

# Synthesis and Characterization of Heteromacro cyclic Compounds via cyclization Reactions

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## Abstract :

In the present study , new type of heteromacro cycles [4,5] were synthesized by the reaction between terminal of (amine , thiol ) of compounds [1-3] with carbonyl compounds (4 – amino benzoyl chloride ,4-methanal ethyl benzoate , 4-methanal benzaldehyde) by condensation reaction .The synthesized compounds have been investigated using different chemical techniques , such as (Uv-Visible spectra ,FT-IR-spectra ,H.NMR-spectra ,(C.H.N)-analysis , and melting points ) .

## Introduction :

The importance of this compounds has long been recognized in the synthetic organic chemistry ,which have a wide variety of biological activity such as pharmacological activities ,which include anti fungal<sup>(1,2)</sup> ,anti bacterial<sup>(3,4)</sup> ,anti tumor ,antitubercular<sup>(5,6)</sup> and anti convulsant<sup>(6)</sup>.

In this article , synthesized heteromacrocycles are result from condensation reaction as the ring – closing step . these compounds are promising candidates for developing new supramolecular structures , they are reported to have antibacterial activity , the structural modification of organic molecule has considerable biological relevance and other uses<sup>(7-10)</sup> , which are contain (amide, imine , sulphide , thiazol ) groups<sup>(6-11)</sup> due to activity of these compounds .

These compounds are stable at room temperature and are non hygroscopic , have good yield , from a synthetic point of view , they are containing reactive functional groups are important for the above – listed applications .

## Experimental :

All chemical used were supplied from Merck & BDH-chemical company.

All measurements were carried out by :

-Melting points :electro thermal 9300 , melting point engineering LTD , U.K .

-FT-IR spectra : fourrier transform infrared shimadzu (8300) (FT-IR) ,KBr-disc was performed by CO.S.Q. Iraq .

-H-NMR spectra: in centre lab – institute of earth and environmental science , AL – byat university , Jordan .

-Elemental analysis (C.H.N) : EA-017 Mth in centre lab –institute of earth and environmental science , AI-byat university , Jordan .

-Uv–Visible spectra :shimadzu–1700 , double beam with computerized , Japan .

### **Synthesis of 6-Mercapto-2-(4-amino benzamide)-benzothiazole [1]:**

A mixture of (0.05mole , 9.1 gm ) of 6-Mercapto -2-(4-amino benzothiazole & (0.05 mole , 7.77 gm)of 4- amino benzoyl chloride were heated under reflux for (2 hrs) , the reaction mixture was cooled , the precipitate was filtered of & recrystallized from ethanol to produce (16.4g) 84% of bill yellow crystal compounds [1].

### **Synthesis of Bis{6-(mercapto-2-benzamide)-benzothiazol}-4-benzamide methyl imine [2]:**

Refluxing mixture of (0.04 mole ,12.04 g) of compounds[1] with (0.02 mole ,3.56 g) of 4-formal- ethyl benzoate were reacted for two hours refluxing until the participitate formed ,after cooling, the precipitate was filtered off & recrystallized to produce(15.2g) 81% of yellow crystal compounds [2] .

### **Synthesis of Bis{6-(4-aminobenzoyl sulphide-2-benzamide )-benzothiazol}-4-benzamide methyl imine [3]:**

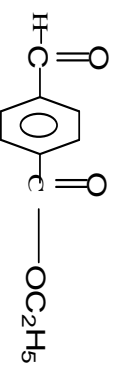
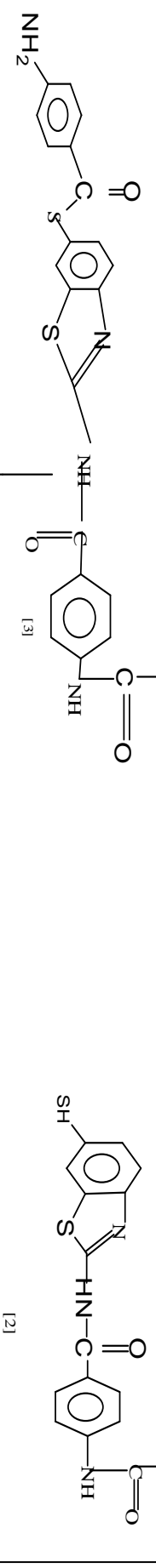
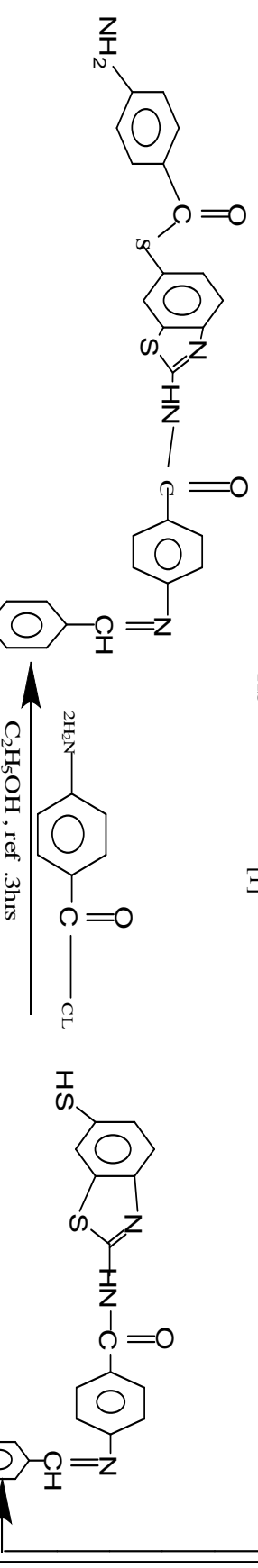
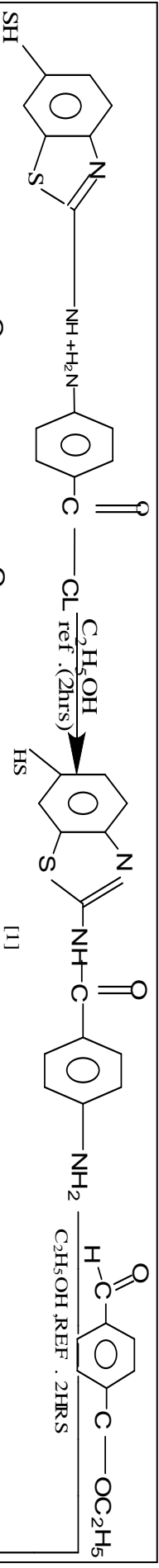
A mixture of (0.04 mole , 28.6g) of compound [2] and (0.08 mole , 12.44 g) of 4-amino benzoyl chloride were reacted by condensation for (3hrs) refluxing until the participitate formed, after cooling , the precipitate was filtered off & recrystallized to produce(45.3g) 83% from bill orange crystal compounds[3].

### **Synthesis of compounds [4,5]:**

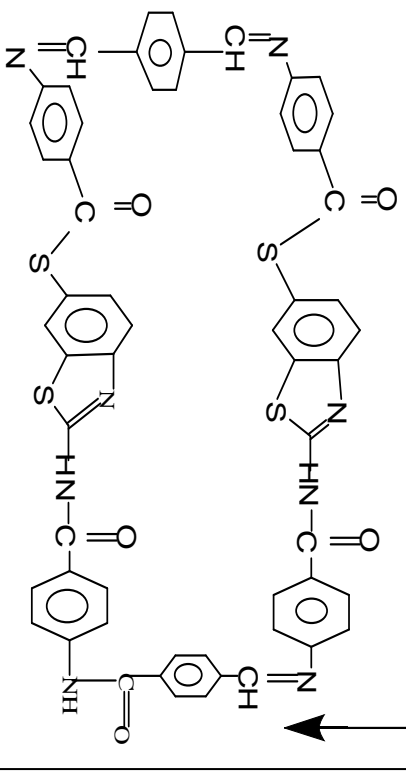
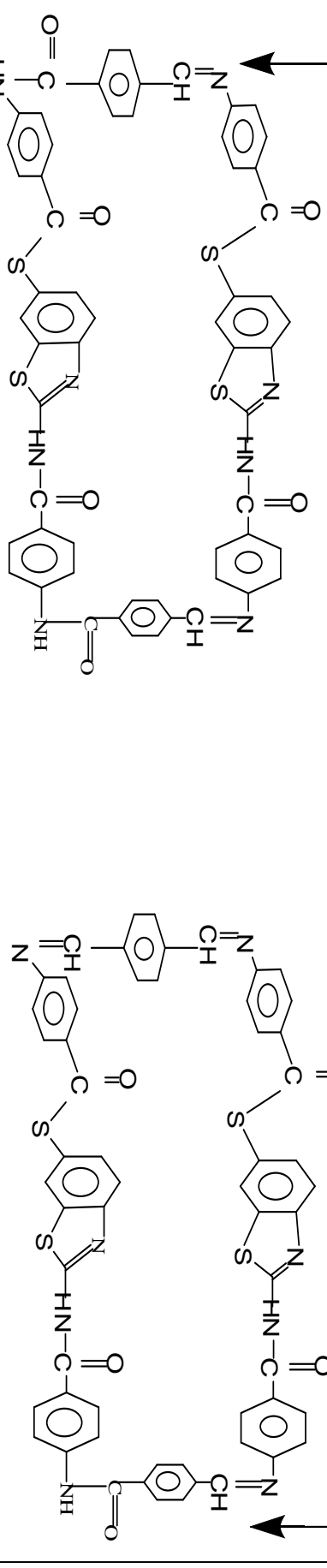
(0.02 mole , 19.08 g) of compound [3] was reacted with one of [(0.02 mole , 3.56 gm) of 4-formal–ethyl benzoat , (0.02 mole , 2.68g) of 4-formal benzaldehyde] respectively by reflux for (4hrs) & recrystallized to yield(23.2g ,21.1g) (82% , 80%) from(orange, red) compounds [4,5] respectively :

Compound [4] : Bis – {(6-benzoyl sulphide -2-benzamide ) benzothiazol -4-benzamide methyl imine } – hetromacrocycle .

Compound [5]: Bis-{(6-benzoyl sulphide -2-benzamide)-benzothiazol} -4-benzamide – tris (methyl imine ) – hetromacrocycle.



C<sub>2</sub>H<sub>5</sub>OH, REF. 4HRS



## Result and Discussion:

All the synthesized compounds[1-5] have been characterized by their melting points and spectroscopic methods , such as (Uv-visible , FT.IR ,H.NMR spectrum, and (C.H.N)-analysis):

### FT.IR Spectra:

In FT.IR spectra ,the reaction is followed by disappearance of (-NH<sub>2</sub>) absorption band at (3420)cm<sup>-1</sup> in compound [1] , and appearance two band :at (1610)cm<sup>-1</sup> .(1690)cm<sup>-1</sup> due to (HC=N)of azomethine group<sup>(7-9)</sup> and (  $\text{HN}-\overset{\text{O}}{\parallel}{\text{C}}-$  ) carbonyl of amide group , respectively in compound [2] . while FT.IR spectra of compound [3] showed disappearance of (S-H) absorption band at (2455) cm<sup>-1</sup> and appearance absorption (3455)cm<sup>-1</sup> due to (-NH<sub>2</sub>) group<sup>(11-14)</sup> .In compound [4] we are observed disappearance of (-NH<sub>2</sub>) absorption band and appearance absorption band at (1616)cm<sup>-1</sup> due to (HC=N) azomethine group and (1690)cm<sup>-1</sup> due to (  $\text{HN}-\overset{\text{O}}{\parallel}{\text{C}}-$  )amide group<sup>(15-18)</sup> . While FT.IR Spectra of compound [5] showed disappearance of (-NH<sub>2</sub>) ,absorption band appearance absorption band at (1631)cm<sup>-1</sup> due to (HC=N) azomethine group ,other informative bands<sup>(19-21)</sup> are listed in table (1) . The presence these bands consider as indication to formation these compounds .

### H.NMR-Spectrum:

H.NMR –spectrum of compounds in figures (4-6) : showed the following characteristics chemical shift were appeared : singlet signal at  $\delta$  9.79 for one proton of azomethine<sup>(20,21)</sup> group (-CH=N), peak at  $\delta$  9.96 for proton of amide group (  $\text{HN}-\overset{\text{O}}{\parallel}{\text{C}}-$  ) in compound [2] , signal at  $\delta$  8.5 for two proton of amine group (-NH<sub>2</sub>) ,signal at  $\delta$  9.70 for proton of azomthine group (-CH=N) peak at  $\delta$  9.9 for proton of amide group (  $\text{HN}-\overset{\text{O}}{\parallel}{\text{C}}-$  ) in compound [3], while the compound [4,5] are disappear the signals at  $\delta$  8.5 for protons of amine group (-NH<sub>2</sub>) and appear signals at  $\delta$  9.71 for proton of imine<sup>(20,21)</sup> (-CH=N) and at  $\delta$  9.9 for proton of amide group (  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}$  ) ,multistate leaning on each other at  $\delta$  7.5-7.8 that could be attributed to the protons of benzene ring in these compounds .

This is other evidence to formation of compounds [1-5], and other peaks<sup>(18-21)</sup> in figures (4-6).

## UV-Visible and (C.H.N)-Analysis:

UV-spectra of compounds [1-5] have electron transition ( $n-\pi^*$ ) due to the heteroatom (S,N) in these compounds beside of transition ( $\pi-\pi^*$ ) of conjugated system, the UV-spectra of these compounds show absorption maxima (315-405) nm due to oxochromic groups ( $-\text{NH}_2, -\text{SH}, \text{--}\overset{\text{O}}{\parallel}{\text{C}}\text{--NH}$ ) with conjugated system of compounds [1-5].

It was found from (C.H.N) –analysis, from compared the calculated data from compounds [1-5] are in good agreement with experimentally, the results were compactable and this is other evidence for formatted compounds, the data of analysis,  $\lambda_{\text{max}}$  and melting points are listed in table (2).

## Acknowledgment :

I would like to express my thanks to Mr.Muhanad –Abu-Alsoaud in centre Lab-Institute of Earth and Environmental Science –Al-Bayt University H.J.K in Jordan for providing (C.H.N) element analytical, and H.NMR –spectrum.

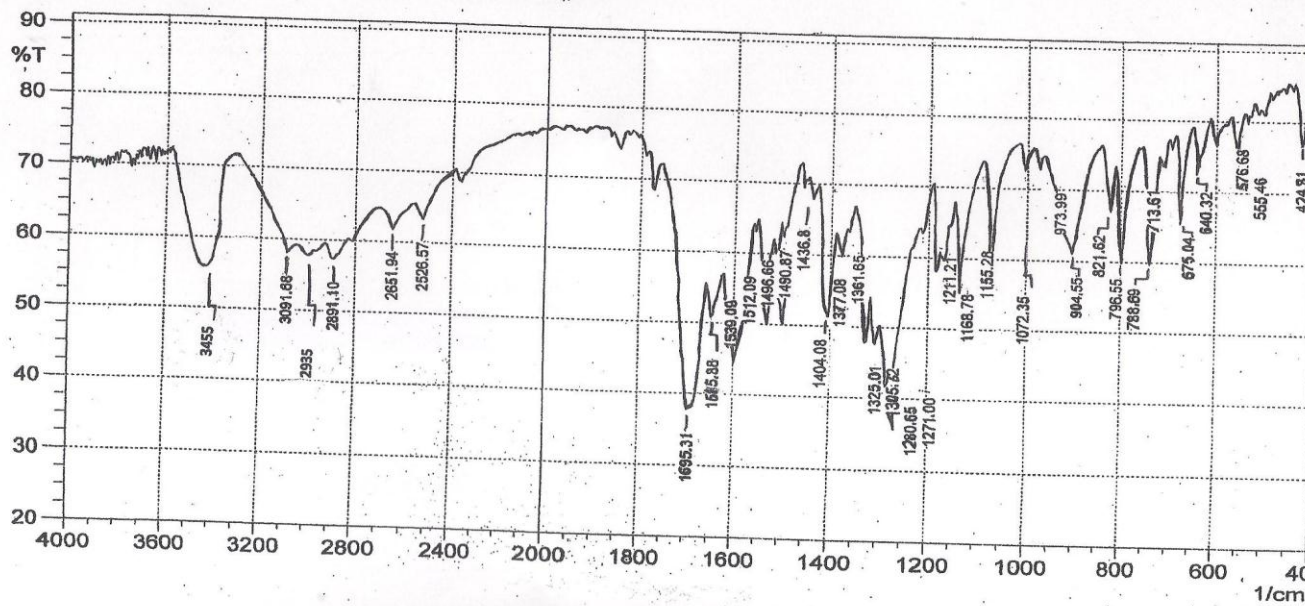
**Table (1) :FT.IR data (cm<sup>-1</sup>)of compounds[1-5]**

Comp. No.	$\nu(\text{N-H})$	$\nu(\text{S-H})$	$\nu(\text{CH=N})$ Azomthine	$\left( \begin{array}{c} \text{O} \\ \parallel \\ \text{HN-C} \end{array} \right)$ carbonyl of amide	$\nu(\text{C-S})$ Sulphide
[1]	3420m	2470w	-----	1685s	-----
[2]	-----	2455w	1610s	1690s	-----
[3]	3455m	-----	1615s	1695s	1325vs , 675s
[4]	-----	-----	1616s	1690s	1315vs , 682s
[5]	-----	-----	1631s	1690s	1323s , 682s

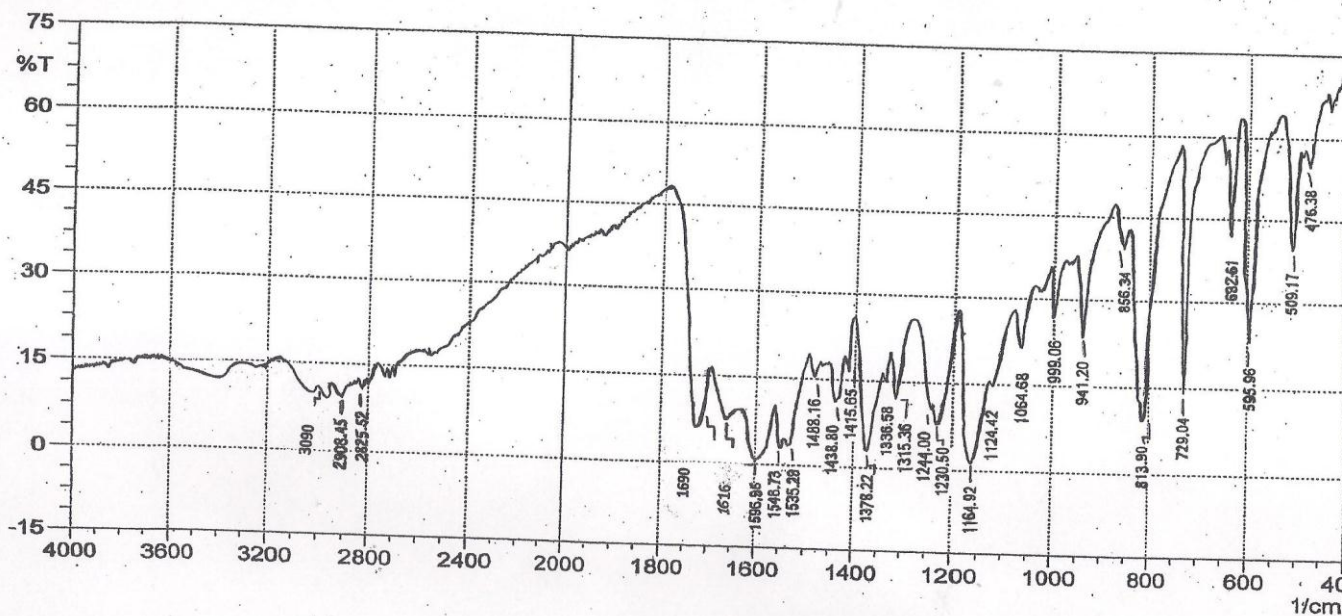
s=strong , m=medium , w=weak , v=very

**Table (2):Melting points,M.F , $\lambda_{\text{max}}$  and (C.H.N)-Analysis of compounds[1-5]**

Comp . No.	M.F M.Wt <sub>(g/mole)</sub>	m.p ( $^{\circ}$ )	$\lambda_{\text{max}}$ (nm)	Calc / Found C%	H%	N %
[1]	$\text{C}_{14}\text{H}_{11}\text{N}_3\text{O S}_2$ 301	161	310	55.813 55.609	3.654 3.538	13.953 13.710
[2]	$\text{C}_{36}\text{H}_{24}\text{N}_6\text{O}_3\text{S}_4$ 716	182	335	60.335 60.213	3.351 3.274	11.731 11.654
[3]	$\text{C}_{50}\text{H}_{34}\text{N}_8\text{O}_5\text{S}_4$ 954	221	360	62.893 62.648	3.563 3.571	11.740 11.599
[4]	$\text{C}_{58}\text{H}_{36}\text{N}_8\text{O}_6\text{S}_4$ 1068	243	392	65.168 65.096	3.370 3.310	10.486 10.348
[5]	$\text{C}_{58}\text{H}_{36}\text{N}_8\text{O}_5\text{S}_4$ 1052	247	405	66.159 66.145	3.422 3.309	10.646 10.573



Fig(1) : FT-IR Spectra of compound (3)



Fig(2) : FT-IR Spectra of compound(4)



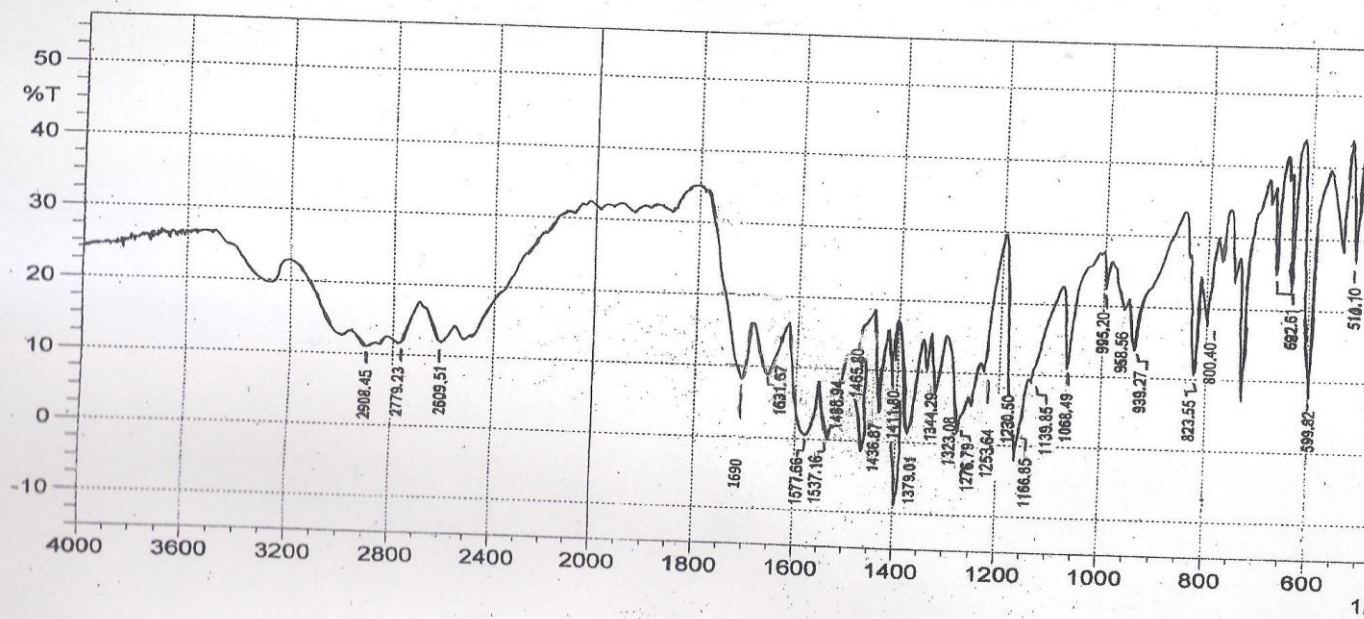
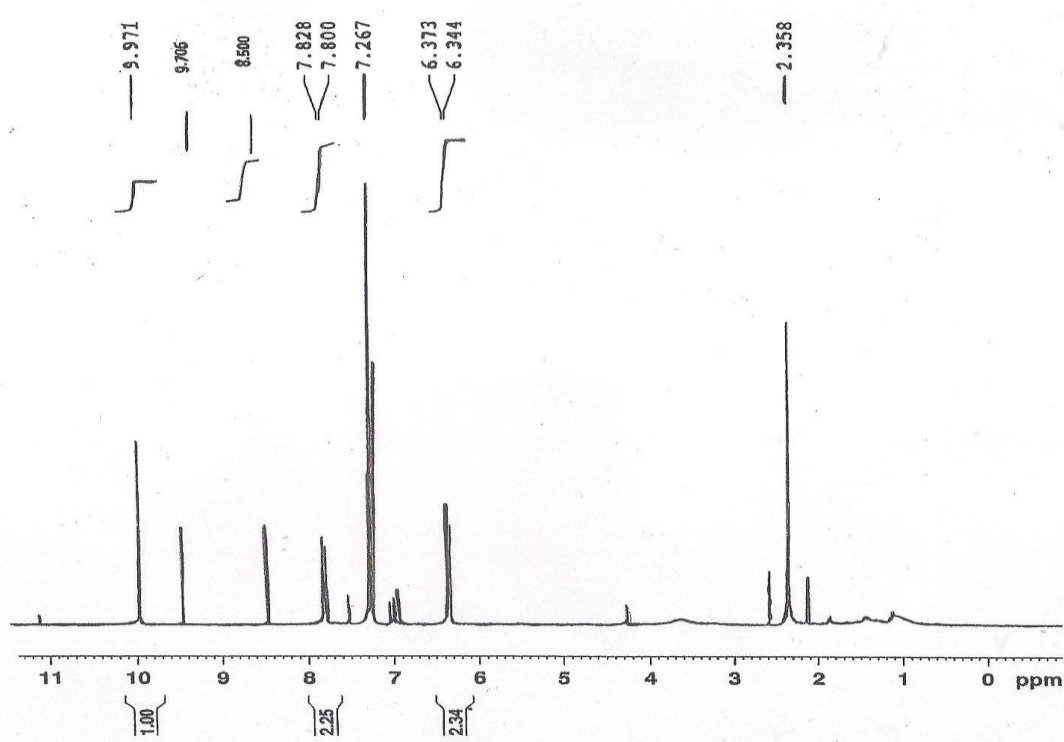


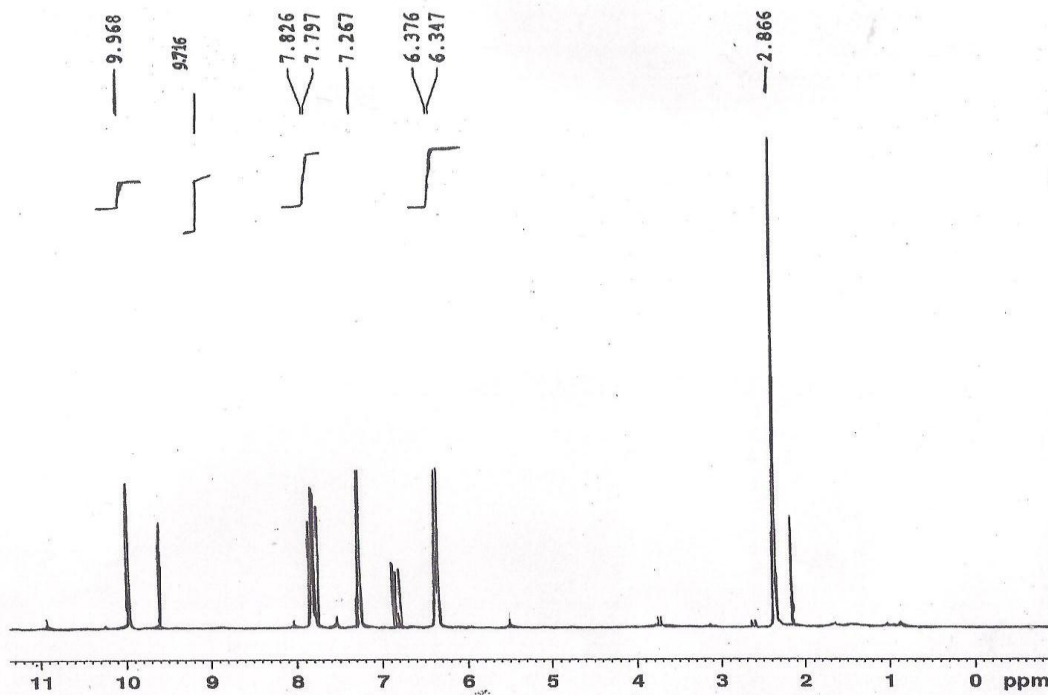
Fig (3) FT-IR Spectrum of compound(5)



Current Data Parameters  
 NAME  
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 PROCNO  
 F2 - Acquisition Parameters  
 Date\_ Time  
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 PULPROG  
 TD  
 SOLVENT  
 NS  
 DS  
 SWH 8333  
 FIDRES  
 AQ 3.9322  
 RG 18  
 DW 60  
 DE  
 TE  
 D1 1.0000  
 MCREST 0.0000  
 MCWRK 0.0150  
 ===== CHANNEL f1  
 NUC1  
 P1  
 P11  
 SFO1 300.131  
 F2 - Processing parameters  
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 SF 300.130  
 NDB  
 SSB  
 LB  
 GB  
 PC

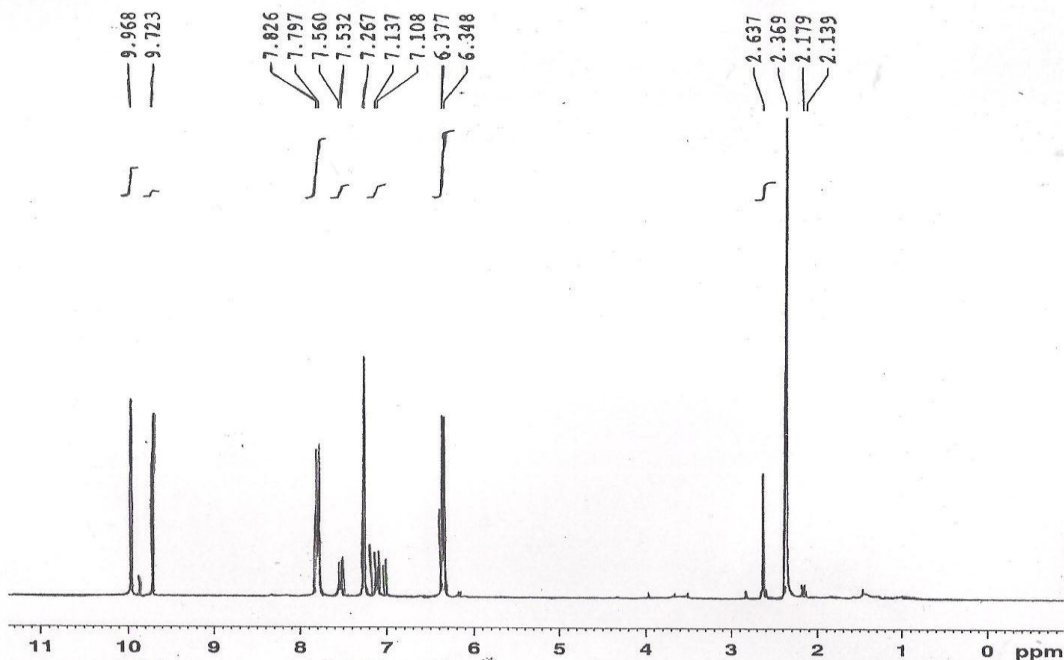
Fig (4): H.NMR-Spectra of compound (3)





Current Data Parameters  
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 PROCNO  
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 Time   
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 PULPROG 655  
 TD  
 SOLVENT  
 NS  
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 FIDRES 0.1272  
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 RG  
 DW 60.6  
 DE 6  
 TE 29  
 D1 1.00000  
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 MCWRK 0.01500  
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 PL1 -3  
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 SF 300.1300  
 WDW  
 SSB  
 LB  
 GB  
 PC

Fig(5): H.NMR -Spectra of compound (4)



Current Data Parameters  
 NAME  
 EXPNO  
 PROCNO  
 F2 - Acquisition Parameters  
 Date\_   
 Time   
 INSTRUM  
 PROBHD 5 mm DUL  
 PULPROG  
 TD  
 SOLVENT  
 NS  
 DS  
 SWH 833  
 FIDRES 0.1  
 AQ 3.93  
 RG  
 DW 6  
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 TE  
 D1 1.000  
 MCREST 0.000  
 MCWRK 0.015  
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 PL1  
 SFO1 300.13  
 F2 - Processing parameters  
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 WDW  
 SSB  
 LB  
 GB  
 PC

Fig(6): H.NMR -Spectra of compound (5)

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تخليق مركبات حلقيّة كبيرة غير متجانسة عن طريق تفاعلات الحوّلقة

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الخلاصة :

تم في هذه الدراسة تخليق نوع جديد لمركبات حلقيّة عيانية غير متجانسة [5,4] من تفاعل مجاميع الثايول و الأمين في مركبات [ 1-3] مع مركبات الكاربونيل (4- أمينو - كلوريد البنزويل , 4- فورمال بنزوات الأثيل , 4- فورمال بنزليدهايد ) باستخدام تفاعل التكتيف . شُخصت المركبات المحضرة بمختلف التقنيات الكيميائية تمثلت ب(طيف الاشعة فوق البنفسجية - المرئية , طيف الاشعة تحت الحمراء , طيف الرنين النووي البروتوني المغناطيسي , التحليل الكمي الدقيق للعناصر) ومن ثم قياس درجات أنصهارها.