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New Formazan Compounds (Synthesis, Identification, Physical Properties)

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ABSTRACT

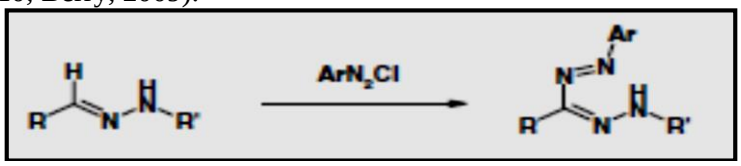
New various formazane compounds synthesized in this work which acts important pharmaceutical compounds in most fields like antifungal, antimalaria, antioxidant, antimicrobial against types of bacteria. Various formazan compounds were synthesized via azotation reaction after condensation reaction with carbanion of imine group to produce target compounds (carban-imine-azo).

All reactions are followed by TLC chromatographic papers and all the synthesized compounds have been identified by using various chemical techniques, like (^{1}H.NMR-spectra, ^{13}C.NMR-spectra, (C, H, N)-analysis, FTIR-spectra), melting points and physical properties.

KEY WORDS: formazan, Cabranion, Oxadiazol, Imidiazol, Azo, Imine, Schiff base.

1. INTRODUCTON

Formazan compounds are an important and class of organic compounds. Their chemistry applications have attracted the interest of several research groups due to their wide pharmaceutical, medical, industrial and chemical applications in various fields as well as their utility in analytical chemistry and synthesis of heterocyclic compounds (Marjadi, 2009; Tezcan, 2010; Kalidhar, 2011). At present, there are several survey articles and scientific books devoted to the synthesis, chemical with physical properties and chemical reactions of formazan (Shawali, 2015; Senoz, 2012; Buzykin, 2010; Berry, 2009).



Formazans compounds have important pharmaceutical and biological applications; the tetrazolium salts are classified as promoter of vitality formazans are known for their uses of medical activities like (antiviral, anticancer, antimicrobial (Nagham, 2014; 2017; 2015), anti-inflammatory, antifungal, anti-HIV, etc. Several formazans show promising anti-fertility and anti-malaria activity. Formazans and their complexes are colored compounds (Nagham, 2014; Sherif, 2015; Shawali, 2009; Nagham, 2016) due to ($\pi - \pi$ *) transitions of (π –electrons) in the formazan structures of (-N=N-C=N-NH-). Which has caused intensive interest among scientists. Since the preparation of the first formazans by Pechman, noted that Formazans are colored compounds because of the (p–p*) and (n–p*) electronic transitions of the (azo-imine) chromophore (Nagham, 2016; Senoz, 2012). Oxidation of formazan compounds results in their conversion into colorless tetrazolium salts. Formazans are used for testing of anticancer drugs, investigation of tumor cell activity and sperm viability and in other applications (Kalsi, 1988; Sigeikin, 2006; Edwards, 2004). Which are also applied in Brucella-ring test in milk and to investigate dehydrogenase (Gilroy, 2007; Kalsi, 1990; Nagham, 2017) activity inhibition of a soil bacterium caused by soil contaminated with lead, copper ion and in coordination with ions in complexes.

2. EXPERIMENTAL AND APPARATUS

All chemicals used (purity 99.98%) and investigation of the compounds was carried out by melting point, FT-IR, 1H-NMR, 13C NMR, and (CHNS) - analysis. Melting points were determined by open capillary method and are uncorrected. TLC spots were tested via using iodine vapors. IR spectra were recorded on 4100 FT-IR spectrometer using KBr disc technique. 1H NMR and 13C NMR were recorded on a Brucker 500 MHz spectrometer using tetramethylsilane as standard. Chemical shifts were recorded in parts per million (ppm).

Synthesis of Compounds (1-4): The compounds were synthesized according to studying (Nagham, 2017), a mixture from benzil (0.001 mol) and phenyldiamine (0.001 mol) in the presence of sulfuric acid (6ml) and absolute ethanol then refluxing the mixture for (5h) the precipitate was filtered and dried with re-crystallized to yield 76% of compound (1), which (0.001 mol) of compound (1) react with (0.001 mol) ethyl-2-chloroacetate in the presence of absolute ethanol and potassium carbonate and then refluxing the mixture for (5h) the precipitate was filtered and dried with re-crystallized to yield 72% of compound (2), A mixture (0.001 mol) of compound (2) with (0.001mol) of semicarbazide in the presence of absolute ethanol and refluxed (16hrs), the precipitate was filtered and dried with re-crystallized to yield 74% of compound (3), which (0.001 mol) reacts with (0.001mol) of chlorobenzaldehyde the presence of absolute ethanol with drops of glacial acetic acid and reflux for (4h), the precipitate was filtered and dried with re-crystallized to yield 76% of compound (4).

Synthesis of Compound (5): According to procedures (Nagham,2017, 2016,2015), 4-methyl aniline dissolved in 3 ml hydrochloric acid with sodium nitrite solution in (0- 5)C, then added compound (4) to the mixture, after 48 hrs filtered and dried with re-crystallized to yield 86% of compound (5), which acts formazane compound.

Synthesis of Compounds (6-9): 1,3-diphenyl propandione (0.001mol) and thiosemicarbazide (0.001 mol) were refluxed in ethanol with (6ml) sulfuric acid for (16hrs) to give compound (6), which (0.001 mol) reacts with (0.001 mol) ethyl-2-chloroacetate in the presence of absolute ethanol and reflux for (5h), the precipitate was filtered and dried with re-crystallized to yield 70% of compound (7), A mixture (0.001 mol) of compound (7) with (0.001mol) of phenyldiamine in the presence of absolute ethanol and refluxed (7hrs), the precipitate was filtered and dried with re-crystallized to yield 72% of compound (8). A mixture (0.001mol) of compound (7) with (0.001mol) of 4-methyl benzaldehyde in the presence of absolute ethanol and reflux for (16hrs) the precipitate was filtered and dried with re-crystallized to yield 70% of compound (9).

Synthesis of Compound (10): According to procedures (Nagham, 2014; 2017; 2015), 4-methyl aniline dissolved in 3 ml hydrochloric acid with sodium nitrite solution in (0- 5)C, then added compound (9) to the mixture, after 48 hrs filtered and dried which with re-crystallized presence of absolute ethanol to yield in the 82% of compound (10), which acts formazane compound.

Synthesis of Compound (11): A mixture (0.001 mol) of compound (6) with 4-methyl benzaldehyde (0.001 mol) in the presence of drops (glacial acetic) with absolute ethanol and reflux for (16h), the precipitate was filtered and dried which with re-crystallized presence of absolute ethanol to yield in the 72% of compound (11).

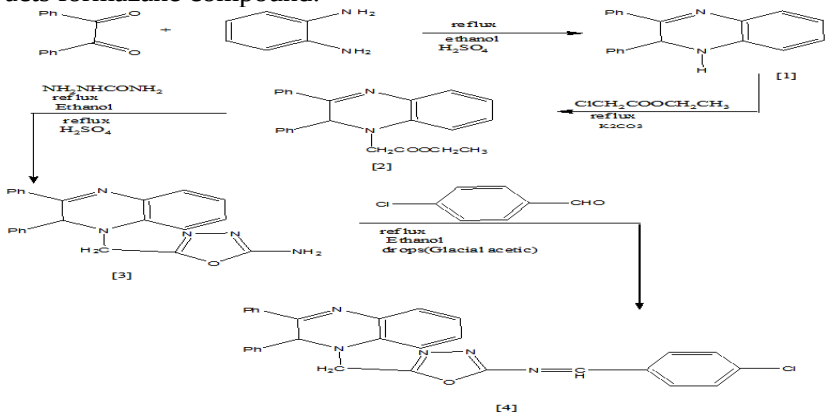
Synthesis of Compound (12): According to procedures (Nagham, 2014; 2017; 2015), 4-methyl aniline dissolved in 3 ml hydrochloric acid with sodium nitrite solution in (0- 5)C, then added compound (11) to the mixture, after 48 hrs filtered and dried which with re-crystallized presence of absolute ethanol to yield in the 84% of compound (12) which acts formazane compound.

Synthesis of Compounds (13-14): A mixture of diethyl oxalate (0.01 mol) and thiosemicarbazide (0.002 mol) in the presence of sulfuric acid (8ml) absolute ethanol and reflux for (16h), the precipitate was filtered and dried with re-crystallized to yield in the 70% of compound (13), which (0.001 mol) of compound (13) with (0.002mol) 4-hydroxbenzaldehyde react with (drops) glacial acetic in the presence of absolute ethanol and reflux for (8h) the precipitate was filtered and dried with re-crystallized to yield 72% of compound (14).

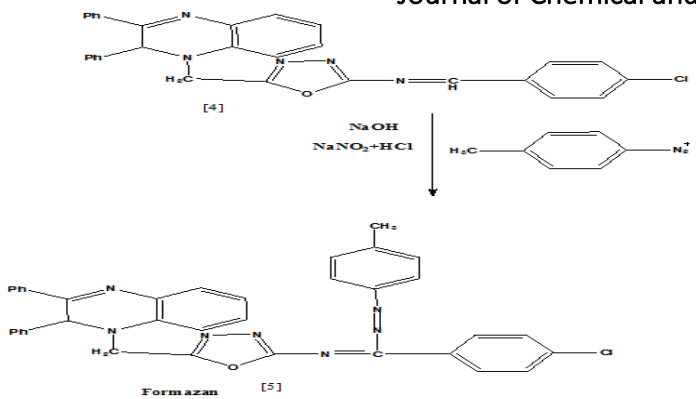
Synthesis of Compound (15): According to procedures (Nagham, 2014; 2017; 2015), 4-methyl aniline dissolved in 3 ml hydrochloric acid with sodium nitrite solution in (0- 5)C, then added compound (14) to the mixture, after 48 hrs filtered and dried which with re-crystallized presence of absolute ethanol to yield in the 86% of compound (15) which acts formazane compound.

Synthesis of Compounds (16-19): Treatment of terephthalic acid (0.001 mol) and phenyldiamine (0.001 mol) in the presence of hydrochloric acid with (6ml) in presence of absolute ethanol and then refluxing the mixture for (7h) the precipitate was filtered and dried with re-crystallized to yield 72% of compound (16), which (0.001 mol) reacted with ethanol and with 6 ml sulphuric acid for esterification, then refluxing the mixture for (6h) the precipitate was filtered and dried with re-crystallized to yield 72% of compound (17), A mixture (0.001 mol) of compound (17) with (0.001mol) of phenyldiamine in the presence of absolute ethanol and refluxed (16hrs), the precipitate was filtered and dried with re-crystallized to yield 80% of compound (18), which (0.001 mol) of compound (18) reacts with (0.001mol) of 4-methylbenzaldehyde the presence of absolute ethanol and glacial acetic (drops) and reflux for (5h), the precipitate was filtered and dried with re-crystallized to yield 72% of compound (19).

Synthesis of Compounds (20): According to procedures (Nagham and Nemah, 2016; Nagham, 2016), 4-methyl aniline dissolved in 3 ml hydrochloric acid with sodium nitrite solution in (0- 5)C, then added compound (19) to the mixture, after 48 hrs filtered and dried with re-crystallized presence of absolute ethanol to yield in the 84% of compound (20) which acts formazane compound.



Scheme.1. Preparation of Compounds (1-4)



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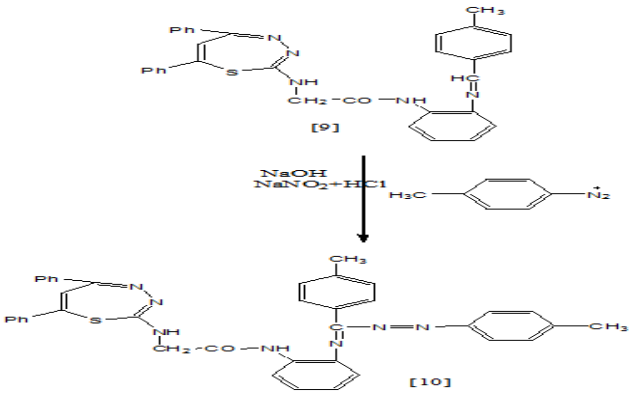
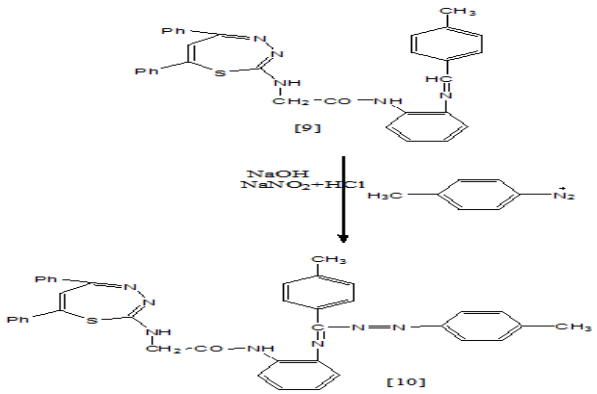
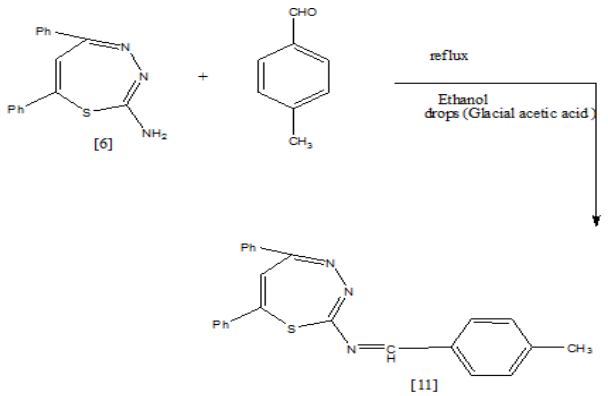


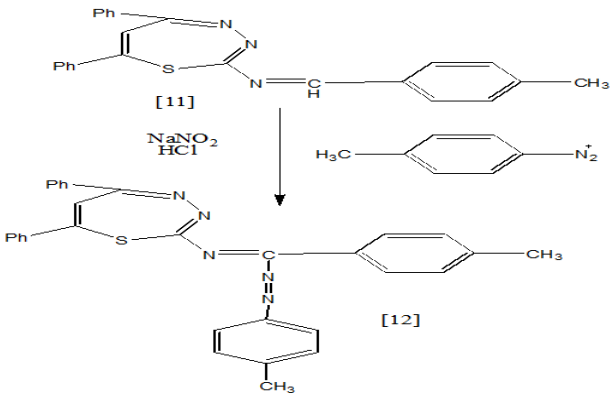
Scheme.3. Preparation of Compounds (6-9)



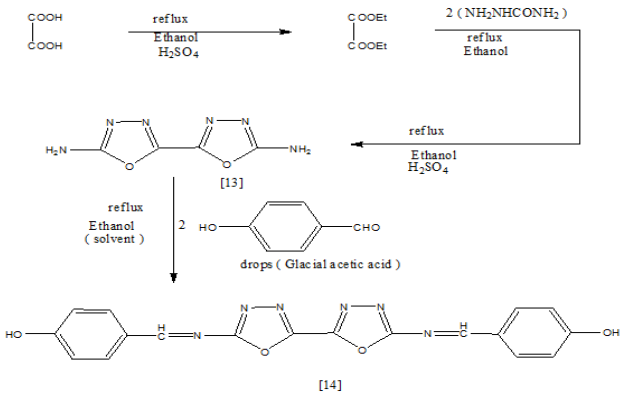
Scheme.4. Preparation of Compound (10)



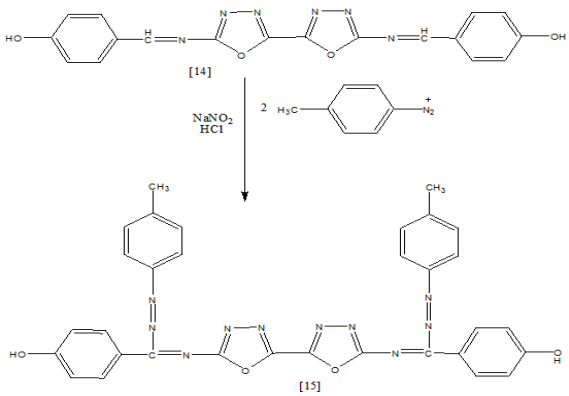
Scheme.5. Preparation of Compound (11)



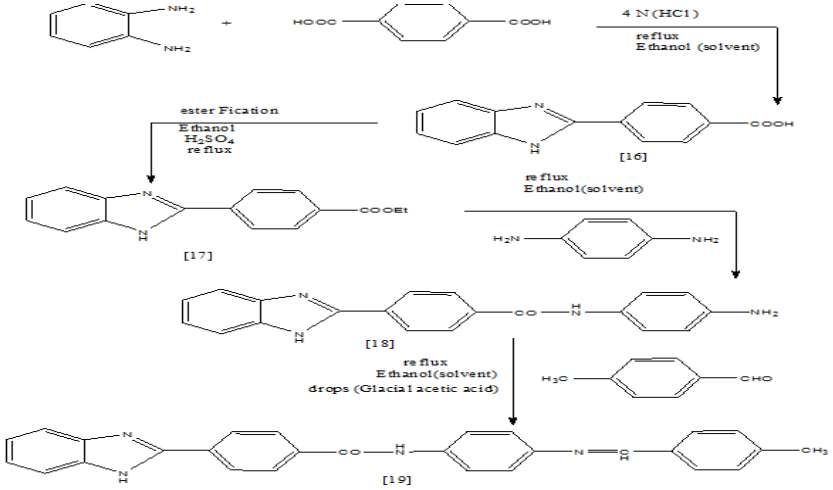
Scheme.6. Preparation of Compound (12)



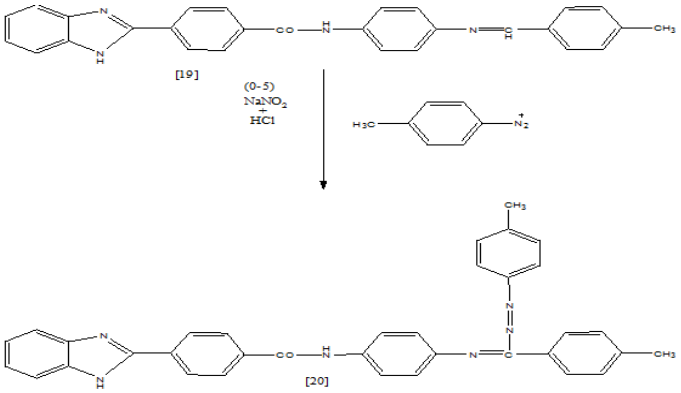
Scheme.7. Preparation of Compounds (13, 14)



Scheme.8. Preparation of Compound (15)



Scheme.9. Preparation of Compounds (16-19)



Scheme.10. Preparation of Compound (20)

3. RESULTS AND DISCUSION

Newly synthesized compounds (1-20) were investigated via many techniques (FTIR-spectra, (C, H, N)-analysis, melting points, H.NMR-spectra and some of them by ^{13}C NMR-spectra.

FTIR-spectra: Their spectra showed absorption bands at (1654) cm^{-1} due to (C=N) endo cycle, absorption band at (3350) cm^{-1} due to (NH), absorption band at (3040) cm^{-1} due to (C-H) aromatic in compound (1). Absorption band at (1647) cm^{-1} due to (C=N) endo cycle, absorption band at (1716) cm^{-1} due to (-COO) carbonyl of ester, absorption band at (2935) cm^{-1} due to (CH) aliphatic absorption band at (3055) cm^{-1} due to (CH) aromatic compound (2). Showed absorption bands at (1627-1604) cm^{-1} due to (C=N) endo cycle, absorption band at (3321,3207) cm^{-1} due to (NH), absorption band at (2900) cm^{-1} due to (CH) aliphatic, absorption band at (3039)$^{cm-1}$ due to (C-H) aromatic, absorption band at (1174) cm^{-1} due to (C-O-C), cycle in compound (3). Absorption band at (1666) cm^{-1} due to (C=N) endo cycle, absorption band at (3050) cm^{-1} due to (C-H) aromatic, absorption band at (2972) $^{cm-1}$ due to (C-H) aliphatic, absorption band at (1160) cm^{-1} due to (C-O-C), absorption band at (1643) cm^{-1} due to (CH=N) absorption band at (792) cm^{-1} due to (C-Cl) compound (4). Absorption bands at (1630) cm^{-1} due to (C=N) endo cycle, absorption band at (2904) cm^{-1} due to (C-H) aliphatic, absorption band at (3072) cm^{-1} due to (CH) aromatic, absorption band at (1166)cm^{-1} due to (C-O-C), absorption band at (1617)cm^{-1} due to (C=N), absorption band at (790)cm^{-1} due to (C-Cl) absorption band at (1413, 1506)cm^{-1} due to (N=N-) in compound (5), appearance absorption bands at (3220, 3305) cm^{-1} due to (NH), absorption band at (3090)cm^{-1} due to (=CH), absorption band at (3020)cm^{-1} due to (C-H) aromatic absorption band at (750)cm^{-1} due to (C-S) in compound (6), absorption band at (1618) cm^{-1} due to (C=N) endo cycle, absorption band at (3385) cm^{-1} due to (NH), absorption band at (1705) cm^{-1} due to (-COO) ester, absorption band at (2990) cm^{-1} due to (C-H)aliphatic, absorption band at (3064) cm^{-1} due to (CH) aromatic, absorption band at (3100) cm^{-1} due to (=CH)absorption band at (750) cm^{-1} due to (C-S) compound (7), absorption bands at (1630) cm^{-1} due to (C=N) endo cycle, absorption band at (3200, 3260) cm^{-1} due to (NH), absorption band at (1680) cm^{-1} due to (CO-NH) amide, absorption band at (3140)cm^{-1} due to (NH-) of amide, absorption band at (2928)cm^{-1} due to (C-H) aliphatic, absorption band at (3066)cm^{-1} due to (C-H) aromatic, absorption bands at (3101) cm^{-1} due to (=CH), absorption band at (1690)cm^{-1} due to (CO-NH) carbonyl of amide, absorption band at (766)cm^{-1} due to (C-S) in compound (8). Absorption bands at (1647) cm^{-1} due to (C=N) endo cycle, absorption band at (1685) cm^{-1} due to (CO-NH) carbonyl of amide, absorption band at (2937)cm^{-1} due to (C-H) aliphatic' absorption band at (3076)cm^{-1} due to (C-H) aromatic absorption band at (750)cm^{-1} due to (C-S) absorption band at (3100)cm^{-1} due to (=CH) absorption

band at (1627)cm^{-1} due to (CH=N) in compound (9). Absorption bands at (1654) cm^{-1} due to (C=N) endo cycle, absorption band at (3255)cm^{-1} due to (NH) absorption band at (1695) cm^{-1} due to (CO-NH) amide, absorption band at (2900)cm^{-1} due to (C-H) aliphatic, absorption band at (3043)cm^{-1} due to (C-H) aromatic, absorption band at (3100)cm^{-1} due to (=CH) absorption band at (1620)cm^{-1} due to (C=N) absorption band at (1469'1525)cm^{-1} due to (N=N) 'absorption band at (777)cm^{-1} due to (C-S) in compound (10). Absorption bands at (1640) cm^{-1} due to (C=N) endo cycle, absorption band at (2972) cm^{-1} due to (C-H) aliphatic, absorption band at (1610) cm^{-1} due to (CH=N), absorption band at (3020)cm^{-1} due to (C-H) aromatic, absorption band at (3090)cm^{-1} due to (=CH) absorption band at (729)cm^{-1} due to (C-S); in compound (11). Absorption bands at (1650) cm^{-1} due to (C=N) endo cycle, absorption band at (3100) cm^{-1} due to (=CH), absorption band at (1610) cm^{-1} due to (C=N), absorption band at (744)cm^{-1} due to (C-S), absorption band at (3080)cm^{-1}due to (C-H) aromatic, absorption band at (2940)cm^{-1} due to (C-H) aliphatic absorption band at (1417'1500)cm^{-1} due to (N=N-) in compound (12). Absorption bands at (1653) cm^{-1} due to (C=N) endo cycle, absorption band at (3224'3322) cm^{-1} due to (NH), absorption band at (1170) cm^{-1} due to (C-O-C), in compound (13), absorption bands at (1655) cm^{-1} due to (C=N) endo cycle, absorption band at (1159)cm^{-1}due to (C-O-C), absorption band at (3329)cm^{-1} due to (OH) carboxylic acid absorption band at (3016)cm^{-1} due to (C-H)aromatic, absorption band at (1627)cm^{-1} due to (CH=N) in compound (14), absorption bands at (1651) cm^{-1} due to (C=N) endo cycle, absorption band at (11163)cm^{-1} due to (C-O-C), absorption band at (3000)cm^{-1} due to (C-H) aromatic absorption band at (2927)cm^{-1} due to (C-H) aliphatic absorption band at (3400)cm^{-1} due to (OH) absorption band at (1617)cm^{-1} due to (C=N) absorption band at (1456'1500)cm^{-1} due to (N=N-) " in compound (15). Absorption bands at (1649) cm^{-1} due to (C=N) endo cycle, absorption band at (3329) cm^{-1} due to (NH), absorption band at (1716) cm^{-1} due to (CO-O) carboxylic acid, absorption band at (2779'3184)cm^{-1} due to (OH), absorption band at (3063)cm^{-1} due to (C-H) aromatic in compound (16), absorption bands at (1643) cm^{-1} due to (C=N) endo cycle, absorption band at (3412) cm^{-1} due to (NH), absorption band at (1710)cm^{-1} due to (-COO) ester, absorption band at (2981)cm^{-1} due to (C-H)aliphatic absorption band at (3000)cm^{-1} due to (C-H)aromatic' in compound (17), absorption bands at (1650)cm^{-1} due to (C=N) endo cycle, absorption band at (3300-3360)cm^{-1} due to (NH), absorption bands at (3000)cm^{-1} due to (C-H) aromatic absorption bends at (3200)cm^{-1} due to (NH) amide absorption band at (1690)cm^{-1} due to (CO-NH) carbonyl of amide' in compound (18), absorption band at (1652)cm^{-1} due to (C=N) endo cycle absorption band at (3400)cm^{-1} due to (NH), absorption bands at (2900)cm^{-1} due to (CH) aliphatic, absorption bands at (3050)cm^{-1} due to (C-H-) aromatic absorption bands at (3150)cm^{-1} due to (NH) amide, absorption band at (1698)cm^{-1} due to (CO-NH) carbonyl of amide, absorption band at (1635)cm^{-1} due to (CH=N) in compound (19), absorption bands at (1655) cm^{-1} due to (C=N) endo cycle, absorption band at (3405) cm^{-1} due to (NH), absorption band at (1690) cm^{-1} due to (CO-NH) amide, absorption band at (2990)cm^{-1} due to (CH) aliphatic, absorption band at (3080)cm^{-1} due to (CH) aromatic, absorption band at (3170)cm^{-1} due to (NH) amide absorption band at (1620)cm^{-1} due to (C=N), absorption band at (1420, 1480)cm^{-1} due to (N=N-)azo in compound (20), other data are listed in table.1, and figures.1-20.

Table.1. FT.IR-data (cm^{-1}) of Compounds (1-20)

Comp.	υ (C=N) endo cycle	υ(NH) or υ(NH_2)	υ (-COO) ester	Other Groups
1	1654	3350	---	(CH)arom:3040
2	1647	---	1716	(CH)aliphatic:2935, (CH)arom:3055
3	1627, 1604	3321, 3203	---	(CH)aliphatic:2900, (CH)arom:3039, (C-O-C):1174
4	1666	---	---	(CH)aliphatic:2972,(CH)arom:3050, (C-O-C):1160, (CH=N)Schiff base:1643, (C-Cl):729
5	1630	---	---	(CH)aliphatic:2904, (CH)arom:3072, (C-O-C):1166, (C=N)Schiff base:1617, (C-Cl):790, (N=N-):1413, 1506
6	1640	3220, 3300	---	(=CH):3090, (CH)arom:3020, (C-S):750
7	1618	3385	1705	(CH)aliphatic:2990,(CH)arom:3064, (=CH):3100, (C-S):740
8	1630	3200, 3260	---	(CH)aliphatic:2928,(CH)arom:3066, (=CH):3102,(C-S):766, (CO-NH) Carbonyl of amide:1690, (NH-) of Amide:3140
9	1647	3325	---	(CH)aliphatic:2937, (CH)arom:3076, (=CH):3100, (C-S):750, (CH=N)Schiff base:1627, (CO-NH) Carbonyl of amide:1685
10	1654	3255	---	(CH)aliphatic:2900, (CH)arom:3043, (N=N-):1469, 1525, (=CH):3100, (C-S):777, (C=N)Schiff base:1620, (CO-NH) Carbonyl of amide:1695
11	1640	---	---	(CH)aliphatic:2972, (CH)arom:3020, (=CH):3090, (C-S):729, (CH=N)Schiff base:1629

12	1650	---	---	(CH)aliphatic:2940, (CH)arom:3080, (=CH):3100, (C-S):744, (C=N)Schiff base:1610, (N=N-):1417, 1500
13	1653	3224, 3322	---	(C-O-C):1170
14	1655	---	---	(CH)arom:3016, (CH=N)Schiff base:1627, (OH):3329, (C-O-C):1159
15	1651	---	---	(CH)arom:3000, (CH)aliph:2972, (C=N)Schiff base:1617, (OH):3400, (C-O-C):1163, (N=N-):1456, 1500
16	1649	3329	---	(CH)arom:3063, (OH):(2779-3184), (CO-O) Carboxylic acid:1716
17	1643	3412	1710	(CH)arom:3000, (CH)aliph:2981
18	1650	3300, 3360	---	(CH)arom:3000, (NH)Amide:3200, (CO-NH)Carbonyl of amide:1690
19	1652	3400	---	(CH)arom:3050, (CH)aliph:2900, (NH)Amide:3150, (CO-NH) Carbonyl of amide:1698, (CH=N)Schiff base:1635
20	1655	3405	---	(CH)arom:3080, (CH)aliph:2990, (NH) Amide:3170, (CO-NH) Carbonyl of amide:1690, (C=N) Schiff base:1620, (-N=N) Azo:1420, 1480

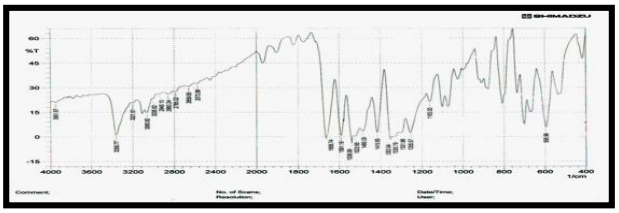


Fig.1. FT.IR of Compound (1)

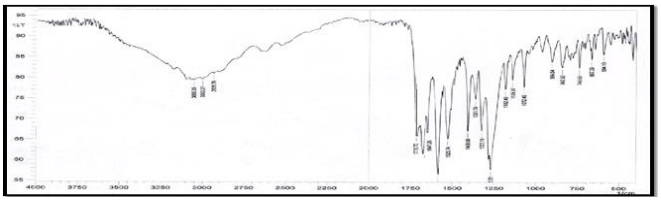


Fig.2. FT.IR of Compound (2)

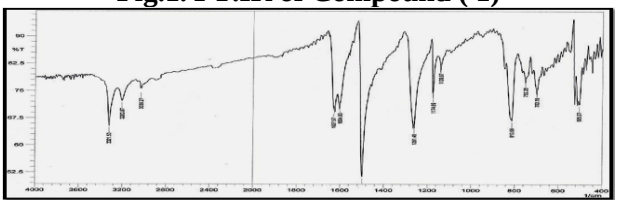


Fig.3. FT.IR of Compound (3)

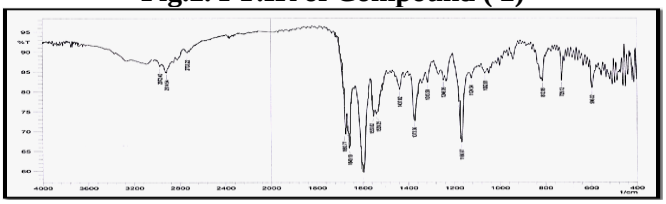


Fig.4. FT.IR of Compound (4)

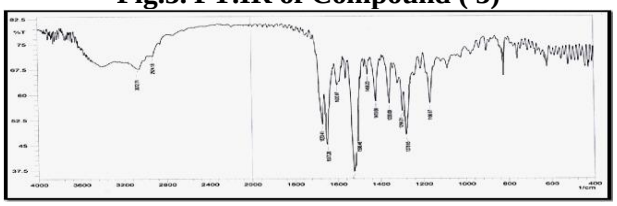


Fig.5. FT.IR of Compound (5)

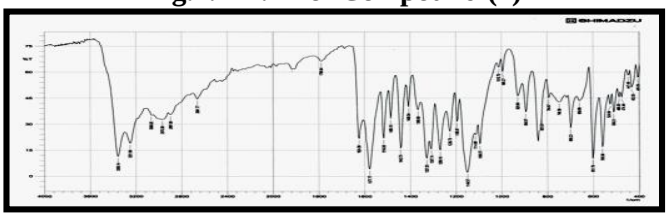


Fig.6. FT.IR of Compound (6)

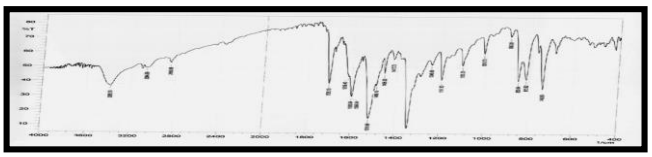


Fig.7. FT.IR of Compound (7)

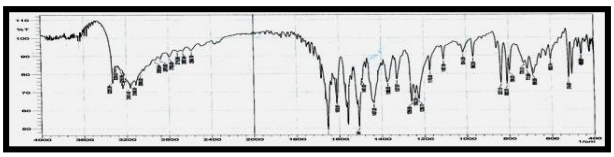


Fig.8. FT.IR of Compound (8)

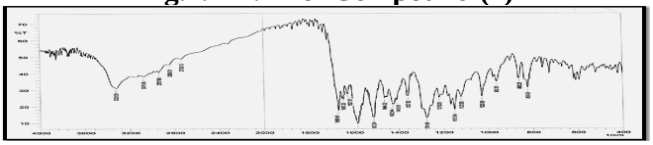


Fig.9. FT.IR of Compound (9)

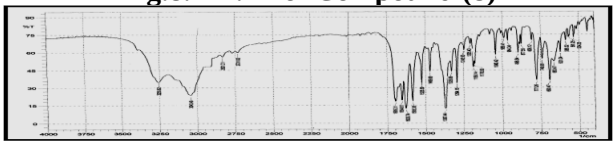


Fig.10. FT.IR of Compound (10)

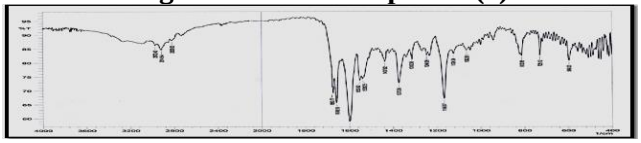


Fig.11. FT.IR of Compound (11)

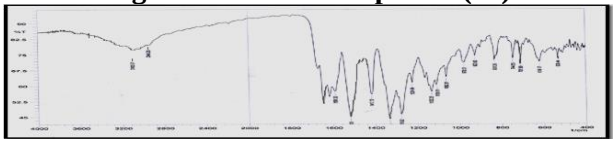


Fig.12. FT.IR of Compound (12)

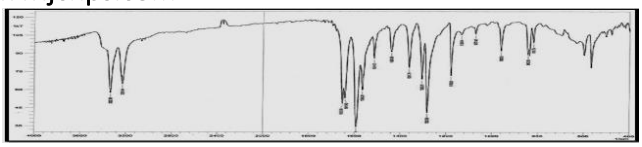


Fig.13. FT.IR of Compound (13)

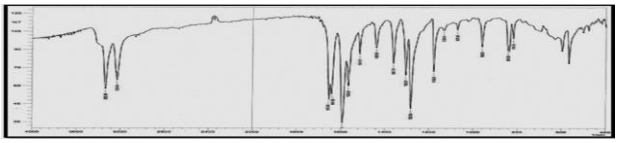


Fig.14. FT.IR of Compound (14)

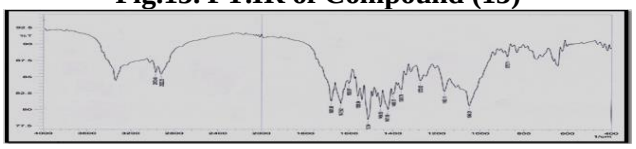


Fig.15. FT.IR of Compound (15)

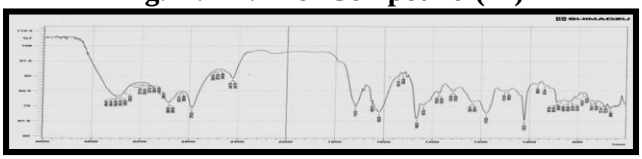


Fig.16. FT.IR of Compound (16)

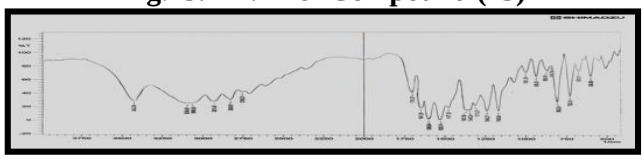


Fig.17. FT.IR of Compound (17)

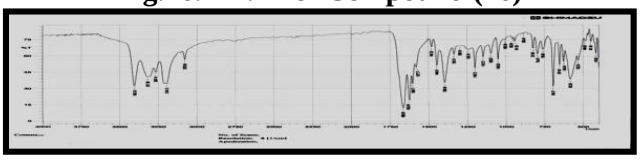


Fig.18. FT.IR of Compound (18)

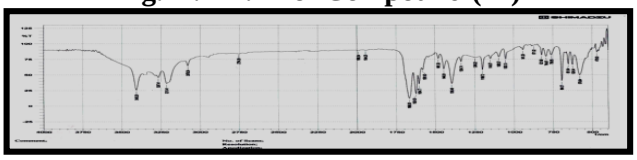


Fig.19. FT.IR of Compound (19)

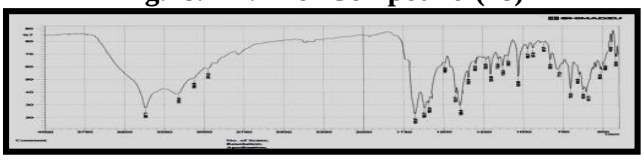


Fig.20. FT.IR of Compound (20)

(C.H.N)- Analysis: All results of micro analysis indicate to synthesize compounds through compared experimental data with calculated data.

Table.2. Physical Properties (C.H.N)-analysis of compound (1-20)

Comp.	M.F.	M.P. ^{0}C	Calc./Found (%)			
			C	H	N	S
1	$C_{20}H_{16}N_2$	148	84.507/84.013	5.633/5.110	9.859/9.191	---
2	$C_{24}H_{22}N_2O_2$	170	77.837/77.210	5.945/5.271	7.567/7.085	---
3	$C_{23}H_{19}N_5O$	194	72.440/72.027	4.986/4.453	18.372/18.109	---
4	$C_{30}H_{22}N_5O$ Cl	198	71.570/71.074	4.369/4.225	13.902/13.474	---
5	$C_{37}H_{28}N_7O$ Cl	215	71.440/71.118	4.505/4.172	15.768/15.201	---
6	$C_{16}H_{13}N_3$ S	136	68.817/68.252	4.659/4.167	15.053/14.74	11.469/11.008
7	$C_{20}H_{19}N_3O_2$ S	176	65.753/65.292	5.205/4.901	11.506/11.139	8.767/8.248
8	$C_{24}H_{21}N_5OS$	184	67.447/67.152	4.918/4.349	16.393/16.074	4.494/4.180
9	$C_{32}H_{27}N_5O$ S	198	72.589/72.126	5.103/4.861	13.232/13.00	6.049/5.751
10	$C_{39}H_{33}N_7O$ S	218	72.333/72.049	5.100/4.863	15.146/14.836	4.945/4.683
11	$C_{24}H_{19}N_3$ S	160	75.590/75.096	4.986/4.421	11.023/10.651	8.398/8.104
12	$C_{31}H_{25}N_5$ S	194	74.549/74.074	5.010/4.629	14.028/13.709	6.412/6.106
13	$C_4H_4N_4$ O_2	142	34.285/33.949	2.857/2.562	40.00/39.618	---
14	$C_{18}H_{12}N_6O_4$	166	57.446/57.027	3.191/3.001	22.340/22.115	---
15	$C_{32}H_{24}N_{10}O_4$	202	62.745/62.197	3.921/3.364	22.875/22.319	---
16	$C_{14}H_{10}N_2O_2$	162	70.588/70.142	4.201/3.871	11.764/11.176	---
17	$C_{16}H_{16}N_2O_2$	154	71.641/71.253	5.970/5.319	10.447/10.172	---
18	$C_{20}H_{16}N_4O$	182	73.170/72.793	4.878/4.241	17.073/16.651	---
19	$C_{28}H_{22}N_4O$	196	78.139/77.865	5.116/4.769	13.023/12.685	---
20	$C_{35}H_{28}N_6O$	220	76.642/76.130	5.109/4.782	10.218/10.110	---

The ^{1}H.NMR spectra: All spectra indicate to synthesized compounds, which showed signals at{ δ(6.93-7.90) for protons of phenyl group and δ(8.15) for protons of amine group (NH_2) and δ(1.20) for protons of (-CH-) }endo cycle) and δ(2.50) for protons of DMSO-d6(solvent) in compound (1), which converted to signals at {δ(6.50-7.84) for proton of phenyl group and δ (2.09) for protons of (-CH_2-COO) and δ (1.30) for protons of (-CH-) endo cycle and δ (3.40-3.70) for protons of (COO-CH_2CH_3)-for protons of and δ (3.75-3.90) for protons of (COO-CH_2-$_{CH3)}$ in compound (2), which converted to signals at {δ(6.58-7.84) for proton of phenyl group and δ (1.90) for protons of (-CH_2-) and δ (6.04) for protons of amine (NH_2) and δ (1.40) for protons of (-CH-) endo cycle in compound (3), which converted to signals at {δ(8.51) for proton of imine group (CH=N) and δ (7.03-7.90) for protons of phenyl group and δ (1.10) for protons of (-CH_2-) and δ (1.40) for protons (-CH-) endo cycle in compound (4), which converted to

signals at {Ɓ(6.59-7.91) for proton of phenyl group and Ɓ (1.30) for protons of (-CH_2-) and Ɓ (0.80) for protons of (CH_3) and Ɓ (2.00) for protons of (-CH-) endo cycle in compound (5), which converted to signals at {Ɓ(6.23) for proton of amide group (NH_2) and Ɓ (7.20-7.94) for protons of phenyl group in compound (6), which converted to signals at {Ɓ(7.09-7.95) for proton of phenyl group and Ɓ (6.23) for protons of (NH_2) and Ɓ (2.00) for protons of (-CH_2-COO) and Ɓ (2.60-3.00) for protons of (COO-CH_2-CH_3)) and Ɓ (3.10-3.99) for protons of (COO-CH_2-CH_3) in compound (7), which converted to signals at {Ɓ(6.78-7.95) for proton of phenyl group and Ɓ (9.18) for protons of (NH-CO)amide and Ɓ (5.62-5.81) for protons of (NH_2) and Ɓ (3.5) for protons of (N-CH_2CO)) in compound (8), which converted to signals at {Ɓ(7.17-7.94) for proton of phenyl group and Ɓ (8.33) for proton of imine (CH=N) and Ɓ (9.00) for protons of (NH-CO)} amide and Ɓ (5.68) for protons of (NH_2) amine and Ɓ (3.51) for protons of (N--CH_2-CO) and Ɓ (1.20) for protons of (Ph-CH_3) in compound (9), which converted to signals at {Ɓ(9.06) for proton of amide (NH-CO-) and Ɓ (5.58) for protons of (NH)amine and Ɓ (6.78-7.95) for protons of phenyl group and Ɓ (3.40) for protons of (N--CH_2- CO) and Ɓ (1.00-1.10) for protons of (Ph-CH3) in compound (10), which converted to signals at {Ɓ(6.95-7.99) for proton of phenyl ring and Ɓ (8.58) for proton of (CH=N)imine and Ɓ (1.10) for protons of (Ph-CH3) in compound (11), which converted to signals at {Ɓ(7.03-7.98) for proton of phenyl group and Ɓ (1.00-1.30) for protons of (Ph-CH3) in compound (12), which converted to signals at {Ɓ(6.04) for proton of (NH) amine in compound (13), which converted to signals at{Ɓ(7.00-7.97) for proton of phenyl ring and Ɓ (8.51) for proton of imine (CH=N) and Ɓ (11.78) for protons of (OH) Phenol in compound (14), which converted to signals at{Ɓ(7.32-7.99) for protons of phenyl group and Ɓ (11.81) for proton of (OH) Phenol and Ɓ (1.10-1.20) for protons of (Ph-CH3) in compound (15), which converted to signals at{Ɓ(6.72-7.87) for proton of phenyl ring and Ɓ (8.28) for protons of (CH=N)imine and Ɓ (8.75) for protons of (NH_2) and Ɓ (9.36) for protons of (NH-CO)}amide and Ɓ (0.95) for protons of (Ph-CH3) in compound (19), which converted to signals at{Ɓ(6.80-7.89) for proton of phenyl ring and Ɓ (8.88) for protons of (NH2)amine and Ɓ (9.68) for proton of (NH-CO)}amide and Ɓ (1.00-1.20) for protons of (Ph-CH3) in compound (20), other peaks are listed in table (3) and figures (21-37).

Table.3. 1H.NMR- data (δ - ppm) of Compounds

Comp.	Phenyl group	**(CH=N)** Imine	**NH., NH_2 Amine**	**(NH-CO)** Amide	**Other groups**
1	6.93-7.90	---	8.15	---	(-CH-)endocycle:1.20, (DMSO-d6(solvent):2.50
2	6.50-7.94	---	---	---	(-CH_2-COO):2.09, (-CH-)endocycle:1.30, (COO-CH_2-CH_3):(3.40-3.70), (COO-CH_2-CH_3): (3.75-3.90)
3	6.58- 7.84	---	6.04	---	(-CH_2-) : 1. 90, (-CH-) endocycle : 1. 25)
4	7.03- 7.90	8.51	---	---	(-CH2-) : 1.10 -CH-)endocycle:1.40
5	6.59- 7.91	---	---	---	(-CH_2-):1.30, (-CH-)endocycle: 2.00, (CH_3): 0.80
6	7.20-7.94	---	6.23	---	---
7	7.09-7.95	---	6.18	---	(-CH_2-COO): 2.00, (COO-CH_2-CH_3): (2.60 -3.00), COO-CH_2-CH_3): (3.10 -3.99)
8	6.78- 7.95	---	5.62, 5.81	9.18	(N-CH_2-CO): 3.5
9	7.17- 7.94	8.33	5.68	9.00	(N-CH_2-CO): 3.51, (Ph-CH_3): 1.20
10	6.78- 7.95	---	5.58	9.06	(N-CH_2-CO): 3.40, (Ph-CH_3): 1.00, 1.10
11	6.95- 7.99	8.58	---	---	(Ph-CH_3): 1.10
12	7.03- 7.98	---	---	---	(Ph-CH_3): 1.00, 1.30
13	---	---	6.04	---	---
14	7.00-7.97	8.51	---	---	(OH) Phenol : 11.78
15	7.32-7.99	---	---	---	(OH) Phenol : 11.81 (Ph-CH_3): 1.10, 1.20
19	6.72-7.87	8.28	8.75	9.36	(Ph-CH_3): 0.95
20	6.80-7.89	---	8.88	9.68	(Ph-CH_3):1.00, 1.30

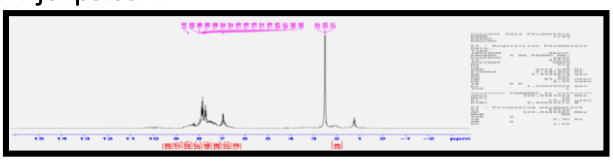


Fig.21. 1H.NMR of Compound (1)

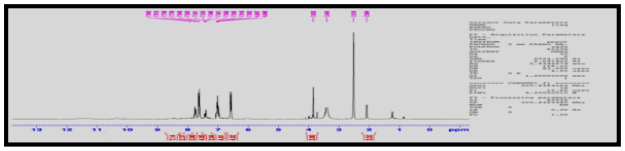


Fig.22. 1H.NMR of Compound (2)

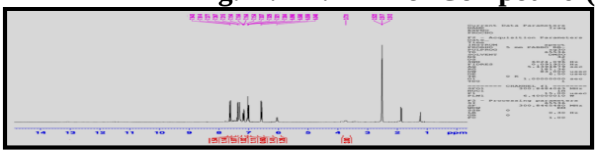


Fig.23. 1H.NMR of Compound (3)

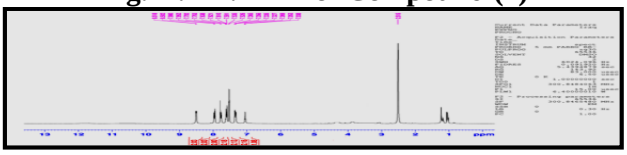


Fig.23. 1H.NMR of Compound (4)

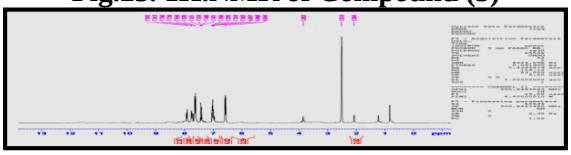


Fig.25. 1H.NMR of Compound (5)

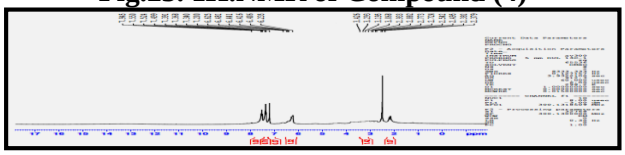


Fig.26. 1H.NMR of Compound (6)

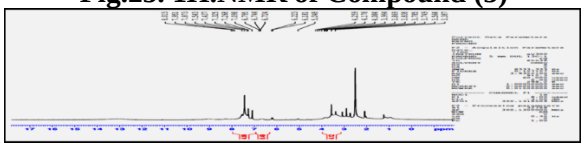


Fig.27. 1H.NMR of Compound (7)

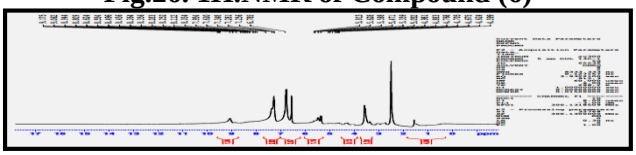


Fig.28. 1H.NMR of Compound (8)

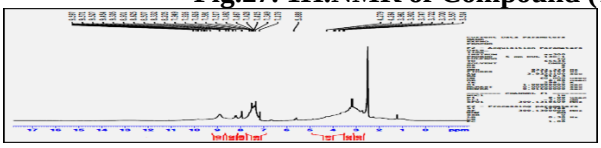


Fig.29. 1H.NMR of Compound(9)

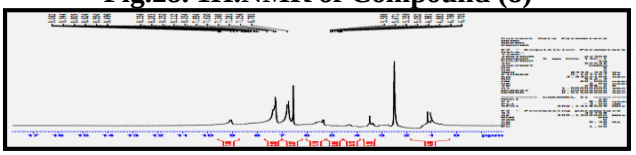


Fig.30. 1H.NMR of Compound (10)

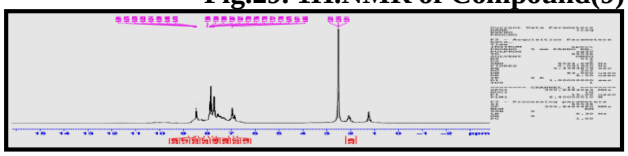


Fig.31. 1H.NMR of Compound(11)

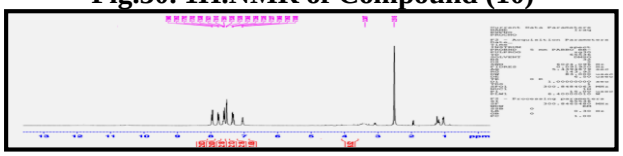


Fig.32. 1H.NMR of Compound(12)

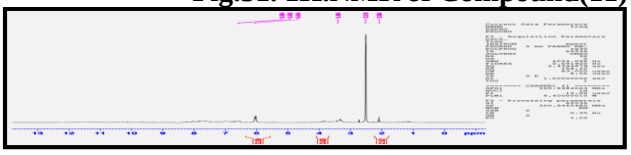


Fig.33. 1H.NMR of Compound(13)

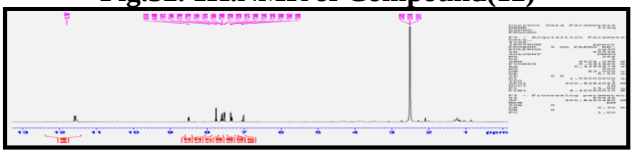


Fig.34. 1H.NMR of Compound(14)

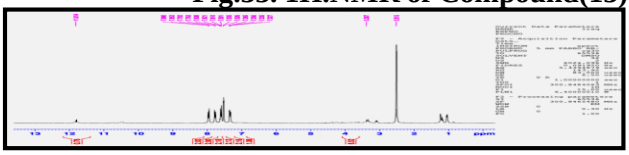


Fig.35. 1H.NMR of Compound(15)

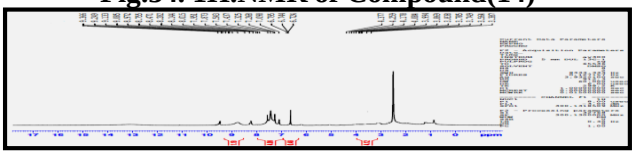


Fig.36. 1H.NMR of Compound(19)

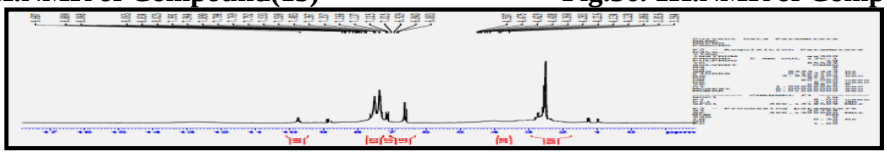


Fig.37. 1H.NMR of Compound(20)

The 13C.NMR spectral: data of some compounds showed signals indicated to functional groups in these compounds, table (4) and figures (38-52).

Table.4. 13C. NMR data of Compounds

Comp.	phenyl	COO- ester	CO-NH Amide	Other peaks
1	116.0 – 134.0	---		(-CH-N -) : 52.0 Solvent (DMSO): 40.0
2	116.0 – 136.0	174.0	----	(-CH-N-CH2-) : 56.0, 62.0 (COO- CH2-CH3): 22.0, 26.0
3	114.0 – 132.0	---	---	(-CH-N-CH2-) : 56.0, 62.0

				(C, Oxadizole): (145.0, 148.0)
4	110.0 – 126.0	---	---	(-CH-N-CH2-) : 58.0, 64.0 (C, Oxadizole): (140.0, 142.0) (CH=N) Imine :159.0
5	108.0 – 130.0			(-CH-N-CH2-) : 60.0, 64.0 (C, Oxadizole): (142.0, 144.0) (N=N-C=N) Formazan :100.0 (Ph-CH3): 12.0
7	108.0- 124.0	176.0	---	-N-CH2-) : 60.0) (C, Thiadiazepine) :(138.0- 146.0) (COO- CH2-CH3): 22.0, 24.0
8	108.0- 126.0	---	168.0	-N-CH2-) : 65.0) (C,Thiadiazepine) :(138.0- 144.0)
9	108.0- 128.0	---	165.0	-N-CH2-) : 62.0) (C,Thiadiazepine) :(140.0- 146.0) (Ph-CH3): 10.0, (CH=N) Imine :156.0
10	110.0- 128.0	---	168.0	-N-CH2-) : 56.0) (C, Thiadiazepine) :(136.0- 142.0) (Ph-CH3): 12.0, 15.0 (N=N-C=N) Formazan : 104.0
11	114.0- 128.0	---	---	(C, Thiadiazepine) :(135.0- 140.0) (Ph-CH3): 10.0 , (CH=N) Imine :152.0
12	114.0- 132.0	---	---	(C, Thiadiazepine) :(138.0- 145.0) (Ph-CH3): 13.0, 15.0 (N=N-C=N) Formazan : 105.0
14	112.0- 128.0	---	---	(CH=N) Imine :155.0, 157.0 (C, Oxadiazole): (136.0 – 142.0)
15	114.0- 132.0	---	---	(Ph-CH3): 14.0, 15.0 (C, Oxadiazole): (138.0 – 145.0) (N=N-C=N) Formazan :(100.0,104.0)
19	110.0- 128.0	---	168.0	(Ph-CH3): 12.0, (CH=N) Imine :156.0 (C, Imidazole): 142.0
20	110.0- 134.0		166.0	(Ph-CH3): 8.0,10.0, (C, Imidazole): 144.0, (N=N-C=N) Formazan : 102.0

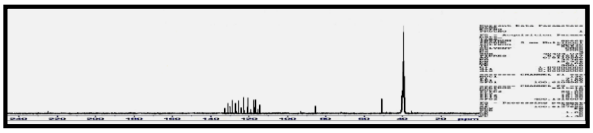


Fig.38. ^{13}C.NMR of Compound (1)

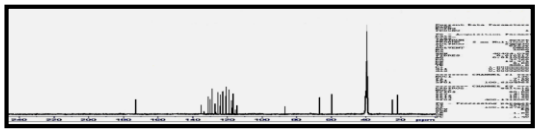


Fig.39. 13C.NMR of Compound (2)

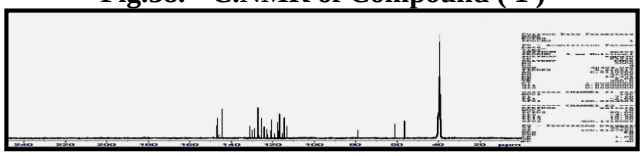


Fig.40. ^{13}C.NMR of Compound (3)

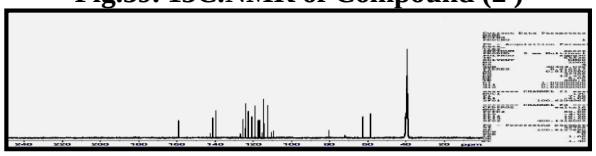


Fig.41. 13C.NMR of Compound (4)

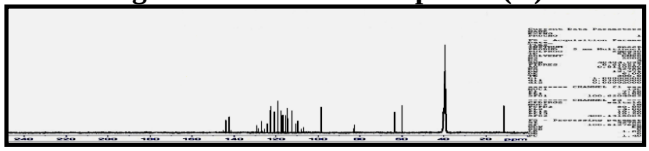


Fig.42. 13C.NMR of Compound (5)

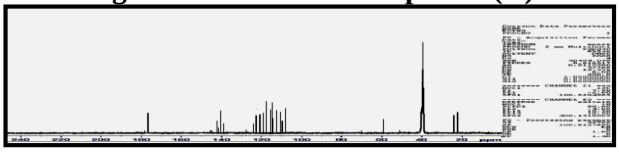


Fig.43. 13C.NMR of Compound (7)

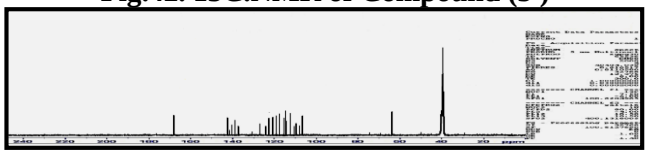


Fig.44. 13C.NMR of Compound (8)

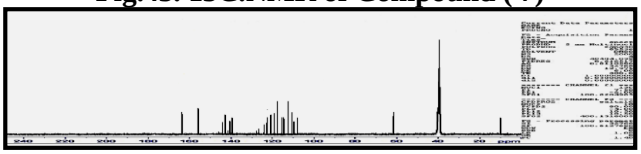


Fig.45. 13C.NMR of Compound (9)

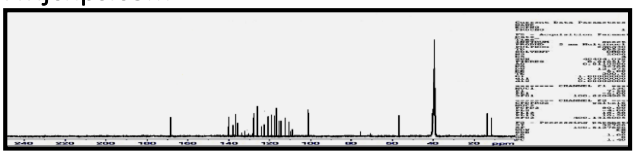


Fig.46. 13C.NMR of Compound (10)

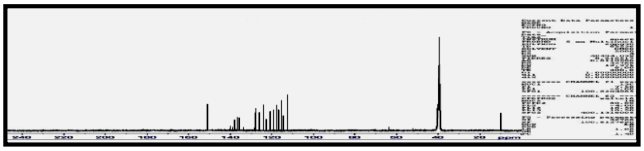


Fig.47. 13C.NMR of Compound (11)

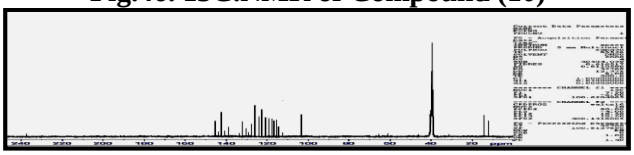


Fig.48. 13C.NMR of Compound (12)

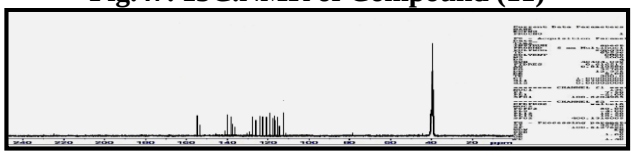


Fig.49. 13C.NMR of Compound (14)

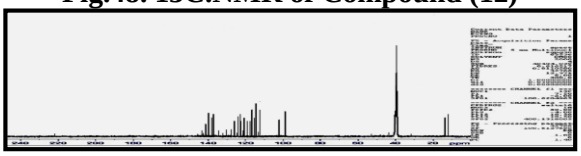


Fig.50. 13C.NMR of Compound (15)

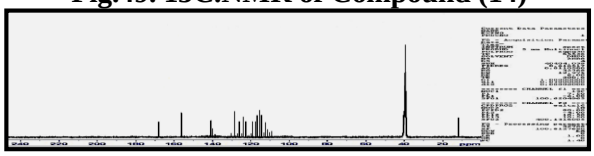


Fig.51. 13C.NMR of Compound (19)

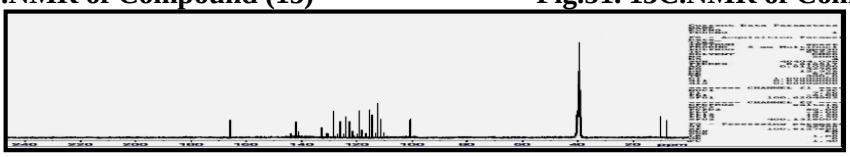


Fig.52. 13C.NMR of Compound (20)

4. CONCLUSION

All formazan compounds gave good resulting, high percentage products more than imine compounds or azo compounds, it was very stable to word high temperatures.

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