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*Synthesis and characterization of some derivatives five hetrocyclic ring

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Abstract

In theis paper,anew series of 3-[(2-hydroxy naphthalene-1-yl)diazenyl)benzoic acid [1],ethyl 3-[(2-hydroxy naphthalene -1-yl)diazenyl]benzoate[2], 3-[(2-hydroxy naph thalene -1-yl)diazeyl] benzohyrrazide[3], [3,5-dimethyl-1H-pyrazole-1-yl] [3-[(2-hydroxy naphthalene-1yl)diazenyl)phenyl]methanone[4],[3-[(3-hydroxy naphthalene-2-yl)-diazenyl)phenyl](5-mercapto-1,3,4-thiadiazole-2-yl) methanone[5], 2-[3- [(3-hydroxy naphthalene-2-yl)diazenyl]benzoyl]-N-phenyl hydrazine carbothio amide [6],1-[(3-(5-mercapto-4-phenyl-4h-1,2,4-teiazole-3-yl)phenyl)diazenyl] naphthalene-2-ol[7], 1-((3-(5-(phenylamino)-1,3,4-thiadiazol-2-yl)phenyl)diazenyl) naphthalen-2-ol[8], (3-((2-butoxynaphthalen-1-yl)diazenyl)phenyl)(5-(butylthio)-1,3,4-thiadiazol-2-yl)methanone[9]. have been synthesized. These compounds were characterized by FT-IR ,spectrum,H^1-NMR spectrum, elemental analysis and the melting point were checked, the purity of the prepared compounds were determind by TLC technique.

Keyword:thiadia , zole, triazole, pyrazole .

Introduction

Hetrocyclic compounds have a wide rang of application are of particular interest in medicinal chemistry[1] and industrial application(2).
Thiadiazole(3) is a 5-member ring system containing two nitrogen and one sulphur atom.They occur in nature in four isomeric forms isomeric forms viz.1,2,3-thiadiazole;1,2,5-thiadiazole;1,2,4-thiadiazole;1,3,4-thiadiazole.fig(1),that is
a-1,2,3-thiadiazole
b-1,2,4-thiadiazole
c-1,3,4-thiadiazole
d-1,2,5-thiadiazole

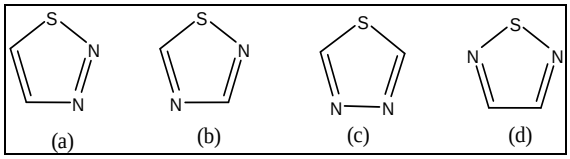


Figure 1:structure of thiadiazole isomers

The drivatives of 1,3,4-thiadiazole was known to possess various pharmacological activities like Anti-microbial[4],Anti-inflammatory[5],Anti-Tubercular[6-7].
Triazole [8] belong to one of the most widely used class of antifungal drugs known as azoles,the molecular formula $C_2 H_3N_3$,having a five membered ring of two carbon atoms and three nirtogen atoms :

***The Research is apart of on M.Sc. thesis in the case of the First researcher**

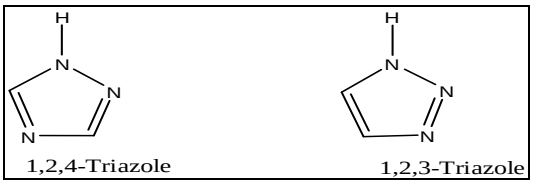
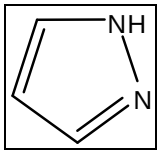


Figure 2:structure of triazole isomers

The drivatives of 1,2,4-triazole was known to possess various pharmacological activities like antimicrobial [9-10], anti-inflammatory [11] .
Pyrazole(12) (Fig.3) refers to the class of simple aromatic ring organic compounds of the hetrocyclic series characterized by a 5-membered ring structure composed of three carbon atoms and two nitrogen atoms in adjacent positions.



(Fig 3: structure of pyrazole)

The pyrazol scaffold represents a commom motif in many pharmaceutical active and remarkable componnds demon strating a wide range of pharmacological activities the most important activities is the anti-microbial[13],analgesic and antiInflammatory[14],antifungal[15]

Expermantal

-All chemical used were supplied from merck and BDH-chemical company
-All measurement were carried out by:
Melting point:-Electro thermal , Melting point 9300-u.k-
-FT.IR spectro:-Test can shimadzu(FT.IR 8000 series,Japan)
-Hot plat stirrer, Jib,L M S-100
-Thin layer chromatography (TLC) was carried out and the plates were developed with iodine vapour.

1-Syntheis 3-((2-hydroxynaphthalen-1-yl)diazenyl)benzoic acid[1]

compound[1] were synthesized by the addition of the (0.001mol,0.12gm) $NaNO_2$ to mixture from (0.001mol,0.13gm)of m-amino benzoic acid dissolved in (15ml,ethanol , 2ml hydrochloric acid) .(0.001mol,0.14gm of 2-naphthol dissolved(15ml)of ethanol and addition to mixture.After filtered off and recrystallized by using ethanol m.p for (270-272)c^0,yield(85%).

2-Synthesis ethyl 3-((2-hydroxynaphthalen-1- yl)diazenyl)benzoate[2]

Treating (0.001mol,0.29gm)of compound [1] with 60ml absolute ethanol (0.001 mol ,0.1ml) consentration sulfuric acid and refuxing the mixture for 8hours, yieded the expected ester[2]m.p(239-241)c^0,yield(85%)

3-Synthesis 3-((2-hydroxynaphthalen-1-yl)diazenyl) benzohydrazide [3](16)

Compound(3)were synthesis by the addition of the hydrazine hydrate(0.001mol,0.1ml to(0.001mol,0.32gm)[2]in15ml of absolute ethanol then the mixture was refuxed for

10 hours .After cooling the product was filtered off and recrystallized by using ethanol m.p for (178-180)c^0 ,yield(62%).

4-Synthesis (3,5-dimethyl-1H-pyrazol-1-yl)(3-((2-hydroxynaphthalen-1-yl) diazenyl) phenyl)methanone[4]

A mixture of compound[3](0.001mol,0.30gm)and acetylaceton (0.001mol,0.1ml) in absolute ethanol(15ml)was heated at reflux temperature for 10hours. the reaction mixture was cooled and the formed precipitate was filtered off to give the titled compound [4],m.p(219-220) c^0,yield(84%).

5-Synthesis (4-((2-hydroxynaphthalen-1-yl) diazenyl)phenyl) (5-mercapto-1,3,4-thiadiazol-2-yl)methanone[5]

To a mixture of compound)[3](0.001mol,0.30gm)in ethanol (20ml)was added a solution of KOH(0.001mol,0.056gm)in ethanol(15ml) Followed by CS_2 (0.001mol, ,0.448ml).the reaction mixture was string for 24 hours then it was concentration ,acidified with sulfuric acid and the resulting soild was collected,washed with ether and recrtstallized to give compound [5]m.p(230-232)c^0,yield(68%).

6-Synthesis 2-(3-((2-hydroxynaphthalen-1-yl)diazenyl)benzoyl)-N-phenyl hydrazine [6]

Compound[6] were synthesized by the addition of the phenyl iso thio cyanate(0.001 mol,0.13ml)to(0.001mol,0.3gm)[3] in 15ml of absolute ethanol then the mixture was refuxed for 13hours.After cooling the product was filtered off and recrystallized by using ethanol m.p(100-102)c^0,yield(90%).

7-Synthesis 1-((3-(5-mercapto-4-phenyl-4H-1,2,4-triazol-3-yl) phenyl) diazenyl) naphthalen-2-ol[7][(16)]

compound[6](0.001mol,0.44gm)and(15ml)of 2N sodium hydroxide solution was refluxed with stirring for 20 hours . After cooling the solution was acidified with hydrochloric acid and the precipitate was filtered m.p(118-120)c^0,yield(86%).

8-Synthesis 1-((3-(5-(phenylamino)-1,3,4-thiadiazol-2-yl)phenyl) diazenyl) naphthalen-2-ol[8][(16)]

compound[6](0.001mol,0.3gm)was added portion wise to (5ml)of concentrated sulfuric acid at 0c with continuous stirring .the reaction mixture was strred further for 18hours at room temperature and then allowed to stand overnight .Neuralization with dilute sodium bicarbonate prepcipitated acrude soild,which was filtered and recrystallized from ethanol,m.p(72-74)c^0,yield(83%).

9-Synthesis (3-((2-butoxynaphthalen-1-yl)diazenyl)phenyl)(5-(butylthio)- 1,3,4-thiadiazol-2-yl)methanone[9]

compound[9] were synthesized by the addition of the chloro butan (0.02mol,0.18ml) to (0.001mol,0.35gm)[5]in (15ml)of absolute ethanol then the mixture was refuxed for13 houts .After cooling the product was filtered off and recrystallized byusing ethanol m.p(188-190)c^0, for yield(70%).Table (1)showed the physical properties of the synthesized compounds.

Results and Discussion:

1-Synthesis 3-((2-hydroxynaphthalen-1-yl)diazenyl)benzoic acid[1]

The compound [1]was synthesized by the
reaction of m-amino benzoic acid with 2-Naphthol in absolute ethanol
The FTIR spectrum of compound [1],Fig(2), show the appearance of the characteristic absorption band in the region (3389.04)cm^{-1} due to (OH)group, and disappearance of the band at(3410.26) cm^{-1} due to (NH_2)group for m-amino benzoic acid , anew band appeared at(1454)cm^{-1} due to the of(N=N)group,The ^{1}H-NMR spectrum,Fig(3) show singlet at (15.651.ppm) due to H phenolic,The second single singlet at (13.351ppm) due to H carboxylic acid and the mult singlet between(6.8-8.5 ppm) due to H aromatic the phenyl and naphthyl ring.

2-Synthesis ethyl 3-((2-hydroxynaphthalen-1-yl)diazenyl)benzoate[2]

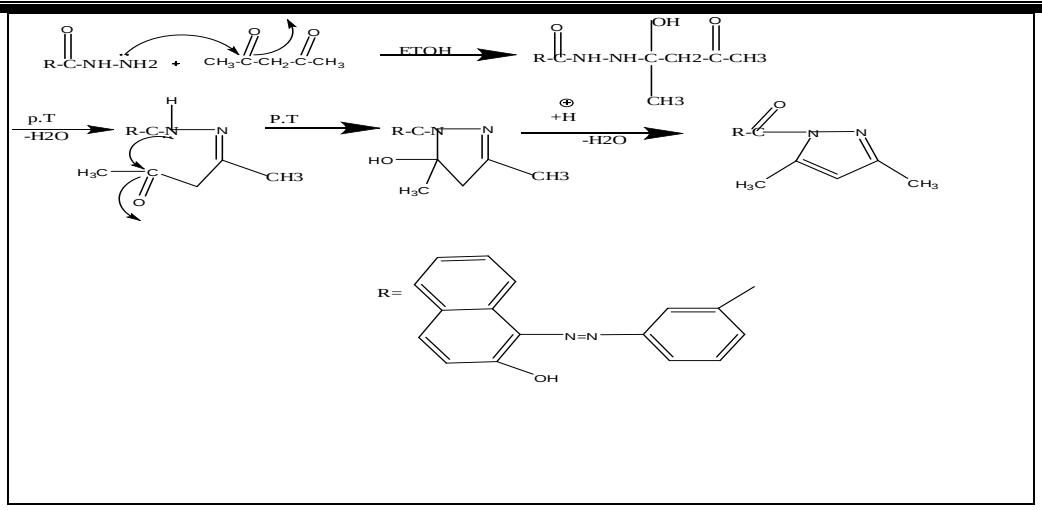
The compound [2] prepared through the reaction of compound [1]with sulfuric acid concentration.
The FTIR spectrum of compound[2],Fig(3), show the disappearance of the C=O carboxylic acid band of compound[1] at (1680)cm^{-1} respectively,also disappearance of (OH) of acid at(3389. 04) cm^{-1} and appearance of band at(1708.99)cm^{-1} due to the stretching vibration of the C=Oof the formed ester.

3- Synthesis 3-((2-hydroxynaphthalen-1-yl) diazenyl) benzohydrazide [3]

The compound [3] prepared through the reaction of compound[2] with hydrazine hydrate in absolute ethanol.
The FTIR spectrum of compound[3],Fig(4), show the appearance of the characteristic absorption band in the regions(3346.6-3446.9)cm^{-1} due to asymmetric and symmetric stretching vibration of the (NH-NH_2) group, the FTIR spectra also show the disappearance of absorption band in the region (1708.99)cm^{-1} due to the stretching vibration of the carbonyl group of ester, while a new band appeared at (1699.34) cm^{-1} due to the stretching vibration of amide,The ^{1}H-NMR spectrum Fig(6) show singal singlet at (15.45 ppm) due to H phenolic ,the singal singlet at(5.4ppm) due to H the N-H amine ,the double singlet between(8.4-8.6 ppm) due to H the NH amide and the multi singlet between(6.7-7.9 ppm) due to H aromatic the phenyl and naphthyl ring.

4-Synthesis(3,5-dimethyl-1H-pyrazol-1-yl)(3-((2-hydroxynaphthalen-1-yl) diazenyl) phenyl)methanone[4]

The compound [4]were prepared through the reaction of compound[3] with acetyl acetone.
IR spectra of compound[4],Fig(5), show the disappearance of NH_2 and NH bands in the region (3346-3446)cm^{-1} and appearance of OH band (3190.37)cm^{-1} in addition to the C=N of pyrazole at (1556.61)cm^{-1} ,The ^{1}H-NMR spectrum (Fig.8) show single singlet at(2.2ppm and 3.5ppm) due to H the methyl group for pyrazole ring,the single singlet at (6.3ppm) due to H the pyrazole ring ,the single singlet at(15.3ppm) due to H phenolic and the multi singlet at(6.6ppm-8.8ppm) due to H aromatic the phenyl and naphthyl ring. . The mechanism of the reaction is shown in scheme below.



.scheme(1) synthesis of pyrazole derivative

5-Synthesis(3-((2-hydroxynaphthalen-1-yl)diazenyl)phenyl)(5-mercapto -1,3,4-thiadiazol-2-yl)methanone[5]

The IR spectra of compound [5],Fig(6), show the appearance of (SH) at (2656.07)cm^{-1},band of(C=N) for thiadiazole appeared at (1620.26)cm^{-1} and of C-S at (1153.47) cm^{-1} , The ^{1}H-NMR spectrum (Fig.10) show single singlet at (15.634ppm) due to H phenolic,the second single singlate at(4.3ppm) due to H mercapto group and the multi single between(6.8-8.4ppm) due to H aromatic the phenyl and naphthyl ring .

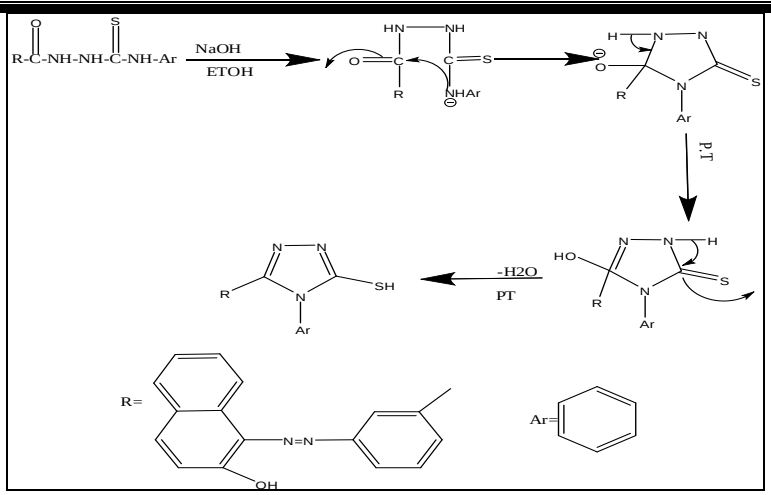
6-Synthes2-(3-((2-hydroxynaphthalen-1-yl) diazenyl)benzoyl)-N-phenylhydrazine carbothioamideis[6]

The compound[6] were prepared through the reaction of compound[3] with phenyl iso thio cyanate.

IRspectra of compound[6],Fig(7), show the disappearance of the two absorption bands at (3346-3446)cm^{-1} due to NH-NH_2 group of compound[3] and the appearance of the two absorption band at(3100- 3184.58)cm^{-1} due to the three group of N-H and appearance band of C=S at (1377.22)cm^{-1}, amideC=O appeared at (1681.98)cm^{-1}.the ^{1}H-NMR spectrum (Fig.12) show single singlet at(10.7ppm) due to H the N-H amide group ,the second single singlet at(9.8ppm)due to the N-H the phenyl,the double singlet at(4.4ppm)due to H the N-H amine group ,the single singlet at(15.70ppm) due to H phenolic and the multi singlet at (6.8-8.5ppm) due to Haromatic the phenyl and naphthyl ring .

7-Synthesis 1-((3-(5-mercapto-4-phenyl-4H-1,2,4-triazol-3-yl)phenyl) diazenyl) naphthalen-2-ol[7]

The IR spectrum of compound[7],Fig(8), show disappearance of the bands at (3100-3184.58cm^{-1}) due to NH-NH group with appearance of a weak band due to –SH group at (2754cm^{-1}),also show the disappearance of the band at(1681.98)cm^{-1} due to C=O of amide with appearance of a bond at (1564.32)cm^{-1}assingnable to C=N of triazole ring.The mechanism of the reaction is shown in scheme below.



Scheme(2) synthesis of triazole derivative

8-Synthesis 1-((3-(5-(phenylamino)-1,3,4-thiadiazol-2-yl) phenyl) diazenyl)naphthalen-2-ol[8]

The compound [8] was synthesis from the reaction of compound [6] with H_2SO_4

The IR spectrum of compound[8],Fig(9), inducated the disappearance of the band at(3100-3184.58)cm^{-1}due to two group NH-NH and apprarance of one N-Hgroup band at3500cm^{-1} and appearance of C=N at 1616.83cm^{-1}.

9-Synthesis(3-((2-butoxynaphthalen-1-yl)diazenyl)phenyl)(5-(butylthio)- 1,3,4-thiadiazol-2-yl)methanone[9]

The compound [9] was synthesized from the reaction of compound [5] with butyl chloride.

The FTIR spectrum of compound[9],Fig(10), inducated the disappearance of SH group band at(2656.07)$cm^{-1}$of the compound[9]disappearance of OH group band at(3398.69) cm^{-1} and appearance of C-H aliphatic at (2870.71)cm^{-1}

Table (1):physical properties of the synthesized compounds

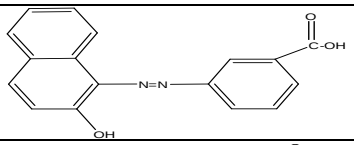
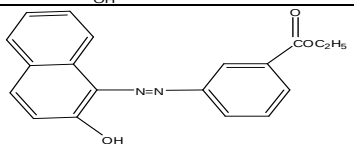
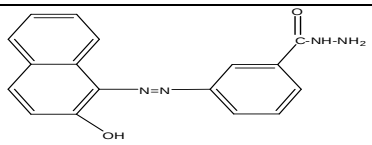
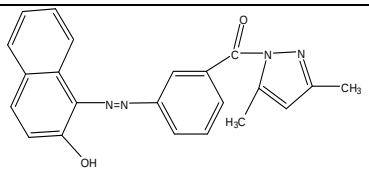
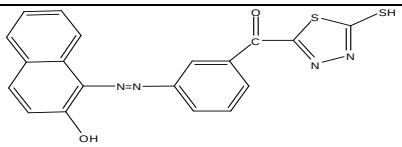
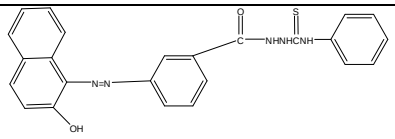
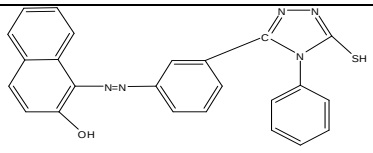
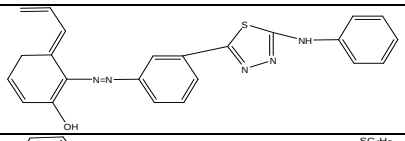
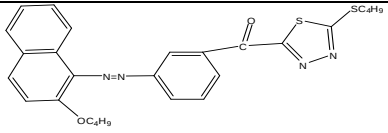
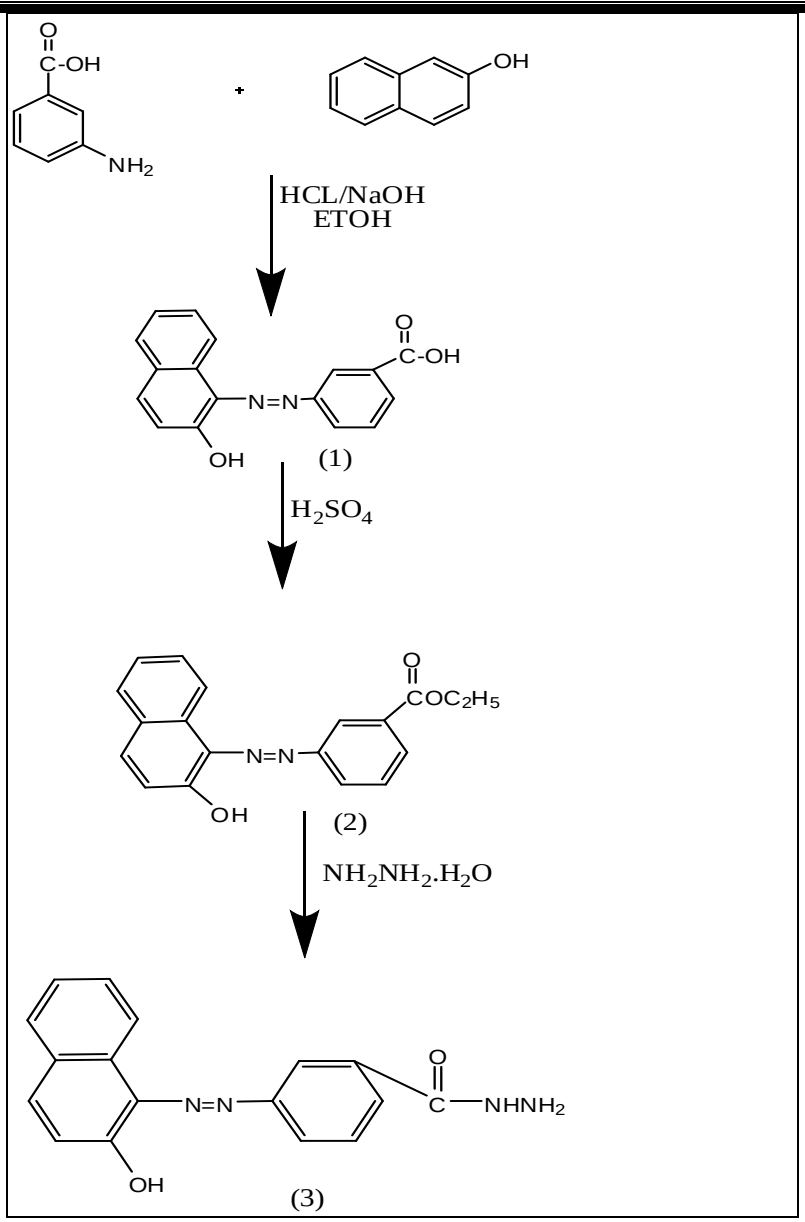
Comp.No	The structure	m.p c^0	colour	Yield%	Elemental Analysis C. H.N cal/found
1		270-272	red	85	---
2		239-241	red	85	-------
3		178-180	Dark red	62	-----
4		219-220	Dark red	84	71.351 4.864 15.135 71.189 4.905 15.205
5		230-232	brown	68	58.163 3.061 14.285 57.981 3.102 14.214
6		100-102	blak	90	--------
7		118-120	Dark red	68	--------
8		72-74	brown	83	--------
9		120-122	red	70	64.285 5.555 11.111 64.476 5.627 11.214

Table (2): IR spectra data(cm^{-1}) of compounds(1-9)

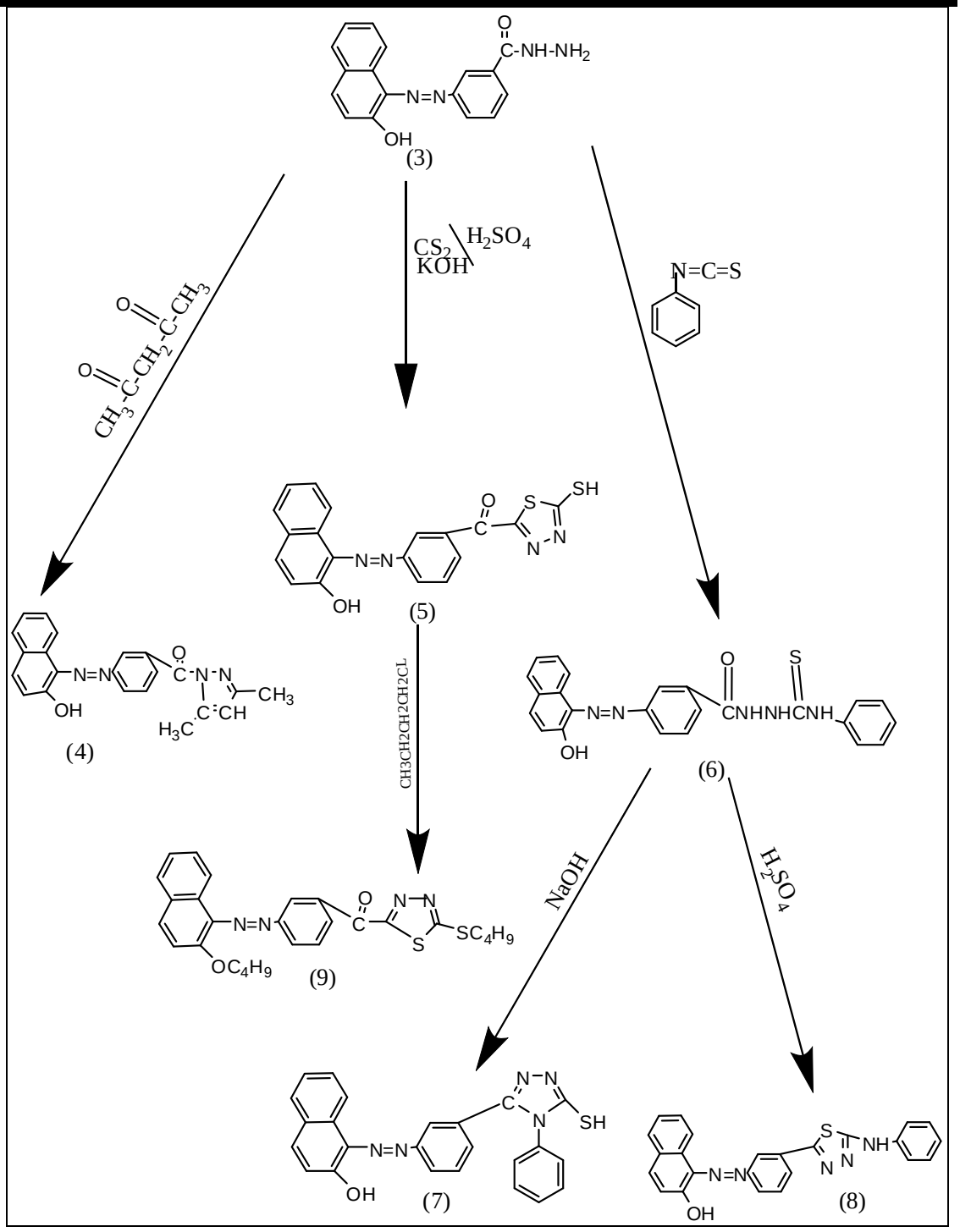
Comp.No.	νN-H	νO-H	νC-H Oram.	νC-H Aleph	νC=O	νC=N	νN=N	others
1	---------	3389.04	3039.91	--------	1680.05	-------	1454.38	--------
2	---------	3421.83	3000	2922.25	1708.99	--------	1450.52	----------
3	3346-3446	-------	3059.20	--------	1699.34	--------	1506.46	---------
4	---------	3190.37	3032.20	2900	1712.85	1500.53-1556.61	--------	---------
5	--------	3398.69	3063.06	--------	1695.49	1620.26	1450.52	V(SH)2656.07
6	3184.58	--------	3000	--------	1681.98	------	-------	V(c=s)1377.22
7	--------	3273.31	3049.56	--------	-------	1564.32	1496.81	ν(SH)2754
8	3500	3300-3500	-------	--------	--------	1600.83	1444.73	---------
9	---------	--------	3030.27	2870.17	-------	1651.12	1452.45	ν(O-R) 1319.35

Table(3): H^1-NMR spectra Data(ppm) of compounds [1, 3, 4, 5 and 6]

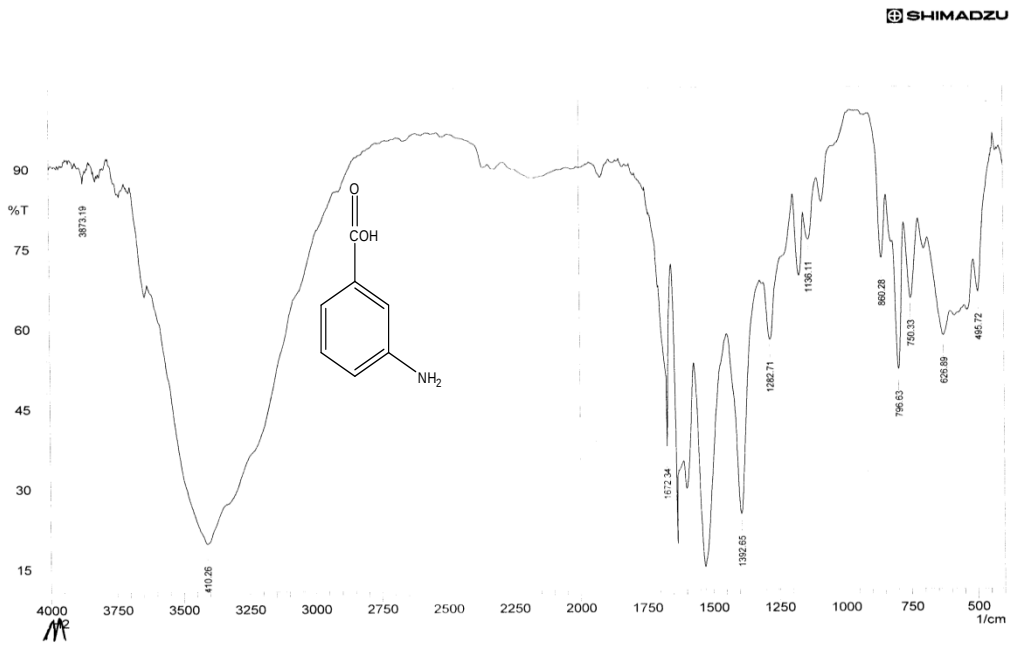
Comp.No	δ(O-H) Phenolic S,1H	δ(O-H) Carboxylic S,1H	δ(H) Arom. m , H	δ(N-H)	δ(NH)	Other
1	15.651	13.35	6.8-8.5			
3	15.451	-	6.7-7.9	t, 1H 8.4-8.6	d,2H 5.4	
4	15.3	-	6.6-8.8	-	-	s ,6H,$(CH_3)_2$ δ2.2and 3.5 s ,1H,(H-pyrazole) δ6.3
5	15.634	-	6.8-8.4	-		s ,1H,(SH) δ4.3
6	15.70	-	m,15H, 6.8-8.5	d,1H δ 10.7	δd,1H,4.4	s,1H,(N-H) δ9.8



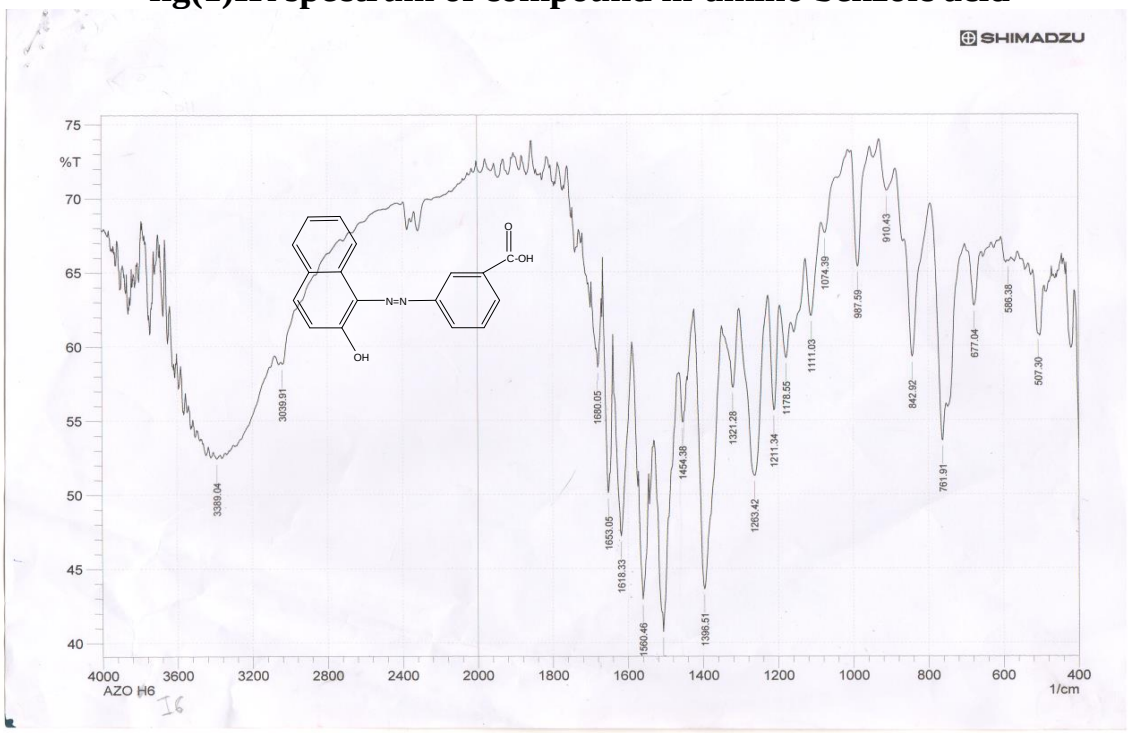
Scheme(3)synthesis of compounds(1),(2),(3)



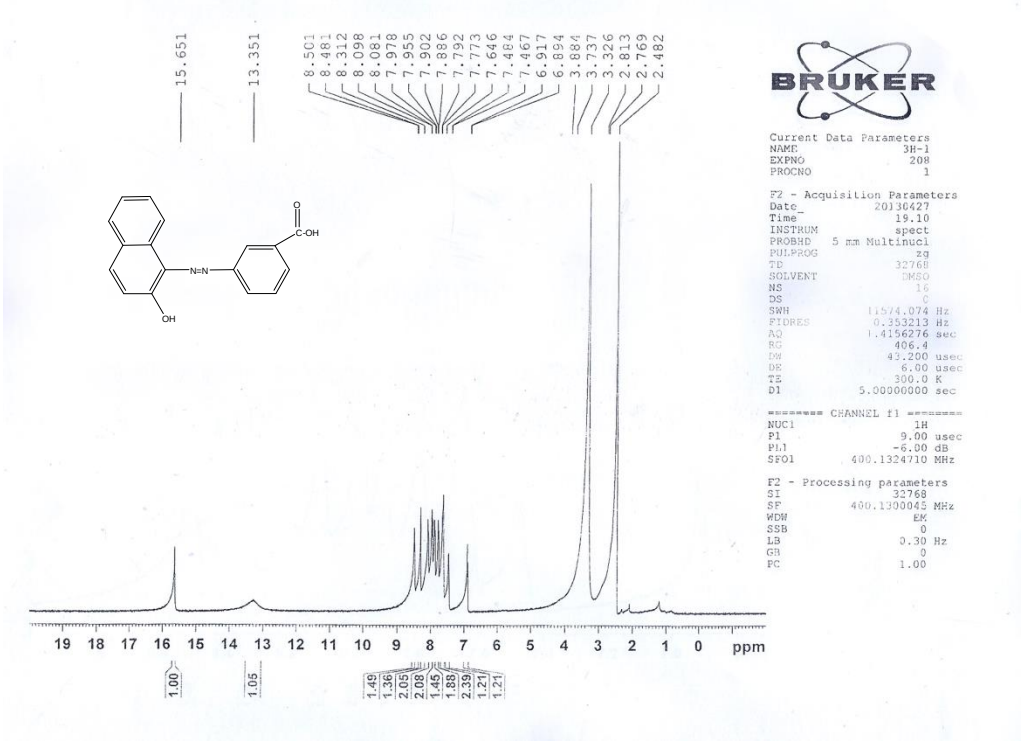
Scheme(4)synthesis of derivatives five hetrocyclic ring



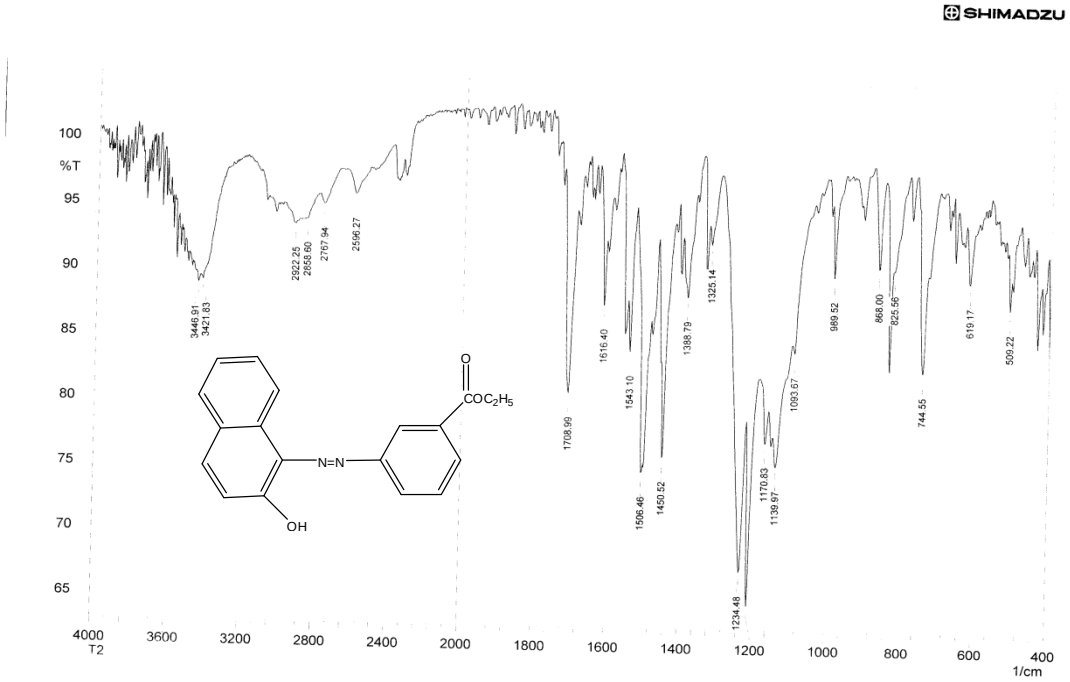
fig(1)IR spectrum of compound m-amino benzoic acid



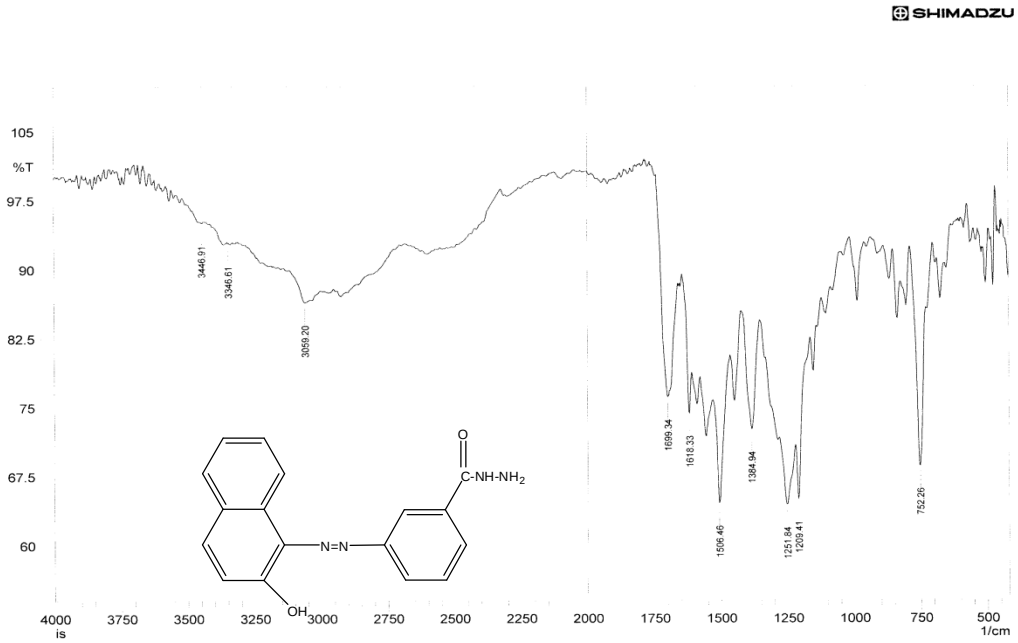
Fig(2):IR spectrum of compound[1]



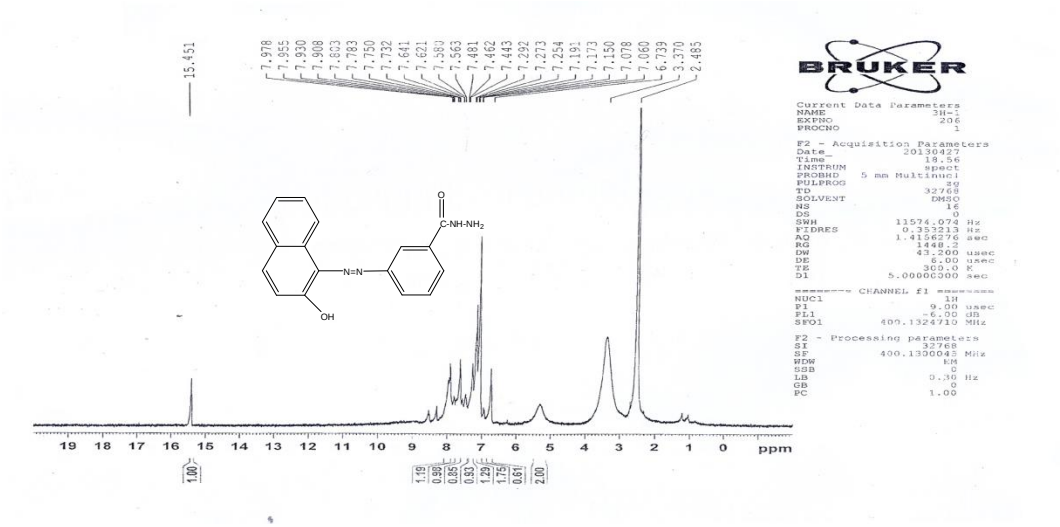
Fig(3):^{1}H-MNR spectrum of compound[1]



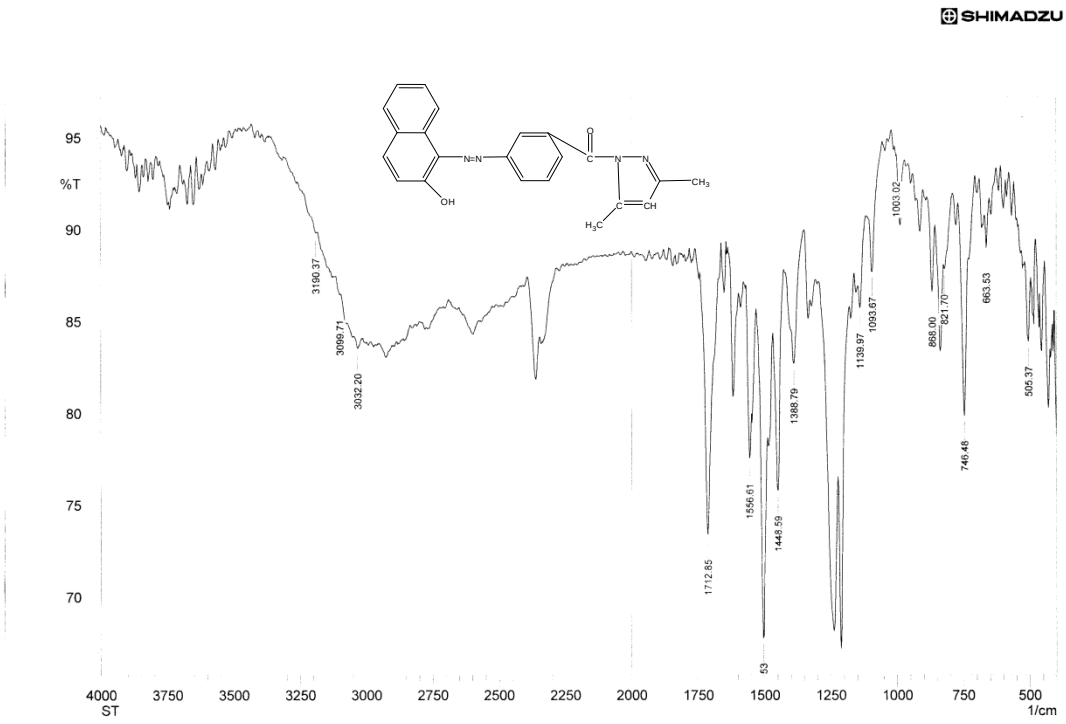
Fig(4) IR spectrum of compound[2]



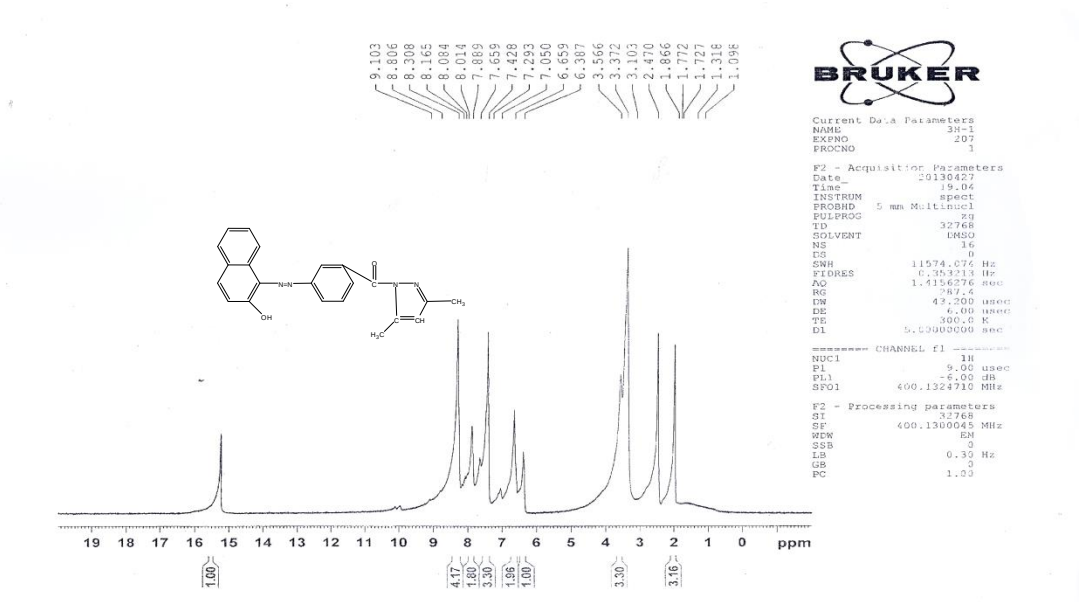
Fig(5):IR spectrum of compound[3]



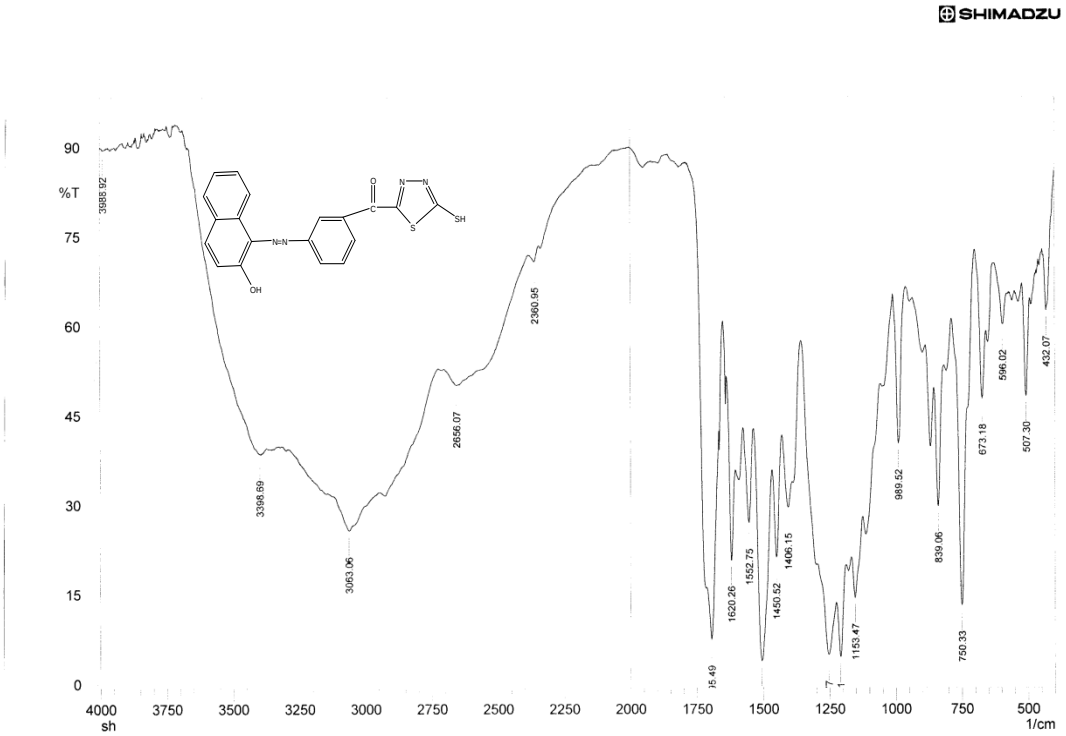
Fig(6):^{1}H-NMR spectrum of compound[3]



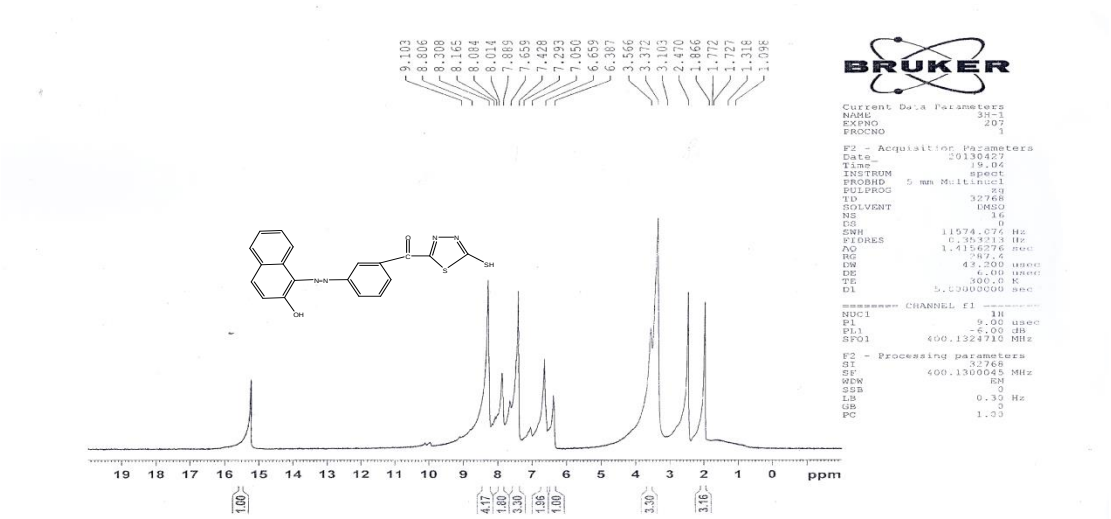
Fig(7):IR spectrum of compound[4]



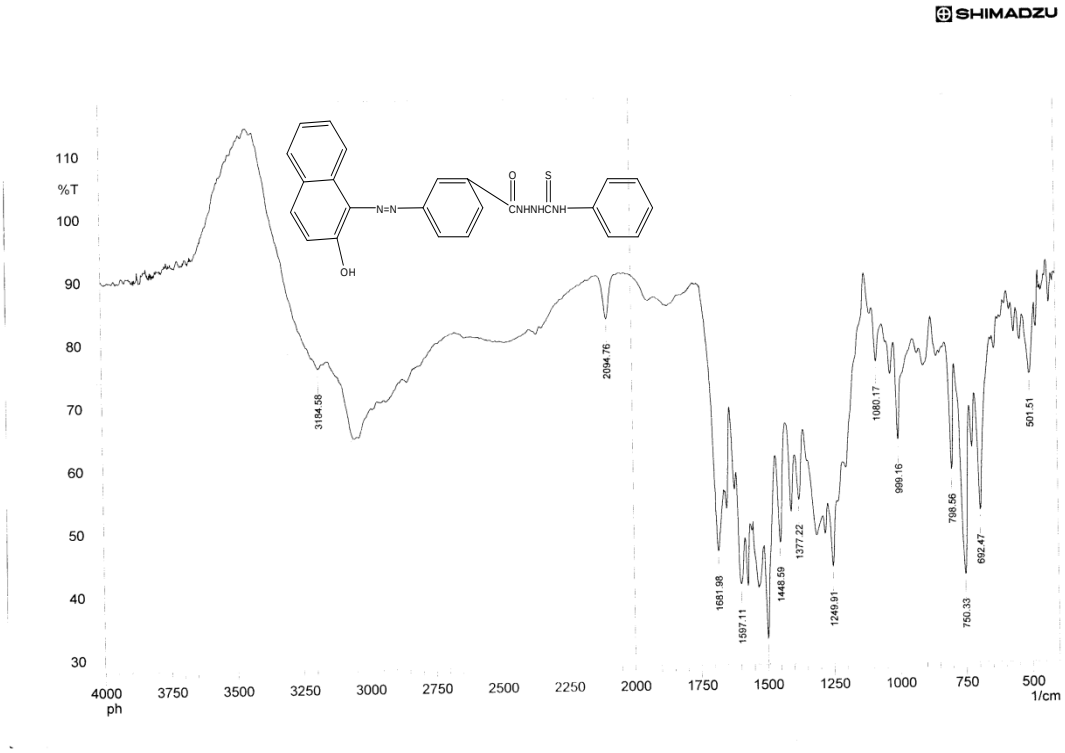
Fig(8):^{1}H-NMR spectrum of compound[4]



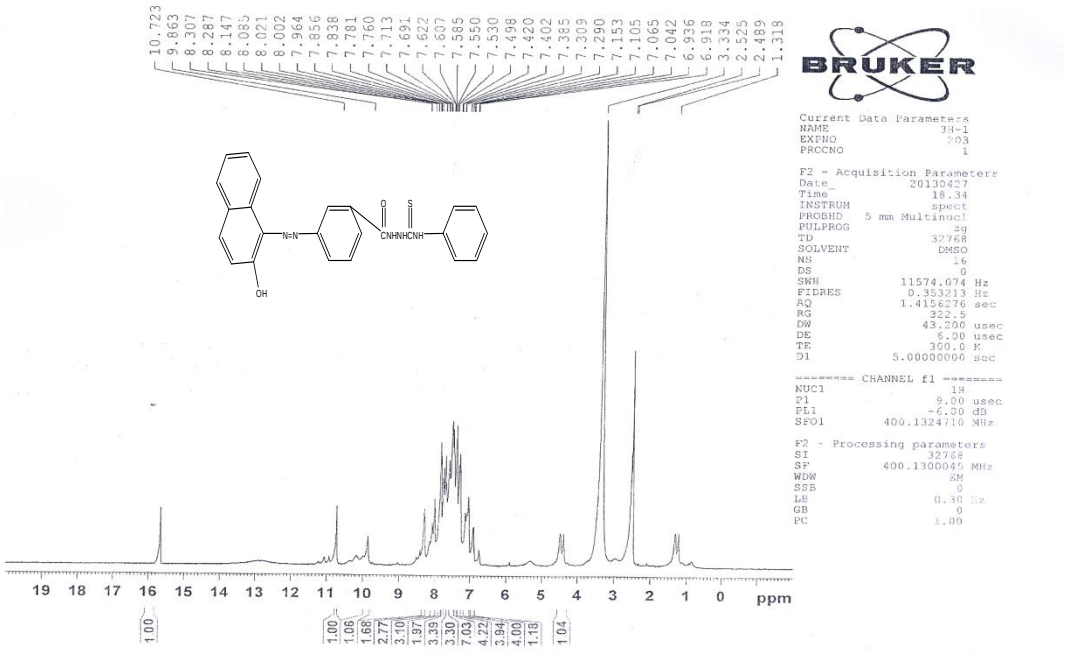
Fig(9):IR spectrum of compound [5]



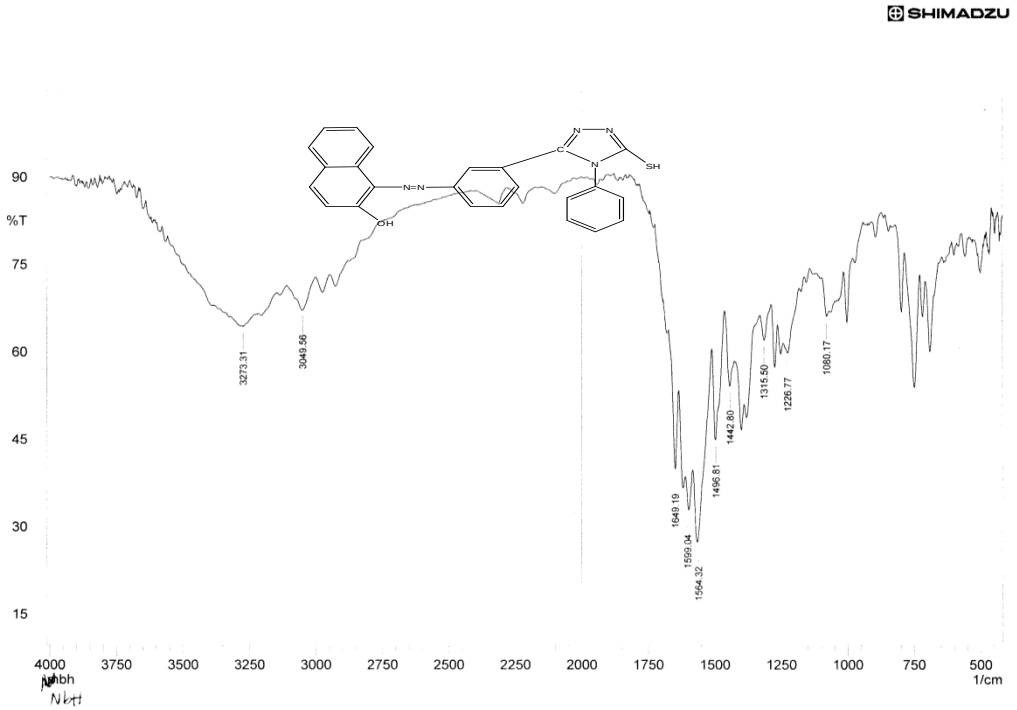
Fig(10):^{1}H-NMR spectrum of compound [5]



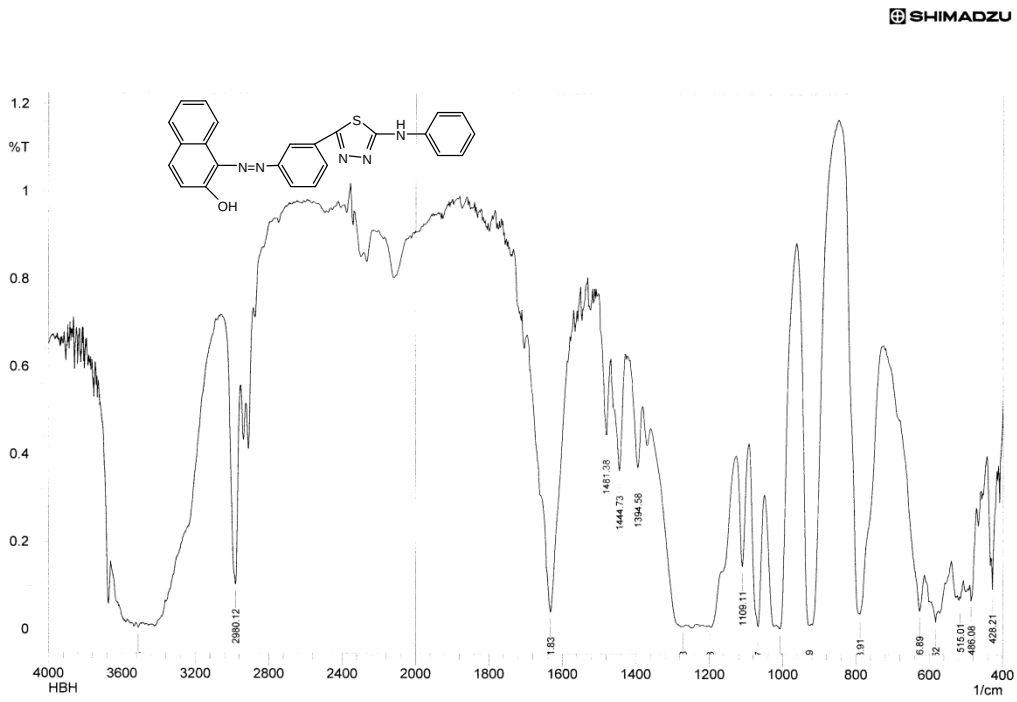
Fig(11) IR spectrum of compound[6]



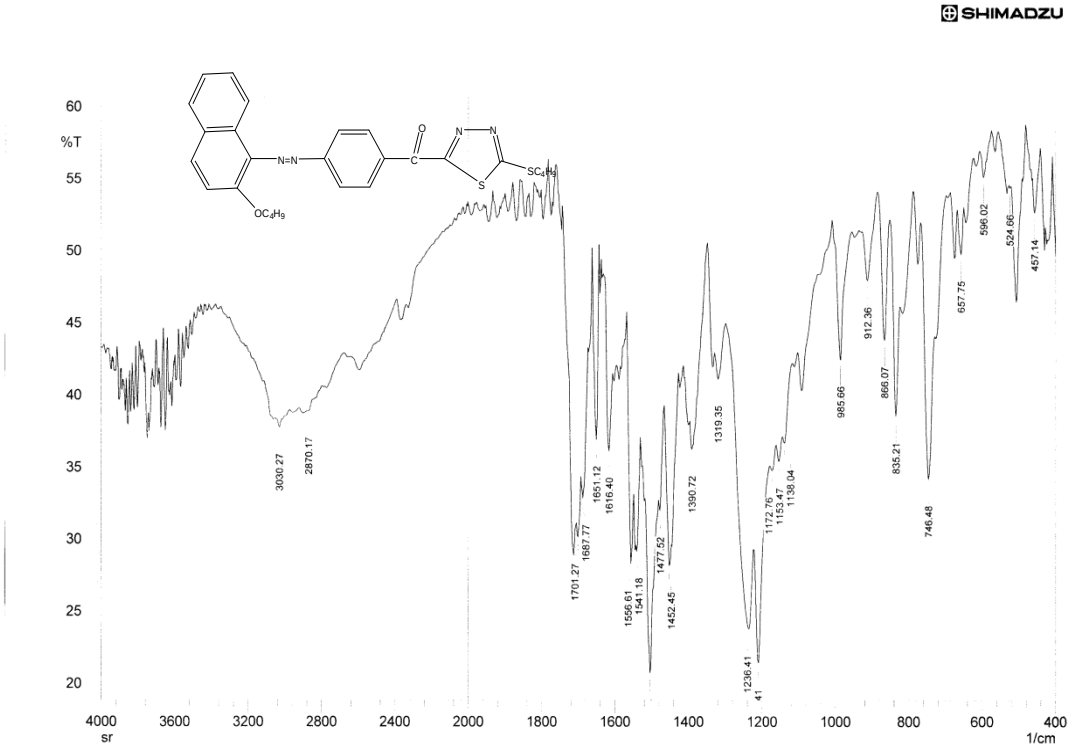
Fig(12) ^{1}H-NMR spectrum of compound[6]



Fig(13):IR spectrum of compound[7]



Fig(14)IR spectrum of compound [8]



Fig(15):IR spectrum of compound[9]

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*تحضير وتشخيص بعض مشتقات الحلقة الخماسية غير المتجانسة

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الخلاصة :-

تم في هذا البحث تحضير عدد من المركبات تشمل3-[(2-هيدروكسي نفثالين-1-يل)ديازنيل بنزوك اسد] (1) ،ايثل3-[(2-هيدروكسي نفثالين -1-يل)ديازنيل]بنزويت(2)،3-[(2-هيدروكسي نفثالين-1-يل) ديازنيل] بنزوهايدرازايد(4)،[5,3-داي مثيل-1H-بايرازول-1-يل] [3-((2-هايدروكسي نفثالين -1-يل) ديازنيل) فنيل]ميثانونين(4)،[3-((3-هايدروكسي نفثالين -2-يل)ديازنيل)فنيل] [5-مركبتو-4,3,1-ثاياديازول-2-يل] ميثانونين(5)،2-[3-((3-هيدروكسي نفثالين-2-يل)ديازانيل)بنزويل]-N-فنيل هايدرازين كاربوثايوامايد(6)،1-[(3-(5-مركبتو-4-فنيل-4H-4،2,1-ترايازول-3-يل)فنيل)ديازانيل]نفثالين-2-اول(7)،1-[(3-(5-(فنيل امين)-4,3,1-ثاياديازول-2-يل)فنيل)ديازانيل]نفثالين-2-اول(8)،[3-((2-هيدروكسي نفثالين-1-يل)ديازانيل)فنيل](5-ثايوبيوتل)-4،3,1-ثاياديازول-2-يل-ميثانون(9). شخصت المركبات المحضرة بواسطة اطياف الاشعة تحت الحمراء واطياف الرنين النووي المغناطيسي البروتوني والتحليل الدقيق للعناصر كذلك تم التاكد من نقاوة المركبات المحضرة عن طريق تقنية كروموتوغرافيا الطبقة الرقيقة .

الكلمات المفتاحية : ثاياديازول ، ترايازول ، بايرازول

***البحث مستل من رسالة ماجستير للباحث الاول .**