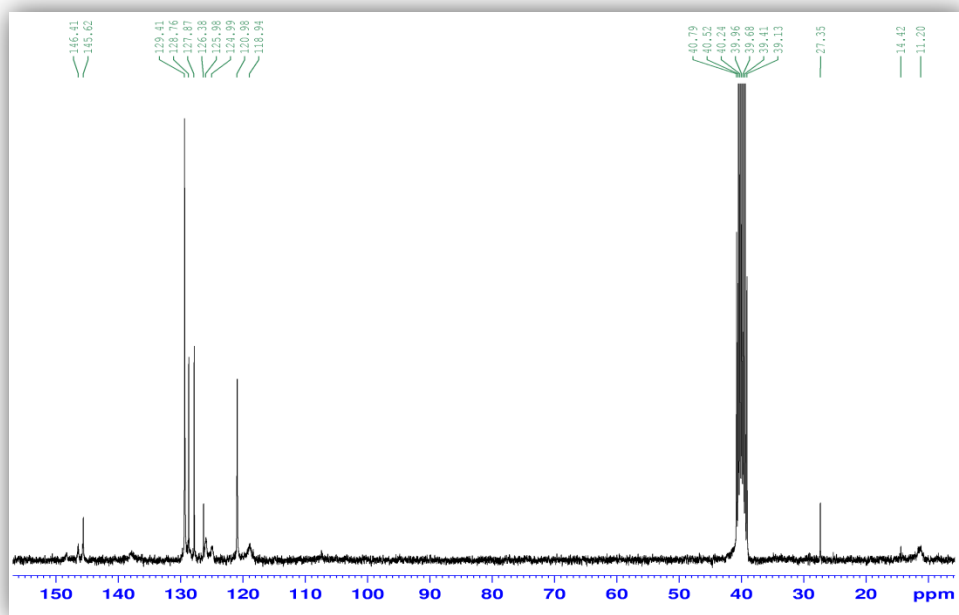


Figure 20b: ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) of of (*E*)-4,4'-(3-Phenylprop-2-ene-1,1-diyl)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)

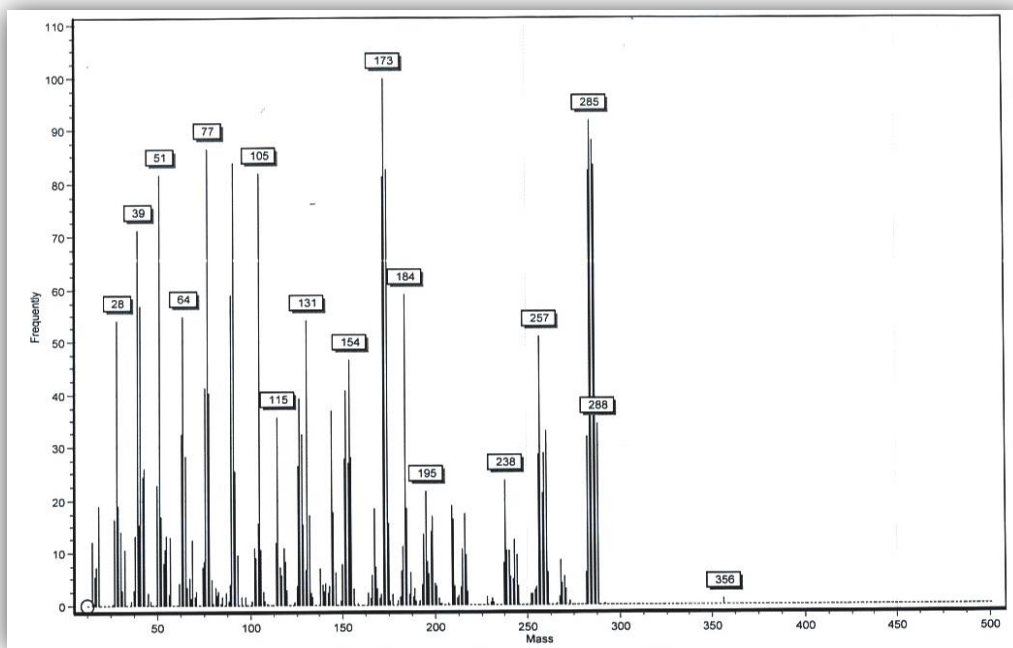


Figure 20c: Mass spectrum of (*E*)-4,4'-(3-Phenylprop-2-ene-1,1-diyl)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)

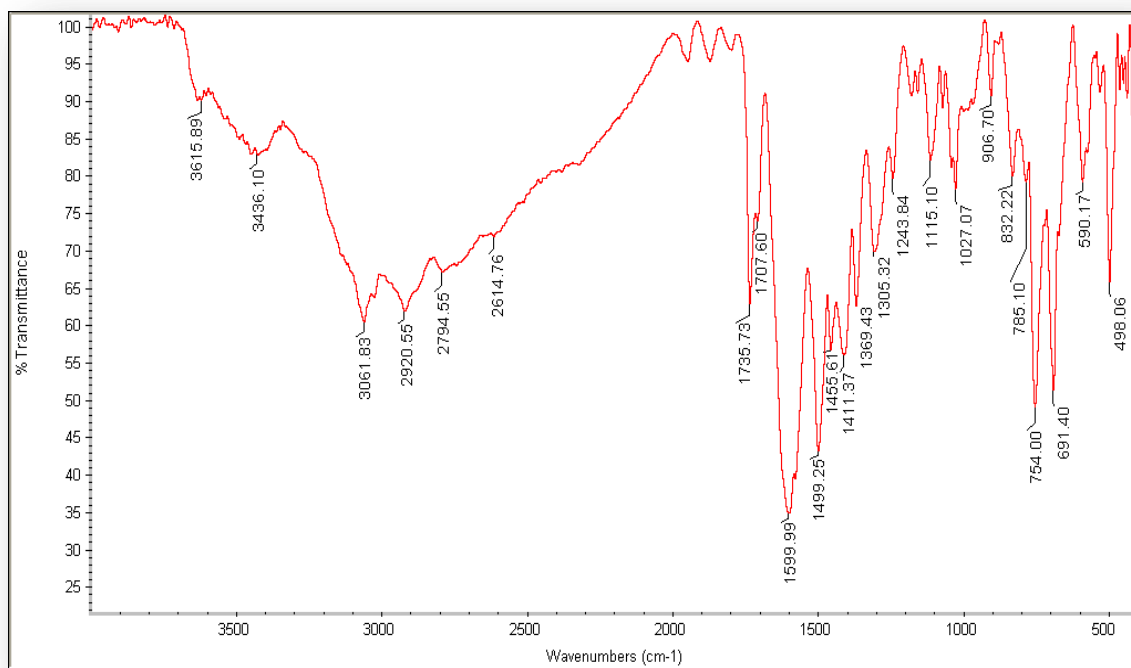
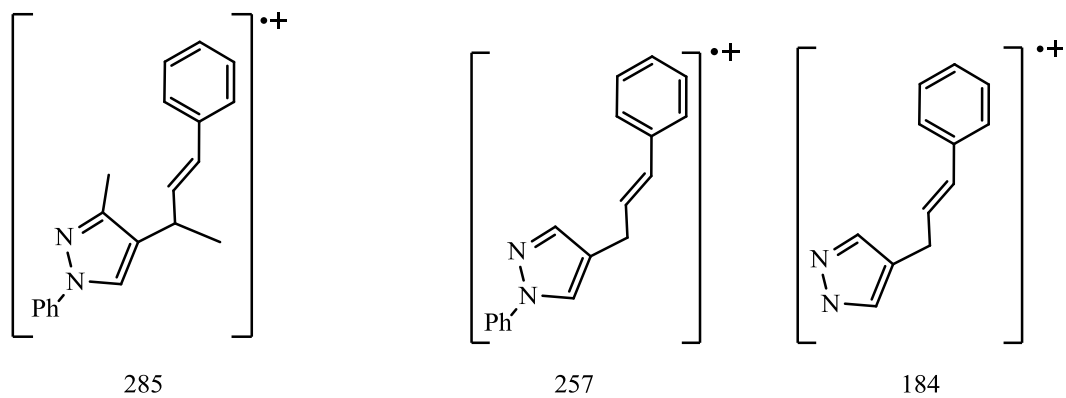


Figure 20d: FT-IR (KBr) spectrum of (*E*)-4,4'-(3-Phenylprop-2-ene-1,1-diyl)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol).

4,4'-(Phenylmethylene)bis(3-methyl-1H-pyrazol-5-ol) (3u)

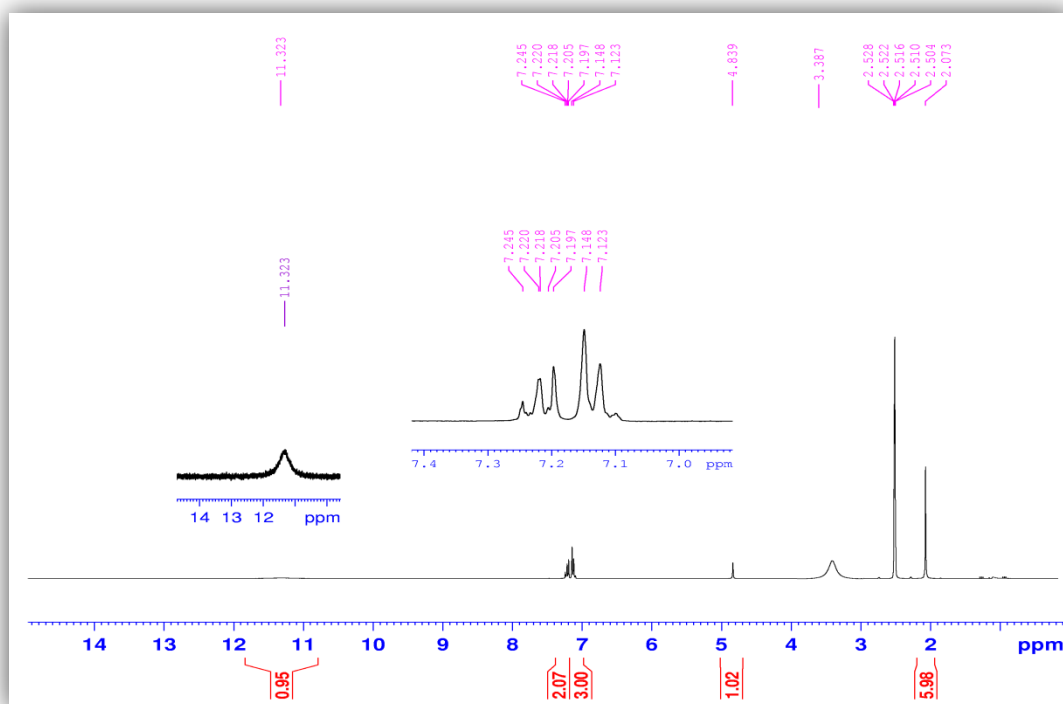
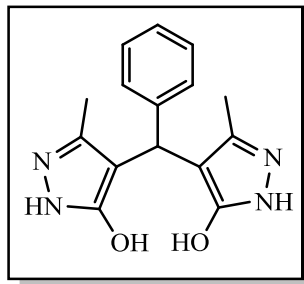


Figure 21a: ¹H NMR (300 MHz, DMSO-*d*₆) of 4,4'-(Phenylmethylene)bis(3-methyl-1H-pyrazol-5-ol).

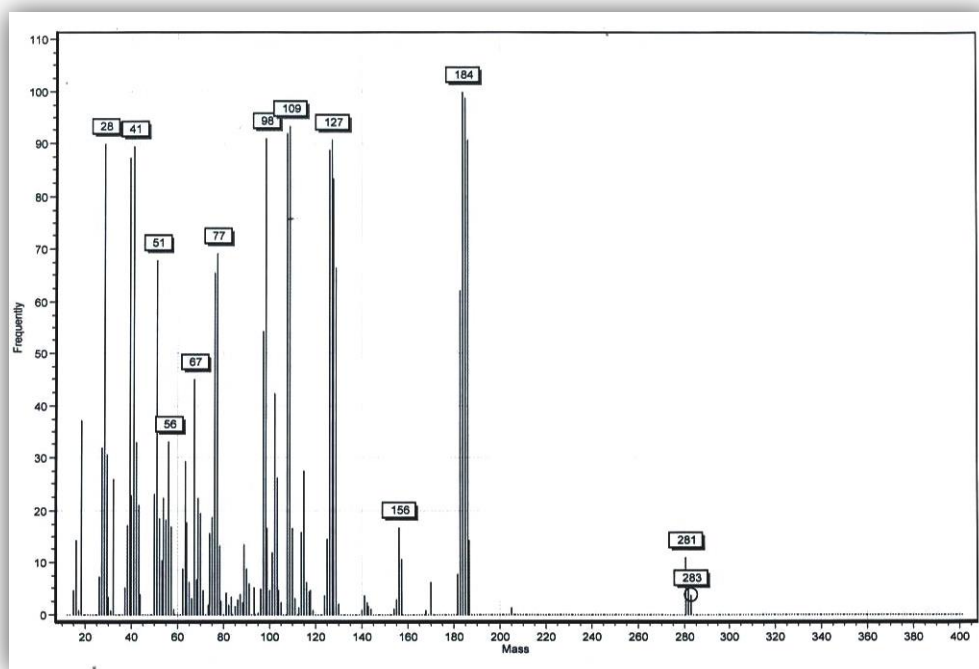
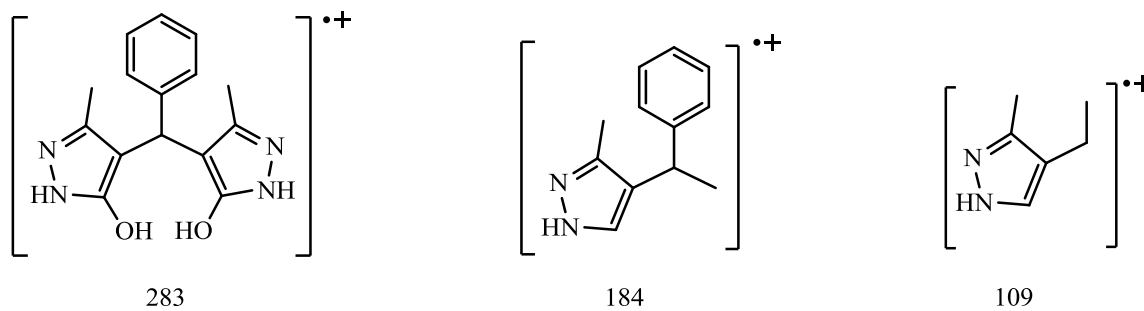


Figure 21b: Mass spectrum of 4,4'-(Phenylmethylene)bis(3-methyl-1*H*-pyrazol-5-ol).



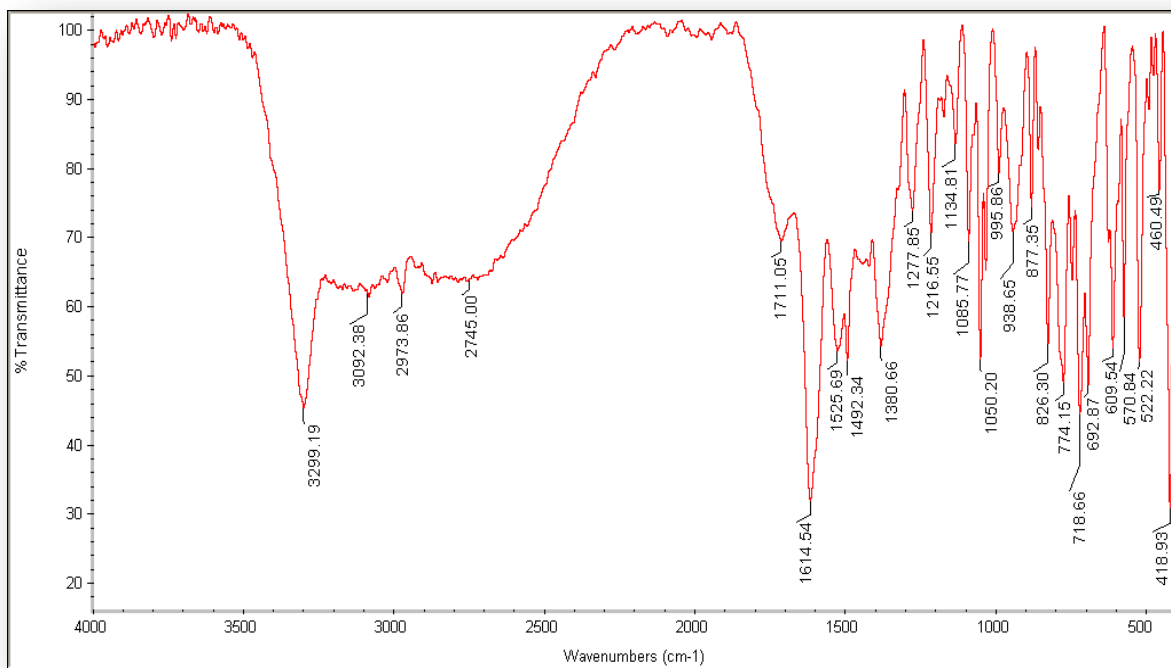


Figure 21c: FT-IR (KBr) spectrum of 4,4'-(Phenylmethylene)bis(3-methyl-1H-pyrazol-5-ol).

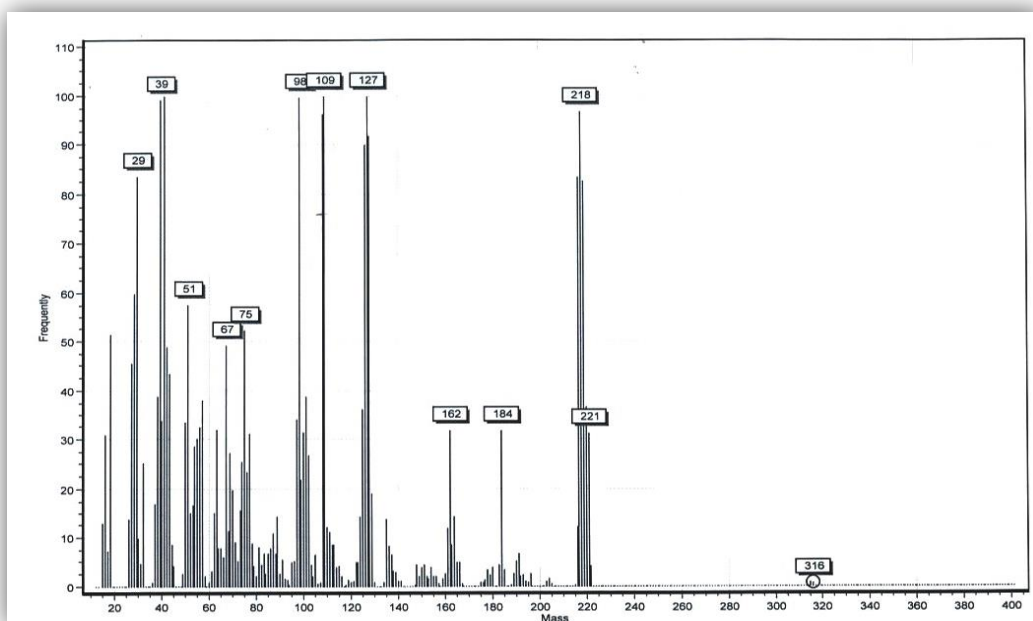


Figure 22b: Mass spectrum of 4,4'-((4-Chlorophenyl)methylene)bis(3-methyl-1*H*-pyrazol-5-ol).

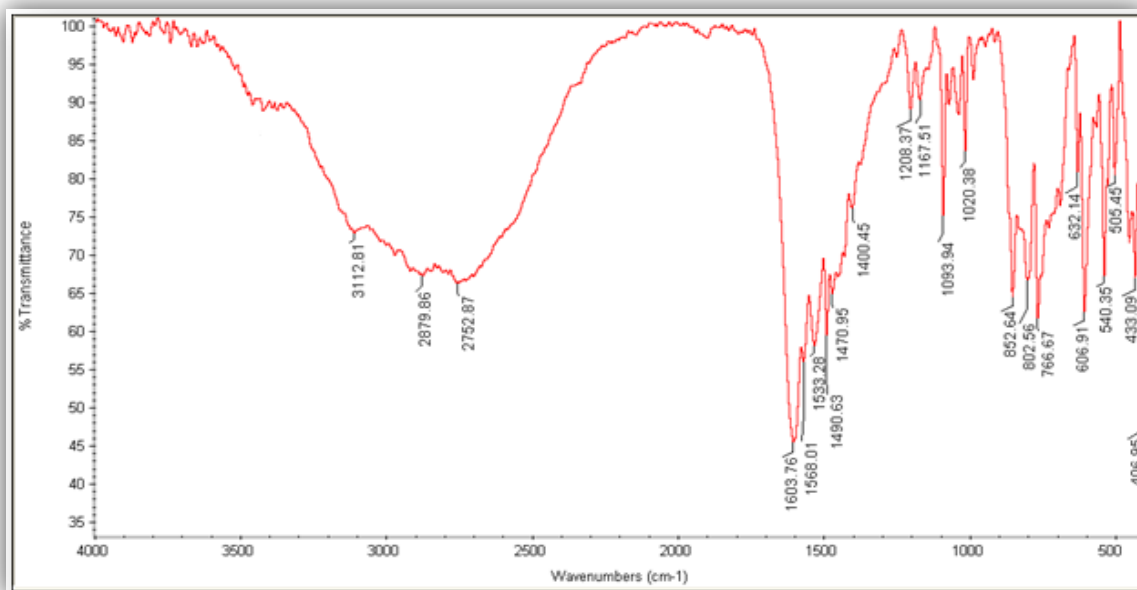


Figure 22c: FT-IR (KBr) spectrum of 4,4'-((4-Chlorophenyl)methylene)bis(3-methyl-1*H*-pyrazol-5-ol).

4,4'-(*p*-Tolylmethylene)bis(3-methyl-1*H*-pyrazol-5-ol) (3w)

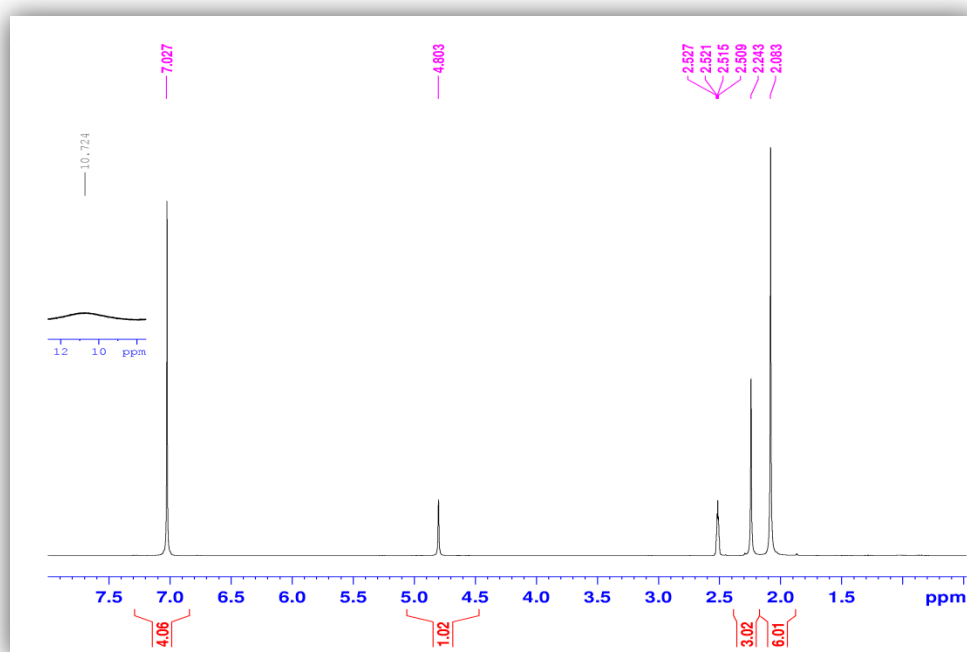
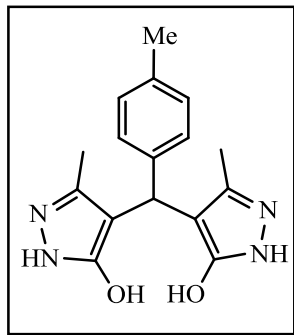


Figure 23a: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) of 4,4'-(*p*-Tolylmethylene)bis(3-methyl-1*H*-pyrazol-5-ol).

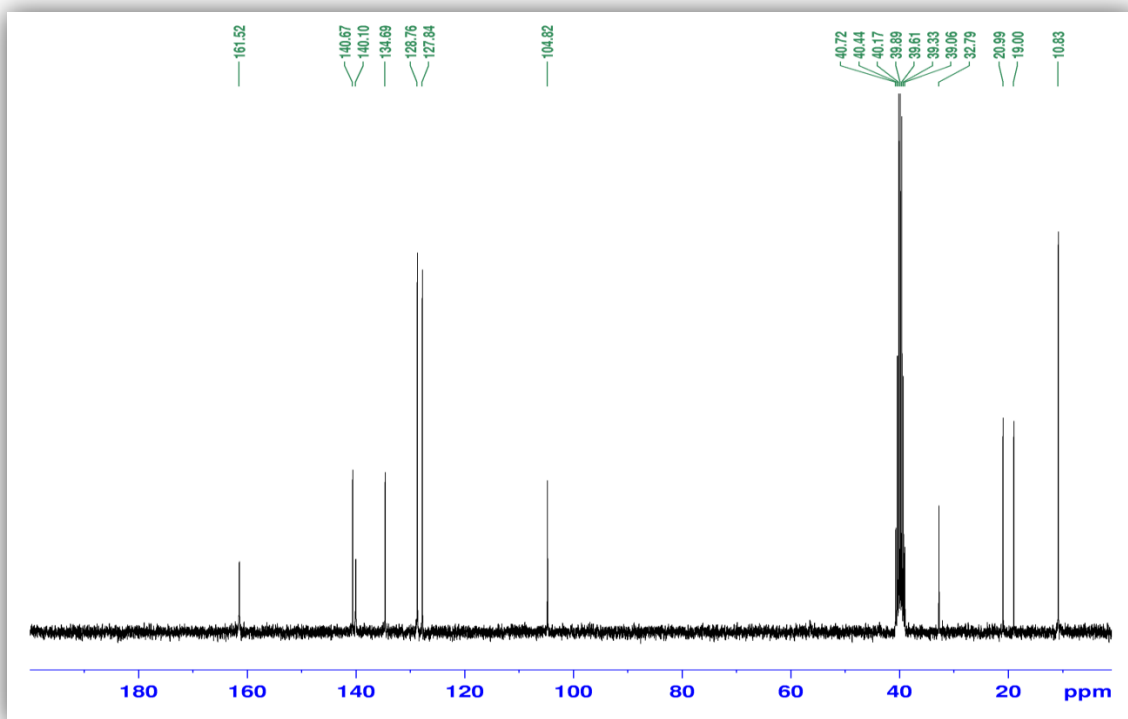


Figure 23b: ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) of 4,4'-(*p*-Tolylmethylene)bis(3-methyl-1*H*-pyrazol-5-ol)

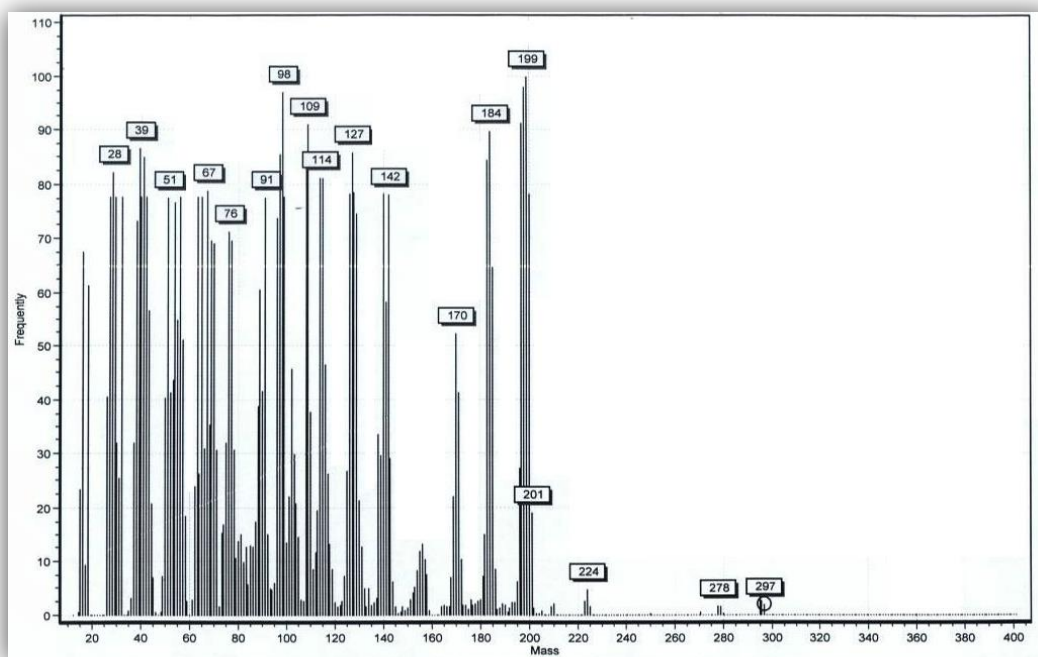


Figure 23c: Mass spectrum of 4,4'-(*p*-Tolylmethylene)bis(3-methyl-1*H*-pyrazol-5-ol).

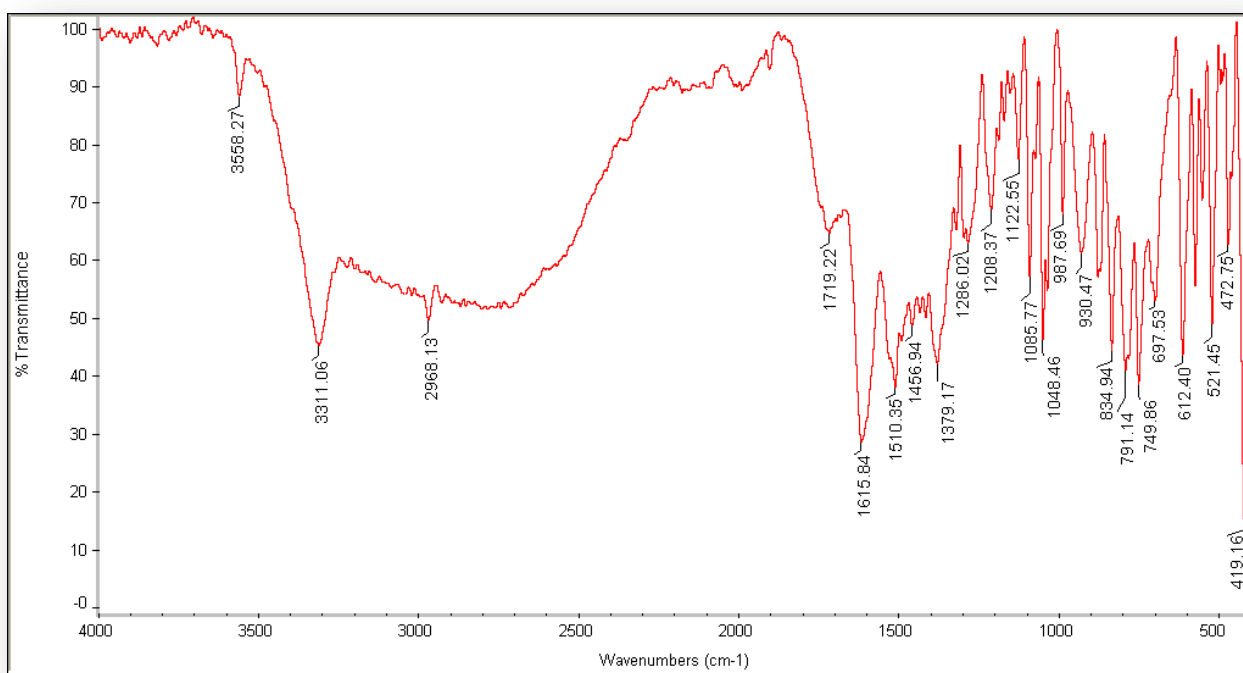


Figure 23 d: FT-IR (KBr) spectrum of 4,4'-(*p*-Tolylmethylene)bis(3-methyl-1*H*-pyrazol-5-ol).

(E)-4-(4-(Dimethylamino)benzylidene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one

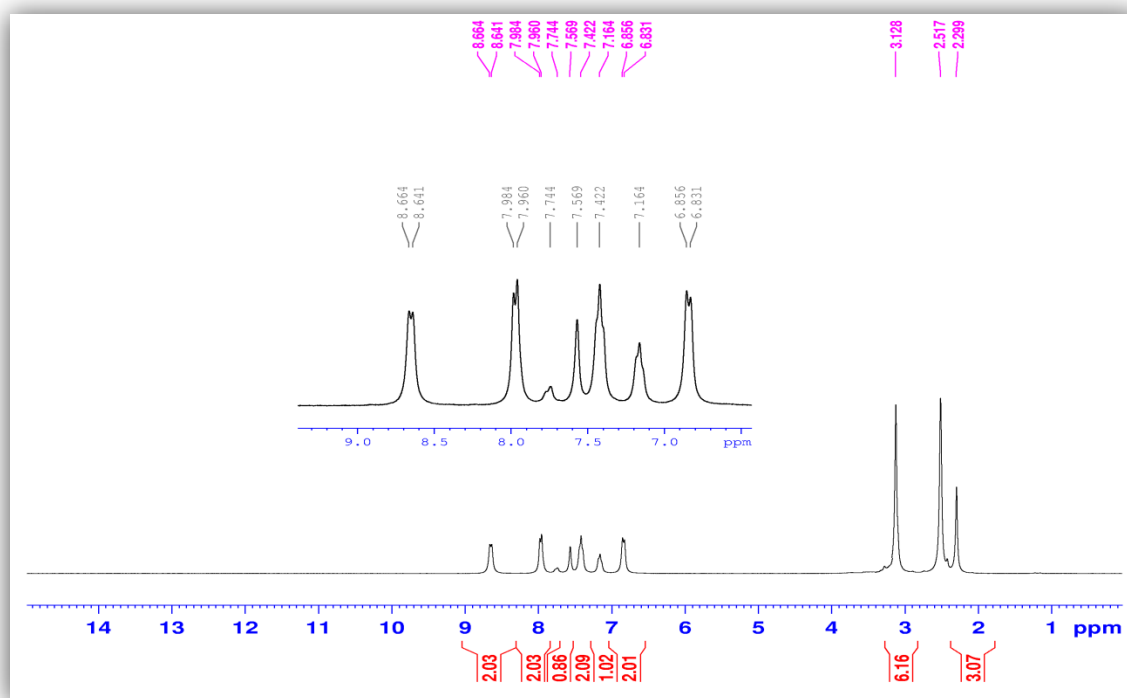
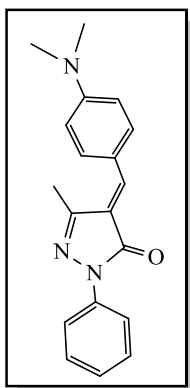


Figure 24a: ^1H NMR (300 MHz, $\text{DMSO}-d_6$) of (E)-4-(4-(Dimethylamino)benzylidene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one.

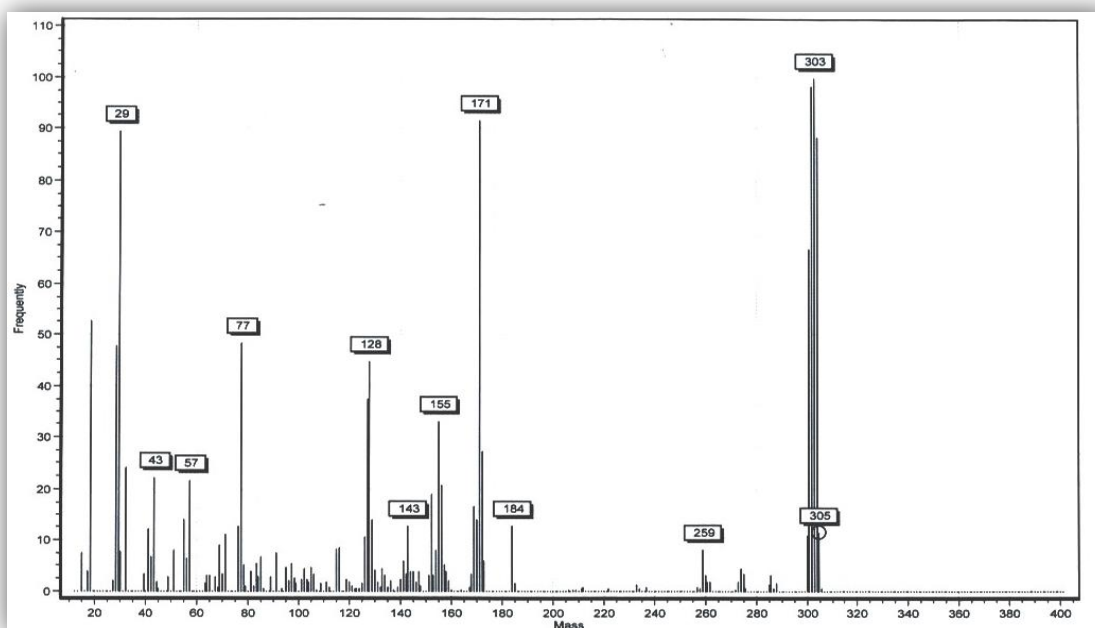


Figure 24b: Mass spectrum of *(E)*-4-(4-(Dimethylamino)benzylidene)-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one.

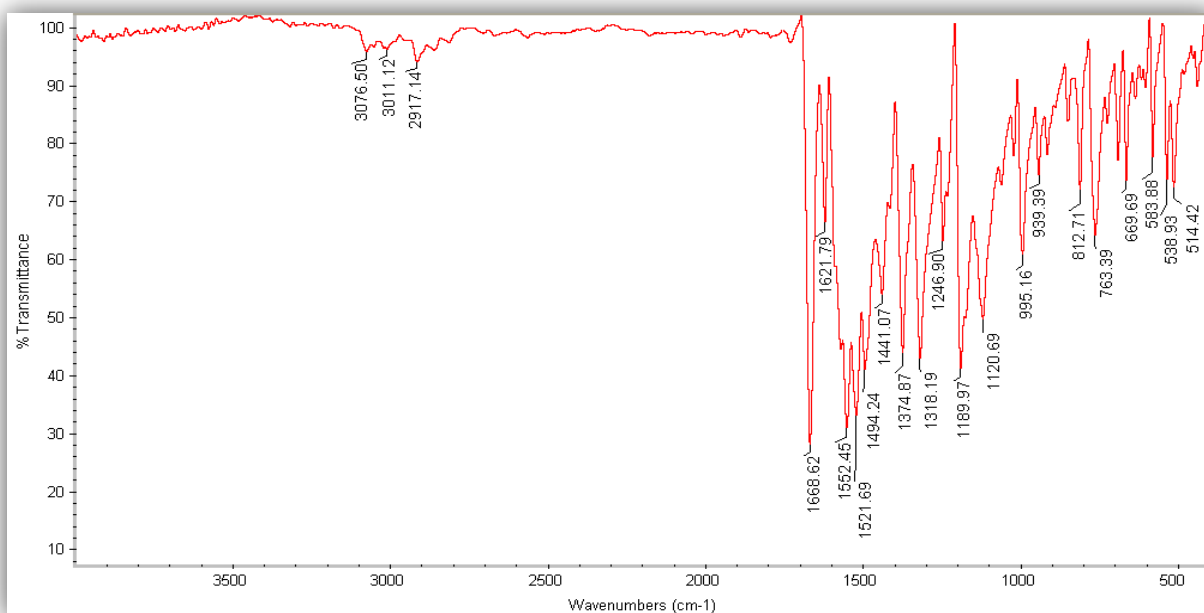


Figure 24c: FT-IR (KBr) spectrum of *(E)*-4-(4-(Dimethylamino)benzylidene)-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one.