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Preparation and diagnosis of new picolinic acid derivatives

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Abstract

In this study, a new series of heterocyclic rings derived from picolinic acid was prepared. The quaternary reaction of acid hydrazone with chloroacetyl chloride was intended to obtain the azitidine-2-on ring known as beta-lactam and the preparation of the seventh ring of acid hydrazone reaction with the anhydride and phthalic anhydride To obtain a 3.1-oxabine loop. The five-ring of the picolinic acid hydrazide reaction with CS_2 was also destined to obtain a 4,3,1-oxadiazole-2-thaion ring. The new compounds were diagnosed using FT-IR techniques and resonance technique Nuclear Magnetic H-NMR and ^{13}C-NMR.

1. Introduction

picolinic acid is a hexagonal ring with extracts such as nicotinic acid and isonicotinic acid. Five carbon atoms, a nitrogen atom and a carbonyl group are present in seat 2 for acetic acid and position 3 and 4 respectively for nicotinic acid and isonicotinic acid [1,2] .Metallic ions are formed in a bifurcated model with soluble atoms such as oxygen and nitrogen present in picolinic acid to form stable complexes with ions such as Cr, Zn, Cu, Iron Fe ,picolinic acid derivatives are also used as supplementary materials for the absorption of base metals and are also useful as food diapers and are also used as disinfectants in food, medicine and textile industries [3,4] .They are also exercised as constructing blocks in photovoltaic devices[5]. They are also ideal systems for environmental studies[6]. It was also shown to show the molecular-hydrogen bonds in a solid state for the formation of new chains[7] .Three of the pyridine monocrystalline acids corresponding to diazo diphenyl methane were also studied in 20 solvents. It was determined that the reaction was highly following on the interfaces of the ring Nitrogen [8,9].which were also observed when studying cyclic-changing carboxylic acids in their interaction with ethanol, but the reaction command was reflected in several solvents, especially in the proton solvents[10] .There has recently been a lack of information regarding the effect of solvents on the composition Molecular and picolinic acid and electronic properties of this acid[11]. Despite a lot of research work on picolinic acid, there is a dearth of information on the solvents effect on the molecular structure and electronic properties of picolinic acid[12]. Therefore, the aim of this work is to theoretically study the solvents effect on the molecule and also to show the effect of basis sets on geometry, vibrational frequencies and NMR. The knowledge of the solvents effect both on the geometry and electronic properties will be helpful when making predictions about the reactivity and interactions of picolinic acid in different solvents..

2. Materials and methods of work:-

2.1.Chemicals and equipment

Physical and spectroscopic measurements were performed using several devices where the melting point of the prepared vehicles using the electro thermal engineering (S-N 10853) was tested in the research labs-Chemical Industries-Technical Institute/ Kirkuk. The UV and visible spectra of SHIMADZU, UVPROBE, and VERSION 1.11 spectrometers were recorded. The spectra were recorded at 25 ° C and for all measurements using a double dipole sulfoxide (DMSO) solvent, ethanol solvent and quartz cells (1 cm) - The Chemical Industries Division - Technical Institute / Kirkuk, and the infrared spectroscopy was recorded using the Perkin-Elmer FT-IR Spectrophotometer, KBR disk scale 400-4000 cm^{-1} in the chemistry labs-Faculty of Education-Tikrit University. Nuclear Magnetic Resonance Spectrometer (1H-NMR) 1H-NMRUltra shield 300

MHZ Bruker 2003 Yasat at Al - Bayt University - Jordan. Chemicals that are produced by companies (Fluka, Aldrich, BDH, Merck) have been used.

2.2 Preparation of vehicles

2.2.1. Preparation of picolinic acid (picolinohydrazide) [13-14] W1

Hydrazine picolinic acid was prepared by dissolving (0.1059 mol, 16 gm) of ethyl picolinate in (0.40 mol, 20 g) hydrazine hydrate (85%) with ethanol as solvent and escalated reaction for 24 hours) And subsequently cooled the mixture and dissolved solvent down vacuum pressure (using a vacuum pump). The precipitated precipitation was filtered and reconstituted using ethanol [15]. to give a white precipitate with its molecular formula $C_6H_7N_3O$ and its melting point of 101 ° C with a rate of 97% and molecular weight 137.06 mol / gm.

2.2.2 Preparation of picolinic acid hydrazones w2-w4

(0.0094 mol, 1.3gm) of picolinohydrazide with 0.0094 mol. of benzeldehyde or one of its metabolites was prepared in 20 ml of absolute ethanol, the mixture was increased for 4 hours and the precipitate was cooled, washed and reconstituted [16]. Table (1) shows some physical properties and percentages of prepared compounds.

2.2.3 Preparation of 5-pyriden 1,3,4-oxadiazole-2-thion w5

(0.005 mol, 0.685 gm) of (picolinohydrazide) in hydrochloric acid 0.01 ml and 0.56 g of KOH solution dissolved in 100 mL of ethanol and then gradually added to the solution (0.20 mol, 12 gm) From CS_2. The mixture increases until the H_2S emission is stopped. It is indicated by its odor and the blackness of the filter paper is wet with the lead, the steam is evaporated and then added to the crushed ice, diluted with diluted HCL, then cooled, separated and reconstituted with ethanol to yield a yellowish precipitation. Molecular formula $C_7H_5N_3OS$ and melting point 226 ° C With an output of 70% and molecular weight 179.02 mol / gm.

2.2.4 Preparation of azetidine-2-One compounds known as betalactam w6

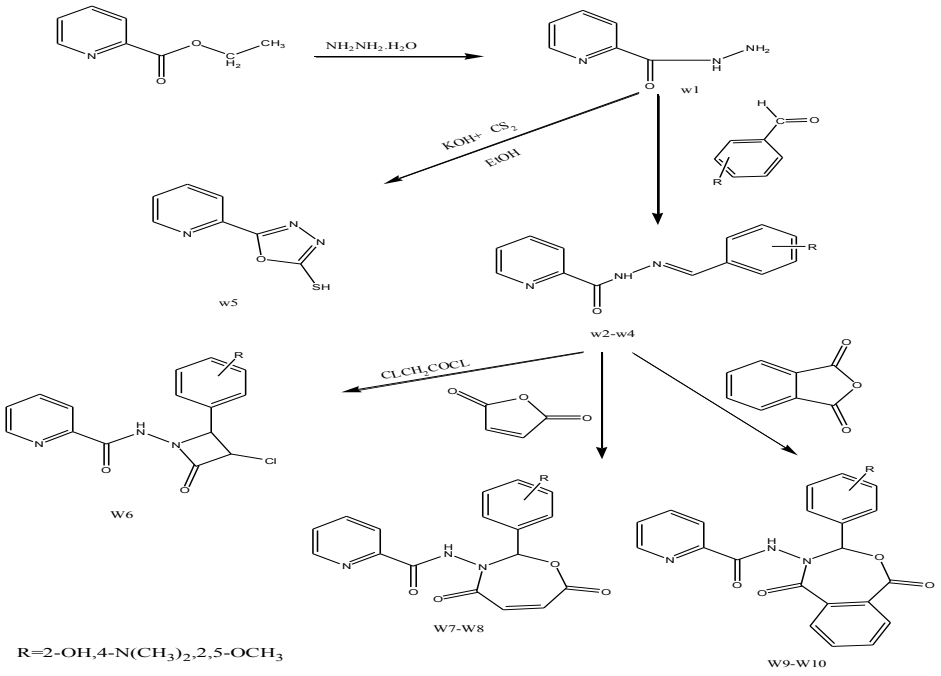
(0.001 mol, 0.3 gm) of the picolinic acid (E) -N'-benzylidenepicolinohydrazide derivatives (0.001 mol, 0.22 gm) were mixed with chloroacetyl chloride and (0.001 mol, 0.1 g) of triethyl Trimethylamine using 1,4-Dioxane as a solvent, escalate the reaction for 12 hours and then mix at room temperature to cool and then add The mixture is then added to the ice cream and then precipitated and reconstituted by ethanol or benzene[17]. The yellow yield is given as a molecular formula $C_{15}H_{12}ClN_3O_4$ and its melting point is 250 c^0, with a yield of 48% and molecular weight 333.05 mol /gm.

2.2.5 Composition of compounds (7,4-dioxo-2-phenyl-7,4-dihydro-3,1-oxazepin-3-yl) picolymide w7-w8

(0.001mol, 0.25gm) of picolinic acid (E) -N'-benzylidenepicolinohydrazide derivatives (with 0.001 mol, 0.098 gm) were eliminated from the maleic anhydride in 20 ml dry gasoline with dicosane drops, For 6 hours, then cool the precipitate, wash and restitinate it using ethanol. Table 2 shows some physical properties and percentage of prepared compounds.

2-6-6. Preparation of compounds (5,1-dioxo-2-phenyl-5,1-dihyhydro-3,1-oxazepin-4-yl) picolymide W9-w10

(0.001 mol, 0.25gm) of picolinic acid (E)-N'-benzylidenepicolinohydrazide derivatives (with 0.001 mol, 0.14 g) were phthalic anhydride in 20 ml of dry gasoline with dicosane drops, For 6 hours and then cool the precipitate and wash and restitinate it using ethanol (Table 3) illustrates some physical properties and percentages of compounds.



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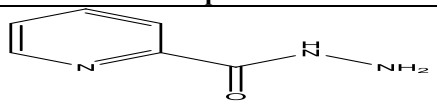
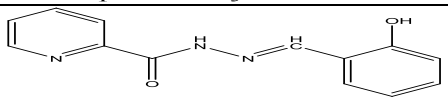
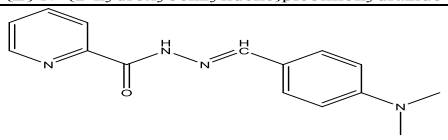
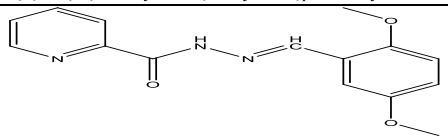
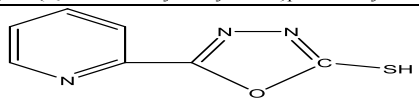
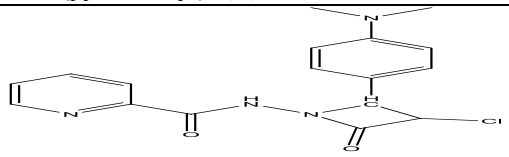
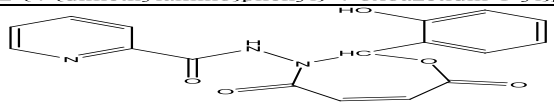
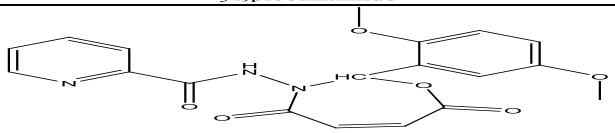
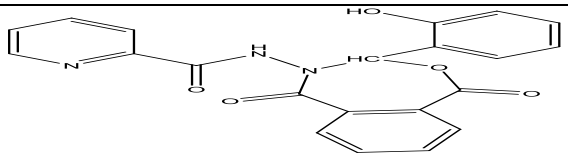
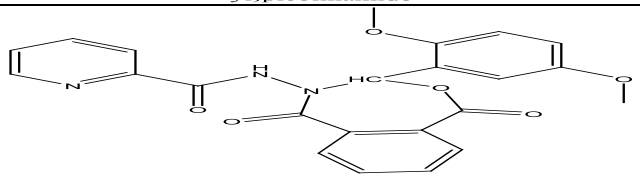
No	Compounds
W1	 picolinohydrazide
W2	 (*E*)-*N*′-(2-hydroxybenzylidene)picolinohydrazide
W3	 (*E*)-*N*′-(4-(dimethylamino)benzylidene)picolinohydrazide
W4	 (*E*)-*N*′-(2,5-dimethoxybenzylidene)picolinohydrazide
W5	 5-(pyridin-2-yl)-1,3,4-oxadiazole-2-thiol
W6	 *N*-(3-chloro-2-(4-(dimethylamino)phenyl)-4-oxoazetidin-1-yl)picolinamide
W7	 *N*-(2-(2-hydroxyphenyl)-4,7-dioxo-4,7-dihydro-1,3-oxazepin-3(2*H*)-yl)picolinamide
W8	 *N*-(2-(2,5-dimethoxyphenyl)-4,7-dioxo-4,7-dihydro-1,3-oxazepin-3(2*H*)-yl)picolinamide
W9	 *N*-(3-(2-hydroxyphenyl)-1,5-dioxo-1,5-dihydrobenzo[*e*][1,3]oxazepin-4(3*H*)-yl)picolinamide
W10	 *N*-(3-(2,5-dimethoxyphenyl)-1,5-dioxo-1,5-dihydrobenzo[*e*][1,3]oxazepin-4(3*H*)-yl)picolinamide

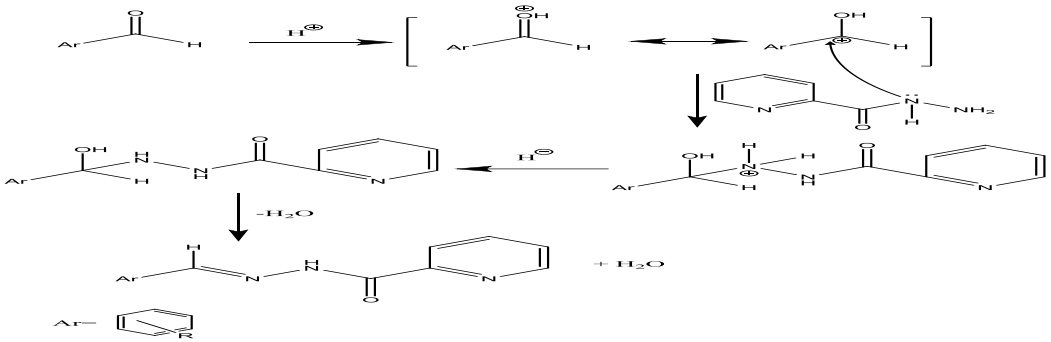
3. Results and discussion

3.1 Diagnosis of picolinic acid picolinohydrazide (w1): -

In the study of the infrared spectra of this compound, two groups of amino acid (NH2) were present at (3317,3201)cm $^{-1}$ due to the corresponding and non-symmetric peak, as well as the curvature of the NH (1596 cm^{-1}), a reference to the interaction of picolinohydrazide In addition, a absorption package of 3058 cm $^{-1}$ was developed for the aromatic CH, consisting of the aromatic bands (C = C), which appeared at 1449-1559 cm $^{-1}$, in addition to the survival of the C = N series of pyridine Where it appeared at 1650 cm $^{-1}$ with the disappearance of the absorption bands dating to the C =O ester), which appears at 1730 cm $^{-1}$ and the emergence of the absorption bands dating to the extension (C = O) Amen, which appeared at 1676 cm $^{-1}$ and has Net matching packages literature.

3.2. Diagnosis of picolinic acid hydroxonate derivatives (E-n'-benzylidenepicolinohydrazide):

Proposed mechanical reaction.



The infrared spectra showed a absorption range within the range of 3168-3313 cm -1 (NH), and two uptake bands within the range 2980-3100cm $^{-1}$ and 1444-1575cm $^{-1}$ were available (C = CH Ar) and (C = N), as well as an absorption bands that appeared within the range of 1280-1390cm $^{-1}$ (C-N) as well as the absorption bands within the range 670 (1), (2), (3) represents the infrared spectra of the compounds w4,w3, w2. Table (4) shows the most important IR frequencies of the above mentioned vehicles.

The ^{1}H-NMR spectrum of W2 showed a single wide beam at 12.66 ppm attributed to the proton of the NH group and the emergence of another single package at 11.01 ppm. The hydroxyl group (OH) was shown with a multiple beam within the range 7.12-8.11 ppm (Ar-CH), and a single peak at 8.68 ppm was attributed to the N = CH group as shown in Figure (4).

3.3. Diagnosis of the 5-pyridine compound 4,3,1-oxadiazole-2-thion.

The infrared spectra showed the interaction by studying the infrared spectra of the recorded compound (w4). The disappearance of the ammonium carbonyl group (C = O) and the appearance of two basic absorption bands were observed at (1037-1074) and 1140-1292 (cm^{-1}), which are the symmetric and asymmetric bands respectively of the(C-O-C) group which confirm the formation of the oxadiazole ring.

The appearance of the C-N peak at 1639-1661 cm^{-1}, a distinctive and powerful package for what exists in the literature, was observed as the (S-H) uptake at 3394 cm $^{-1}$, which is also a powerful beak.

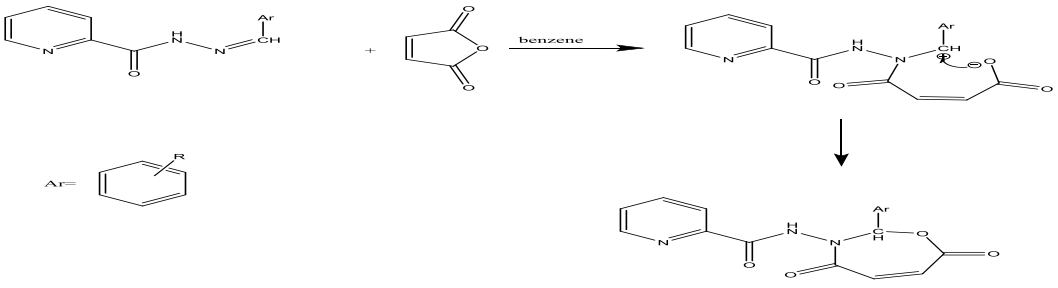
The other relatively stable packages of oxadiazole derivatives have been shown in other bundles (=CH and C = C) in the range (3040-3094), (1417-1575) cm $^{-1}$ and aggregates (NN) and (CN) in the range (1030-1037) and (1315-1329) cm $^{-1}$ and Figure (5) shows the IR spectrum of the compound (w5).

3-4. Diagnosis of azetidine-2-ON compounds known as betalactam.

Infra-red compounds were identified with an uptake range within the range 3218-3300mm $^{-1}$ for the NH spectrum. Two absorption bands were also shown within the range 2925-3100 cm -1 and 1465-1530 cm $^{-1}$, (C-H),(C=C), and the absorption of a absorption beak within the range of 1523-1620 cm $^{-1}$ was acceptable (C = N). A absorption package was also found within the range 1678-1726 cm $^{-1}$, Lactam), as well as a absorption package within the range 676-694 cm $^{-1}$ (CNC), as well as an absorption beak within the range 720-780 cm -1 for the C-CL model and Figure 6 shows the infrared spectrum of vehicles (w6)

3-5. Diagnosis of compounds (7,4-dioxo-2-phenyl-7,4-dihydro-3,1-oxazepin-3-yl)

Proposed mechanical reaction.

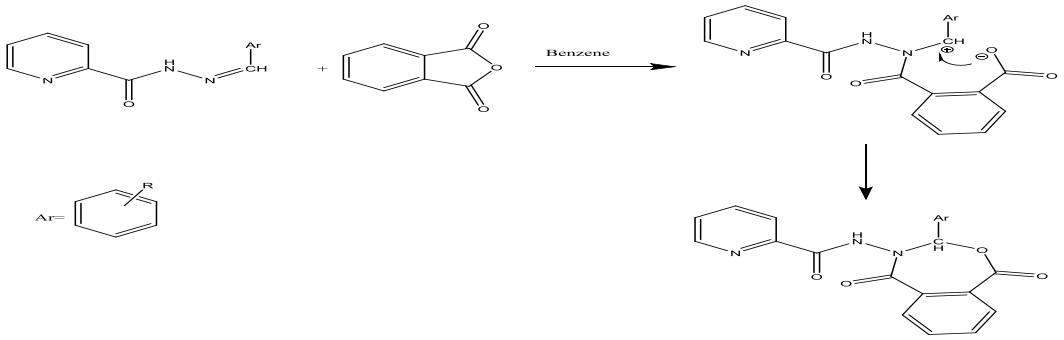


The compounds were measured by infrared measurement and a absorption package was observed within the range 1700-1740 cm $^{-1}$, which is suitable for the group of Lactone Esters (COO), as well as an absorption peak within the range of 1650-1705 cm $^{-1}$, which is suitable for the CO-N), And a absorption peak within the range of 1470-1570 cm $^{-1}$ was found, and a suction peak was found within the range 1600-1635 cm $^{-1}$, which is extended to C = N, and a package within the range of 1565-1614 cm $^{-1}$, (8) represents the infrared spectrum of w7 and w8.

The^{1} H-NMR spectrum as shown in Fig. 9 of W7 has a spectrum of multiple bands Within the range 7.13-8.45 ppm is attributable to (1). The other packages

were at 7.10 ppm due to proton. The group of oxasepine (N-CH-O) is a single peak and the table (5) represents Infrared spectrum of vehicles above ..

3.6 Diagnosis of compounds (5,1-dioxo-2-phenyl-5,1-dihydro-3,1-oxazepine-4-yl)picolymene Proposed mechanical reaction



The compoundswhich examined with the infrared measurement and a absorption package within the range 1700-1746cm^{-1} were found to be suitable for the group of Lactone Esters (COO), as well as a absorption package within the range of 1650-1705 cm $^{-1}$, which is suitable for the CO-N) And a absorption package within the range of 1470-1570 cm $^{-1}$ was found, and a suction package was found within the range 1600-1635 cm $^{-1}$ which is extended to C = N, and a package within the range of 1565-1614 cm $^{-1}$ (C = C) in the represents the IR spectrum of W9, W10.

Table (1) shows some physical properties and percentages of prepared compounds W2-W4. Yield%

Comp No.	R	Color	Molecular Formula	M.P c°	Yield%
W2	2-OH	yellow	$C_{13}H_{11}N_3O_2$	165-167	63
W3	$N(CH_3)_2$	white	$C_{15}H_{16}N_4O$	205-207	77
W4	2,5-OCH3	yellow	$C_{15}H_{15}N_3O_3$	144-146	83

Table (2) shows some physical properties and percentages of prepared compounds W7-W8. Yield%

Comp No.	R	Color	Molecular Formula	M.P c°	Yield%
W7	2-OH	yellow	$C_{17}H_{13}N_3O_5$	149-151	46
W8	2,5-OCH_3	pink	$C_{19}H_{17}N_3O_6$	193-195	41

Table (3) shows some physical properties and percentages of prepared compound W9-W10. Yield%

Comp No.	R	Color	Molecular Formula	M.P c°	Yield%
W9	2-OH	yellow	$C_{21}H_{15}N_3O_5$	155-157	52
W10	2,5-OCH_3	pink	$C_{23}H_{19}N_3O_6$	182-184	45

Table (4) Represents the infrared spectrum of compounds w2-w4

Comp. No.	R	IR,(KBr)cm^{-1}									
		Fixed bands in structure								Changed bands in structure	
		υN-H	υC=O	υ(=CH)Ar	υC-H aliph	υC=N	υC=C ar	υC-N	υN-N		
W2	2-OH	3272	1678	3064	2870	1623	1486-1524	1368	997	υO-H (3480)	υC-O (1153)
W3	4-$N(CH_3)_2$	3293	1676	3060	2915	1600	−1486 1516	1363	996	----	----
W4	2,5-OCH_3	3168	1660	3007	2947	1608	−1496 1533	1361	996	υC-O-C (1170)	----

Table (5) Represents the infrared spectrum of compounds w7-w8

Comp. No.	R	IR,(KBr)cm^{-1}									
		Fixed bands in structure								Changed bands in structure	
		υN-H	υC=O lactone	υ(=CH)ar	υC-H aliph	υC=N	υC=C ar	υC-N	υC=O amide	υN-N	
W7	2-OH	3200	1724	3045	2850-2920	1619	1484-1521	1381	1672	980	υO-H 3343	υC-O 1203
W8	2,5-OCH_3	3197	1725	3059	−2850 2892	1630	−1492 1535	1352	1686	995	υC-O-C 1222	----

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Table (6) Represents the infrared spectrum of compounds w9-w10

Comp. No.	R	IR,(KBr)cm^{-1}										
		Fixed bands in structure									Changed bands in structure	
		υN-H	υC=O lactone	υ(=CH)Ar	υC-H Aliph	υC=N	υC=CAr	υC-N	υC=O amide	υN-N		
W9	2-OH	3242	1724	3045	2872-2915	1620	1483-1521	1373	1660	983	υO-H 3524	υC-O 1142
W10	2,5-OCH_3	3161	1724	3006	−2835 2948	1630	−1493 1535	1352	1664	995	υC-O-C 1171	----

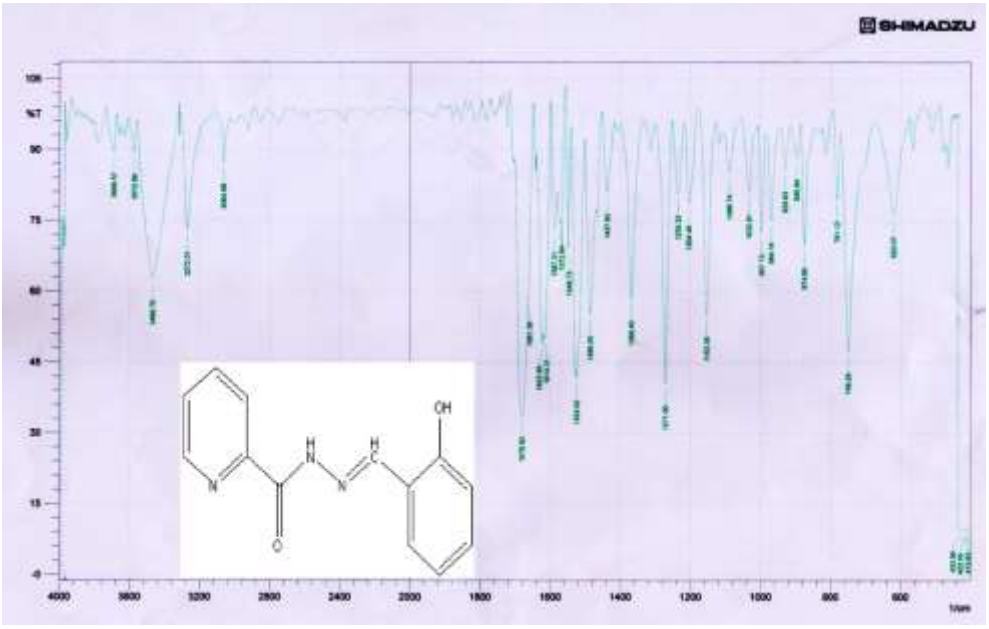

Table (1) Represents the infrared spectrum of compound w2

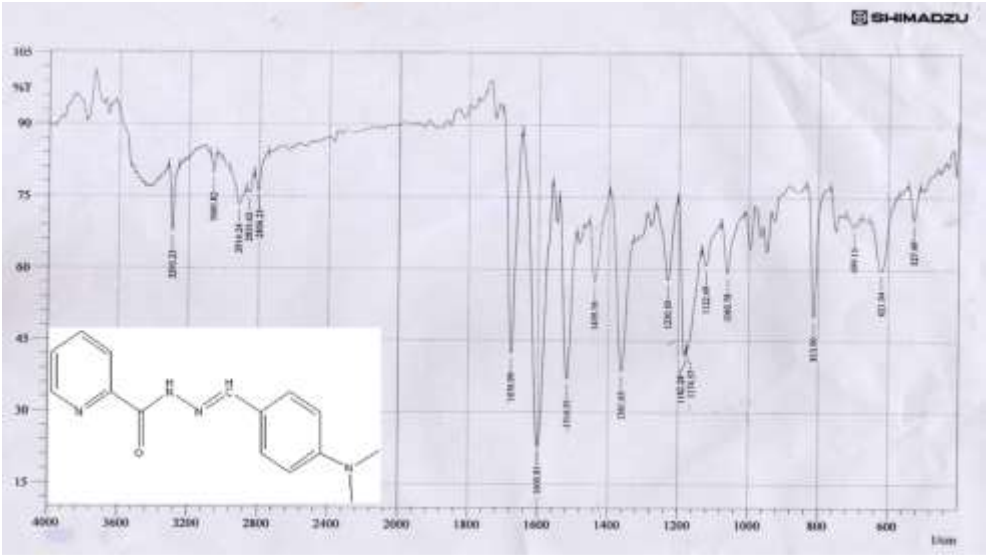

Table (2) Represents the infrared spectrum of compound w3

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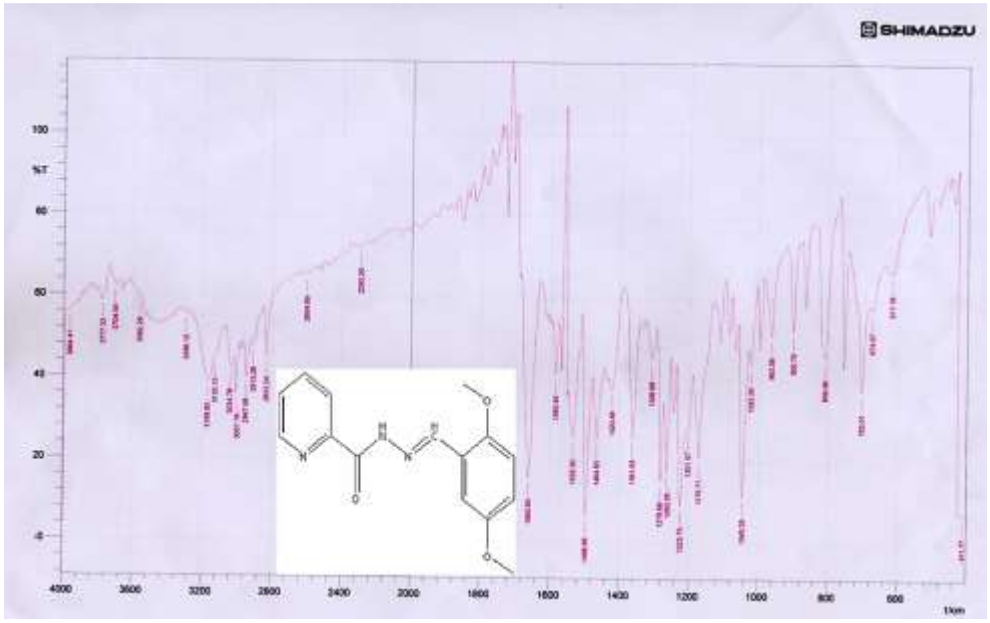

Table (3) Represents the infrared spectrum of compound w4

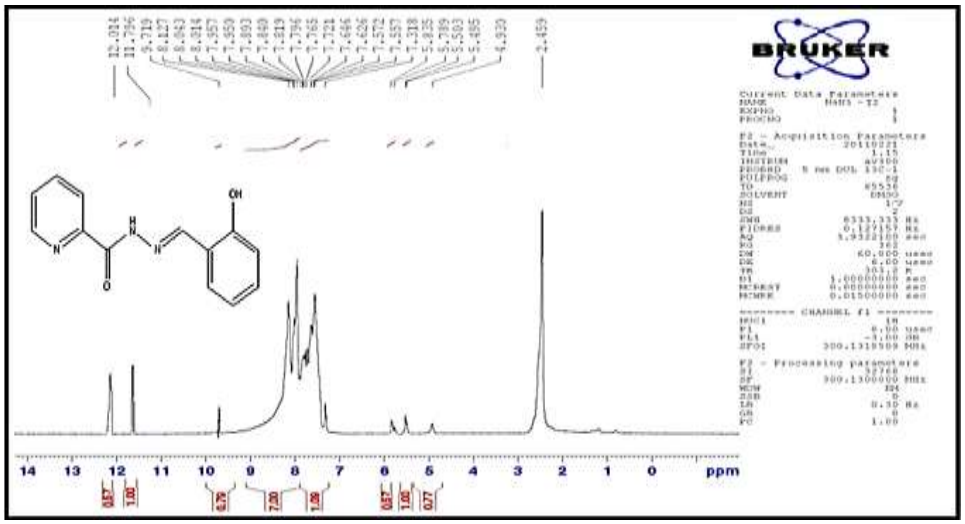

Table (4) Represents the spectrum of the nuclear resonance of the H-NMR proton of compound w2

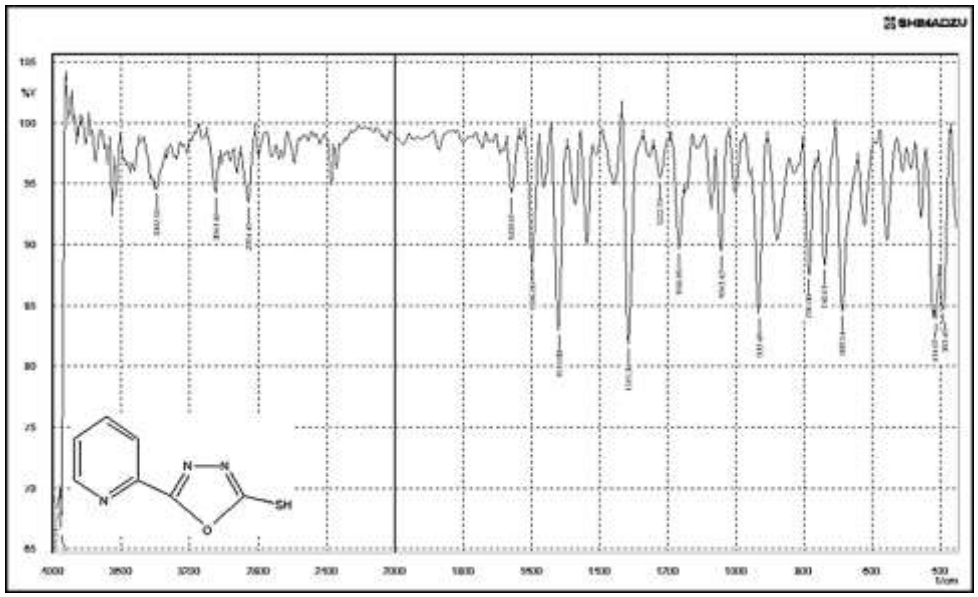

Table (5) Represents the infrared spectrum of compound w5

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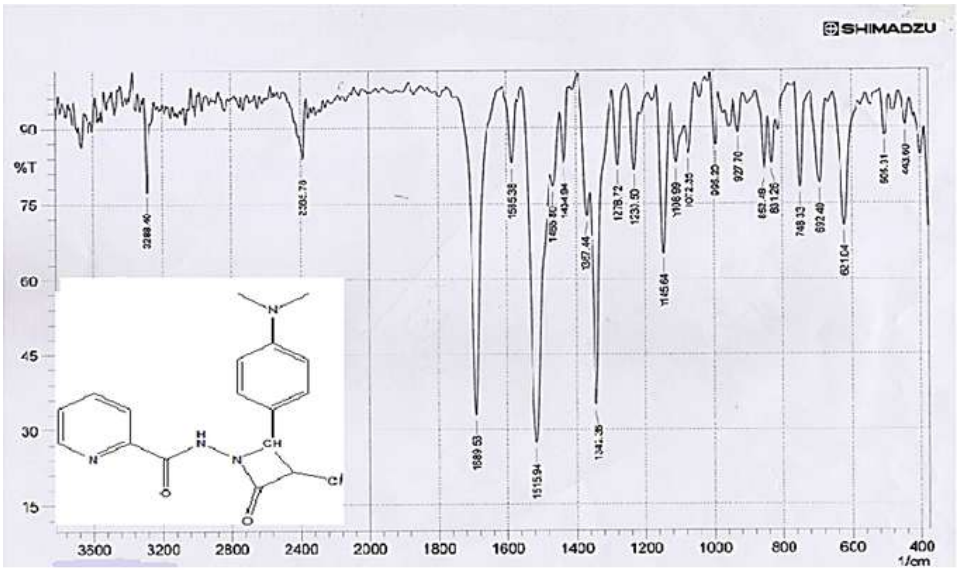
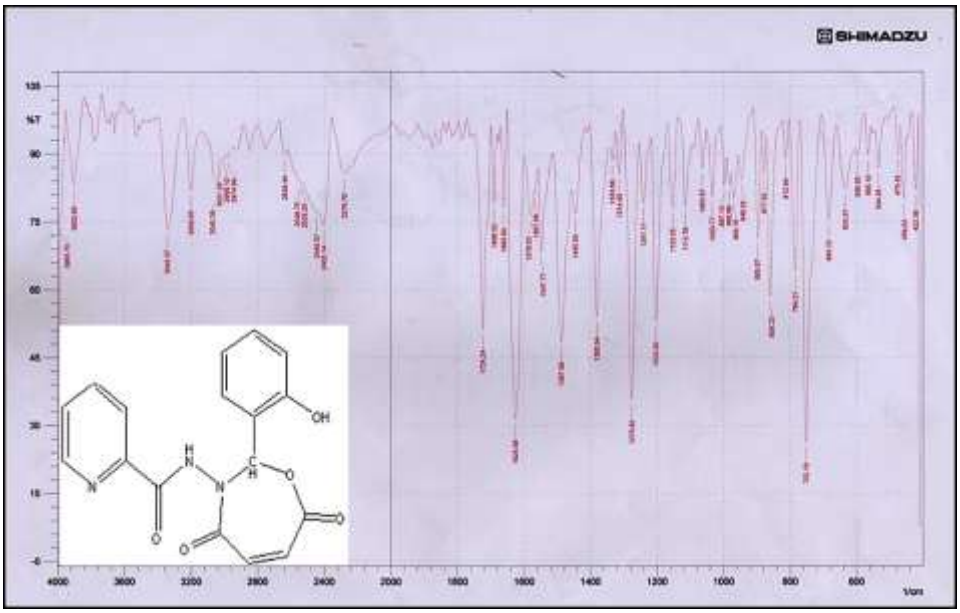
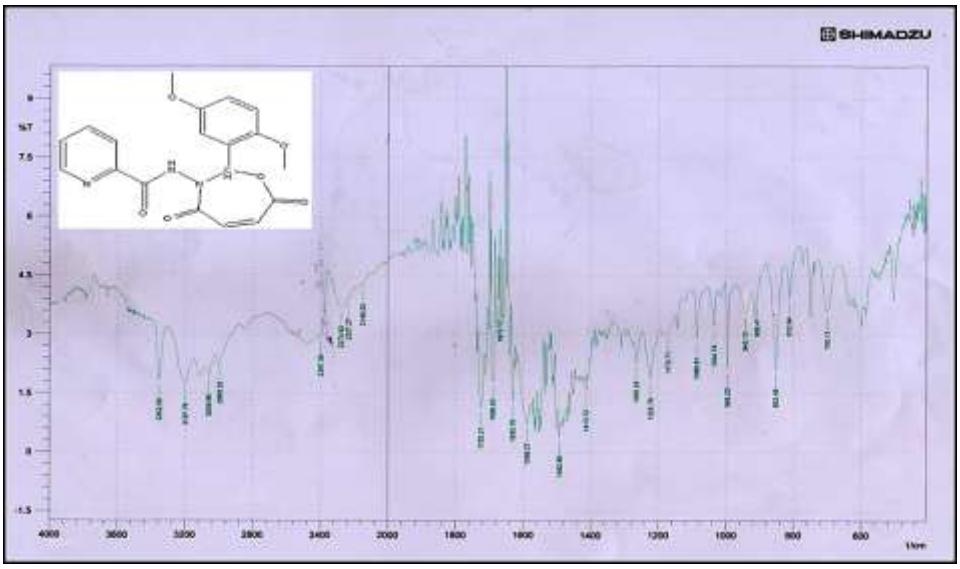


Table(6) Represents the infrared spectrum of compound w6



Table(7) Represents the infrared spectrum of compound w7



Table(8) Represents the infrared spectrum of compound w8

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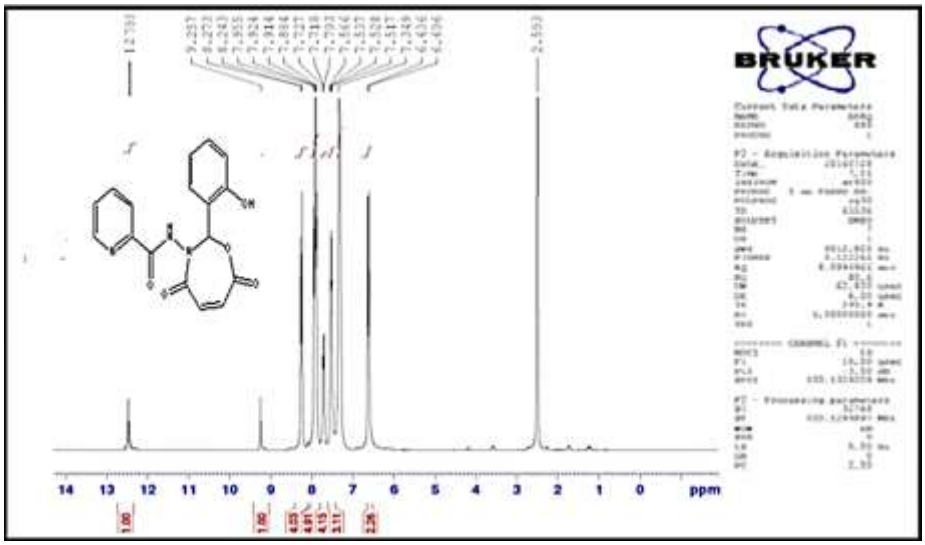
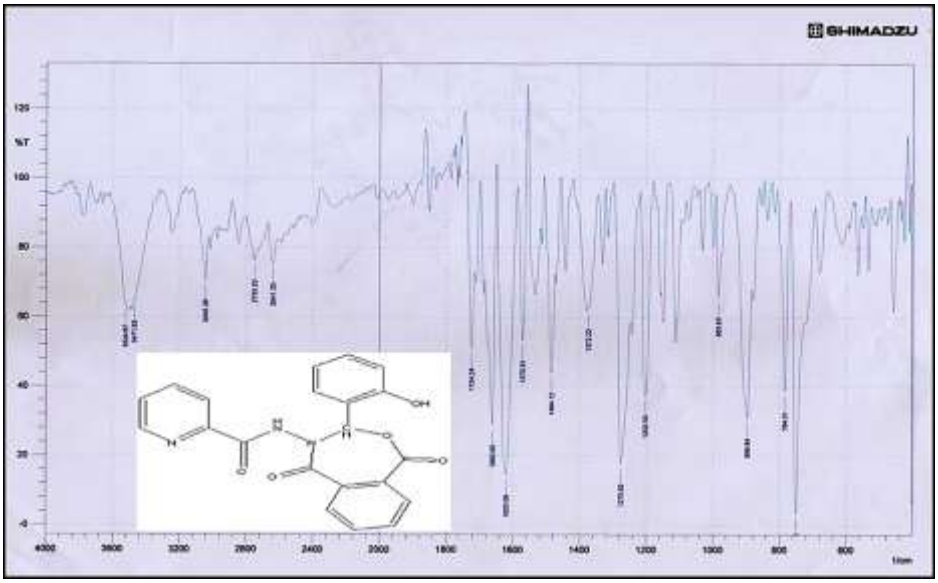
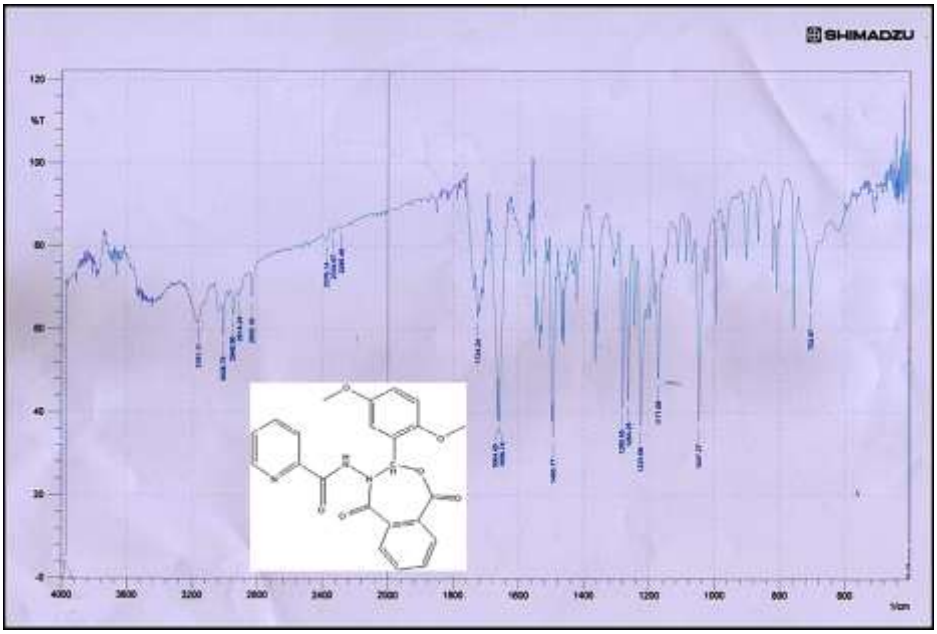


Table (9) Represents the spectrum of the nuclear resonance of the H-NMR proton of compound w7



Table(10) Represents the infrared spectrum of compound w9



Table(11) Represents the infrared spectrum of compound w10

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تحضير وتشخيص لبعض مشتقات حامض البيكولينيك الجديدة

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الملخص

تم في هذا البحث تحضير سلسلة جديدة من الحلقات غير المتجانسة المشتقة من حامض البيكولينيك حيث تم تحضير الحلقة الرباعية من تفاعل هيدرازونات الحامض مع كلورو استيل كلورايد للحصول على حلقة الازيتيدين-2-اون المعروفة بالبيتا لاكتام وتحضير الحلقة السباعية من تفاعل هيدرازونات الحامض مع المالك انهيدريد والفثالك انهيدريد للحصول على حلقة 3,1-اوكسازبين ،كما تم تحضير الحلقة الخماسية من تفاعل هيدرازايد حامض البيكولينيك مع ثنائي كبريتيد الكربون للحصول على حلقة 4,3,1-اوكسادايازول-2-ثايون،تم تشخيص المركبات الجديدة باستخدام تقنيات الاشعة تحت الحمراء وتقنية الرنين ^{1}H-NMR . و^{13}C-NMR.