

Preparation and Spectroscopic Identification of Some Sulphamerazine Imines

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Abstract

Sulphamerazine Imines derived from Sulphamerazine and selected aromatic aldehydes, namely, 2-Hydroxy-1-naphthaldehyde, 4-Hydroxy benzaldehyde, salicaldehyde, 3-Ethoxy Salicaldehyde and p-Tolualdehyde have been synthesized and characterized by IR, ¹HNMR and GC. Mass spectroscopy .The results revealed that , all compounds exit in imino form where the chemical shift (σ) of the imino proton (HC=N) are within the range 8.5- 9.6 . The strong intrahydrogen bonding was observed in compounds containing OH group in ortho position of aldehydes (compounds 1,3 and 4) as indicated by the downfield OH proton signals which appeared within the range 12-15.5 ppm .

Key words : Sulphamerazine , Schiff base .

Introduction:

The condensation of primary amine with carbonyl compounds was first reported by Schiff [1]. Aromatic aldehydes react smoothly under mild conditions and at relatively low temperatures in a suitable solvent or without it[2]. Sulpha drugs and their imine derivatives represent an interesting class of compounds which posses a wide range of biological activities[3 , 4] . The Schiff base derived from sulpha drugs and aldehydes or ketones have ability to form metal complexes[5,6] . With all these considerations in mind we have synthesized a series of sulphamerazine imines , then confirmed their structure by IR, ¹HNMR and mass spectroscopy.

Experimental;

1-Materials and measurements :

All chemicals and solvents are obtained from Fluka and Aldrich chemical co. and are used without further purification .

Melting points were recorded on Gallenkamp melting point apparatus without correction.

IR spectra were recorded on a shimadzu spectrometer as a KBr disks.

¹HNMR spectra were recorded with a Bruker 500 (500MHz)spectrophotometer using d₆-DMSO as a solvent and TMS as internal standard .

GC-mass spectra were recorded with a Fisons Trio 1000 spectrometer.

2-Preparation :

(a) Compound 1 ; A 25ml round bottomed flask. was charged with 0.264 g (1 mmol)of sulphamerazine , 0.172 g (1 mmol) of 2-Hydroxy-1-naphthaldehyde and 15ml absolute ethnl . The mixture was refluxed for 1.5 h. The yellow deposit which was formed was filtered off ,washed with cold ethanol and recrystallized from ethanol followed by drying at ~ 70C° over night .Yield 0.258 g (61%) as yellow crystals m.p. 250-252 °C.

(b) Compound 2 ; A 25 ml round bottomed flask. was charged with 0.122g (1 mmol) of 4-Hydroxy salicaldehyde , 0.264 g (1mmol) of sulphamerazine and 15ml absolute ethanol .The mixture was refluxed for 6 hrs. then the solvent was evaporated and the solid orange product was recrystallized from ethyl acetate followed by drying at ~ 70°C over night . Yield 0.202 g (55%) as yellow crystals , m.p. 147-148 °C

(c) Compound 3 : The mixture of 0.264 g (1mmol) of sulphamerazine and excess (10ml) of salicyladehyde was heated together (fusion) for 1.5 h., the yellow solid obtained after cooling was filtered off washed with hot ethanol for several times followed by drying at~ 70°C over night .Yield 0.272g (71%) as yellow crystals m.p. 262-263 °C.

(D) Compound 4 : A 50 ml round bottomed flask was charged with 0.166g (1mmol) of 3-Ethoxy salcinaldehyde , 0.26g (1mmol) of sulphamerazine and 25ml of absolute ethanol . The mixture was refluxed for 2h. , the orange solid which was formed was separated while the solution hot ,filtered and washed with ethanol and recrystallized from benzene followed by drying at $\sim 70^{\circ}\text{C}$ over night .Yield 0.337g (82%) as orange crystals m.p. $192\text{-}195^{\circ}\text{C}$.

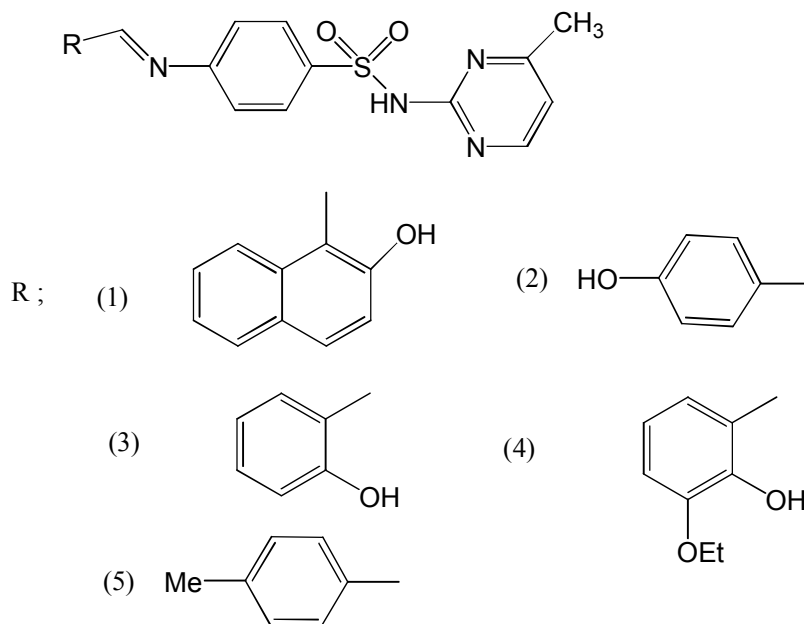
(E) Compound 5 :The mixture of 0.264g (1mmol) of sulphamerazine and excess (10ml) of p-Tolualdehyde was heated together for 2 h., cooled and the yellow solid filtered off and washed with ethanol and the product recrystallized from benzene then dried at $\sim 70^{\circ}\text{C}$ over night , yield 0.33(90%) as yellow crystals m.p. $252\text{-}254^{\circ}\text{C}$

Note: reaction were monitored by TLC using either Ethyl acetate :Benzene (7:3) or Dichloromethane – Acetone (20:1) as eluent

Result and discussion :

The 1:1 molar ratio reaction between aldehyde and sulphamerazine had led to the formation of sulphamerazine imine in a good yield , the resulting compounds are sparingly or insoluble in most of the

common organic solvents at room temperatures except in DMF and DMSO .The general formulae can be represented by the structures shown .



IR spectra ;

The IR spectra of compounds 1,2,3 and 4 show a broad band at $\sim 3450\text{ cm}^{-1}$ which assigned to $\nu\text{ OH}$, while the $\nu\text{ NH}$ bands in these compounds shown in the range $3350\text{-}3200\text{ cm}^{-1}$. Also a broad band at $1622\text{-}1585\text{ cm}^{-1}$ due to the stretching vibration of hydrogen bonded azomethine group . The shift to lower wavenumber (1585 cm^{-1}) observed in compound 3 spectrum (Fig 1) illustrated the strong

hydrogen bonding between hydroxyl group and azomethine group. In all compounds a bands at $\sim 1330\text{ cm}^{-1}$ and $\sim 1150\text{ cm}^{-1}$ has been ascribed to asymmetric and sym. stretching of SO_2 group[7].The IR data of the studied compounds are show in Table (1).

Table 1 : IR spectra data of compounds (cm⁻¹)

Compounds	v OH v NH	C-H aromatic C-H aliphatic	v C=N	O=S=O Asym. Sym.
(1)	3450 br 3380 br	3036 m 2927-2855 m	1622 s	1339 s 1152 vs
(2)	3450 br 3223 w	3050 m 2960-2850 w	1610s	1321 m 1152 s
(3)	3423 br 3325 br	3062 w 2952 w	1585 br	1325 s 1147 s
(4)	3350 w 3210 br	3037 m 2977-2873 m	1586 br	1337 s 1155 vs
(5)	---- 3200 br	3078 2921-2856	1630 s	1330s 1151 s

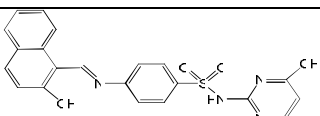
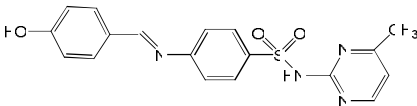
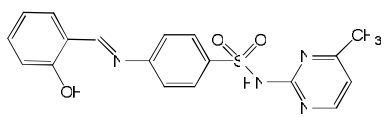
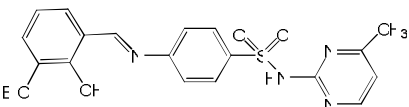
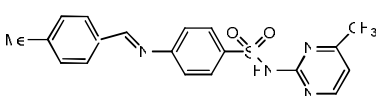
v : stretch, br:broad , s:strong , m:medium , w:weak

¹HNMR spectra;

Figs. 2 and 3 and Table (II) show the ¹HNMR spectral data of compounds 1-5 , in general the spectra displayed a singlet signal at ~2.3 ppm that attributed to the protons of CH₃ group of sulphamerazine moiety . The signals due to the aromatic protons appeared at the region σ 6.8-8.5 ppm . The broad signal at σ about 11 ppm is

assigned to the NH proton. All compounds exist in the imine form where the chemical shift of the imino proton (HC=N) is within the range of 8.5-9.6 ppm[8] . The relatively downfield chemical shift of the OH group in the compounds with OH group at position 2 (12-15) ppm indicated the strong hydrogen bonding between OH group and imino group[9].

Table II: H¹NMR characterization of compounds (σ ppm)

compound	σ in ppm and J in Hz chemical shift
(1) 	2.3(s,3H,CH ₃) , 6.9-8.5(m,12H,Ar-H) 9.6(d,J=4.85,1H,HC=N),11.76(br,1H,NH) 15.3(d,J=4.75,1H,OH)
(2) 	2.31(s,3H,CH ₃) , 5.98(s,1H,OH) , 6.9-8.3(m,10H,Ar-H), 9.2(s,1H,HC=N),11.22(br,1H,NH)
(3) 	2.34(s,3H,CH ₃) , 6.8-8.4(m,10H,ArH), 8.93(s,1H,HC=N),11.83(br,1H,NH), 12.22(br,1H,OH)
(4) 	1.3(t,3H,CH ₂ CH ₃ ,J=6.9) , 2.3(s,3H,CH ₃), 4.9(q,2H,CH ₂ ,J=6.95) , 6.9-8.3(m,9H,Ar-H) 8.97(s,1H,HC=N) , 11.8(br,1H,NH), 12.67(s,1H,OH)
(5) 	2.2(s,3H,Me) , 2.37(s,3H,CH ₃),7-8(m,10H Ar-H) , 8.53(s,1H,HC=N) , 11.79(br,1H,NH)

S:singlet, d:doublet , t:triplet , q:quartet , br:broad , m: multiple

Mass spectra :

The mass spectra of the studied compounds characterized by the molecular ion backs $[M^+]$ which appear at m/z correspond to the molecular weights of the imperial formulae .The relative intensity of molecular ion of all compounds

is less than 10% except compound 4 where the relative intensity of $[M^+]$ is 58% at $m/z= 412$ as show in Fig 3 . which means to the first approximation that this compound is more stable than the others within the applied condition .

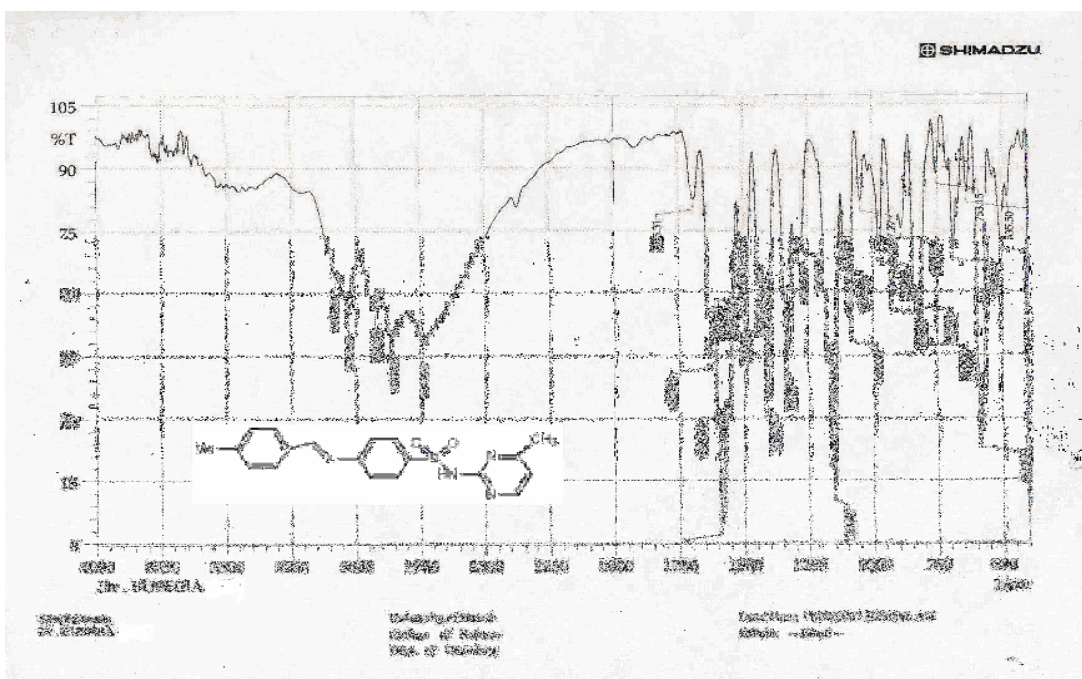
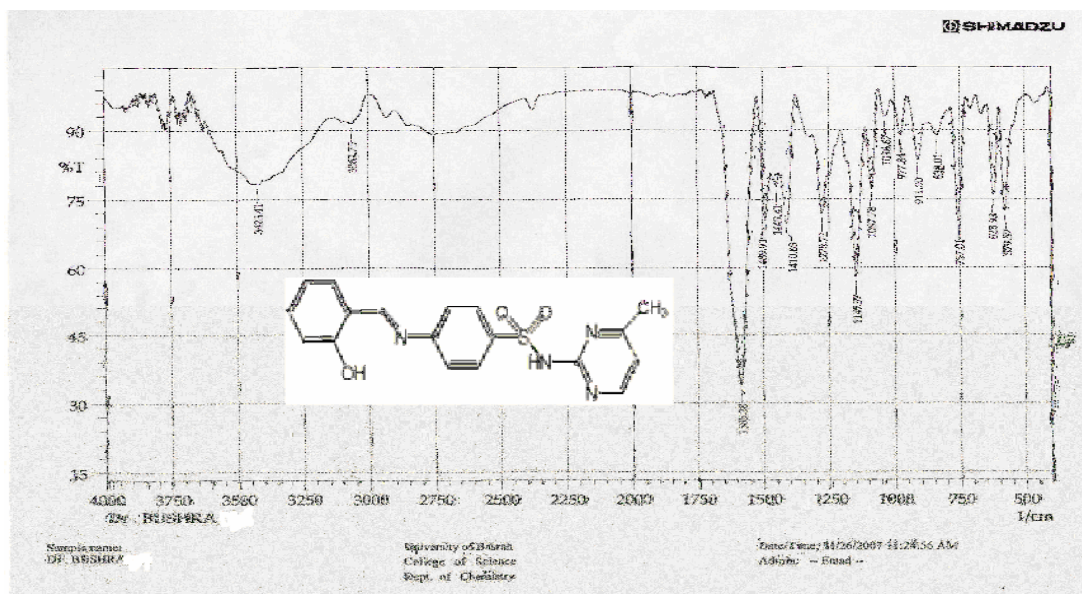


Fig 1 : IR spectra for compounds 3 and 5

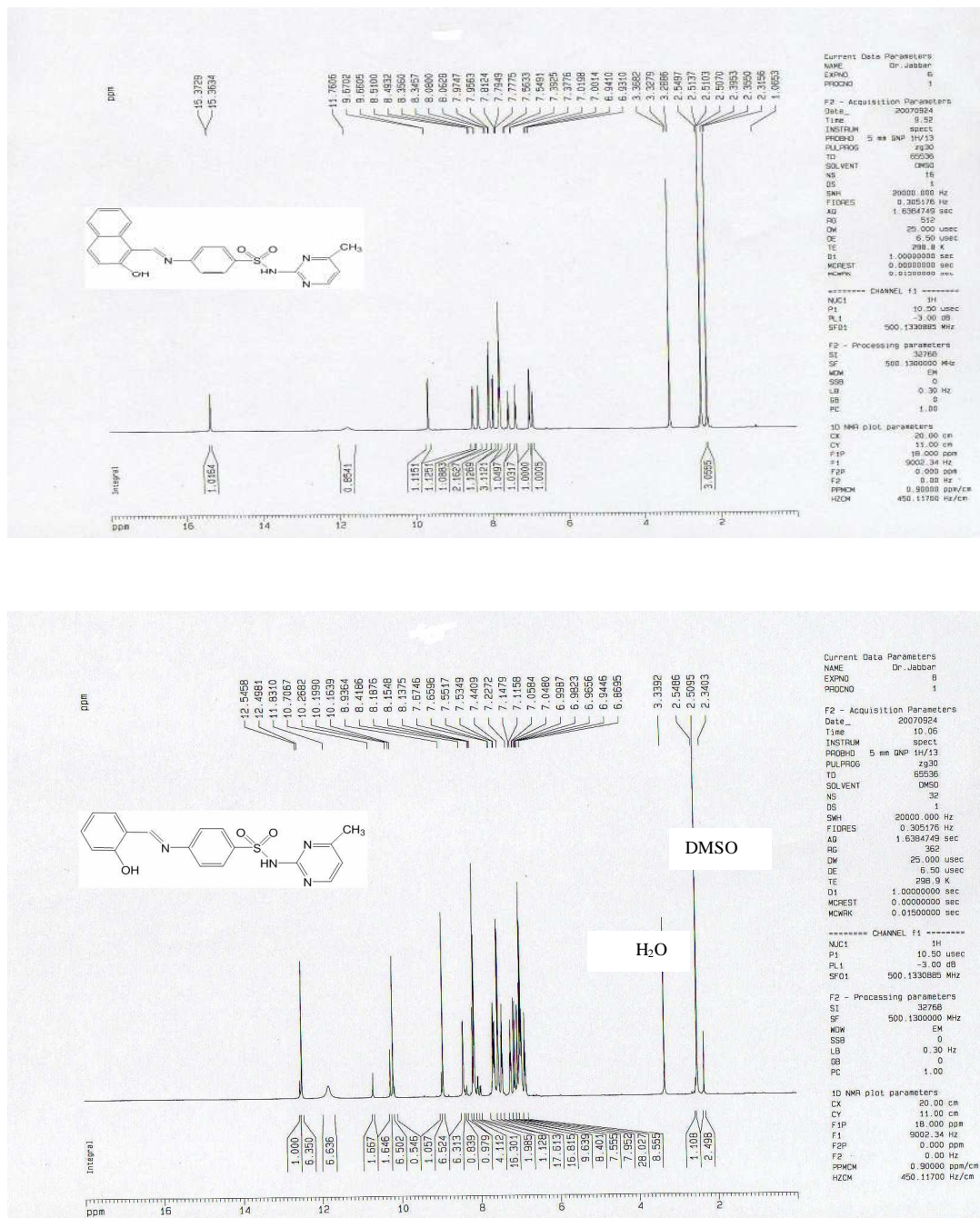


Fig 2 : ¹HNMR spectra for compounds 1 and 3

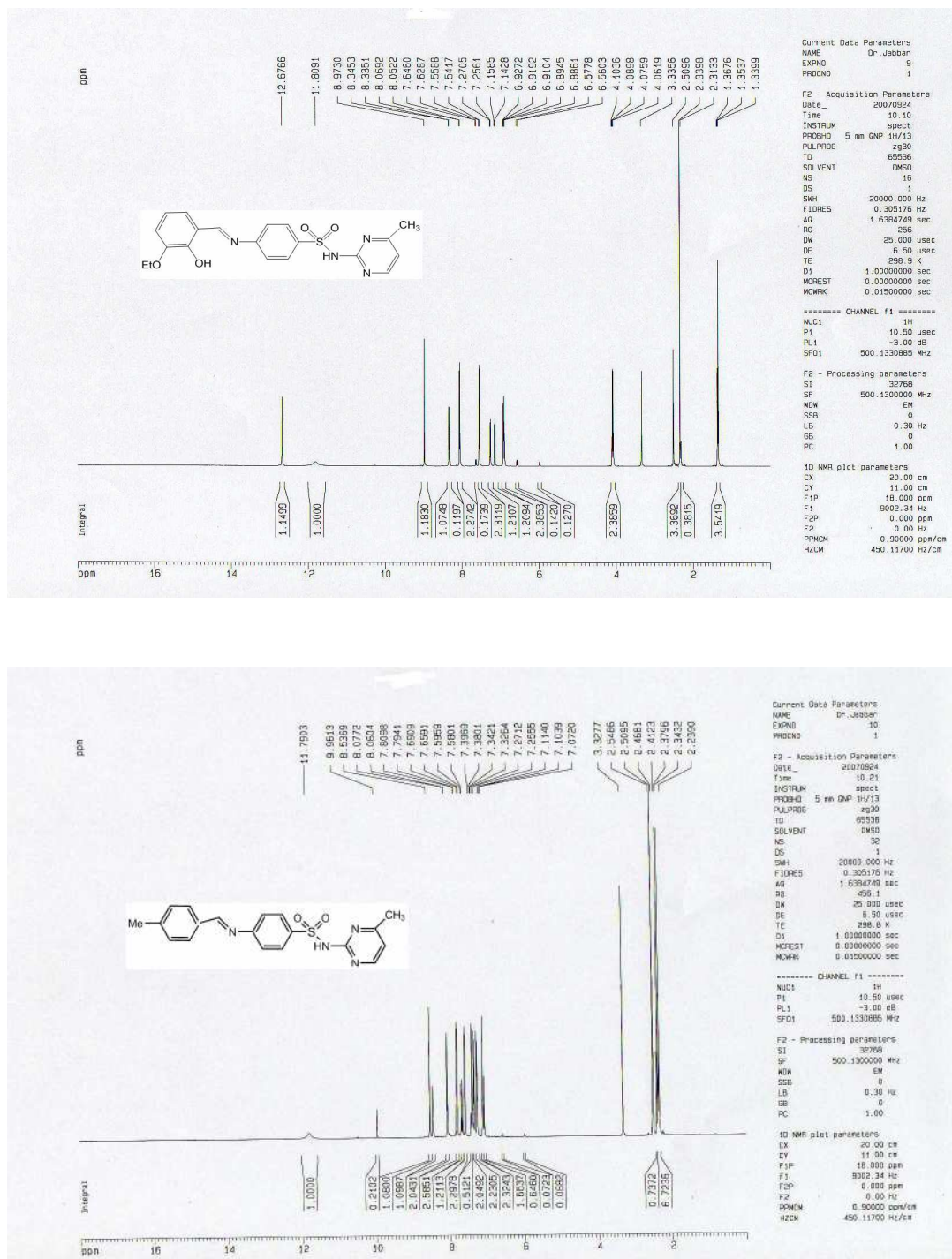


Fig 3 : ¹H NMR spectra for compounds 4 and 5

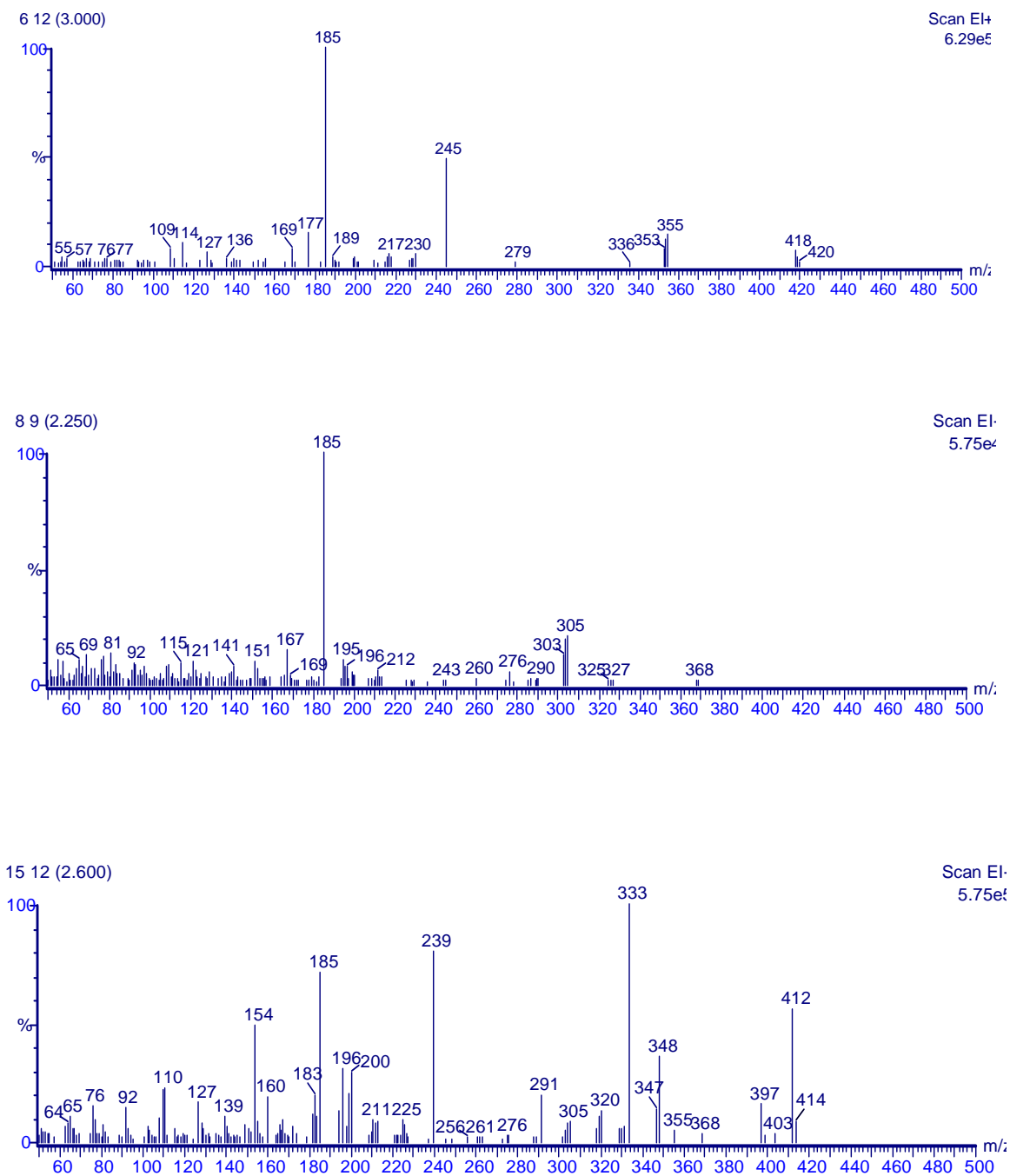


Fig 4 : Mass spectra for compounds 1 , 3 and 4

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الخلاصة

حضرت في هذه الدراسة خمسة من الایمينات المشتقة من السلفاميرازين وبعض الالديهيدات الاروماتية وهي 2-هيدروكسي -1- نفتالديهيد , 4- هيدروكسي بنزليهيد , سلسالديهيد , 3- ايثوكسي سالسالديهيد , 4- مثيل بنزليهيد , شخصلت جمیع المركبات المحضرة بتقنية الاشعة تحت الحمراء وطيف الرنين النووي المغناطيسي وطيف الكتلة , وبينت النتائج ان المركبات على هيئة ايمين (HC=N) من خلال اشارة بروتون مجموعة (HC=N) في المنطقة 8.5-9.6 ppm في طيف ال ¹HNMR . كما بينت النتائج التآصر الهيدروجيني الضمني في المركبات الحاوية على مجموعة OH في الموقع اورثو في الالديهيد , اي في المركبات 1,3,4 حيث لوحظ وقوع اشارات بروتون OH في المجال الاوطأ 12 – 15.5 ppm .