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Synthesis, Identification, Chromatographic Studying of Formazane – Phenylenediamine Derivatives

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ABSTRACT

The research included two lines to prepare new derivatives of Formazan of medical and industrial importance, and the preparation carried out according to the following lines: The first line: four formazan derivatives were prepared by coupling the base of the preparation with aromatic amines (P-nitro aniline, O-hydroxy aniline, P-chloro aniline, 4-amino-5-methyl-2-phenyl-1.2-dihydro-3H-pyrozol-3-one) in a basic medium with the azotation step. As for the imine used, it was prepared through the condensation reaction of anthranilic with (o-phenylenediamine) in an acidic medium to form the first amine, which was treated with four types of aldehydes (vanilline, 2-nitro benzaldehyde, o-hydroxy benzaldehyde, p-hydroxybenzaldehyde) to form four new derivatives of the imine compound., The second line: two derivatives of formazan were prepared by reaction of two derivatives of the new imine compounds with two types of amines (P-chloro aniline, benzo imidazole-2-amine) in a basic medium where they were lubricated to accumulate the formazan compounds. As for the new Schiff base compounds, they were prepared from the condensation reaction of anthranilic with (p-phenylene diamine) in the presence of sulfuric acid (H2SO4) to form the first amines, which were treated with two types of aldehydes (vanilline P-nitro benzaldehyde,) to form Schiff bases. Each reaction is followed by TLC technology as well as measurement of the melting point of the prepared compounds. Study the chromatographic behavior of the prepared compounds. All compounds prepared were identified using different chemical techniques, such as (1H.NMR spectra, ^{13}C.NMR-spectra, FT.IR-spectra), melting points and physical properties.

KEYWORDS

Phenylenediamine, Schiff Base, Azo, Formazane, Chromatographic-Studying, Imine.

Introduction

Formazans are characterized by bond (-N=N-C=N). Sometimes formazan compounds[(1-3)] are derived from amine, so their general[(4-8)] formula is

but if it is derived from hydrazine, then its formula is[(9-12))]

Where (R) is a homogeneous or heterogeneous cyclic compound, either (X) is a cyclic substitution group or a group of (NO_2, CN, OH, SH) [(13, 14)]. And because of their wide applications, these compounds entered the field of coordination chemistry as ligand in the formation of complexes for some elements such as cobalt and iron[(15-20)] because they contain an electronic double that is not participant on the nitrogen atom[(21-25)] .

Formazan compounds are generally characterized by low melting points despite the large size of their molecules, and

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they are soluble in chloroform[26, 27], acetone, and ethanol, and are less soluble in water. This type of compound has synthetic isomers [28-31].

Formazan compounds have the ability to form inter-hydrogen bonds within the molecule between the electronic duplex located on the nitrogen atom and the hydrogen atom attached to the nitrogen cycle[32]. Formazan compounds was derived from benzothiazole have anti-bacterial activity. Where they were used as dyes for cotton, wool, and sawdust, and these derivatives showed resistance to washing processes due to their high stability[7, 33]. Formazans derived from sulfamethoxazole are bioactive [34-37]. Formazan derivatives may contain other groups associated with it showing colors, such as (OH, NH), or they may contain two or three azo groups, and the latter is preferred over compounds containing one group in dyeing because of their stronger application of color to tissue and cellulose fibers[38]. Formazan derivatives prepared by a diamine technician have proven pharmacological efficacy as anti-fungi, anti-malarial, antioxidant, antimicrobial, and certain types of bacteria [38].

Experimental and Apparatuses

All chemicals used (purity 99.98%), FT.IR-spectra: were recorded on Shimadzu 8300, KBr-disc, ^{1}HNMR-spectra were recorded on varian 300MHZ spectrometer using TMS ^{13}C.NMR–spectra carried out with DMSO-d6 as a solvent, The Melting points were determined on Gallenkamp M.F.B 600-010f melting point apparatus., Chromatography Technique in Baghdad in Science Ministry and Technology.

Synthesis of Compound [B_1]

The compound was prepared by dissolving (0.01M) (1.37gm) of anthranilic acid in (30ml) of absolute ethanol with constant stirring, then adding (0.01M) (1.08 gm) of the compound ortho-phenylenediamine and then adding 2-3 drops of acid. Concentrated sulfuric (H_2SO_4) and the process of sublimation at a temperature of (76C$^{\circ}$) for a period of (7hr), in which the reaction process was followed up by (TLC). After that, the product was cooled, dried and recrystallized with absolute ethanol, its weight and percentage (80%) according to studies[6-12].

Synthesis of Compounds [B_2-B_5]

(0.01M) of compound [B1] dissolved in (30ml) of ethanol, Then added (0.01M) of a compound (vanillin, para-nitro-benzaldehyde, ortho-hydroxybenzaldehyde, para-hydroxybenzyldehyde) with (1-2) drops of glacial acetic acid to it. Sublimation process was carried out at (76 °C) for a period of (5 hours), then the product was cooled, dried, purified by filtration and recrystallized with absolute ethanol and its percentage was (78, 85, 80, 82)% of the compound [B2], the compound [B3] and the compound [B4] and compound [B5] respectively, according to studies[6-12].

Synthesis of Compounds [B_6]

The compound was prepared by dissolving (0.01M) (1.37gm) of anthranilic acid in (30ml) of absolute ethanol with constant stirring, then adding (0.01M) (1.08gm) of the compound para-phenylene diamine and then adding (2-3) drops of Concentrated sulfuric acid (H2SO4) and the process of sublimation at a temperature of (76C$^{\circ}$) for a period of (5hr). The course of the reaction was followed up by (TLC), after which the product was cooled, dried and recrystallized with absolute ethanol, its weight and percentage (83%) according to studies[6-12].

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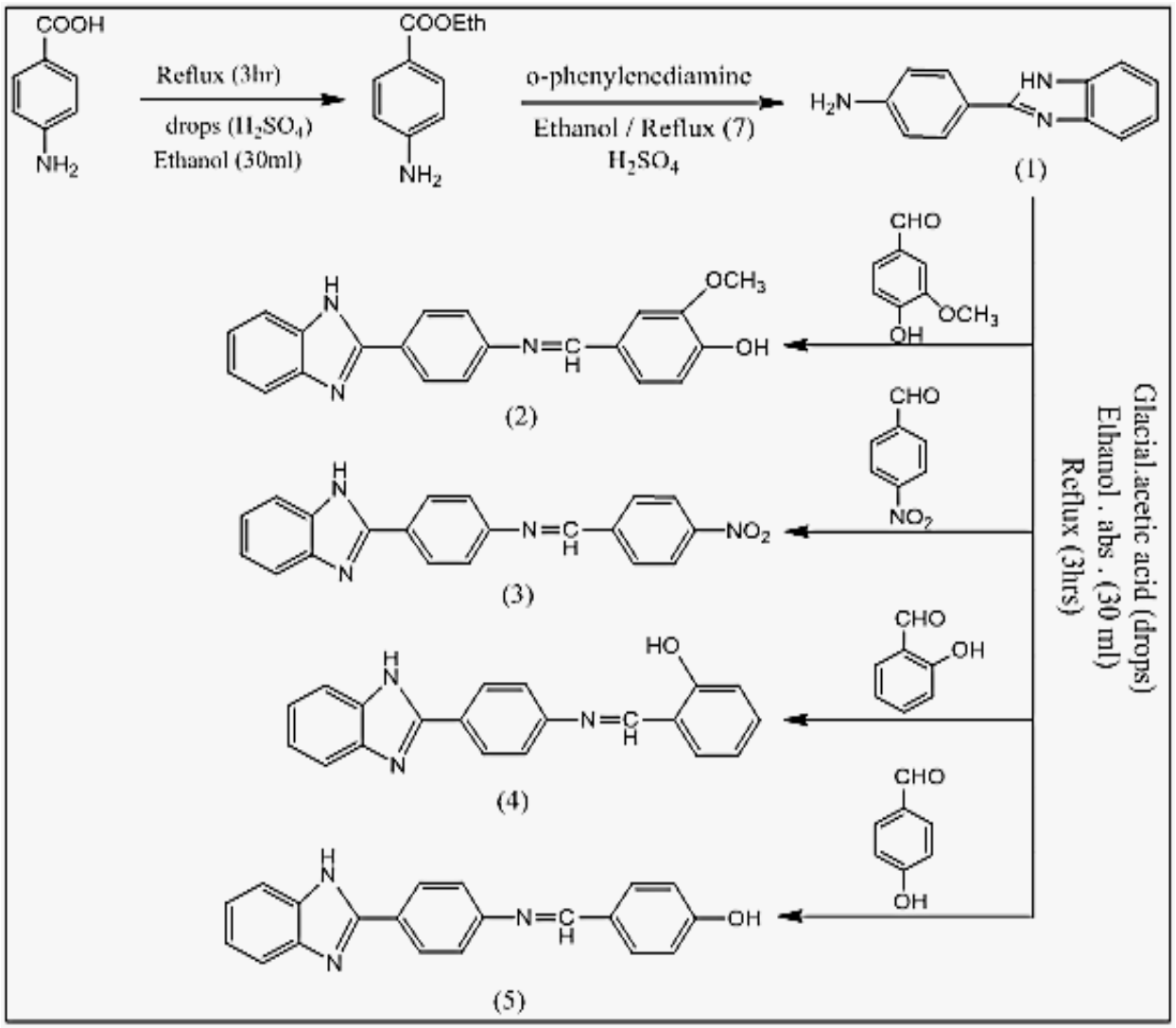
Synthesis of Compounds [$B_7 – B_9$]

(0.01M) of compound [B6] was weighed and (30 mL) of ethanol was added to it. Then added (0.01M) of the compound (vanillin, para-nitro-benzaldehyde, ortho-hydroxybenzaldehyde with (2) drops of glacial acetic acid. The reflux process was carried out at (76 ° C) for a period of (5 hours), then the product was cooled, dried, purified by filtration, and recrystallized with absolute ethanol, and its percentage was (80, 83, 80)% of the compound [B7], the compound [B8] and the compound [B9] respectively according to studies[6-12].

Synthesis of Formazan Compounds [$B_{10} – B_{15}$]

One of the compounds (o- amino phenol, p- chloro aniline, p- nitro aniline, 4-amino-5-methyl-2-phenyl-1'2-dihydro-3H-pyrazol-3-one, benzothiazol-2-amine, p-chloro aniline, 4-(1H-benzo[d]imidazole-2-yl)aniline) was dissolved in 4 ml of hydrochloric acid with a solution of sodium nitrite in (0-5C°). Then the compound (B2, B3, B4, B5, B7, B8, B9) is added to the mixture in basic medium, after 48 hours, filtered and dried then the absolute ethanol was recrystallized to produce the formazan compound and the product (85, 88, 80, 85, 83, 90, 85)%, respectively according to studies[6-12].



Scheme 1. Preparation of compounds [1-5]

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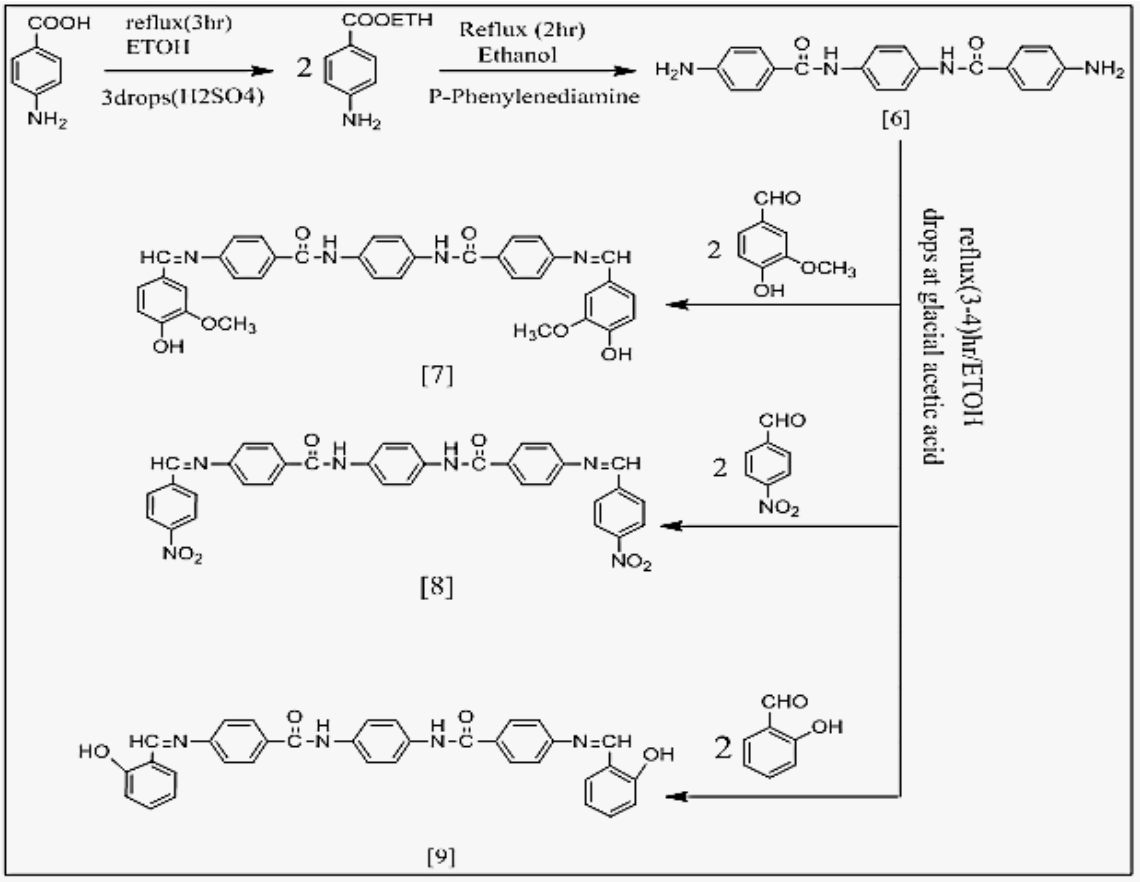
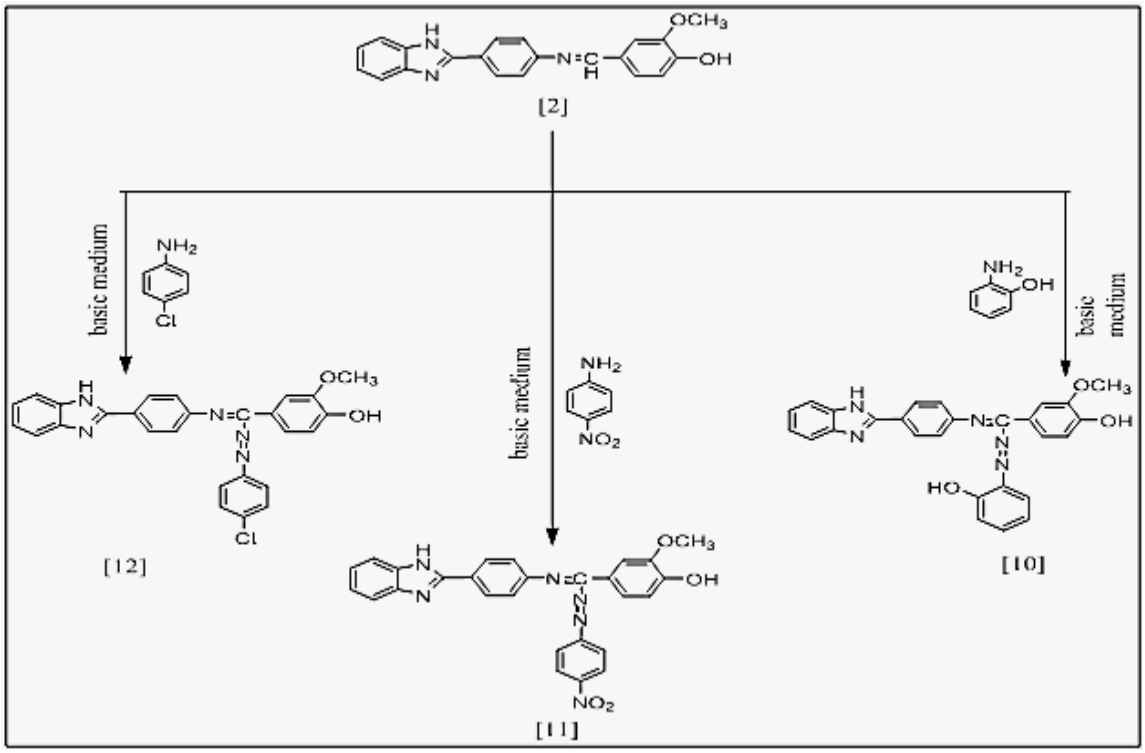


Scheme 2. Preparation of compounds [6-9]



Scheme 3. Preparation of compounds [10-12]

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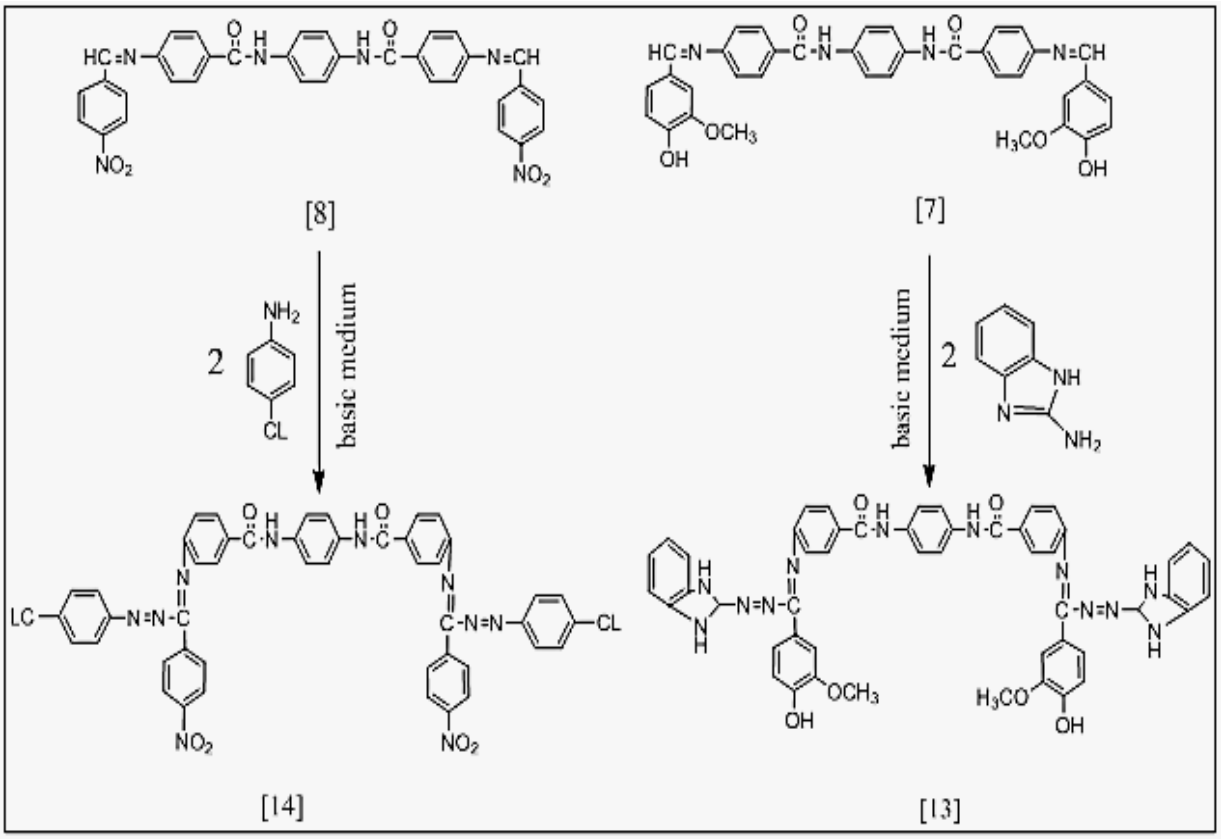
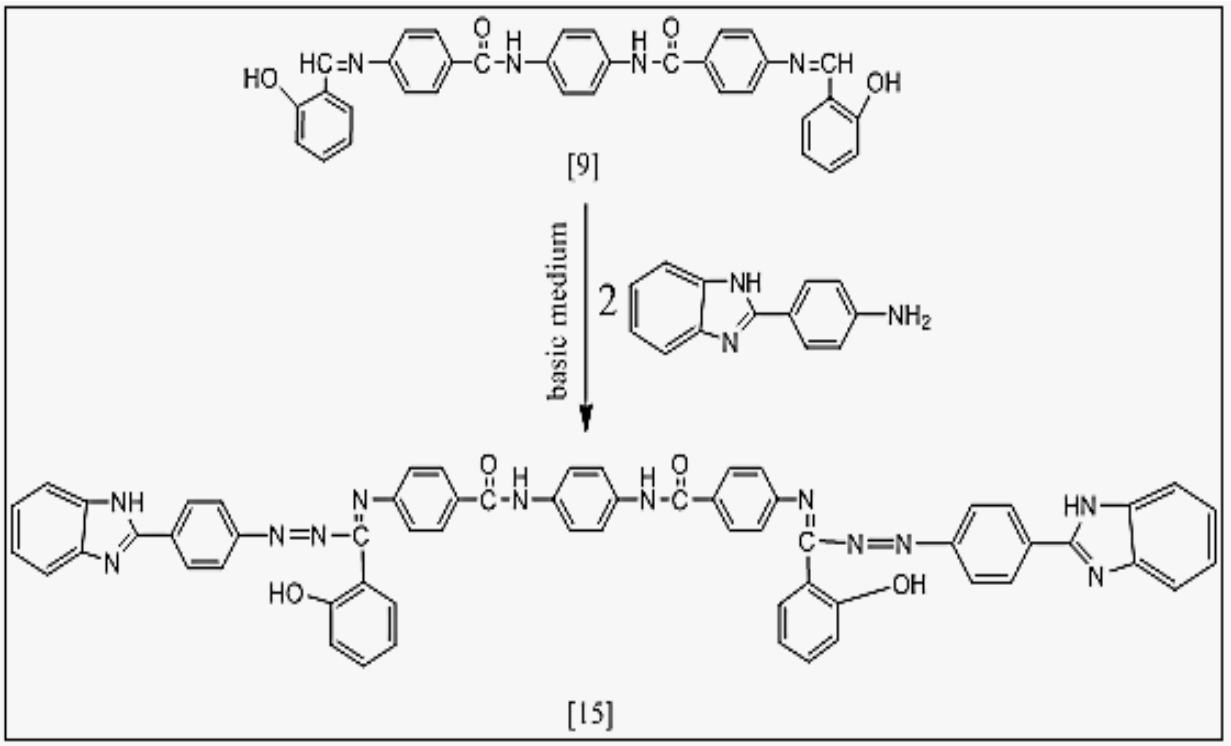


Scheme 4. Preparation of compounds [13-14]



Scheme 5. Preparation of compounds [15]

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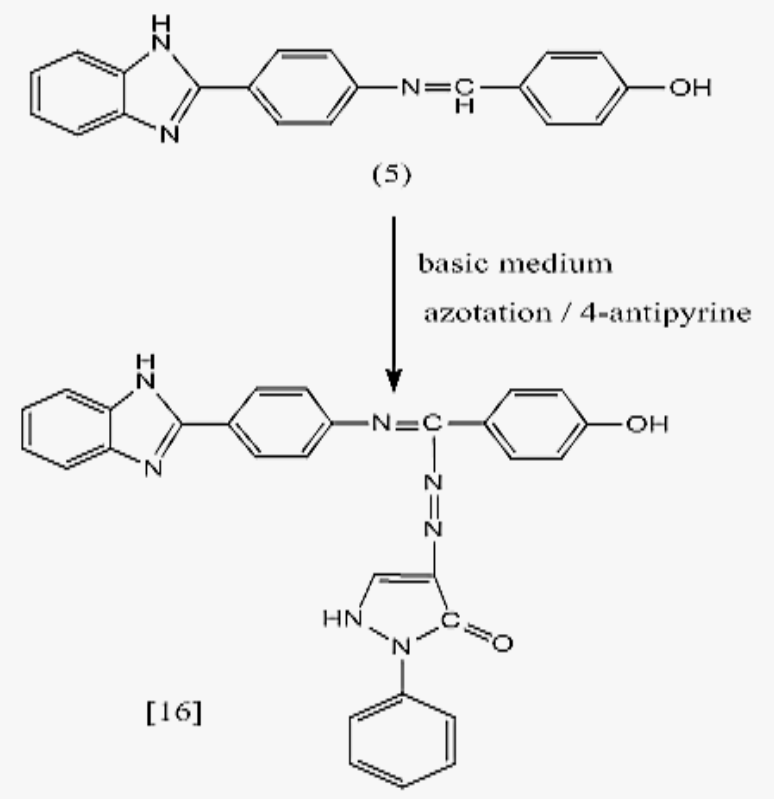

Scheme 6. Preparation of compounds [16]

Results and Discussion

Newly synthesized compounds [1-16] were detected by using a variety of technical methods [FT.IR spectra, melting points, ^{1}H.NMR spectra, and ^{13}C.NMR spectra in some cases also chromatography studies]:

FT.IR-spectra

FT.IR-Spectra showed absorption bends at (3200) cm^{-1} due to (NH), absorption band at (3471, 3417) cm^{-1}due to (NH_2) cm^{-1} amine group, absorption bends at (1664) cm^{-1} due to (C=N) imine group endocycle of benzimidazole in compound [B_1]. Also appearance of the absorption band at (1654)cm^{-1} due to (C=N), the absorption band at (6161)cm^{-1} due to imine group (C=N), the absorption band at (3024) cm^{-1} due to (C-H) aromatic, the absorption band at (2995)cm^{-1} due to (C-H) aliphatic, the absorption band at (3354) cm^{-1} due to (O-H) phenol, the absorption band at (3169) cm^{-1} due to (N-H) secondary amine and disappearance of the primary amine absorption package indicating the reaction and formation of compound [B2]. the appearance of the absorption band at (1315, 1514) cm^{-1} due to (NO_2) nitro group, the absorption band at (1681) cm^{-1} due to the (C = N) endocycle, the absorption range at (1608) cm^{-1} due to imine group, The absorption range at (3311) cm $^{-1}$ due to (N-H) secondary amine in the compound [B3].appearance of the absorption band at (3433) cm^{-1} due to (O-H) of phenol, absorption band at (3387) cm^{-1} due to the (N-H) amine, absorption range at (3028) cm^{-1} due to (C-H) aromatic, The absorption range at (1643) cm $^{-1}$ due to (C=N) endocycle Absorption range at (1608) cm^{-1} due to (CH=N) imine group, in the compound [B4]. appearance of the absorption band at (3410) cm^{-1} due to (O-H) of phenol, absorption band at (3172) cm^{-1} due to the (N-H) amine, absorption range at (1662) cm^{-1} due to (C=N) endocycle, The absorption range at (1618) cm $^{-1}$ due to (CH=N) imine group. Absorption range at (3088) cm^{-1} due to (C-H) aromatic, in the compound [B5]. Appearance of the absorption band at (3475,3387) cm^{-1} due to (NH2), absorption band at (3315) cm^{-1} due to the (N-H), absorption range at (1681) cm^{-1} due to (CO-N) of amide, The absorption range at (3000) cm $^{-1}$ due to (C-H) aromatic, in the compound [B6]. appearance of the absorption band at (3410) cm^{-1} due to (O-H) of phenol, absorption band at (3172) cm^{-1} due to the (H-N), absorption range at (1662) cm^{-1} due to (CO-N) of amide, The absorption range at (1618) cm $^{-1}$ due to (CH=N) imine group, Absorption range at (1165) cm^{-1} due to (-OCH3) ether, absorption range at (2991) cm-1 due to (C-H) aliphatic and absorption band at (3088) cm^{-1} due to the (C-H) aromatic in the compound [B7]. appearance of the

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absorption band at (3315) cm^{-1} due to (H-N), absorption band at (1681) cm^{-1} due to the (CO-N) of amide, absorption range at (1606) cm^{-1} due to (CH=N) imine group, The absorption range at (3034) cm^{-1} due to (C-H) aromatic, Absorption range at (1317, 1512) cm^{-1} due to (NO_2) nitro group, in the compound [B8].appearance of the absorption band at (3552) cm^{-1} due to (O-H), absorption band at (3412) cm^{-1} due to the (N-H), absorption range at (1618) cm^{-1} due to (CH=N) imine group, The absorption range at (3068) cm^{-1} due to (C-H) aromatic, Absorption range at (1662) cm^{-1} due to (CO-N) of amide, in the compound [B9]. appearance of the absorption band at (3441) cm^{-1} due to (O-H) phenol, absorption band at (3219) cm^{-1} due to the (N-H), absorption range at (1654) cm^{-1} due to (C=N) endocycle of imidazole, The absorption range at (1155) cm^{-1} due to (OCH3) ether, Absorption range at (2929) cm^{-1} due to (C-H) aliphatic, absorption range at (1635) cm^{-1} due to (C=N) of formazane, absorption band at (1367,1415,1456) cm^{-1} due to the (-N=N-) of formazan in the compound [B10]. appearance of the absorption band at (3550) cm^{-1} due to (O-H), absorption band at (3414) cm^{-1} due to the (N-H), absorption range at (1681) cm^{-1} due to (C=N) endocycle of imidazole, The absorption range at (1232) cm^{-1} due to (OCH3) ether, Absorption range at (2962) cm^{-1} due to (C-H) aliphatic, absorption range at (1635) cm^{-1} due to (C=N) of formazan, absorption band at (1382,1435,1483) cm^{-1} due to the (-N=N-) of formazan, absorption band at (769) cm^{-1} due to the (C-Cl), in the compound [B11]. appearance of the absorption band at (3441) cm^{-1} due to (O-H) phenol, absorption band at (3319) cm^{-1} due to the (N-H), absorption range at (1653) cm^{-1} due to (C=N) formazan, The absorption range at (1172) cm^{-1} due to (OCH3) ether, Absorption range at (2966) cm^{-1} due to (C-H) aliphatic, absorption range at (3030) cm^{-1} due to (C-H) of, absorption band at (1382,1406,1438) cm^{-1} due to the (-N=N-) of formazan, absorption band at (1307,1516) cm^{-1} due to the (NO2), in the compound [B12]. Appearance of the absorption band at (3444) cm^{-1} due to (O-H) phenol, absorption band at (3350) cm^{-1} due to the (N-H), absorption range at (1620) cm^{-1} due to (C=N) formazan, The absorption range at (1222) cm^{-1} due to (OCH3) ether, Absorption range at (2989) cm^{-1} due to (C-H) aliphatic, absorption band at (1346,1384,1463) cm^{-1} due to the (-N=N-) of formazan, absorption band at (1662) cm^{-1} due to the (CO-N) carbonyl of amide, absorption band at (1643) cm^{-1} due to the (C=N) endocycle of thiazole, absorption band at (617) cm^{-1} due to the (C-S), in the compound [B13]. absorption band at (3468) cm^{-1} due to the (N-H), absorption range at (1625) cm^{-1} due to (C=N) formazan, The absorption range at (1689) cm^{-1} due to (CO-N) carbonyl of amide, Absorption range at (1350,1519) cm^{-1} due to (N02), absorption band at (788) cm^{-1} due to the (C-Cl), absorption band at (1625) cm^{-1} due to the (C=N) of formazan, absorption band at (1382,1400,1469) cm^{-1} due to the (-N=N-) of formazan in the compound [B14]. appearance of the absorption band at (3373) cm^{-1} due to (O-H), absorption band at (3207) cm-1 due to the (N-H), absorption range at (1631) cm^{-1} due to (C=N) formazan, The absorption range at (1690) cm^{-1} due to (CO-N) carbonyl of amide, Absorption range at (3321) cm^{-1} due to (NH) amide, absorption band at (1307,1355,1429) cm^{-1} due to the (-N=N-) of formazan, appearance of the absorption band at (1654) cm^{-1} due to (C=N) endocycle of imidazole, in the compound [B15]. appearance of the absorption band at (3410) cm^{-1} due to (O-H), absorption band at (3224) cm^{-1} due to the (N-H) in imidazole, absorption range at (1690) cm^{-1} due to (CO-N) of amide, The absorption range at (1670) cm^{-1} due to (C=N) endocycle of imidazole, Absorption range at (2916) cm^{-1} due to (C-H) aliphatic, absorption band at (1371,1433,1508) cm^{-1} due to the (-N=N-) of formazan, appearance of the absorption band at (1651) cm^{-1} due to (C=N) of formazan, appearance of the absorption band at (3313) cm^{-1} due to (N-H) in antipyrine, appearance of the absorption band at (1327) cm^{-1} due to (C-N) in antipyrine, in the compound [B16].

^{1}H.NMR-Spectrum

The emergence of a signal in all spectra of (^{1}H. NMR) for all compounds at (2.50) due to the used dmso-d6 solvent., H.NMR-Spectrum of compounds showed signal at ϭ (5.23) for one proton of amine group (NH2), signal at ϭ (3.70) ϭ for protons of amine (N H) in imidazole ring, two signal at and ϭ (6.74-7.66) for protons of aromatic rings in the compound [B1]. Showed signal at ϭ (8035) for one proton of imine group (CH=N), signal at ϭ (4.22) for protons of amine (N-H) in imidazole, signal at (3.44) for protons of the methoxy group (-OCH3), signal at ϭ (10.90) for protons of hydroxyl group (OH) in phenol, signal at ϭ (7.97-6.70) for protons of aromatic rings in the compound [B2]. Also appearance of signal at ϭ (4.20) for one proton of amine group (NH) in imidazole ring, signal at ϭ (8.19) for protons of imine group (N=CH) in the compound as a result of the formation of the Schiff base in the new compound and the disappearance of the amine signal (NH2). In the compound [B3]. A signal at ϭ (8.50) for the imine group protons (N = CH), sign at ϭ (10.0) for hydroxyl group (OH) protons in phenol, signal at ϭ (7.90-6.86) for aromatic ring protons in compound [B4]. Appearance a signal at ϭ (9.30) for one proton of the amide group (CO-NH), a signal at (4.20) for the amine group protons (NH_2), signal at ϭ (7.71-6.64) for aromatic ring protons, in the compound [B6]. show a signal at ϭ (9.97) for one proton of the amide group (CO-NH) in the imidazole ring, a signal at ϭ (8.30) for the imine group protons (N = CH), sign at ϭ (10.89) for hydroxyl group (OH) protons in phenol, signal at ϭ (7.95-6.97) for aromatic ring protons Signal at ϭ (3.75) for methoxy group protons (-OCH3), in the compound [B7]., a signal at ϭ

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(9.76) for one proton of the amide group (CO-NH), a signal at (8.45) for the imine group proton (CH=N), signals at ϭ (7.96-6.72) for aromatic ring protons, in the compound [B8]., a signal at ϭ (9.0) for one proton of the amide group (CO-NH), a signal at ϭ (8.26) for the imine group proton (CH=N), signals at ϭ (7.95-6.60) for aromatic ring protons, sign at ϭ (10.27) for hydroxyl group (OH) protons in phenol, in the compound [B9]. Showed a signal at ϭ (5.14) for one proton from the amine group (NH) in the imidazole ring, and signals at ϭ (7.85-6.69) for the protons of the aromatic ring, and a signal at (10.32) and another at ϭ (10.77) for the hydroxyl group of the proton (OH) repetitive and different environments. In the compound in the phenol rings, the signal at ϭ (3.77) for the protons of the methoxy group (-OCH3). And disappearance of the signal belonging to the proton of the amine group as a result of its association with a formazan group (-N = N-C = N-) [B10]. Show a signal at ϭ (5.5) for one proton from the amine group (NH) in the imidazole ring, signals at ϭ (7.85-6.75) for the aromatic ring protons, sign at (10.32) for the hydroxyl proton group (OH) in the phenol, A signal at ϭ (3.78) for the protons of the methoxy group (-OCH3)., And disappearance of the signal belonging to the proton of the amine group as a result of its association with formazan group(-N = N-C = N-) In the compound [11]. Showed a signal at ϭ (5.65) for one proton from the amine group (NH) in the imidazole ring, and signals at (7.94-6.86) for the protons of the aromatic ring, and a signal at (10.17) for the hydroxyl group of the proton (OH). In the compound in the phenol, the signal at (3.5) for the protons of the methoxy group (-OCH3), And disappearance of the signal belonging to the proton of the amine group as a result of its association with formazan group (-N = N-C = N-) in the compound [12]. A signal at ϭ (9.03) for one proton from the amide group (NH-CO), signals at ϭ (7.90-6.67) for the protons of the aromatic ring, and a signal at ϭ (10.27) for the hydroxyl group of the proton (OH). In the compound, the signal at ϭ (3.75) for the protons of the methoxy group (-OCH3), And disappearance of the signal belonging to the proton of the amine group as a result of its association with the azoo-group to form a formazan complex (-N = N-C = N-) in the compound [13]. A signal at ϭ (9.52) for one proton from the amide group (NH-CO), signals at ϭ (7.83-6.55) for the protons of the aromatic ring, and disappearance of the signal belonging to the proton of the amine group as a result of its association with a formazan group (-N = N-C = N-) in the compound [14]. A signal at ϭ (9.07) for one proton from the amide group (NH-CO), signals at (7.69-6.64) for the protons of the aromatic ring, and a signal at ϭ (10.27) for the hydroxyl group of the proton (OH). Showed a signal at ϭ (5.5) for one proton from the amine group (NH), and disappearance of the signal belonging to the proton of the amine group as a result of its association with a formazan group (-N = N-C = N-) in the compound [15].

Showed a signal at ϭ (5.5) for one proton from the amine group (NH), signals at (7.83-6.77) for the protons of the aromatic ring, and a signal at (10.9) for the hydroxyl group of the proton (OH). A signal at ϭ (4.25) for one proton from the amine group (NH) in antipyrine ring, signal at ϭ (1.12) for protons from the methyl group (CH3), In the compound [16]

The ^{13}C.NMR spectra:

All compounds measured in C^{13}.NMR spectroscopy appeared at (40.0) due to the solvent (dmso-d6).

The compound was characterized with a spectrum of C.NMR13, show a signal due to the carbon of the amine group (CH=N) appeared at (150.0 ppm). A signal appeared at (60.0 ppm) due to the methoxy group (-OCH3). Several signals at (141.0-120.0 ppm) due to the carbon atoms in the aromatic rings in the compound [2]. Show a signal due to the carbon of the amine group (CH=N) appeared at (155.0 ppm). A signal appeared at (162.0 ppm) due to the carbon of amid group (CO-N). A signal appeared at (52.0 ppm) due to the carbon of methoxy group (-OCH3). Several signals at (146.0-115.0 ppm) due to the carbon atoms in the aromatic rings in the compound [7]. A signal appeared at (98.0 ppm) due to carbon from the formazan group (-N = N-C = N-) As a result of the disappearance of the carbon signal belonging to the amine group in the Schiff base to form the new compound, Formazan. A signal appeared at (160.7-163.0ppm) due to the carbon carbonyl group in amid (CO-N) recurring. An signal appeared at (58.0ppm) due to carbon in the Methoxy group (-OCH3). Several signals at (140.0-119.6 ppm) due to carbon atoms in the aromatic rings in the compound [12]. A signal appeared at (98.0 ppm) due to carbon from the formazan group (-N = N-C = N) As a result of the disappearance of the carbon signal belonging to the amine group in the Schiff base to form the new compound, Formazan. A signal appeared at (160.7-163.0ppm) due to the carbon carbonyl group in several amide groups in compound (CO-N). An signal appeared at (58.0ppm) due to carbon in the Methoxy group (-OCH3). Several signals at (140.0-119.6 ppm) due to carbon atoms in the aromatic rings in the compound [13].

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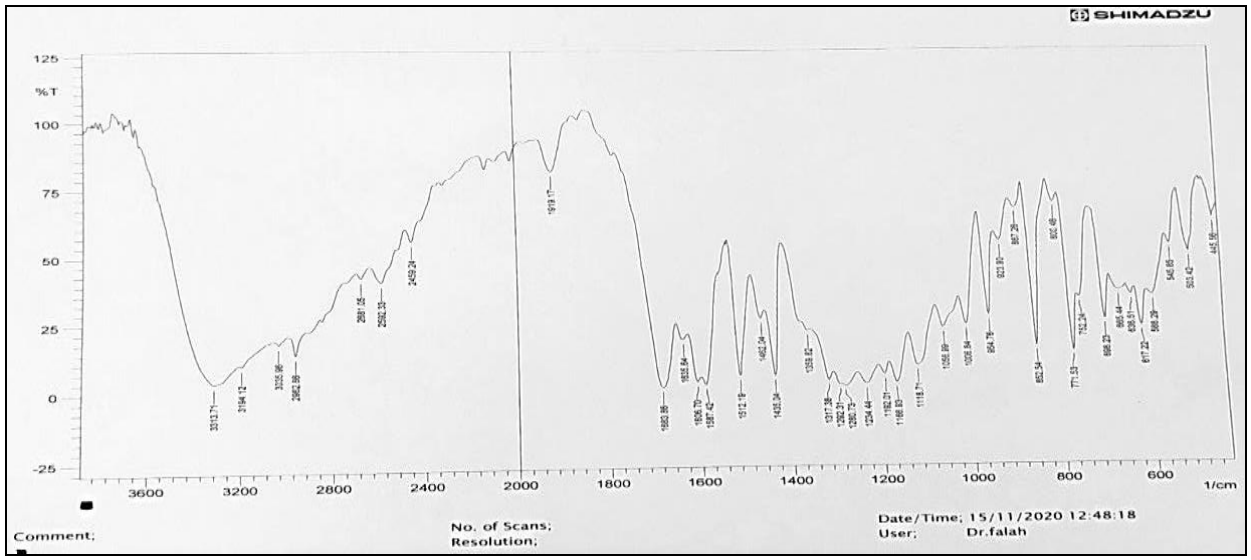

Fig. 1. FT.IR- Spectra of compound [1]

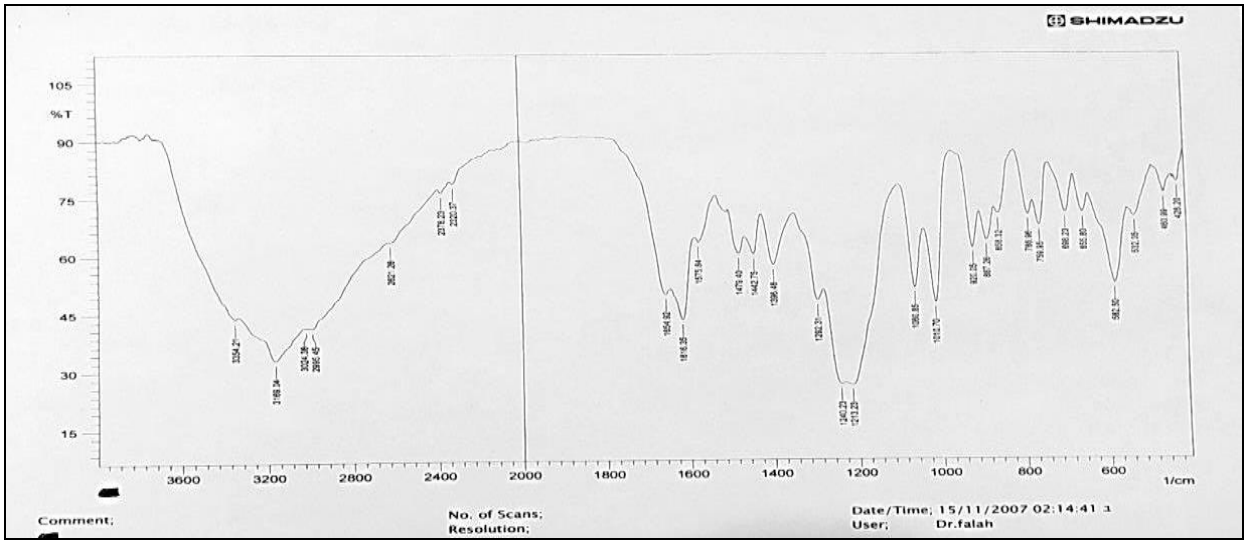

Fig. 2. FT.IR- Spectra of compound [2]

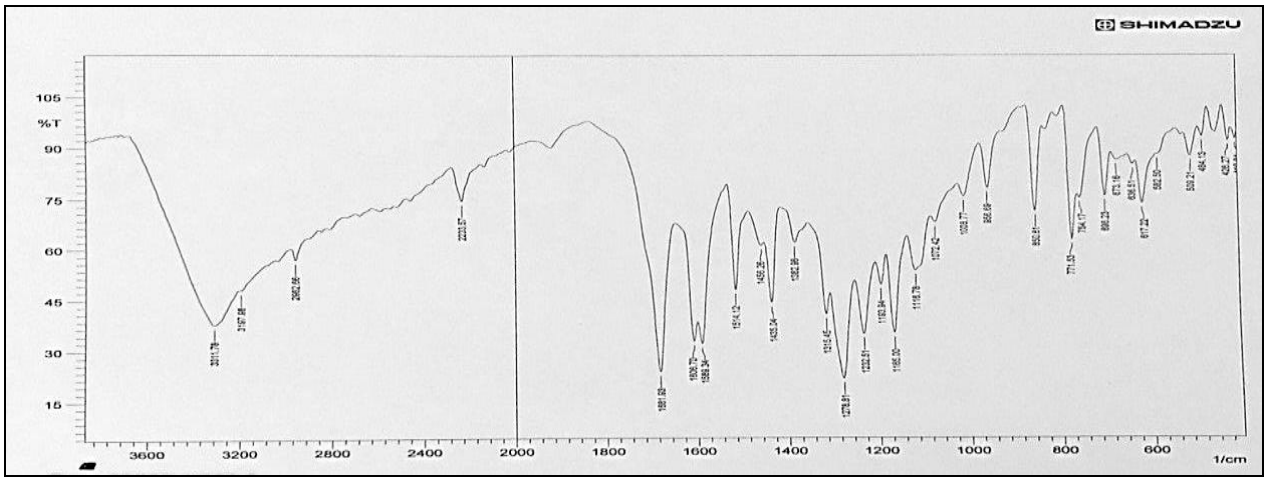

Fig. 3. FT.IR- Spectra of compound [3]

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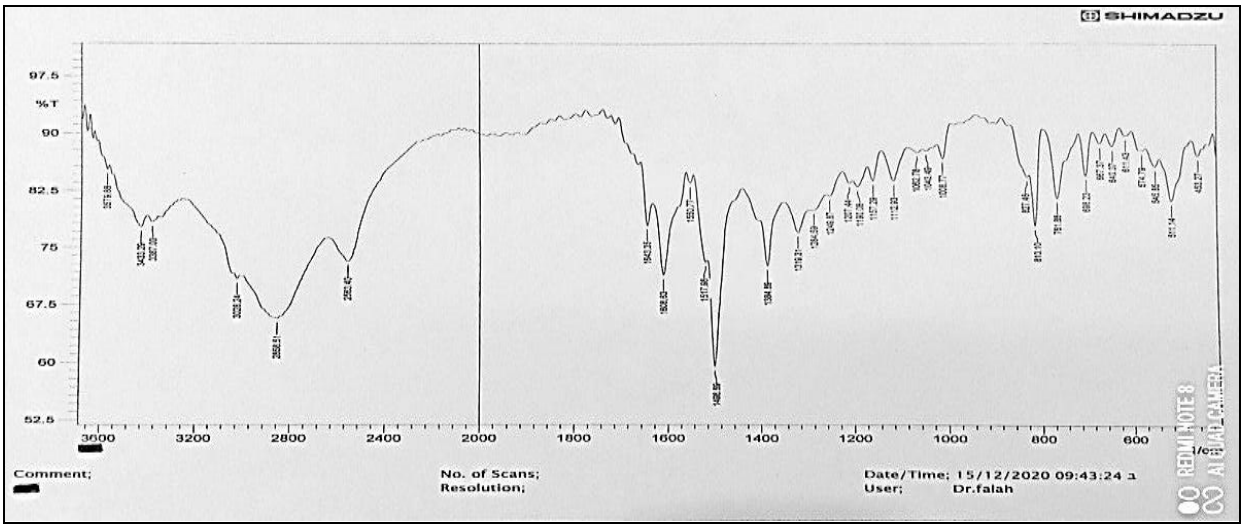

Fig. 4. FT.IR- Spectra of compound [4]

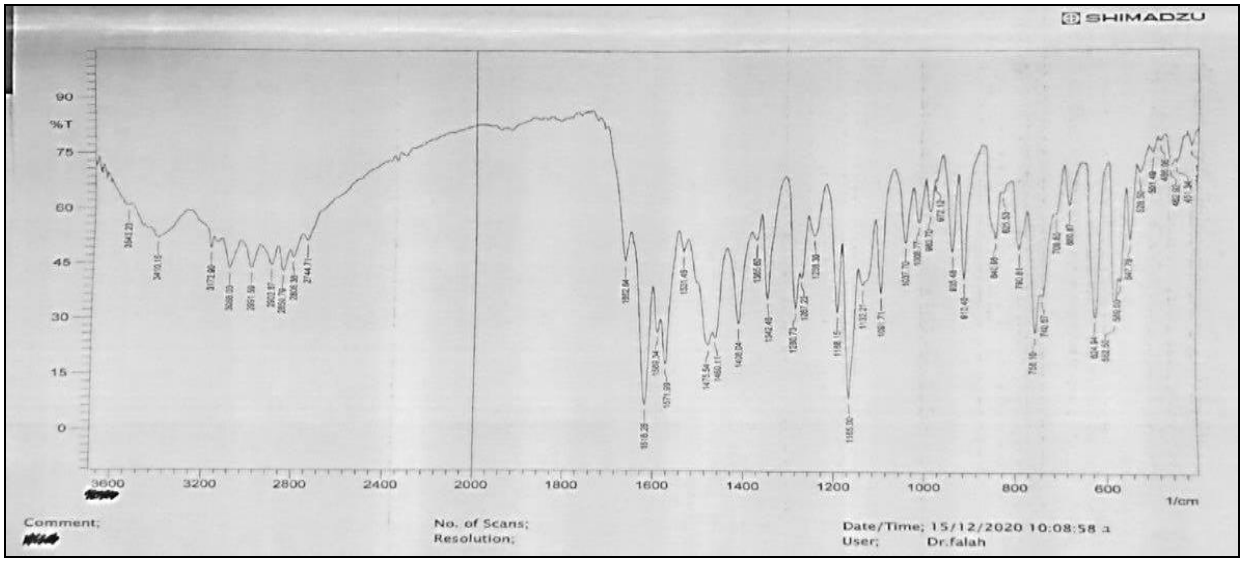

Fig. 5. FT.IR- Spectra of compound [5]

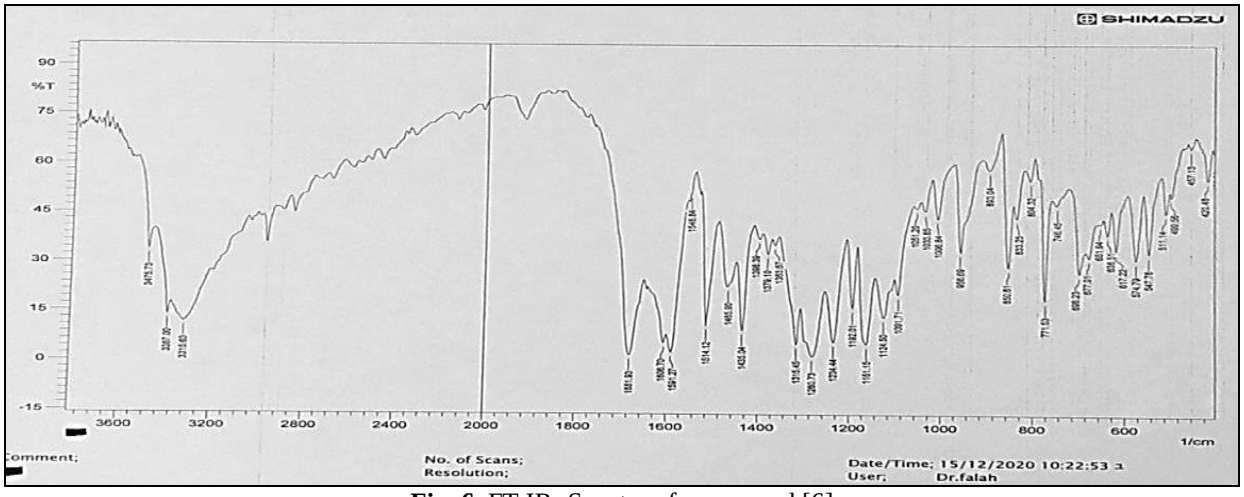

Fig. 6. FT.IR- Spectra of compound [6]

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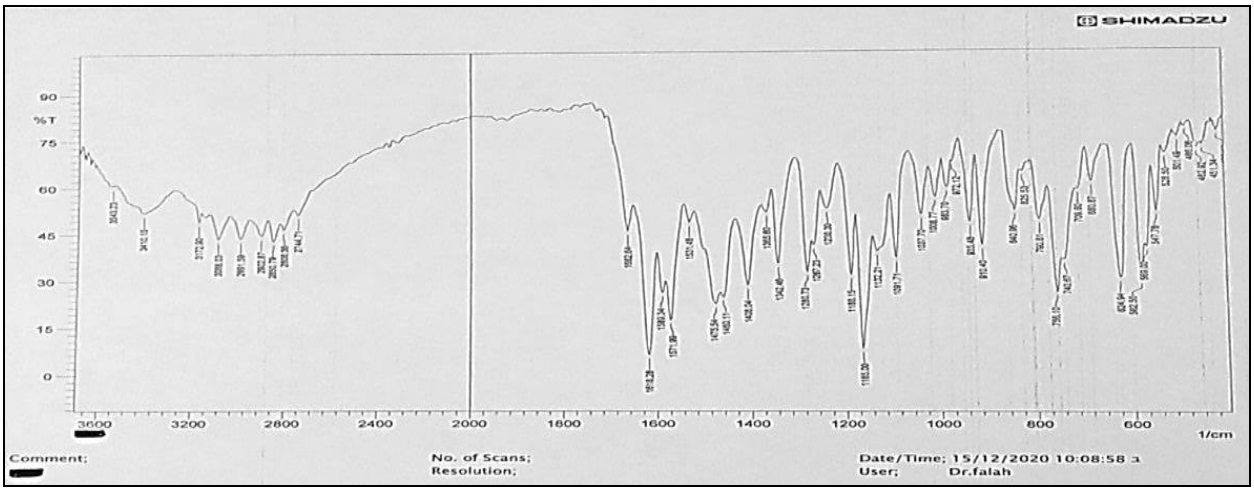

Fig. 7. FT.IR- Spectra of compound [7]

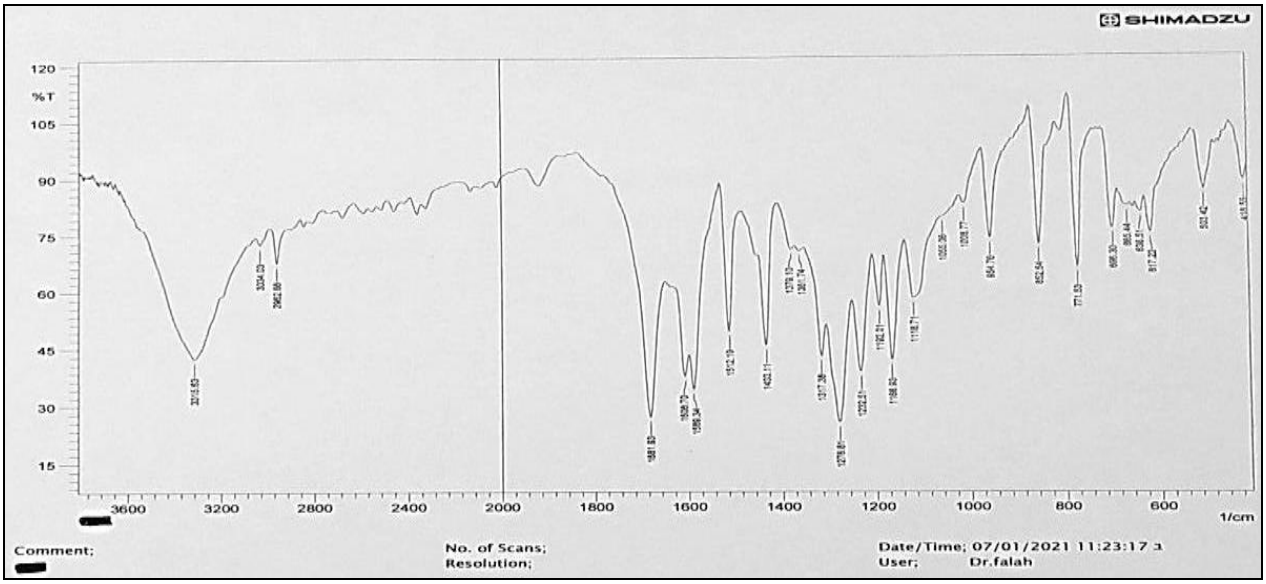

Fig. 8. FT.IR- Spectra of compound [8]

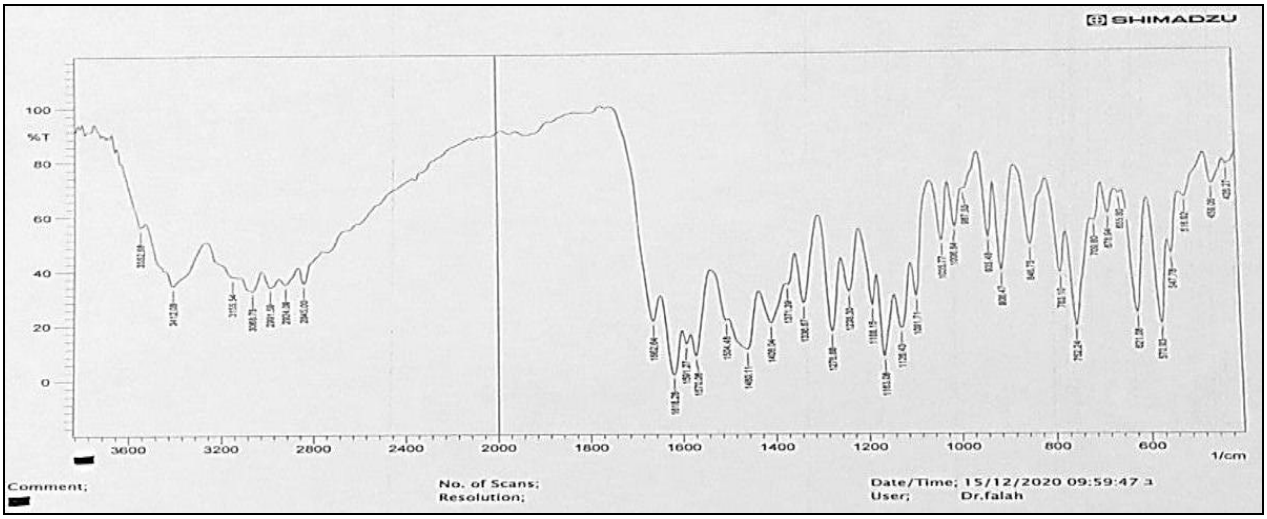

Fig. 9. FT.IR- Spectra of compound [9]

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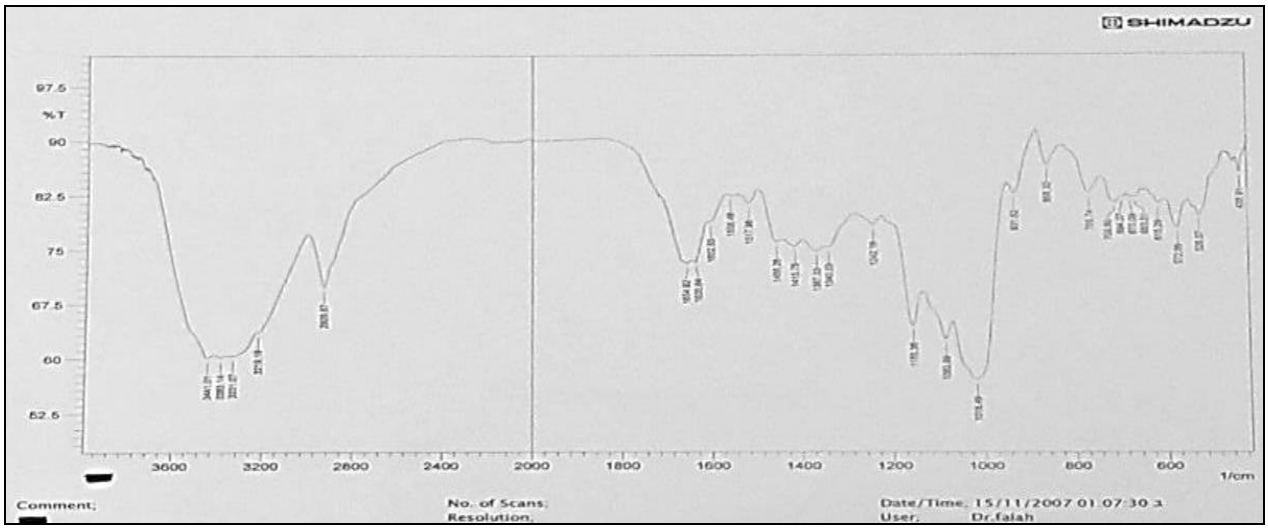

Fig. 10. FT.IR- Spectra of compound [10]

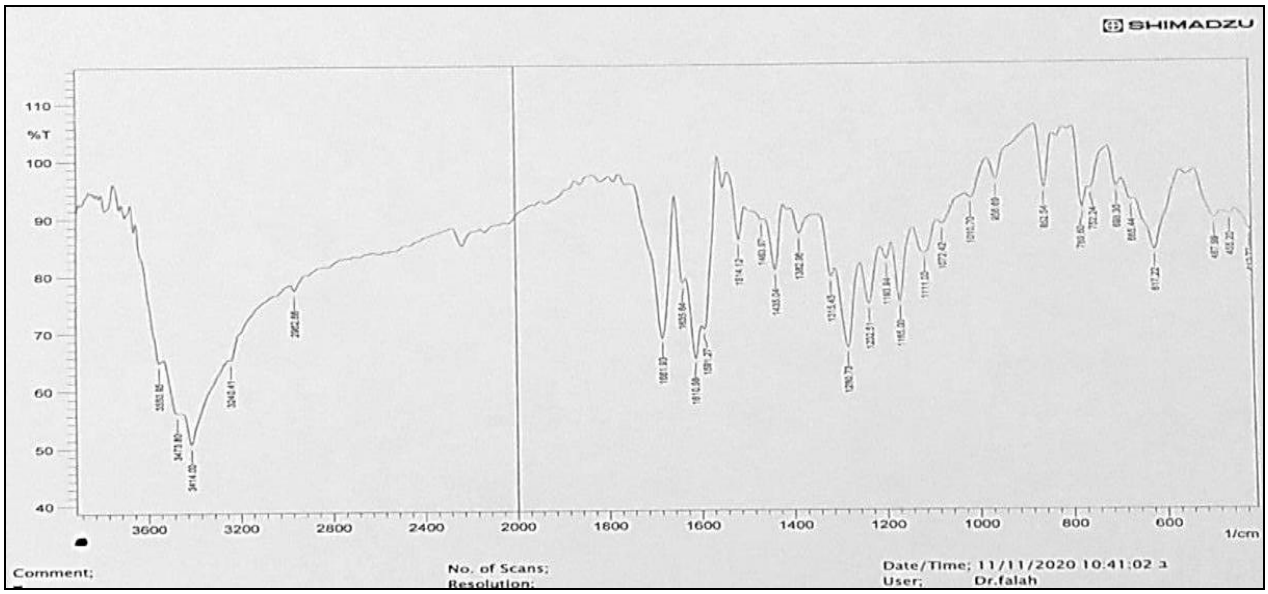

Fig. 11. FT.IR- Spectra of compound [11]

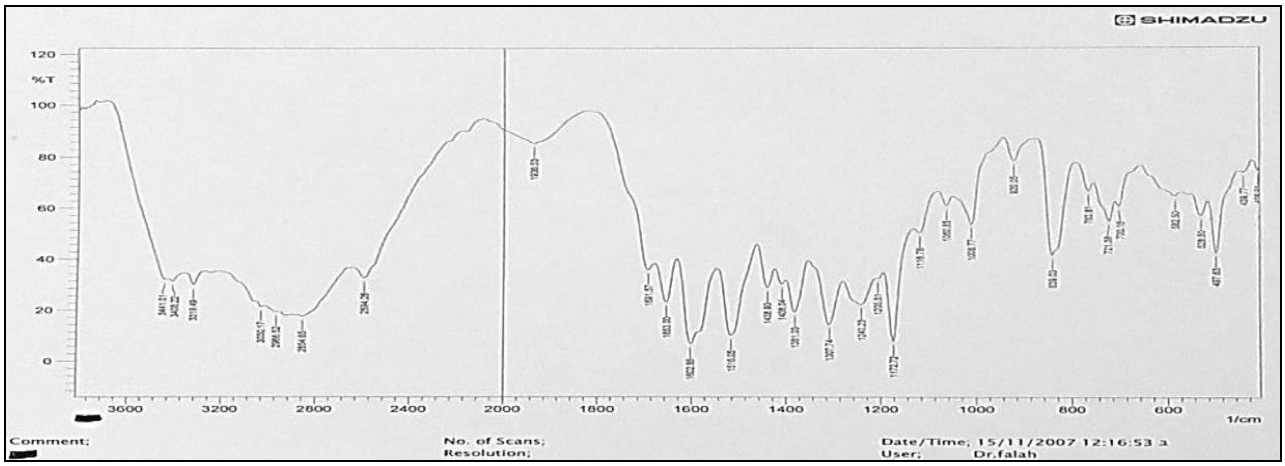

Fig. 12. FT.IR- Spectra of compound [12]

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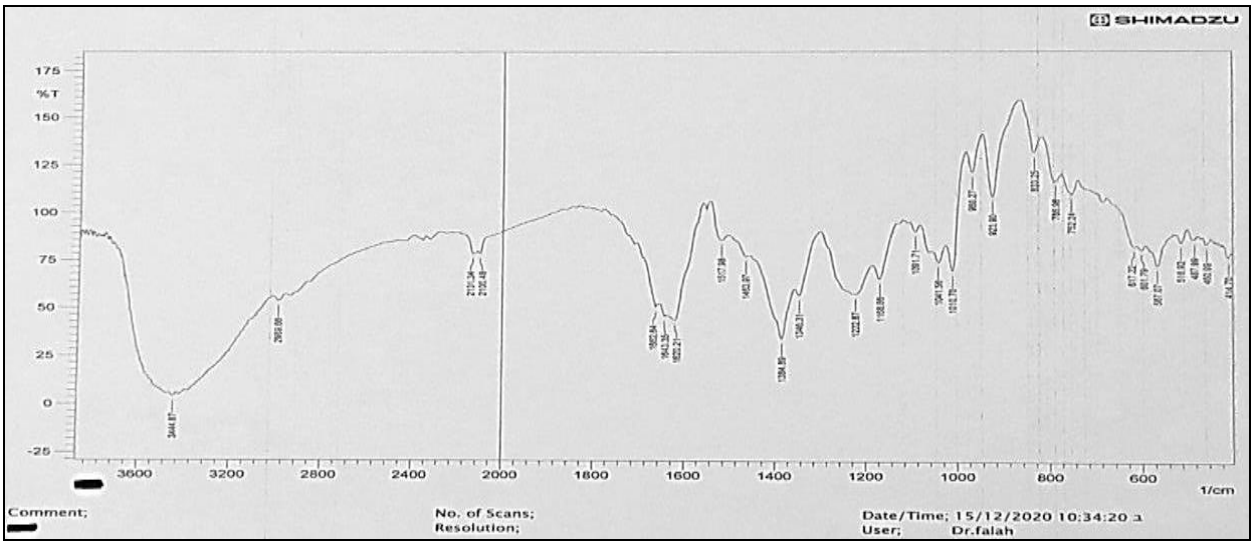

Fig. 13. FT.IR- Spectra of compound [13]

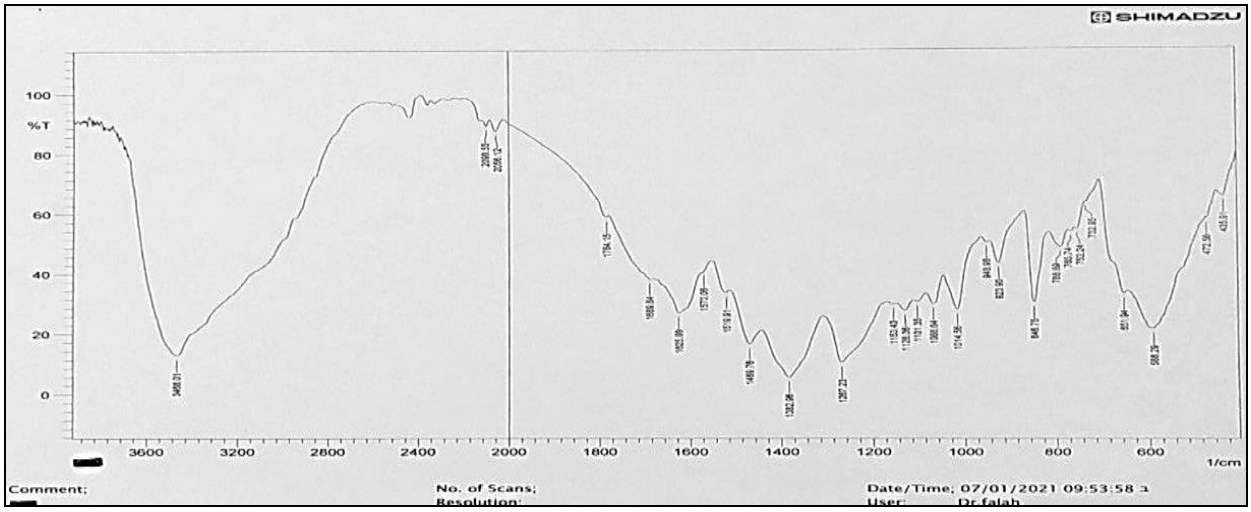

Fig. 14. FT.IR- Spectra of compound [14]

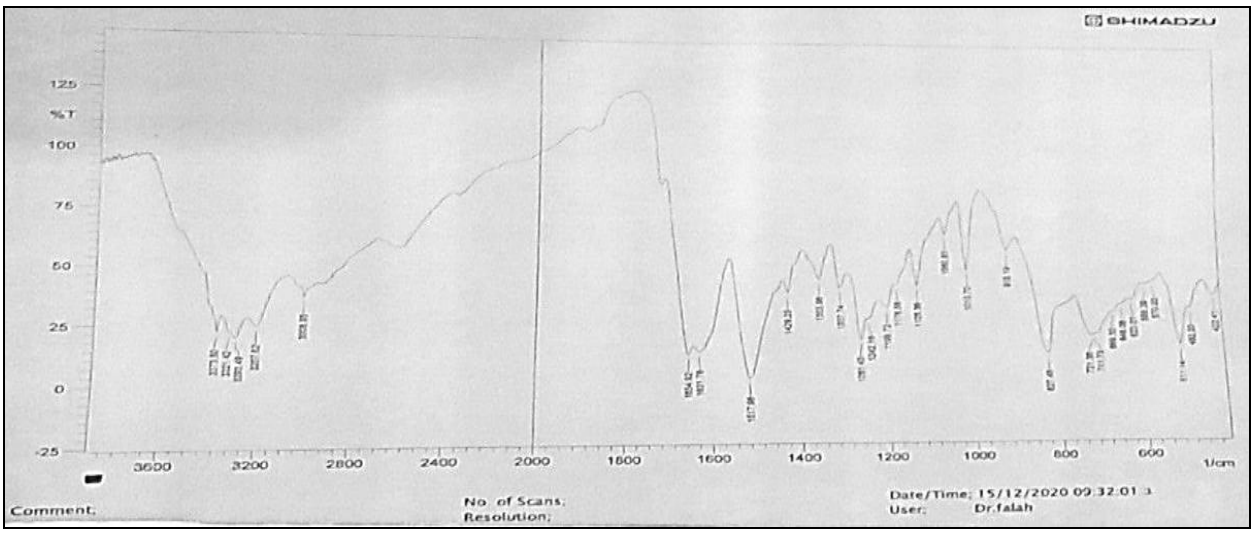

Fig. 15. FT.IR- Spectra of compound [15]

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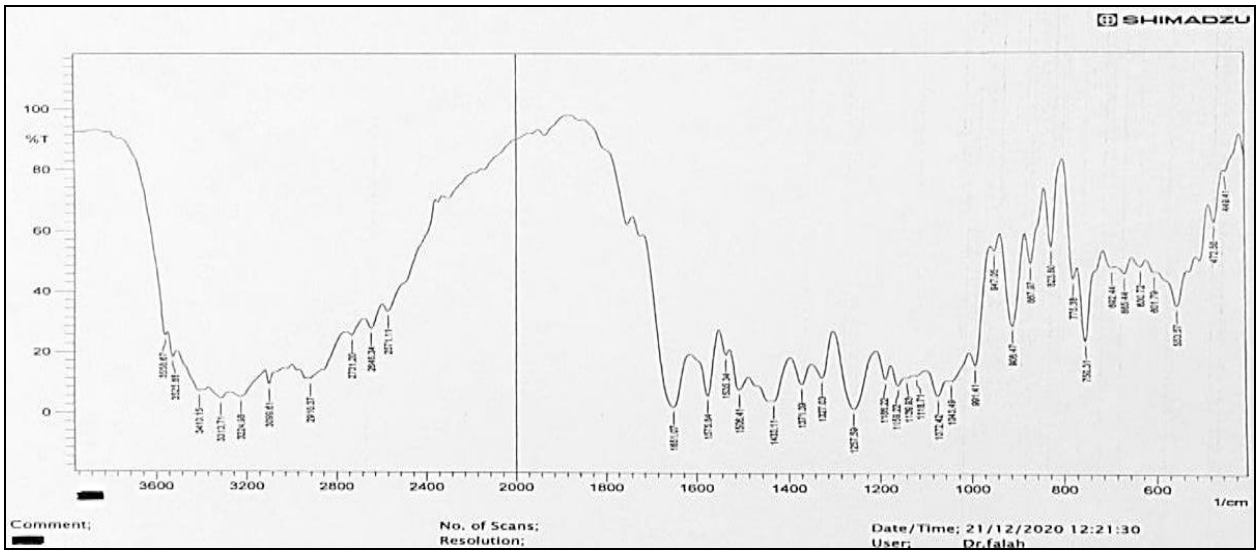

Fig. 16. FT.IR- Spectra of compound [16]

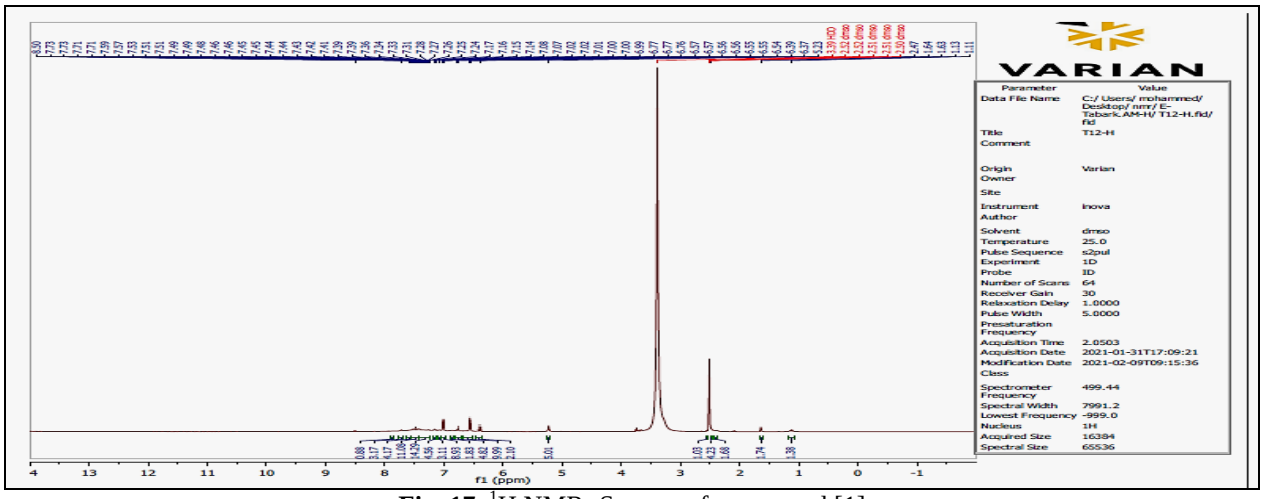

Fig. 17. ^{1}H.NMR- Spectra of compound [1]

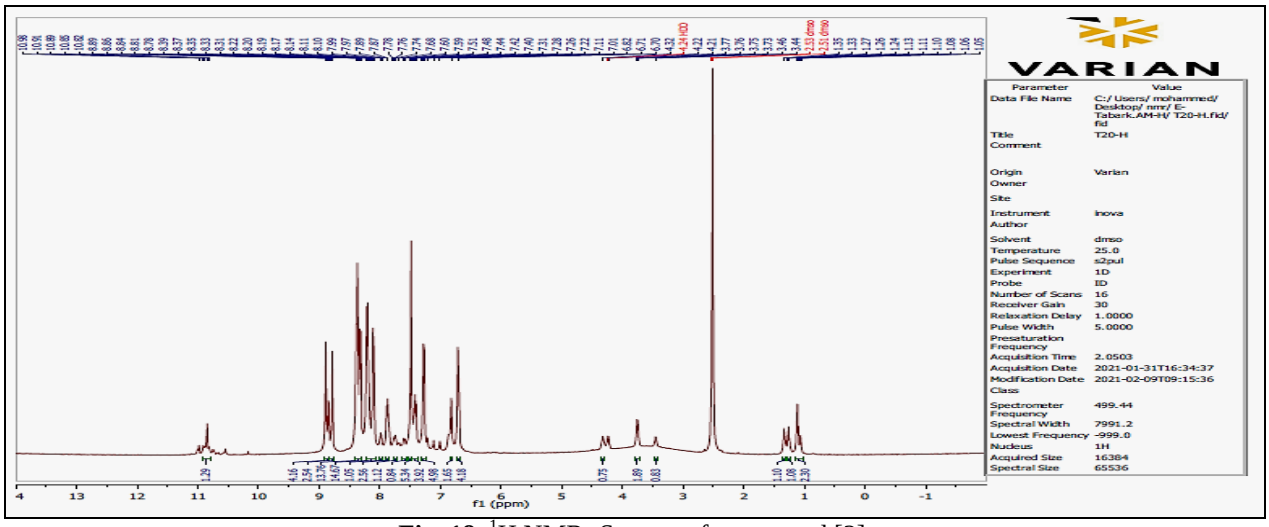

Fig. 18. ^{1}H.NMR- Spectra of compound [2]

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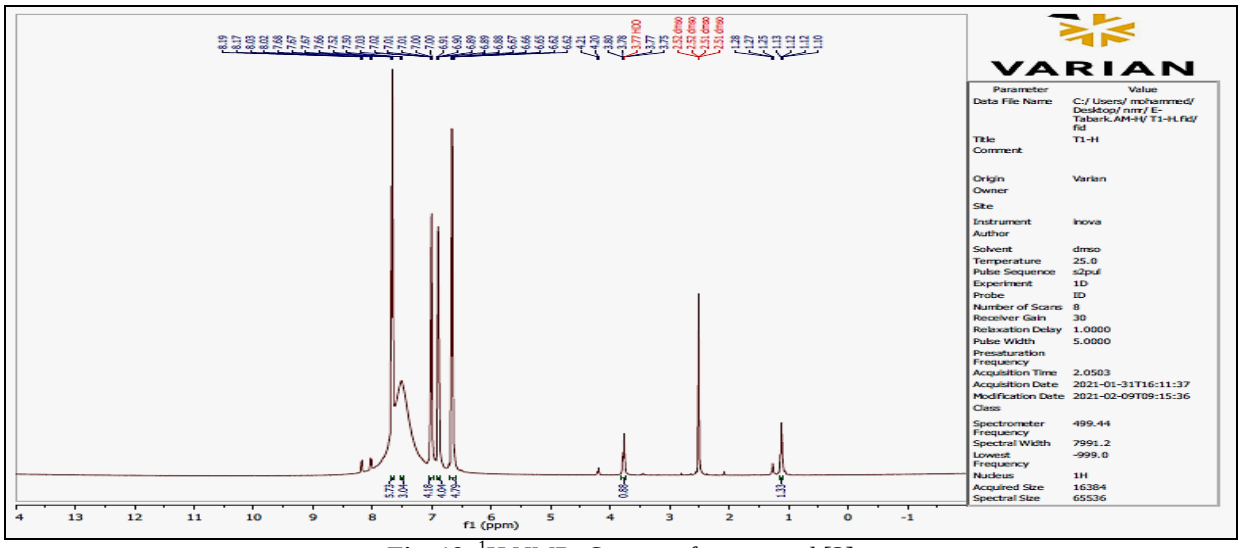

Fig. 19. ^{1}H.NMR- Spectra of compound [3]

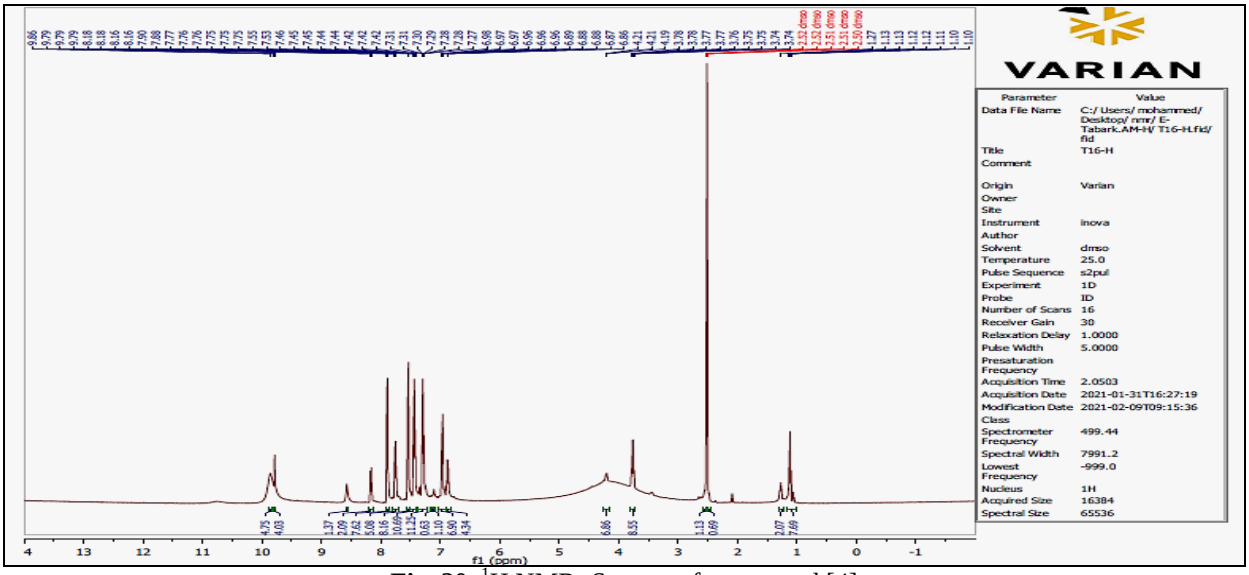

Fig. 20. ^{1}H.NMR- Spectra of compound [4]

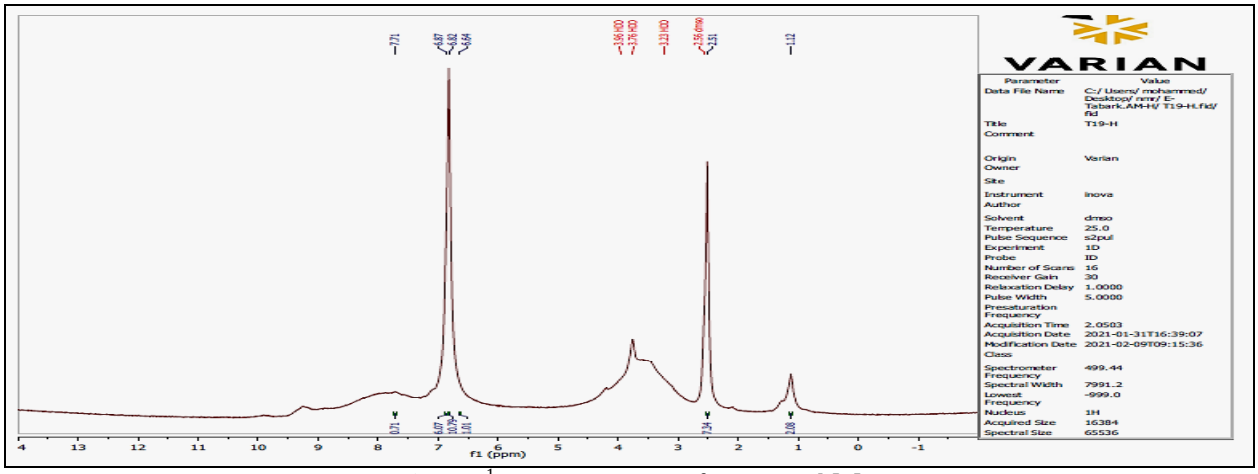

Fig. 21. ^{1}H.NMR- Spectra of compound [6]

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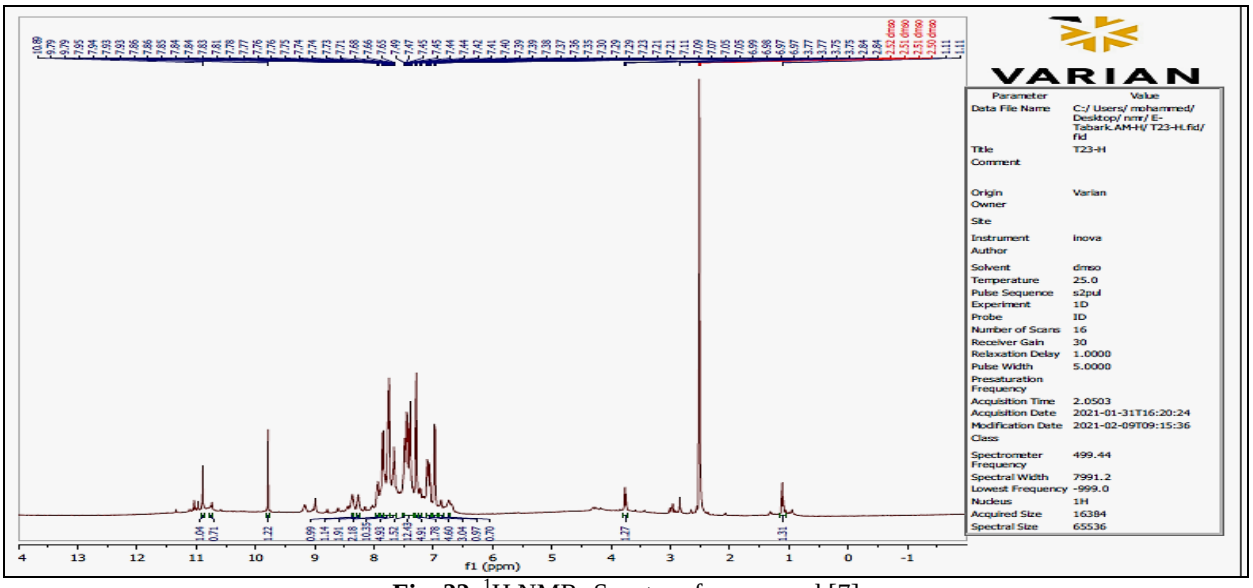

Fig. 22. ^{1}H.NMR- Spectra of compound [7]

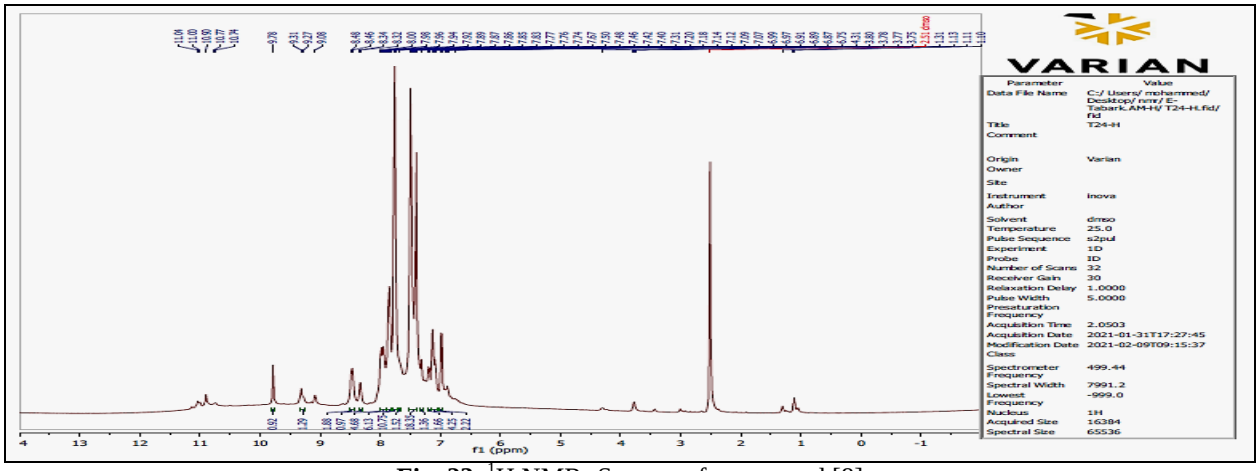

Fig. 23. ^{1}H.NMR- Spectra of compound [8]

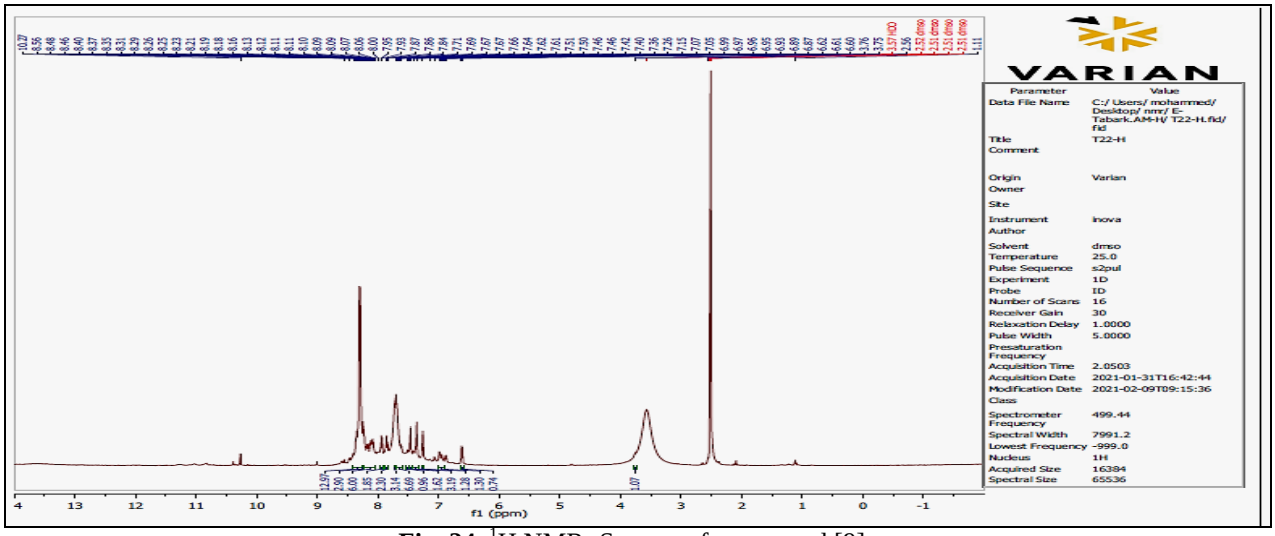

Fig. 24. ^{1}H.NMR- Spectra of compound [9]

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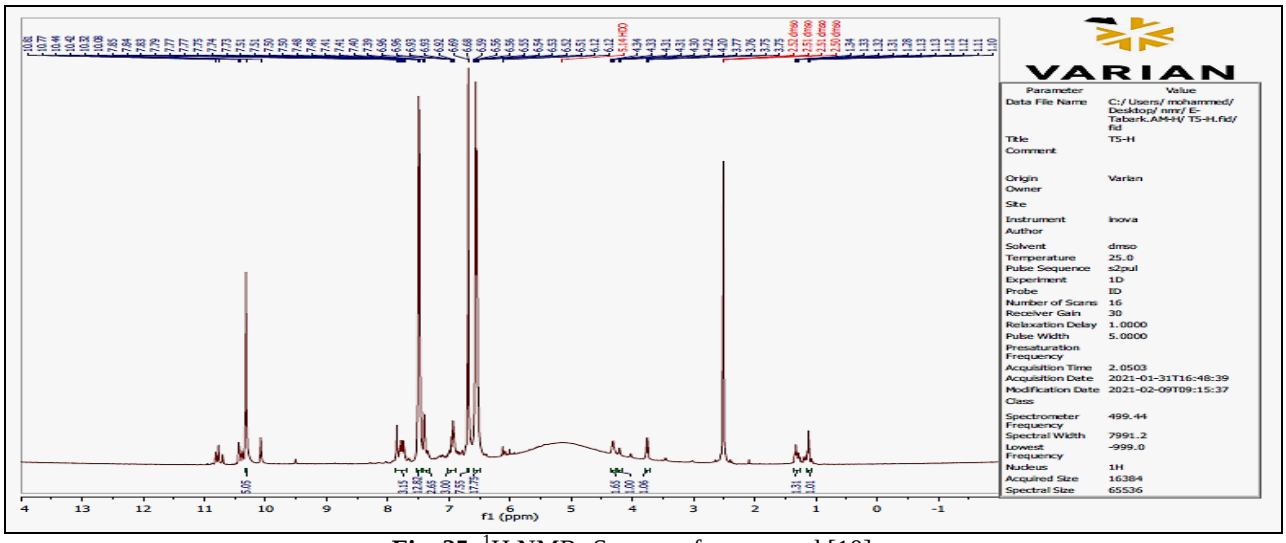

Fig. 25. ^{1}H.NMR- Spectra of compound [10]

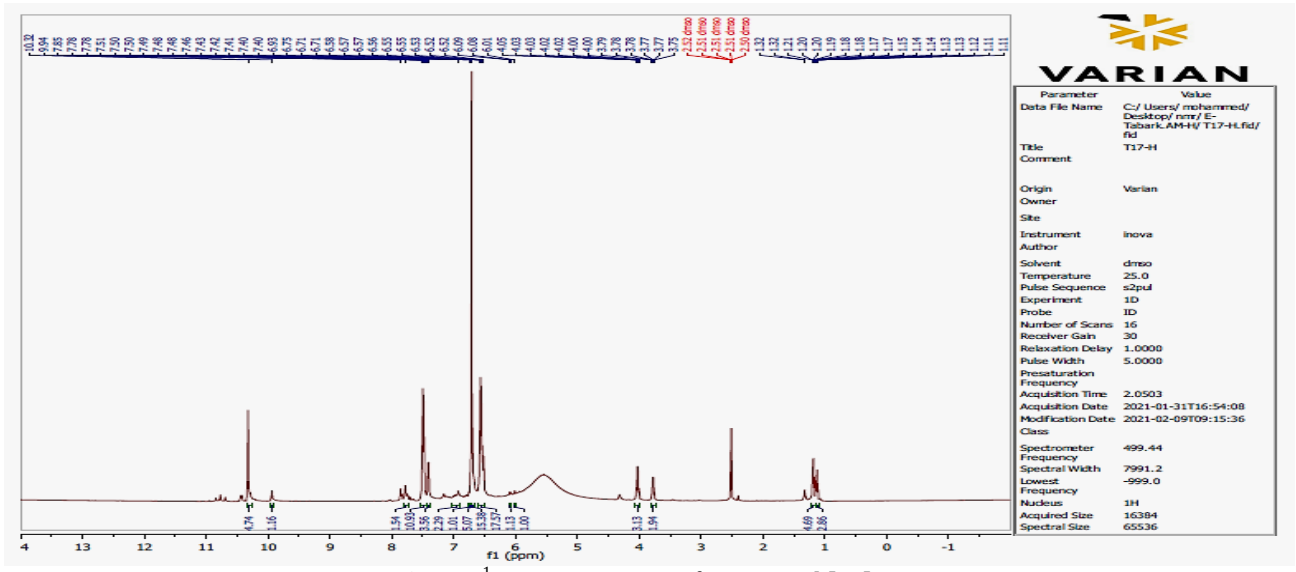

Fig. 26. ^{1}H.NMR- Spectra of compound [11]

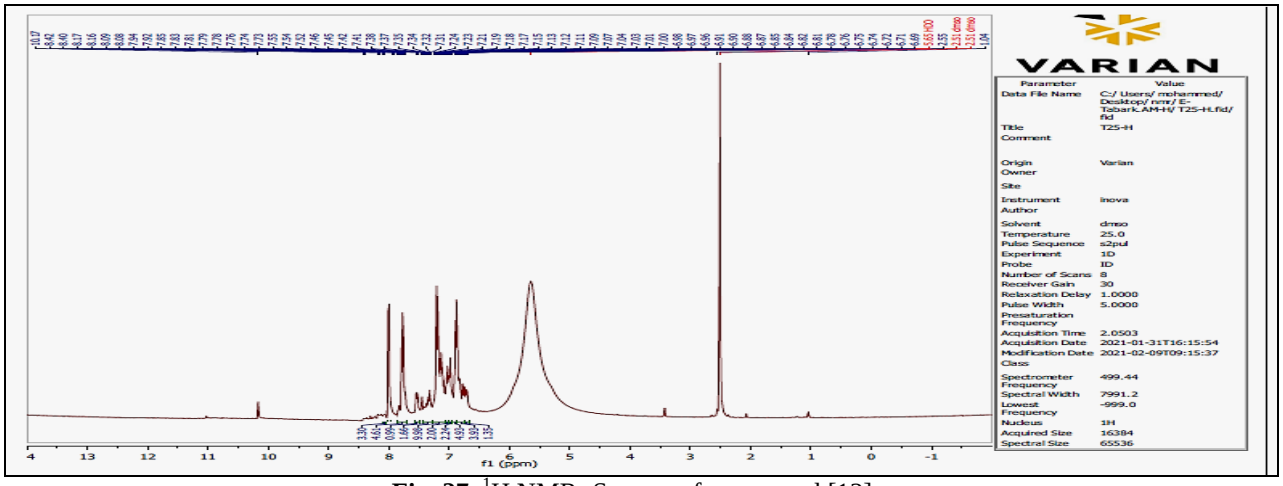

Fig. 27. ^{1}H.NMR- Spectra of compound [12]

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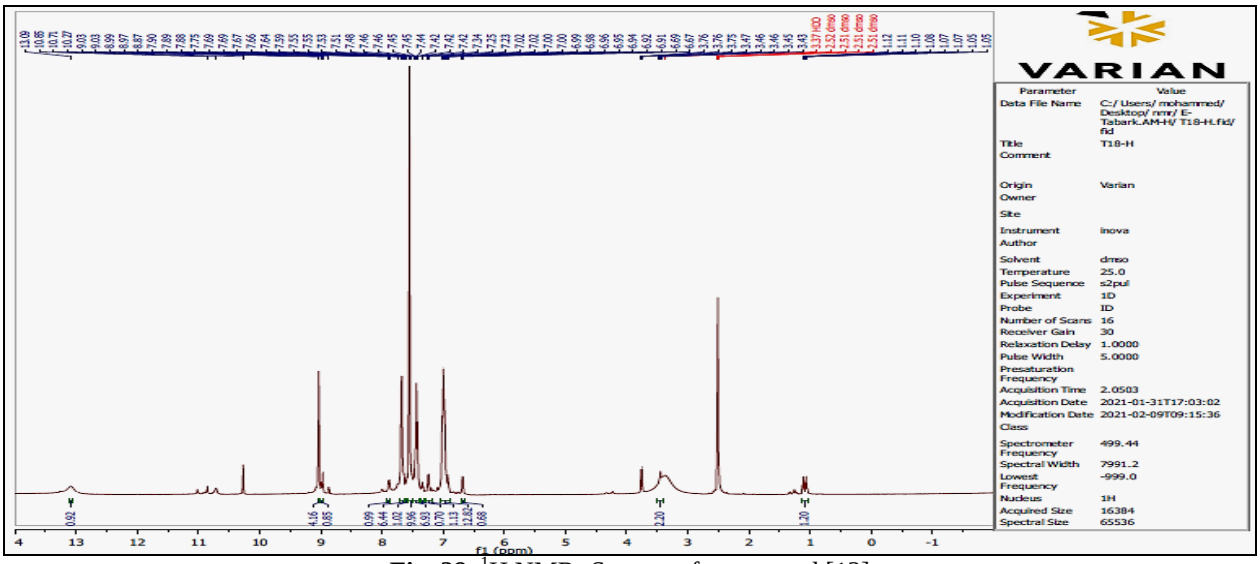

Fig. 28. ^{1}H.NMR- Spectra of compound [13]

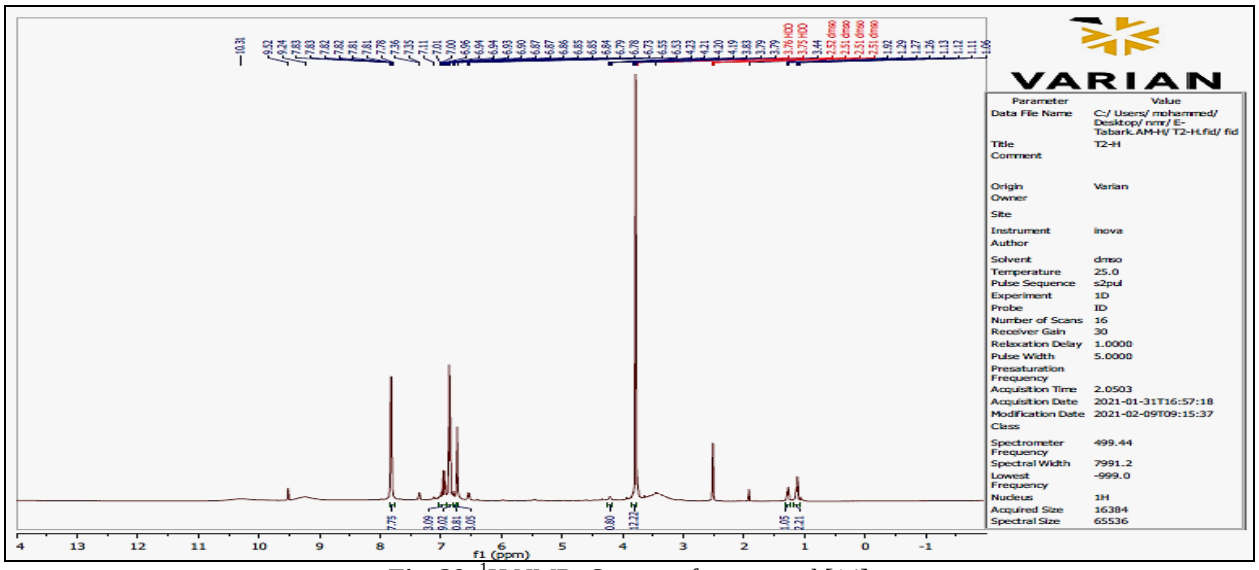

Fig. 29. ^{1}H.NMR- Spectra of compound [14]

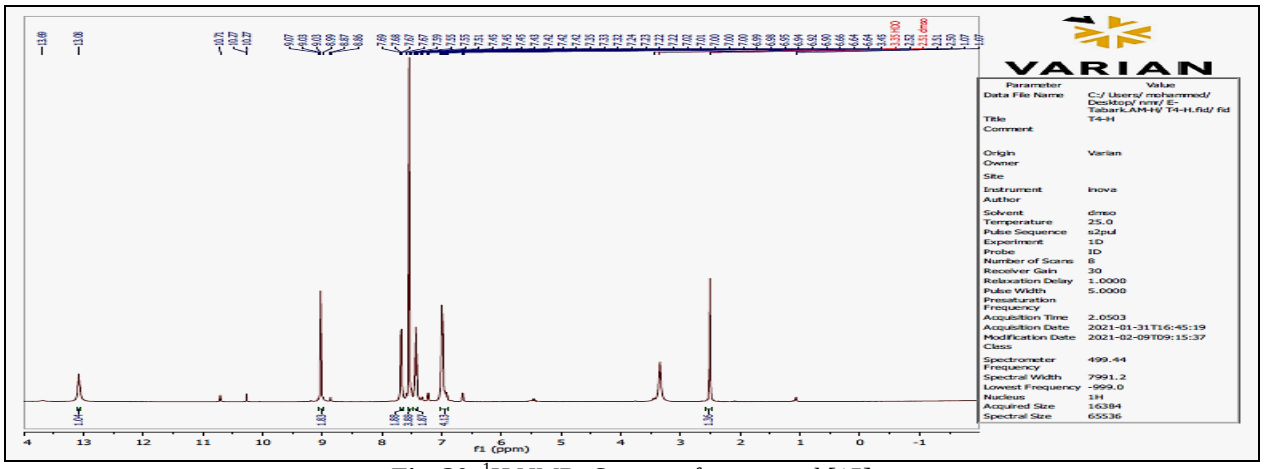

Fig. 30. ^{1}H.NMR- Spectra of compound [15]

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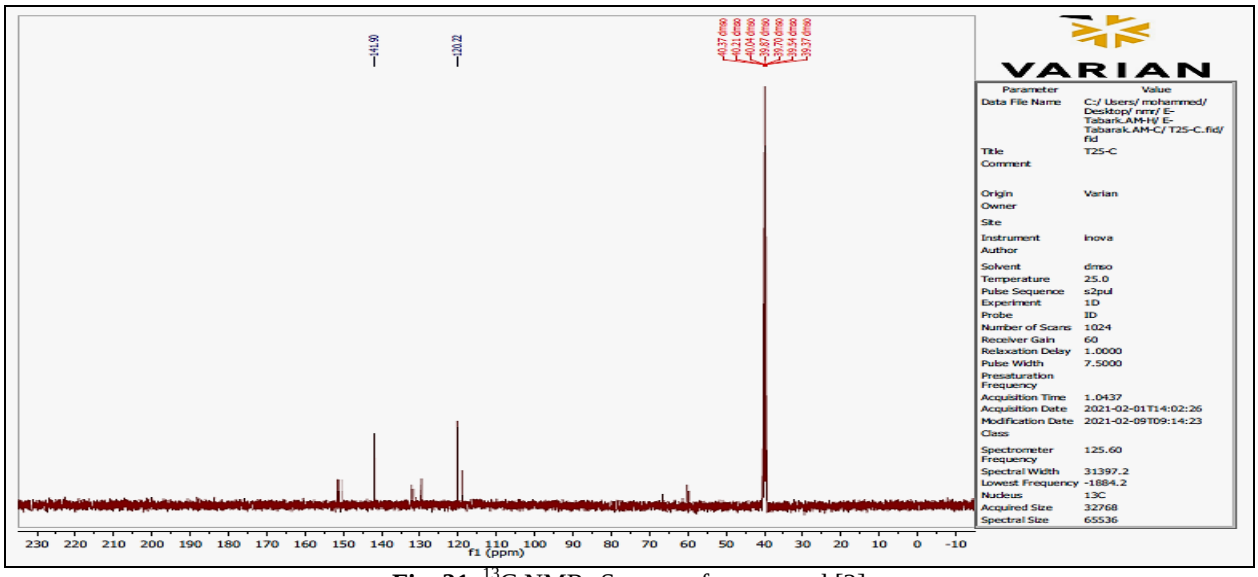

Fig. 31. ^{13}C.NMR- Spectra of compound [2]

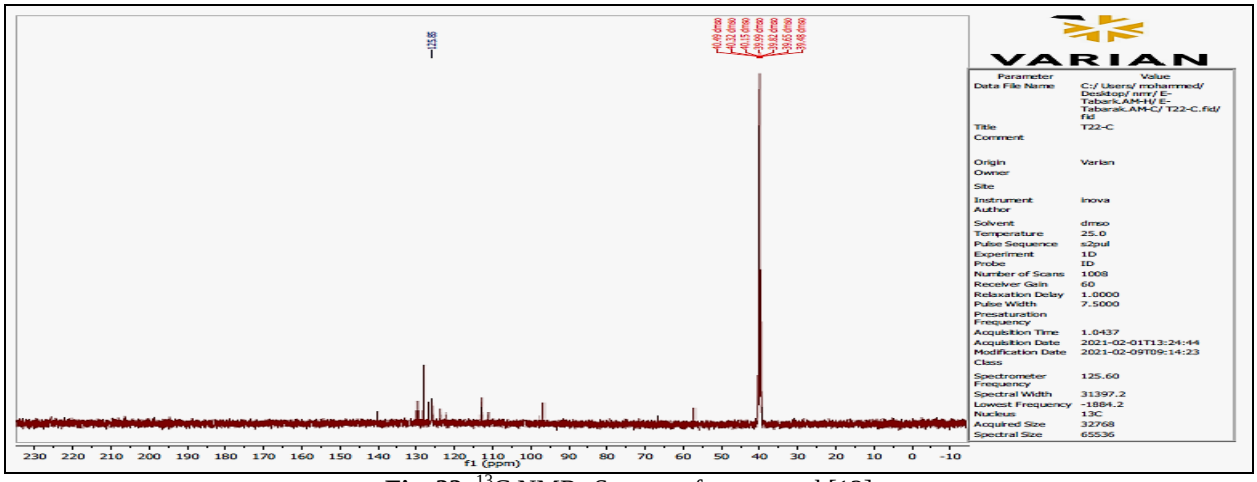

Fig. 32. ^{13}C.NMR- Spectra of compound [12]

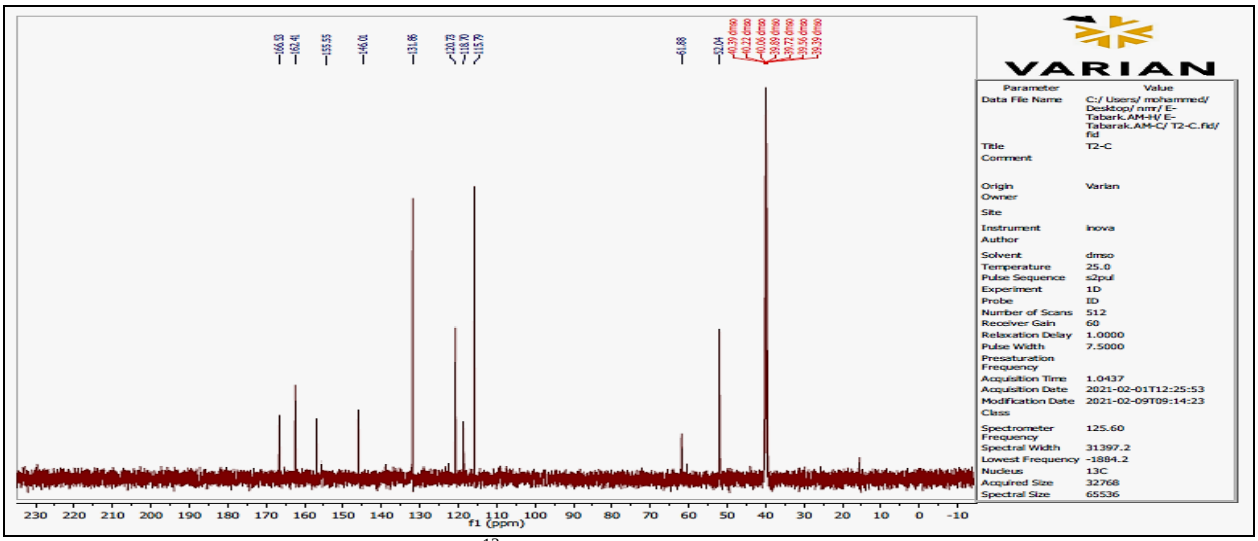

Fig. 33. ^{13}C.NMR- Spectra of compound [7]

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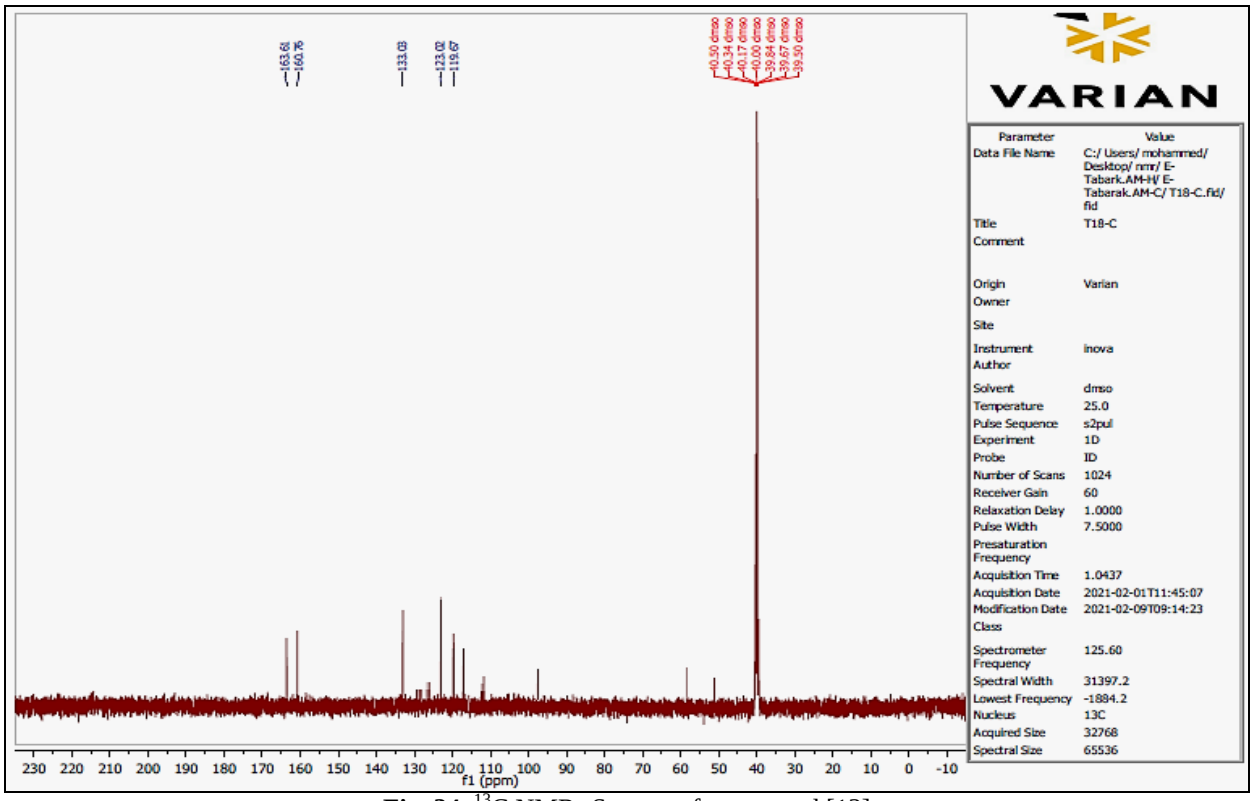

Fig. 34. ^{13}C.NMR- Spectra of compound [13]

Analysis of Compounds [10, 12, 13, 14, 15] by Gas Chromatography[21, 22]

Preparation of diluted solutions ((concentration of 1ppm for vehicles)) of compounds [**10, 12, 13, 14, 15**] after dissolved with ethanol was also attended by a mixture of compounds which prepared by mixing 10ml of each solution individually after shaking continuous., injected models by using a syringe(Hamilton) with a capacity of 10ml individually and then injected the mixture, and then install the measurement conditions through the use of nitrogen a gas flow of 25ml/min bus speeds and injection temperature was 25C° degrees higher than the temperature separation column and then use a flame ionization detector is 50C° higher than the temperatures of the column either column temperature programmed gradual increase of (90-160)C°, taking into consideration the maximum temperature to avoid damage to the column according to studies[21, 22]., Figures (35-39) illustrate the process of separating the compounds under study. It became clear from the figures that the first compound that was separated and compound (10) which is the lowest molecular weight and lowest polar compounds, where the separation depended on the polar influences of the compounds and also on the molecular weight of the compounds in the separation process, followed by the compound (12), then the compound (14), then the compound (15) In the end, the peak (13) was because it contained influences resulting from the polar groups in the boat that increased the time of its detention in the column. All data are shown in Table (1) and figures (35-39):

Table 1. Specification Used Capillary Columns

Liquid phase	Composition	Formula	Column dimension	Max operatory Temp.(M.O.T)	Polarity
DP5-25	2,3-di-o-propionyl-6-t-butyl silyl derivative of ɣ-cyclodextrin phase		0.25mm I.D 0.12 Mm d.f	(300) C°	Low polar
FS-BP10	14%Cyanopropyl phenyl poly siloxane		0.25mm I.D 0.25Mm d. f	-20C°-280C°-(300)C°	Moderately polar

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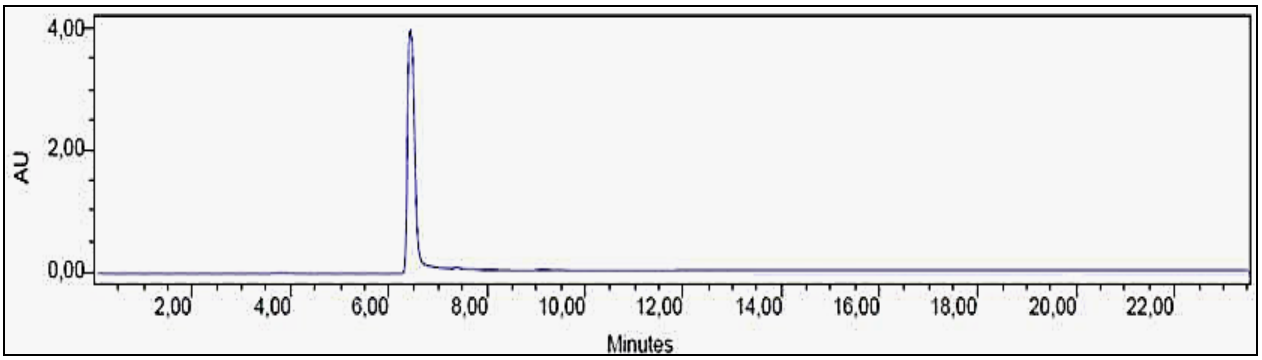

Fig. 35. Chromatogram of Comp.[10]

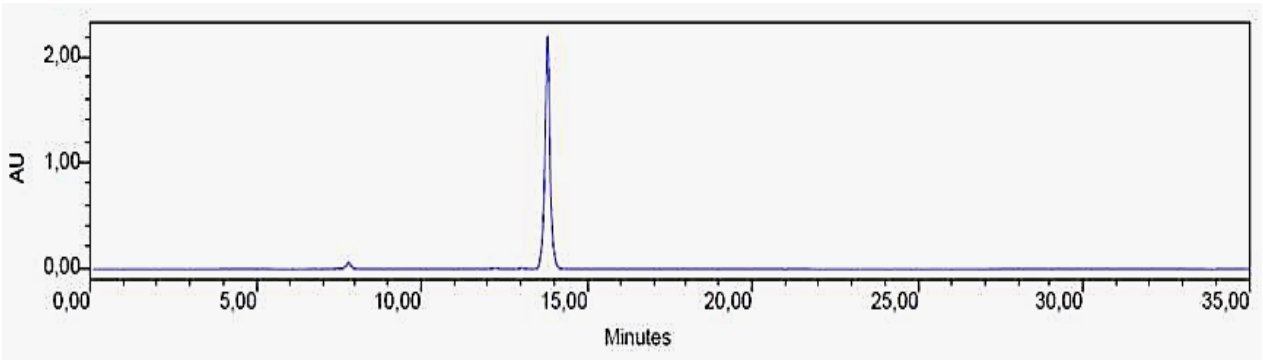

Fig. 36. Chromatogram of Comp.[12]

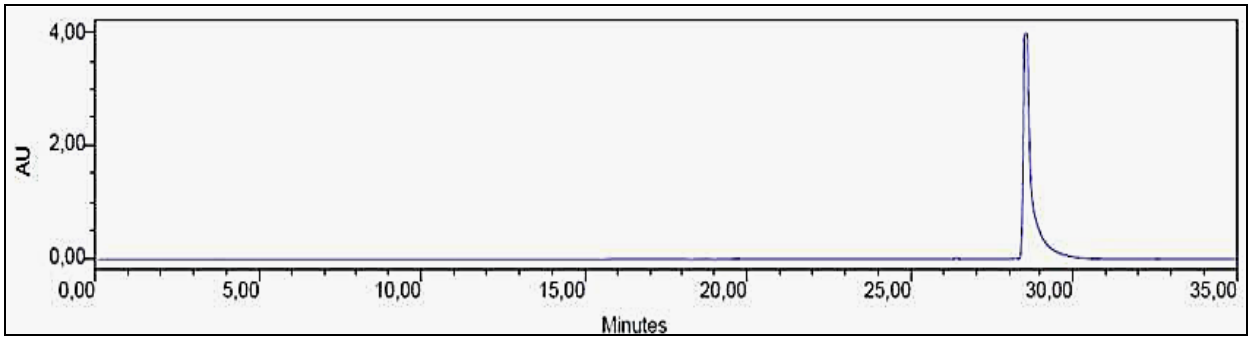

Fig. 37. Chromatogram of Comp.[13]

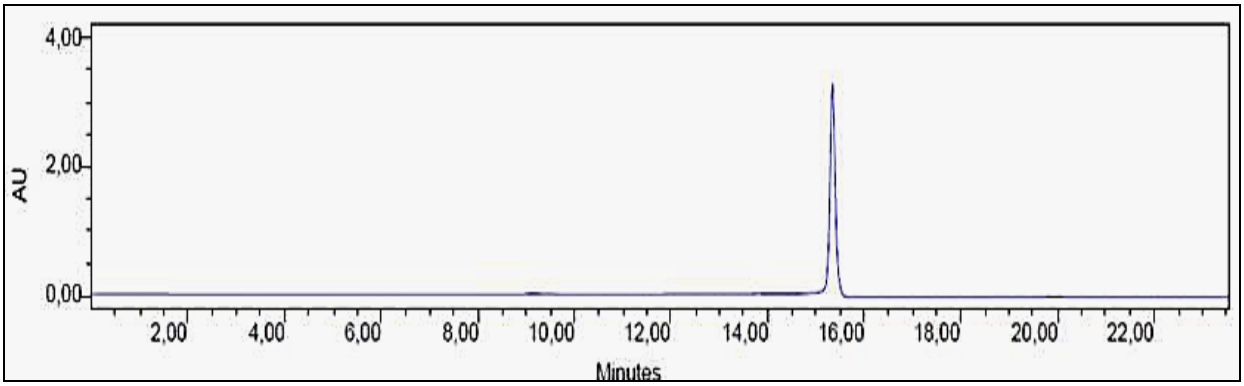

Fig. 38. Chromatogram of Comp.[14]

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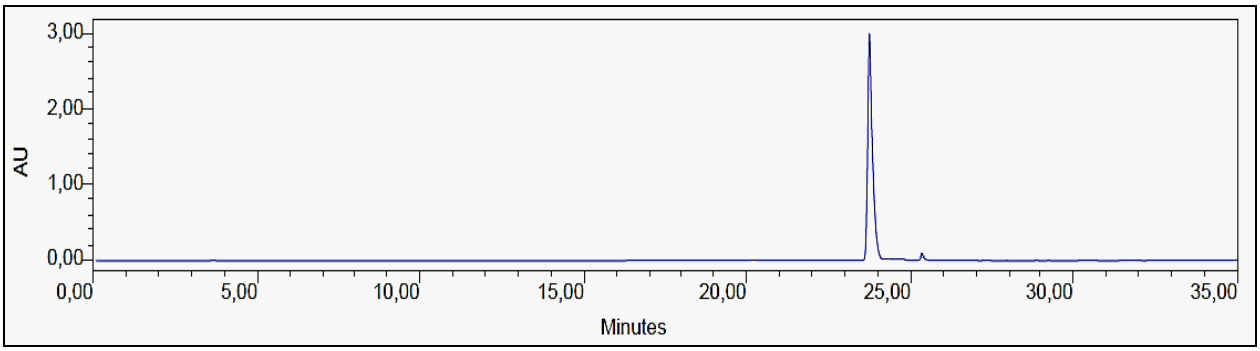

Fig. 39. Chromatogram of Comp. [15]

References

[1] Martins NM, Mahmudov KT, da Silva MFCG, Martins LM, Pombeiro AJ. Copper (II) and iron (III) complexes with arylhydrazone of ethyl 2-cyanoacetate or formazan ligands as catalysts for oxidation of alcohols. *New Journal of Chemistry*. 40, 12, 2016.

[2] Al-Araji YH, Shneine JK, Ahmed AA. Chemistry of formazan. *International Journal of Research in Pharmacy and Chemistry.* 2015; 5(1): 41-76.

[3] TÜRKOĞLU G, Cinar ME. Experimental and computational studies on the absorption properties of novel formazan derivatives. *Turkish Journal of Chemistry.* 2017; 41(5):710-27.

[4] Ha Al-Somaidaie, Gazwan. Synthesis, Characterization and study of antibacterial activity in vitro of some hydrazones and formazan dyes containing benzothiazole moiety. *Karbala journal of pharmaceutical sciences*, 2013, 4.5: 81-90

[5] Alkhazraji, Shima Ibraheem Chyad; IDHAM, Hussein Abbood. Synthesis of Some Formazan Derivatives from Schiff's Bases and Studying of Biological Activity. *Diyala Journal for Pure Science*, 2017, 13.4-part 2

[6] M NAbdul Maged; Nagham Mahmood Aljamali., Preparation of Benzothiazole-Formazane Reagents and Studying of (Spectral, Thermal, Scanning Microscopy, Biological Evaluation). *International Journal of Pharmaceutical Research*, 2021, 13.1. DOI: https://doi.org/10.31838/ijpr/2021.13.01.641.

[7] Nagham Mahmood Aljamali, Dhuha Rahi. New Formazan Compounds (Synthesis, Identification, Physical Properties). *Journal of Chemical and Pharmaceutical Sciences*, 2017, 10, 3: 1461-1472.

[8] Nagham Mahmood Aljamali.,"Review on (Azo, Formazane, Sulfazane)-Compounds", *International Journal of Innovations in Scientific Engineering*, 2019, Vol. No. 10, Jul-Dec., 19-45.

[9] Nagham Mahmood Aljamali., *"The Various Preparation Methods in Synthetic Chemistry"*. 1 Edt., Evincepub Publishing house, 2019. ISBN: 978-93-88277-82-2.

[10] Nagham Mahmood Aljamali. *"Reactions and Mechanisms"*. 1 Edt., IJMRA Publication, 2018., ISBN: 978-93-87176-25-6.

[11] Nagham Mahmood Aljamali. *"Experimental Methods for Preparation of Mannich Bases, Formazan, Normal and Cyclic Sulfur Compounds"*, 1st edition Evince pub Publishing House; 2018, ISBN: 978-93-87905-19-1.

[12] Nagham Mahmood Aljamali., *"Alternative Methods in Organic Synthesis"*. 1th–Edition, Eliva Press SRL, 2020. ISBN: 9798680201176.

[13] Nagham Mahmood Aljamali. 2016. "Synthesis and Biological Study of Hetero (Atoms and Cycles) Compounds", *Der Pharma Chemica*, 8(6), 40-48.

[14] Nagham Mahmood Aljamali. Synthesis of Antifungal Chemical Compounds from Fluconazole with (Pharma-Chemical) Studying. *Research journal of Pharmaceutical, biological and chemical sciences*, 2017, 8(3), 564 -573.

[15] Mieaad M, Nagham Mahmood Aljamali, Wassan Ala Shubber, Sabreen Ali Abdalrahman. "New Azomethine- Azo Heterocyclic Ligands via Cyclization of Ester". *Research Journal of Pharmacy and Technology*, 2018, 11(6), 2555-2560. DOI: 10.5958/0974-360X. 2018. 00472.9.

[16] Hussniya A. Aldifar, Mohammad F. Ali, Abdulrahim M. Khlafulla. Preparation and Characterization of Some of Formazan Derivatives. *Research & Reviews: A Journal of Pharmacology*, 2017.

[17] Moussa, Shaaban H. "Tetrazolium/formazan test as an efficient method to determine fungal chitosan antimicrobial activity." *Journal of Mycology* 2013 (2013).

[18] Tezcan, Habibe, Elif uzluk, and Mehmet Levent Aksu. "Electrochemical and spectroscopic properties of 1: 2 Ni complexes of 1, 3-substitued (CH3, OCH3) phenyl-5-phenylformazans." *Electrochimica acta* 53.18 (2008): 5597-5607.

[19] Nagham Mahmood Aljamali, Intisar Obaid Alfatlawi. "Synthesis of Sulfur Heterocyclic Compounds and Study of Expected Biological Activity". *Research J. Pharm. and Tech.*, 2015, 8, 9, 1225-1242, DOI:10.5958/0974-360X.2015.00224.3.

[20] Nagham Mahmood Aljamali.; Saher Mahmood Jawd.; Zainab MJ., Intisar, Obaid. Alfatlawi.; 2017, "Inhibition activity of (Azo–acetyl acetone) on bacteria of mouth"., *Research Journal of Pharmacy and Technology* 10(6):1683-1686, DOI: 10.5958/0974-360X.2017.00297.9

[21] Nagham Mahmood Aljamali., "(Synthesis, Investigation, Chromatography, Thermal) - Behavior of (Five, Seven)- Membered Ring with Azo and Anil Compounds". *Pak. J. Biotechnol.*, 15(1): 219-239 (2018).

[22] Rajaa Abdul Ameer Ghafil, Nour A Alrazzakb, Nagham Mahmood Aljamali., Synthesis of Triazole Derivatives via Multi Components Reaction and Studying of (Organic Characterization, Chromatographic Behavior, Chem-Physical Properties). *Egypt. J. Chem.* Vol. 63, No. 11, pp. 4163 - 4174 (2020). DOI: 10.21608/EJCHEM.2020.23541.2399.

[23] Ahmad, T; Kandil, F and Moustapha, M. Preparation and Characterization of Some New Azo Dyes, Azomethine Dyes and Heterocyclic-Schiff Bases Derivatives. *AASCIT Journal of Chemistry*, 2015, 2(2): 24-31.

[24] Shinde, A.T; Deshmukh, N.J; Kottapalle G.D and Zangade. S.B. Synthesis Antimicrobial Evaluation of Some New FluoroFormazans. *Journal of Pure and Applied Chemistry Research*, 2016, 5 (2) 61-66.

[25] Gurusamy M, Rejaul K, Nand M.J, Faruk A, Rajib H, Deepak K, and Tiewlasubon U. Synthesis and biological evaluation of formazan Derivatives. *Journal of Advanced Pharmaceutical Technology & Research*, 2016, 1(4): 396-400

[26] Venkatesan, P., B. Anand, and P. Matheswaran. "Influence of formazan derivatives on corrosion inhibition of mild steel in hydrochloric acid medium." *E-Journal of Chemistry* 6.S1 (2009): S438-S444.

[27] Shireen R. Rasool, Nagham Mahmood Aljamali, Ali Jassim Al-Zuhairi., Guanine substituted heterocyclic derivatives as bioactive compounds. *Biochem. Cell. Arch.* Vol. 20, Supplement 2, pp. 3651-3655, 2020. DocID: https://connectjournals.com/03896.2020.20.3651.

[28] Nagham Mahmood Aljamali.,"Synthesis and Chemical Identification of Macro Compounds of (Thiazol and Imidazol)". *Research J. Pharm. and Tech*, 2015, 8, 1, 78-84., DOI: 10.5958/0974-360X.2015.00016.5.

[29] Maulucci G, Labate V, Mele M, Panieri E, Arcovito G, Galeotti T, Østergaard H, Winther JR, De Spirito M, Pani G (October 2008). "High-resolution imaging of redox signaling in live cells through an oxidation-sensitive yellow fluorescent protein". *Science Signaling.* 1 (43): pl3. doi:10.1126/scisignal.143pl3.

[30] Imad Kareem Alwan Alsabri, Hasaneen Kudhair Abdullabass,Nagham Mahmood Aljamali.,Invention of (Gluta.Sulfazane-Cefixime) Compounds as Inhibitors of Cancerous Tumors. *Journal of Cardiovascular Disease Research*, 2020, 11, 2. 44-55. DOI: 10.31838/jcdr.2020.11.02.09.

[31] Aseel Mahmood Jawad, Nagham Mahmood Aljamali, Saher Mahmood Jwad., Development and Preparation of ciprofloxacin Drug Derivatives for Treatment of Microbial Contamination in Hospitals and Environment. *Indian Journal of Forensic Medicine & Toxicology*, 2020, 14, 2, p: 1115-1122.

[32] Hasaneen Kudhair Abdullabass, Aseel Mahmood Jawad, Nagham Mahmood Aljamali. Synthesis of drugs

derivatives as inhibitors of cancerous cells. *Biochem. Cell. Arch*, Vol. 20 (2) – October 2020. DocID: https://connectjournals.com/03896.2020.20.5315.

[33] Nagham Mahmood Aljamali, Imad Kareem Alwan Alsabri., Development of Trimethoprim Drug and Innovation of Sulfazane-Trimethoprim Derivatives as Anticancer Agents. *Biomedical & Pharmacology Journal*, March 2020. Vol. 13(2), 613-625. http://dx.doi.org/10.13005/bpj/1925.

[34] Miad Mohmed, Nagham Mahmood Aljamali,Sabreen Ali Abdalrahman., Wassan Ala Shubber., "Formation of Oxadiazole Derivatives Ligands from Condensation and Imination Reaction with References To Spectral Investigation, Thermal and Microbial Assay". *Biochem. Cell. Arch.,* 2018, 18(1), 847-853.

[35] Nagham Mahmood Aljamali, (2015). Review in Azo Compounds and its Biological Activity. *Biochem Anal Biochem*, 4, 169, doi:10.4172/2161-1009.1000169.

[36] Nagham Mahmood Aljamali. 2014. Synthesis and Investigation of Formazane compounds (Azo– Imine) and their complexes. *Asian J. Research Chem*, 7(2), 225-231.

[37] Fei, Na; Sauter, Basilius; Gillingham, Dennis (2016). "The pK a of Brønsted acids controls their reactivity with diazo compounds". *Chemical Communications.* 52(47): 7501–7504.

[38] Filimonov, Victor D.; Trusova, Marina; Postnikov, Pavel; Krasnokutskaya, Elena A.; Lee, Young Min; Hwang, Ho Yun; Kim, Hyunuk; Chi, Ki-Whan (2008). "Unusually Stable, Versatile, and Pure Arene-diazonium Tosylates: Their Preparation, Structures, and Synthetic Applicability". *Organic Letters.* 10(18): 3961–3964.