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Synthesis ,Charactrization and Evaluation Biological Activity of some New Formazan Compounds Derived from Schiff Bases and Azo Compounds

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Abstract
The titled compounds ((twenty compounds)) were synthesized from series reactions of two types compounds (azo and imine) - compounds ., we prepared ten compounds from Schiff bases which react after that with diazo compounds to produce formazane compounds .All the synthesized compounds have been investigated using different chemical techniques, such as (^{1}H.NMR–spectra, , (C.H.N)-analysis, FT.IR–spectra) some of them in ^{13}C.NMR–spectra , melting points and biological study
Keywords: different , melt , range.

1. Introduction

Formazan compound, of the general formula , are an important and distinct class of organic compounds. Their chemistry has attracted the interest of many research groups due to their wide biological and industrial applications as well as their utility in analytical chemistry and synthesis of heterocyclic compounds (Ahmed 2015 , Martin et al 1999, Sainoto et al 1996) . At present, there are several review articles and books devoted to the synthesis, physical properties and chemical reactions of formazan

(Nagham 2014 , Nagham 2015). All literature reveals that many formazans have been reported to possess wide spectrum of biological activities. In the following, a complete coverage of the recently reported pharmacological applications of various formazan derivatives (Buzykin et al Times New Roman 1922 , Bednyaig 1975) .Several formazans were reported to show promising anticonvulsant and therapeutic activities , Also, the formazans were prepared and tested for anticancer and anti-HIV activities .However, none of such compounds was found active at the dose level tested (Ninhan et al 1955, Reid 1951 , Shawali 2009).

they have been found to possess wide spectrum of biological activities such as antiviral, antimicrobial, anti-inflammatory, antifungal, anticancer, anti HIV. Based on these findings and in continuation of our studies of the chemistry of both 3-chloro-1, 5-diarylformazans and the related hydrazonoyl halides , it was thought necessary to present this review. Our objective is to shed light on the recent developments in biological activities of various functionalized formazans (Nagham 2016) .Only recent reports that have been published during the period from 1980 to 2013 are covered. Compounds of type, which were erroneously named, in some articles as formazans, will not be included in this review as they are amidrazone derivatives and not formazans (Shawali 2005 ,Nagham 2015).

2. Experiment and Apparatuses

All chemicals used (purity 99.98%), FT.IR-spectra: were recorded on shimadzu 8300, KBr -disc, HNMR-spectra were recorded on varian 300MHz spectrometer using TMS as an internal standard and elemental analysis (C.H.N)-elemental (analyses system GmbH)-measurements and ^{13}C.NMR–spectra , were carried out in Department of chemistry in Canada. The melting points were determined in open capillary tubes by electro thermal 9300LTD, UK. , biological study carried out in Bio – lab in biological department.

2.1. Synthesis of Compounds {1- 4} :

According to procedures[4-8] ,ethanolic mixture of (0.01mole) of P-chloro benzaldehyde with (0.01mole) from ((benzoyl hydrazine , pyridoyl hydrazine , phenyl thioemicarbazide , p-nitro aniline)) were refluxed for (3hrs) in presence of drops from glacial acetic acid to produce precipitate of Schiff bases compounds [1, 2, 3, 4] ,the precipitates were filtered and dried then re crystallized to yield compounds [1, 2, 3, 4] .

2.2. Synthesis of Compounds {5 -8} :

According to procedures[4-8] ,ethanolic mixture of (0.01mole) of O- hydroxy benzaldehyde with (0.01mole) from ((benzoyl hydrazine , pyridoyl hydrazine , phenyl thioemicarbazide , p-nitro aniline)) were refluxed for (2hrs) in presence of drops from glacial acetic acid to produce precipitate of Schiff bases compounds [5, 6, 7, 8] ,the precipitates were filtered and dried then re crystallized to yield compounds [5, 6, 7, 8] .

2.3.Synthesis of Compounds {9 , 10} :

According to procedures[17],ethanolic mixture of (0.01mole) of formal indole with (0.01mole) from ((pyridoyl hydrazine , p-nitro aniline)) were refluxed for (3hrs) in presence of drops from glacial acetic acid to produce precipitate of Schiff bases compounds [9 ,10] ,the precipitates were filtered and dried then re crystallized to yield compounds [9, 10] .

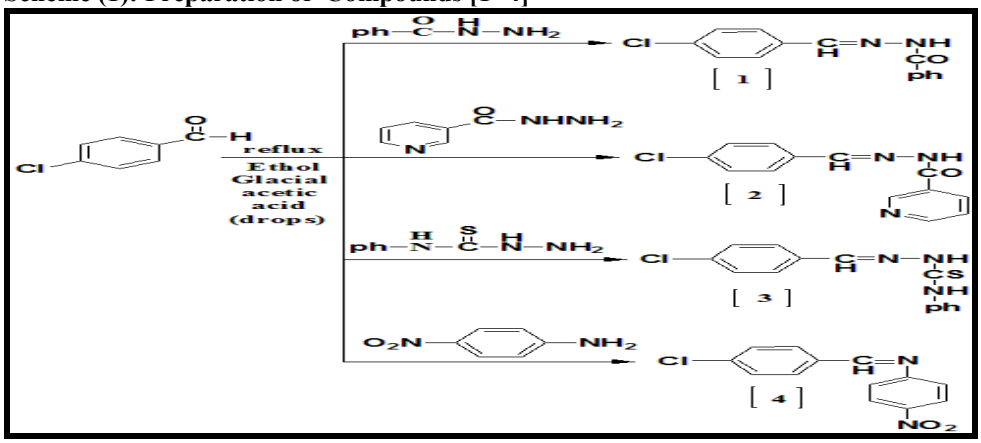
2.4.Synthesis of Compounds {11 -14} :

According to procedures[17], 2-Amino imidazole dissolved in 3 ml hydrochloric acid with sodium nitrite solution in (0- 5)C , then added compound [1, 2, 3, 4] to the mixture , after 48 hrs filtered , dried and re crystallized from ethanol to give compounds [11 , 12, 13, 14]respectively.

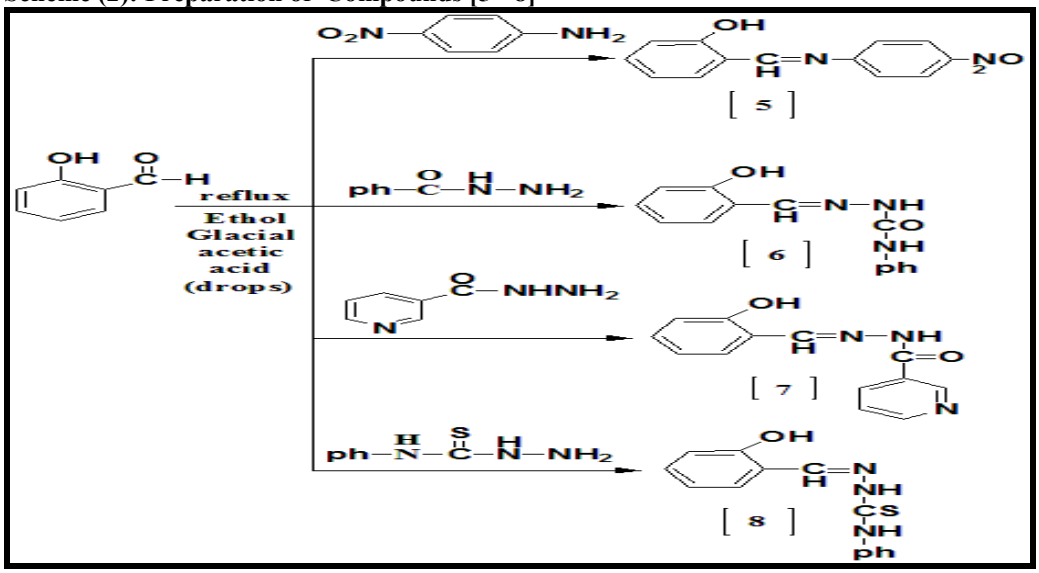
2.5.Synthesis of compounds {15- 20} :

According to procedures[4-8 ,17], 2-Amino thiazole dissolved in 3 ml hydrochloric acid with sodium nitrite solution in (0- 5)C ,then added compound [5, 6, 7, 8, 9, 10] respectively to the mixture , after 48 hrs filtered , dried and re crystallized from ethanol to give compounds [15 , 16, 17, 18 ,19, 20] respectively.

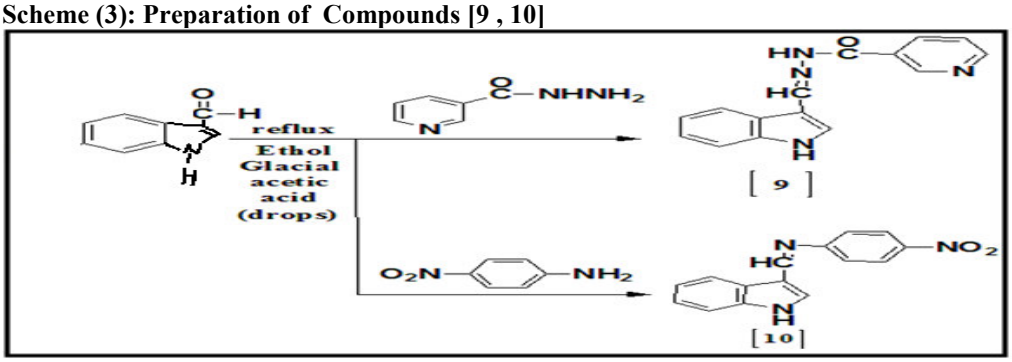
Scheme (1): Preparation of Compounds [1- 4]



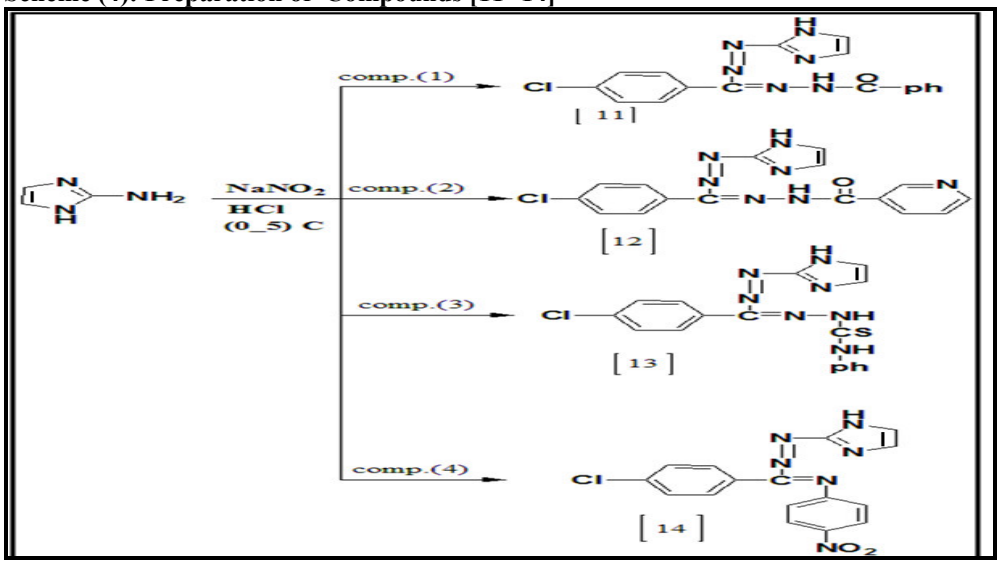
Scheme (2): Preparation of Compounds [5 - 8]



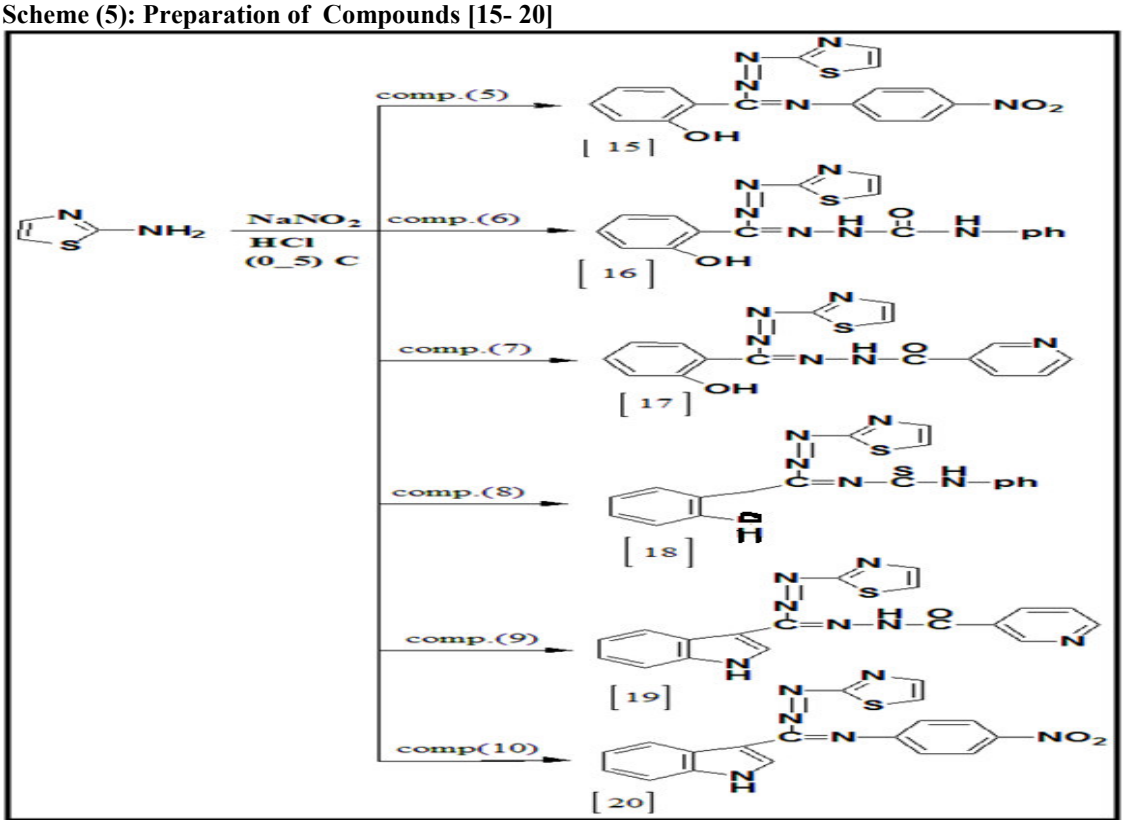
Scheme (3): Preparation of Compounds [9 , 10]



Scheme (4): Preparation of Compounds [11- 14]



Scheme (5): Preparation of Compounds [15- 20]

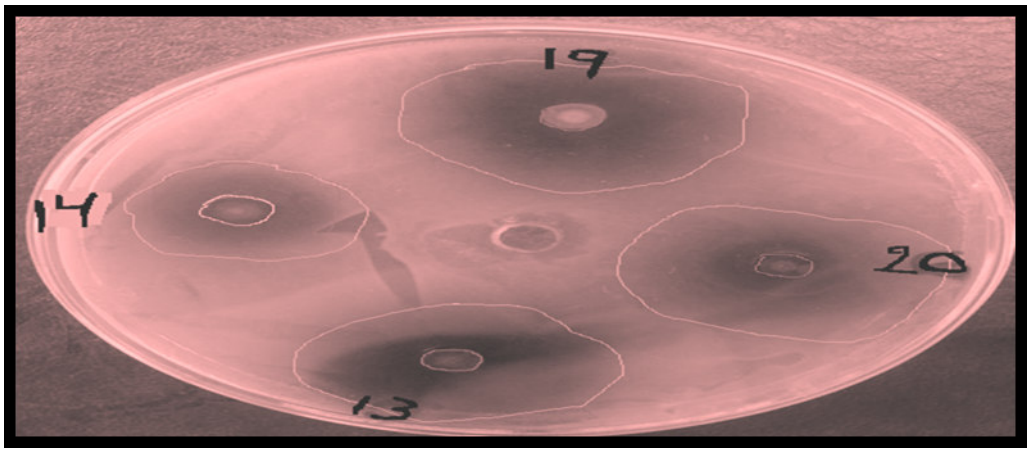


3. Biological Activity of Compounds :

According to procedures[17,18],Some of the prepared compounds are tested for the biological activities , The antibacterial activity(0.2ml) of the synthesized compounds were tested against both Gram-negative and Gram-positive bacteria using their($1X10^{-3}$) concentration in DMSO as a solvent. The inhibition zone against the growth of the verified bacteria for the compounds is given in table (1)

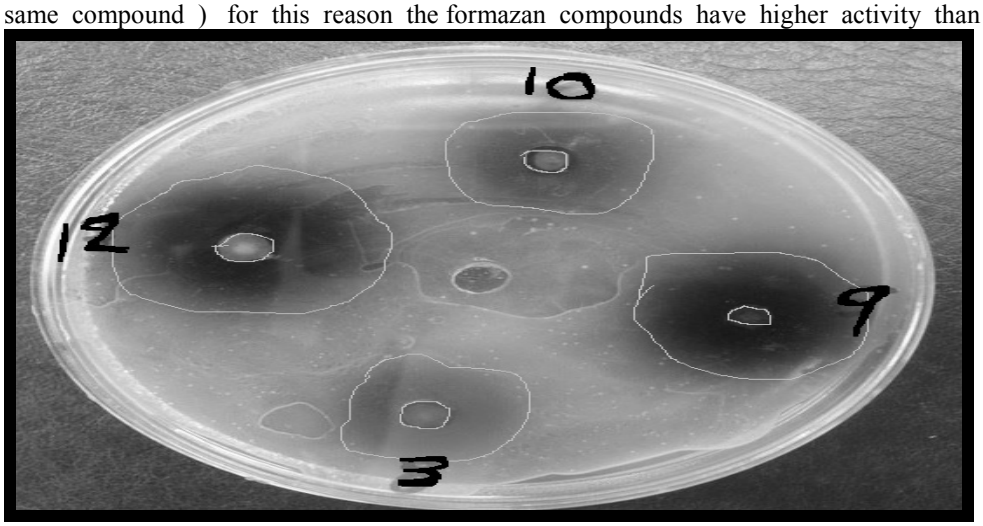
Table (1): Effect of compounds on inhibition Zone of Bacteria in (mm.).

Comp. No.	G+ : Staphylococcus. Aureus	*G-: E- Coli*	*Salmonella .typhi*
{1}	12	10	8
{2}	14	10	10
{3}	16	12	12
{4}	12	12	12
{9}	18	14	14
{10}	16	14	16
{11}	26	26	24
{12}	28	20	20
{13}	28	22	24
{14}	24	20	22
{19}	34	24	20
{20}	30	20	20



Picture (1) – Inhibition of other compound on Staphylococcus. Aureus

From this results , the formazane compounds are more reactive as antibacterial than imine compounds (Schiff base)) because their structures which included (azo groups with imine groups in same compound) for this reason the formazan compounds have higher activity than Schiff bases



Picture(1) : Inhibition of compound on Staphylococcus. Aureus

4.Results and Discussion:

All synthesized compounds were characterized by [FT.IR-spectra, (C.H.N)-analysis, melting points, H.NMR-spectra and some of them by ^{13}C.NMR-spectra].

4.1.FT.IR-spectra :showed appearance absorption bands at (1610-1635)cm^{-1} due to Schiff base (CH=N) in compounds [1- 10], which shifted to (1625- 1650) cm^{-1} due to to(C=N) and (1440- 1520) cm^{-1}to(-N=N -) group in compound [11-20] in formazan compounds, figures (1-20)

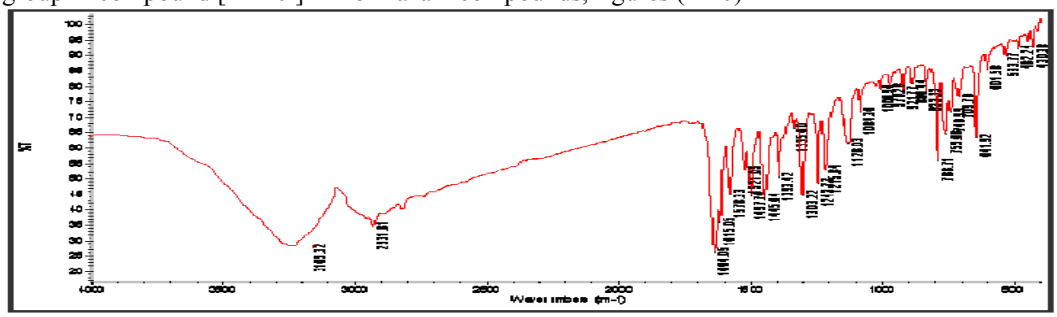


Fig.(1) FTIR Spectrum of the compound {1}

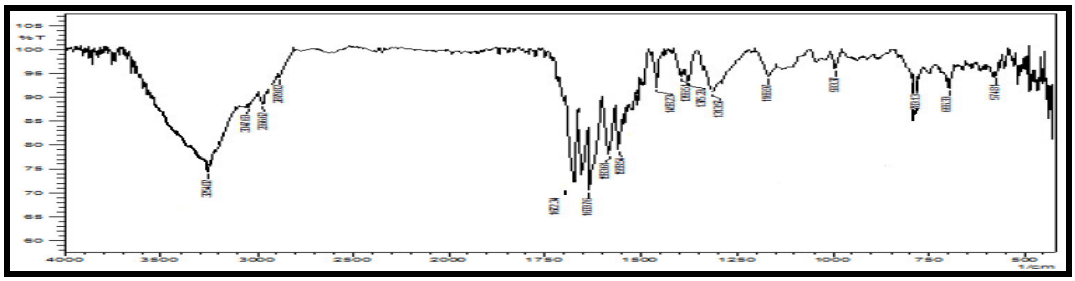


Fig.(2) FTIR Spectrum of the compound {2}

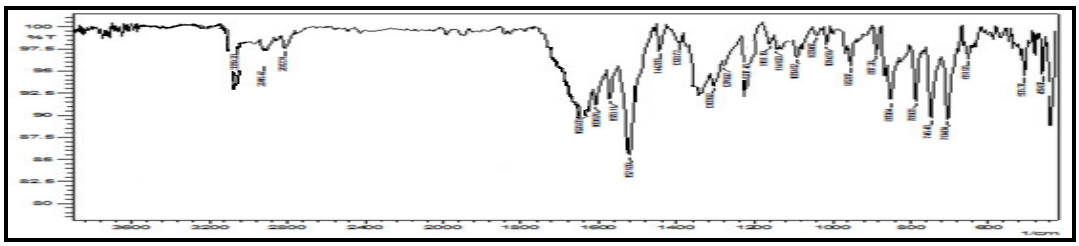


Fig.(3) FTIR Spectrum of the compound {3}

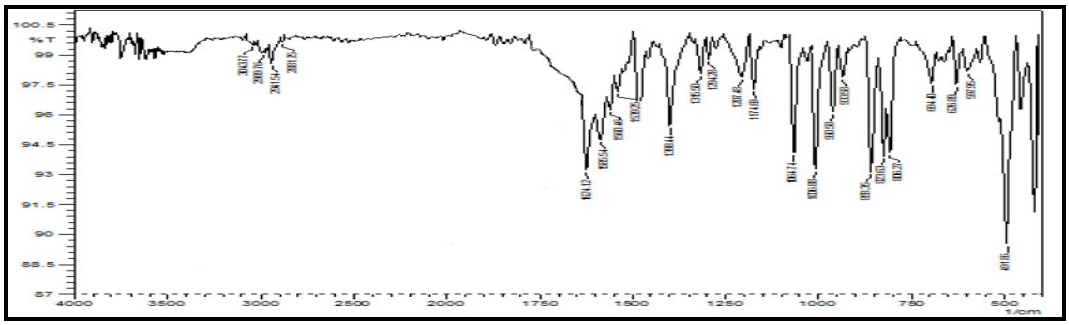


Fig.(4) FTIR Spectrum of the compound {4}

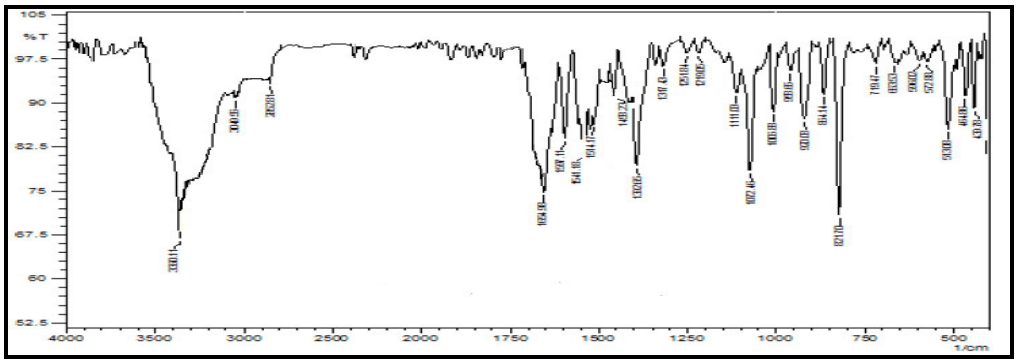


Fig.(5) FTIR Spectrum of the compound {5}

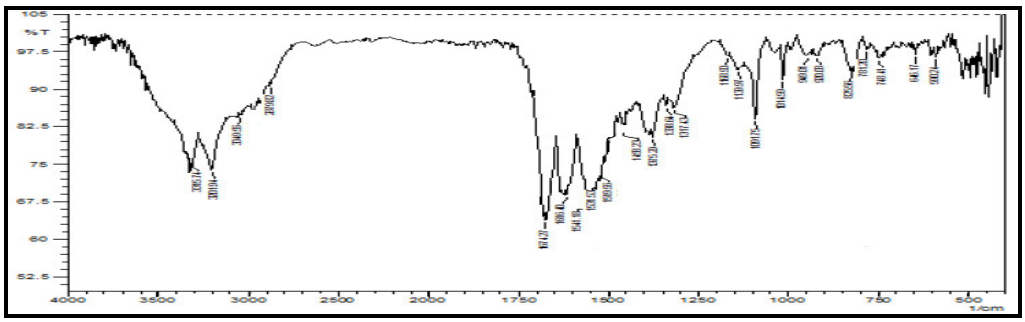


Fig.(6) FTIR Spectrum of the compound {6}

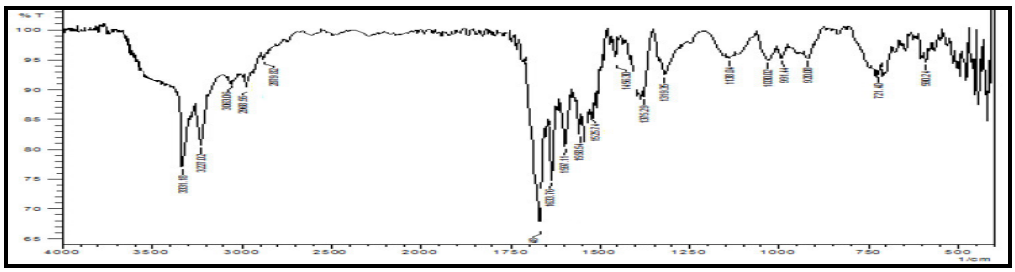


Fig.(7) FTIR Spectrum of the compound {7}

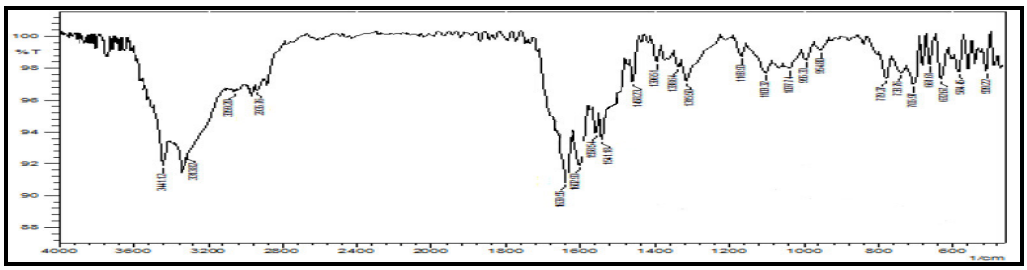


Fig.(8) FTIR Spectrum of the compound {8}

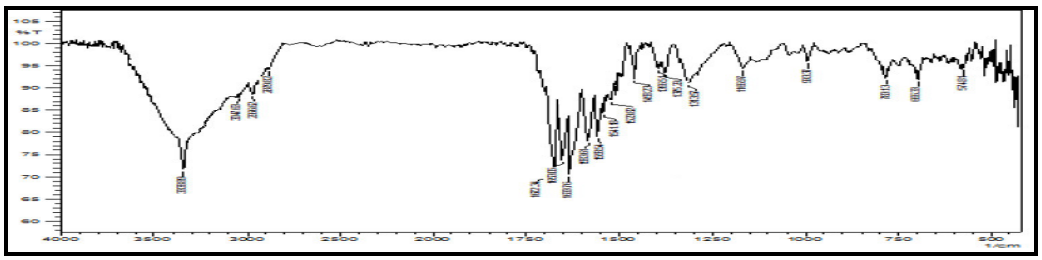


Fig.(9) FTIR Spectrum of the compound {9}

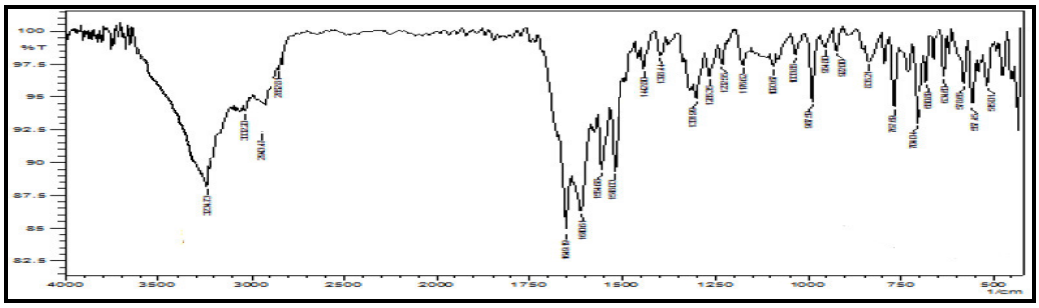


Fig.(10) FTIR Spectrum of the compound {10}

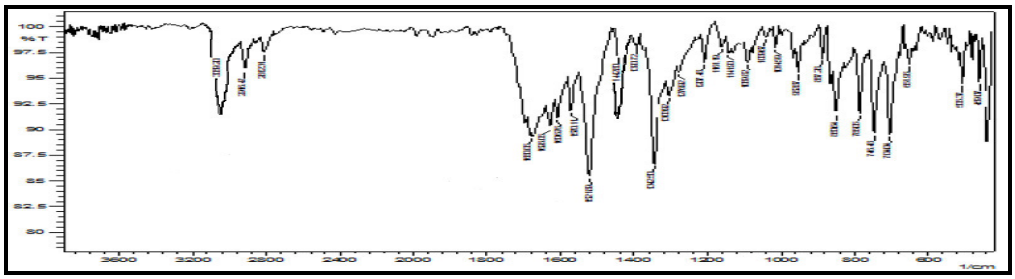


Fig.(11) FTIR Spectrum of the compound {11}

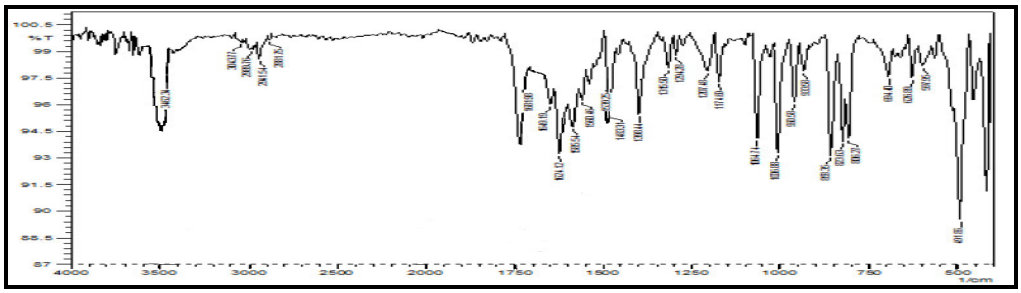


Fig.(12) FTIR Spectrum of the compound {12}

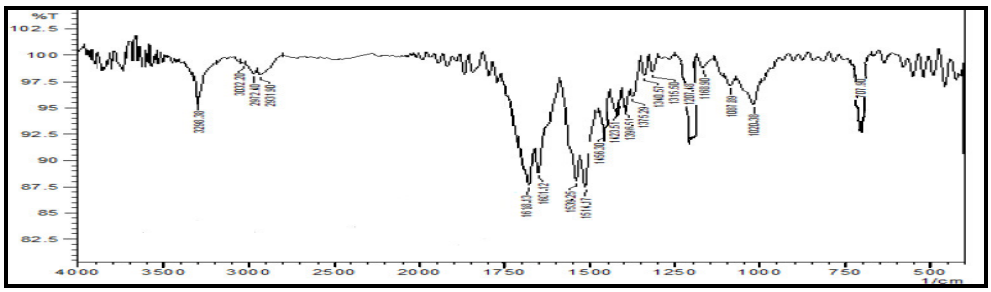


Fig.(13) FTIR Spectrum of the compound {13}

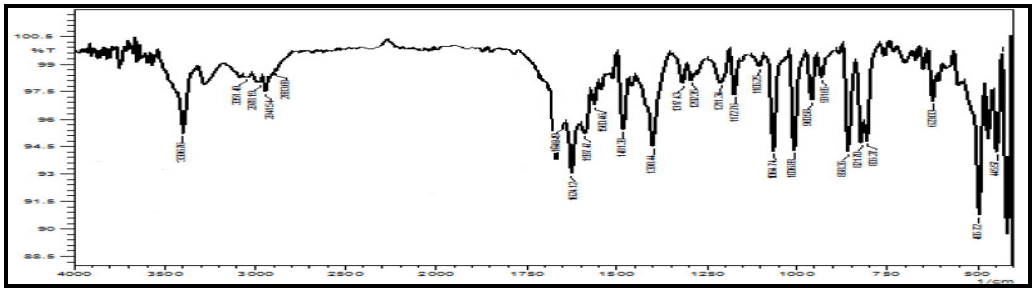


Fig.(14) FTIR Spectrum of the compound{14}

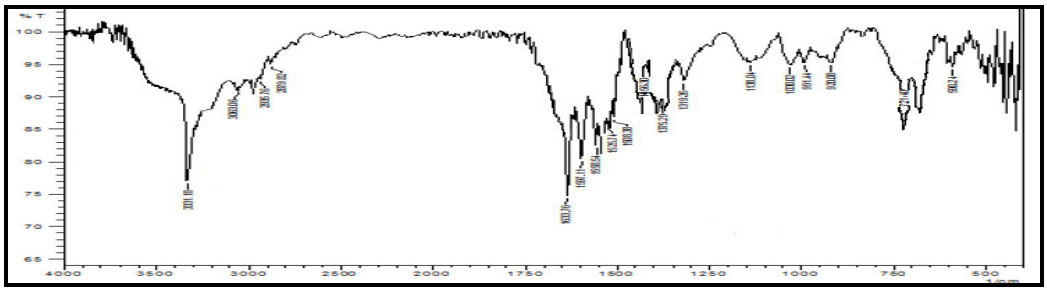


Fig.(15) FTIR Spectrum of the compound {15}

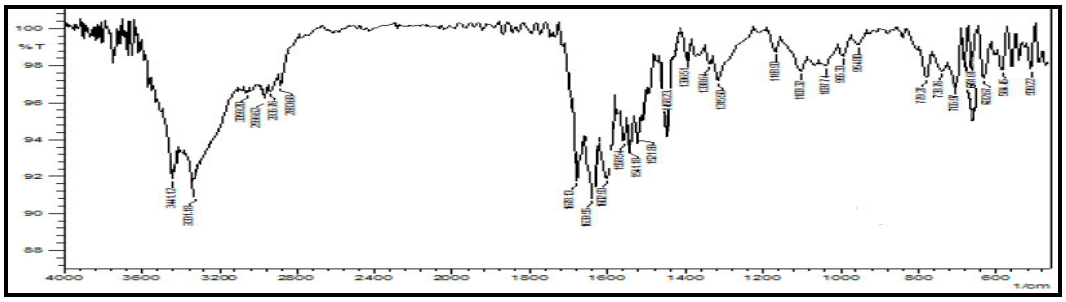


Fig.(16) FTIR Spectrum of the compound {16}

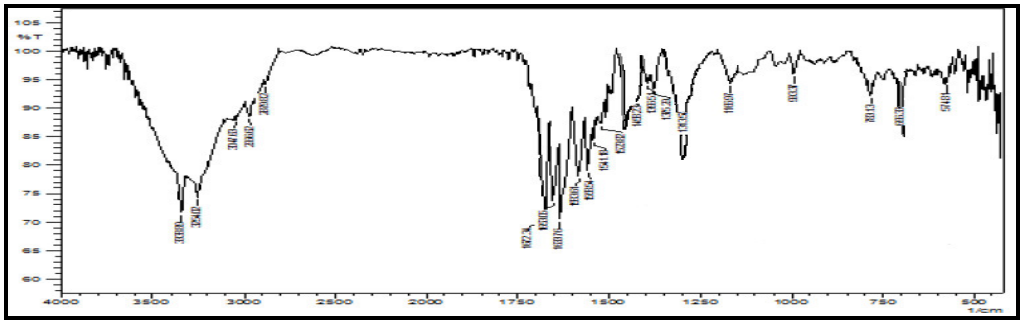


Fig.(17) FTIR Spectrum of the compound {17}

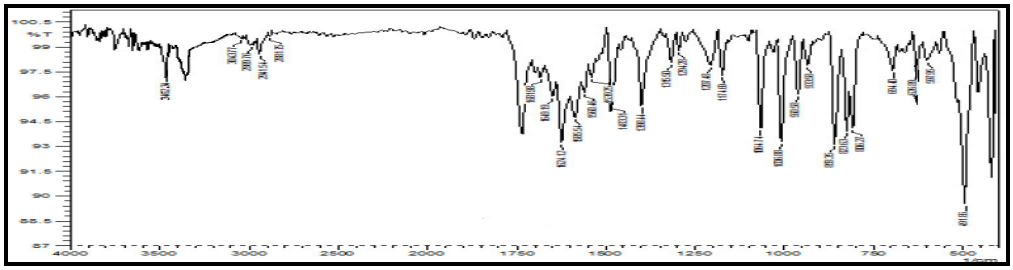


Fig.(18) FTIR Spectrum of the compound {18}

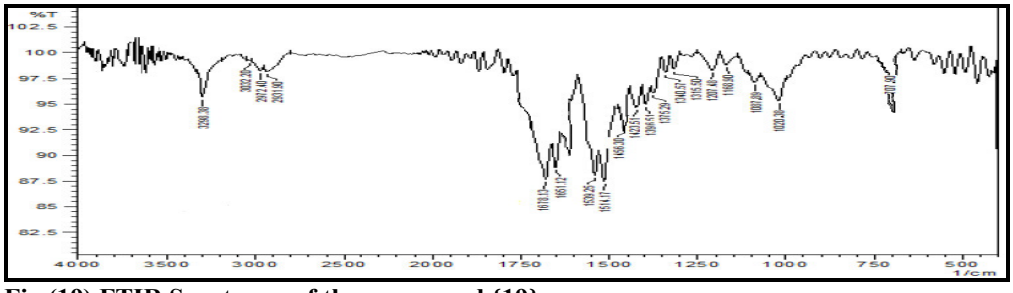


Fig.(19) FTIR Spectrum of the compound {19}

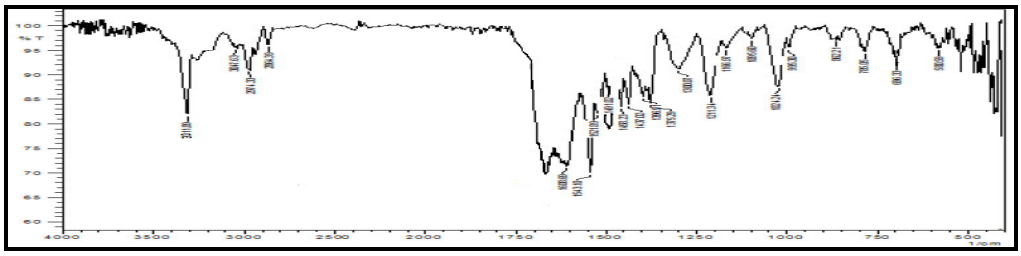


Fig.(20) FTIR Spectrum of the compound {20}

4.2. (C.H.N)- Analysis: (C.H.N)- Analysis, some physical properties in table (2, 3)**,**

Table (2): (C.H.N)-analysis of compounds [1-20].

Compounds	C%	H%	N%	S%
	found(Average)	found(Average)	found(Average)	found(Average)
[1]	64.213	4.021	10.364	/
[2]	59.641	3.277	16.001	/
[3]	57.618	3.898	14.082	10.621
[4]	59.217	3.119	10.342	/
[5]	64.103	3.916	11.142	/
[6]	65.336	4.724	16.138	/
[7]	64.221	4.197	17.231	/
[8]	61.124	4.188	15.154	11.258
[9]	67.708	4.078	21.053	/
[10]	67.301	4.014	15.179	/
[11]	57.006	3.113	23.148	/
[12]	53.811	3.058	27.174	/
[13]	52.641	3.137	25.071	8.001
[14]	53.721	2.801	23.318	/
[15]	54.066	2.942	19.317	8.638
[16]	60.686	3.887	25.011	/
[17]	54.108	3.164	23.199	8.711
[18]	58.006	3.202	21.118	16.069
[19]	57.122	3.182	25.817	8.070
[20]	56.931	2.899	22.024	8.119

From the data of results , we observed that the found data are compactable with calculated data which indicate of formation these compounds

Table (3): Physical properties of compounds [1-20].

Compounds	F.M	M.P C°	Product %	R_f
[1]	$C_{14}H_{11}N_2OCl$	170	82	0.86
[2]	$C_{13}H_{10}N_3OCl$	162	78	076
[3]	$C_{14}H_{12}N_3OsCl$	182	80	0.72
[4]	$C_{13}H_9N_2O_2Cl$	148	76	0.78
[5]	$C_{13}H_{10}N_2O_3$	154	80	0.66
[6]	$C_{14}H_{13}N_3O_2$	178	82	0.80
[7]	$C_{13}H_{11}N_3O_2$	166	77	0.82
[8]	$C_{14}H_{13}N_3OS$	190	80	0.70
[9]	$C_{15}H_{12}N_4O$	198	78	0.74
[10]	$C_{15}H_{11}N_3O_2$	184	82	0.69
[11]	$C_{17}H_{13}N_6OCl$	218	84	0.63
[12]	$C_{16}H_{12}N_7OCl$	204	86	0.70
[13]	$C_{17}H_{14}N_7SCl$	226	82	0.83
[14]	$C_{16}H_{11}N_6O_2Cl$	208	80	0.68
[15]	$C_{16}H_{11}N_5O_3S$	232	84	0.72
[16]	$C_{17}H_{14}N_6O_2S$	238	78	0.80
[17]	$C_{16}H_{12}N_6O_2S$	236	80	0.66
[18]	$C_{19}H_{14}N_6S_2$	248	80	0.84
[19]	$C_{18}H_{13}N_7OS$	242	78	0.70
[20]	$C_{18}H_{12}N_6O_2S$	244	74	0.66

4.3.The ^{1}H.NMR spectra : showed signals at δ(8. 20 – 8. 80) for protons of imine group (CH= N)Schiff bases in compounds [1 - 10]., which disappeared in compounds [11- 20] to formation of formazane[4-8] compounds , and other signals in figures (21-31), this result indicates to formation all compounds in this paper .

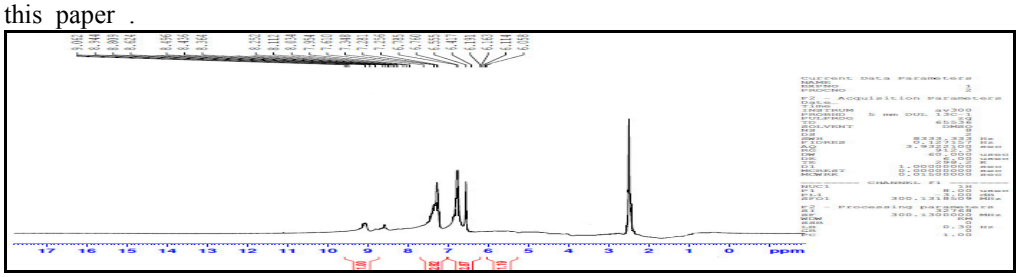


Fig (21): 1H.NMR of Compound [1]

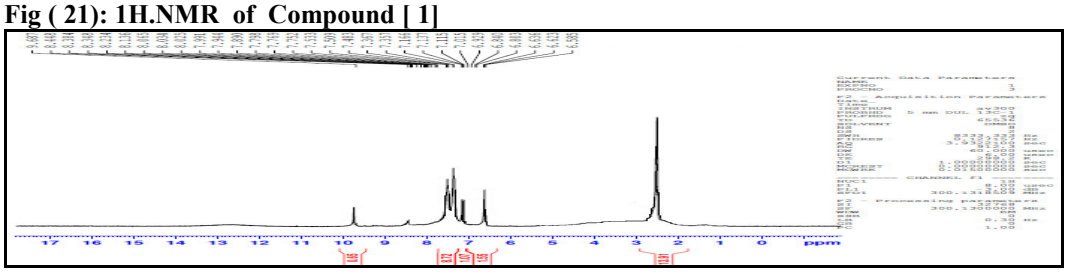


Fig (22): 1H.NMR of Compound [2]

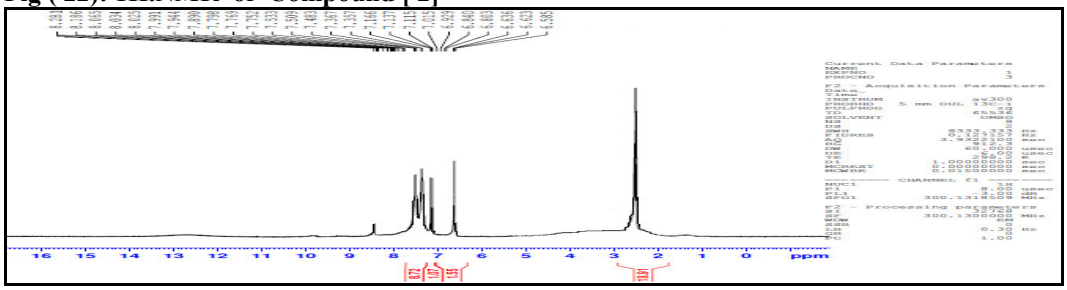


Fig (23): 1H.NMR of Compound [3]

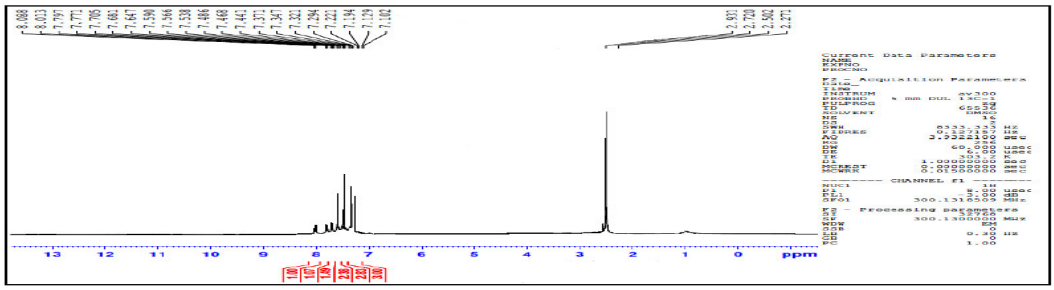


Fig (24): 1H.NMR of Compound [4]

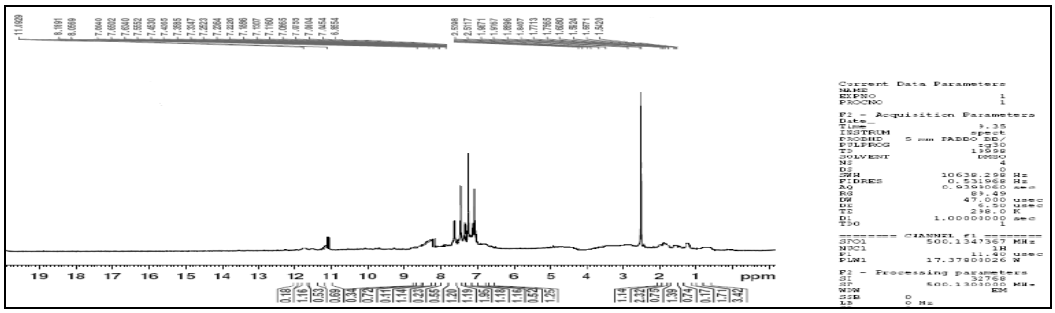


Fig (25): 1H.NMR of Compound [5]

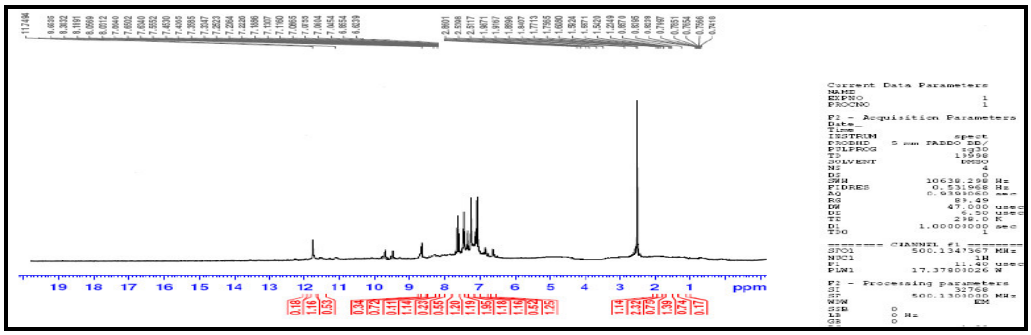


Fig (26): 1H.NMR of Compound [6]

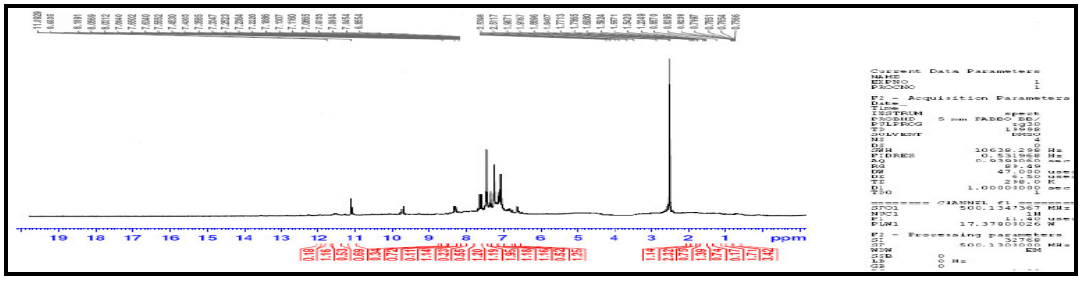


Fig (27): 1H.NMR of Compound [7]

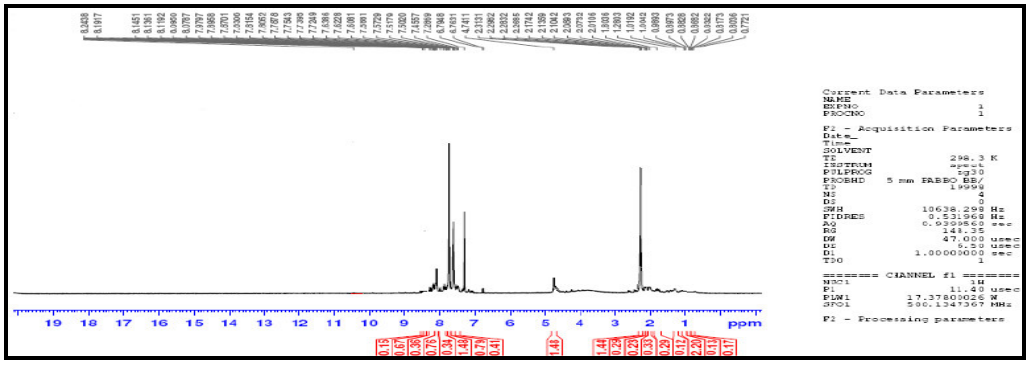


Fig (28): 1H.NMR of Compound [10]

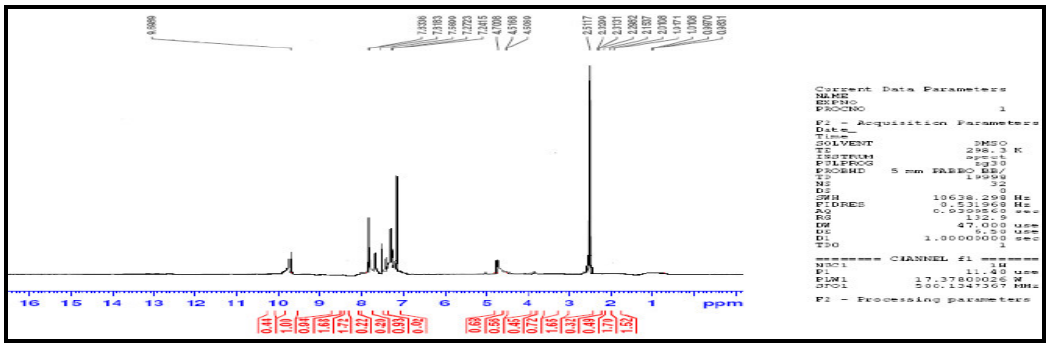


Fig (29): 1H.NMR of Compound [11]

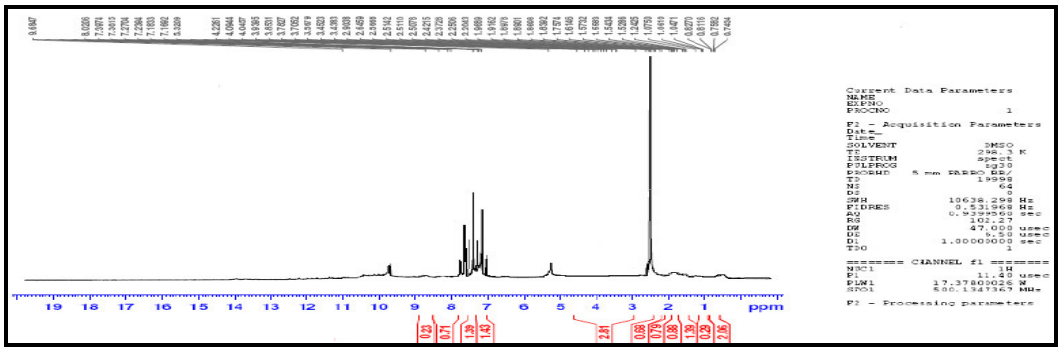


Fig (30): 1H.NMR of Compound [12]

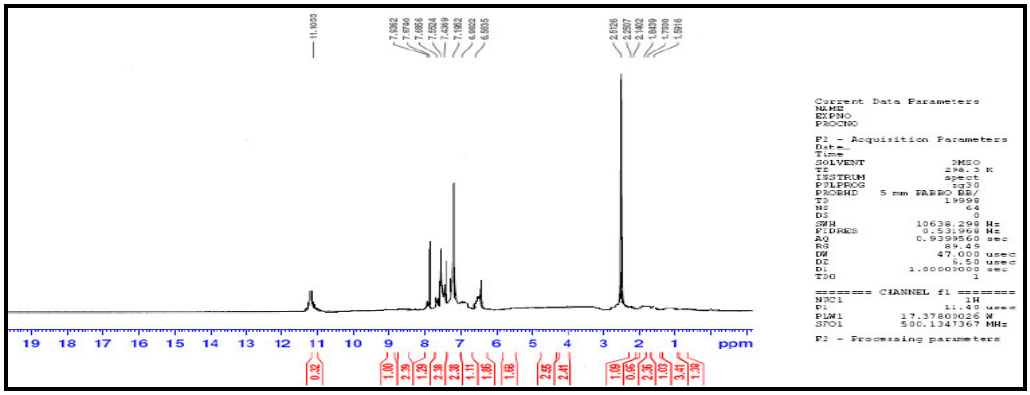


Fig (31): 1H.NMR of Compound [15]

4.4.The ^{13}C.NMR - spectra : values of some compounds showed signals indicated to functional groups (Nagham 2016 , Shalwani 2005) in these compounds , all compounds .we noted data of carbon spectra and showed good indicators for production of ,figures (32- 40) :

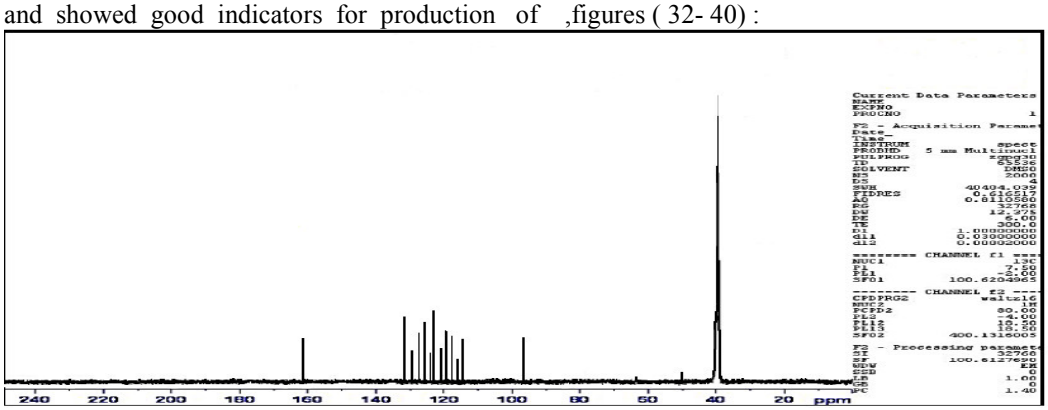


Fig (32): 13C.NMR of Compound [1]

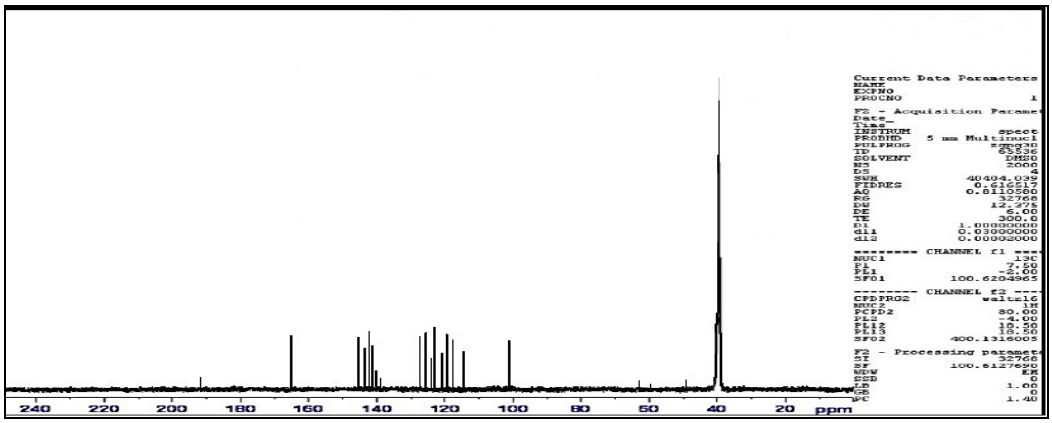


Fig (33): 13C.NMR of Compound [2]

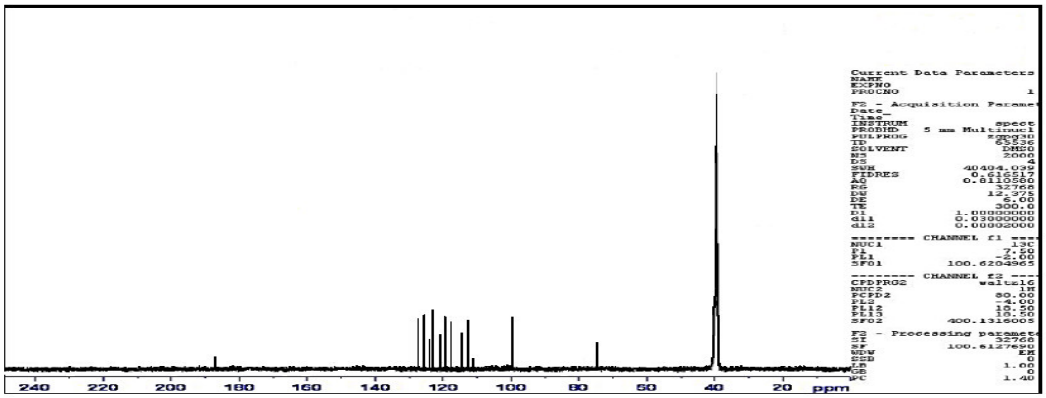


Fig (34): 13C.NMR of Compound [3]

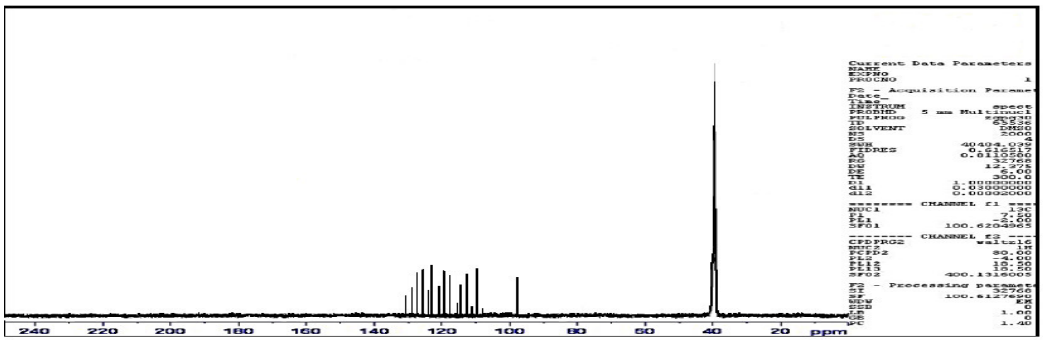


Fig (35): 13C.NMR of Compound [4]

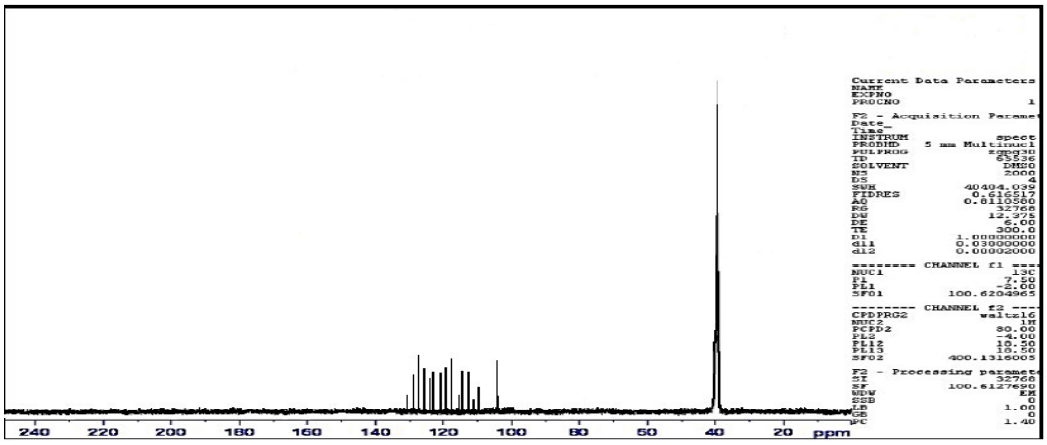


Fig (36): 13C.NMR of Compound [5]

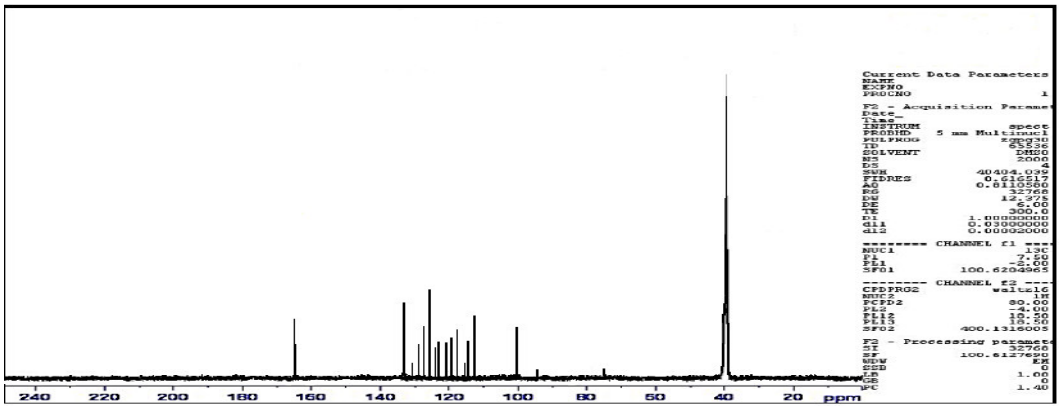


Fig (37): 13C.NMR of Compound [6]

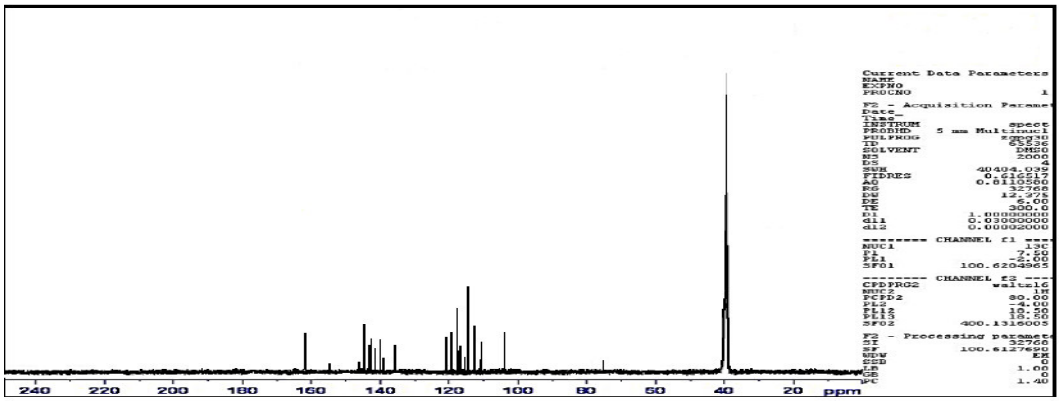


Fig (38): 13C.NMR of Compound [7]

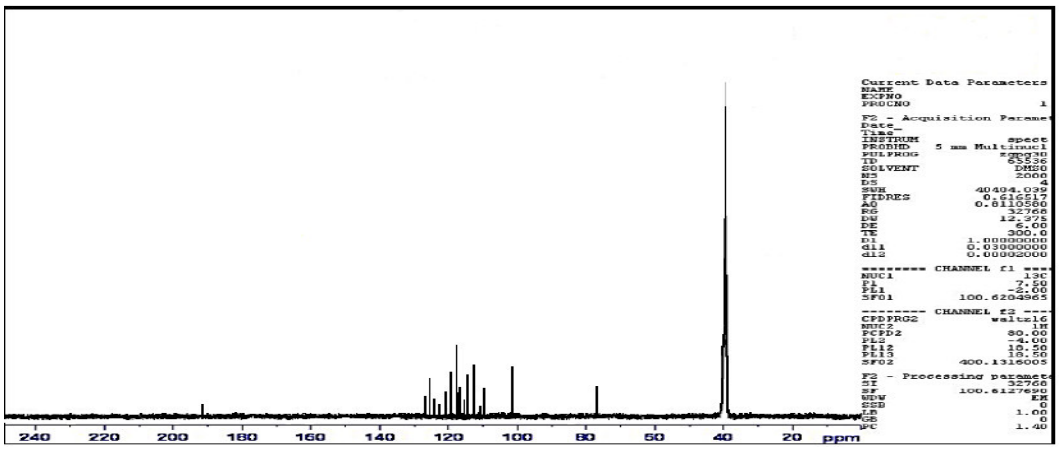


Fig (39): 13C.NMR of Compound [8]

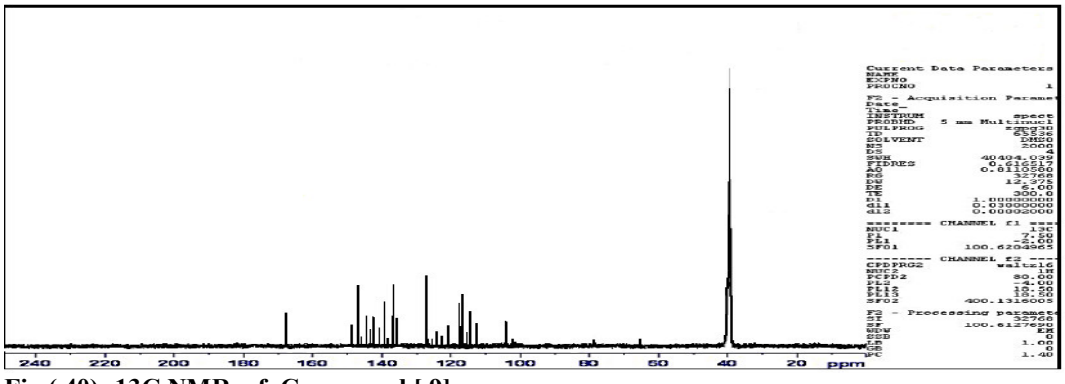


Fig (40): 13C.NMR of Compound [9]

5. Conclusion

All results in this work indicate to formatted compounds from imine compounds and formazan compounds as a ligands , and indicate that these compound have antimicrobial activity against bacterial .

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