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Department of Chemistry

Synthesis ,Characterization and Study the Mesomorphic Behavior of Some New Mesogenes Containing Hetrocyclic Ring

A Thesis
Submitted to the Council of College of Education for Pure Science, Ibn Al-Haitham, University of Baghdad, in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Chemistry

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيم
الرَّحْمَنُ (١) عَلَّمَ الْقُرْآنَ
(٢) خَلَقَ الإنْسَانَ (٣)
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(٦)

صدق الله االعظيم

سورة الرحمن من الآية (١-٦)

I certify that this thesis was prepared under my supervision at Department of Chemistry, College of Education For Pure Science (Ibn Al Haitham), Baghdad University, as a partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

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This work is

Dedicated

To

My Mother

Tareq

Acknowledgment

I would like to extend my thanks and gratitude to God for my conciliation to complete my research. I would also like to thank my supervisor Asst .Prof. Dr. Nisreen H. Karam for suggesting the proposal and her continuous support, her generousity to provide me with

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I wish her health, happiness and long live

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Abstract

Our work includes synthesis, characterization and study of the liquid crystalline behavior of some new heterocyclic compounds derived from 1,3-phenylendiamine and 1,4-phenylendiamine compounds, as follows:

The first synthetic route includes the synthesis of N,N-(1,3- or 1,4-Phenylene)bis(2-chloroacetamide) $[I]_{a,b}$ then conversion to corresponding N,N-(1,3or 1,4--phenylene)bis(2-azidoacetamide) $[II]_{a,b}$ by reaction with sodium azide.

These compounds reacted with acrylic acid to give compounds $[III]_{a,b}$ where converted to ester compounds $[IV]_{a,b}$ by reacted with methanol in the presence of H_2SO_4. Also ester compounds $[IV]_{a,b}$ reaction with hydrazine hydrate 80% to form acid hydrazide compounds $[V]_{a,b}$, The compounds n- alkoxy benzaldehyde$[V]_n$ synthesized from 4-hydreoxybenzaldehyde with alkyl bromide , these compounds reacted with acid hydrazide $[V]_{a,b}$ to produce Schiff bases compounds $[VII]_n$, $[VIII]_n$ where (n=1,2,3,5,6,7,8) . The second synthetic route includes the synthesis benzimidazole compounds$[IX]_{a,b}$ from reaction compounds $[III]_{a,b}$ with o-phenylene diamine . Also synthesized acid chloride compounds $[X]_{a,b}$ by react compounds $[III]_{a,b}$ with thionylchloride, In addition, to these compounds

reacted with different aromatic amines to give amide compounds $[XI]_{a-d}$ and $[XII]_{a-d}$ While thiazolidine-4one compounds $[XIII]_{a,b}$ synthesized via react acid chloride compounds $[X]_{a,b}$ with potassiumthiocyanate in acetone.

The third synthetic route includes preparation the compound 4-(prop-2-yn-1-yloxy)benzaldehyde [XIV] from reaction of 4-hydroxybenzaldehyde with propargylbromide . These compound react with compounds $[II]_{a,b}$ to give 1,2,3-triazole compounds $[XV]_{a,b}$, that react with different aromatic amines to produce Schiff bases compounds $[XVI]_{a-d}$ and $[XVII]_{a-d}$. Finally, the fourth synthetic route includes synthesized oxazoles compounds $[XVIII]_{a,b}$ and thiazoles compounds $[XIX]_{a,b}$ by the reaction of compounds $[I]_{a,b}$ with urea or thiourea in absolute ethanol. Then these compounds react with different aromatic aldehydes in pipyridine and THF to give compounds $[XX]_{a-c}$ and $[XXI]_{a-c}$ when use urea and to give compounds $[XXII]_{a-c}$ and $[XXIII]_{a-c}$ when use thiourea .

All the synthesized compounds were characterized FT-IR , ^{1}HNMR and mass spectroscopy (of some of them).

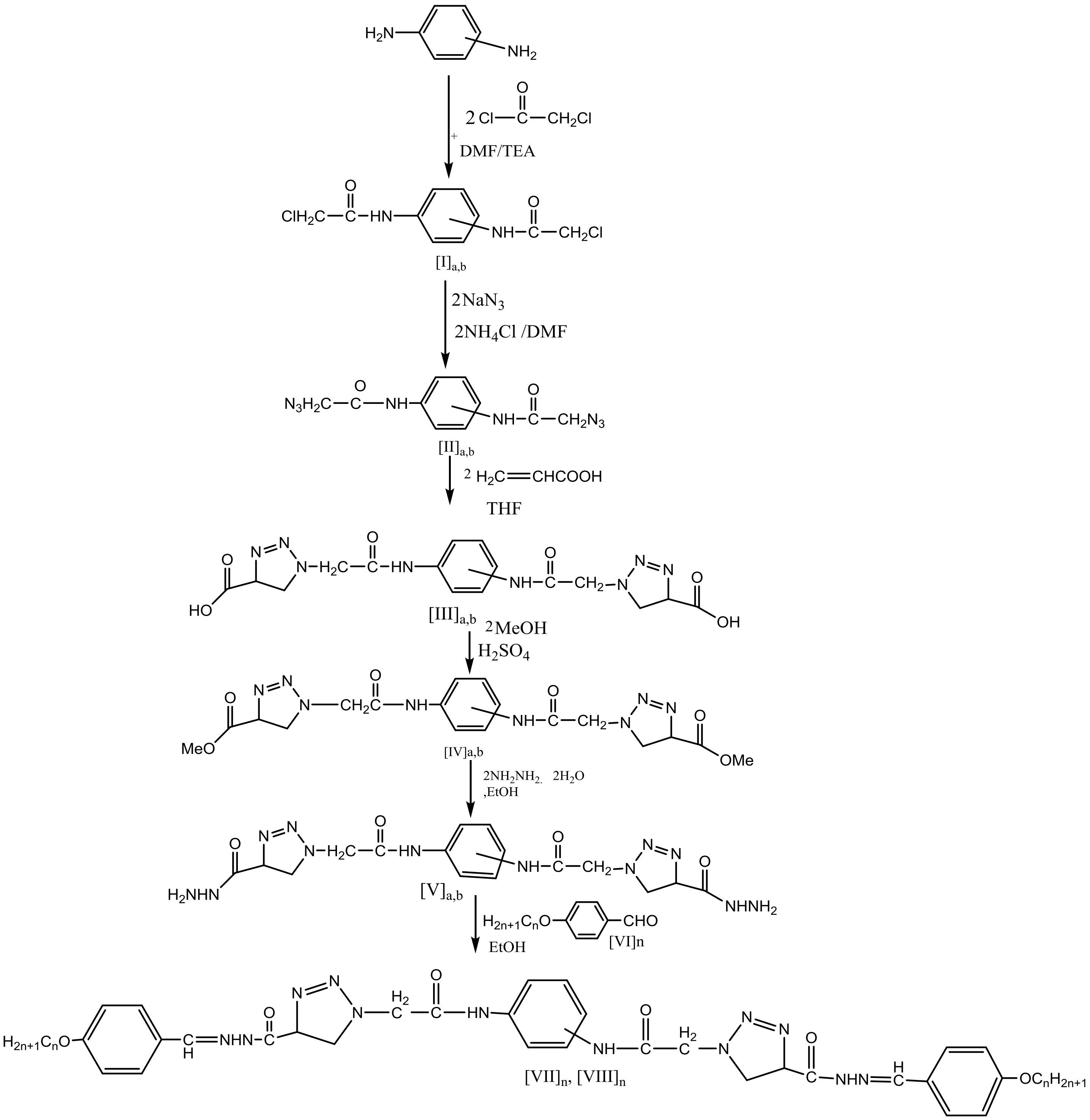
The liquid crystalline behavior of all compounds were studied by using optical polarizing microscope (OPM) and differential scaning calorimetry (DSC) (of some of them). and the results were as follows :-

All Schiff bases $[VII]_n$ and $[VIII]_n$ exhibited enantiotropic liquid crystalline behavior .

The compounds$[VII]_1$. $[VII]_2$, $[VII]_3$, $[VII]_5$ and $[VII]_6$ exhibit enantiotropic nematic phase while the compound $[VII]_7$ exhibited enantiotropic smectic A and nematic phases In addition to, the compound.$[VII]_8$ exhibited enantiotropic smectic B phases beside to nematic phase

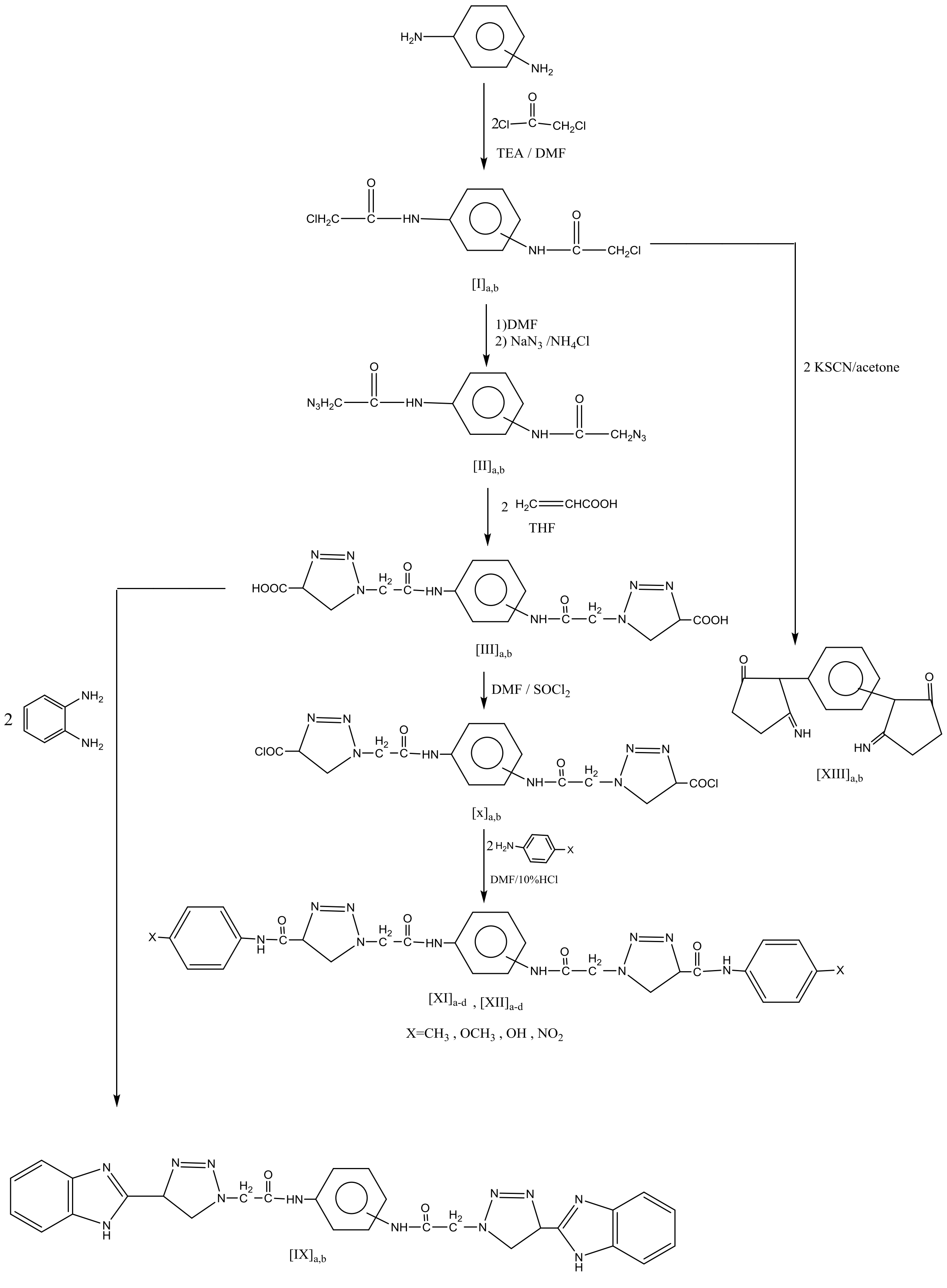
The compound $[VIII]_1$ didn't show any liquid crystalline properties. While the compounds $[VIII]_2$, $[VIII]_3$, $[VIII]_5$ and $[VIII]_6$ showed enantiotropic nematic phase. The compound $[VIII]_7$ displays enantiotropic SmA phase only . In addition to the compound$[VIII]_8$ showed SmA and nematic phases . The benzimidazole compounds $[IX]_{a,b}$ exhibited smecticic B phase . While amide compounds $[XI]_{a-d}$ and $[XII]_{a-d}$ did not show any liquid crystalline properties but only. transition from crystal to isotropic phase.
Also the thiazolidine-4-one compounds $[XIII]_{a,b}$ did not show any liquid crystalline properties only transition from crystal to isotropic phase. As while as , the Schiff bases compounds $[XVI]_{a-d}$ and $[XVII]_{a-d}$ didn't showed any liquid crystalline behavior. While , the Schiff bases of oxazole compounds $[XX]_{a-c}$ showed SmA phase but the compounds $[XXI]_{a-c}$ didn't showed any liquid crystalline behavior . Finally the Schiff bases of thiazole compounds$[XXII]_a$ and $[XXII]_c$ showed enantiotropic nematic phase .While the compound $[XXII]_b$ showed SmC and nematic phases . While the compound $[XXIII]_a$ showed enantiotropic SmB phase , but the compounds $[XXIII]_b$ and $[XXIII]_c$ showed enantiotropic nematic phase.

This work can be summarized by the following Schemes (1,2,3 and 4)

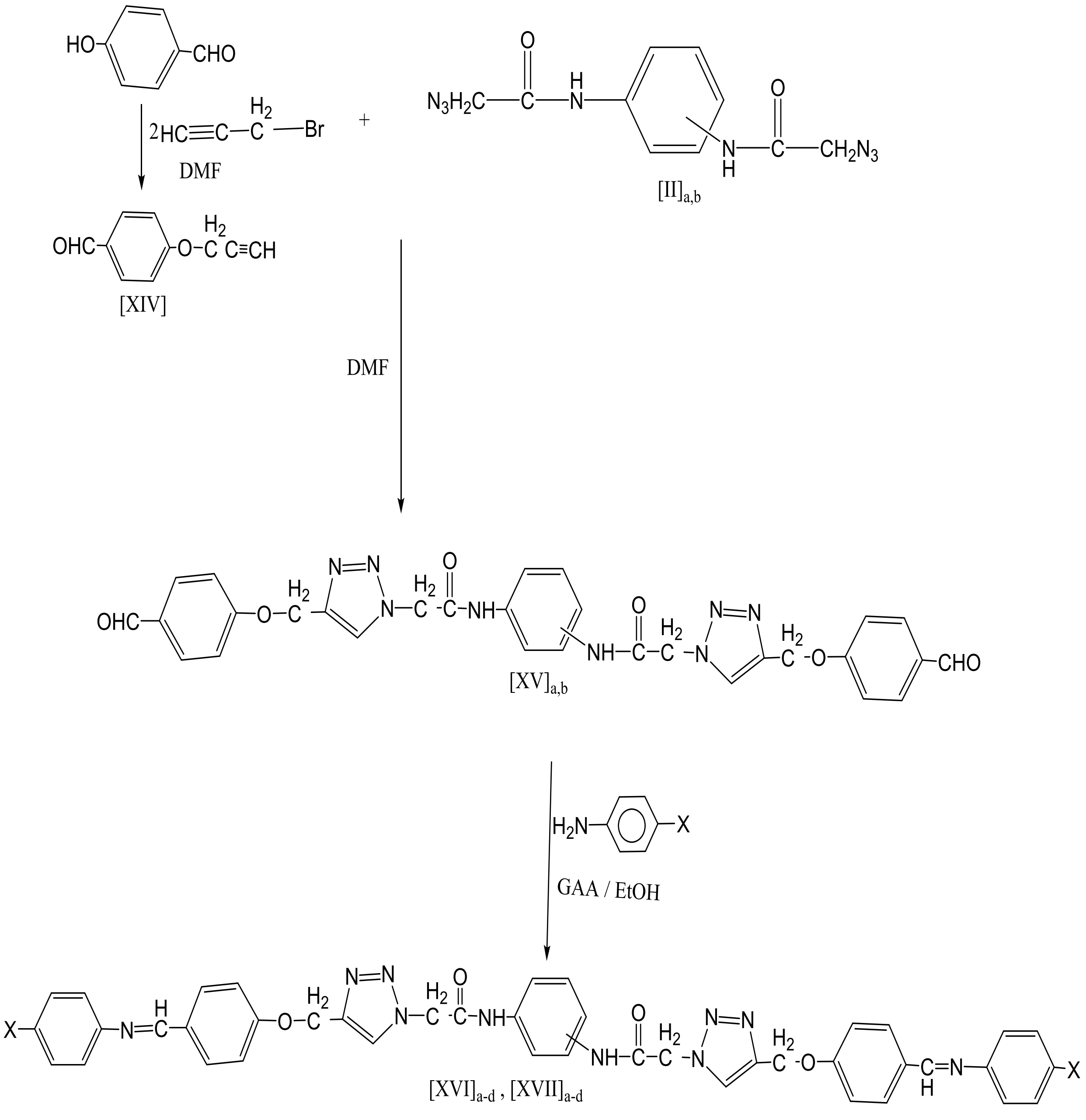


n= 1,2,3,5,6,7,8

Scheme (1) IV

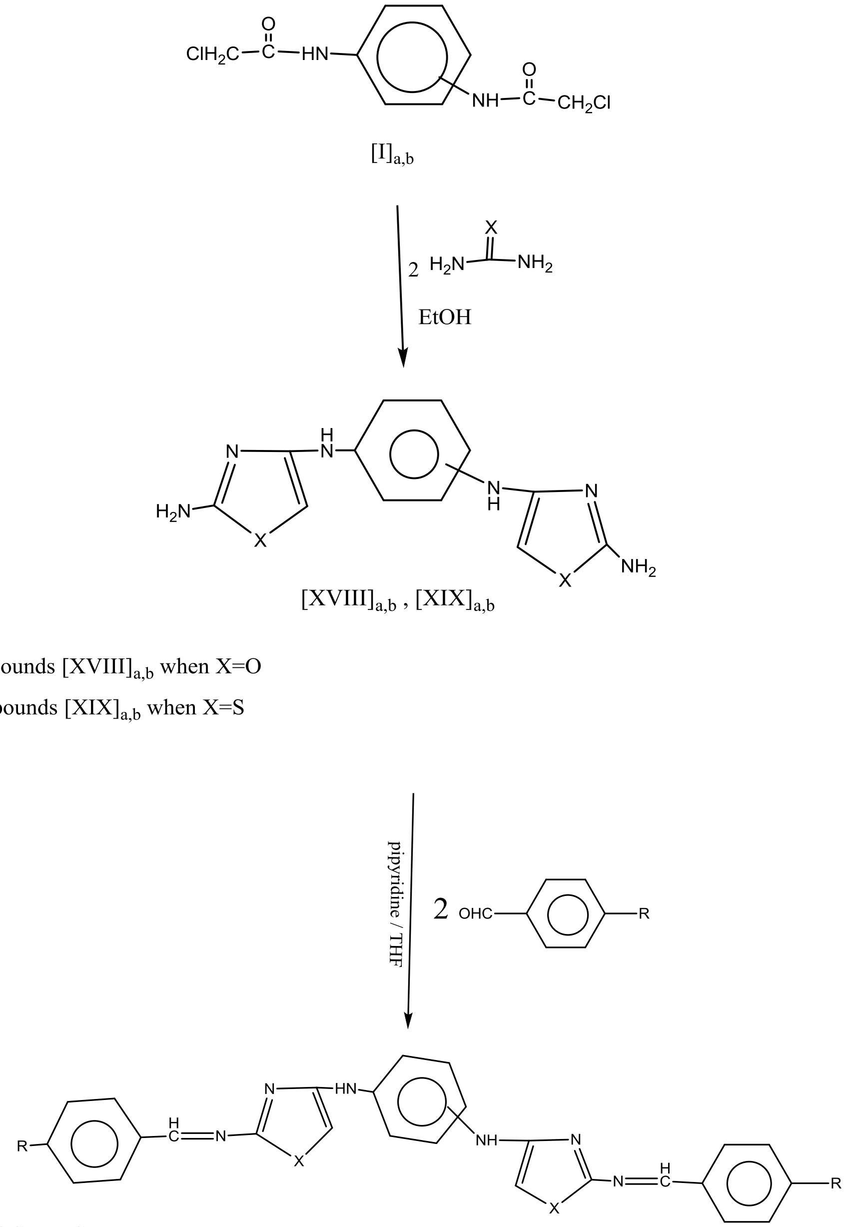

H2N
NH2
2Cl—C(O)—CH2Cl
TEA / DMF
ClH2C—C(O)—HN
NH—C(O)—CH2Cl
[I]a,b
1)DMF
2) NaN3 /NH4Cl
2 KSCN/acetone
N3H2C—C(O)—HN
NH—C(O)—CH2N3
[II]a,b
2 H2C═CHCOOH
THF
HOOC
COOH
N═N
[III]a,b
DMF / SOCl2
ClOC
COCl
[x]a,b
2 H2N—C6H4—X
DMF/10%HCl
X
[XI]a-d , [XII]a-d
X=CH3 , OCH3 , OH , NO2
2
NH2
NH2
O
NH
HN
[XIII]a,b
N
H
[IX]a,b

Scheme II



X= CH_3 , OCH_3 , OH , NO_2

Scheme III



$[I]_{a,b}$

$[XVIII]_{a,b}$, $[XIX]_{a,b}$

The compounds $[XVIII]_{a,b}$ when X=O

The compounds $[XIX]_{a,b}$ when X=S

R =OH, OCH_3 , CH_3

$[XX]_{a-c}$, $[XXI]_{a-c}$
$[XXII]_{a-c}$ $[XXIII]_{a,b}$

The compounds $[XXII]_{a-c}$ and $[XXIII]_{a-c}$ when X=S

Scheme IV

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List of Schemes

List of abbreviations

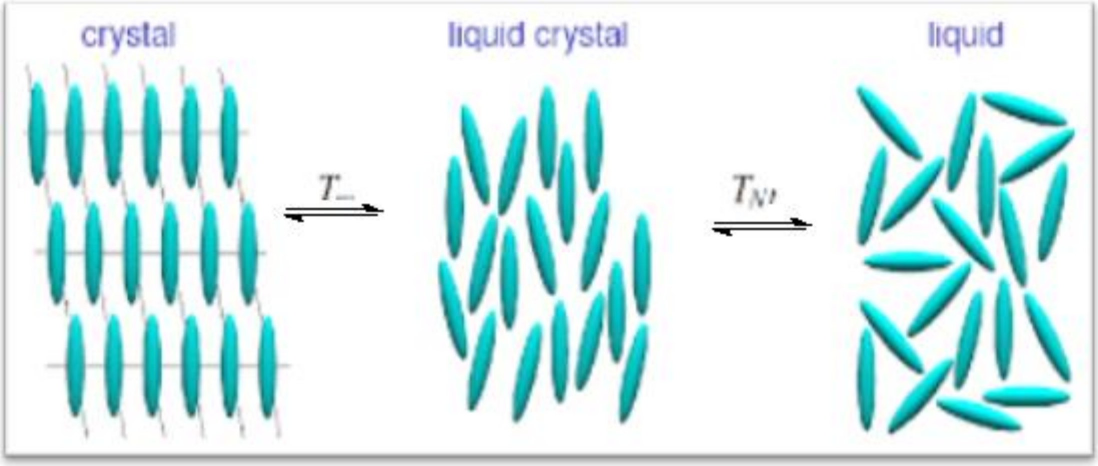
DMF	N,N-dimethyl formamide
Py	pyridine
GAA	Glacial acetic acid
DMSO-d_6	Dimethyl sulfoxide deuterated
Conc.	Concentration
Abs.	absolute
gm	Gram
mL	Milliliter
mp	Melting Point
^oC	Degree centigrade
M	Molarity
FT-IF	Fourier Transform Infrared
^{1}HNMR	Proton Nuclear Magnetic ResonaNCE
cm^{-1}	Centimeter of Wave number
asym .	asymmetry
sym	symmetry
δ	Chemical shift
ppm	Part per million
s	singlet
d	doublet
t	Triplet
OPM	Optical Polarized Microscopy
DS C	Differential Scanning Calorimetry
L C	Liquid crystalline
Cr	Crystal phase
I	Isotropic
N	Nematic phase
Sm	Smectic phase
TMS	Trimethylsilan

1. Introduction

1.1 Liquid crystal

Liquid crystals are substance in a state which has properties between those of conventional liquids and those of solid crystals (1). For example, a liquid crystal may flow like a liquid , but its molecules may be oriented in a crystal-like way Figure (1-1).

The exist many different types of liquid-crystal phases , which can be distinguished by their different optical properties (such as refraction). When looking under a microscope using a polarized light source, different liquid crystal phases will apopear to have distinct texture . The contrasting areas in the textures correspond to domains where the liquid-crystal molecules are oriented in different directions. Within a domain , however , the molecules are well ordered(1) .



Figure(1-1) states of matter(1)

1.2 Types of liquid crystals

Liquid crystals can be devided into lyotropic and thermotropic phases Figure (1-2).

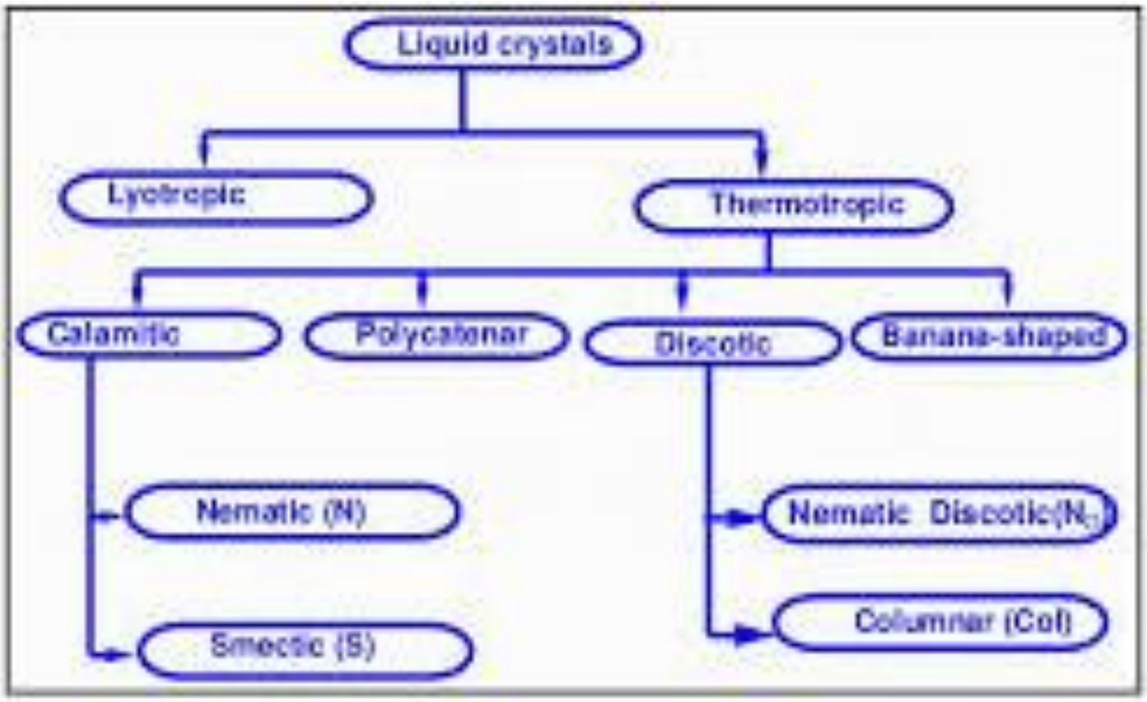


Figure (1-2) : Types of liquid crystals

1.2.1 Lytropic liquid crystals

Lytropic liquid crystal phases are abundant in living systems but can also be found in the mineral world . For examples , cell membranes and many protiens are liquid crystals . Other examples of liquid crystals are solutions of soap and various related detergents and the tobacco mosaic virus, and some clays(2)

A lytropic crystal contains of two or more components that exhibit liquid crystalline properties in certain concentration ranges, in the lyotropic phases; solvent molecules fill the space around the compounds to provie fluidity to the system . The amphiphilic compounds are characterized by two distict moieties , a hydrophilic polar "head" and hydrophobic polar "tail" These types of molecules are soaps (3) Figure (1-3)

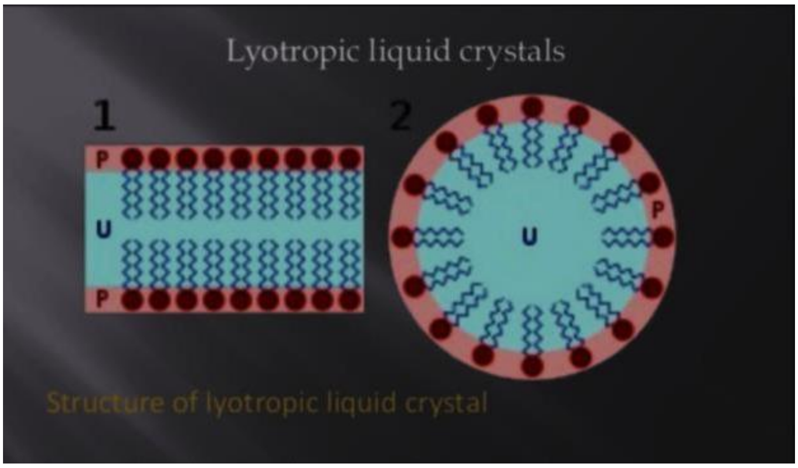


Figure (1-3): Cell membranes(3) lytropic liquid crystal arrangement the tails are immersedin oil (blue): bilayer (left) and micelle (right)

1.2.2 Thermotropic liquid crystals

A Liquid crystal the components order is determined or changed by temperature is being thermotropic. If temperature is high, the hightin energy and therefore in motion of the components will make a phase transition , the liquid crystal will become an isotropic liquid . If per contra temperature is low support a thermotropic phase , the liquid crystal will change to glass phase.

A range of temperatures at which we observe thermotropic LCs and most of these have sevsral "subphases"(nematic , smectic…..), which we may observe by modifying the temperature . Figure (1-4)

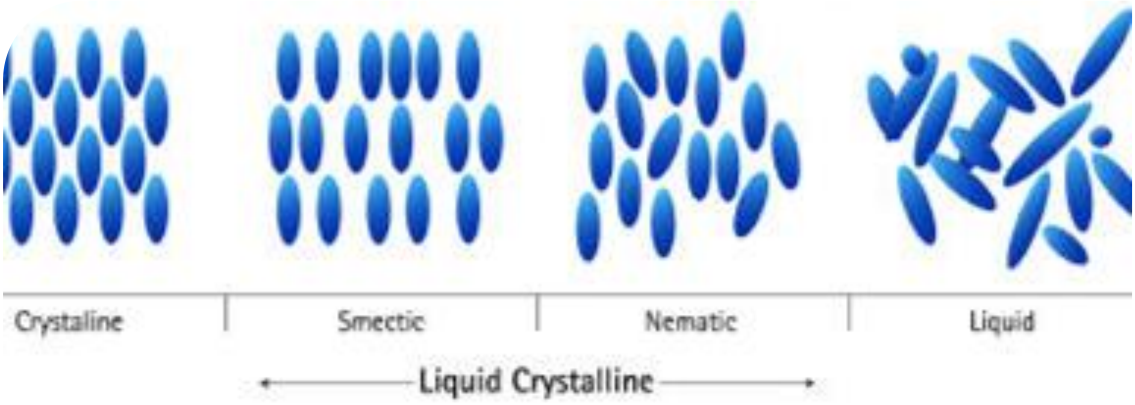


Figure (1-4) Schematical phase sequence of a liquid crystal

1.2.2.1. Calamitic liquid crystals

Calamitic or rod-like LCs are those mesomorphic compounds that posses an elongated shape$^{(3)}$, responsible for the form anisotropy of the molecular structure as the result of the molecular length (L) being significantly greater than the molecular breadth (b), as depicted in the cartoon representation in figure (1-5)

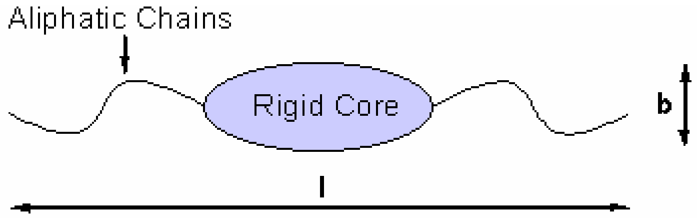


Figure (1-5): Schematic representation of calamitic liquid crystals, where length(l) >> breadth(b).

Calamitic LCs can exhibit three common of mesophases

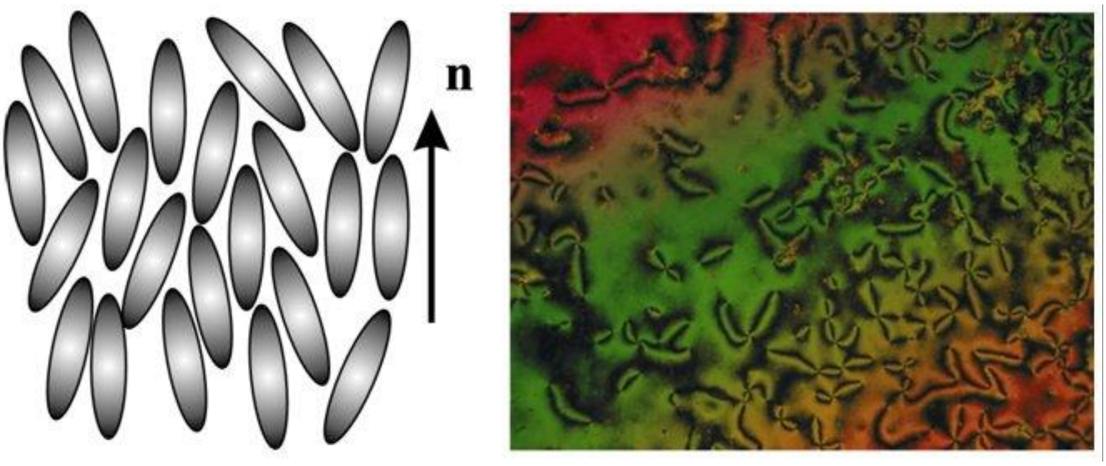
i) Nematic phase

ii) Chloesteric phase

iii) Smectic phase

i) Nematic phase

One of the most common LC phases is the nematic. The word nematic comes from the Greek νήμα (Greek: nema), which means "thread". This term originates from the thread-like topological defects observed in nematics, which are formally called 'disclinations'. In a nematic phase, the calamitic or rod-shaped organic molecules have no positional order, but they self-align to have long-range directional order with their long axes roughly parallel.(4) Figure (1-6)



Figure(1-6) Molecular arrangement and nematic thread-like texture(4)

Thus, the molecules are free to flow and their center of mass positions are randomly distributed as in a liquid, but still maintain their long-range directional order. Most nematics are uniaxial: they have one axis that is longer and preferred, with the other two being equivalent can be approximated as cylinders or rods. However, some liquid crystals are biaxial nematics, meaning that in addition to orienting their long axis, they also orient along a secondary axis. Nematics have fluidity similar to that of ordinary isotropic liquids but they can be easily aligned by an external magnetic or electric field. Aligned nematics have the optical properties of uniaxial crystals and this makes them extremely useful in liquid-crystal displays (LCD).(5)

ii) **Chiral phases**

The chiral nematic phase exhibits chirality . This phase is often called the cholesteric phase because it was first observed for cholesterol derivatives. Only chiral molecules can give rise to such a phase. This phase exhibits a twisting of the molecules perpendicular to the director, with the molecular axis parallel to the director. The finite twist angle between adjacent molecules is due to their asymmetric packing Figure (1-7).

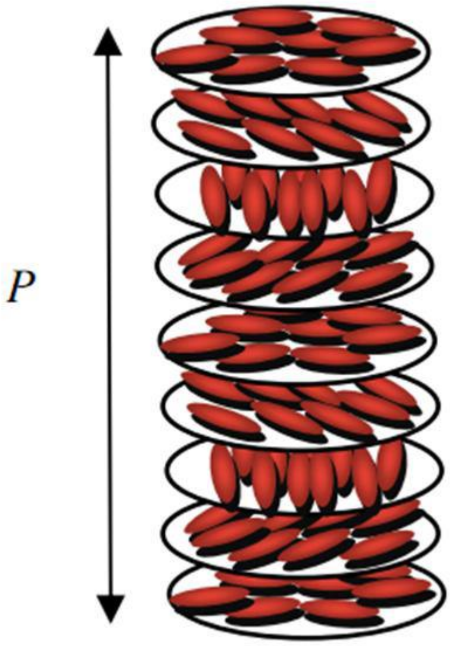


Figure (1-7) Chiral nematic phase

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which results in longer-range chiral order. The chirality induces a finite azimuthal twist from one layer to the next, producing a spiral twisting of the molecular axis along the layer normal.(6,7)

The chiral pitch, p, refers to the distance over which the LC molecules undergo a full 360° twist but note that the structure of the chiral nematic phase repeats itself every half-pitch, since in this phase directors at 0° and ±180° are equivalent Figure (1-8). The pitch, p, typically changes when the temperature is altered or when other molecules are added to the LC host allowing the pitch of a given material to be tuned accordingly. In some liquid crystal systems, the pitch is of the same order as the wavelength of visible light. This causes these systems to exhibit unique optical properties, such as Bragg reflection and low-threshold laser emission,(8) and these properties are exploited in a number of optical applications. For the case of Bragg reflection only the lowest-order reflection is allowed if the light is incident along the helical axis, whereas for oblique incidence higher-order reflections become permitted.

Cholesteric liquid crystals also exhibit the unique property that they reflect circularly polarized light when it is incident along the helical axis and elliptically polarized if it comes in obliquely.(9)

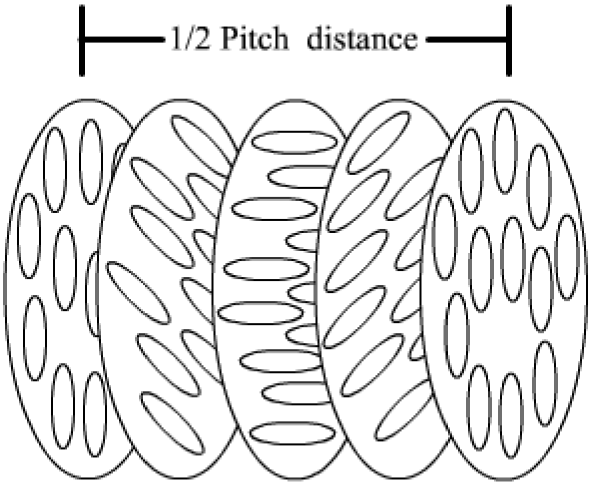


Figure (1-8) Chiral phases

iii) Smectic phase

As compared to the nematic phase, smectic phases are characterized by an additional positional ordering of the mesomorphic molecules in layers. In general, the smectic layers can slide freely over one another so that each layer is in principle a two dimensional liquid
In this phase , the molecules are tilted , describe different smectic phases. Many kinds of (smecticphases) have been detected. These types have been named ; smetic A, B, C, D, E, F, G, H, I, J, K, M, O, Q and X phases. with respect to the layers, and the system is now "biaxial" in character, typical textures formed by smectics are shown in Figure (1-9)

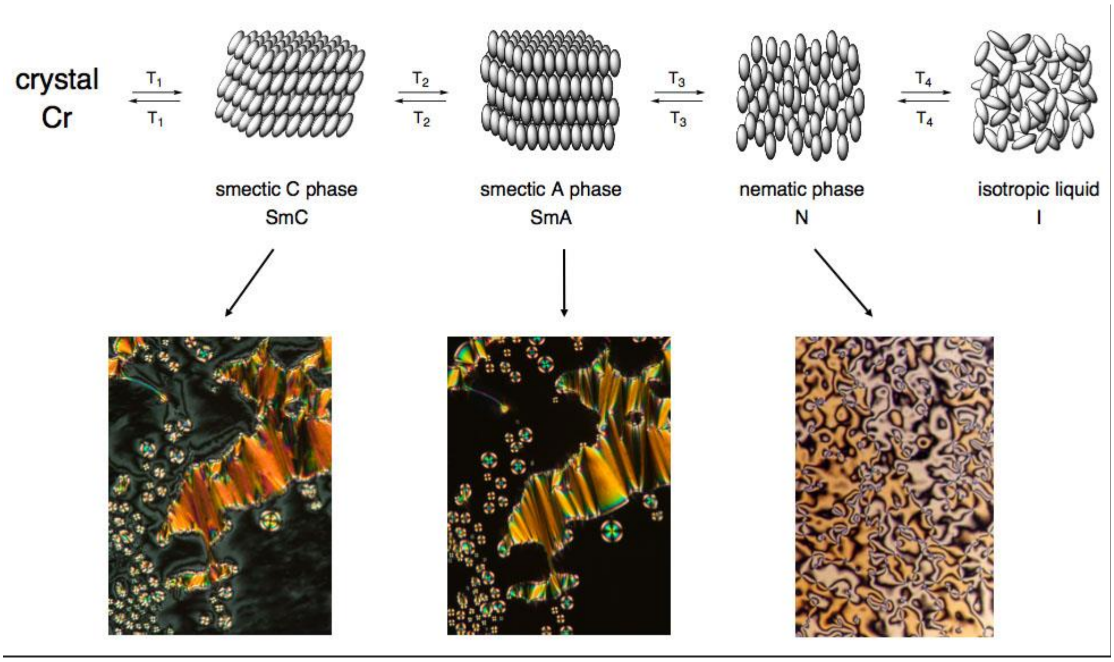


Figure (1-9) Typical textures of liquid crystal phases(9)

1.2.2.2. Discotic liquid crystals

Discotic liquid crystals are mesophases formed from disc-shaped molecules known as discotic mesogens. These phases are often also referred to as columnar phases. Discotic mesogens are typically composed of an aromatic core surrounded by flexible alkyl chains. The aromatic cores allow charge transfer in the stacking direction through the π conjugate systems. The charge transfer allows the discotic liquid crystals to be electrically semiconductive along the stacking direction.(10) Applications have been focusing on using these systems in photovoltaic devices,(11) organic light emitting diodes (OLED),(12) and molecular wires.(13) Discotics have also been suggested for use in compensation films for LCD displays.

a. Nematic discotic phase

Nematic discotic (ND) is the least ordered mesophase(14) , where the molecules have only orientationnal order being aligned on average with the director as illustrated in Figure (1-10).

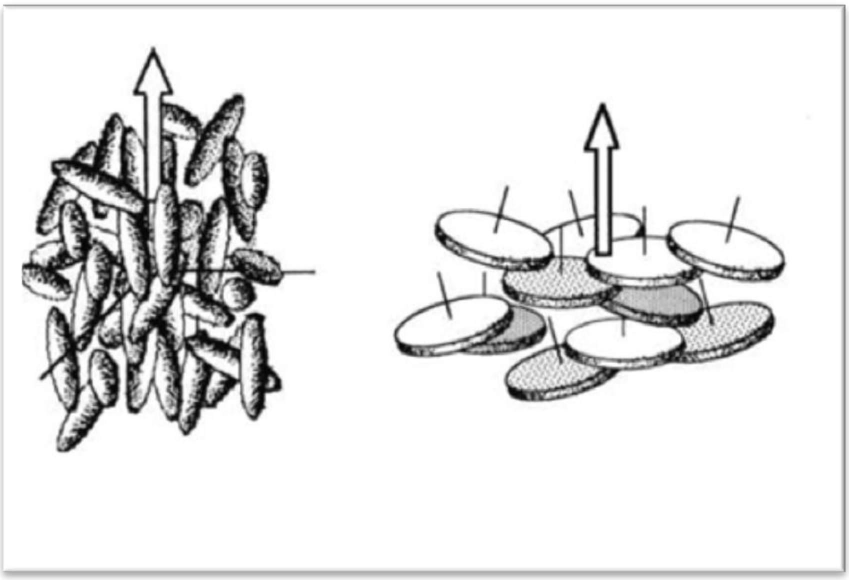


Figure (1-10) Schematic representation of the nematic discotic phase(14).

b. columnar phase

The columnar phase is a class of mesophases in which molecules assemble into cylindrical structures to act as mesogens. Originally, these kinds of liquid crystals were called discotic liquid crystals or bowlic liquid crystals (15)because the columnar structures are composed of flat-shaped discotic or bowl-shaped molecules stacked one-dimensionally Figure (1-11).

Figure (1-11) discotic columnar phase

Since recent findings provide a number of columnar liquid crystals consisting of non-discoid mesogens, it is more common now to classify this state of matter and compounds with these properties as columnar liquid crystals.

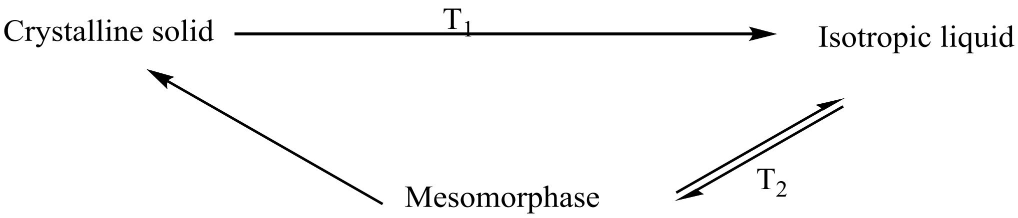
Takuzo Aida and co-workers recently reported cyclic peptides that self-assemble into polar columnar organizations. These materials can be unidirectionally aligned over large areas by application of an external electric field.(15)

1.3 Order of appearance

Thermotropic liquid crystals are classified into three types:

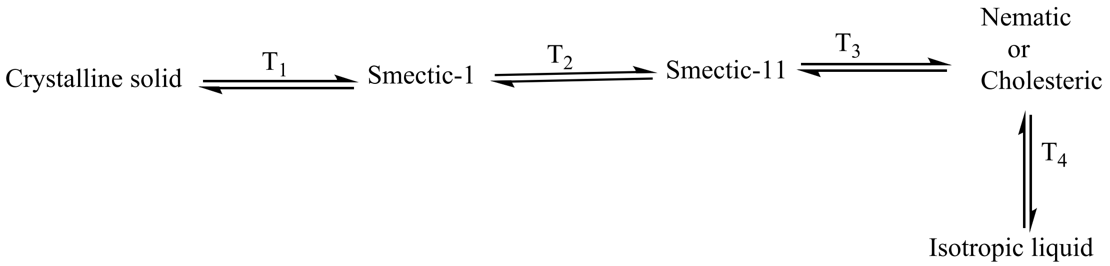
1. Enantiotropic liquid crystals : Can be appeared by heating and cooling

2. Monotropic liquid crystals: Only be appeared by cooling



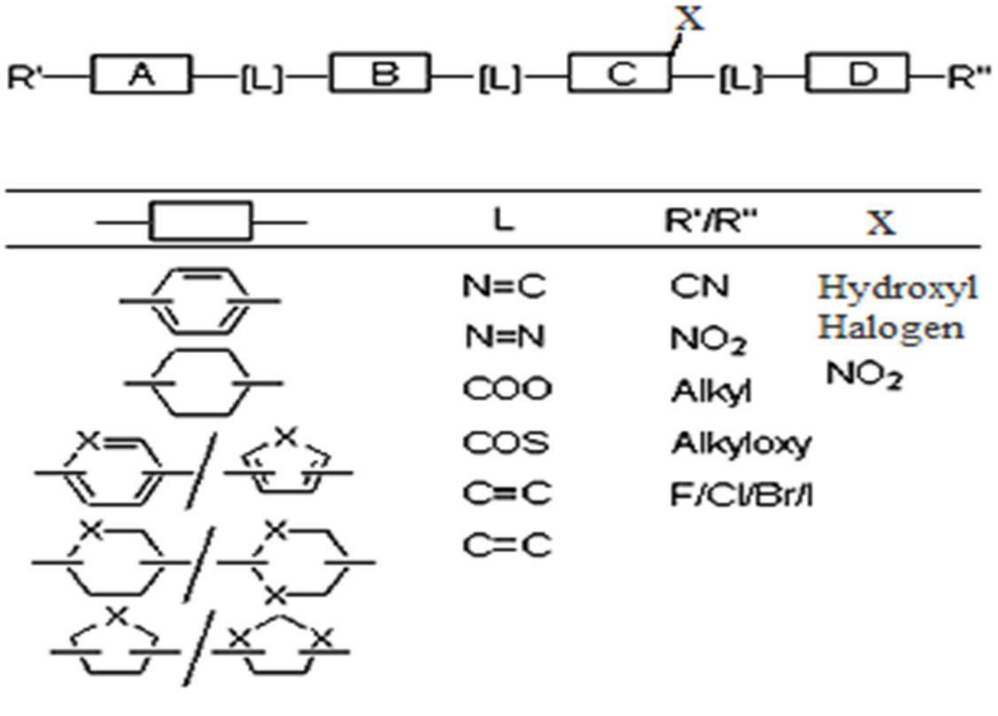
1.4 Polymorphism liquid crystals

Polymorphism mesogens(16-18) represent a hybrid class of thermotropic LCs , which can be described with intermediate molecular features substances which have exclusively smectic mesophase structure or exclusively nematic mesophase structure. But some can exist as both types of mesophase, smectic followed by nematic. This phenomenon is known as polymorphism.



1.5 General structural of liquid crystals.

Organic compounds that form mesophase are characterized by being long, narrow, linear molecules. Both permanent dipoles and polarizable moieties are required. The vast majority of thermotropic liquid-crystalline substanses are based on the following structure:



where A,B,C, D describe ring systems, one or more bridging groups, (L) that bind the rings together. (L), which preserve the linearity of molecule and by being unsaturated also extend conjugation between two rings

,such as: (-C≡C- , -CH=N- , -N=N-, …etc). Nematic phases, such as nitro, cyano and methoxy group which strongly promote nematic properties. molecular long axis promote, smectic properties(19) . Terminal groups, R' and R": the terminal substituents are important factors that affect the anisotropy of molecular interactions. Normally, they control both the nature and the type of mesophases. If terminal substituent groups are of high polarizability they favor formation of less order mesophases, i.e., nematic mesophase, such as nitro, cyano and methoxy groups which strongly promote nematic properties. On the other hand, terminal groups which contribute strongly to the resultant dipole acting across the molecular long axis promote, smectic properties. The thermal stability of the mesophase formed depends in large measure on stable structural, steric, and electronic effects, in the central and terminal groups(20). X is the lateral groups such as hydroxyl, halogen

1.6 Application of liquid crystals

A large number of new liquid crystal compounds have been prepared which have specific properties for different applications as:

1.6.1- Display application

Liquid crystals find wide use in liquid crystal displays, which rely on the optical properties of certain liquid crystalline substances in the presence or absence of an electric field(21). In a typical device, a liquid crystal layer typically 4 μm thick sits between two polarizers that are crossed oriented at 90° to one another. The liquid crystal alignment is chosen so that its relaxed phase is a twisted one. This twisted phase reorients light that has passed through the first polarizer, allowing its transmission through the second polarizer and reflected back to the observer if a reflector is provided. The device thus appears transparent.

When an electric field is applied to the LC layer, the long molecular axes tend to align parallel to the electric field thus gradually untwisting in the center of the liquid crystal layer. In this state, the LC molecules do not reorient light, so the light polarized at the first polarizer is absorbed at the second polarizer, and the device loses transparency with increasing voltage. In this way, the electric field can be used to make a pixel switch between transparent or opaque on command. Color LCD systems use the same technique, with color filters used to generate red, green, and blue pixels. Chiral smectic liquid crystals are used in ferroelectric LCDs which are fast-switching binary light modulators. Similar principles can be used to make other liquid crystal based optical devices.(21)

Liquid crystal tunable filters are used as electrooptical devices,(22) e.g., in hyperspectral imaging.

1.6.2- Medical Applications

Thermotropic chiral LCs whose pitch varies strongly with temperature can be used as crude liquid crystal thermometers, since the color of the material will change as the pitch is changed. Liquid crystal color transitions are used on many aquarium and pool thermometers as well as on thermometers for infants or baths(23).

1.6.3- Gas-liquid chromotography

Other liquid crystal materials change color when stretched or stressed. Thus, liquid crystal sheets are often used in industry to look for hot spots, map heat flow, measure stress distribution patterns, and so on. Liquid crystal in fluid form is used to detect electrically generated hot spots for failure analysis in the semiconductor industry. The most important things in (GC) is the search for good stationary phase, including the selectivity, there are many studies for this trend, one of the important phases under investigation is liquid crystalline stationary phase (LCSPs) (24).

1.6.4- Other applications

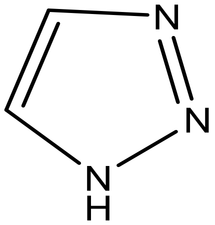
Liquid crystal lasers use a liquid crystal in the lasing medium as a distributed feedback mechanism instead of external mirrors. Emission at a photonic bandgap created by the periodic dielectric structure of the liquid crystal gives a low-threshold high-output device with stable monochromatic emission. (25)

Polymer dispersed liquid crystal (PDLC) sheets and rolls are available as adhesive backed smart film which can be applied to windows and electrically switched between transparent and opaque to provide privacy.

Many common fluids, such as soapy water, are in fact liquid crystals. Soap forms a variety of LC phases depending on its concentration in water.(26)

1.7. 1,2,3-Triazole

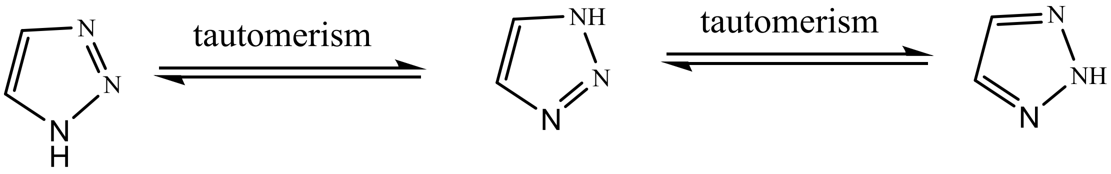
1,2,3-Triazole[1] is one of a pair of isomeric chemical compounds with molecular formula $C_2H_3N_3$, called triazoles, which have a five-membered ring of two carbon atoms and three nitrogen atoms. 1,2,3-Triazole is a basic aromatic heterocycle.(27)



1*H*-1,2,3-triazole

[1]

Three constitutional triazole isomers, which ocour in nature, 1,2,3-triazole, may exhibit tautomersim: the NH hydrogen atom can be attached to the, 1st , 2nd , and 3rd nitrogen atom . The triazole tautomersim is a subject of previous studies(28-37)



1*H*-1,2,3-triazole

[1]a [1]b [1]c

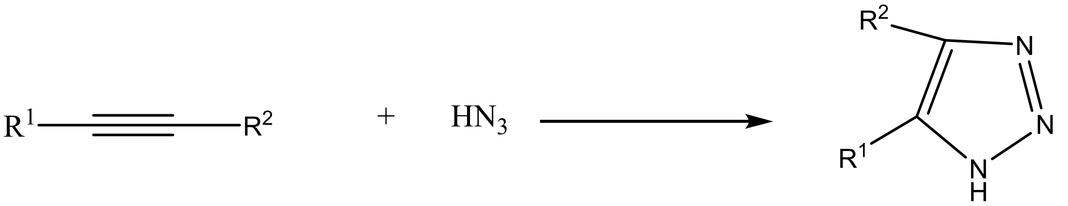
Substituted 1,2,3-triazoles can be produced using the azide alkyne Huisgen cycloaddition in which an azide and an alkyne undergo a 1,3-dipolar cycloaddition reaction.

1,2,3-Triazole finds use in research as a building block for more complex chemical compounds, including pharmaceutical drugs such as tazobactam.

1.8. Synthesis of 1,2,3-triazole derivatives

The Azide-Alkyne Huisgen Cycloaddition is a 1,3-dipolar cycloaddition between an azide and a terminal or internal alkyne to give a 1,2,3-triazole. Huisgen(38) was the first to understand the scope of this organic reaction. American chemist K. Barry Sharpless has referred to this cycloaddition of click chemistry(39) and "the premier example of a click reaction."(40) Many workers synthesized 1,2,3-triazole derivatives as following :

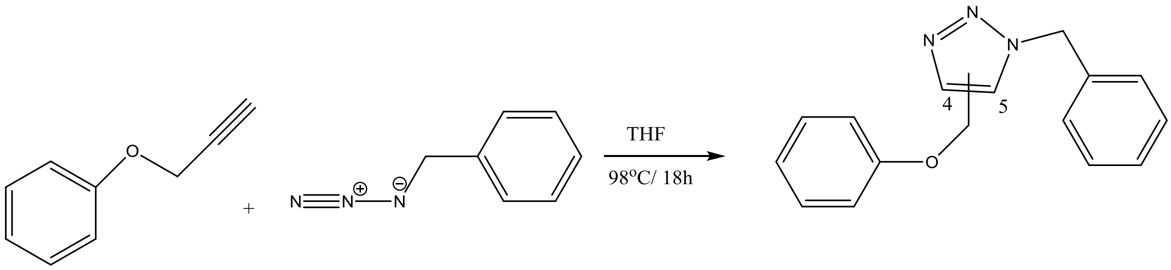
Dimrorth, Fester, and Ber (41) were reacted alkynes [2] with hydrazoic acid [3] to form compound [4]



[2] [3] [4]

R^1=H, Ph, TMS R^2=Me, CHO

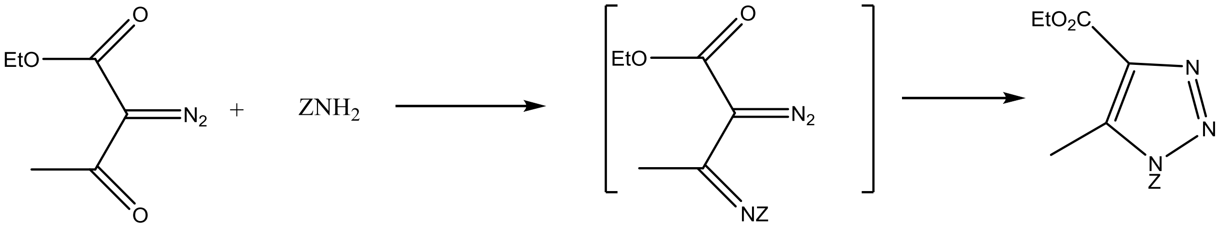
In the reaction bellow(42) alkyne[5] reacts neatly with azide[6] to afford the triazole [7] as a mixture of 1,4-adduct and 1,5-adduct at 98 °C in 18 hours.



[5] [6] [7]

The standard 1,3-cycloaddition between an azide 1,3-dipole and an alkene as dipolarophile has largely been ignored due to lack of reactivity as a result of electron-poor olefins and elimination side reactions. Some success has been found with non-metal-catalyzed cycloadditions, such as the reactions using dipolarophiles that are electron-poor olefins or alkynes.

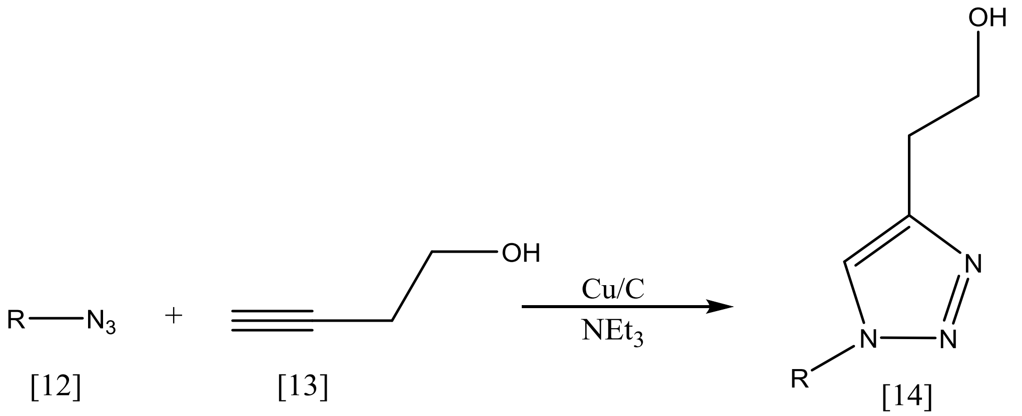
The synthesis of triazole derivatives[10]was obtained by reaction of ethyl 2-diazo-3-oxobutanoate [8] with phenylhydrazine, semicabazide ,hydroxylamine ,aniline, or ammonia(43)



[8] [9] [10] [11]

Z = NHPh , $NHCO_2NH_2$, OH , Ph , H

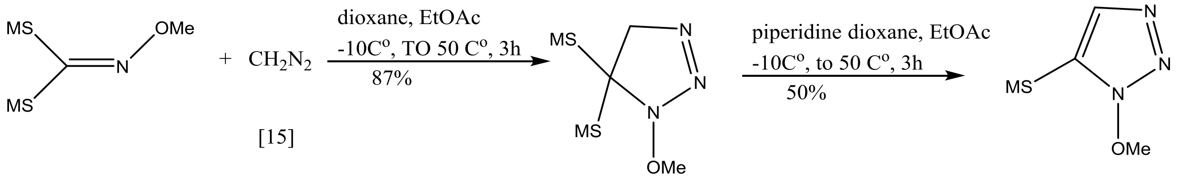
The common starting material for the synthesis of all substituted-1,2,3-triazoles [14] was different azide [12] which was coupled to a variety of but-3-yn-1-ol in the presence of the recently introduced heterogeneous Cu/C catalyst system.(44)



[12] [13] [14]

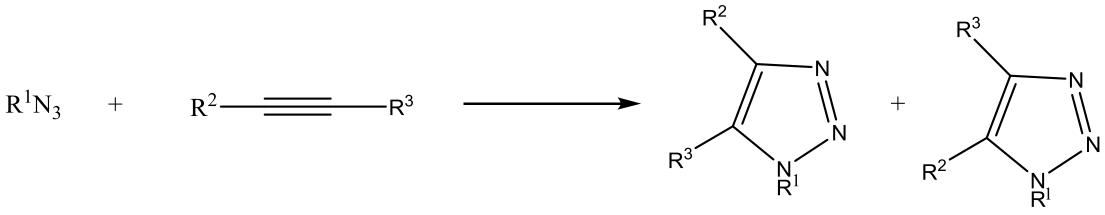
R- Benzyl ,Cyclohyxyl , 2-Hydroxyethyl

Also prepared 1,2,3-triazole [17] derivatives from reaction of compound [15] with diazomethane [14] to give compound [17]$^{(45)}$



[15] [16] [17]

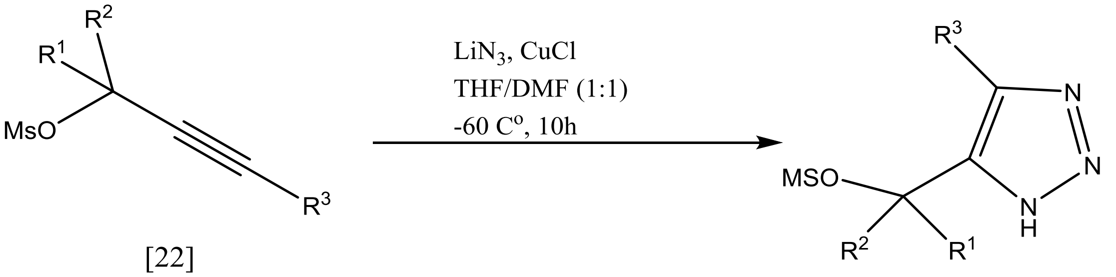
While , Azides [18] were added to unsymmetrical disubstituted alkynes [19] to form mixtures of isometric triazoles [20] , [21]$^{(46-49)}$



[18] [19] [20 [21]

R^1= Ph, 4-MeOC_6H_4, 1-naphthyl; R^2=Ph, CH_2OH, Me ; R^3= CO_2Me, Bz, CO_2Et,

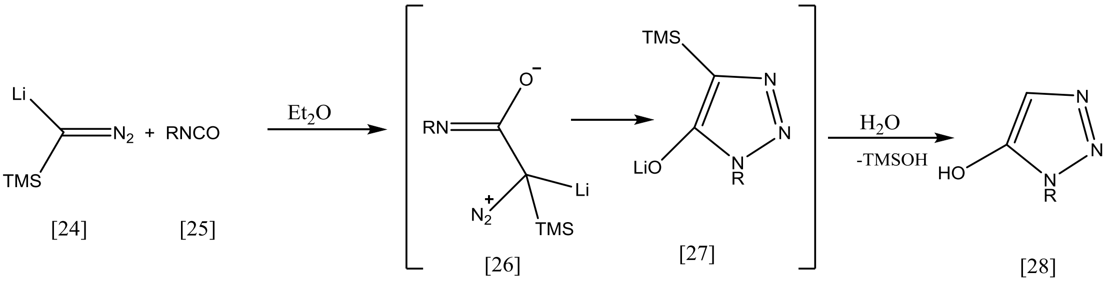
Also, propargyl sulfonates [22] reacted with lithium azide/CuCl complex in solvent as THF/DMF after acidification to produce 1,2,3-triazole compounds [23] $^{(50)}$



[22] [23]

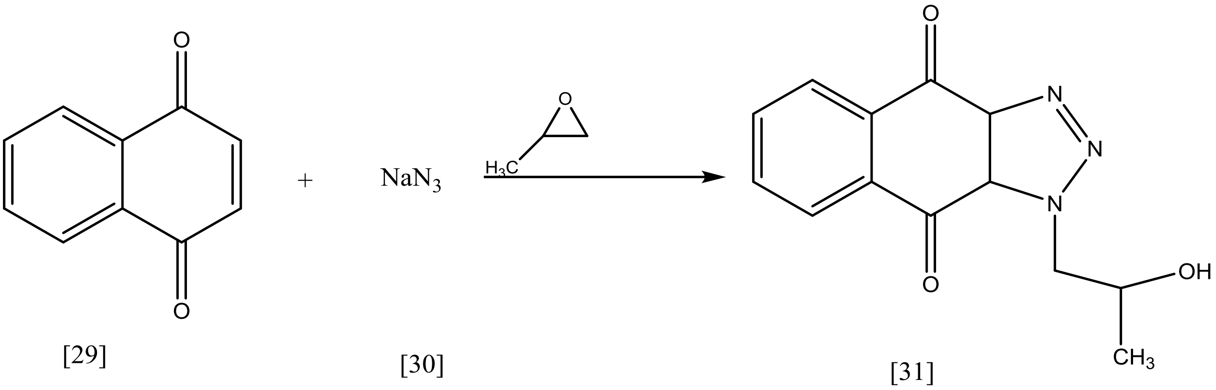
R^1= t-Bu, Ph, 3-$O_2NC_6H_4$; R^2=H, Ph; R^3=t-Bu, ph

As well as reaction the compound [diazo(trimethylsilyl)methyl]lithium [24][with isocynate [25] gave compound [27] and when added the water to the later compound gave 1-substituted 1H-1,2,3-triazol-5-ols [28](51)



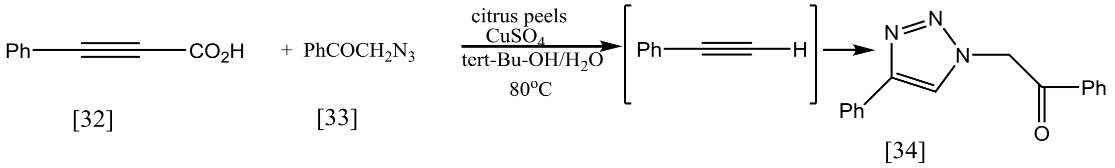
[24] [25] [26] [27] [28]

Naphthoquinone [29] can react with sodium azide [30]via a [2+3] cycloaddition, (52-53) or with various nucleophiles through a Michael addition Michael addition and/or oxidation process.(54-57) to produce naphthoquinone derivative [31]

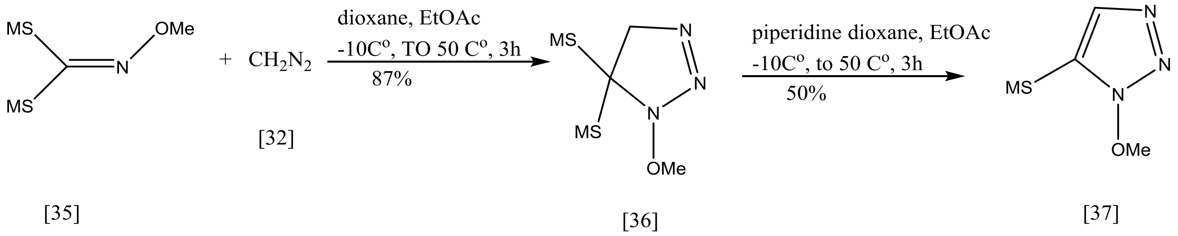


[29] [30] [31]

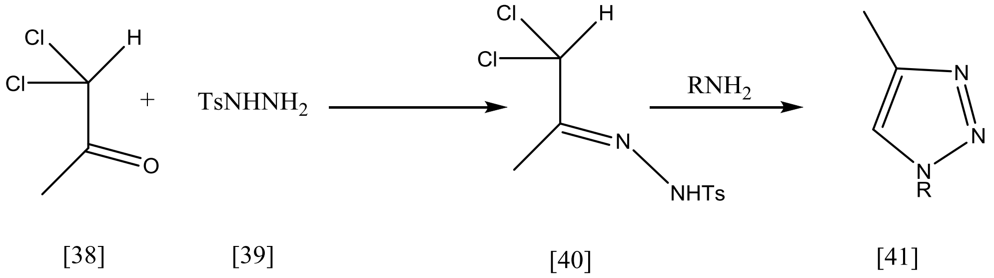
As well as Wintner(58), synthesized compound [34] from decarboxylation reactions are well-known in organic chemistry. By reaction compound [32] with azido compound [33]



While from react nitriles [35] with respect to their reactivity toward diazomethane [36] yields of N-methyl-triazoles $[37]_{a\text{-}c}$(59)

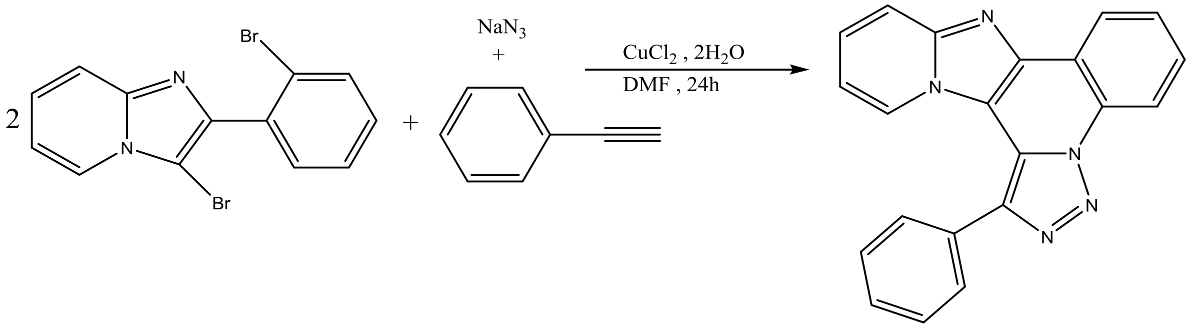


While 1,1-dichloro ketone [38] and tosylhydrazones [39] used in prepare the compound [40] was converted into 1-benzyl or 1-allyl-4-methyl-1H-1,2,3-triazoles(60) [41]



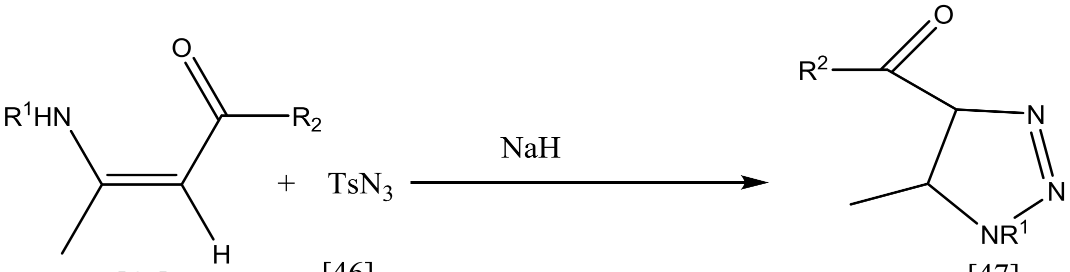
R= Ph-CH_2-CH=CH_2

The synthesis of 1,2,3-triazoles via $CuCl_2$-catalyzed click reaction, direct arylation sequence (61). Panteleev et al. have described interesting results on fused 1,2,3-triazole [44] through cycloaddition followed by direct arylations.(62)



[42 [43] [44]

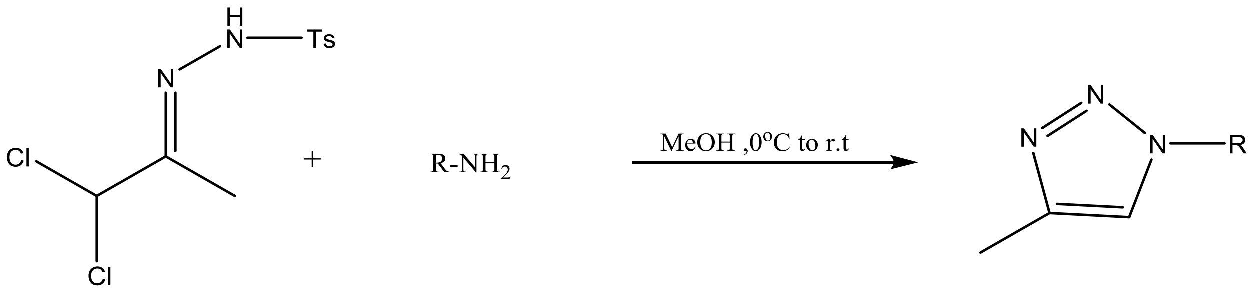
In addition, the triazoles derivatives [47] were synthesized by the reaction of compound [45] with tosyl azide [46] the later compound can act as diazo transfer reagents (63)



[45] [46] [47]

R^1= alkyl, aryl; R^2= Me, OEt

In this approach(64), an dichloro tosyl hydrazine[48] is condensed with amine [49] to form a 1,4-substituted triazole [50] under mild reaction conditions



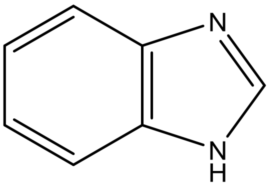
[48] [49] [50]

R= Aallyl , Bn

1.9 -Azole derivatives

1.9.1 Benzimidazole derivatives

Benzimidazole is a heterocyclic aromatic organic compound. This compound is bicyclic in nature which consists of the fusion of benzene and imidazole.

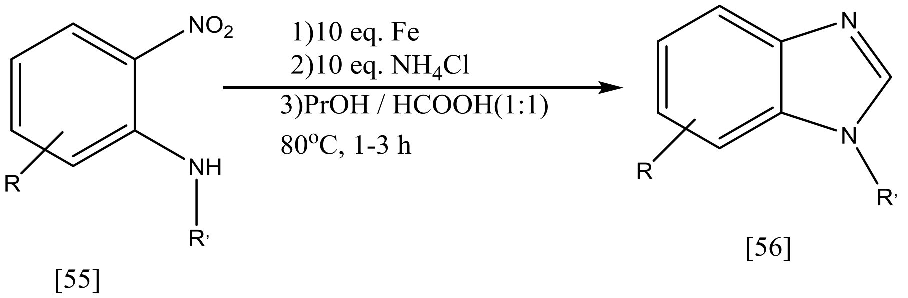


[54]

It is an important pharmacophore and a privileged structure in medicinal chemistry. Nowadays is a moiety of choice which possesses many pharmacological properties. The most prominent benzimidazole compound in nature is N-ribosyl-dimethylbenzimidazole, which serves as an axial ligand for cobalt in vitamin B12.(65) The Benzimidazole used dates many years back(66). In 1990 various benzimidazole derivatives were synthesized with substitution of fluorine, propylene, tetrahydroquinoline and cyclised compound which resulted in compounds with increased stability, bioavailability and significant biological activity(67,68) It was also shown that substitution on pyridine by electron donating group increases activity. In 1991 benzimidazole derivatives were synthesized by derivatization at N-H of benzimidazole by electron donating group and substitution with long chain of propyl, acetamido, thio, thiazole-amino, tetramethyl piperidine on pyridine resulting in good antiulcer activity(69,70). Nowadays Infectious microbial diseases are causing problems world-wide, because of resistance to number of antimicrobial agents (β-lactam antibiotics, macrolides, quinolones, and vancomycin). A variety of clinically significant species of microorganisms has become an important health problem globally(71)

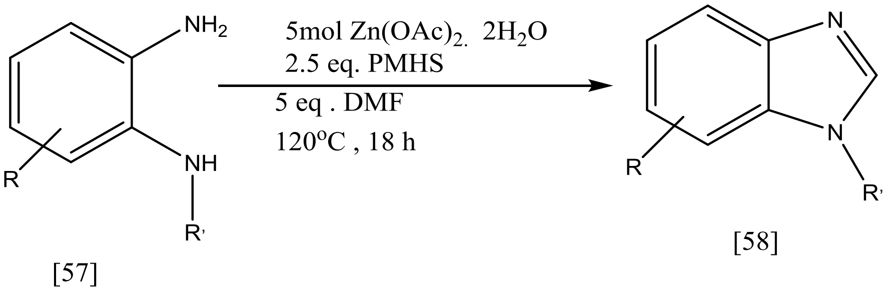
1.9.2-Synthesis of benzimidazole derivatives

A one-pot procedure for the conversion of aromatic and heteroaromatic 2-nitroamines[55] into bicyclic 2*H*-benzimidazoles[56] employs formic acid, iron powder, and NH_4Cl as additive to reduce the nitro group and 72)(effect the imidazole cyclization with high-yielding



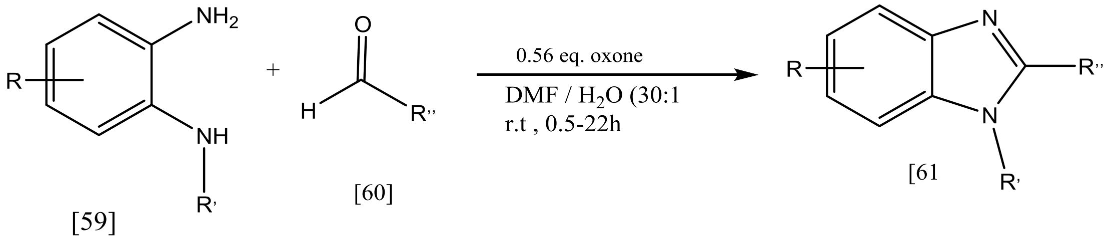
R= H , Ph , Et

Nale, and Bhanage(73) use of various substituted 1,2-phenylenediamines[57] and N,N-dimethyl formamide (DMF) as C_1 sources in a $Zn(OAc)_2$ catalyzed cyclization in the presence of polymethylhydrosiloxane (PMHS) to provides benzimidazoles [58] in good yields.

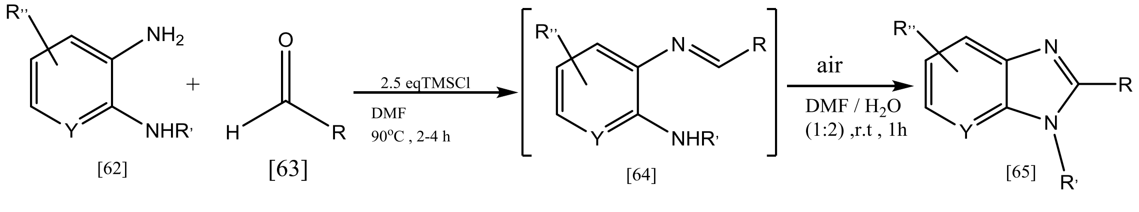


R= H , Me ,Ph , R'= Ar

Beaulieu. et. al(74) added oxone to a mixture of a substituted 1,2-phenylenediamine [59]and an aldehyde [60] in wet DMF to results in rapid formation of benzimidazoles[61] under very mild conditions. Products are isolated in high purity in most cases by simple aqueous precipitation.

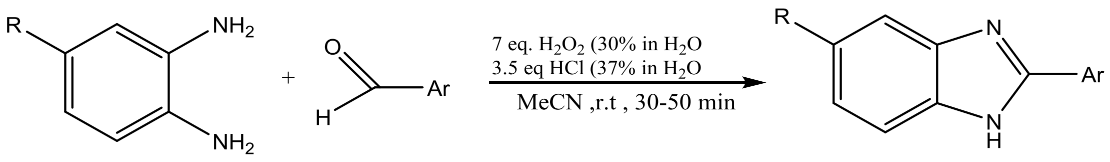


A set of benzimidazoles or 3*H*-imidazo[4,5-b]pyridines[65] was readily prepared from (hetero)aromatic ortho-diamines[62] and aldehydes [63]using trimethylsilanechloride (TMSCl) in DMF as a promoter and water-acceptor agent, followed by oxidation with air oxygen(75) at room temperature .



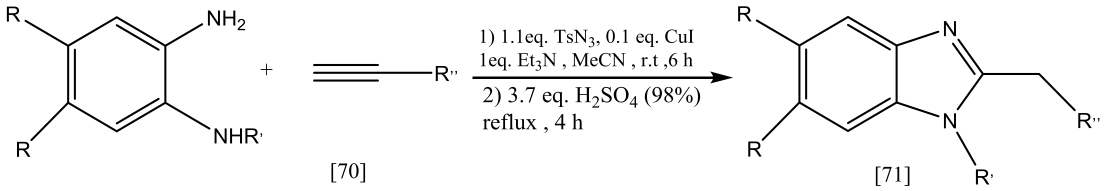
Y= CH , N

A simple and efficient procedure for the synthesis of substituted benzimidazoles [68] through a one-pot condensation of 1,2-phenylenediamines [66] with aryl aldehydes[67] in the presence of H_2O_2 and HCl in acetonitrile at room temperature features short reaction time, easy and quick isolation of the products and excellent yields$^{(76)}$.



[66] [67] [68]

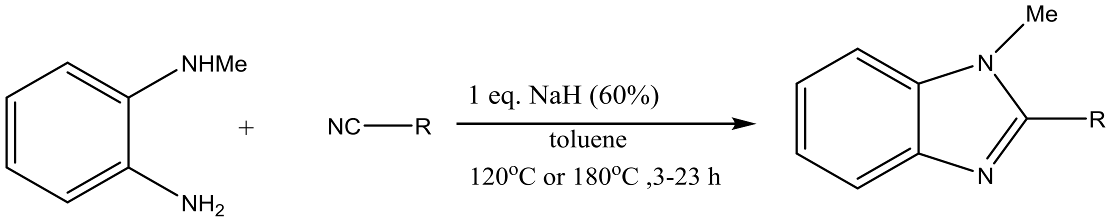
She. et. al$^{(77)}$ synthesized benzimidazoles [71] in good yields by efficient and general cascade reactions of o-aminoanilines[69] with terminal alkynes[70] and *p*-tolylsulfonyl azide



[69] [70] [71]

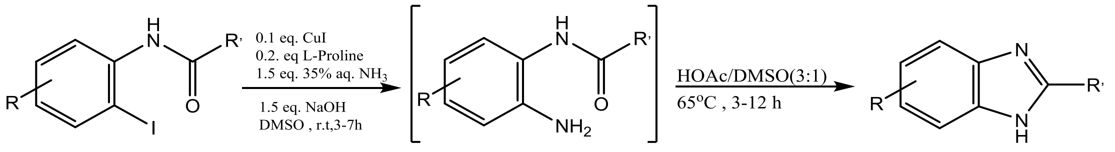
R: H , Me , Cl
R'= H, Me
R''=Ar , alkyl

In addition , Sluiter and Christoffers$^{(78)}$ used a NaH-mediated reaction of *N*-methyl-1,2-phenylenediamine [72] and carbonitriles [98] in toluene allows the formation of *N*-methylbenzimidazole [74]



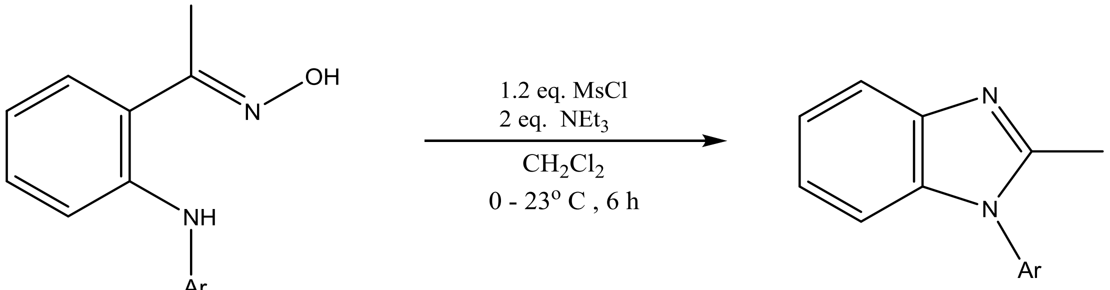
[72] [73] [74]

Diao, et. al$^{(79)}$ used CuI/L-proline catalyzed coupling of aqueous ammonia with 2-iodoacetanilides[75] affords aryl amination products at room temperature, which undergo in situ additive cyclization under acidic conditions or heating to give substituted 1*H*-benzimidazoles[77]



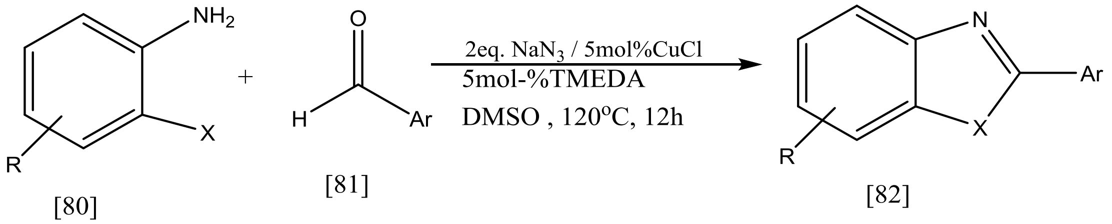
[75] [76] [77]

While, Wray and stambuli$^{(80)}$ were synthesized avrious *N*-aryl benzimidazoles [79] from common arylamino oximes [78] in good to excellent yields by using triethyl amine (TEA) as base in the reaction



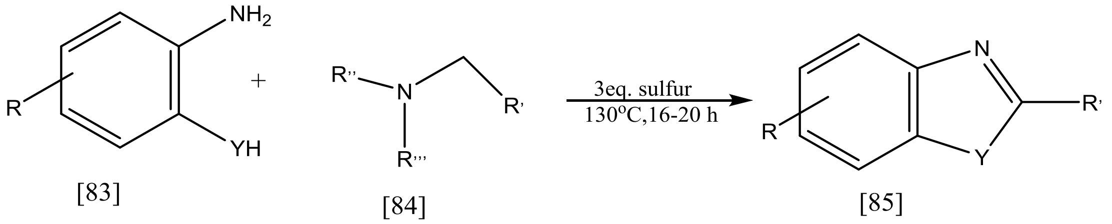
[78] [79]

Kim. et. al(81) used three-component reaction of 2-haloanilines [80], aldehydes[81], and NaN_3 enabled the synthesis of benzimidazoles[82] in good yields using catalytic amounds of CuCl and N,N,N′.N′-tetramethylethylenediamine(TMEDA) in dimethyl sulfoxide(DMSO) at 120°C for 12 hrs. The reaction tolarated many functional groups such as ester, nitro, and chloro



$X=NH_2$, $Ar= C_6H_5^-$

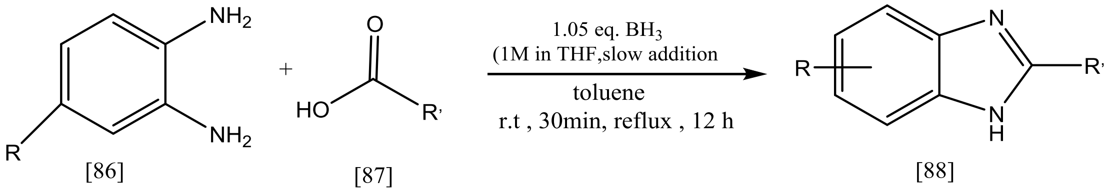
While Nguyen et. al(82) use of elemental sulfur as traceless oxidizing agent enables a remarkably simple solvent-free and catalyst-free synthesis of benzazoles[85] from *o*-hydroxy/amino/mercaptan aniline substituted [83] and alkylamines [84].



y= NH, NMe, S, O

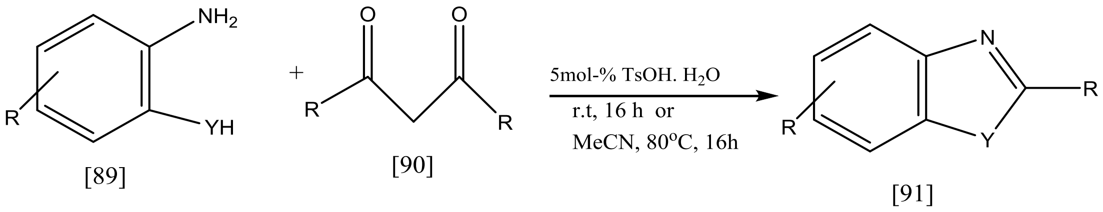
R'= Ar, alkyl R''= H, alkyl R'''=H, alkyl

As well as, a mild and efficient one-pot synthesis enables the preparation of 2-substituted benzimidazoles[88] from substituted 1,2-phenylenediamines [86] , carboxylic acids [87] and borane tetrahydrofuran (THF)in toluene. (83).



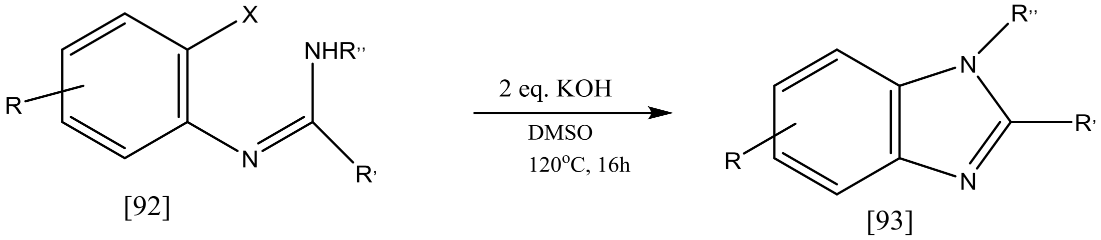
R= H,Me,Cl. Br
R'= Ar , alkyl,benzyl , vinyl

In addition to that, Mayo et. al(84) synthesized 2-substituted benzimidazole [91] in good yields by cyclization reactions of 2-amino thiophenols and anilines[89] with β-diketones[90] under oxidant and metal-free conditions.



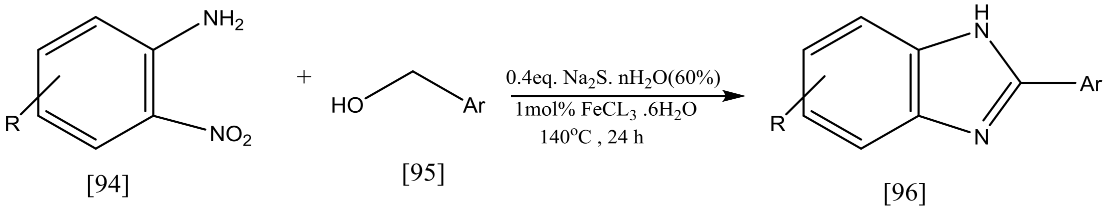
Y= NH , S , R'= Me , Et , iPr , Ph

Baars et. al$^{(85)}$ synthesized substituted benzimidazoles[93] in good yields by intramolecular *N*-arylations [92] of amidines added potassium hydroxide in DMSO at 120°C for mediated.



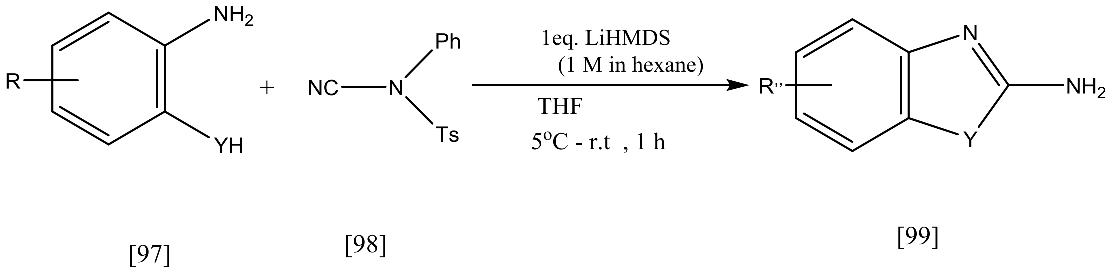
X= F , Br , I
R'= alkyl , Ar
R''= Ph , alkyl , benzyl

Also using sodium sulfide in combination with iron(III) chloride hexahydrate promote an unbalanced redox condensation reaction between o-nitroanilines[94] and alcohols [95] leading to benzimidazole compound [96]. Beside the role as a precursor for an iron-sulfur catalyst, hydrated sodium sulfide is also an excellent noncompetitive, multi-electron reducing agent$^{(86)}$



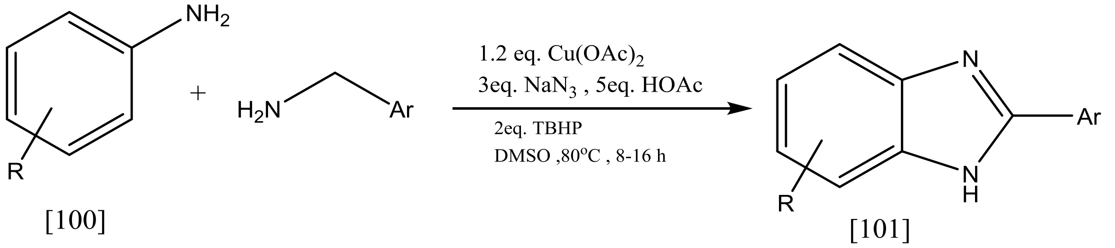
Ar = C_6H_4-OCH_3

2-aminobenzoxazole and 2-aminobenzimidazole derivatives [99] synthesized by the reaction substituted 2-aminophenols or 1,2-phenylenediamine [97] with *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (NCTS) [98] in the presence of lithium hexamethyldisilazide (LiHMDS). $^{(87)}$

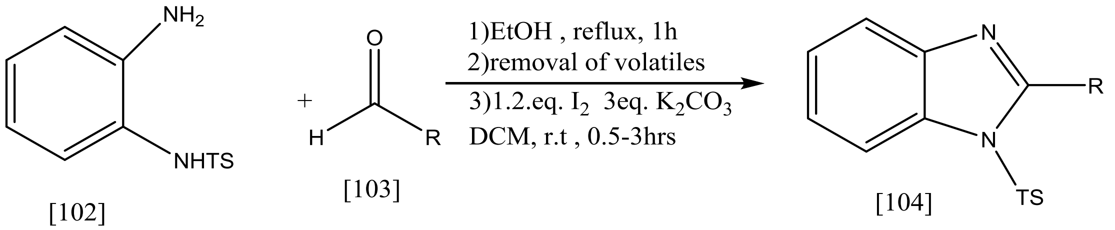


Y = O , NH

Mahesh et. al.(88) used a copper(II)-catalyzed oxidative cross-coupling of substituted anilines [100], primary alkyl amines, and sodium azide provides benzimidazoles[101] in the presence of tert-Butyl hydroperoxide (TBHP) at moderate temperature via a domino C-H functionalization, transimination, ortho-selective amination, and a cyclization sequence.

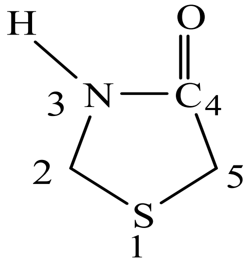


Recently the benzimidazole derivatives [104] synthesized(89) by imine substrates were readily obtained by condensation of simple 1,2-phenylenediamine derivatives[102] and a broad range of aldehydes[103] with molecular iodine under basic conditions



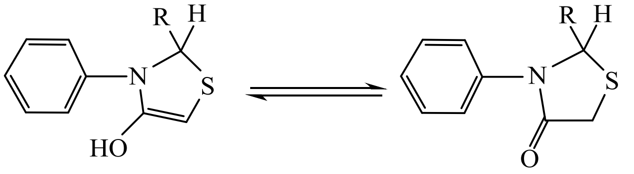
1.9.3 Thiazolidin-4-one:-

Thiazolidin-4-one [105] is an important five member heterocyclic compounds having sulfur in addition to nitrogen atoms with carbonyl group at position (4).



[105]

Thiazolidin-4-one have enol and keto tautmerisum $[106]_{a,b}$$^{(90,91)}$.



enol form
$[106]_a$

keto form
$[106]_b$

R= CH_3,C_2H_5

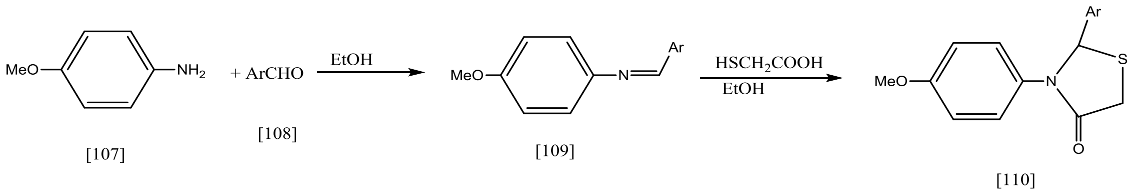
A brief review revealed thiazolidine derivatives belonging to an important group of heterocyclic compounds that have a long history in medicinal chemistry. In particular, thiazolidine-4-ones represent a class of heterocyclic compounds with a wide variety of pharmacological activities. (92) Furthermore, compounds containing a thiazolidine nucleus have a broad spectrum of biological activities, including anti-tumor, (93)anti-HIV, (94) antibacterial , (95) anti-microbial,(96) anti-inflammatory(97) and analgesic properties(98). Thiazolidinones and their derivatives have attracted continuing interest because of their potential roles as antitumor and anticancer agents in chemotherapy.(99, 100)

1.9.4. Synthesis of thiazolidin 4-one dervatives

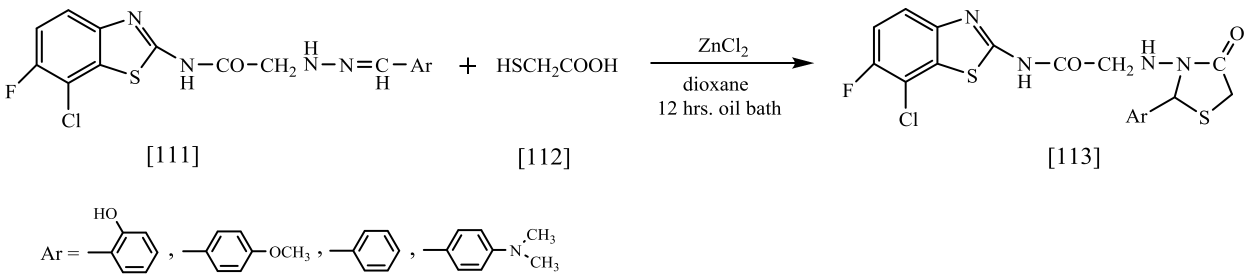
The thermal methodologies for the synthesis of thiazolidinone-4-ones are very efficient, leading to good or excellent product yields. However, the thermal methods require a very long reaction time that raises the possibility of creating impure products. Microwave irradiation is another heating method based on the potential of some compounds to transform electromagnetic energy into heat. This process, that enhances chemical reaction rates and manufactures cleaner products. (101)

The thiazolidine-4-one derivatives synthesized by many methods as followed :-

Synthesized series of 3-(4-methoxy phenyl)-2-aryl thiazolidin-4-one [110] by the reaction of thioglycolic acid with Schiff bases [109]. Which were synthesized by condensation of 4-methoxy aniline [107] with different substituted aromatic aldehydes[108] (102) in EtOH as a solvent

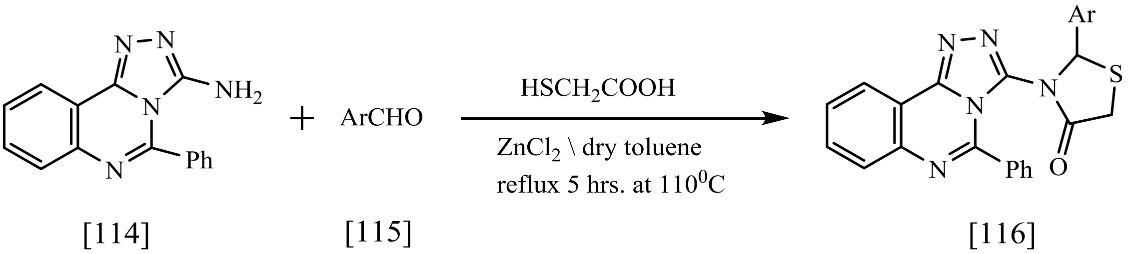


Shailaja et. al. (103) reported the synthesis of 4-thiazolidinone derivatives [113] by the reaction of compound [111] and thioglycolic acid [112] by using anhydrous $ZnCl_2$ in solvent such as1,4-dioxane .



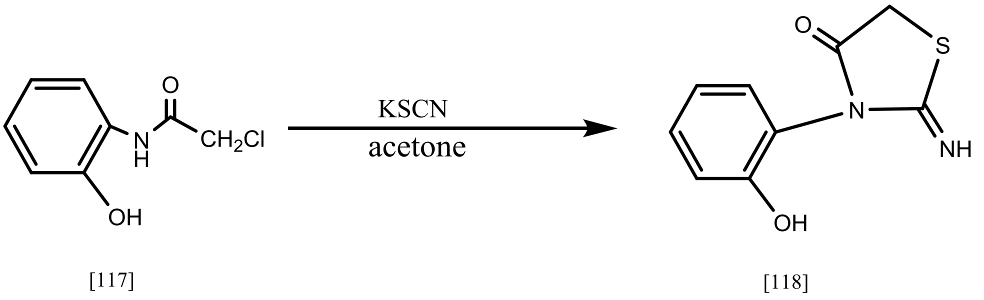
.

Reddy and Sunitha$^{(104)}$ synthesized 2-aryl-3-(5-phenyl[1,2,4]triazolo[4,3-c]quinazolin-3-yl)-1,3-thiazolidin-4-ones [116] by refluxing of 3-amino -5-phenyl[1,2,4]triazolo[4,3-c]quinazolin [114] with benzaldehyde and substituted benzaldehyde [115] followed by thioglycolic acid using $ZnCl_2$ in dry toluene .

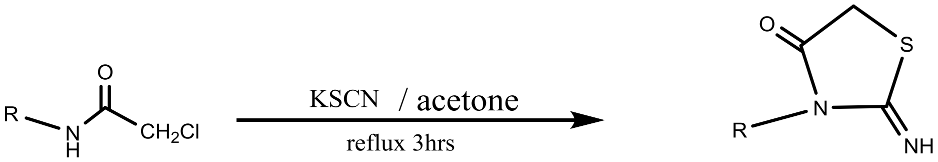


Ar = C_6H_5 , 4-ClC_6H_4 , 4-$NO_2C_6H_4$, 4-HOC_6H_4 , 3-$NO_2C_6H_4$, 2-ClC_6H_4 , 2-HOC_6H_4 , 4-$N(CH_3)_2C_6H_4$

While, Gemechu$^{(105)}$synthesized 3-(2-hydroxyphenyl-2-iminothiazolidine -4-one [118] by reaction of 2-chloro-N(-2-hydroxyphenyl)-acetamide [117] with KSCN in acetone as a solvent



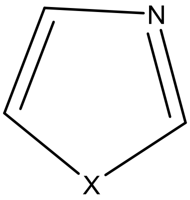
In addition , Saxena et.al. (106) synthesized thiazolidin-4-one derivatives [120] from compound [119] and KSCN in acetone as asolvent



[119] [120]

1.9.5. 1,3-azole derivatives

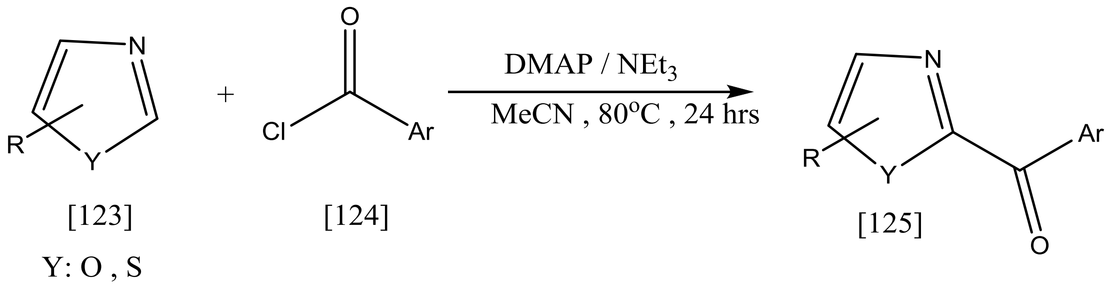
Oxazole and thiazle are the parents compounds(107) for a vast class of heterocyclic aromatic organic compounds. These are azoles[121] with an oxygen and a nitrogen separated by one carbon this called oxazole , but azoles [122] containing sulfur atom called thiazole. Oxazoles are aromatic compounds but less or aromatic than the thiazoles.



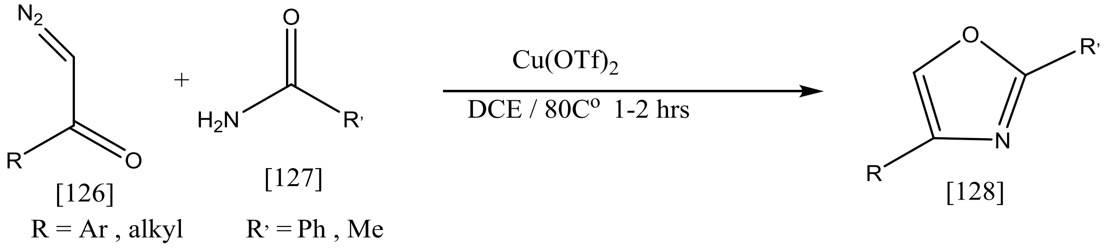
[121] , [122]
X =O, S

1.9.6. Synthesis of 1,3-azoles derivatives

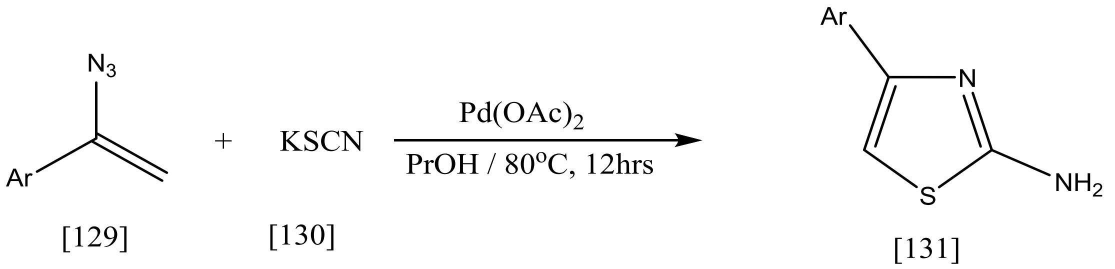
Also Lassalas et.al(108) synthesized 2-ketoazoles [125] Regel-type transition-metal-free direct C-2 aroylation of (benzo)oxazoles, (benzo)thiazoles [123] with acid chloride [124] using *N*,*N*-dimethyl-4-amino pyridine (DMAP) as a catalyst. .



Reddy et. al$^{(109)}$ used Copper(II) triflate as a catalyst enables a coupling of α-diazoketones[126] with amides [127] to provide 2,4-disubstituted oxazoles [128].

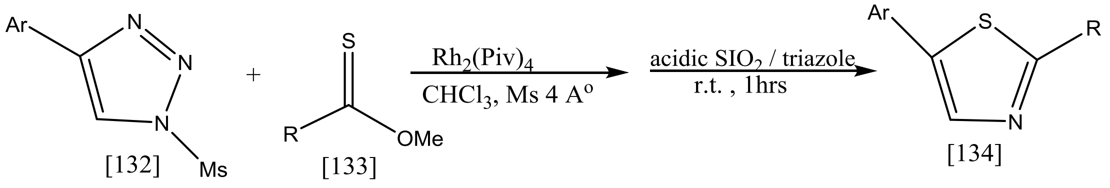


Chen et. al$^{(110)}$ using vinyl azides [129] and potassium thiocyanate [130] to form 4-substituted -2-aminothiazoles [131]



Also Miura et.al$^{(111)}$ used 1-sulfonyl-1,2,3-triazoles [132] with thionoesters [133] in the presence of a rhodium(II) catalyst providing 3-

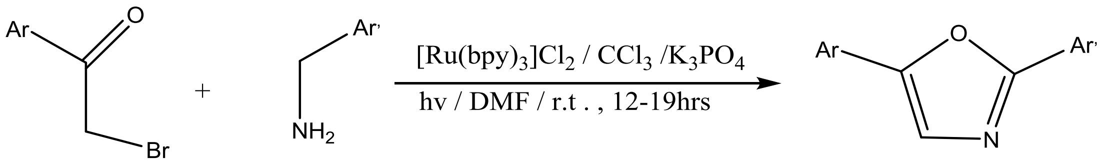
sulfonyl-4-thiazolines, which subsequently aromatize into the corresponding 2,5-disubstituted thiazoles [134] by elimination of the sulfonylgroup.



[132] [133] [134]

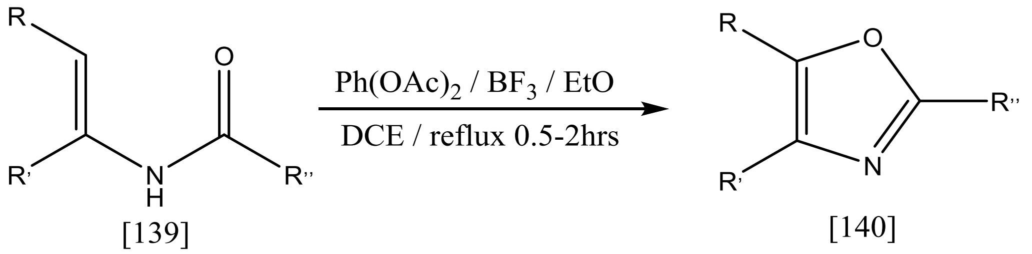
R: Ar , vinyl , Bn , C_9H_{19}

While Chatterjee. et. al(112) synthesized substituted oxazoles [137] from reaction α-bromoketones [135] with benzylamines [136] by visible-light photocatalysis at room temperature.



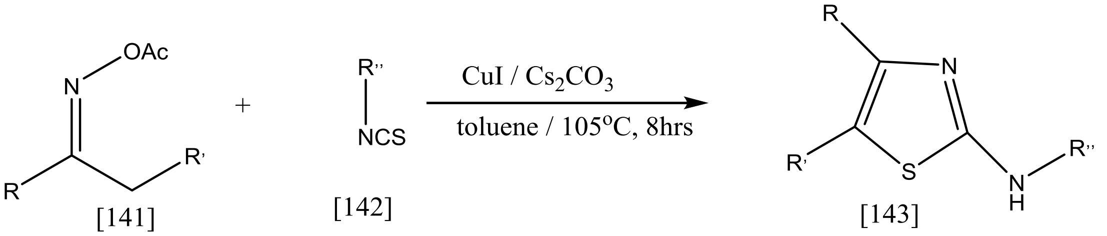
[135] [136] [137]

Also Chen. L et. al(113) synthesized of 2,4,5-trisubstituted oxazole [140] from reaction compound [139] with $Ph(OAc)_2$ BF_3 and EtO in DCE BY reflux for 0.5-2hrs . This provides a wide range of substituted oxazoles in good yields.



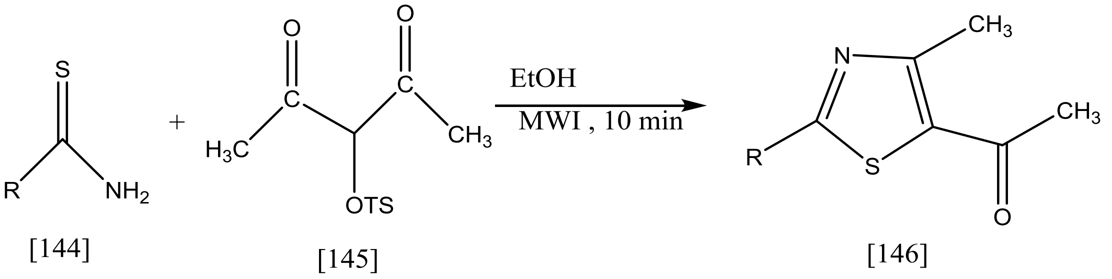
R = Ar , Me , COMe , CO_2Me
R' = CO_2Me , Me , Ar , COPh , H
R'' = alkyl , Ar

A copper-catalyzed coupling of oxime acetates [141] with isothiocyanates [142] provides 4,5-disubstituted 2-N-substituted-aminothiazoles(114) [143]

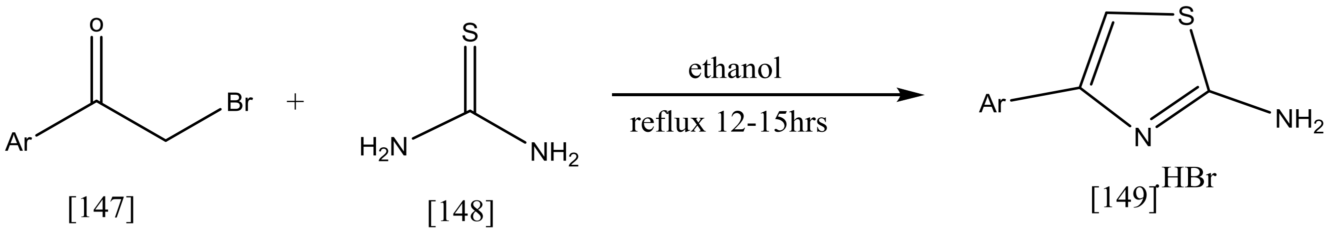


R: Ar , 1° alkyl
R': H , 1° alkyl
R'': Ar , alkyl , Bn

By using microwave irradiation method Vaddula et al.(115) synthesized new thiazole compounds [146] only in 10 min

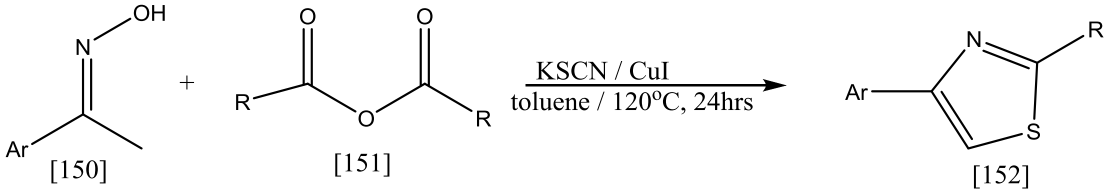


In addition Facchinetti et.al(116) synthesized 5-substituted 2-aminothiazoles [149] from condensation of 2-bromoacetophenones [147] with thiourea [148] .



[147] [148] [149]

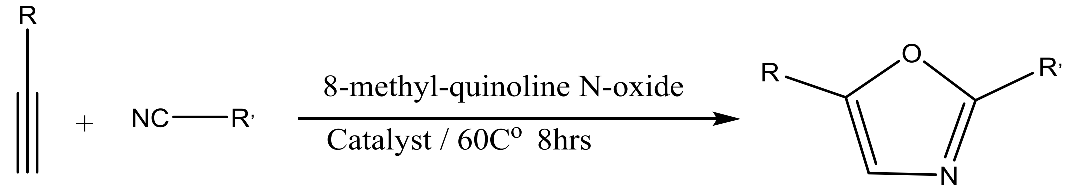
The condensation of oximes[150] with acid anhydrides[151] and potassiumthiocyanate (KSCN) in copper catalyzed provides thiazoles [152] in very good yields under mild reaction conditions(117).



[150] [151] [152]

R: alkyl

Yang. et . al(118) synthesized of 2,5-disubstituted oxazole [154] from reaction alkynes [95] with nitriles [153] .



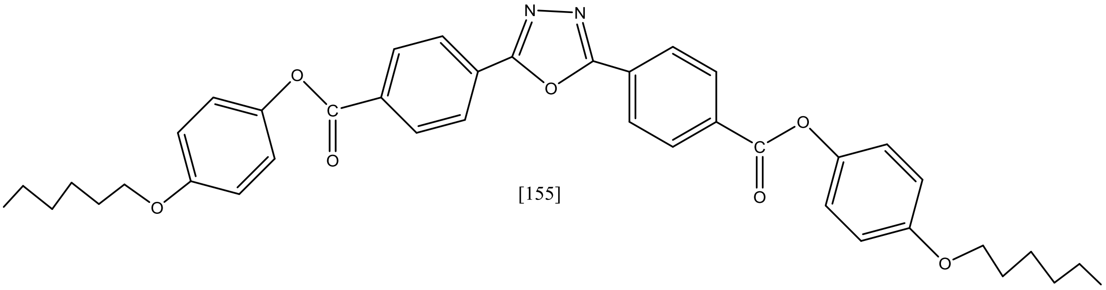
[95] [153] [154]

R = Ar , alkyl R' = alkyl , Ar

1.10 The literature survey of heterocyclic liquid crystal

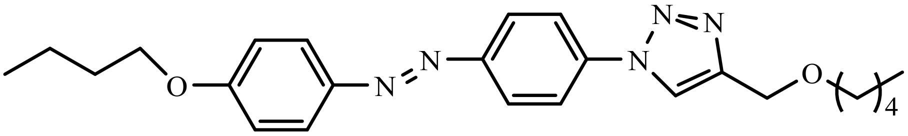
Heterocyclic are of great importance as core units in liquid crystals due to their ability to impart lateral and / or longitudinal dipoles combined with changes in the molecular shape . Therefore many workers designed heterocyclic compounds have LC properties containing thiophene(119) , thaizole , oxazole ,isoxazole (120) , oxadaizole, thiadaizole , pyridine(121) , pyrazole(122,123) , pyrazolone(124) , oxazepine , triazole and teterazole, as Followes :

Semmler et .al (125) , prepared first bent-core 2,5-diphenyl-1,3,4-oxadiazoles [162] with two additional benzene rings which showed SmC and SmA mesophase .



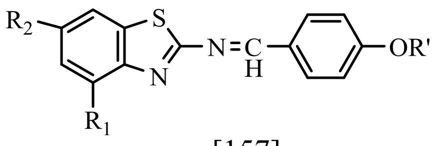
[155]

On the other hand ,Srividhya et. al.(126) reported the synthesis of a new 1,2,3-triazole type [156] of liquid crystalline heterocyclics . This compound displays smectic A phase by cooling from isotropic to crystalline



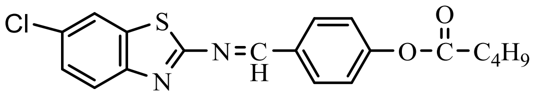
[156]

Also ,Tomma(127) have synthesized and studied liquid crystalline properties of some benzothiazoles derivatives [157] and [158].



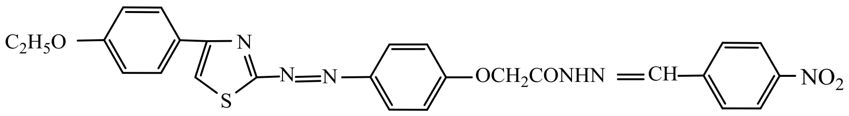
[157]

R_1	R_2	R'
H	CH_3O	OCH_3
H	CH_3O	OC_5H_{11}
H	CH_3O	OC_5H_{11}
NO_2	NO_2	OC_5H_{11}



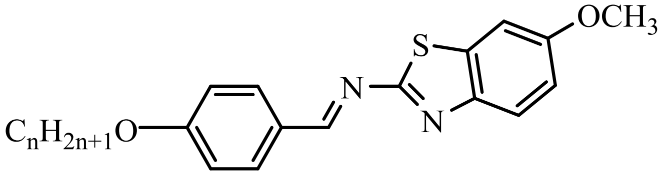
[158]

Al-Dujaili et.al.(128)synthesized and studied liquid crystal properties of compound [159] containing 1,3-thiazole unit this compound showed only nematic schlioren texture .



[159]

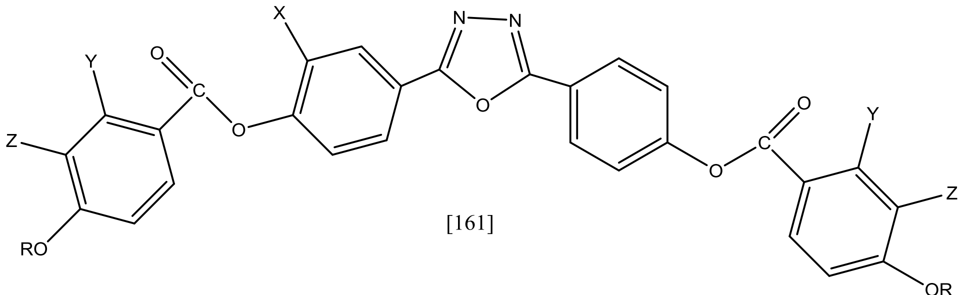
Foo and Ha(129) synthesized and studied the effect of alkyl chain length on the mesomorphic properties for new rod-shaped 6-methoxy-2-(4-N-alkyloxybenzylidenamino) benzothiazoles [160]



n = 10 , 12 , 14 , 16 , 18

[160]

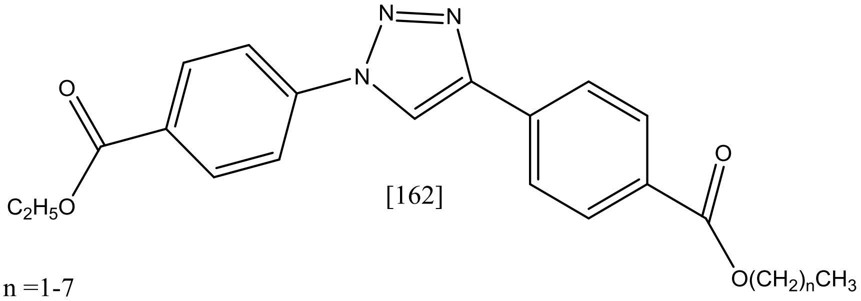
Nguyen et .al(130) synthesized some new compounds [161] that possess lateral floro or methyl group . All these derivatives exhibit nematic phase.



[161]

X=F , Y=H , Z=CH_3
X=F , Y=CH_3 , Z=H
X=F , Y = Z = H

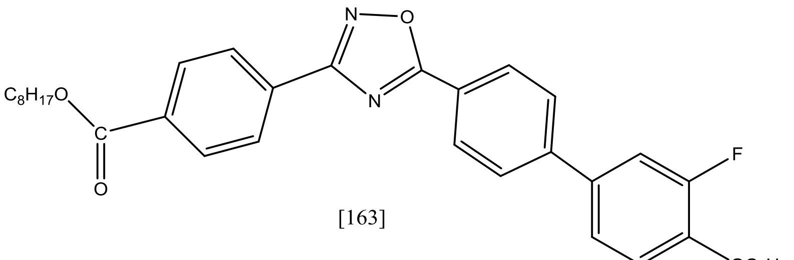
Li et.al (131) synthesized a series of heterocyclic compounds containing 1,2,3-triazole ring [162] most of these compounds exhibited SmA mesophase



[162]

n =1-7

A novel compounds of liquid crystals containing oxadiazole cores [163]with unsymmetrical substitution are synthesized and characterized by subrao et . al(132) . These compounds possess high thermal stability and exhibit smectic phases .

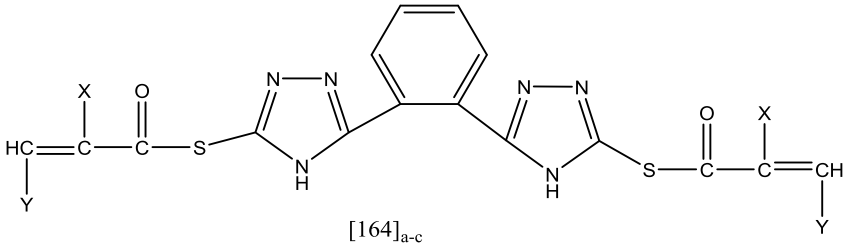


[163]

n= 8,10,12,15,16

In addition ,Karam

et. al. (133) , synthesized and studied liquid crystalline behavior of thio ester bent core compoundes containing 4H-1,2,4-triazole-3-thios moiety[164]$_{a-c}$



[164]$_{a-c}$

X=H , Y=H
X=H , Y=C_6H_5
X=CH_3 , Y=H

The aim of the work

1,2,3-triazole , benzimidazole , 1,3-oxazole , 1,3-thiazole and thiazolidine-4-one derivatives are important heterocyclic moieties both mesomorphic properties and industrially useful , thus , the aim of this work is:

1- Synthesis and characterization of new derivatives of 1,2,3-triazole , benzimidazole , 1,3-azole and thiazolidine-4-one.

2- Study the effect of heterocyclic five membered ring on the liquid crystal properties of the synthesized compounds.

3- Study the effect of amine , amide and alkoxy as a terminal group and imine as a linkage group in the synthesized compounds on liquid crystalline properties.

2. Chemicals and Techniques

2.1. Chemicals

The following chemicals in Table (2-1) were obtained from different companies.

Table (2-1) : listed liquid and solid chemicals with companies used in this work

Company supplied	**Name of material**	**Purity %**
Aldrich	1,2-phenylenediamine	99
	1,3- phenylenediamine	99
	1,4-phenylenediamine	98
	Chloroacetylchloride	99
	Ethyl acetate	97
	Acrylic acid	99
	1-Bromo ethane	98
	1-Bromo propane	99.8
	1-Bromo pentane	99
	1-Bromo hexane	98
	1-Bromo heptane	99
	1-Bromo octane	99
	p-nitroaniline	97
	pipyridine	96
BDH	Potassium hydroxide	96
	Anisidine	99

Fluka	Diethyl ether	98
	Sodiumcarbonate	96
	4-hydroxy benzaldehyde	99
	Tetrahydrofuran (THF)	98
	Ammonia solution	99.5
	p-hydroxyaniline	98
	4-methoxybenzaldehyde	99
	Thiourea	99
GCC	N,N-Dimethylformamide (DMF)	98
Merck	Benzene	99.5
	Sodium azide	99
	Dimethyl sulphoxide (DMSO)	99
	Hydrazine hydrate	80
	Magnesium sulphate	99
	Sodium becarbonate	98
	Pyridine	99
	Tolidine	99.5
	4-methylbenzaldehyde	99
	Urea	99.7
	glacial acetic acid	98
Riedal-deHaën	Triethylamine (TEA)	99.5
	Ethanol absolute	99.8
	Hydrochloric acid	35-36
	Sulfuric acid	98

2.2. Techniques

2.2.1. Spectroscopy

a) Fourier transform infra-red spectrophotometer (FTIR)

FTIR spectra were recorded on a SHIMADZU (IR Affinity-1) FTIR spectroscopy at College of Education for Pure Science(Ibn-Al-Haitham), University of baghdad and SHIMADZU (IR Affinity-1) FTIR spectroscopy at College of Education for Pure Science, University of Diyala and FTIR-600 spectrometer, (UK) at College of Education for Pure Science (Ibn-Al-Haitham)\ Central Service Laboratory , University of Baghdad .

b) Nuclear magnetic resonance spectrometer (^{1}HNMR)

^{1}HNMR spectra were carried out using Ultra Shield 400 MHz and Ultra shield 500MHz, Bruker, Switzerland, at University of Tehran , Center Lab (in Iran) ,also some spectra were carried out by Ultra shield 300MHz Bruker, Switzerland at University of Kasi , Turkey are reported in ppm(δ), DMSO and $CDCl_3$ were used as a solvent with TMS as an internal standard .

c) Mass spectroscopy:

The mass spectra recorded on Shimadzo model: GCMS QP 1000 EX, (made in Japan) at College of Science, Asfhan University / Iran .

2.2.2. Melting points measurements

Uncorrected melting points were determined by using Stuart , SMP 10 , (UK) .

2.2.3. Thin layer chromatography(TLC)

The TLC was preformed on aluminum plate coated with layer of silica gel, supplied by Merck. The compounds were detected by iodine vapor.

2.2.4. Hot-stage polarizing microscopy

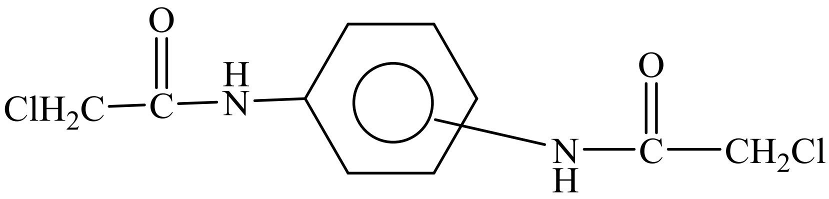
The transition temperatures and textures of the mesophases were determined using polarized optical microscope model Leica DM2500 M , College of Education for Pure Science (Ibn-Al-Haitham)\ Central Service Laboratory , University of Baghdad .

2.2.5. Differential scanning calorametry (DSC)

DSC measurements were recorded by the STA PT-1000 LINSIS , German origin , heat rate was average 5 ^{o}C /minute , College of Education for Pure Science (Ibn-Al-Haitham)\ Central Service Laboratory , University of Baghdad .

2.3. Synthetic Methods

2.3.1 Preparation of N,N-(1,3-Phenylene)bis(2-chloroacetamide) $[I]_a$ and N,N-(1,4-Phenylene)bis(2-chloroacetamide) $[I]_b$

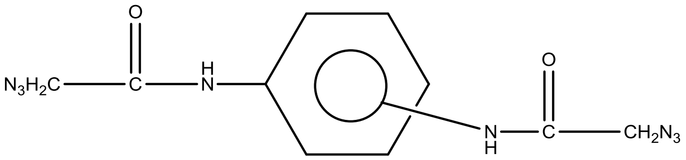


$[I]_{a,b}$

A mixture of 1,3-phenylenediamine or 1,4-phenylenediamine (1,08 gm , 0.01 mol), in DMF (15 mL) was mixed triethylamine (TEA) (18mL) and chloroacetylchloride (2.26gm ,0.02 mol) was stirred in ice bath for (3 hrs). After cooling the mixture addition to ice water then filtration dried and recrystallized from ethanol .

The compound $[I]_a$, has a white color, yield 76% , m.p =212-214^{o}C
The compound $[I]_b$, has a grey color, yield 72% , m.p =315-317^{o}C

2.3.2 Synthesis of N,N-(1,3-phenylene)bis(2-azidoacetamide) $[II]_a$ and N,N-(1,4-phenylene)bis(2-azidoacetamide) $[II]_b$



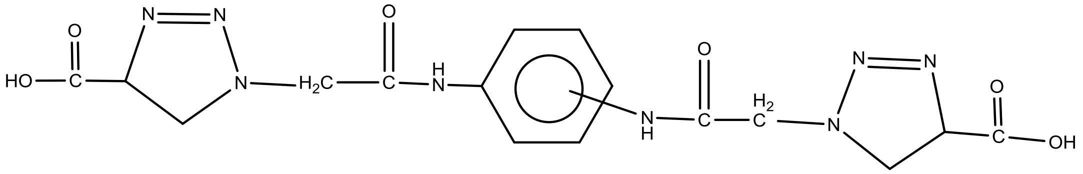
$[II]_{a,b}$

To a solution of compound $[I]_a$ or $[I]_b$ (0.26gm , 0.001mol) in 3mL DMF added sodium azide(133-135) (0.13gm , 0.002mol) and ammonium chloride (0.106gm , 0.002mol) were added. The mixture was refluxed for (4hrs) with continuous stirring for (4hrs) after that the resulting solution cool in water ice and the product obtained was collecting .

The compound $[II]_a$, has a brown color, yield 76% , m.p =122-124 °C

The compound $[II]_{b,}$ has a dark red color, yield 72% , m.p =131-133C°

2.3.3 Synthesis of 1,1-((1,3 -phenyenebis(azanediyl))bis(2-oxoethane-2,1-diyl)bis(4,5-dihydro-1H-1,2,3-triazole-4-carboxylic acid) $[III]_a$ and 1,1-((1,4 -phenylenebis(azanediyl))bis(2-oxoethane-2,1-diyl)bis(4,5-dihydro-1H-1,2,3-triazole-4-carboxylic acid) $[III]_b$

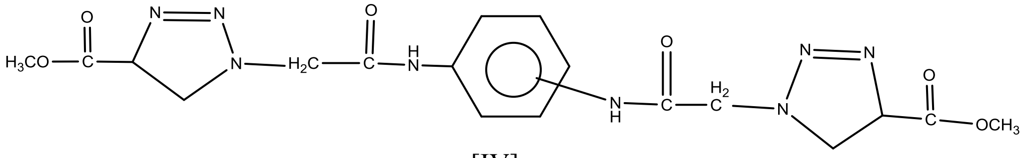


$[III]_{a,b}$

In THF (3mL)were added compound $[II]_a$ or $[II]_b$ (0.05gm , 0.0002) mol) and acrylic acid (0.028gm , 0.0004mol)the mixture was refluxed for (24hrs) The solvent was evaporated under the reduced pressure.The precipeted was dried and recrystallized from ethanol

The compound $[III]_{a,}$ has a pink color, yield 81% , m.p =218-220C^o. The compound $[III]_{b,}$ has a purple color, yield 70% , m.p =287-289C^o

2.3,4 Synthesis of dimethyl1,1-((1,3-phenyenebis(azanediyl))bis(2-oxoethane-2,1-diyl)bis(4,5-dihydro-1H-1,2,3-triazole-4-carboxylate) $[IV]_a$and dimethyl1,1-((1,4-phenyenebis(azanediyl))bis(2-oxoethane-2,1-diyl)bis(4,5-dihydro-1H-1,2,3-triazole-4-carboxylate $[IV]_b$



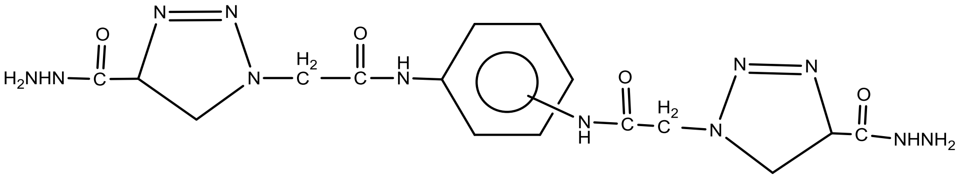
$[IV]_{a,b}$

In 100 mL methanol absolute about 102.8gm, 0.246mol) of compound $[III]_a$ or $[III]_b$ was added and then (3mL) of sulfuric acid was added, The mixture was refluxed for 6hrs then cooled at room temperature after that added solution sodiumbecarbnate 5% and the precipeted washing in water and recrystallized from ethanol

The compound $[IV]_{a,}$ has a brown color, yield 72% , m.p =277-279C^o

The compound $[IV]_{b,}$ of dark brown color, yield 76% , m.p =305-307C^o

2.3.5-Synthesisof N,N-(1,3-phenyene)bis(2-(4-(hydrazinecarbonyl) 4,5- dihydro-1H1,2,3-triazole-1yl) acetamide$[V]_a$andN,N-(1,4-phenyene) bis(2-(4-(hydrazinecarbonyl)4,5-dihydro-1H1,2,3-triazole-1yl) acetamide $[V]_b$



$[V]_{a,b}$

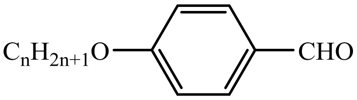
To compound $[IV]_a$ or $[IV]_b$ (2.67gm , 0.006mol) 13mL of hydrazine hydrate 80% was added then 15mL absolute ethanol the reaction mixture was refluxed for 3hrs then resulting solution was allowed to cooled to room temperature and

recrystallized from ethanol

The compound $[V]_{a,}$ has a brown color, yield 68% , m.p =237-239C^o

The compound $[V]_{b,}$ has a dark brown color, yield 76% , m.p =249-251C^o

2.3.6 Preparation of 4-n-alkoxybenzaldehyde $[VI]_n$

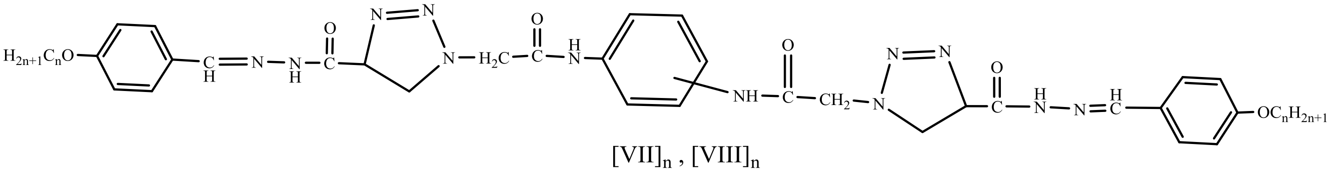


$[VI]_n$

n = 2.3,5,6,7,8

To a solution of potassium hydroxide(4.87gm , 0,087mol) in absolute ethanol 50 mL, (10.6gm , 0,087mol) of 4-hydroxybenzaldehyde was added then (0.13mol) of alkylbromide, the reaction mixture was refluxed for 6hrs then added, 50mL water. The product was extracted by using ethylether (50mL). The organic layer washed in 25mL solution of sodium hydroxide 10%, then 25mL water , after that the solvent was evaporated(136) to produce the compounds $[VI]_n$.

2.3.7 Synthesis of N,N-((1,3 -phenylene)bis(2-(4-(-2(4-methoxybenzylidene)hydrazine-1-carbonyl) 4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamide)$[VII]_n$ and N,N-((1,4 -phenylene)-bis(2-(4-(2(4-methoxybenzylidene)hydrazine-1-carbonyl)4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamide) $[VIII]_n$

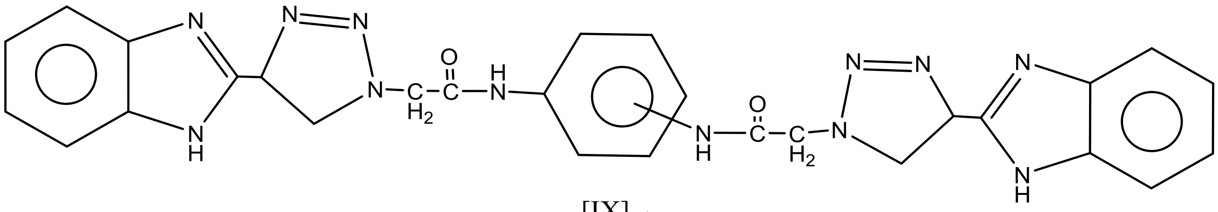


$[VII]_n$, $[VIII]_n$

n = 1,2,3,5,6,7.,8

A mixture of compound $[V]_a$ or $[V]_b$ (0.446gm , 0.001mol) with 4-n-alkoxybenzaldehyde compounds $[VI]_n$ (0.002mol) and 5mL absolute ethanol, the solution heating for (3-4hrs) then cooled after that filtered and recrystallized from ethanol to give the compound $[VII]_n$ and $[VIII]_n$, the nomenclature structural formula, molecular formula, yields and physical properties for these compounds were listed in Tables (2-2) and (2-3), respectively.

2.3.8 Synthesis of N,N'-(1,3-phenylene)bis(2-(4-(1H-benzo[d]imidazol-2-yl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamide) $[IX]_a$ and N,N'-(1,4-phenylene)bis(2-(4-(1H-benzo[d]imidazol-2-yl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamide) $[IX]_b$



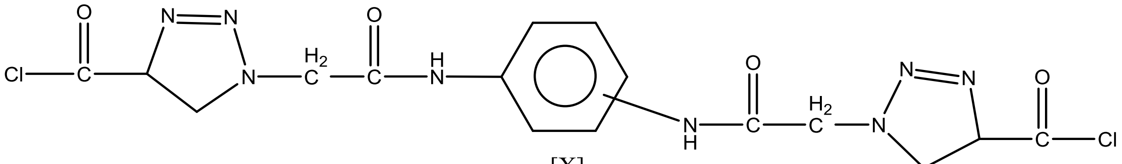
$[IX]_{a,b}$

To compound [III]$_a$ or [III]$_b$ (0.418gm , 0.001mol) added 3mL of DMF then added (0.216gm , 0.002mol) of 1,2-phenylenediamine and refluxed for10hrs. Added drops of ammonia to the mixture and filtered then the precipeted was dried and recrystallized from ethanol.

The compound [IX]$_a$, has a brown color, yield 77% , m.p =251-253C^o

The compound [IX]$_b$, has a purple color, yield 72% , m.p =274-276C^o

2.3.9 Synthesis of 1,1'-((1,3-phenylenebis(azanediyl))bis(2--oxoethane-2,1-diyl))bis(4,5-dihydro-1H-1,2,3-triazole-4-carbonyl chloride [X]$_a$ and 1,1'-((1,4-phenylenebis(azanediyl))bis(2-oxoethane-2,1-diyl))bis(4,5-dihydro-1H-1,2,3-triazole-4-carbonyl ((chloride [X]$_b$



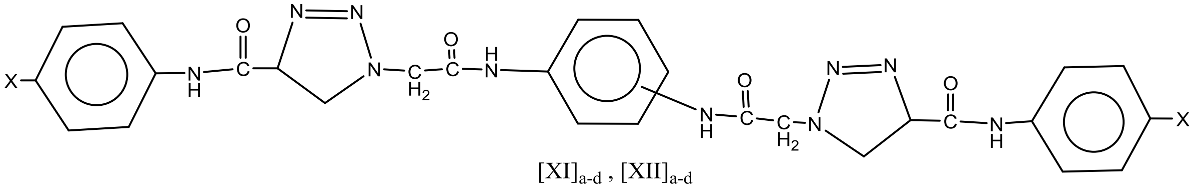
[X]$_{a,b}$

In DMF 3mL added compounds [III]$_a$ or [III]$_b$ (0.3gm , 0.0007mol) then added (0.16gm , 0.0014 mol) of thionylchloride the reaction mixture refluxed for 3hrs then the resulting was cool to room temperature , and recrystallized from ethanol .

The compound [X]$_a$, has aoff white color, yield 67% , m.p =221-223C^o.

The compound [X]$_b$, has a purple color, yield 64% , m.p =239-241C^o

2.3.10 Synthesis of amide derivatives [XI]$_{a-d}$ and [XII]$_{a-d}$

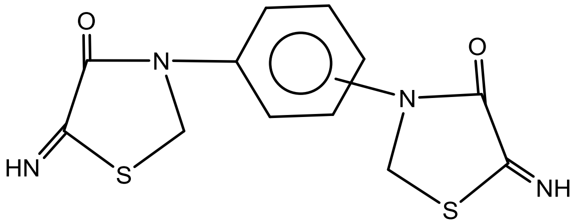


[XI]$_{a-d}$, [XII]$_{a-d}$

X=CH_3 , O-CH_3 , OH , NO_2

To a mixture of 1mL of pyridine and 2mL of DMF added aromatic amine and put a round flask in ice bath then added compound $[X]_a$ or $[X]_b$ and stirrer for 4hrs, after that added hydrochloric acid (10%), then filtered and washing in water then dried and recrystallized from ethanol, the nomenclature structural formula, molecular formula, yields and physical properties for these compounds were listed in Table (2-4)

2.3.11 Synthesis of 3,3-(1,3-phenylene)bis(2-iminothiazolidine-4one)$[XIII]_a$ and 3,3-(1,4-phenylene)bis(2-iminothiazolidine-4one)$[XIII]_b$



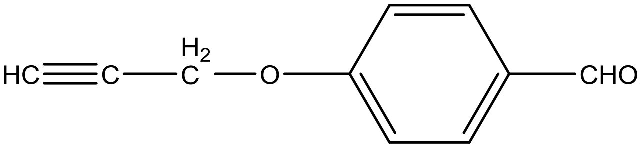
$[XIII]_{a,b}$

To a solution of compounds $[I]_a$ or $[I]_b$ (0,78gm , 0.003mol) and 5mLof acetone added (1.16gm , 0.006mol) of potassium thiocyanate KSCN, the mixture was refluxed for(3-4hrs), then the solvent was evaporated the product dried and recrystallized from ethanol.

The compound $[XIII]_a$ has a crimson color, yield 81% , m.p =243-245°C .

The compound $[XIII]_b$, has a dark red color, yield 78% , m.p =281-283°C

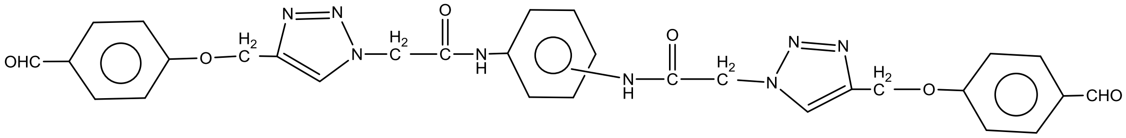
2.3.12 Preparation of 4-(prop-2-yn-1-yloxy)benzaldehyde [XIV]



[XIV]

In DMF 2mL added (0.1gm , 0.0008 mol) of 4-hydroxybenzaldehyde then added (0.12gm , 0.0032mol) of NaOH, a mixture was stirred in ice bath for 10min then added gradually (0.15gm , 0.0009 mol) propergylbromide, srtirrer for 24h at room temperature after that filtered to get the compound(137) [XIV] , color hrs dark red , yield 78% , m.p =201- 203°C

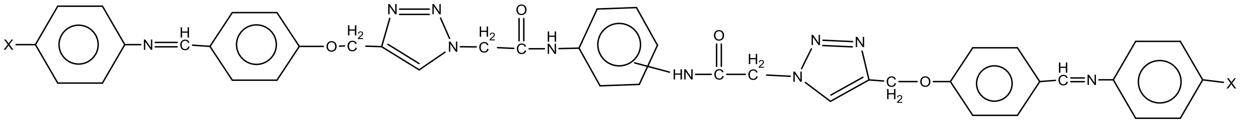
2.3.13.Synthesis of N,N'-(1,3-phenylene)bis(2-(4-((4-formylphenoxy) methyl)-1H-1,2,3-triazol-1-yl)acetamide) $[XV]_a$ and N,N'-(1,4-phenylene)bis(2-(4-((4-formylphenoxy)methyl)-1H-1,2,3-triazol-1-yl)acetamide) $[XV]_b$



$[XV]_{a,b}$

The compound [XIV] (0.96gm , 0.006mol) dissolved in 3mL of THF then added amount of copper(I) iodide and added a solution (0.82gm , 0.003mol) of compound $[II]_a$ or $[II]_b$ in THF, after that stirrer at room temperature for evaporate the solvent Then extraction in ethylacetate and dried of layer organic . The compound $[XV]_a$, a crimson color, yield 81% , m.p =231- 233°C . The compound $[XV]_b$, has a dark red color, yield 78% , m.p =271-273°C .

2.3.14 Synthesis of Schiff bases derivatives $[XVI]_{a-d}$ and $[XVII]_{a-d}$

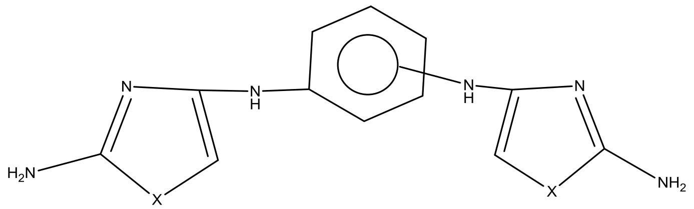


$[XVI]_{a-d}$, $[XVII]_{a-d}$

X = CH_3 , OCH_3 , OH , NO_2

Dissolved (0.53gm, 0.001mol of compound [XV]$_a$ or [XV]$_b$ in 2 mL ethanol absolute then added drops of glacial acetic acid (GAA) and (0.002mol) of different aromatic amine after that stirrer for 6hrs. Then under reduced pressure the solvent was evaporated, dried and recrystallized from diethylether the nomenclature structural formula, molecular formula, yields and physical properties for these compounds were listed in Table (2-5)

2.3.15 Synthesis of oxazole compounds [XVIII]$_{a,b}$ and thiazole compounds [XIX]$_{a,b}$



X = O,S

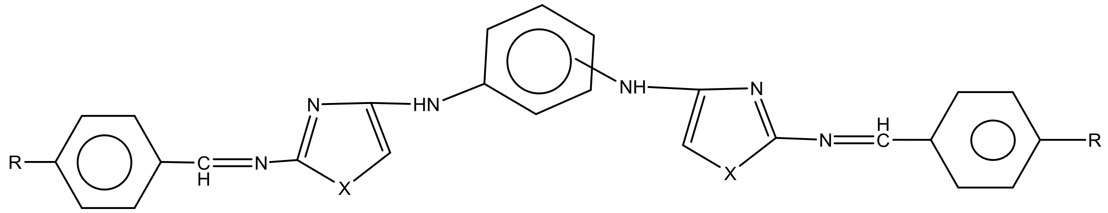
[XVIII]$_{a,b}$, [XIX]$_{a,b}$

[XVIII]$_{a,b}$ when X = O
[XIX]$_{a,b}$ when X = S

To a solution of compound [I]$_a$ or [I]$_b$ (0.01 mol) in ethanol 150 mL, urea (1.2gm , 0.02 mol) or thiourea (1.52gm , 0.02mol) was added. This reaction mixture was heated under reflux for 12-15 hrs with occasional stirring. Then, the reaction mixture was concentrated, and the residue obtained was poured over crushed ice and then filtered and recrystallized from ethanol .

The nomenclature structural formula, molecular formula, yields and physical properties were listed in Table (2-6).

2.3.16 Synthesis of Schiff bases compounds $[XX]_{a-c}$, $[XXI]_{a-c}$, $[XXII]_{a-c}$, $[XXIII]_{a-c}$



R = CH_3 , OCH_3 , OH

[XX]a-c , [XXI]a-c , [XXII]a-c , [XXIII]a-c

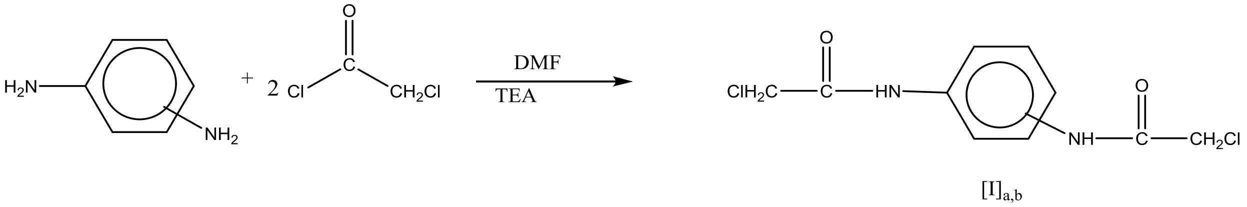
$[XX]_{a-c}$ and $[XXI]_{a-c}$ when X= O
$[XXII]_{a-c}$ and $[XXIII]_{a-c}$ when X= S

To a solution (0.002mol) different aromatic aldehyde and (4mL) of THF added a few drops of piperidine(138), then added (0.001mol) of compound $[XVIII]_{a,b}$ or $[XIX]_{a,b}$ and reflux for 4hrs (in water bath) . The solvent was evaporated and the residue was extracted with diethyl ether, the nomenclature structural formula, molecular formula, yields and physical properties for these compounds were listed in Tables (2-7) and (2-8).

3.1. Results and discussion

3.1.1. Preparation and characterization of N,N-(1,3-Phenylene)bis(2-chloroacetamide) [I]$_a$ and N,N-(1,4-Phenylene)bis(2-chloroacetamide) [I]$_b$

The compounds [I]$_{a,b}$ were prepared by reaction of 1,3-phenylenediamine or 1,4-phenylenediamine with two moles from chloroacetylchloride in DMF and triethylamine (TEA) (as a catalyst)



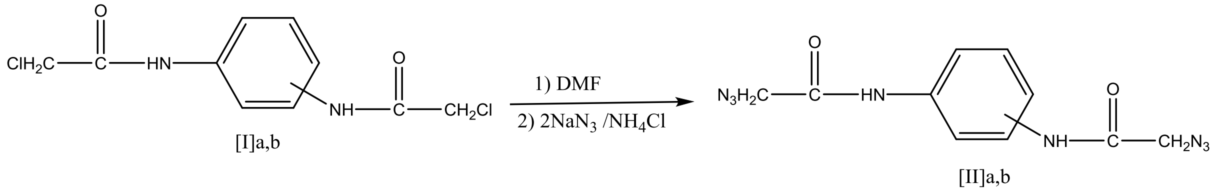
[I]$_{a,b}$

These compounds were identified by melting points and FTIR spectroscopy.

The FTIR spectra for compounds [I]$_{a,b}$, showed the appearance of absorption stretching bands of N-H at (3259) cm^{-}, (3223) cm^{-1} and C═O groups of (amide moiety) at (1681) cm^{-1}, (1673) cm^{-1} respectively and disappearance of stretching bands of NH$_2$ groups. Figure (3-1) the FTIR spectrum for compound [I]$_a$.

3.1.2. Synthesis and Characterization of N,N-(1,3-phenylene)bis(2-azidoacetamide) [II]$_a$ and N,N-(1,4-phenylene)bis(2-azidoacetamide) [II]$_b$

The reaction of one mole of compound [I]$_{a,b}$ with two moles of sodium azide and ammonium chloride in DMF produced compounds [II]$_{a,b}$.



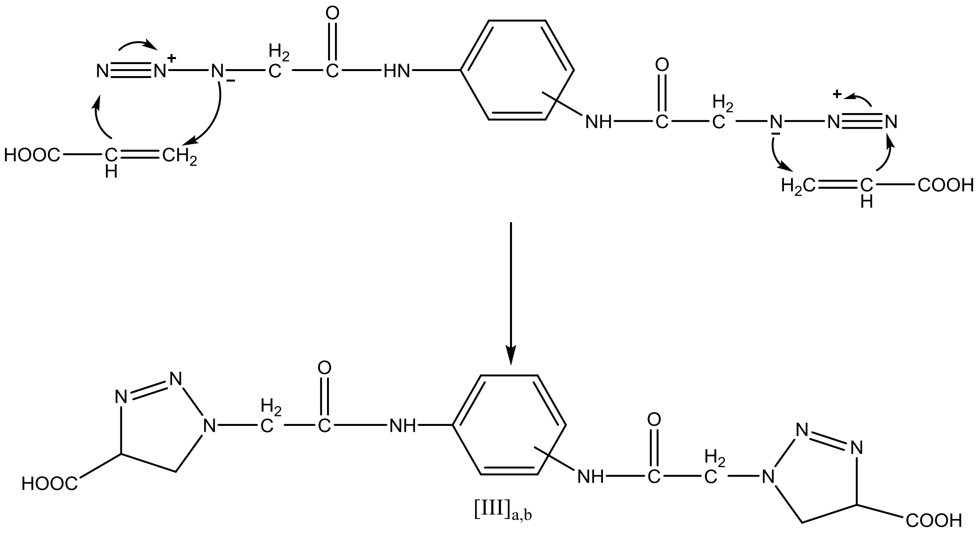
The azidoacetamide $[II]_{a,b}$ were characterized by FTIR spectroscopy.

The FTIR spectra of compounds $[II]_{a,b}$, Figures (3-2),(3-3) showed absorption stretching bands of (N≡N) groups at (2112)cm^{-1} , (2113)cm^{-1} and NH groups at (3267)cm^{-1} , (3265) cm^{-1} as well as stretching absorption bands at (1664)cm^{-1} , (1662)cm^{-1} for C═O (amide) groups, respectively .The ^{1}HNMR spectrum (in DMSO-d6 as a solvent) for compound $[II]_b$ as in Figure (3-4) showed: a singlet signal at δ10.14ppm for two protons of N-H groups, signal appear at δ 7. 55ppm for four protons of benzene ring and a signal at δ 4.03 ppm for four protons of two CH_2 groups .

3.1.3. Synthesis and characterization of 1,1-((1,3 -phenylenebis(azanediyl))bis (2-oxoethane-2,1-diyl)bis(4,5-dihydro-1H-1,2,3-triazole-4-carboxylic acid) $[III]_a$ and 1,1-((1,4 -phenylenebis(azanediyl))bis(2-oxoethane-2,1-diyl)bis(4,5-dihydro-1H-1,2,3-triazole-4-carboxylic acid) $[III]_b$

The compound $[III]_a$ or $[III]_b$ product from reaction of the compound $[II]_a$ or $[II]_b$ with two moles of acrylic acid in THF as a solvent .

The mechanism(139) of this reaction may be outlined as follows, Scheme (3-1) .



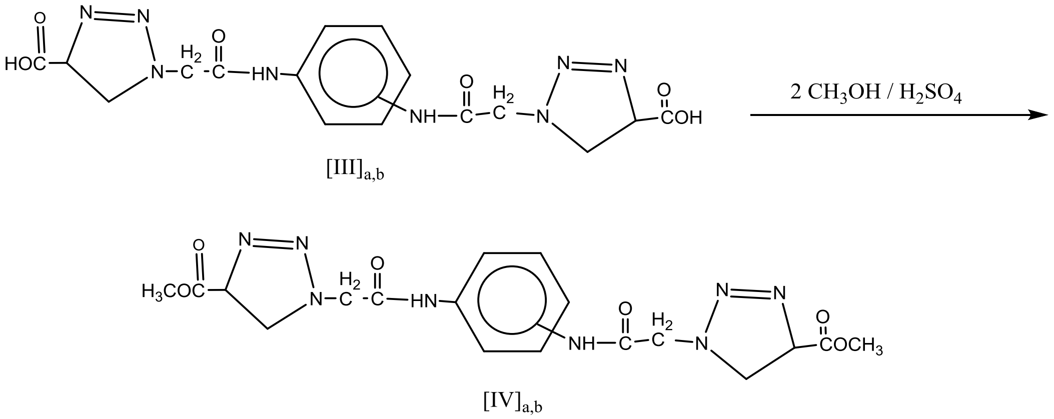
Scheme (3-1)

The carboxylic acid compounds $[III]_{a,b}$ were characterized by FTIR spectroscopy .

The FTIR spectra of these compounds showed appearance bands at 1710cm^{-1} and 1722 cm^{-1} assigned to C=O carboxylic groups and absorption band at 3348cm^{-1} and 3423cm^{-1} for (OH) group, respectively with disappearance of absorption stretching bands of (N≡N) groups for starting materials ,this is agood evidence for cyclization of 1,2,3-triazole ring as in Figures (3-5) and (3-6).

3.1.4. Synthesis and characterization dimethyl1,1-((1,3-phenylenebis (azanediyl))bis(2-oxoethane-2,1-diyl)bis(4,5-dihydro-1H-1,2,3-triazole-4-carboxylate) $[IV]_a$and dimethyl1,1-((1,4-phenylenebis(azanediyl))bis(2-oxoethane-2,1-diyl)bis(4,5-dihydro-1H-1,2,3-triazole-4-carboxylate $[IV]_b$

The ester compounds $[IV]_{a,b}$ formation from the reaction compounds $[III]_{a,b}$ with absolute methanol in sulfuric acid (as a catalyst).



[III]$_{a,b}$

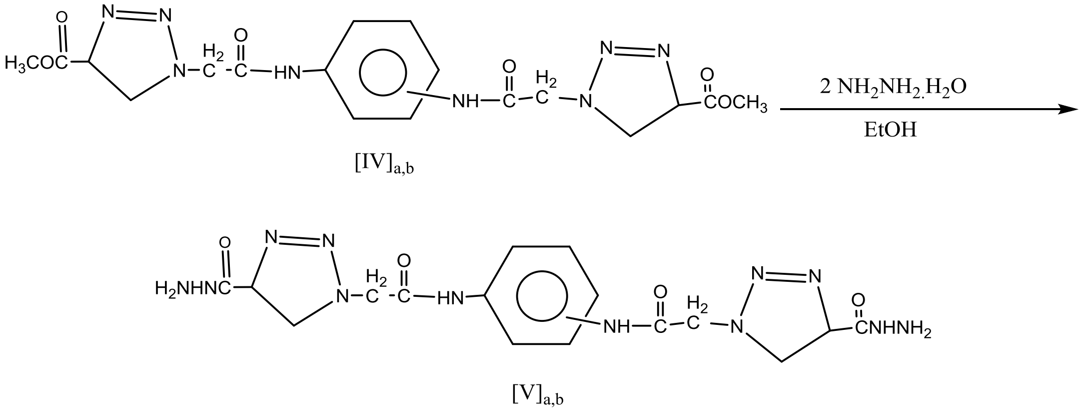
[IV]$_{a,b}$

These compounds [IV]$_{a,b}$ were characterized by FTIR spectroscopy .

The FTIR spectra showed disappearance of absorption bands of C=O and OH groups for carboxylic acid[III]$_{a,b}$ and showed stretching bands at 1730 cm^{-1} and1743 cm^{-1} for carbonyl C=O for ester groups , respectively Figures (3-7) and (3-8) .

3.1.5. Synthesis and characterization of N,N-(1,3-phenyene)bis(2-(4-(hydrazinecarbonyl)4,5-dihydro-1H1,2,3-triazole-1yl) acetamide [V]$_a$ and N,N-(1,4-phenyene)bis(2-(4-(hydrazinecarbonyl)4,5-dihydro-1H1,2,3-triazole-1yl) acetamide [V]$_b$

These compounds were synthesized from reaction of [IV]$_a$ or [IV]$_b$ with two moles from hydrazine hydrate 80% in ethanol .



[IV]$_{a,b}$

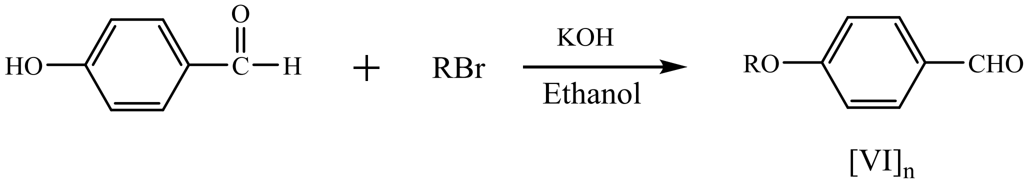
[V]$_{a,b}$

The acid hydrazide compounds $[V]_{a,b}$ were identified by FTIR and ^{1}HNMR spectroscopy .

The FTIR spectra showed absorption stretching bands to asymmetric and symmetric of ($NH-NH_2$) groups in the region(3384-3247)cm^{-1}, (3429-3190)cm^{-1} and stretching bands at1635cm^{-1} , 1649 cm^{-1} to C=O amide groups, respectively. Figure (3-9) FTIR is for compound $[V]_b$ .The ^{1}HNMR spectrum for compound $[V]_b$ showed asinglet signal at δ 11.15ppm for two protons of NH for (-CONH-) groups , asinglet signal at δ 7.64 ppm for two protons NH of acid hydrazide groups , many signals in the δ6.56 ppm for four protons of aromatic protons , also showed douplat signal of δ 7.74 ppm for protons CH_2 of (C_5) of triazole rings , as while as showen triplet signal at δ 7,58 ppm for protons (CH) of C_4 of triazole rings(140) . Also showed signal at δ 5.44ppm for four protons of (NH_2) groups . Finally singlat asignal at δ 3.33 ppm for four protons of ($-COCH_2$) groups Figure (3-10) .

3.1.6. Preparation of n-alkoxy benzaldehyde $[VI]_n$

The compounds $[VI]_n$ were synthesized from the reaction of 4-hydroxybenzaldehyde with alkylbromide and potassium hydroxide in absolute ethanol(137)

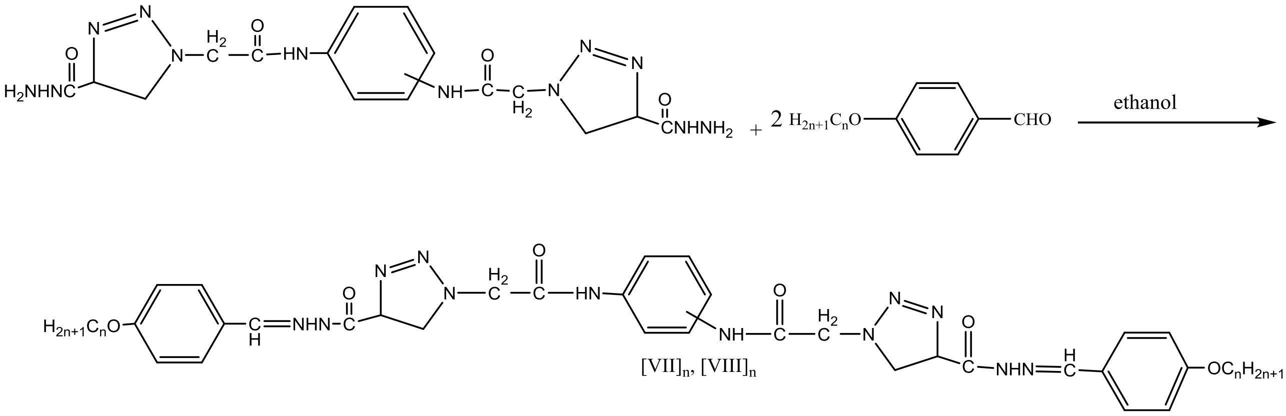


$[VI]_n$

$R = C_nH_{2n+1}$, n =2,3,5,6,7,8

3.1.7. Synthesis and characterization of N,N-((1,3 -phenylene)bis(2-(4-(2(4-methoxybenzylidene)hydrazine-1-carbonyl)4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamide)[VII]$_n$ and N,N -((1,4 -phenylene)bis (2-(4-(2(4-methoxybenzylidene)hydrazine-1-carbonyl)4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamide) [VIII]$_n$

The Schiff bases compounds [VII]$_n$ and [VIII]$_n$ were synthesized by the reaction of acid hydrazide [V]$_{a,b}$ with two moles of different aromatic aldehyde in ethanol.



n= 1,2,3,5,6,7,8

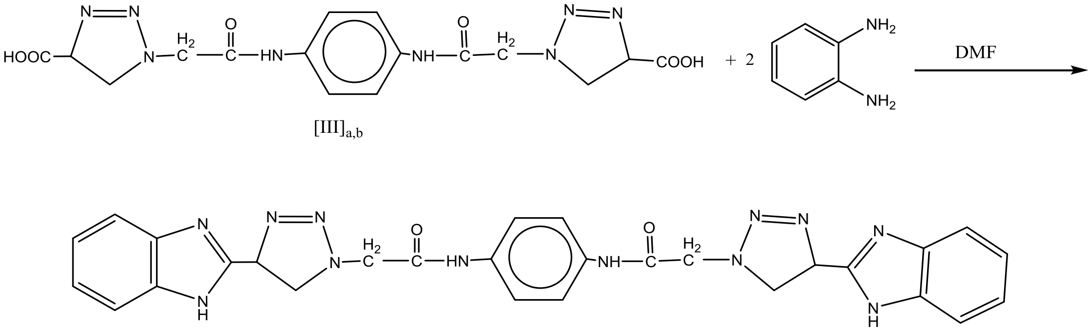
These compounds were characterized by FTIR and ^{1}HNMR spectroscopy .

The FTIR spectra for compounds [VII]$_n$ showed absorption stretching bands for NH groups at region (3298-3262) cm^{-1}and absorption bands for carbonyl groups (C=O) in the region (1664-1649) cm^{-1} also showed absorption bands for(-N=CH) groups at region (1621-1600) cm^{-1} . Figure (3-11) and (3-12) for compounds [VII]$_2$ and [VII]$_8$, respectively . The characterization FTIR absorption bands values for compounds [VII]$_n$ were listed in Table (3-1)

The ^{1}HNMR spectrum for compound [VII]$_3$ (DMSO)Figure(3-13) showed: asinglet signal at δ 10.26ppm for two protons of N-H of H-N-CO-CH_2 groups, asinglet signal at δ 8.60ppm for two protons of (CONHN=)groups ,many signals at δ (6.79-7.70)ppm for twelve aromatic protons and two protons of (N=CH)groups , adouplat signal at δ 7.70ppm for four protons of aromatic group of C_5 triazole ring , atriplet signal at δ 7.23ppm for two protons CH of C_4 triazole ring(140). Signals at δ 4.12ppm for four protons OCH_2 group andfour protons of CH_2CO. Amultiplet signalat δ 1.80 ppm for four protons CH_2CH_3 group and triplet signal at δ 1.20ppm for six protons of two CH_3 groups . The ^{1}HNMR spectrum for compound $[VII]_7$ Figure (3-14) showed: asinglet signal at δ 8.80 ppm for two protons of NH of (NH-CO-CH_2) groups , asinglet signal at δ 8.45ppm for two protons of (CONHN=) ,many signals at δ (6.70-7.75) ppm for twelve aromatic protons and protons of triazole ring , signals at δ 4.13ppm for four protons of OCH_2 groups asinglet signal at δ 3.98ppm for four protons of CO-CH_2 groups many signals at δ 2.15-2.2 ppm for twenty protons of ($-OCH_2(CH_2)_5CH_3$) , atriplet signals at δ0.98ppm for six protons of two CH_3 groups. The FTIR spectra for compounds $[VIII]_n$ showed absorption stretching bands for NH groups of region (3294-3263)cm^{-1} and absorption bands for carbonyl groups(C=O) in the region (1675-1641)cm^{-1} also showed absorption bands for(-N=CH) groups at region (1675-1614)cm^{-1} ,as Figure (3-15) for compound $[VIII)_3$. The characterization FTIR absorption bands for compounds $[VIII]_n$ were listed in Table (3-2) . The ^{1}HNMR spectrum for compound $[VIII]_2$, Figure (3-16) showed: singlet signal at δ 10.21ppm for two protons of N-H of (NH-CO-CH_2) groups , asinglet signal at δ 8.62ppm for two protons of (CONH-N=) groups, asinglet signal at δ 8.26ppm for two protons of (CH=N-) groups , three douplats signals at δ (7.80-6.98)ppm for twelve aromatic protons, adouplat signal at δ 7.70ppm for four protons of CH_2 of C_5 triazole rings , atriplet signal at δ 7.22ppm for two protons of CH of C_4 triazole rings , atriplet signal at δ 4.12ppm for four protons of OCH_2 groups , asinglet signal at δ 2.11ppm for four protons of CO-CH_2 groups, triplet signal at δ 1.39ppm for six protons of CH_3 groups . The ^{1}HNMR spectrum for compound $[VIII]_6$, Figure(3-17) showed singlet asignal at δ 10.43ppm for two protons of NH of (NH-CO-CH_2) groups , asinglet signal at δ 8.63ppm for two protons of (CONH-N=)groups ,singlet signal at δ 8.51ppm for two protons of (CH=N-) groups , Many signals at δ (6.98-7.78)ppm for twelve aromatic protons, signal at δ 7.35ppm for four protons of CH_2 of C_5 triazole rings, signal at δ 7.20ppm for two protons of CH of C_4 triazole rings , triplet signal at δ 4.18ppm for four protons of OCH_2 groups , asinglet signal at δ 2. 25ppm for four protons of CO-CH_2 groups, amultiplet signal at δ 1.3-1.12ppm for sixteen protons of($OCH_2(CH_2)_4CH_3$)groups and triplet signal at δ 0.75 ppm for six protons of CH_3 groups .

3.1.8. Synthesis and characterization N,N'-(1,3-phenylene)bis(2-(4-(1H-benzo[d]imidazol-2-yl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamide) $[IX]_a$ and N,N'-(1,4-phenylene)bis(2-(4-(1H-benzo[d]imidazol-2-yl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamide) $[IX]_b$

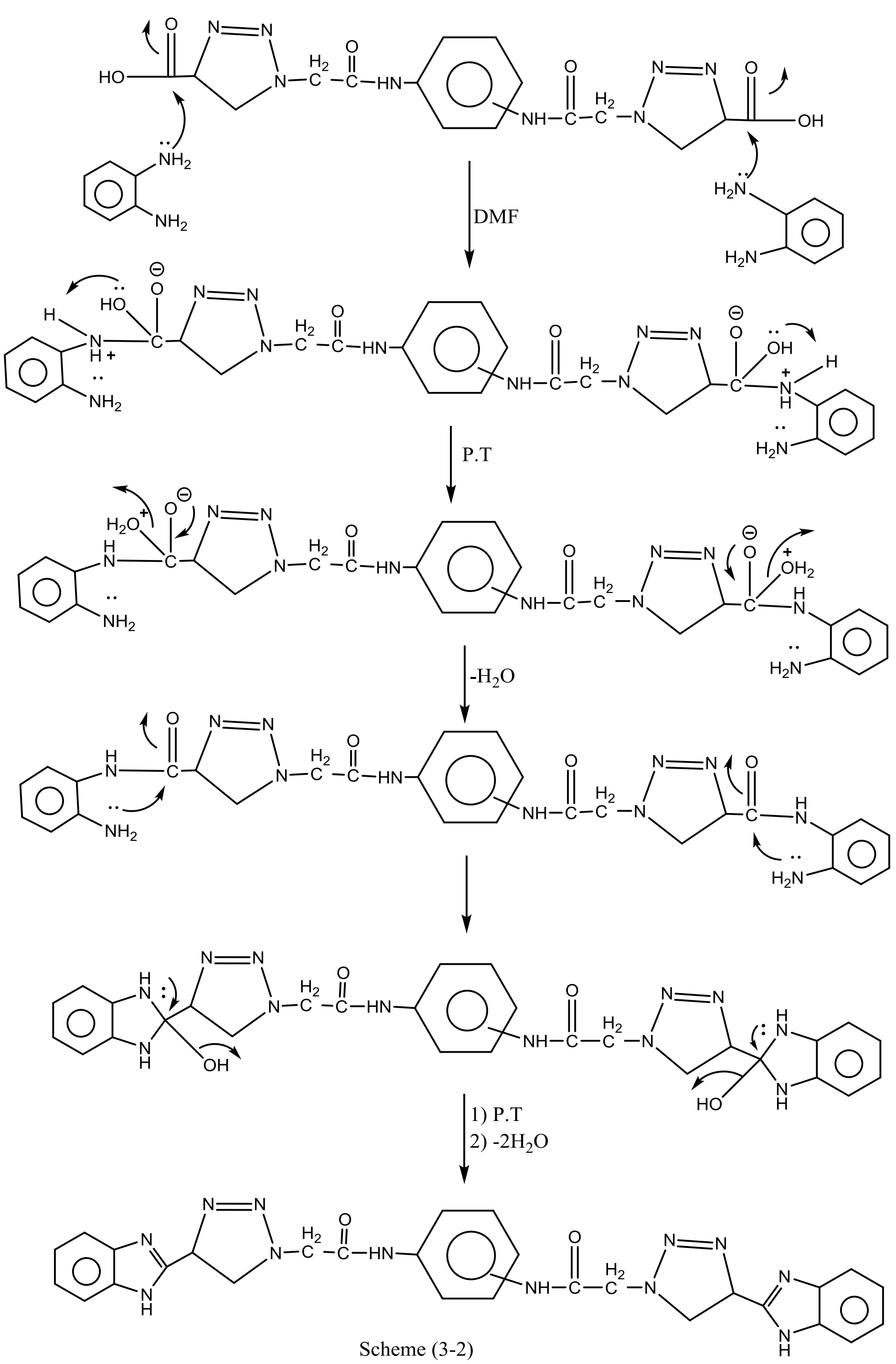
The formation benzimidazole compounds $[IX]_{a,b}$ from the reaction of compounds $[III]_{a,b}$ with two moles of o-phenylenediamine in DMF as asolvent .



$[III]_{a,b}$

$[IX]_{a,b}$

The mechanism$^{(141)}$ of this reaction may be outlined as follows, Scheme (3-2) .



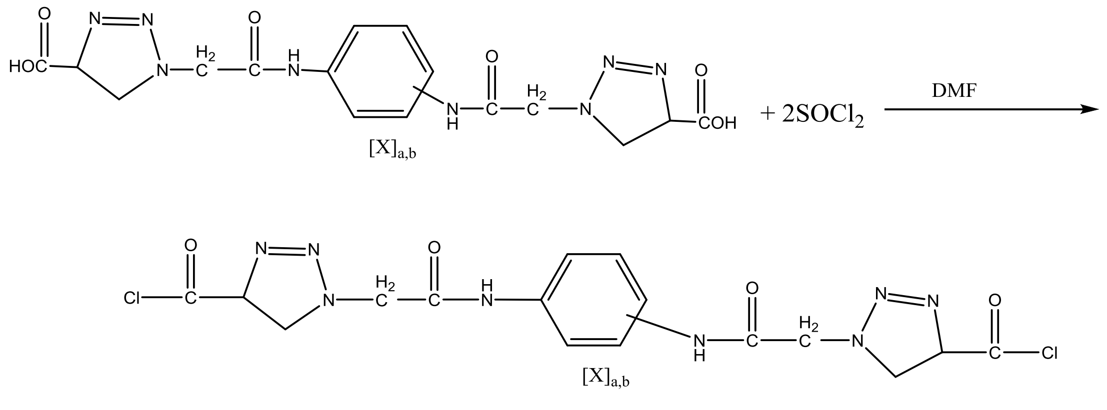
Scheme (3-2)

The benzimidazole compounds $[IX]_{a,b}$ were characterized by FTIR and mass spectroscopy for compound $[IX]_a$

The FTIR spectra showed disappearance of stretching bands of C=O and OH groups for carboxylic acid [III]$_{a,b}$ and NH_2 groups for o-phenylendiamine and showed absorption bands at (1631)cm^{-1}, (1635)cm^{-1} for (C=N) groups respectively . as Figure in(3-18) for compound [IX]$_b$. The mass spectrum of compound [IX]$_{a.}$ Figure(3-19) showed several peaks attributed to the presence of benzimidazle. This spectrum showed interesting peaks(142) (base peak) m/z=108 and showed peak at m/z 562 for molecular whight for compound [IX]$_a$ and peaks at m/z= 109 , 108 , 94 , for benzimidazole units also showed peaks at m/z =170 , 54 , for triazole unit and peaks at m/z =78, 77 , 65 , 51 and 39 for aromaticity of benzene.

-3.1.9. Synthesis and characterization of 1,1'-((1,3-phenylenebis(azanediyl)) bis(2-oxoethane-2,1-diyl))bis(4,5-dihydro-1H-1,2,3-triazole-4-carbonyl chloride) [X]$_a$ and 1,1'-((1,4-phenylenebis(azanediyl))bis(2-oxoethane-2,1-diyl))bis(4,5-dihydro-1H-1,2,3-triazole-4-carbonyl chloride) [X]$_b$

The compound [III]$_a$ or [III]$_b$ reacted with two moles from thionylchloride in DMF product acid chloride compounds[X]$_{a,b}$.

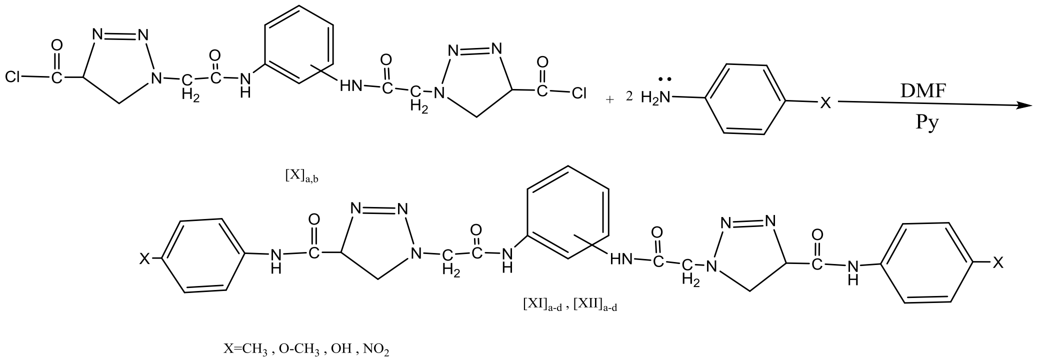


These compounds identified by FTIR spectroscopy .

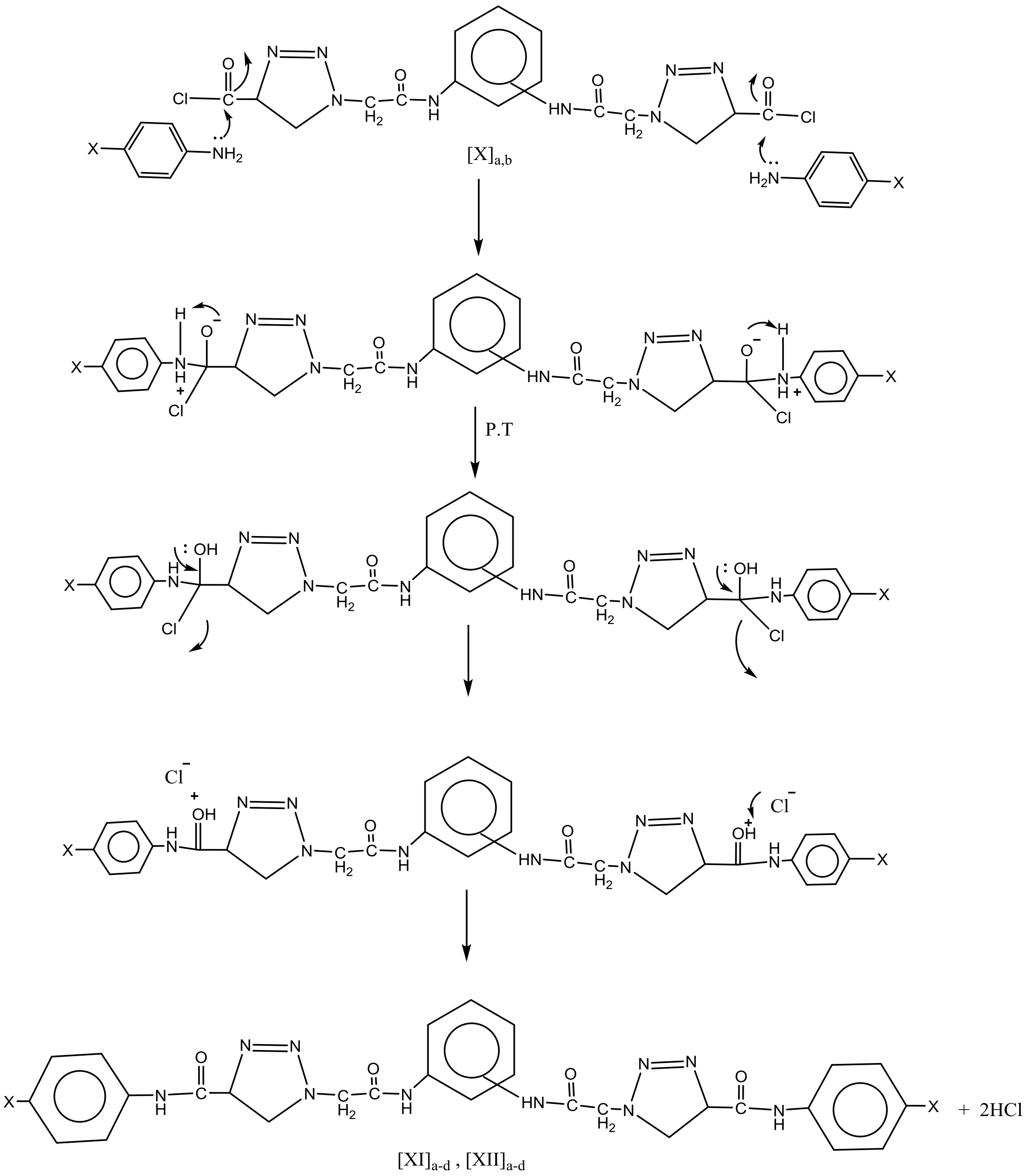
The FTIR spectra showed disappearance of stretching bands of (OH) groups for starting materials and appearance absorption stretching bands for (C-Cl) groups at 706 cm^{-1} and 722 cm^{-1} respectively, as in Figure (3-20) is IR spectrum for compound $[X]_b$.

3.1.10. Synthesis of amide compounds $[XI]_{a-d}$ and $[XII]_{a-d}$

The amide compounds $[XI]_{a-d}$ and $[XII]_{a-d}$ product from reaction compounds $[X]_{a,b}$ with two moles from different aromatic amines.



The mechanism(143) of this reaction is as follows in Scheme (3-3)



X=CH_3 , O-CH_3 , OH , NO_2

Scheme (3-3)

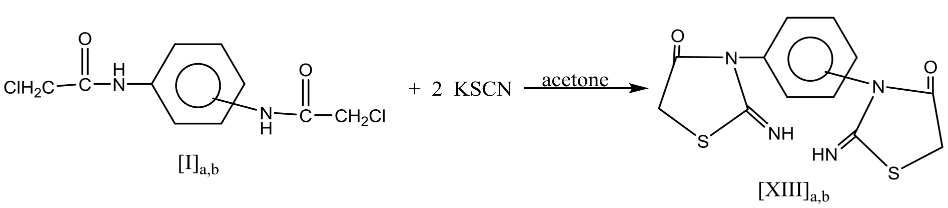
These compounds were characterized by FTIR spectroscopy

The FTIR spectra for the compounds $[XI]_{a\text{-}d}$ and $[XII]_{a\text{-}d}$ showed disappearance stretching bands of C-Cl and NH_2 groups for starting material and showed absorption stretching bands for NH groups at region (3417-3271) cm^{-1} and (3417-3265) cm^{-1} , respectively .

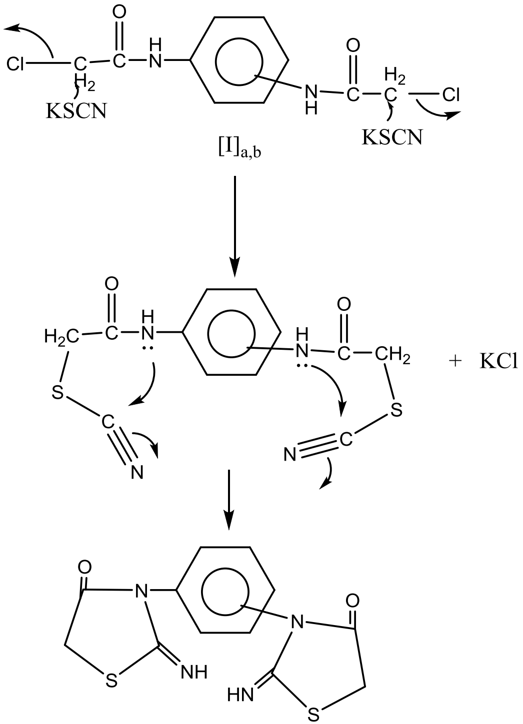
The characterization FTIR absorbtion bands for these compounds were listed in Table (3-3) . The Figures (3-21) , (3-22) and (3-23) showed FTIR spectra for compounds, $[XI]_c$ and $[XII]_a$, respectively . The ^{1}HNMR spectrum for compound $[XI]_a$, Figure (3-24) showed: asinglet signal at δ 9.62ppm for two protons of NH-Ar-NH group and two protons of CO-NH groups , many signals at δ (6.85-7.00)ppm for twelve aromatic protons, signal at δ 3..88ppm for four protons of CH_2 groups and signal at δ 2.20ppm for six protons of CH_3 groups Figure (3-24) for ^{1}HNMR specrum of compound $[XII]_a$ showed: asinglet signal at δ 10.20ppm for two protons of HN-Ar-NH groups and two protons of CONH groups , signals at δ (7.23-7. 30)ppm for twelve aromatic protons, asinglet signal at δ 3.67ppm for four protons of CH_2 groups ,asinglet signal at δ 2.32ppm for six protons of CH_3 groups

3.1.11. Synthesis and characterization of 3,3-(1,3-phenylene)bis(2-iminothiazolidine-4-one)$[XIII]_a$ and 3,3-(1,4-phenylene)bis(2-iminothiazolidine-4-one)$[XIII]_b$

The reaction of one mole of compound $[I]_a$ or$[I]_b$ with two moles of potassium thiocyanate in acetone produced compounds $[XIII]_a$ and $[XIII]_b$.



The mechanism$^{(144)}$ of this reaction as follows schem(3-4)



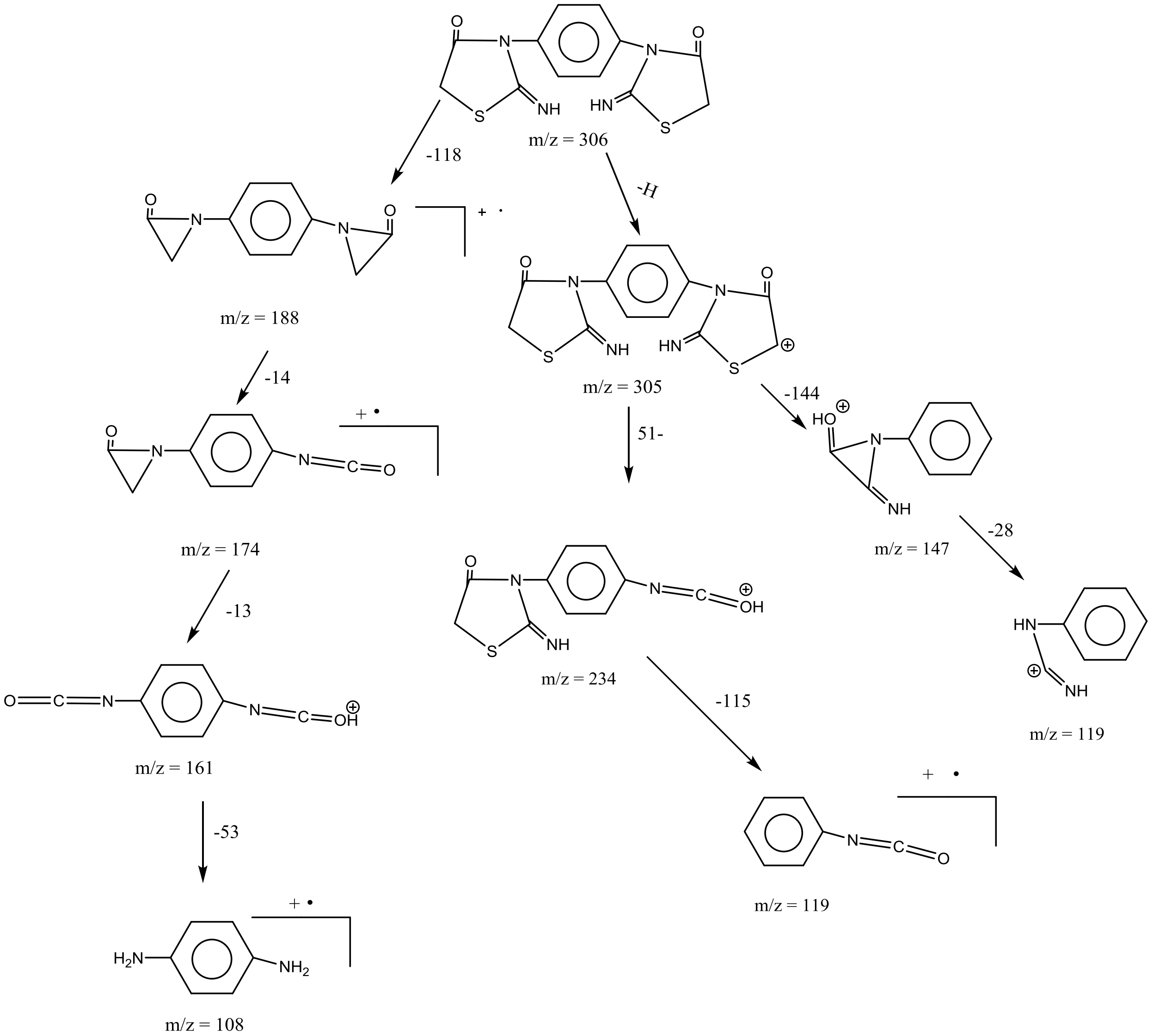
$[I]_{a,b}$

$[XIII]_{a,b}$

Scheme (3-4)

The compounds $[XIII]_{a,b}$ were characterized FTIR , ^{1}HNMR and mass spectroscopy

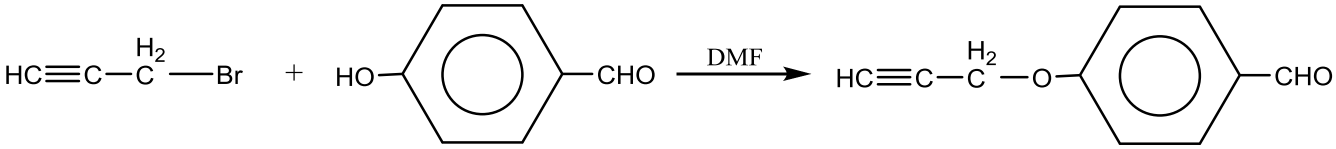
The FTIR spectra of these compounds showed stretching bands at 3251cm^{-1} for NH and1671 cm^{-1}, 1662cm^{-1} for carbonyl groups (C=O) and 1622 cm^{-1}, (1625) cm^{-1} for (C=NH) groups and 698 cm^{-1} , 736 cm^{-1} for (C-S) groups respectively . Figure (3-26) for compound $[XIII]_b.CDCl_3$ The ^{1}HNMR spectrum($CDCl_3$) for compound$[XIII]_b$ as in Figure (3-27) showed: asinglet signal at δ 8.90ppm for two protons of NH groups, douplet at δ (9.01-8.06)ppm for four aromatic protons, singlet signal at δ 6.82ppm for four protons of thiazolidine rings. The mass spectrum of compound $[XIII]_b$ as in Figure(3-28) showed several peaks attributed to the presence of thiazolidine-4-one ring. This spectrum showed interesting peaks(145) (base peak) m/z=107.2 and showed peak at m/z 306 for molecular whight for compound $[XIII]_b$ and peaks at m/z 188 , 174 , 161 , 108 for thiazolidine units The most characteristic fragments of the compound were illustrated in Scheme (3-5).



Scheme (3-5)

3.1.12. Preparation and characterization of 4-(prop-2-yn-1-yl-oxy)benzaldehyde [XIV]

The compound [XIV] was prepared from reaction propargyl bromide with 4-hydroxybenzaldehyde and NaOH in DMF .



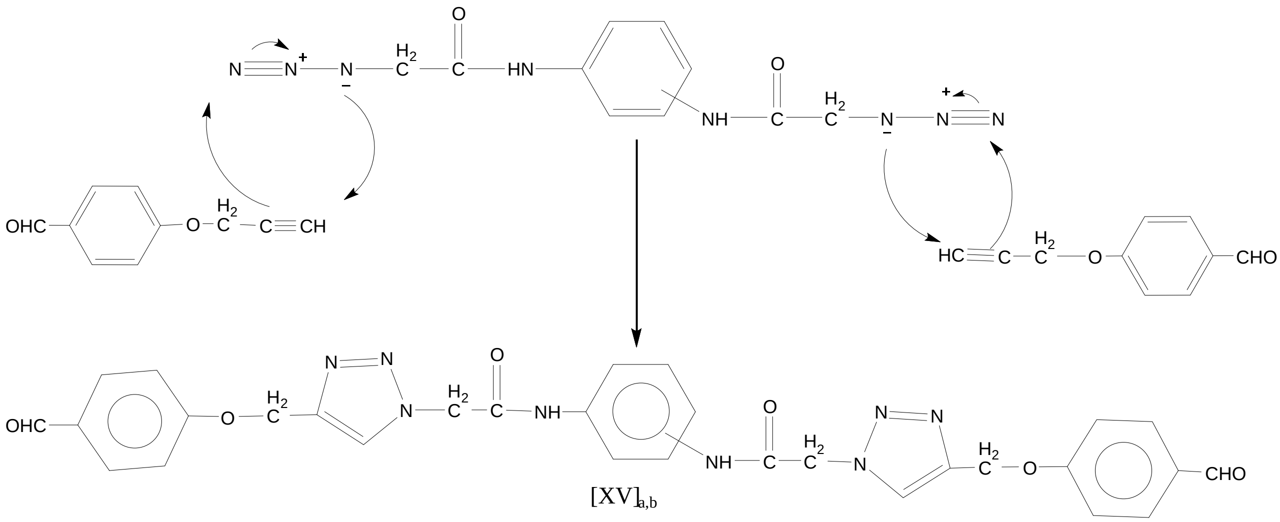
[XIV]

The FTIR spectrum of this compound showed stretching band at 2121cm^{-1} for alkyne(C≡C) group and 1687 cm^{-1} for carbonyl group of aldehyde as in Figure (3-29)

3.1.13. Synthesis and characterization of N,N'-(1,3-phenylene)bis(2-(4-((4-formylphenoxy)methyl)-1H-1,2,3-triazol-1-yl)acetamide) [XV]$_a$ and N,N'-(1,4-phenylene)bis(2-(4-((4-formylphenoxy)methyl)-1H-1,2,3-triazol-1-yl)acetamide) [XV]$_b$

The synthesis of 1,2,3-triazole compounds [XI]$_{a,b}$ via reaction the compound [II]$_a$ or [II]$_b$ with two moles from compound [XIV] in DMF .

The mechanism(146-148) of this reaction is as follows in Scheme (3-7).



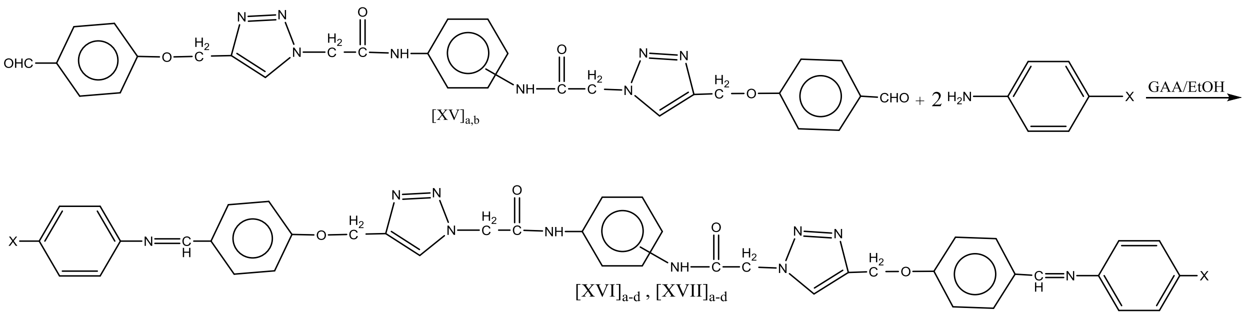
[XV]$_{a,b}$

Scheme(3-7)

The FTIR spectra of These compounds characterized FTIR spectroscopy. compound [XV]$_b$ as in Figure (3-30) showed disappearance stretching bands of triple bonds for starting material and showed stretching bands at (1687)cm^{-1}and (1681)cm^{-1} for carbonyl group of aldehyde for compound [XV]$_a$ and [XV]$_b$ respectively.

3.1.14. Synthesis and characterization of Schiff bases compounds [XVI]$_{a-d}$ and [XVII]$_{a-d}$

The compounds [XVI]$_{a-d}$ and [XVII]$_{a-d}$ product from reaction compounds [XV]$_{a,b}$ with two moles from different aromatic amines with some drops from glacial acetic acid (GAA) in ethanol as a solvent.



[XV]$_{a,b}$

[XVI]$_{a\text{-}d}$, [XVII]$_{a\text{-}d}$

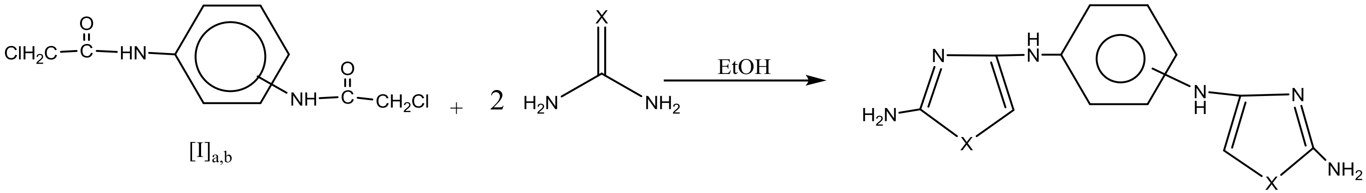
X= CH_3 , OCH_3 , OH , NO_2

The Schiff bases compounds were characterized FTIR and ^{1}HNMR spectroscopy. The FTIR spectra for these compounds[XVI]$_{a\text{-}d}$ and [XVII]$_{a\text{-}d}$ showed the disappearance of absorption stretching bands of aldehyde and amine for starting materials and showed stretching bands for (-N=CH-) groups at the region (1622-1609)cm^{-1} and (1623-1604)cm^{-1}, respectively. Figures (3-31) and (3-32) for compounds [XVI]$_c$ and [XVII]$_a$, respectively .

The characterization FTIR absorption bands for these compounds were listed in Table (3-4) . The ^{1}HNMR spectrum for compound [XVI]$_d$ (DMSO) Figure (3-33) showed: a singlet signal at δ 9.88 ppm for two protons of NH-CO groups , a singlet signal at δ 8.38ppm for two protons CH of triazole rings, a singlet signal at δ 8.20ppm for two protons of CH=N groups . Many signals at δ 7.24-7.89ppm for twenty aromatic protons and signal at δ 2.73ppm for four protons of CH_2O groups and singlet of δ2.28ppm for four protons of $COCH_2$. The ^{1}HNMR spectrum for compound [XVII]$_c$ Figure (3-34) (DMSO) showed: a singlet signal at δ 10.49ppm for two protons of OH groups, a singlet signal at δ 9.89 ppm for two protons of HNCO groups , singlet signal at δ 8.58ppm for two protons CH of triazole rings ,singlet signal at δ 8.34ppm for two protons of CH=N groups , Many signals at δ 6.96-7.90ppm for twenty aromatic protons.

3.1.15. Synthesis and characterization of oxazole compounds $[XVIII]_{a,b}$ and thiazole compounds $[XIX]_{a,b}$.

These compounds were synthesized by reaction compound $[I]_a$ or $[I]_b$ with two moles from urea or thiourea in absolute ethanol .



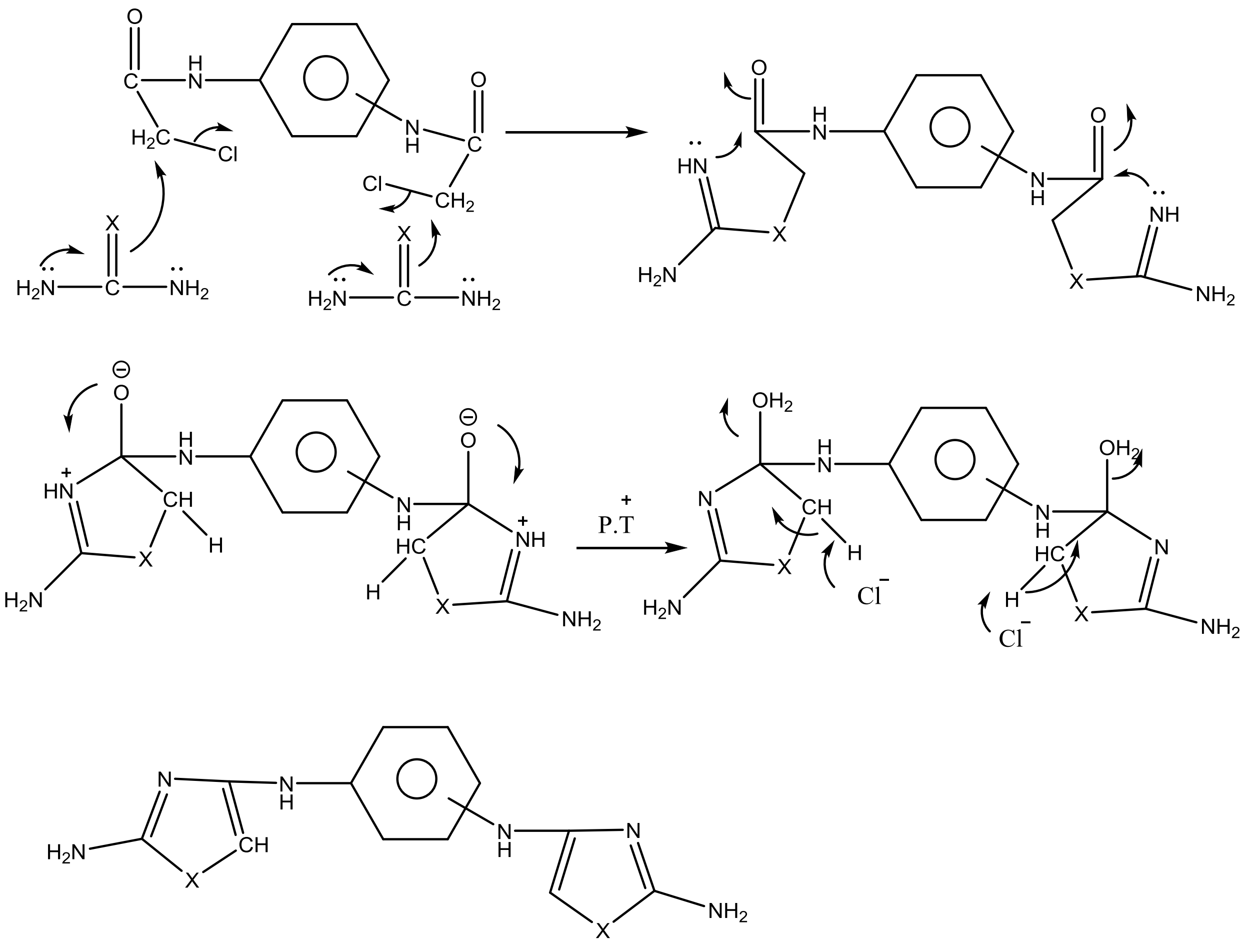
$[I]_{a,b}$

$[XVIII]_{a,b}$, $[XIX]_{a,b}$

The compounds $[XVIII]_{a,b}$ when X=O

The compounds $[XIX]_{a,b}$ when X=S

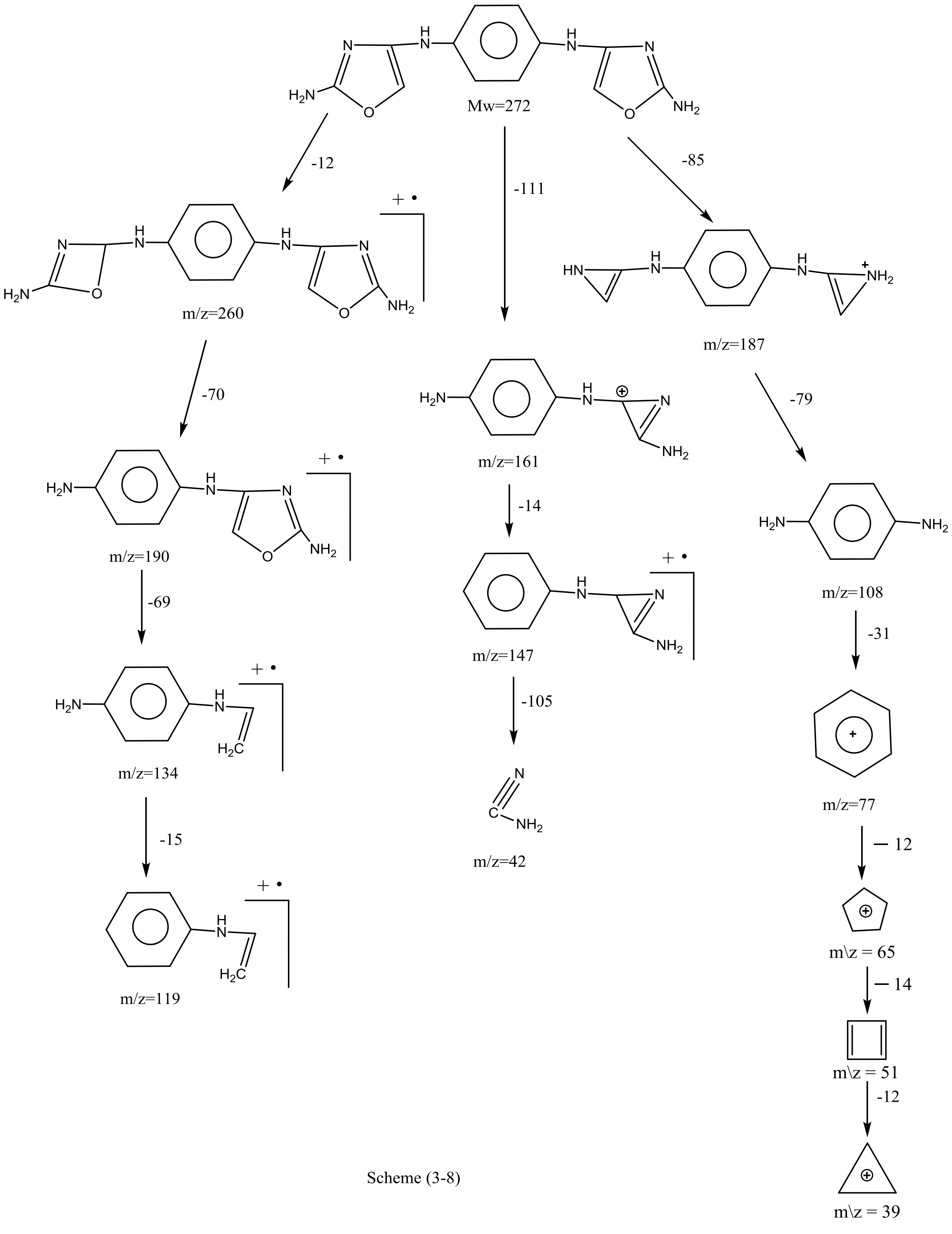
The mechanism of this reaction is as follows, Scheme (3-8)



Scheme (3-7)

The compounds $[XVIII]_{a,b}$ and $[XIX]_{a,b}$ were characterized by ^{1}HNMR and FTIR spectroscopy . The FTIR spectra showed disappearance absorption bands of the carbonyl amide for starting material with showed absorption stretching bands for (C=N) endo cyclic groups at 1649 cm^{-1} , 1634 cm^{-1} for compounds $[XVIII]_{a,b}$ and 1656 cm^{-1} , 1662 $cm^{-1}$for compounds $[XIX]_{a,b}$ respectively . Figures (3-35) and (3-38) for oxazole$[XVIII]_{a}$ and thiazole $[XIX]_{b}$ respectively.

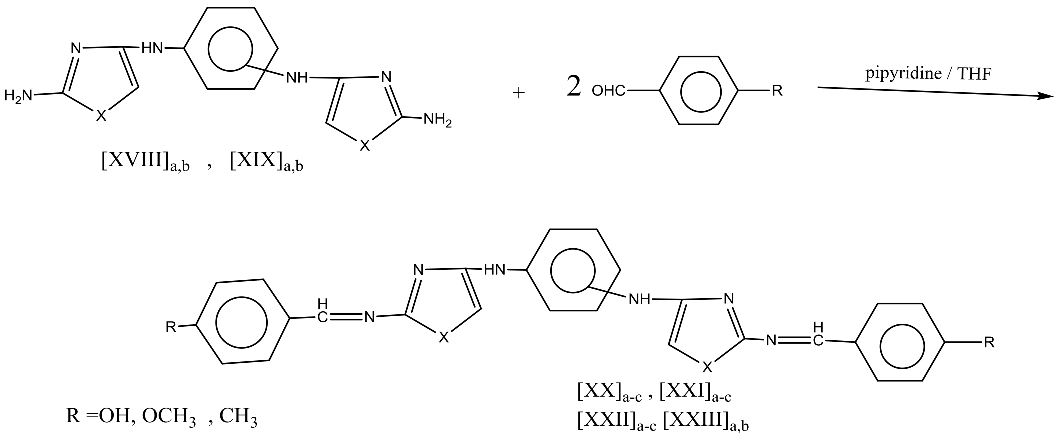
The characterization FTIR absorption bands of compounds $[XVIII]_{a,b}$ and $[XIX]_{a,b}$ were listed in Table (3-5). The ^{1}HNMR spectrum for compound $[XVIII]_{a}$ (DMSO) Figure (3-36) showed : a singlet signal at δ 9.89ppm for two protons of NH groups , many signals at region δ 7.00-7.53ppm for four benzene protons and proton of oxazole ring , a singlet signal at δ 5.39ppm for two protons of NH_2 groups , The ^{1}HNMR for compound (DMSO) $[XIX]_a$ as in Figure (3-39) showed : a signal at δ 8.79ppm for two protons of NH groups , two singlet at δ 8.93and 8.67ppm for four aromatic protons , a signal at δ 3.26ppm for two protons of NH_2 groups. The mass spectrum of compound $[XVIII]_b$ Figure(3-37) showed several peaks attributed to the presence of oxazole ring . This spectrum showed interesting peaks (base peak) m/z=107 and showed peak at m/z 272for molecular whight for compound $[XIII]_b$ and peaks at m/z 187 , 161 , 147 , 134 , 119 , and 42 for oxazole ring and peaks at m/z= 77 , 65 , 51 and 39 for aromaticity of benzene(149). The most characteristic fragments of this compound were illustrated in Scheme (3-9).


Mw=272
-12
-111
-85
m/z=260
m/z=187
-70
-79
m/z=161
m/z=190
-14
m/z=108
-69
m/z=147
-31
-105
m/z=134
m/z=77
-15
− 12
m/z=42
m\z = 65
m/z=119
− 14
m\z = 51
-12
m\z = 39

Scheme (3-8)

3.1.16. Synthesis and characterization of Schiff bases compounds $[XX]_{a-c}$, $[XXI]_{a-c}$, $[XXII]_{a-c}$, $[XXIII]_{a-c}$

The compounds $[XX]_{a-c}$, $[XXI]_{a-c}$, $[XXII]_{a-c}$ and $[XXIII]_{a-c}$ formation from reaction the compound $[XVIII]_{a,b}$ or $[XIX]_{a,b}$ with two moles from different aromatic aldehydes in THF and few drops of pipyridine.



$[XVIII]_{a,b}$, $[XIX]_{a,b}$

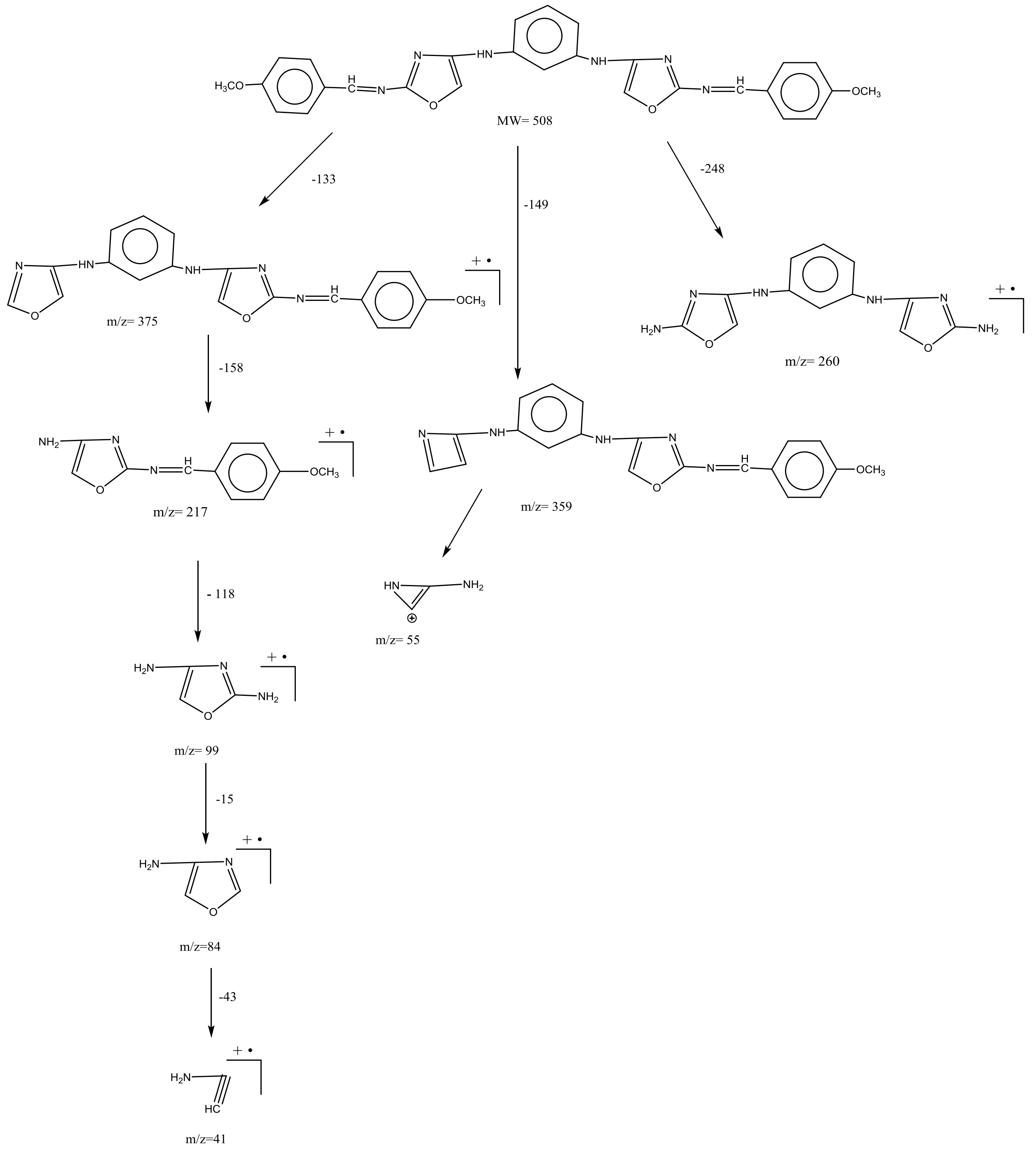
R =OH, OCH_3 , CH_3

$[XX]_{a-c}$, $[XXI]_{a-c}$
$[XXII]_{a-c}$ $[XXIII]_{a,b}$

The compounds $[XX]_{a-c}$ and $[XXI]_{a-c}$ when X=O
The compounds $[XXII]_{a-c}$ and $[XXIII]_{a-c}$ when X=S

The Schiff bases compounds were characterized ^{1}HNMR , FTIR and Mass spectroscopyfor some of them . The FTIR spectra showed disappearance of stretching bands for amine and aldehyde groups for starting material and showed absorption stretching bands of imine groups (-N=CH-) in the region (1656-1619)cm^{-1} and(1658-1612)cm^{-1} for the compounds $[XX]_{a-c}$, $[XXI]_{a-c}$ and $[XXII]_{a-c}$, $[XXIII]_{a-c}$, respectively. The Figures (3-40) , (3-43) for compounds $[XXI]_a$ and $[XXII]_b$, respectively. The characterization FTIR for compounds $[XX]_{a-c}$,$[XXI]_{a-c}$ and $[XXII]_{a-c}$, $[XXIII]_{a-c}$ were listed in Tables (3-6) and (3-7), respectively . The ^{1}HNMR spectrum for compound $[XX]_c$, Figure (3-41) showed : singlet signal at δ 9.60 ppm for two protons of NH groups, singlet asignal at δ 7.77ppm for two protons of CH=N groups, many signals at δ 6.96-7.58ppm for twelve aromatic protons and proton of oxazole ring and a signal at δ 2.54ppm for six protons of CH_3 groups . The mass spectrum of compound $[XX]_b$ Figure(3-42) showed several peaks attributed to the presence of oxazole ring(150). This spectrum showed interesting peaks (base peak) m/z=108 and showed peak at m/z 508 for molecular whight for compound $[XX]_b$ and peaks at m/z 359 , 204 , 189, 55 and 41 for oxazole units .

The most characteristic fragments of compound $[XXII]_b$ were illustrated in Scheme (3-10)


H$_3$CO
OCH$_3$
MW= 508
-133
-149
-248
m/z= 375
m/z= 260
-158
m/z= 217
m/z= 359
- 118
m/z= 55
m/z= 99
-15
m/z=84
-43
m/z=41

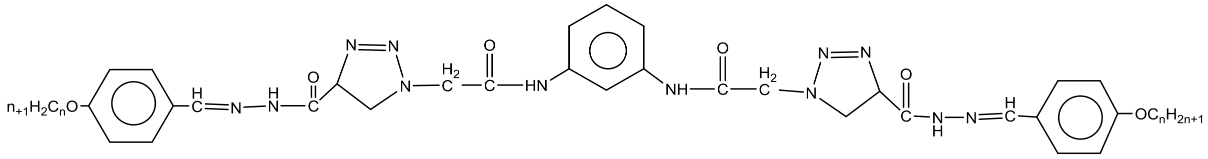
Scheme (3-9)

3.2. Liquid crystalline properties.

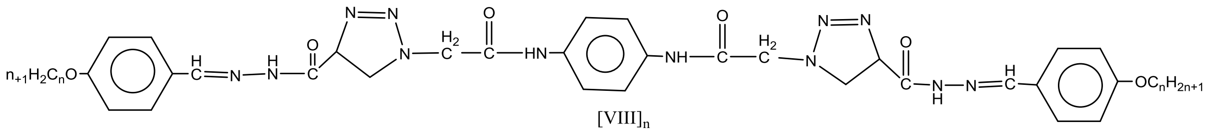
The optical textures for the synthesized compounds were observed by OPM , using the classification systems reported by Sackmann and demus and Richer(151,152) ,and Gray and Good by (153)

The transition temperature and mesophase type (texture identity) of all synthesized compounds were investigated by optical polarizing microscopy (OPM) and some of them by differential scanning calorimetry (DSC) .

3.2.1. The mesomorphic properties of Schiff bases $[VII]_n$ and $[VIII]_n$



$[VII]_n$



$[VIII]_n$

n = 1,2,3,5,6,7,8

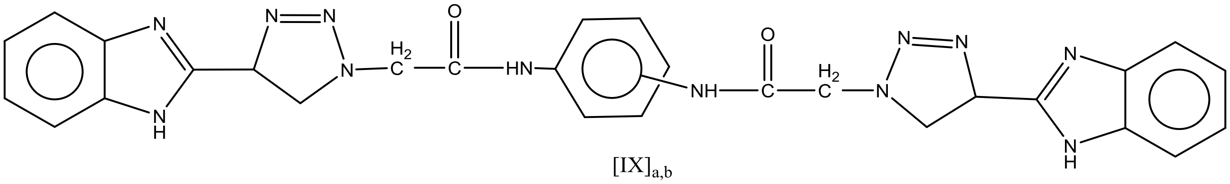
The phase transition temperatures of compounds $[VII]_n$ and $[VIII]_n$, were summarized in Table (3- 8). All the compounds type $[VII]_n$ showed enantiotropic mesophases with wide thermal stability .

The compounds $[VII]_{1,2,3,5,6}$ exhibit enantiotropic nematic phase as in Figures (3-44) , (3-45) , (3-46) , (3-47) , and (3-48) for compounds $[VII]_1$. $[VII]_2$, $[VII]_3$, $[VII]_5$ and $[VII]_6$, respectively while the compound $[VII]_7$ exhibited enantiotropic

Smectic A phases and nematic phases as in Figure (3-49) and the compound.$[VII]_8$ exhibited enantiotropic Smectic B phase beside to nematic phase, Figure (3-50).The demonstration of the smectic mesophase from heptyl and octyl derivatives of the reported series is attributed to the packing of the molecules , which increases the suitable magnitude of anisotropic forces of attractions to cause the sliding layers (a two dimensional array of molecules), Figure (3-51) showed DSC thermogram of compound $[VII]_1$. A plot of the transition temperature against the number (n) of carbon atoms in the alkyl chain for compound $[VII]_n$ is shown in Figure (3-52)

The compound $[VIII]_1$ didn’t show any liquid crystalline properties but only transition from crystal to isotropic phase . While the compounds $[VIII]_{2,3,5,6}$ showed enantiotropic nematic phase as in Figures (3-53) , (3-54) , (3-55) and (3-56) respectively . The compound $[VIII]_7$ display enantiotropic SmA phase only as in Figure (3-57) . In addition to, the compound $[VIII]_8$ showed SmA and nematic phases . The Figure (3-58) of SmA phase for compound $[VIII]_8$ and the DSC thermogram of compound $[VIII]_8$ as in Figure (3-59). A plot of the transition temperature against the number (n) of carbon atoms in the alkyl chain is shown in Figure (3-60). These results could be explained in term of terminal / lateral (t/l) interaction forces ratio when this ratio is high , compounds tend to give less order mesophases nematic phase , on the other hand when this ratio is low the compound tend to give high order mesophase smectic phase (154) .

3.2.2. The mesomorphic properties of benzimidazole compounds $[IX]_{a,b}$.



$[IX]_{a,b}$

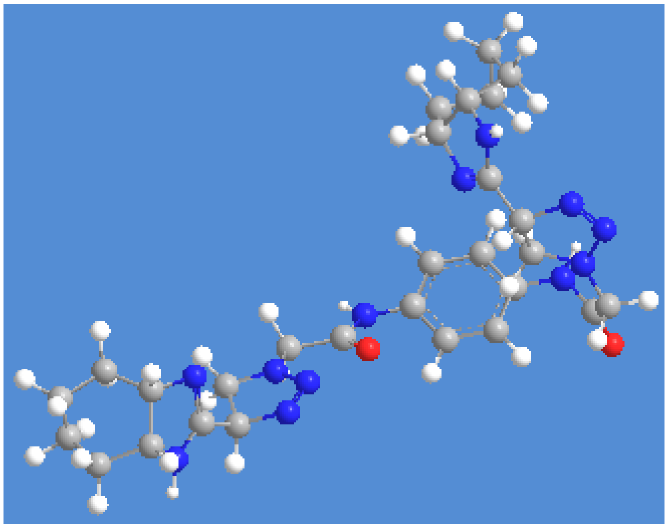


Figure (3-64) Three dimensional structure of compound $[IX]_a$.

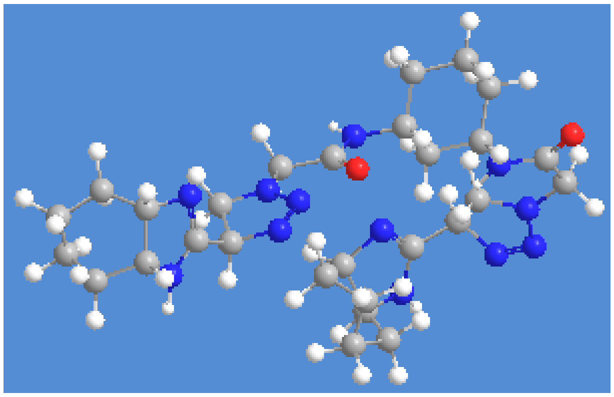
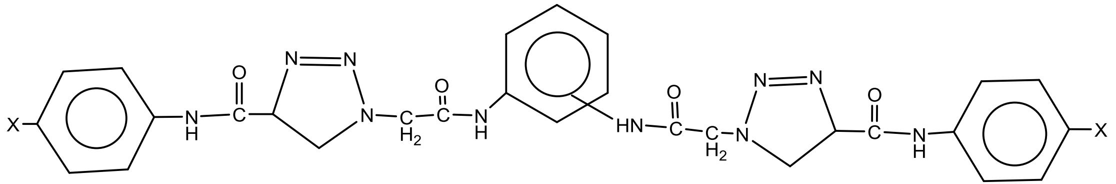


Figure (3-65) Three dimensional structure of compound $[IX]_b$.

The type of transition and transition temperature were summarized in Table (3-9).

All these compound showed mesomorphic behaviour under OPM on the heating. The compounds $[IX]_{a,b}$ showed SmecticB phase Figures (3-61) and (3-62), respectively. Figure (3-63) DSC thermogram of compound $[IX]_b$ The liquid crystal behavior for the compound $[IX]_{a,b}$ The liquid crystal behavior for the compoundS $[IX]_{a,b}$ my be attributed to the presence benzimidazole unit in the structure for these compounds, which increase the rigidity and the lateral forces for the compounds $[IX]_{a,b}$. This result agreement with other study for reported liquid crystal properties of some compounds containing benzimidazole unit(155) The 3D model for compounds $[IX]_a$ and $[IX]_b$, as in Figure (3-64) and (3-65) respectively .

3.2.3. The mesomorphic properties of amide compounds $[XI]_{a-d}$ and $[XII]_{a-d}$

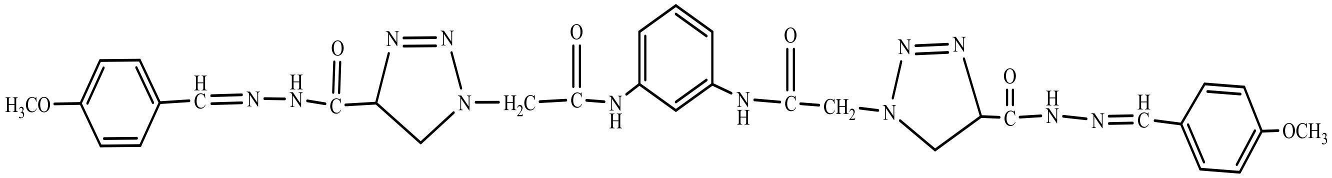


$[XI]_{a-d}$, $[XII]_{a-d}$

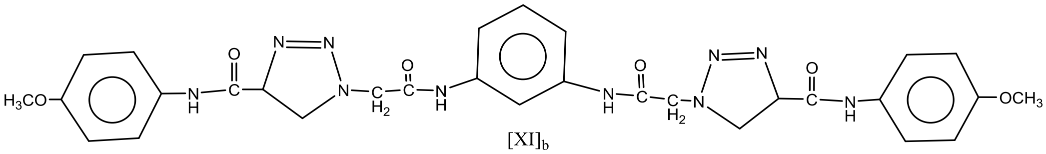
X=CH_3 , O-CH_3 , OH , NO_2

These compounds were studied by OPM and did not showed any liquid crystalline properties but only transition from crystal to isotropic phase were absorved. The transition temperature of these compounds were listed in Table (3-9).

The compounds $[VII]_1$ and $[XI]_b$ are the same structure but the compound $[VII]_1$ contains CH=N group



[VII]$_1$



[XI]$_b$

When we compared between these compounds it was found the compound [VII]$_1$ showed nematic phase but the compound [XI]$_b$ did not showed any liquid crystalline properties, this behavior could be attributed to the presence of CH=N group in the compound [VII]$_1$and the geometrical structure for these compound as in Figures (3-66) and (3-67) for compound [VII]$_1$ and [XI]$_b$ respectively . The C=N (known as imine linking) is linkage group used in connecting the rigid core groups though it provides a stepped cores structure. Besides to retain of linearity for molecular, hence providing higher stability and enabling formation of mesophase (156).

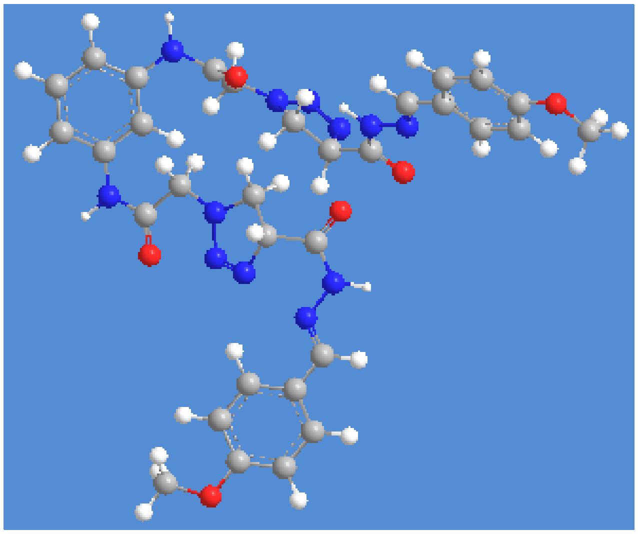


Figure: (3-66) Three dimensional structure of compound [VII]$_1$.

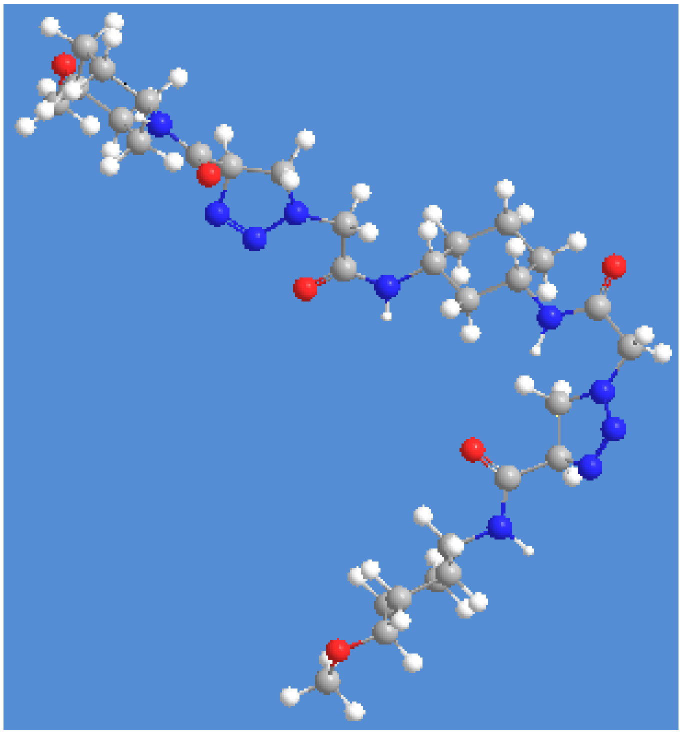
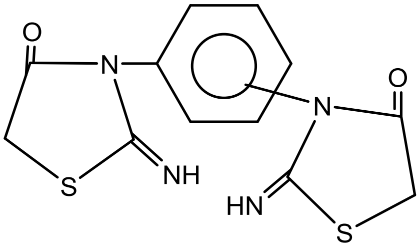


Figure: (3-67) Three dimensional structure of compound $[XI]_{b.}$

3.2.4. The mesomorphic properties of thiazolidine-4-one compounds $[XIII]_{a,b}$



$[XIII]_{a,b}$

These compounds were studied by OPM and did not showed any liquid crystalline properties only transition from crystal to isotropic phase .This behavior could be attributed to the presence of thiazolidine ring, which will affect on the mesomorphic behavior , increases the breadth and reduces in the planarity of the molecules. Both of these effects may explain the absence of liquid crystalline properties in these compounds, as represented in three dimensional structures of the compounds $[XIII]_a$ and $[XIII]_b$ as in Figure (3-68) and (3-69), respectively. The transition temperature of these compounds were listed in Table (3-9)

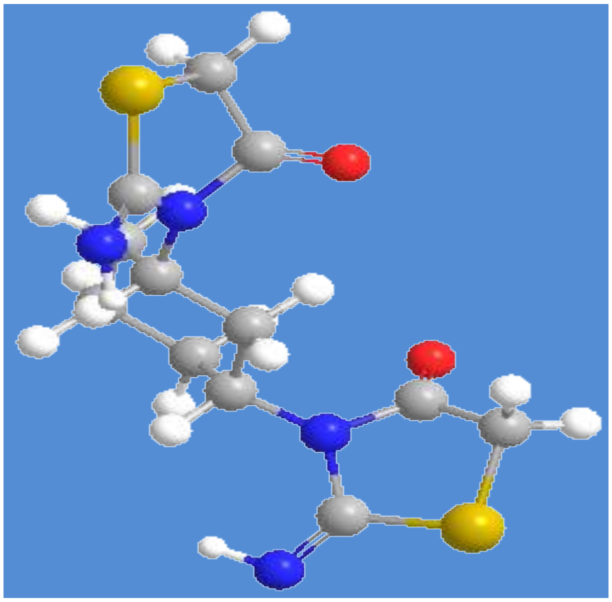


Figure: (3-68) Three dimensional structure of compound $[XIII]_a$.

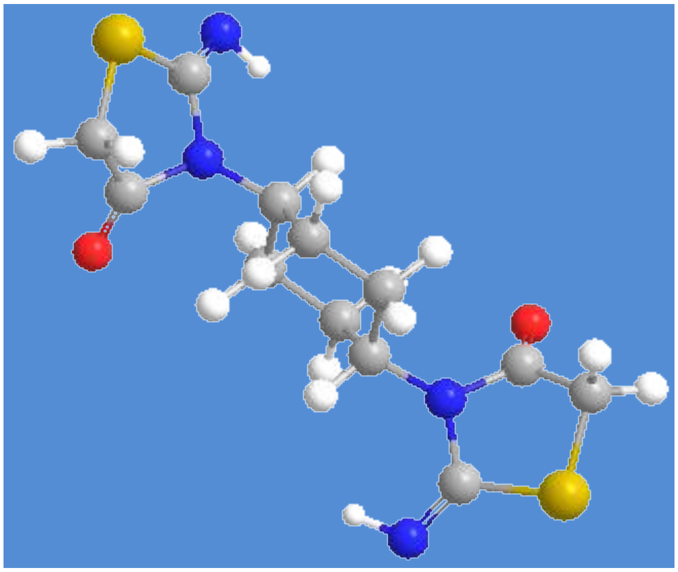
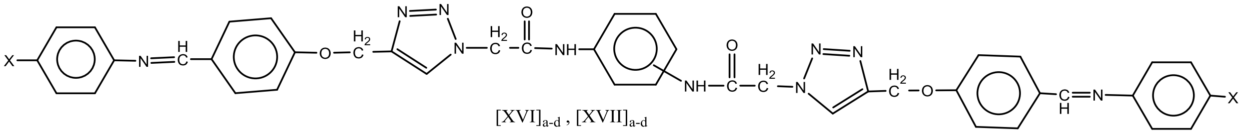


Figure: (3-69) Three dimensional structure of compound $[XIII]_b$.

3.2.5. The mesomorphic properties of Schiff bases compounds $[XVI]_{a-d}$ and $[XVII]_{a-d}$.



$[XVI]_{a-d}$, $[XVII]_{a-d}$

X= CH_3 , OCH_3 , OH , NO_2

The Schiff bases compounds $[XVI]_{a-d}$ and $[XVII]_{a-d}$ were studied by OPM and didn’t show any liquid crystalline behavior , this behavior my be attributed to the geometrical. The transition temperatures for these compounds were listed in Table (3-10) . The strucutresfor these compounds as Figure (3-70) and (3-71) for 3D models for compounds $[XVI]_{a-d}$ and $[XVII]_{a-d}$

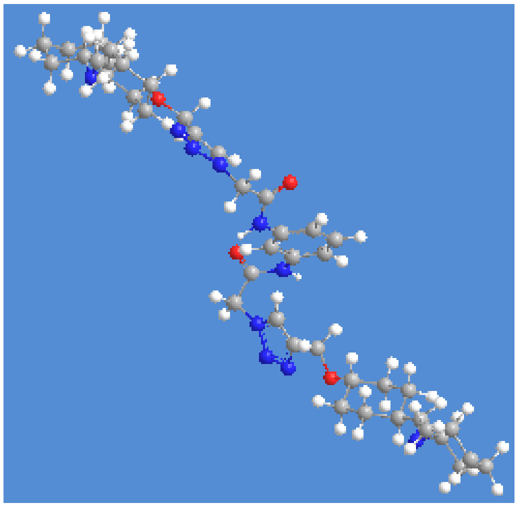


Figure: (3-70) Three dimensional structure of compounds $[XVI]_{a-d}$.

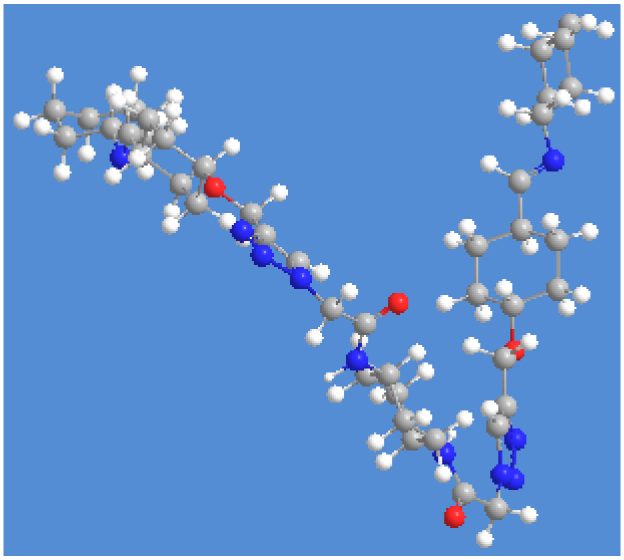
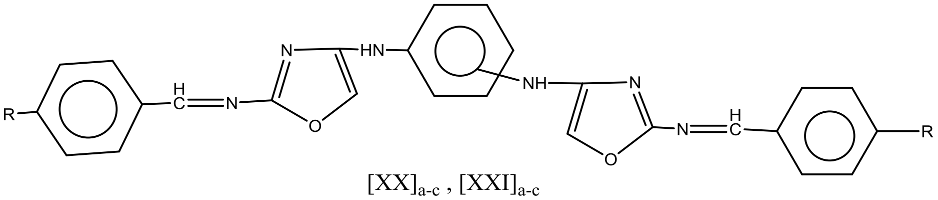


Figure: (3-71) Three dimensional structure of compounds $[XVII]_{a-d}$.

3.2.6. The mesomorphic properties of Schiff bases of oxazole compounds $[XX]_{a-c}$and $[XXI]_{a-c}$.



$[XX]_{a-c}$, $[XXI]_{a-c}$

R = OH , OCH_3 , CH_3

The phase transition temperatures of oxazole compounds $[XX]_{a-c}$ and $[XXI]_{a-c}$ were summarized in Table (3-11). The compounds $[XX]_{a-c}$ showed SmA phase as in Figures (3-72) , (3-73) and (3-74) , respectively .The Figure (3-75) for DSC thermogram for compound $[XX]_{a}$, while the compounds $[XXI]_{a-c}$ were studied by OPM didn't show any liquid crystalline behavior . The transition temperatures for these compounds are listed in Table (3-11) . The Figures (3-76) , (3-77) and (3-78) for 3D models for compounds $[XXI]_{a-c}$

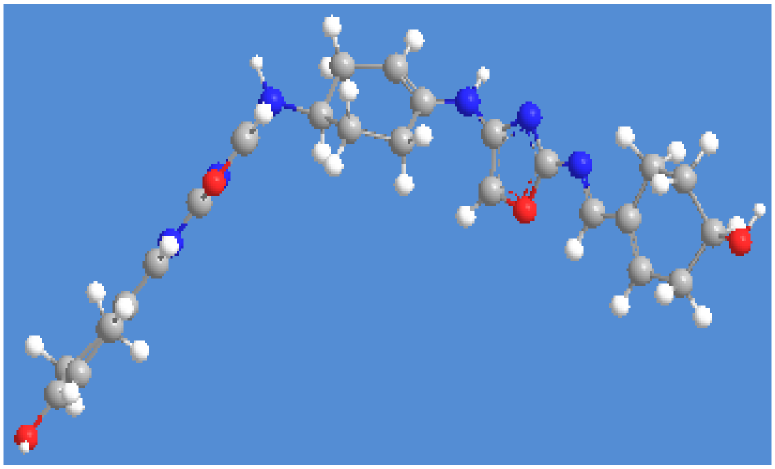


Figure: (3-76) Three dimensional structure of compounds $[XXI]_a$.

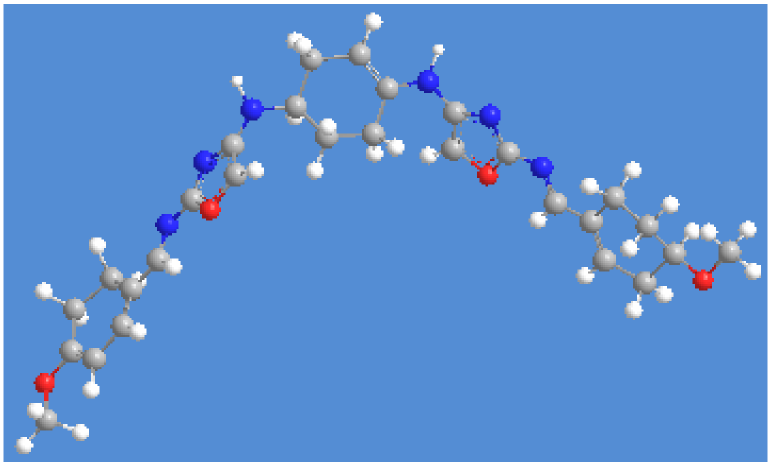


Figure: (3-77) Three dimensional structure of compounds $[XXI]_b$.

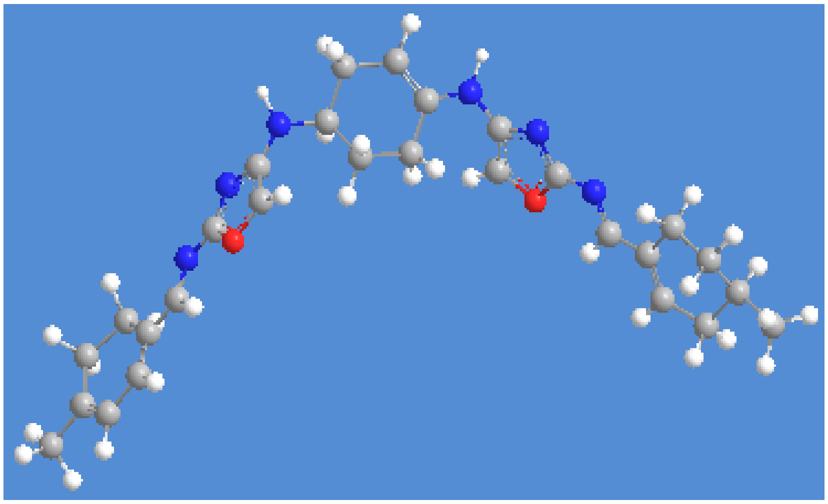
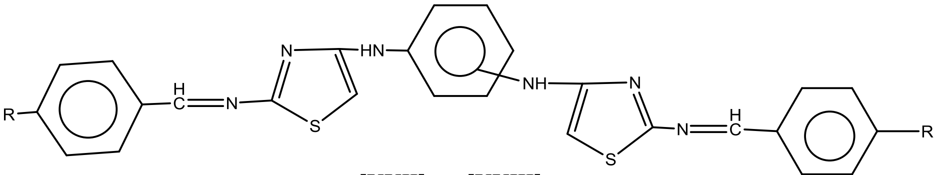


Figure: (3-78) Three dimensional structure of compounds $[XXI]_{c}$.

3.2.7. The mesomorphic properties of Schiff bases of thiazole compounds $[XXII]_{a-c}$and $[XXIII]_{a-c}$.



$[XXII]_{a-c}$, $[XXIII]_{a-c}$

R = OH , OCH_3 , CH_3

The phase transition temperatures for compounds $[XXII]_{a-c}$ and $[XXIII]_{a-c}$ were listed in Table (3-12). The compounds $[XXII]_{a}$ and $[XXII]_{c}$ showed enantiotropic nematic phase as in Figures (3-79) and (3-80) respectively , but the compound $[XXII]_{b}$ showed enantiotropic SmC and nematic phases as in Figure (3-81) for SmC for compound $[XXII]_{b}$. Figure (3-82) for DSC thermogram for compound $[XXII]_{b}$

The compound $[XXIII]_{a}$ showed enantiotropic SmB phase as in Figures (3-83) while the compounds $[XXIII]_{b}$ and $[XXIII]_{c}$ showed enantiotropic nematic phase as in Figures (3-84) and (3-85), respectively .

Conclusions

The following coclusions can be listed for this work:

1- Synthesis of new heterocyclic compounds drived from 1,3-phenylenediamine or 1,4-phenylenediamine. The spectroscopy FTIR, ^{1}HNMR, and mass data give

good evidence to the formation of these compounds.

2- The study of liquid crystalline properties of the synthesized compounds gives: a) The Schiff bases compounds [VII]$_n$ and [VII]$_n$ that terminal groups showed mesomorphic behavior with good thermal stability range excepting the compound [VIII]$_1$ didn't showed any liquid crystal behavior these compounds showed different types of mesomorphases that may be related to the geometry , shape and interaction forces in the molecules which may be attributed to the different terminal an lateral substitutions

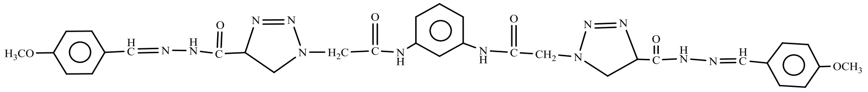
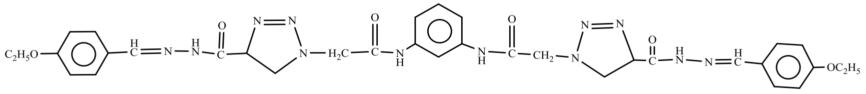
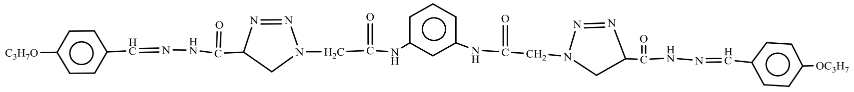
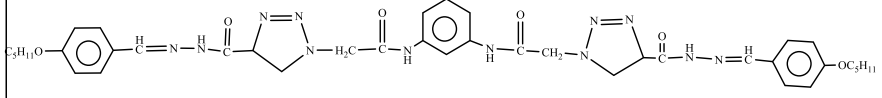
b) The Schiff bases compounds containing oxazole ring [XX]$_{a-c}$ showed mesomorphases behavior but the compounds [XXI]$_{a-c}$ didn't show liquid crystal properties . In addition to the thiazole compounds [XXII]$_{a-c}$ and [XXIII]$_{a-c}$ showed mesomorphic properties and study the effect of the terminal and lateral groups (while as the geometry of the molecules) on type of mesophases behavior.

Suggestion for future work

1. Synthesis and study the liquid crystalline behavior of new chalcon compounds containing 1,2,3- triazoles ring derived from 1,3-phenylenediamine or 1,4- phenylenediamine .

2. Synthesis and study of the liquid crystalline properties of new azo compounds containing on oxazole and thiazole units dervived from 1,3-phenylenediamine or 1,4-phenylenediamine compounds with different aromatic aldehydes.

Table (2-2) : The nomenclature , structure formula , molecular formula yields and physical properties of compounds [VII]$_n$

Comp. No.	Nomenclature	Structural formula	Molecular formula	M. P C^o	Yield %	color
[VII]$_1$	2-(4-(2-(4-methoxybenzylidene) hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)-N-(3-(2-(4-(2-(4-methoxybenzylidene)hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamido)phenyl)acetamide		$C_{32}H_{34}N_{12}O_6$	196	76	yellow
[VII]$_2$	2-(4-(2-(4-ethoxybenzylidene) hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)-N-(3-(2-(4-(2-(4-ethoxybenzylidene) hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamido)phenyl)acetamide		$C_{34}H_{38}N_{12}O_6$	136	72	white
[VII]$_3$	2-(4-(2-(4-propoxybenzylidene) hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)-N-(3-(2-(4-(2-(4-propoxybenzylidene)hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamido)phenyl)acetamide		$C_{36}H_{42}N_{12}O_6$	164	81	white
[VII]$_5$	2-(4-(2-(-4-(pentyloxy)benzylidene) hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)-N-(3-(2-(4-(2-(4-(pentyloxy)benzylidene)hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamido)phenyl)acetamide		$C_{40}H_{50}N_{12}O_6$	140	76	yellow

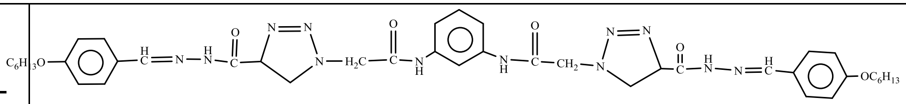
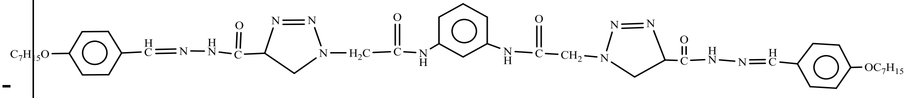
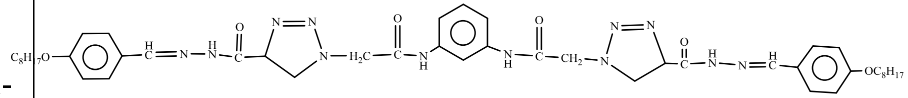
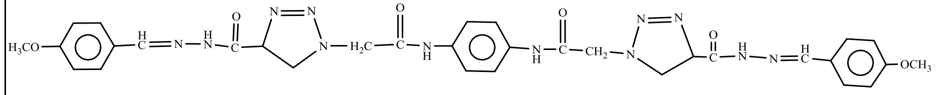
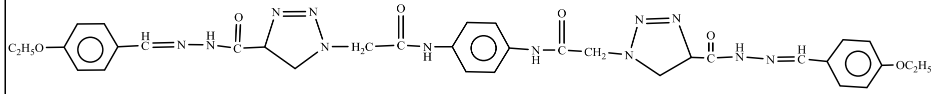
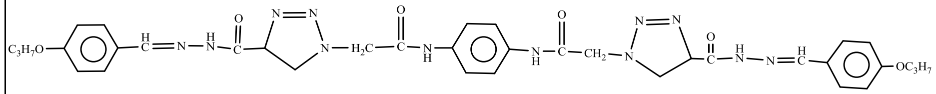
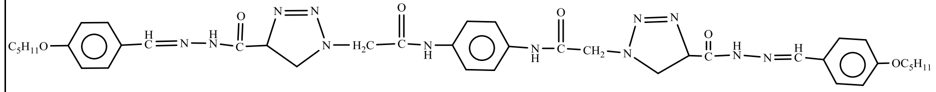
[VII]$_6$	2-(4-(2-(4-(hexyloxy)benzylidene)hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)-N-(3-(2-(4-(2-(4-(hexyloxy) benzylidene) hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamido)phenyl)acetamide		$C_{42}H_{54}N_{12}O_6$	202	78	yellow
[VII]$_7$	2-(4-(2-(4-(heptyloxy)benzylidene)hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)-N-(3-(2-(4-(2-(4-(heptyloxy) benzylidene)hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamido)phenyl)acetamide		$C_{44}H_{58}N_{12}O_6$	194	80	white
[VII]$_8$	2-(4-(2-(4-)(octyloxy)benzylidene)hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)-N-(3-(2-(4-(2-(4-(octyloxy) benzylidene)hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamido) phenyl)acetamide		$C_{46}H_{62}N_{12}O_6$	259	73	white

Table (2-3) : The Nomenclature,structure formula,Molecular formula yields and physical properties of compounds $[VIII]_n$

Comp. No.	Nomenclature	Structural formula	Molecular formula	M. P Cº	Yield %	color
$[VIII]_1$	2-(4-(2-(4-methoxybenzylidene) hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)-N-(4-(2-(4-(2-(4-methoxybenzylidene)hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamido)phenyl)acetamide		$C_{32}H_{34}N_{12}O_6$	198-200	75	white
$[VIII]_2$	2-(4-(2-(4-ethoxybenzylidene)hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)-N-(4-(2-(4-(2-(4-ethoxybenzylidene) hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamido)phenyl) acetamide		$C_{34}H_{38}N_{12}O_6$	158	82	brown
$[VIII]_3$	2-(4-(2-(4-propoxybenzylidene)hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)-N-(4-(2-(4-(2-(4-propoxybenzylidene) hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamido)phenyl)acetamide		$C_{36}H_{42}N_{12}O_6$	176	77	yellow
$[VIII]_5$	2-(4-(2-(-4-(pentyloxy)benzylidene) hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)-N-(4-(2-(4-(2-(4-(pentyloxy)benzylidene)hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamido)phenyl)acetamide		$C_{40}H_{50}N_{12}O_6$	144	68	white

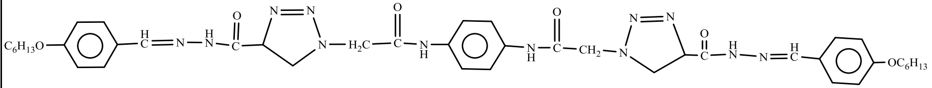
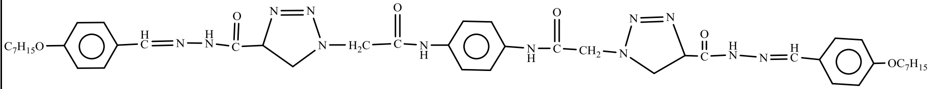
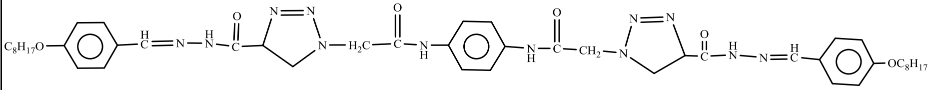
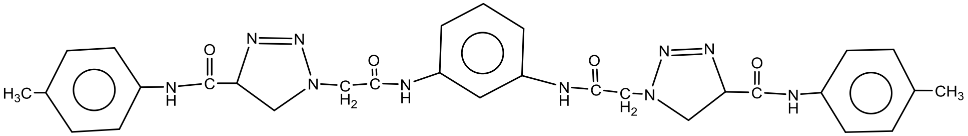
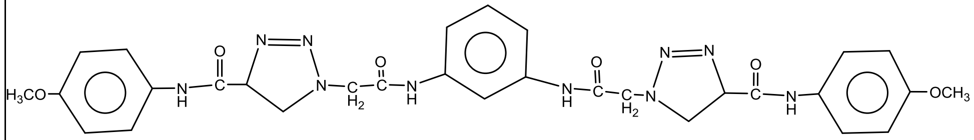
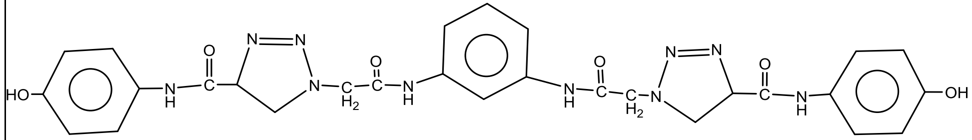
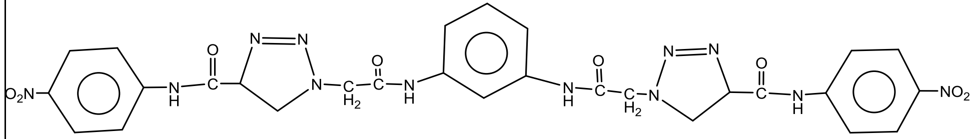
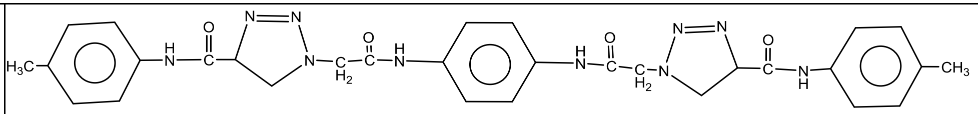
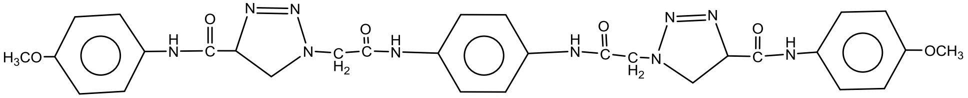
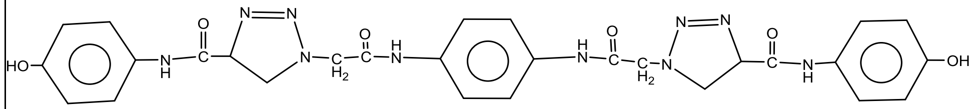
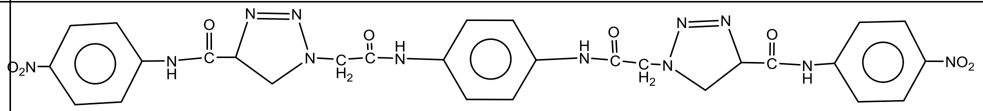
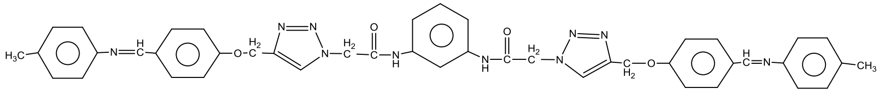
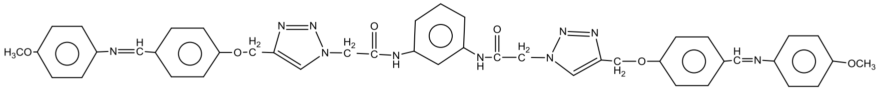
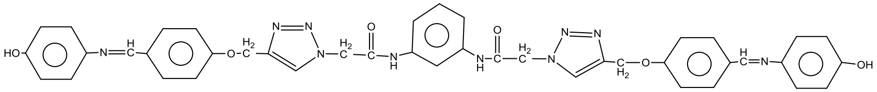
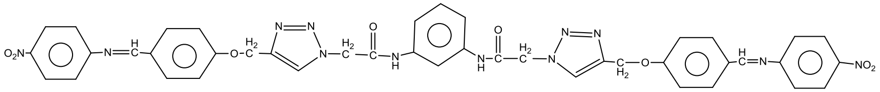
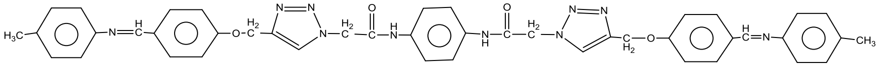
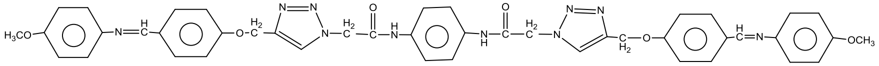
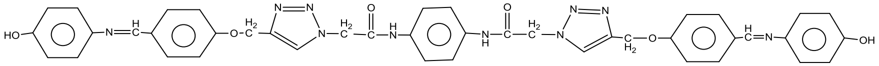
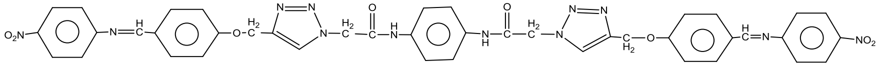
[VIII]$_6$	2-(4-(2-(4-(hexyloxy) benzylidene) hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)-N-(4-(2-(4-(2-(4-(hexyloxy)benzylidene) hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamido) phenyl) acetamide		$C_{42}H_{54}N_{12}O_6$	213	81	white
[VIII]$_7$	2-(4-(2-(4-(heptyloxy)benzylidene) hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)-N-(4-(2-(4-(2-(4-(heptyloxy)benzylidene)hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamido)phenyl) acetamide		$C_{44}H_{58}N_{12}O_6$	215	73	white
[VIII]$_8$	2-(4-(2-(4-(octyloxy)benzylidene)) hydrazine-1-carbonyl) -4,5-dihydro-1H-1,2,3-triazol-1-yl) -N-(4-(2-(4-(2-(4-(octyloxy)benzylidene) hydrazine-1-carbonyl)-4,5-dihydro-1H-1,2,3-triazol-1-yl)acetamido) phenyl) acetamide		$C_{46}H_{62}N_{12}O_6$	295	69	yellow

Table (2-4) : The Nomenclature,structure formula,Molecular formula yields and physical properties of compounds $[XI]_{a-d}$ and $[XII]_{a-d}$

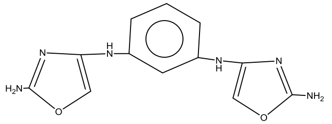
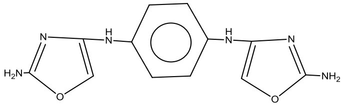
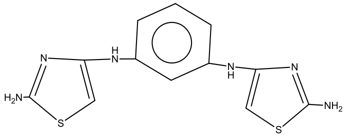
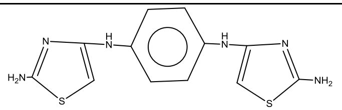
Comp. No.	Nomenclature	Structural formula	Molecular formula	M. P C°	Yield %	color
$[XI]_a$	1,1-((1,3-phenylenebis (azanediyl))bis(2-oxoethane-2,1-diyl))bis(N-(p-tolyl)-4,5-dihydro-1H-1,2,3-triazole-4-(carboxamide		$C_{30}H_{32}N_{10}O_4$	229-231	81	brown
$[XI]_b$	1,1-((1,3-phenylenebis (azanediyl))bis(2-oxoethane-2,1-diyl))bis(N-(4-methoxyphenyl)-4,5-dihydro-1H-1,2,3-triazole-4-(carboxamide		$C_{30}H_{32}N_{10}O_6$	255-257	79	white
$[XI]_c$	1,1-((1,3-phenylenebis (azanediyl))bis(2-oxoethane-2,1-diyl))bis(N-(4-hydroxyphenyl)-4,5-dihydro-1H-1,2,3-triazole-4-(carboxamide		$C_{28}H_{28}N_{10}O_6$	231-233	73	white
$[XI]_d$	1,1-((1,3-phenylenebis (azanediyl))bis(2-oxoethane-2,1-diyl))bis(N-(4-nitrophenyl) -4,5-dihydro-1H-1,2,3-triazole-4-(carboxamide		$C_{28}H_{26}N_{12}O_8$	239-241	68	yellow

[XII]$_a$	1,1-((1,4-phenylenebis (azanediyl))bis(2-oxoethane-2,1-diyl))bis(N-(p-tolyl)-4,5-dihydro-1H-1,2,3-triazole-4-(carboxamide		$C_{30}H_{32}N_{10}O_4$	228-230	73	brown
[XII]$_b$	1,1-((1,4-phenylenebis (azanediyl))bis(2-oxoethane-2,1-diyl))bis(N-(4-methoxyphenyl) -4,5-dihydro-1H-1,2,3-triazole-4-(carboxamide		$C_{30}H_{32}N_{10}O_6$	266-268	62	white
[XII]$_c$	1,1-((1,4-phenylenebis (azanediyl))bis(2-oxoethane-2,1-diyl))bis(N-(4-hydroxyphenyl)-4,5-dihydro-1H-1,2,3-triazole-4-(carboxamide		$C_{28}H_{28}N_{10}O_6$	252-254	78	white
[XII]$_d$	1,1-((1,4-phenylenebis (azanediyl))bis(2-oxoethane-2,1-diyl))bis(N-(4-nitrophenyl)-4,5-dihydro-1H-1,2,3-triazole-4-(carboxamide		$C_{28}H_{26}N_{12}O_8$	247-249	74	yellow

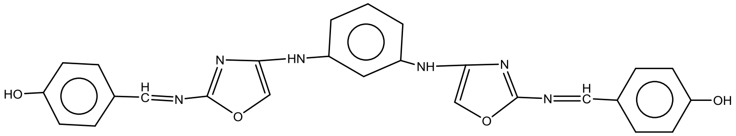
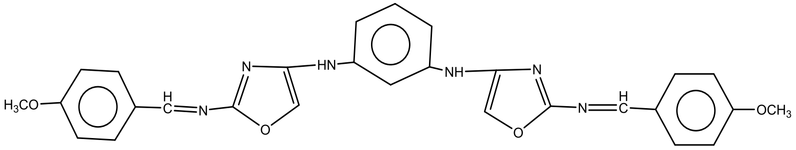
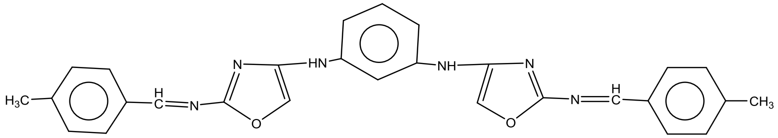
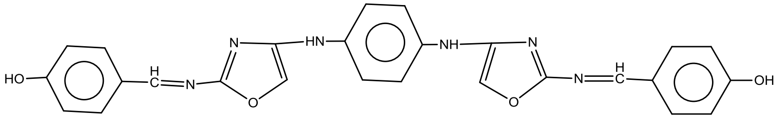
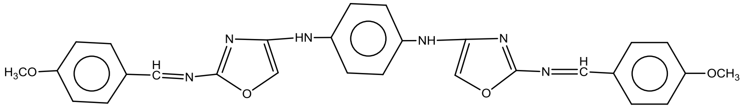
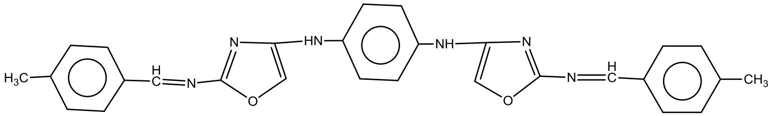
Table(2-5) : The Nomenclature,structure formula,Molecular formula yields and physical properties of compounds $[XVI]_{a-d}$ and $[XVII]_{a-d}$

Comp. No.	Nomenclature	Structural formula	Molecular formula	M. P C°	Yield %	color
$[XVI]_a$	N,N'-(1,3-phenylene)bis(2-(4-((4-((p-tolylimino)methyl)phenoxy)methyl)-1H-(1,2,3-triazol-1-yl)acetamide		$C_{44}H_{38}N_{10}O_4$	261-263	67	Gray
$[XVI]_b$	N,N'-(1,3-phenylene)bis(2-(4-((4-(((4-methoxyphenyl)imino)methyl)phenoxy)met (hyl)-1H-1,2,3-triazol-1-yl)acetamide		$C_{44}H_{38}N_{10}O_6$	267-269	74	White
$[XVI]_C$	N,N'-(1,3-phenylene)bis(2-(4-((4-(((4-hydroxyphenyl)imino)methyl)phenoxy)met (hyl)-1H-1,2,3-triazol-1-yl)acetamide		$C_{42}H_{34}N_{10}O_6$	272-274	85	white
$[XVI]_d$	N,N'-(1,3-phenylene)bis(2-(4-((4-(((4-nitrophenyl)imino)methyl)phenoxy)methyl) (-1H-1,2,3-triazol-1-yl)acetamide		$C_{42}H_{32}N_{12}O_8$	283-285	82	yellow
$[XVII]_a$	N,N'-(1,4-phenylene)bis(2-(4-((4-((p-tolylimino)methyl)phenoxy)methyl)-1H-1,2,3-triazol-1-yl)acetamide		$C_{44}H_{38}N_{10}O_4$	293-295	61	White off
$[XVII]_b$	N,N'-(1,4-phenylene)bis(2-(4-((4-(((4-methoxyphenyl)imino)methyl)phenoxy)met (hyl)-1H-1,2,3-triazol-1-yl)acetamide		$C_{44}H_{38}N_{10}O_6$	> 300	79	brown
$[XVII]_c$	N,N'-(1,4-phenylene)bis(2-(4-((4-(((4-hydroxyphenyl)imino)methyl)phenoxy)met (hyl)-1H-1,2,3-triazol-1-yl)acetamide		$C_{42}H_{34}N_{10}O_6$	> 300	76	brown
$[XVII]_d$	N,N'-(1,4-phenylene)bis(2-(4-((4-(((4-nitrophenyl)imino)methyl)phenoxy)methyl) (-1H-1,2,3-triazol-1-yl)acetamide		$C_{42}H_{32}N_{12}O_8$	> 300	65	yellow

Table(2-6) :The nomenclature , structure formula, molecular formula yields and physical properties of compounds $[XVIII]_{a,b}$ and $[XIX]_{a,b}$

Comp. No.	Nomenclature	Structural formula	Molecular formula	M. P C°	Yield %	color
$[XVIII]_a$	(N^4,$N^{4'}$-(1,3-phenylene)bis(oxazole-2,4-diamine		$C_{12}H_{12}N_6O_2$	198-200	67	White
$[XVIII]_b$	(N^4,$N^{4'}$-(1,4-phenylene)bis(oxazole-2,4-diamine		$C_{12}H_{12}N_6O_2$	212-214	73	White Powder
$[XIX]_a$	(N^4,$N^{4'}$-(1,3-phenylene)bis(thiazole-2,4-diamine		$C_{12}H_{12}N_6S_2$	236-238	69	Dark Yellow
$[XIX]_b$	(N^4,$N^{4'}$-(1,4-phenylene)bis(thiazole-2,4-diamine		$C_{12}H_{12}N_6S_2$	253-255	76	Yellow

Table(2-7) : The physical properties of compounds $[XX]_{a-c}$ and $[XXI]_{a-c}$

Comp. No.	Nomenclature	Structural formula	Molecular formula	M. P C°	Yield %	color
$[XX]_a$	4,4((((1,3-phenylenebis(azanediyl))bis(oxazole-4,2-diyl))bis(azaneylylidene))bis(methaneylylidene))diphenol		$C_{26}H_{18}N_6O_4$	278	74	white
$[XX]_b$	N^1,N^3-bis(2-((4-methoxybenzylidene)amino)oxazol-4-yl)benzene-1,3-diamine		$C_{28}H_{22}N_6O_4$	211	81	brown
$[XX]_c$	N1,N^3-bis(2-((4-methylbenzylidene) amino)oxazol-4-yl)benzene-1,3-diamine		$C_{28}H_{22}N_6O_2$	228	76	Brown
$[XXI]_a$	4,4-((((1,4-phenylenebis(azanediyl)) bis (oxazole-4,2-diyl)) bis(azaneylylidene)) -bis(methaneylylidene))diphenol		$C_{26}H_{18}N_6O_4$	312-314	69	white
$[XXI]_b$	N^1,N^4-bis(2-((4-methoxybenzylidene)amino) oxazol-4-yl)benzene-1,4-diamine		$C_{28}H_{22}N_6O_4$	223-225	63	brown
$[XXI]_c$	N^1,N^4-bis(2-((4-methylbenzylidene)amino) oxazol-4-yl)benzene-1,4-diamine		$C_{28}H_{22}N_6O_2$	244-246	82	white

Table(2-8) : The physical properties of compounds $[XXII]_{a-c}$ and $[XXIII]_{a-c}$

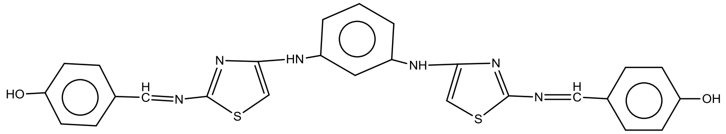
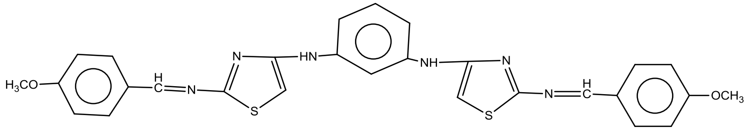
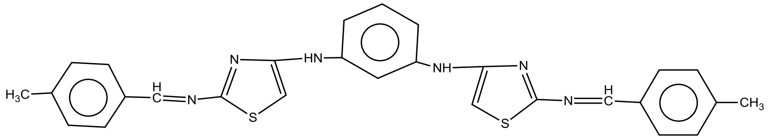
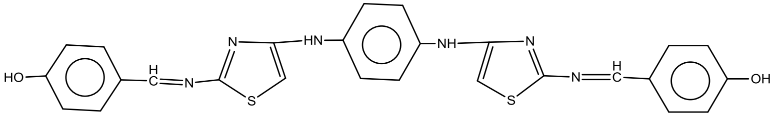
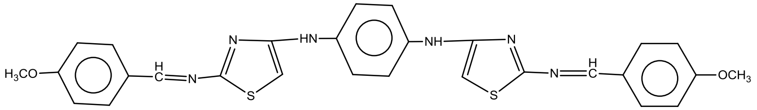
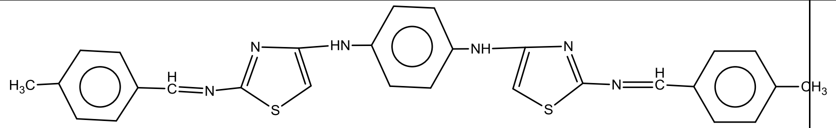
Comp. No.	Nomenclature	Structural formula	Molecular formula	M. P ºC	Yield %	color
$[XXII]_a$	4,4-((((1,3-phenylenebis(azanediyl))bis(thiazole-4,2 -diyl))bis (azaneylylidene))bis (methaneylylidene))diphenol		$C_{26}H_{18}N_6O_2S_2$	283	66	White
$[XXII]_b$	N^1,N^3-bis(2-((4-methoxybenzylidene) amino)thiazol-4-yl)benzene-1,3-diamine		$C_{28}H_{22}N_6O_2S_2$	212	78	Yellow
$[XXII]_c$	N^1,N^3-bis(2-((4-methylbenzylidene) amino)thiazol-4-yl)benzene-1,3-diamine		$C_{28}H_{22}N_6S_2$	277	63	Powder White
[XXIII]	(phenylenebis(azanediyl-1,4))))-4,4 bis (thiazole-4,2(diyl))bis(azaneylylidene))bis- methaneylylidene)) diphenol)		$C_{26}H_{18}N_6O_2S_2$	254	60	Yellow
$[XXIII]_b$	N^1,N^4-bis(2-((4-methoxybenzylidene) amino)thiazol-4-yl)benzene-1,3-diamine		$C_{28}H_{22}N_6O_2S_2$	236	71	White
$[XXIII]_c$	N^1,N^4-bis(2-((4-methylbenzylidene) amino) thiazol-4-yl)benzene-1,3-diamine		$C_{28}H_{22}N_6S_2$	261	81	Yellow

Table (3-1) The characterization FTIR absorption bands of compounds $[VII]_n$

COMP NO.	(Characteristic bands FT-IR spectra(cm $^{-1}$)						
	ν N-H	ν C-H arom	ν C-H aliph	ν C=O	ν C=N	ν C=C aromatic	υ C-O
$[VII]_1$	3267	3087	2927-2839	1664	1617	1600	1233
$[VII]_2$	3287	3051	2927-2837	1649	1620	1600	1247
$[VII]_3$	3296	3034	2929-2856	1656	1610	1601	1241
$[VII]_5$	3262	3062	2937-2893	1649	1621	1600	1239
$[VII]_6$	3290	3043	2916-2881	1660	1613	1604	1244
$[VII]_7$	3298	3043	2926-2881	8165	1609	1604	1251
$[VII]_8$	3270	3043	2951-2866	1658	1620	1602	1264

Table (3-2) The characterization FTIR absorption bands of compounds $[VIII]_n$

COMP NO.	(Characteristic bands FT-IR spectra(cm $^{-1}$)						
	ν N-H	ν C-H .arom	ν C-H aliph	ν C=O	ν C=N	ν C=C aromatic	‹υ C-O
$[VIII]_1$	3276	3051	2943-2866	1662	1615	1604	1246
$[VIII]_2$	3294	3057	2945-2862	1670	1626	1606	1239
$[VIII]_3$	3296	3043	2926-2881	1675	1637	1604	1238
$[VIII]_5$	3285	3075	2926-2862	1641	1618	1611	1241
$[VIII]_6$	3263	3042	2981-2837	1650	1622	1600	1248
$[VIII]_7$	3285	3079	2922-2862	1641	1614	1599	1240
$[VIII]_8$	3282	3063	2920-2850	1659	1625	1604	1243

Table (3-3) The characterization FTIR absorption bands of amide compounds $[XI]_{a-d}$, $[XII]_{a-d}$

COMP NO.	Characteristic bands FT-IR spectra(cm $^{-1}$)					
	ν N-H	ν C-H arom	ν C-H aliph	ν C=O	ν C=C arom	Other absorption band
$[XI]_a$	3325	3089	2915-2855	1643	1602	
$[XI]_b$	3417	3043	2922-2862	1647	1594	**ν**(C-O)1253
$[XI]_c$	3271	3092	2926-2898	1660	1604	**ν**(O-H)3398
$[XI]_d$	3301	3106	2952-2875	1645	1600	**ν**(C-NO_2)1520
$[XII]_a$	3417	3043	2922-2862	1643	1616	
$[XII]_b$	3265	3065	2952-2877	1635	1590	**ν**(C-O)1263
$[XII]_c$	3294	3078	2933-2867	1643	1611	**ν**(O-H)3418
$[XII]_d$	3289	3069	2974-2832	1649	1593	**ν**(C-NO_2)1536

Table (3-4) The characterization FTIR absorption bands of compounds $[XVI]_{a-d}$, $[XVII]_{a-d}$

COMP NO.	(Characteristic bands FT-IR spectra(cm $^{-1}$)					
	ν N-H	ν C-H arom	ν C-H aliph	ν C=O	ν C=N	υ(C –O) ether
$[XVI]_a$	3275	3089	2926-2866	1678	1622	1247
$[XVI]_b$	3250	3076	2933-2842	1668	1612	1246
$[XVI]_c$	3248	3062	2927-2898	1678	1620	1251
$[XVI]_d$	3301	3081	2932-2874	1681	1609	1255
$[XVII]_a$	3275	3043	2926-2866	1678	1616	1247
$[XVII]_b$	3284	3065	2926-2825	1665	1618	1247
$[XVII]_c$	3304	3048	2929-2835	1678	1604	1246
$[XVII]_d$	3289	3069	2920-2832	1649	1623	1252

Table (3-5) The characterization FTIR absorption bands of compounds $[XVIII]_{a,b}$, $[XIX]_{a,b}$

COMP NO.	(Characteristic bands FT-IR spectra(cm $^{-1}$)				
	υ(NH_2) and (NH)	ν C-H .arom	ν C=N	ν C=C	Others
$[XVIII]_a$	3462-3190	3080	1649	1608	C-O(1229)
$[XVIII]_b$	3244-3174	3093	1634	1593	C-O(1235)
$[XIX]_a$	3271-3154	3099	1656	1596	C-S(1224)
$[XIX]_b$	3253-3170	3089	1662	1587	C-S(1220)

Table (3-6) The characterization FTIR absorption bands of compounds $[XX]_{a-c}$ and $[XXI]_{a-c}$

NO. COMP	(Characteristic bands FT-IR spectra(cm^{-1})				
	υ (NH)	**ν C-H arom**	**ν C=N**	**ν C=C**	**other absorption band**
$[XX]_a$	3289	3048	1648	1591	**ν**(O-H) 3253
$[XX]_b$	3200	3093	1650	1601	**ν**C-H aliph. 2956-2885
$[XX]_c$	3184	3089	1622	1598	**ν**C-H aliph. 2974-2812
$[XXI]_a$	3180	3021	1662	1600	**ν**(O-H) 3253
$[XXI]_b$	3172	3048	1656	1610	**ν**C-H. aliph. 2940-2876
$[XXI]_c$	3259	3091	1619	1593	**ν**C-H aliph.

Table (3-7) The characterization FTIR absorption bands of compounds $[XXII]_{a-c}$ and $[XXIII]_{a-c}$

NO. COMP	(Characteristic bands FT-IR spectra(cm^{-1})				
	υ (NH)	**ν C-H arom**	**ν C=N**	**ν C=C**	**other absorption band**
$[XXII]_a$	3280	3048	1651	1599	**ν**(O-H) 3283
$[XXII]_b$	3323	3050	1660	1600	**ν**C-H-aliph. 2946-2875
$[XXII]_c$	3174	3089	1622	1595	**ν**C-H-aliph. 2935-2864
$[XXIII]_a$	3292	3041	1658	1595	**ν**(O-H) 3311
$[XXIII]_b$	3232	3011	1653	1597	**ν**C-H-aliph. 2954-2865
$[XXIII]_C$	3245	3016	1632	1594	**ν**C-H-aliph. 2942-2871

Table (3-8) The type of transition, transition temperatures (T/°C) of compounds $[VII]_n$ and$[VIII]_n$

Compound	Phase transition	Compound	Phase transition
[VII] 1	$\mathrm{Cr} \xrightleftharpoons[140]{162} \mathrm{N}$ $\mathrm{N} \xrightleftharpoons{200} \mathrm{I}$	**[VIII] 1**	$\mathrm{Cr} \xrightarrow{240} \mathrm{I}$
[VII] 2	$\mathrm{Cr} \xrightleftharpoons{120} \mathrm{N}$ $\mathrm{N} \xrightleftharpoons{140} \mathrm{I}$	**[VIII] 2**	$\mathrm{Cr} \xrightleftharpoons{135} \mathrm{N}$ $\mathrm{N} \xrightleftharpoons{165} \mathrm{I}$
[VII] 3	$\mathrm{Cr} \xrightleftharpoons{140} \mathrm{N}$ $\mathrm{N} \xrightleftharpoons{171} \mathrm{I}$	**[VIII] 3**	$\mathrm{Cr} \xrightleftharpoons{160} \mathrm{N}$ $\mathrm{N} \xrightleftharpoons{180} \mathrm{I}$
[VII] 5	$\mathrm{Cr} \xrightleftharpoons{130} \mathrm{N}$ $\mathrm{N} \xrightleftharpoons{145} \mathrm{I}$	**[VIII] 5**	$\mathrm{Cr} \xrightleftharpoons{115} \mathrm{N}$ $\mathrm{N} \xrightleftharpoons{150} \mathrm{I}$
[VII] 6	$\mathrm{Cr} \xrightleftharpoons{183} \mathrm{N}$ $\mathrm{N} \xrightleftharpoons{204} \mathrm{I}$	**[VIII] 6**	$\mathrm{Cr} \xrightleftharpoons{150} \mathrm{N}$ $\mathrm{N} \xrightleftharpoons{218} \mathrm{I}$
[VII] 7	$\mathrm{Cr} \xrightleftharpoons{196} \mathrm{SmA}$ $\mathrm{SmA} \xrightleftharpoons{189} \mathrm{N}$ $\mathrm{N} \xrightleftharpoons{206} \mathrm{I}$	**[VIII] 7**	$\mathrm{Cr} \xrightleftharpoons{190} \mathrm{SmA}$ $\mathrm{SmA} \xrightleftharpoons{219} \mathrm{I}$
[VII] 8	$\mathrm{Cr} \xrightleftharpoons{175} \mathrm{SmB}$ $\mathrm{SmB} \xrightleftharpoons{200} \mathrm{N}$ $\mathrm{N} \xrightleftharpoons{268} \mathrm{I}$	**[VIII] 8**	$\mathrm{Cr} \xrightleftharpoons[116]{209} \mathrm{SmA}$ $\mathrm{SmA} \xrightarrow{268} \mathrm{N}$ $\mathrm{N} \xrightarrow{312} \mathrm{I}$

Table (3-9) The type of transition, transition temperatures (T/°C) of compounds $[XI]_{a-d}$, $[XII]_{a-d}$

Compound	Phase transition
$[IX]_a$	$Cr \overset{194}{\rightleftharpoons} SmB$ $SmB \overset{211}{\rightleftharpoons} I$
$[IX]_b$	$Cr \xrightarrow{233} SmB$ $SmB \xrightarrow{263} I$
$[XI]_a$	$Cr \xrightarrow{219} I$
$[XI]_b$	$Cr \xrightarrow{225} I$
$[XI]_c$	$Cr \xrightarrow{231} I$
$[XI]_d$	$Cr \xrightarrow{235} I$
$[XII]_a$	$Cr \xrightarrow{228} I$
$[XII]_b$	$Cr \xrightarrow{266} I$
$[XII]_c$	$Cr \xrightarrow{242} I$
$[XII]_d$	$Cr \xrightarrow{246} I$
$[XIII]_a$	$Cr \xrightarrow{247} I$
$[XIII]_b$	$Cr \xrightarrow{288} I$

Table (3-10) The type of transition, transition temperatures (T/°C) of compounds $[XVI]_{a-d}$, $[XVII]_{a-d}$

Compound	Phase transition
$[XVI]_a$	$Cr \xrightarrow{261} I$
$[XVI]_b$	$Cr \xrightarrow{267} I$
$[XVI]_c$	$Cr \xrightarrow{272} I$
$[XVI]_d$	$Cr \xrightarrow{281} I$
$[XVII]_a$	$Cr \xrightarrow{293} I$
$[XVII]_b$	$Cr \xrightarrow{300} I$
$[XVII]_c$	$Cr \xrightarrow{314} I$
$[XVII]_d$	$Cr \xrightarrow{333} I$

Table (3-11) The type of transition, transition temperatures (T/°C) of compounds $[XX]_{a\text{-}c}$ and $[XXI]_{a\text{-}c}$

Compound	Phase transition
$[XX]_a$	$\mathrm{Cr} \xrightarrow{240} \mathrm{SmA}$ $\mathrm{SmA} \xrightarrow{287} \mathrm{I}$
$[XX]_b$	$\mathrm{Cr} \overset{158}{\rightleftharpoons} \mathrm{SmA}$ $\mathrm{SmA} \overset{210}{\rightleftharpoons} \mathrm{I}$
$[XX]_c$	$\mathrm{Cr} \overset{188}{\rightleftharpoons} \mathrm{SmA}$ $\mathrm{SmA} \overset{234}{\rightleftharpoons} \mathrm{I}$
$[XXI]_a$	$\mathrm{Cr} \xrightarrow{312} \mathrm{I}$
$[XXI]_b$	$\mathrm{Cr} \xrightarrow{223} \mathrm{I}$
$[XXI]_c$	$\mathrm{Cr} \xrightarrow{244} \mathrm{I}$

Table (3-12) The type of transition, transition temperatures (T/°C) of compounds $[XXII]_{a\text{-}c}$, $[XXIII]_{a\text{-}c}$

Compound	Phase transition
$[XXII]_a$	Cr $\xrightleftharpoons{219}$ N N $\xrightleftharpoons{290}$ I
$[XXII]_b$	Cr $\xrightarrow{102}$ Smc Smc $\xrightarrow{165}$ N N $\xrightarrow{215}$ I
[XXII]c	Cr $\xrightleftharpoons{220}$ N N $\xrightleftharpoons{280}$ I
$[XXIII]_a$	Cr $\xrightleftharpoons{185}$ SmB SmB $\xrightleftharpoons{256}$ I
$[XXIII]_b$	Cr $\xrightleftharpoons{198}$ N N $\xrightleftharpoons{240}$ I
$[XXIII]_c$	Cr $\xrightleftharpoons{200}$ N N $\xrightleftharpoons{266}$ I

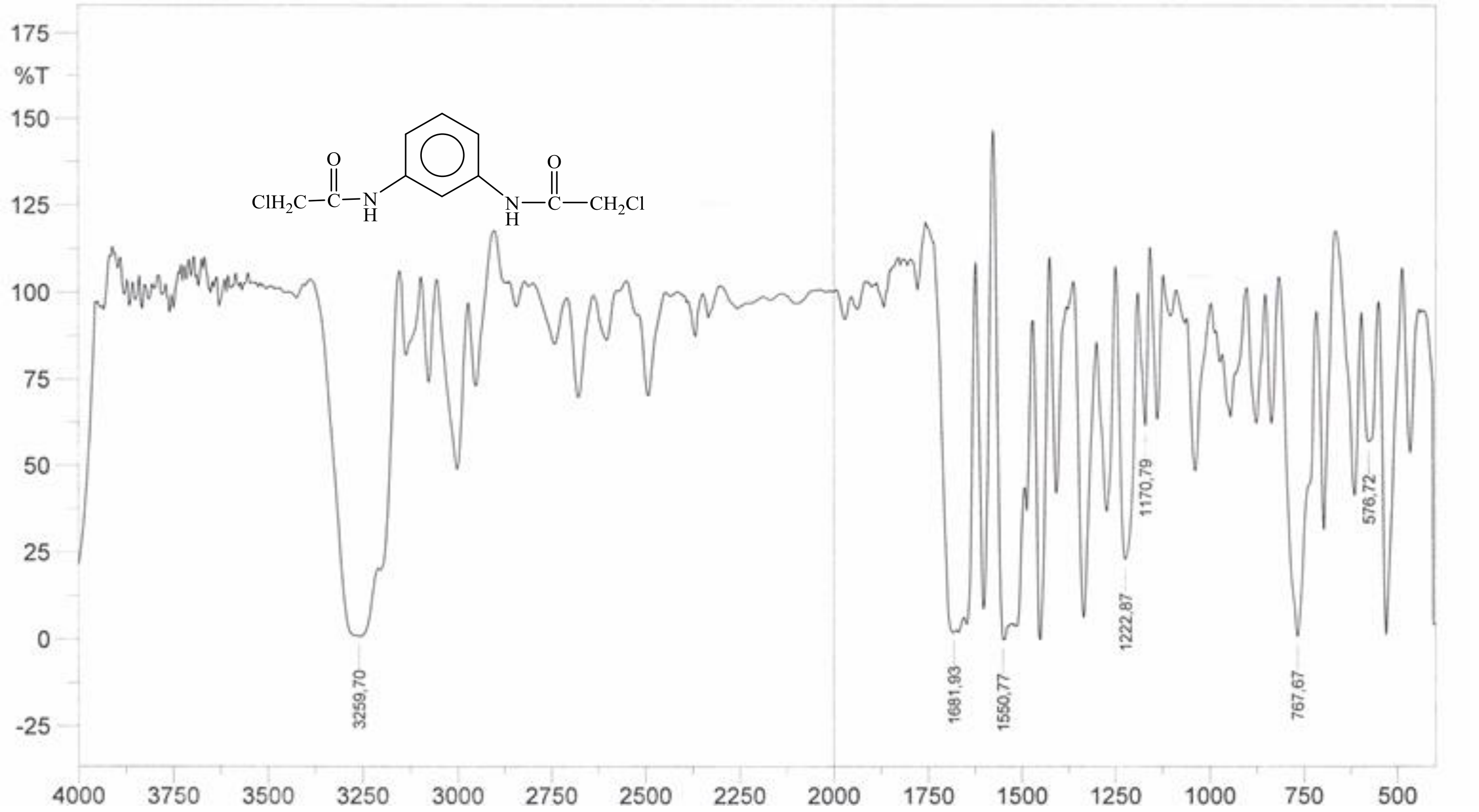


Figure (3-1) FT-IR spectrum for compound[I]$_a$

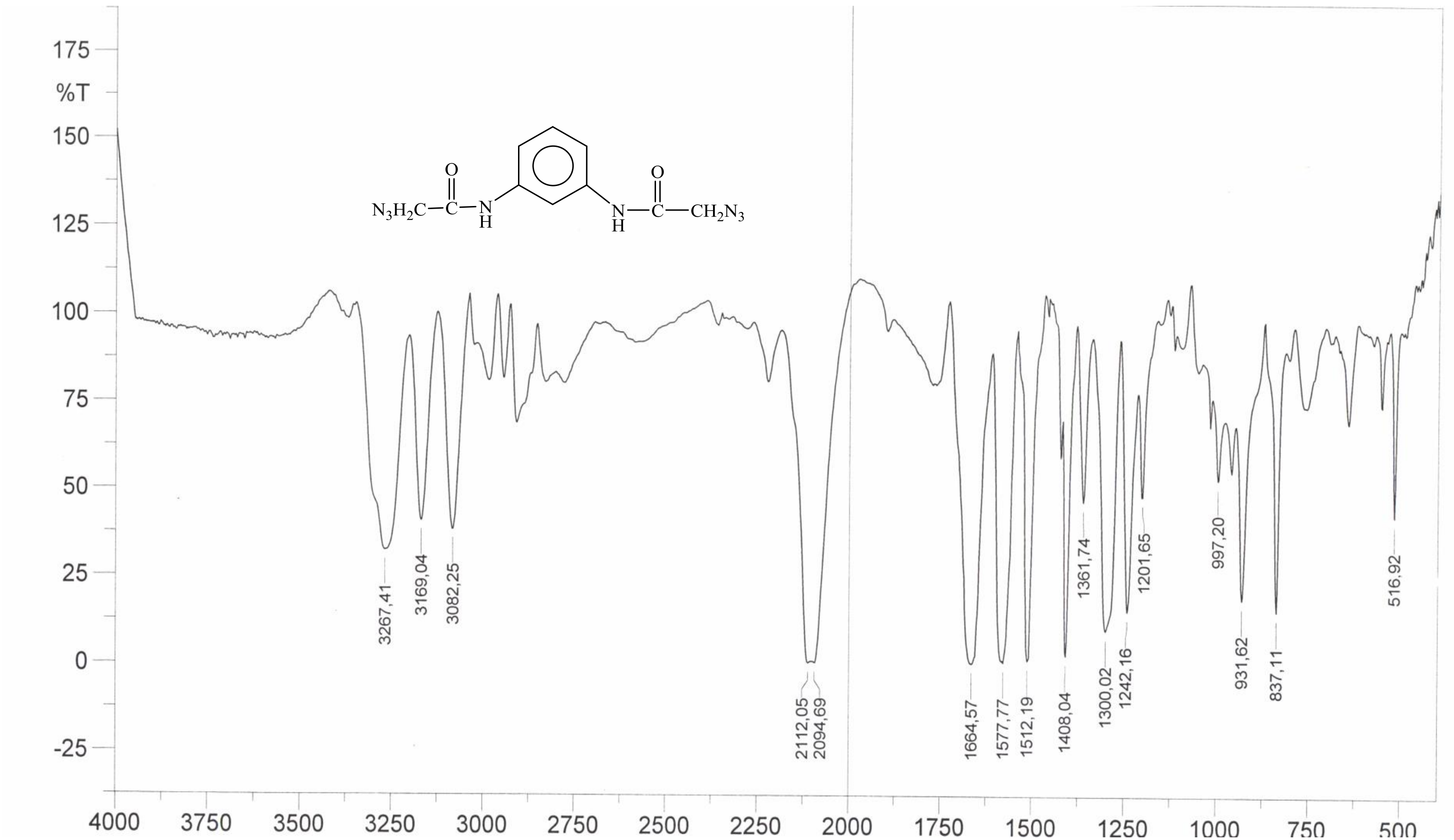


Figure (3-2) FT-IR spectrum for compound[II]$_a$

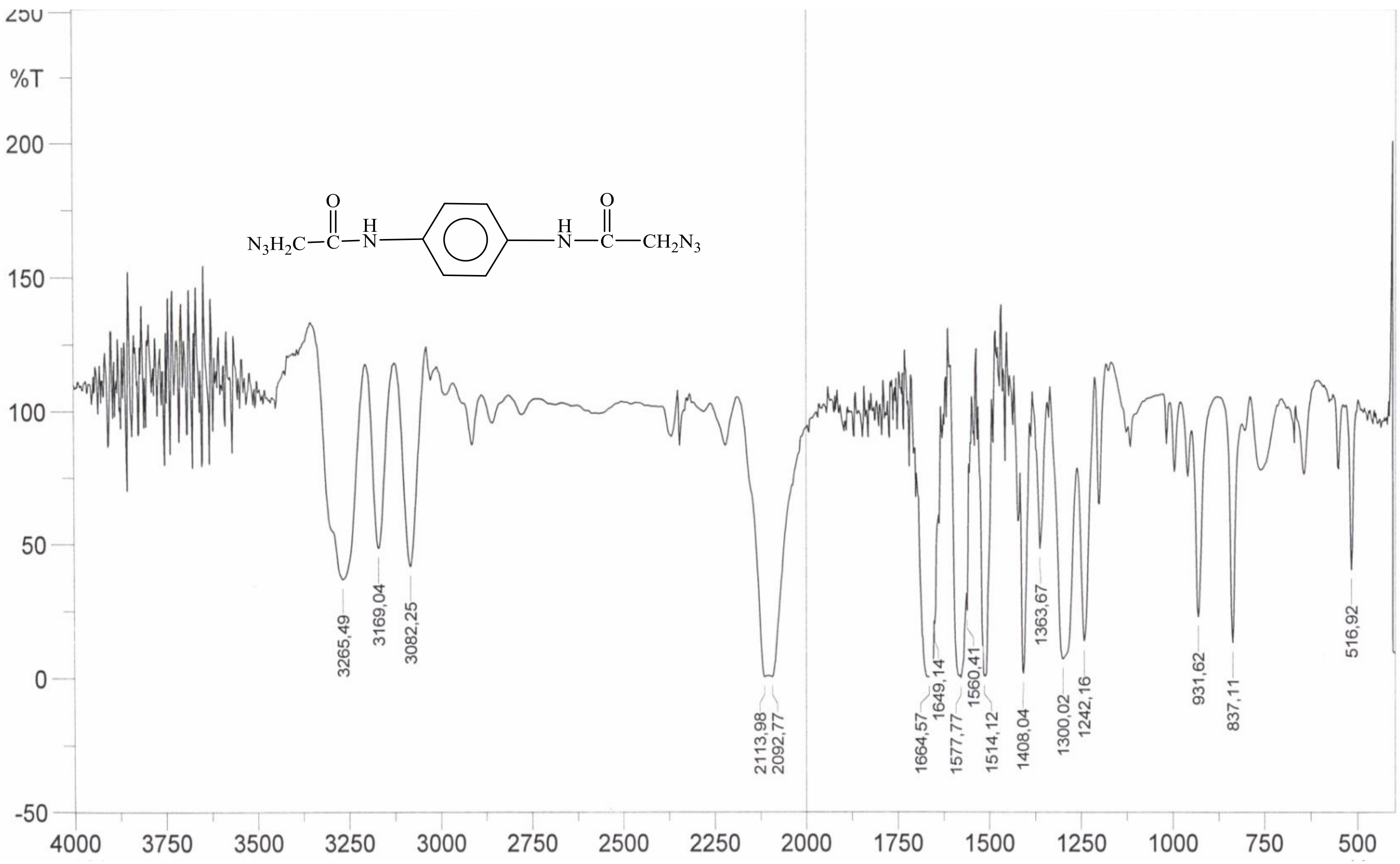


Figure (3-3) FT-IR spectrum for compound[II]$_b$

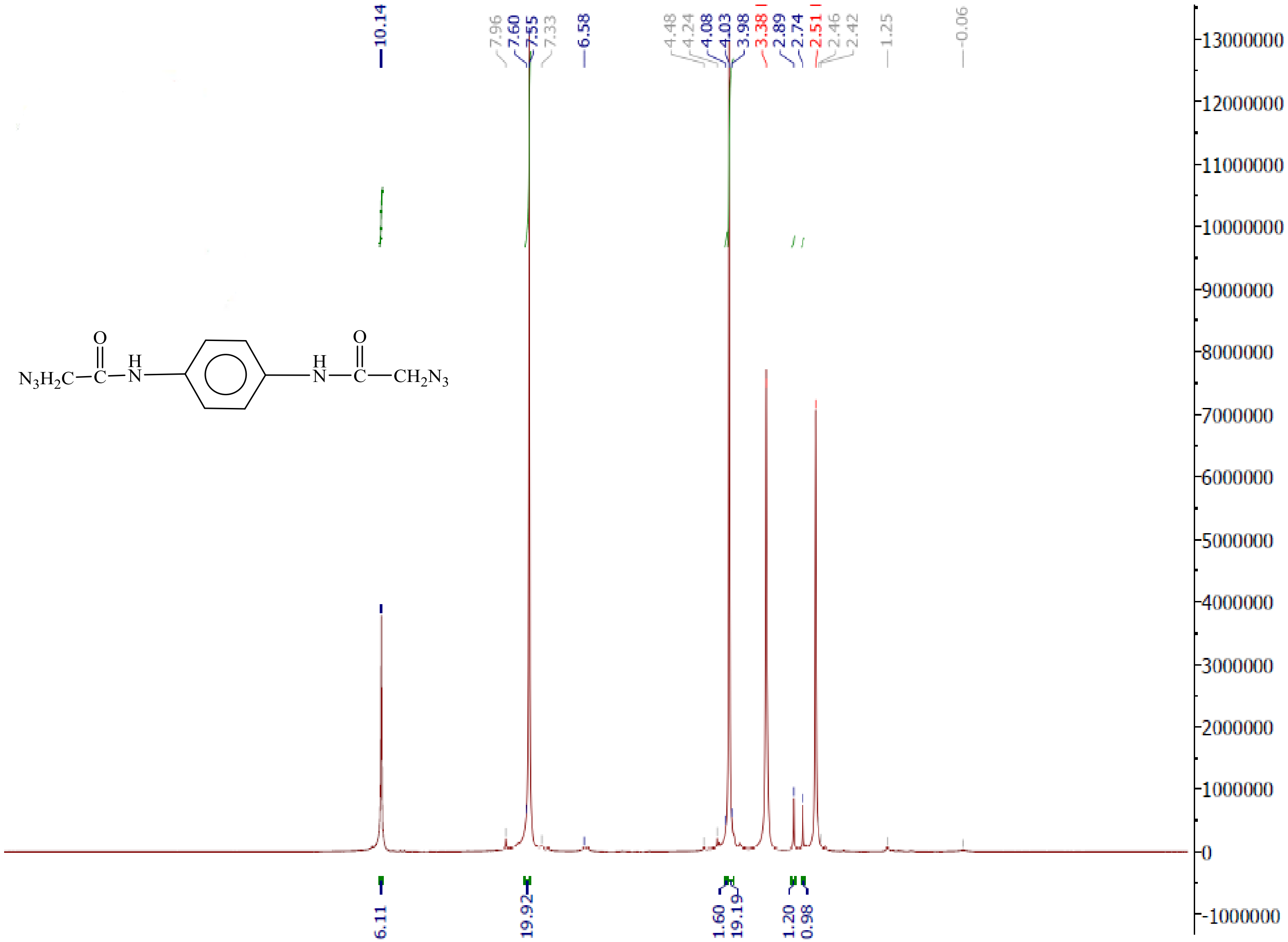


Figure (3-4) ^{1}HNM R spectrum for compound[II]$_b$

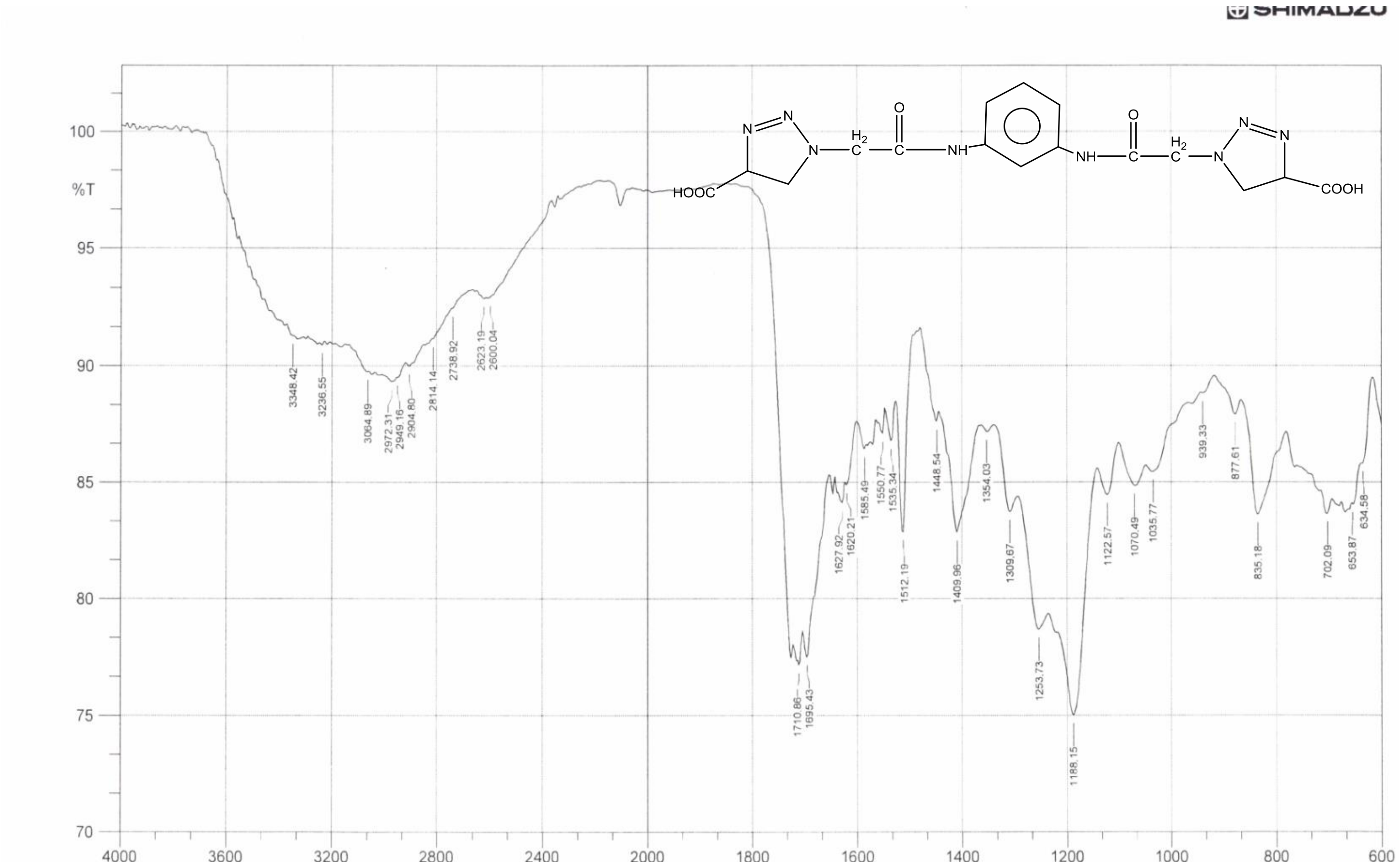


Figure (3-5) FT-IR spectrum for compound[III]$_a$

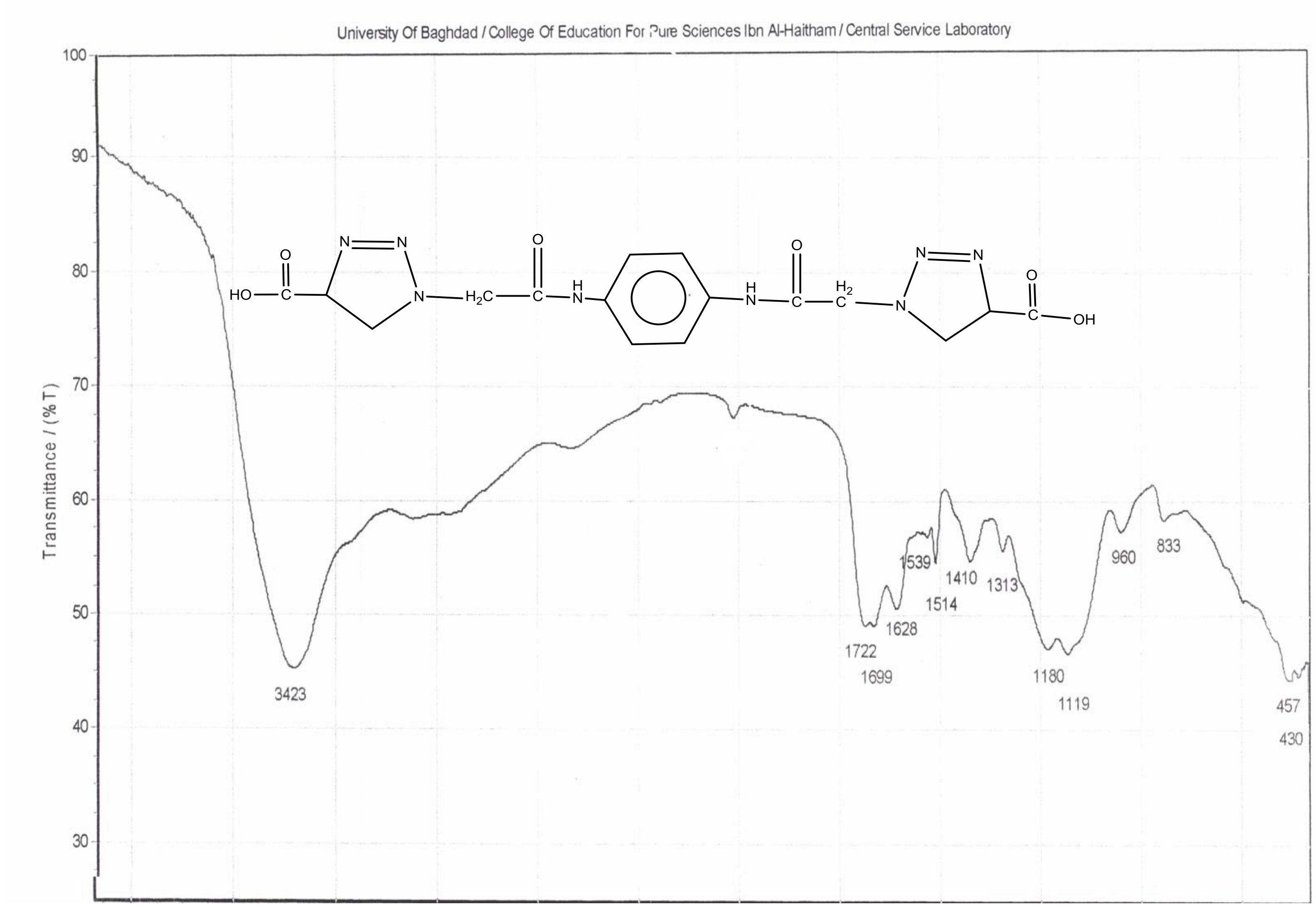


Figure (3-6) FT-IR spectrum for compound[III]$_b$

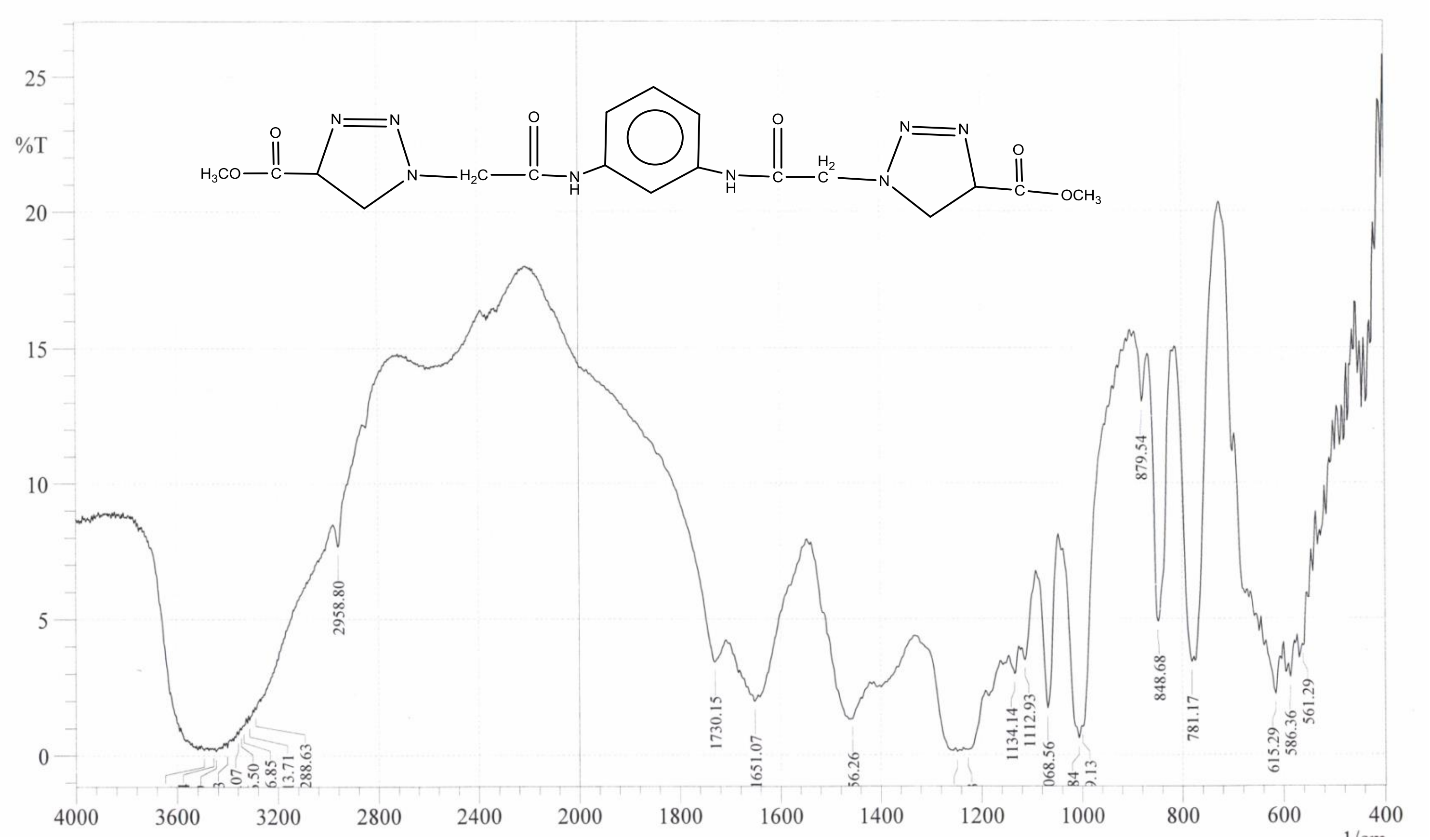


Figure (3-7) FT-IR spectrum for compound[IV]$_a$

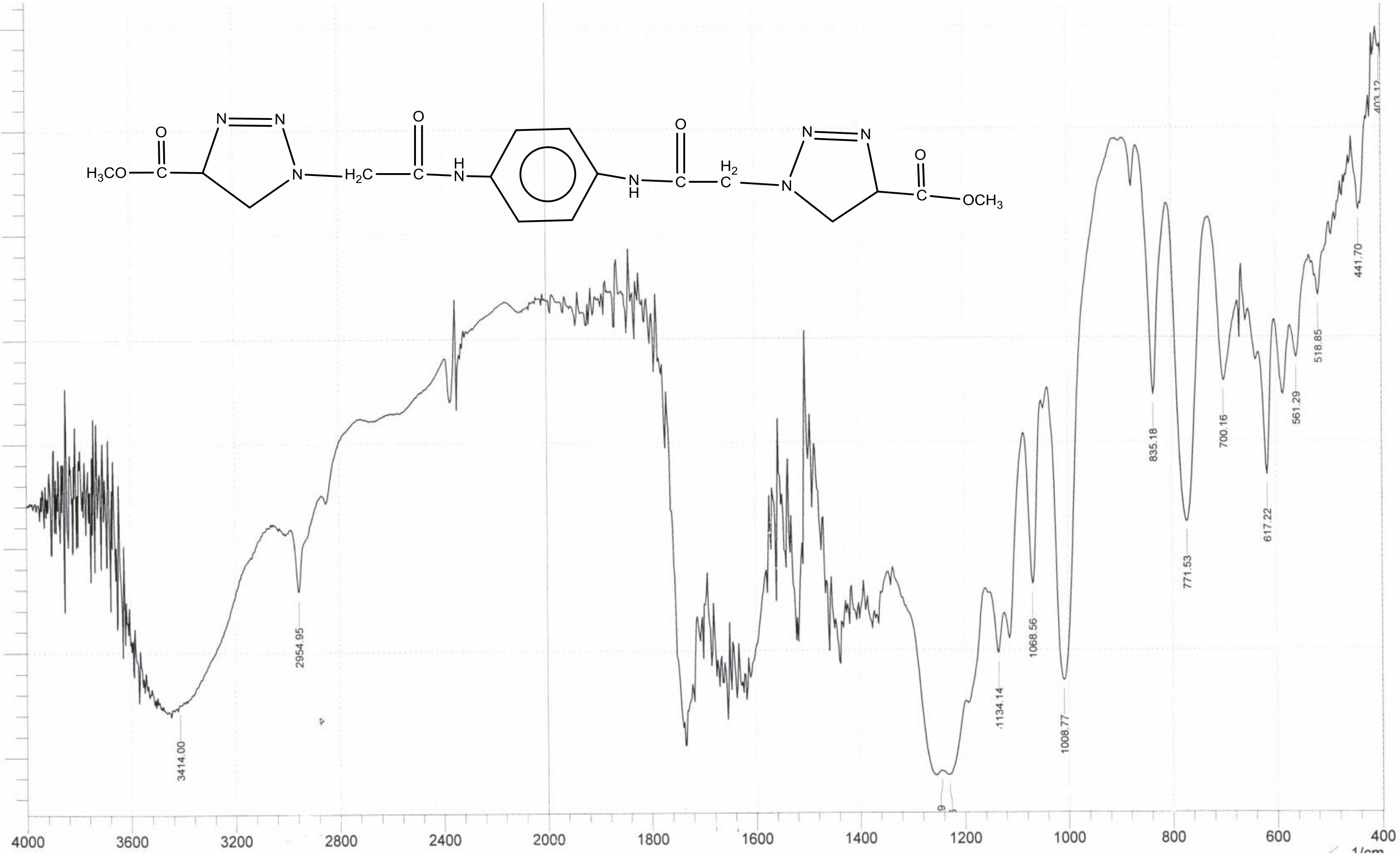


Figure (3-8) FT-IR spectrum for compound[IV]$_b$

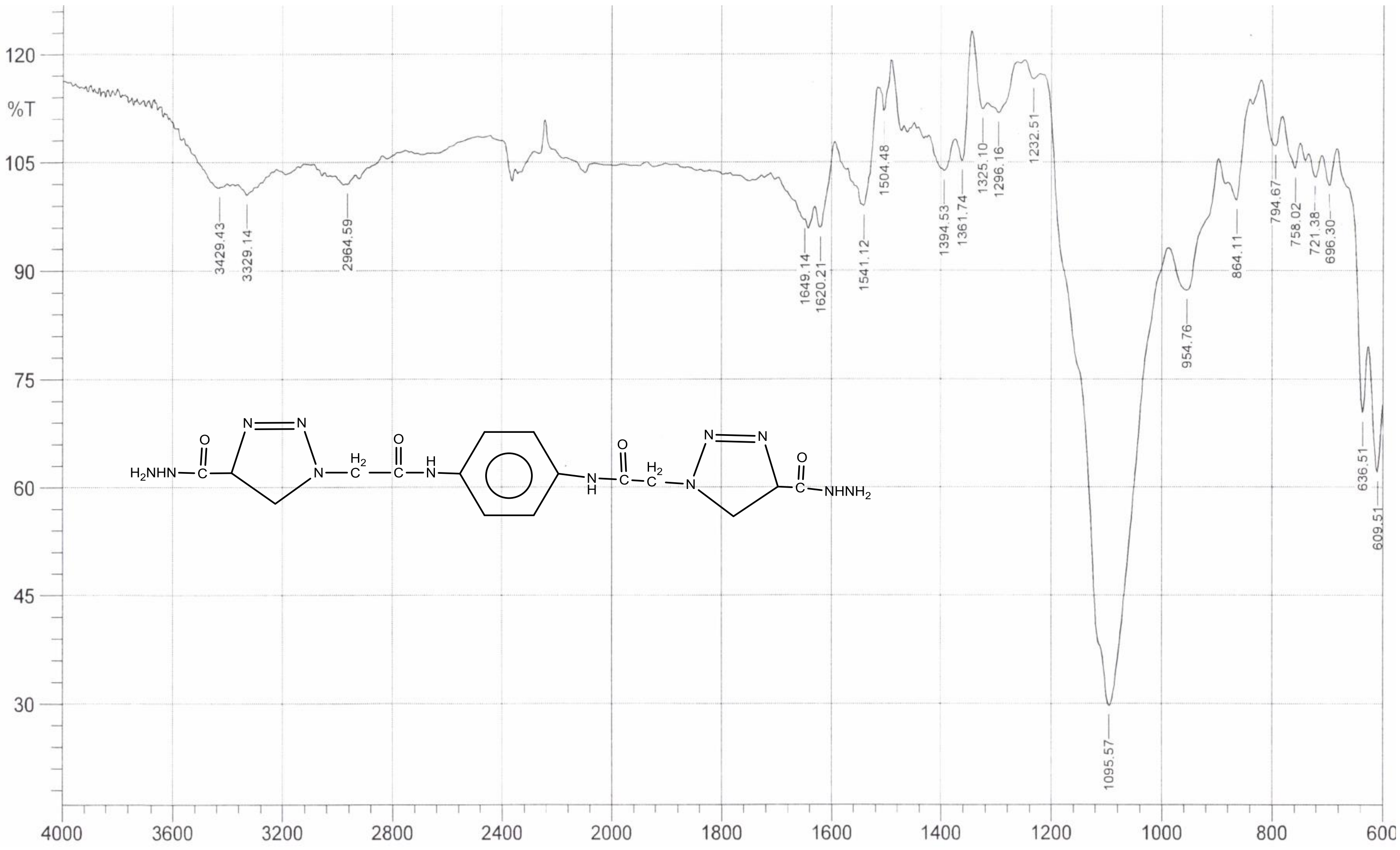


Figure (3-9) FT-IR spectrum for compound[V]$_b$

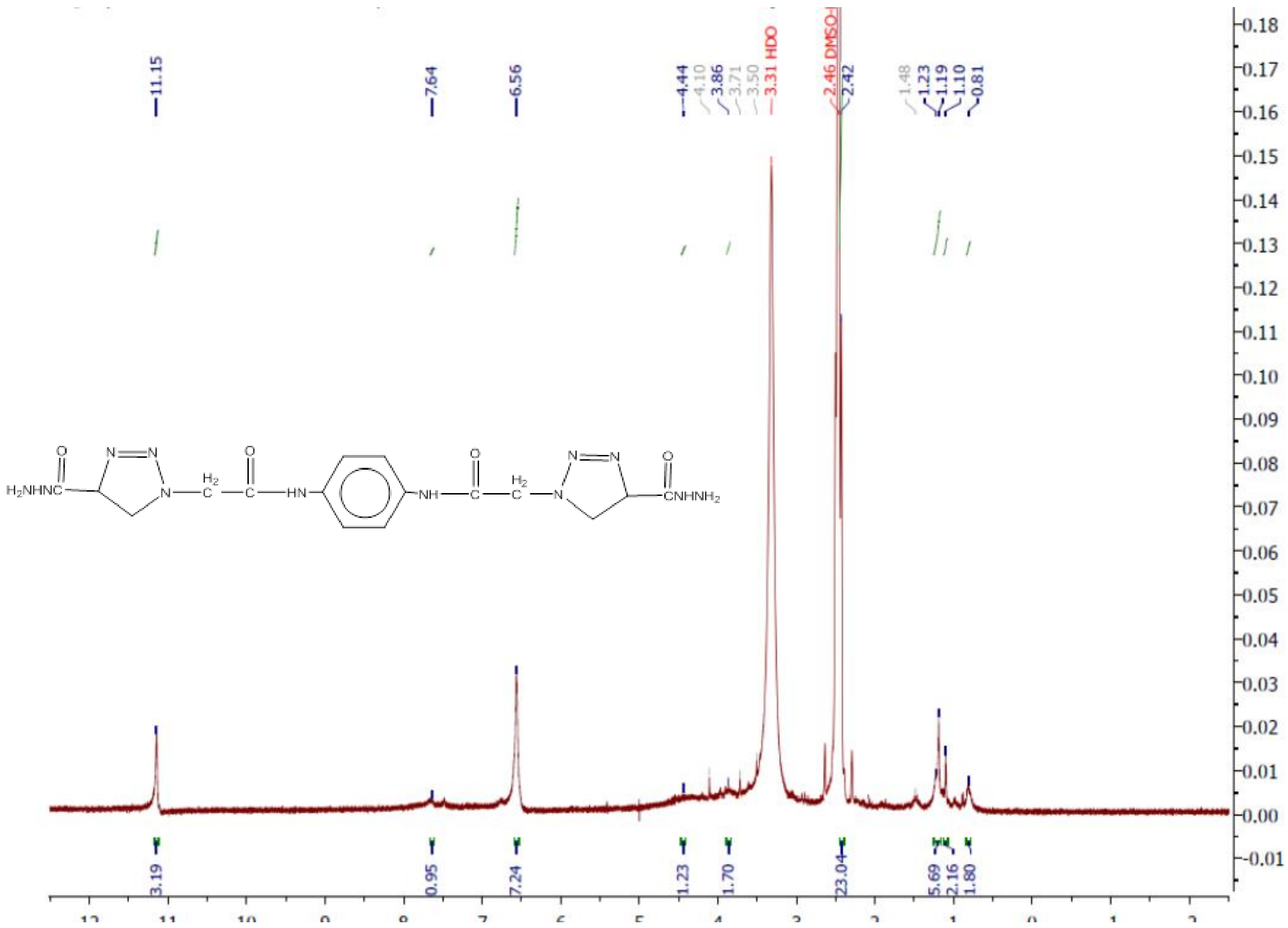


Figure (3-10) ^{1}HNMR spectrum for compound[V]$_b$

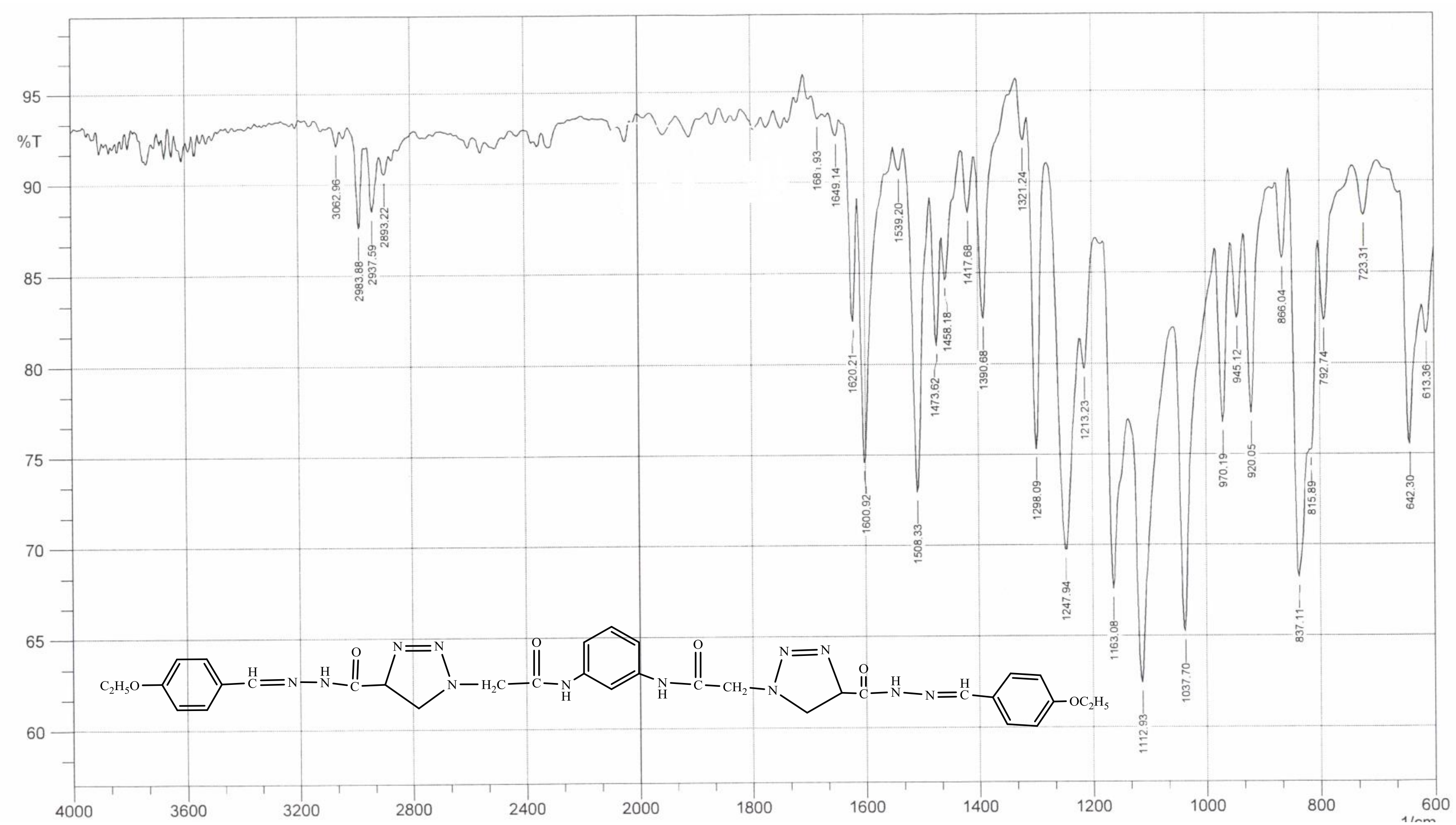


Figure (3-11) FT-IR spectrum for compound[VII]$_2$

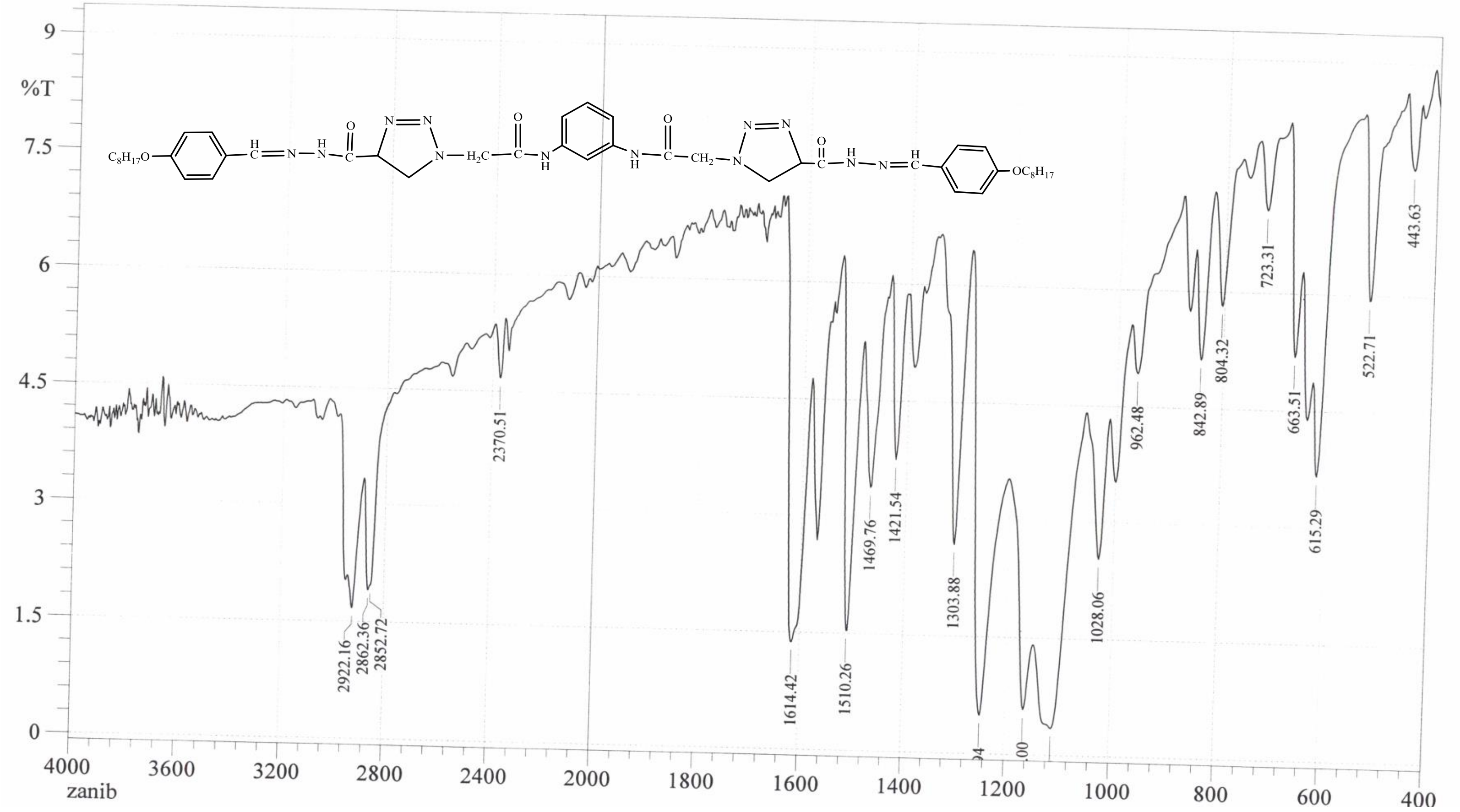


Figure (3-12) FT-IR spectrum for compound[VII]$_8$

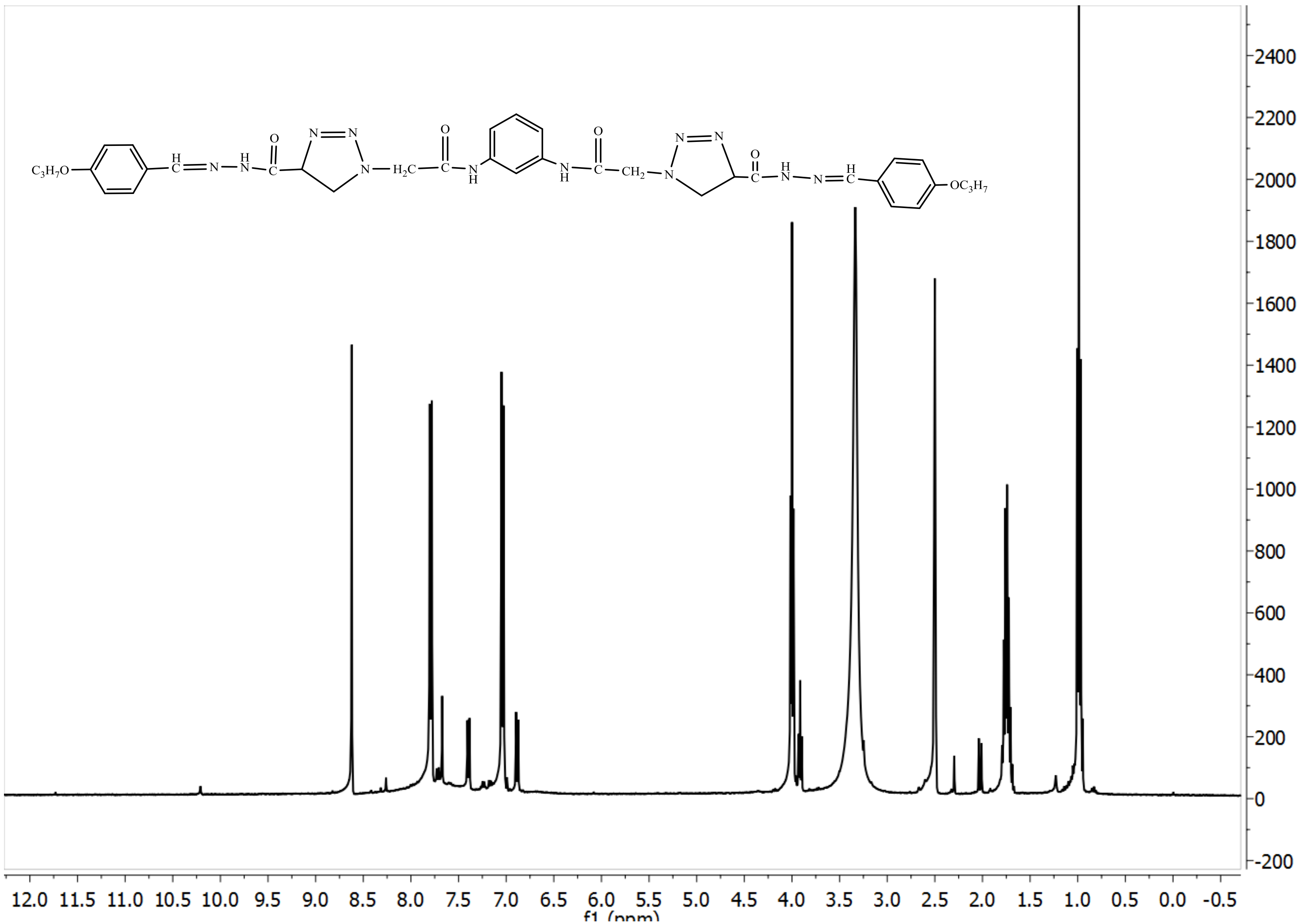


Figure (3-13) ^{1}HNMR spectrum for compound[VII]$_3$

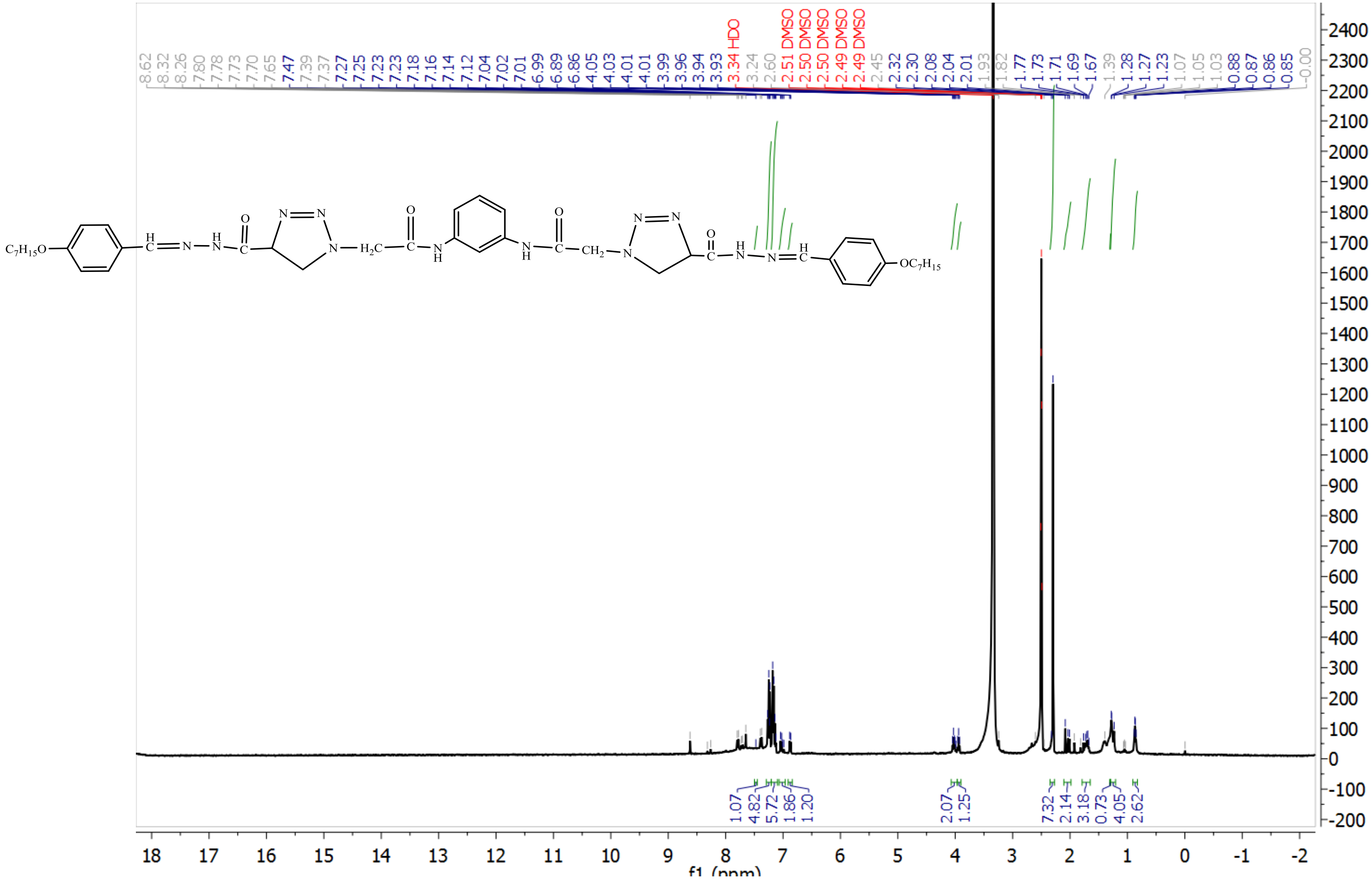


Figure (3-14) ^{1}HNMR spectrum for compound[VII]$_7$

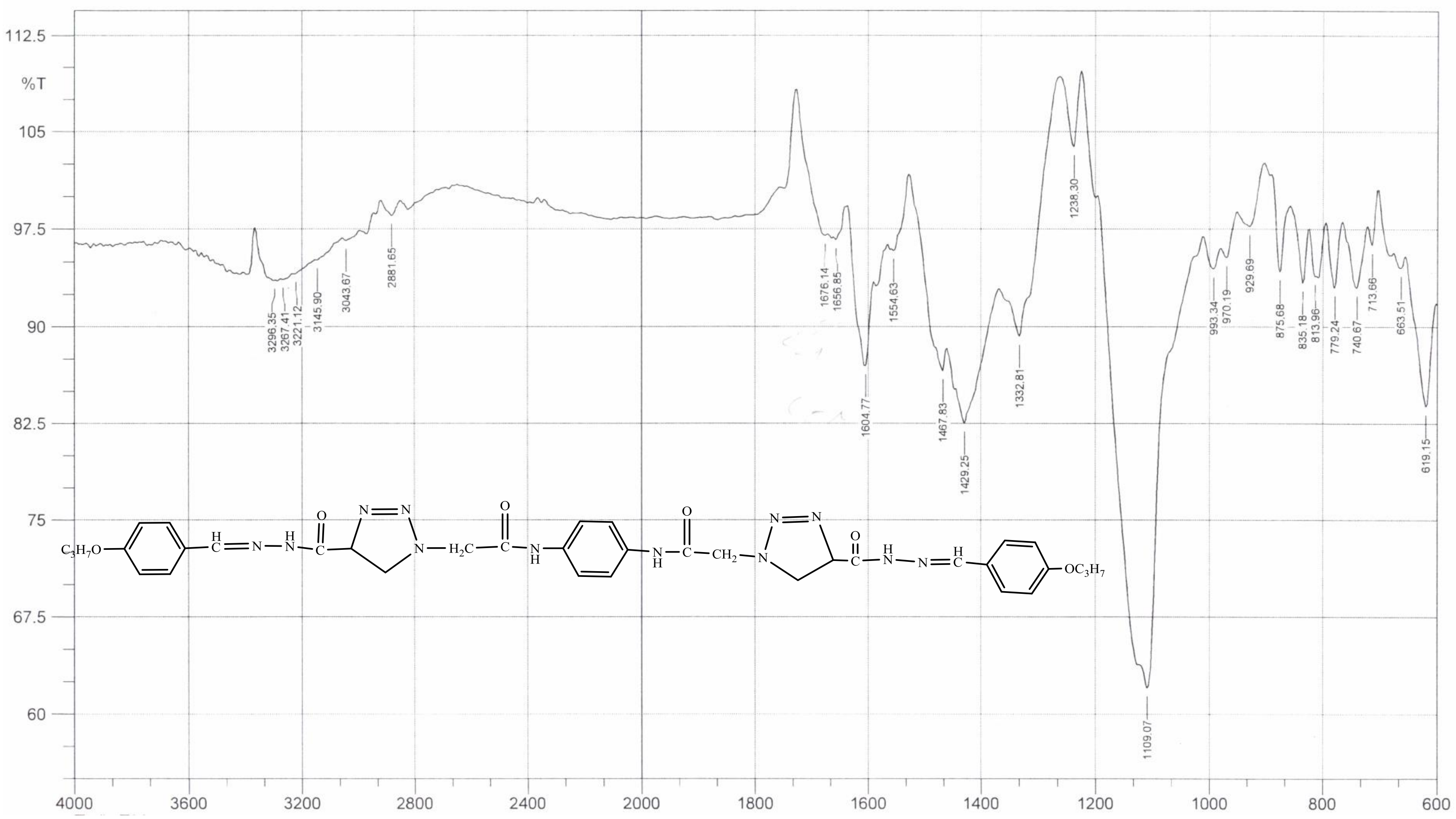


Figure (3-15) FT-IR spectrum for compound[VIII]₃

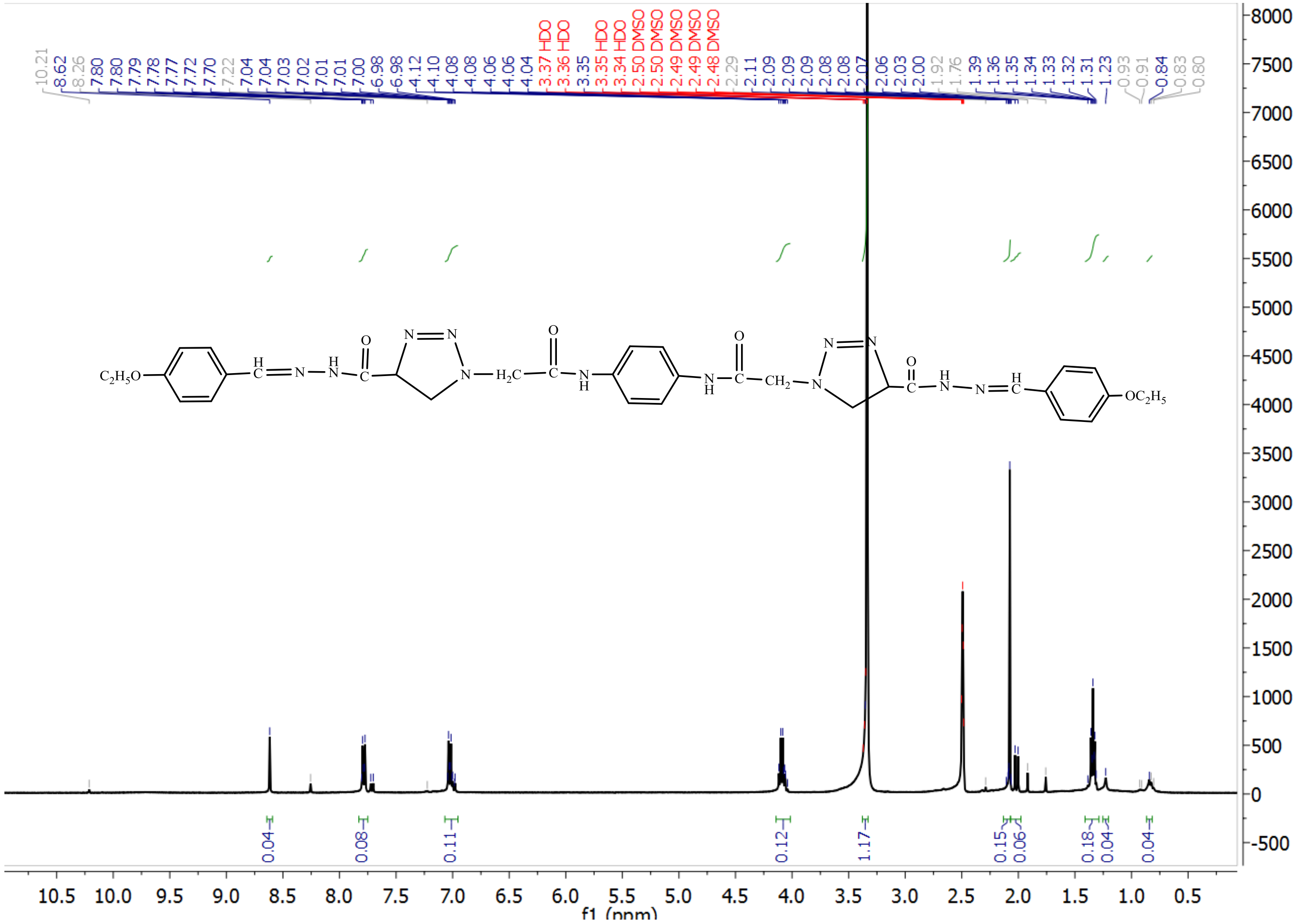


Figure (3-16) ^{1}HNMR spectrum for compound[VIII]$_2$

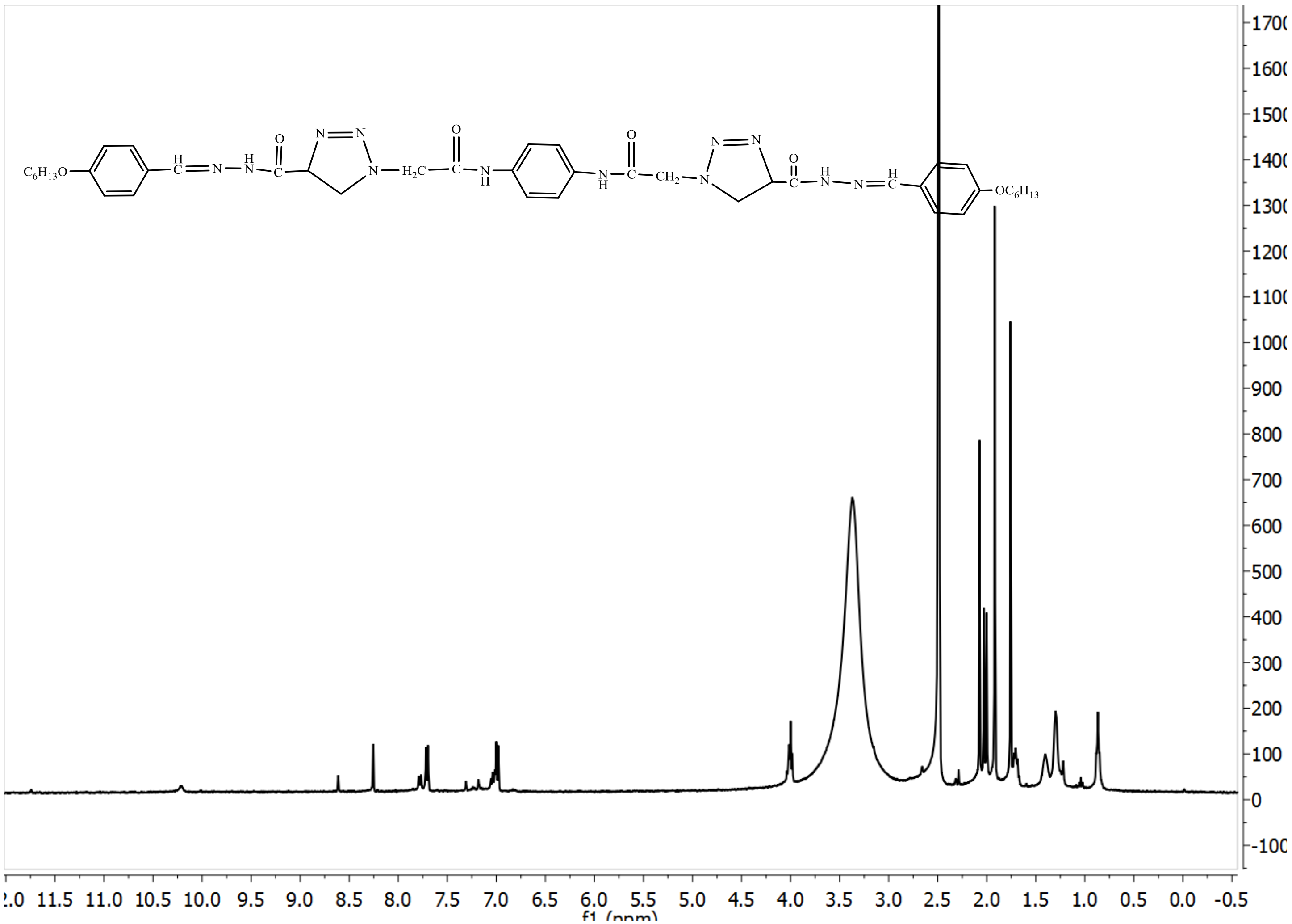


Figure (3-17) ^{1}HNMR spectrum for compound[VIII]$_6$

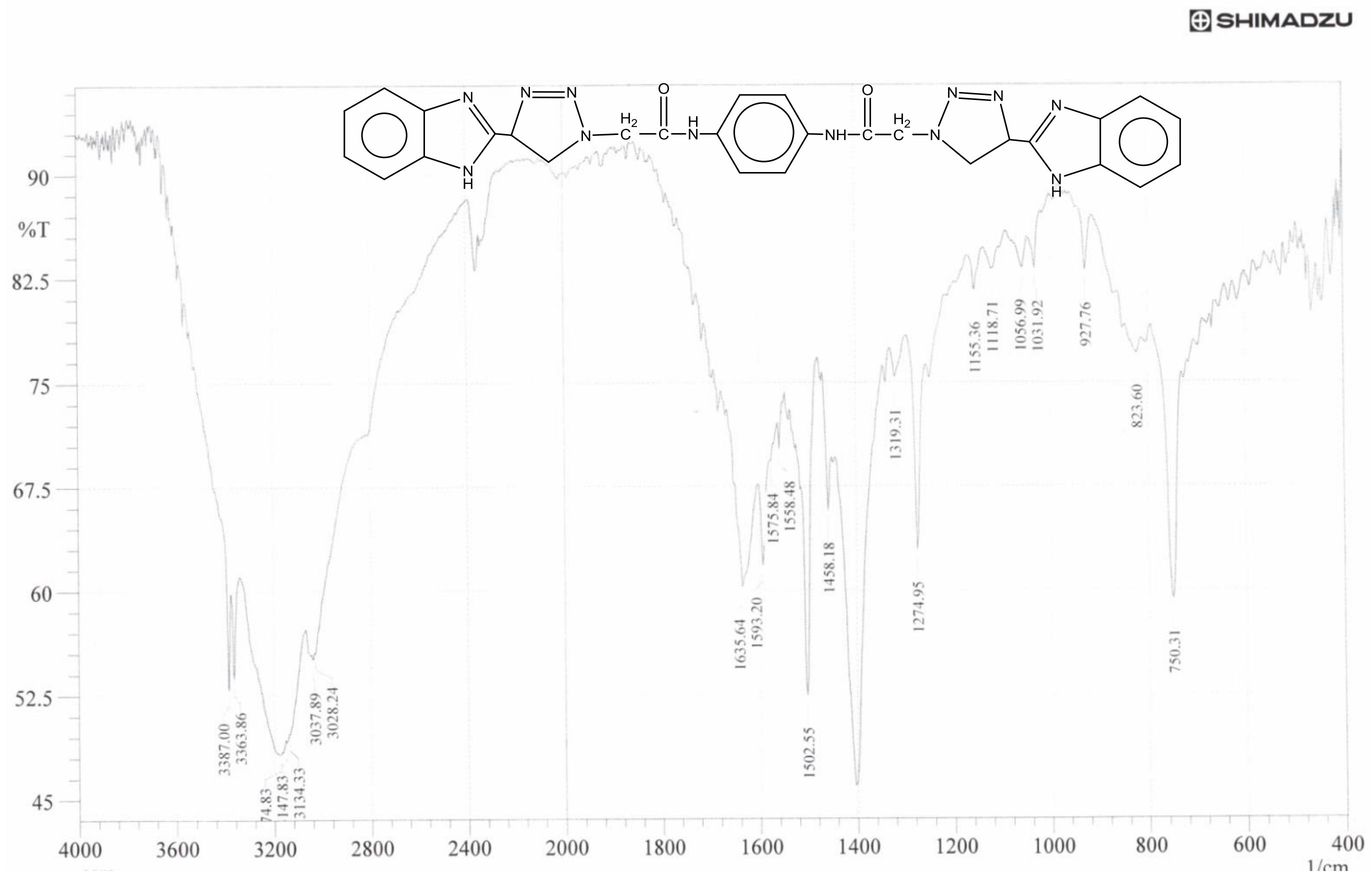


Figure (3-18) FT-IR spectrum for compound[IX]$_b$

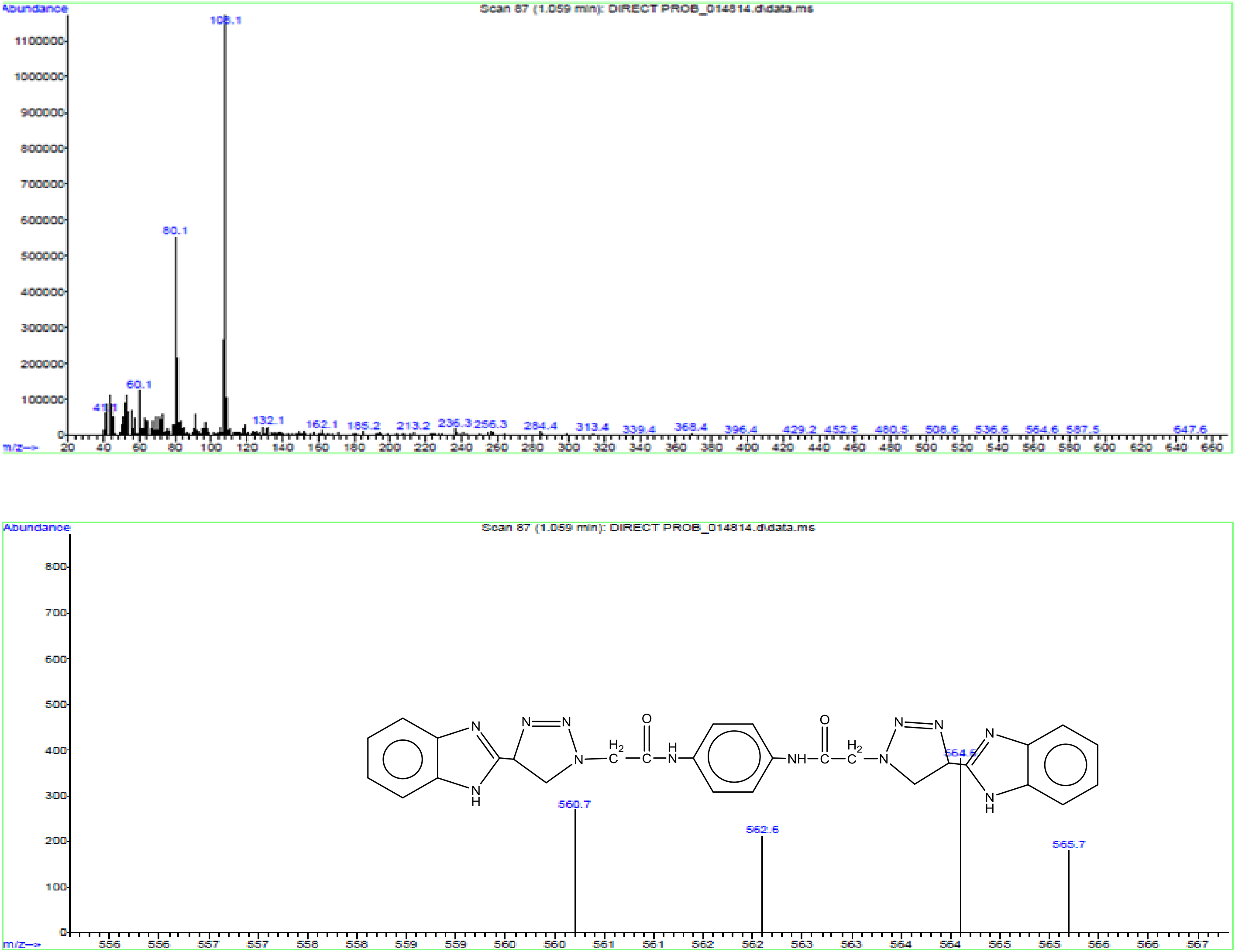


Figure (3-19) mass spectrum for compound [IX]

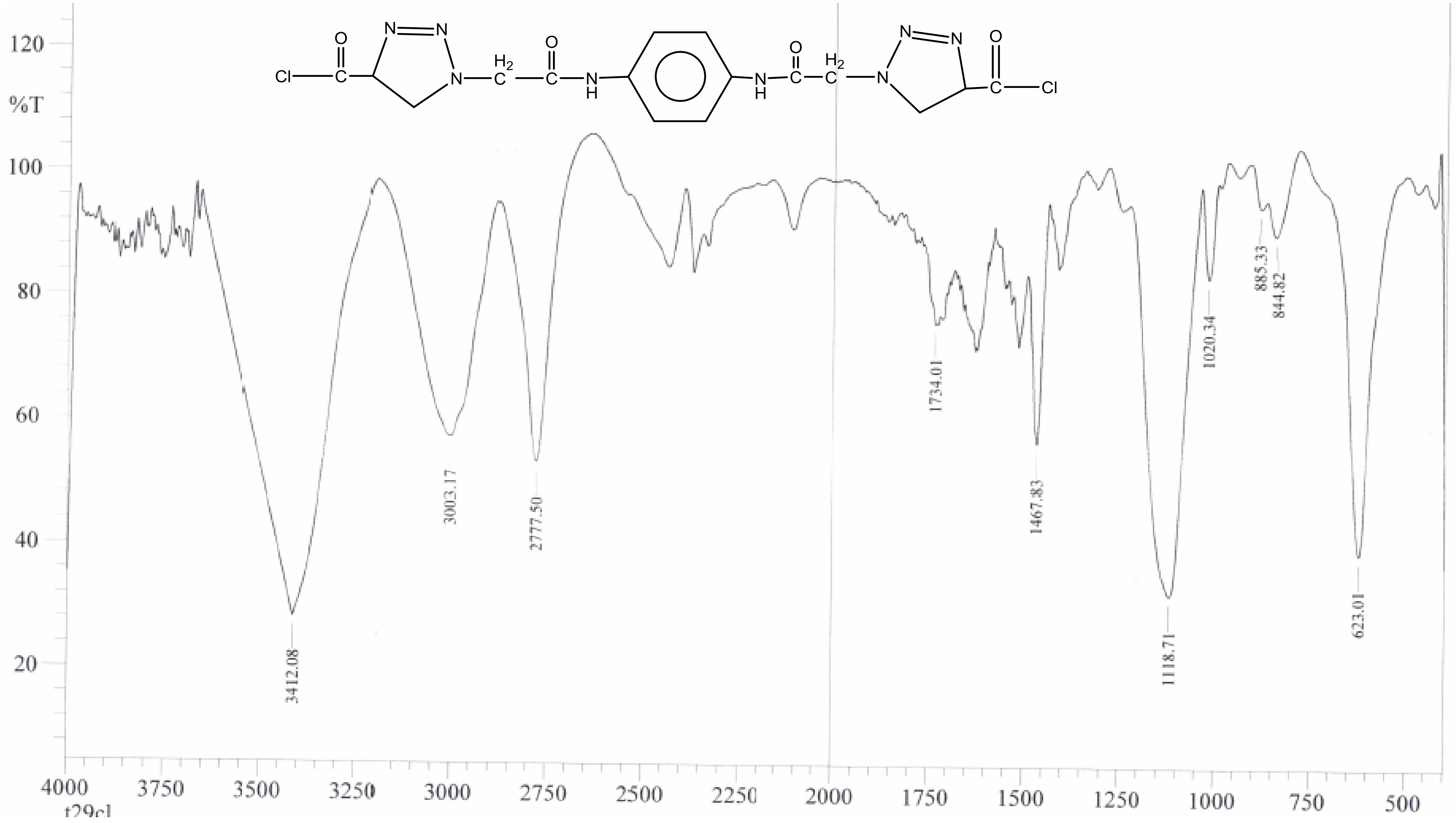


Figure (3-20) FT-IR spectrum for compound[X]$_b$

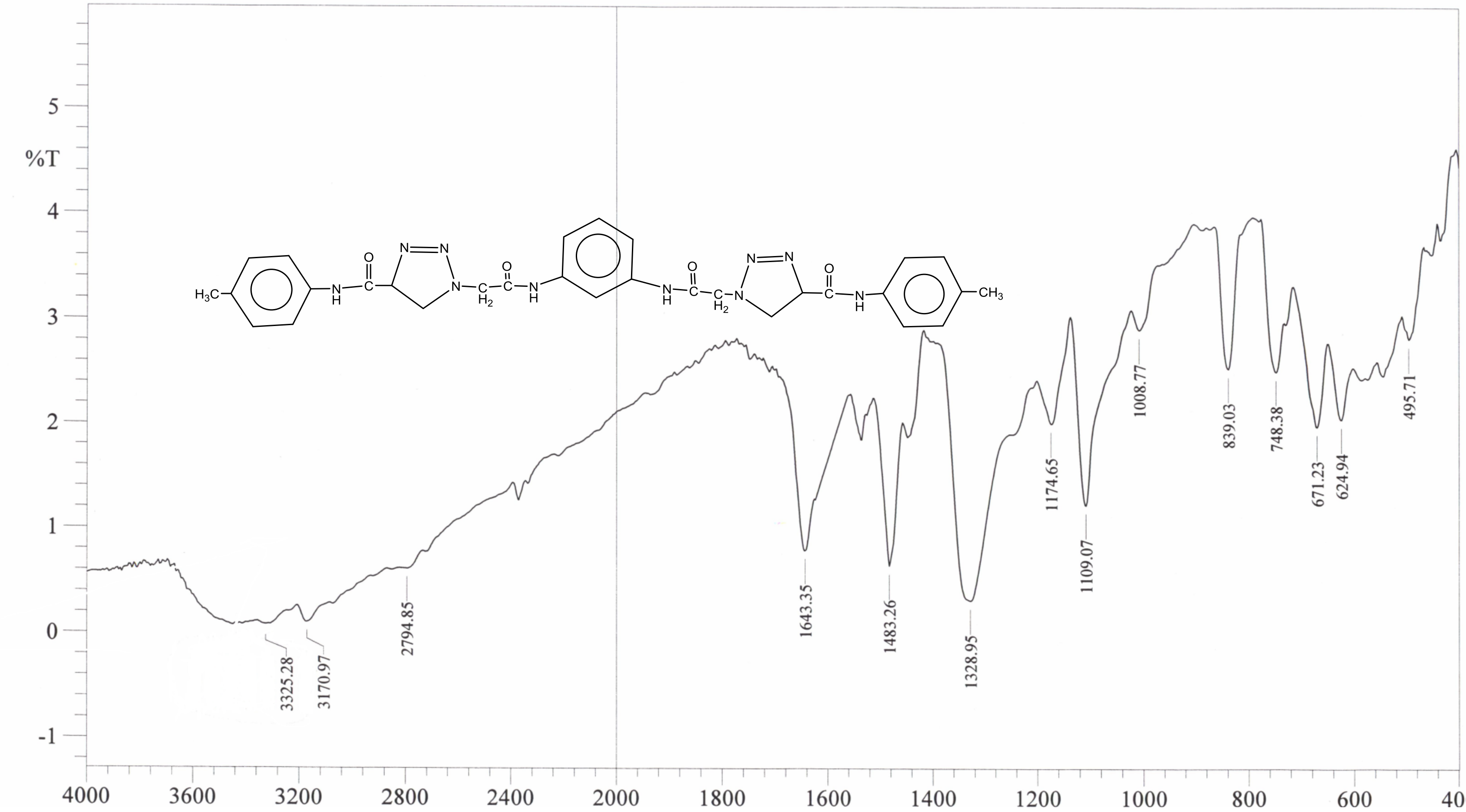


Figure (3-21) FT-IR spectrum for compound[XI]$_a$

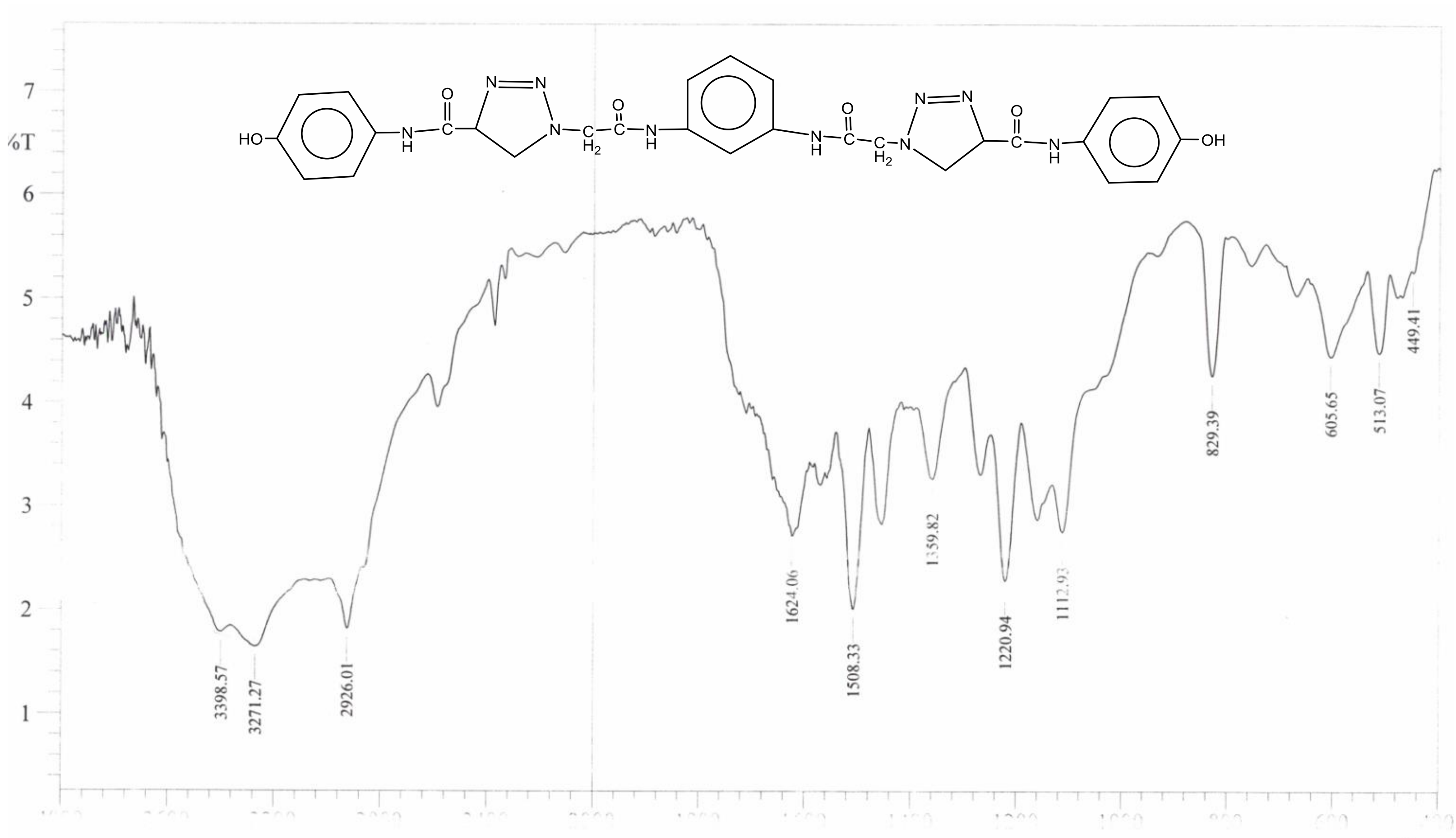


Figure (3-22) FT-IR spectrum for compound[XI]$_c$

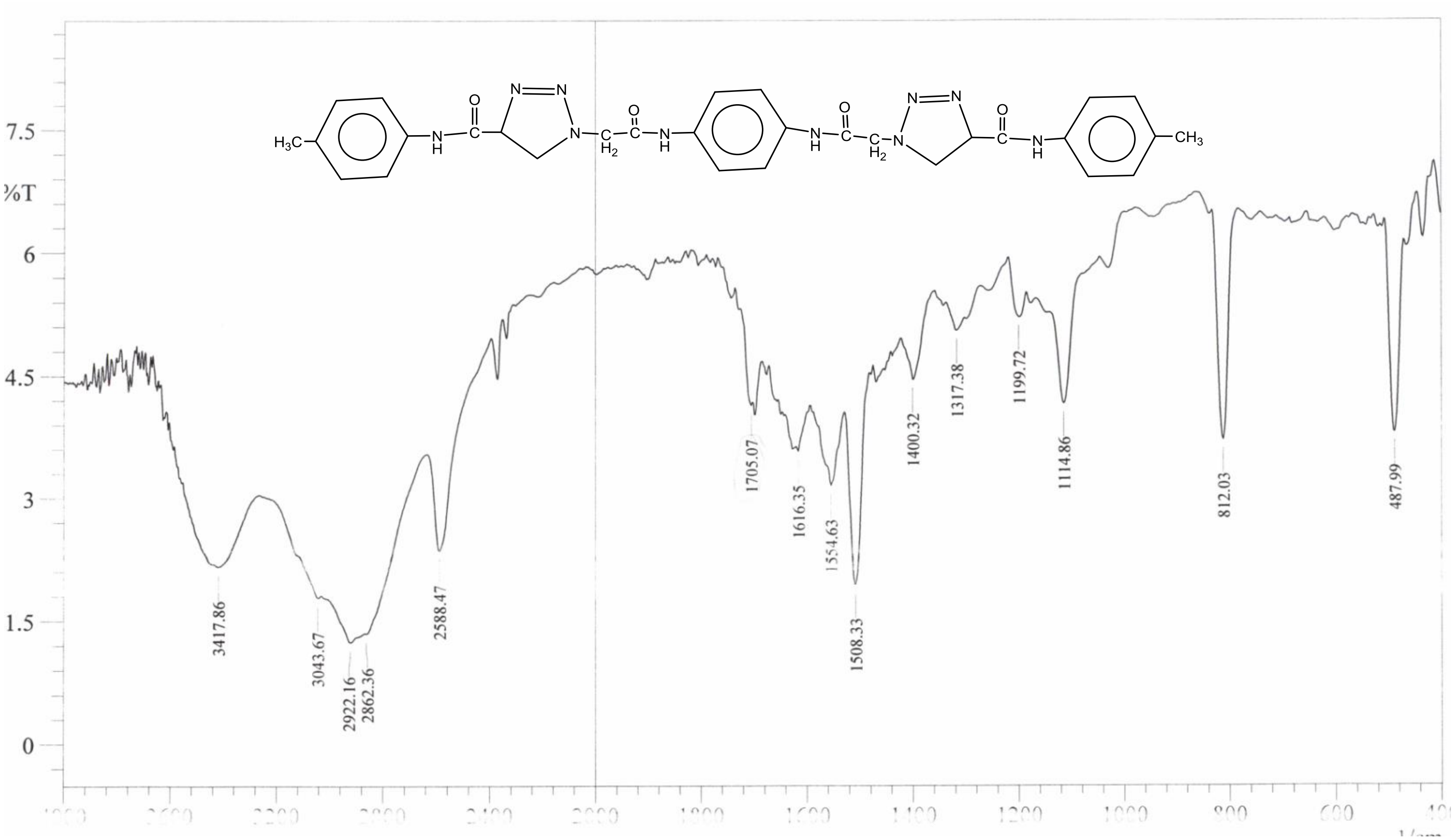


Figure (3-23) FT-IR spectrum for compound[XII]$_a$

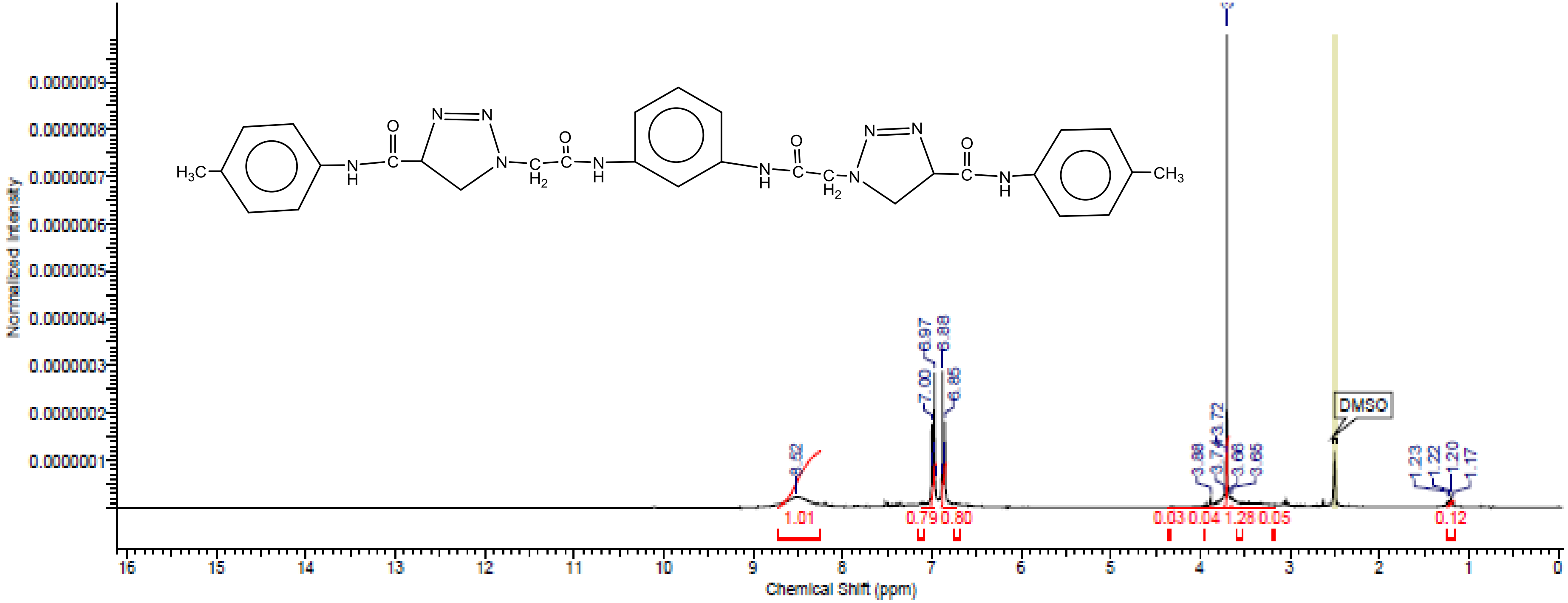


Figure (3-24) ^{1}HNMR spectrum for compound[XI]$_a$

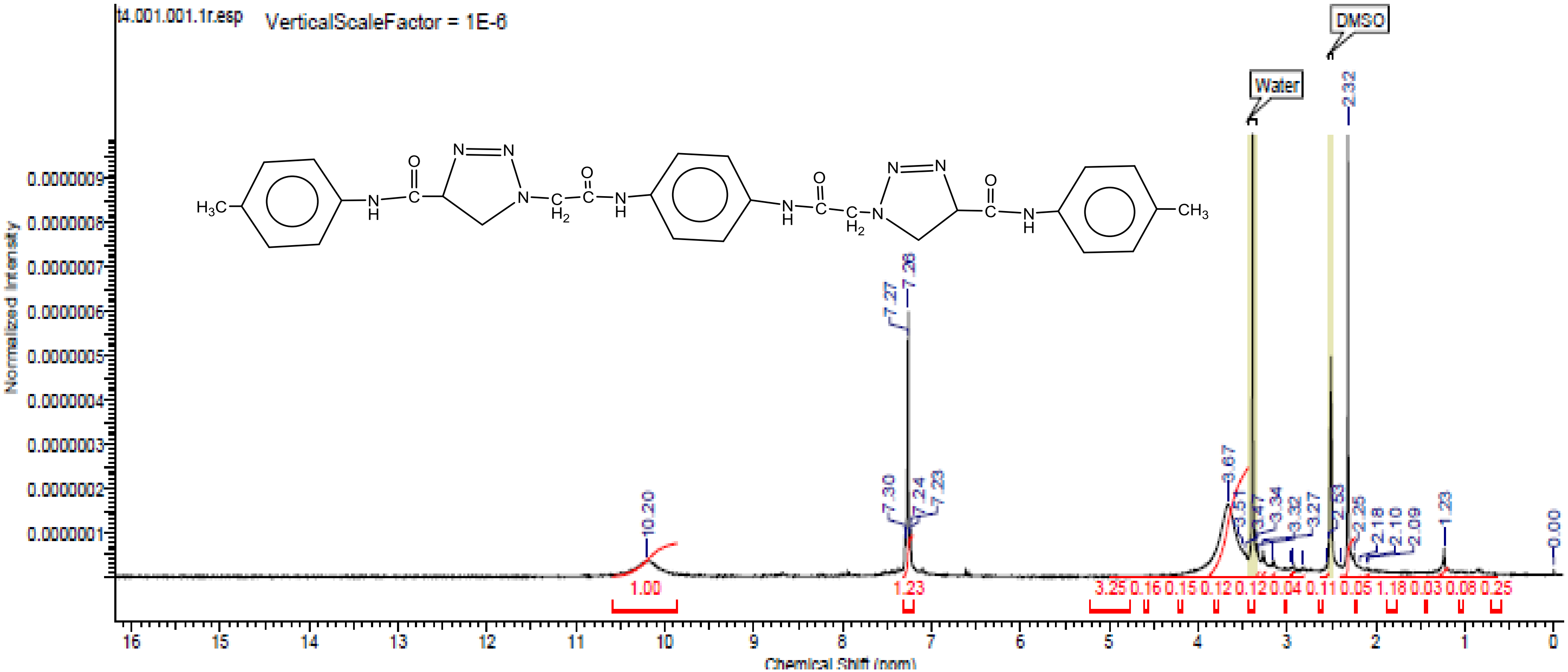


Figure (3-25) ^{1}HNMR spectrum for compound[XII]$_a$

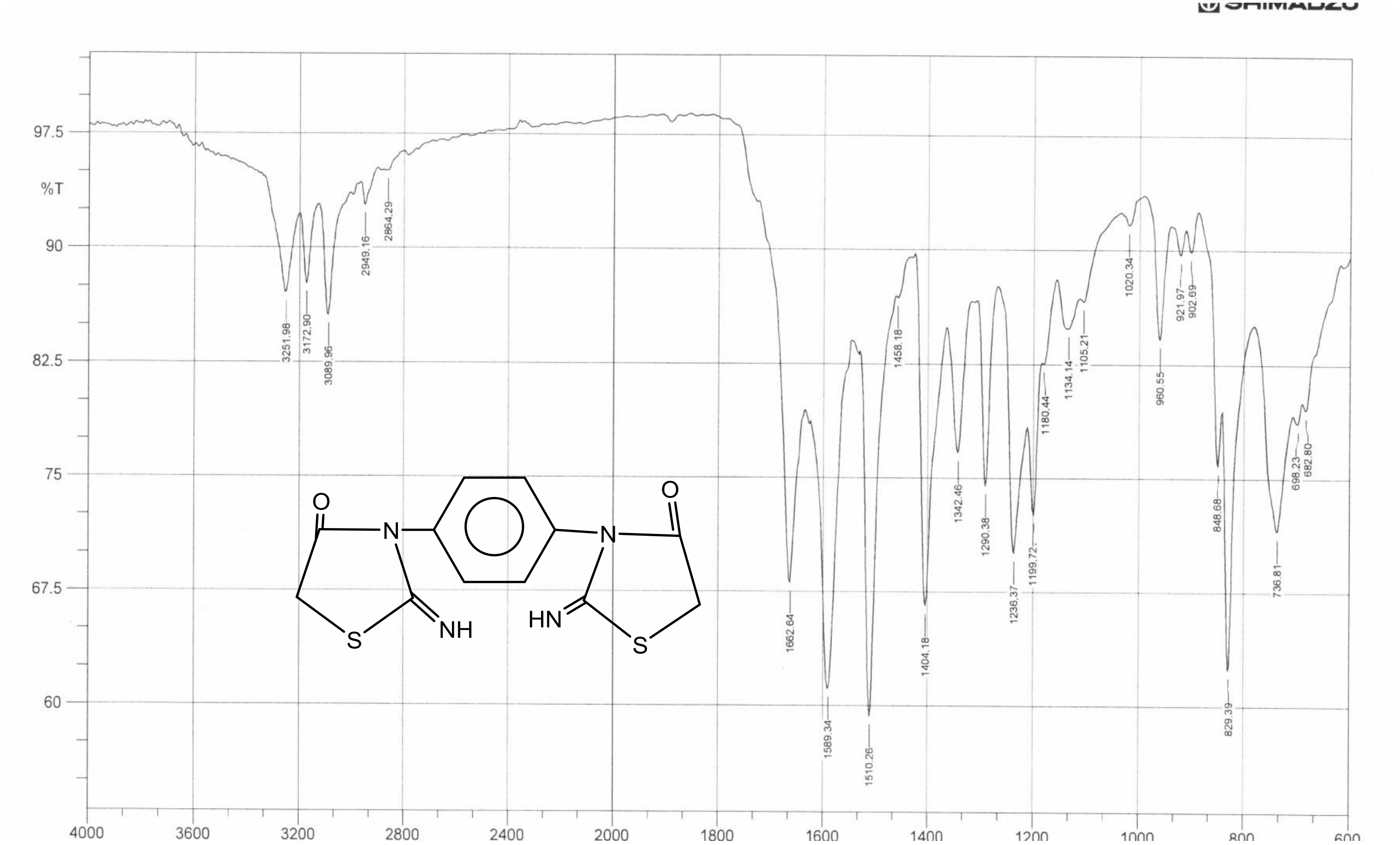


Figure (3-26) FTIR spectrum for compound[XIII]$_b$

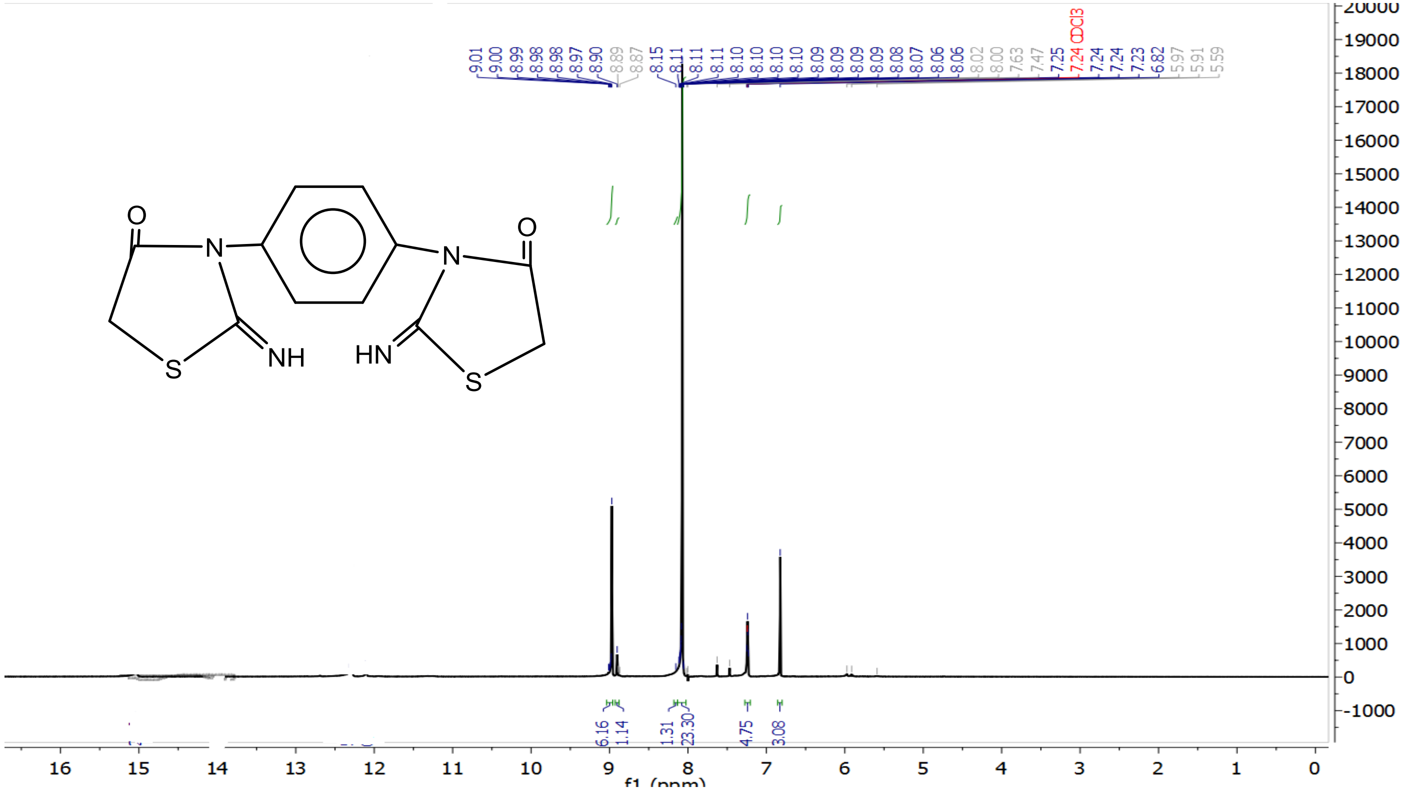


Figure (3-27) ^{1}HNMR spectrum for compound[XIII]$_b$

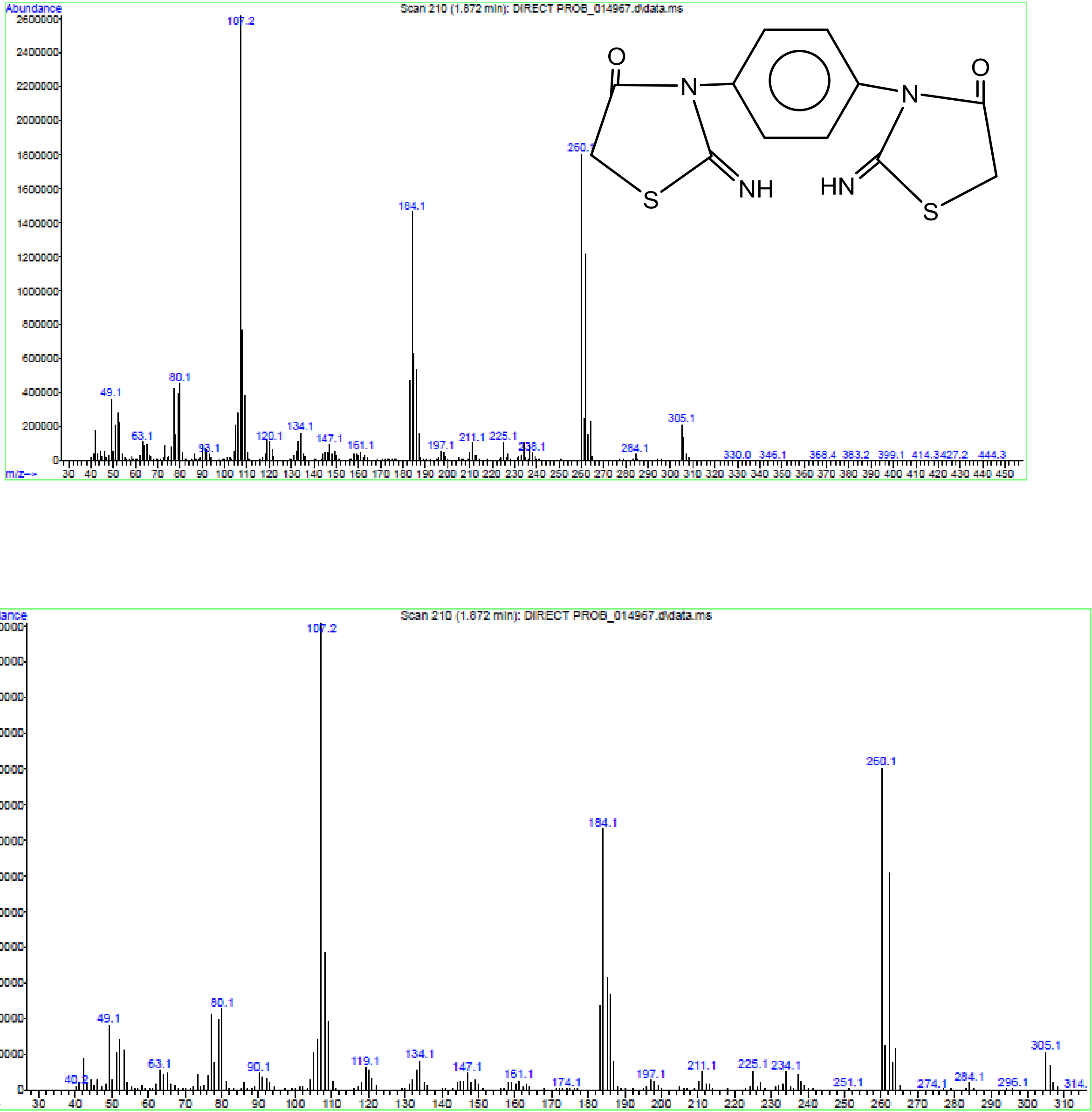


Figure (3-28) mass spectrum for compound [XIII]$_b$

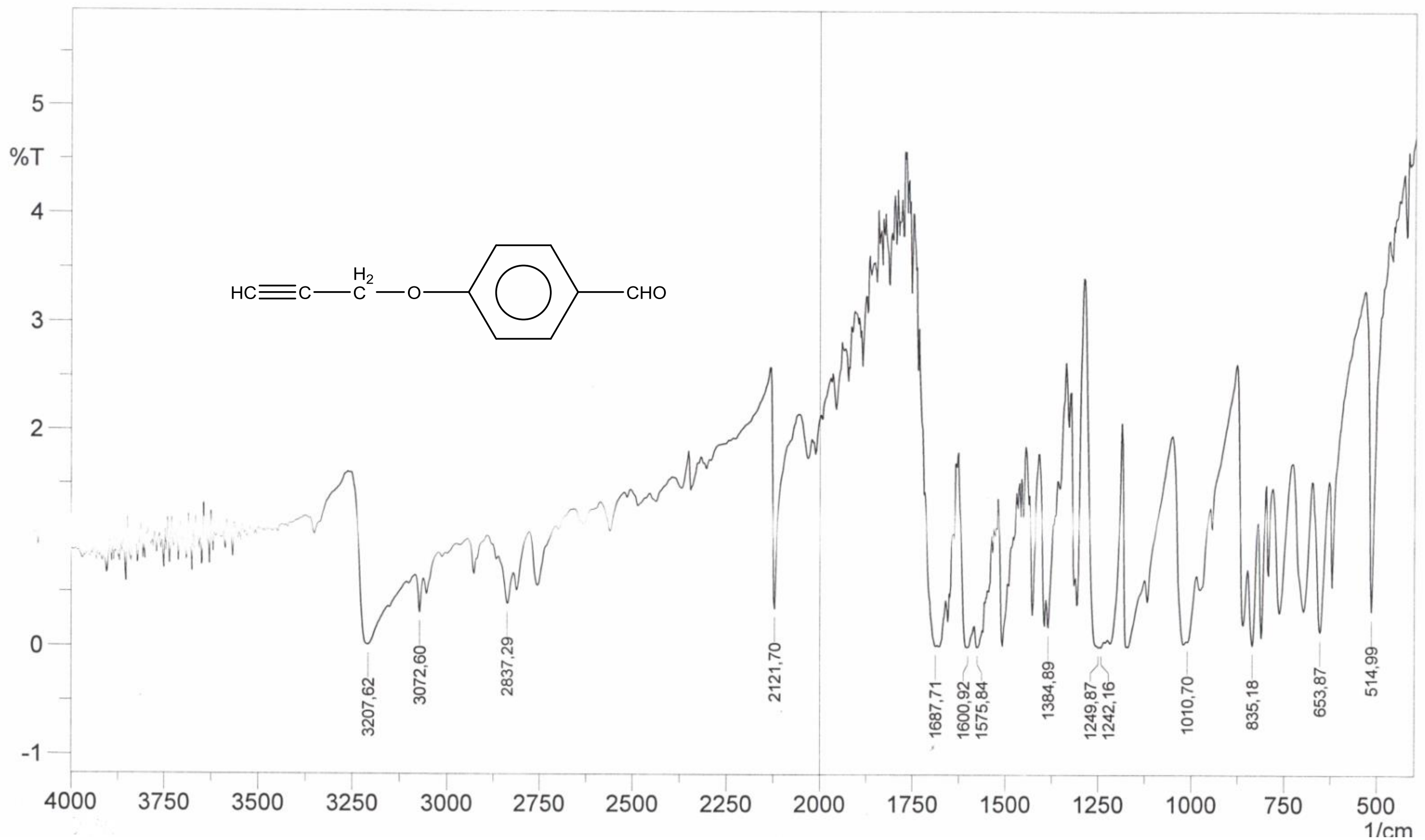


Figure (3-29) FT-IR spectrum for compound [XIV]

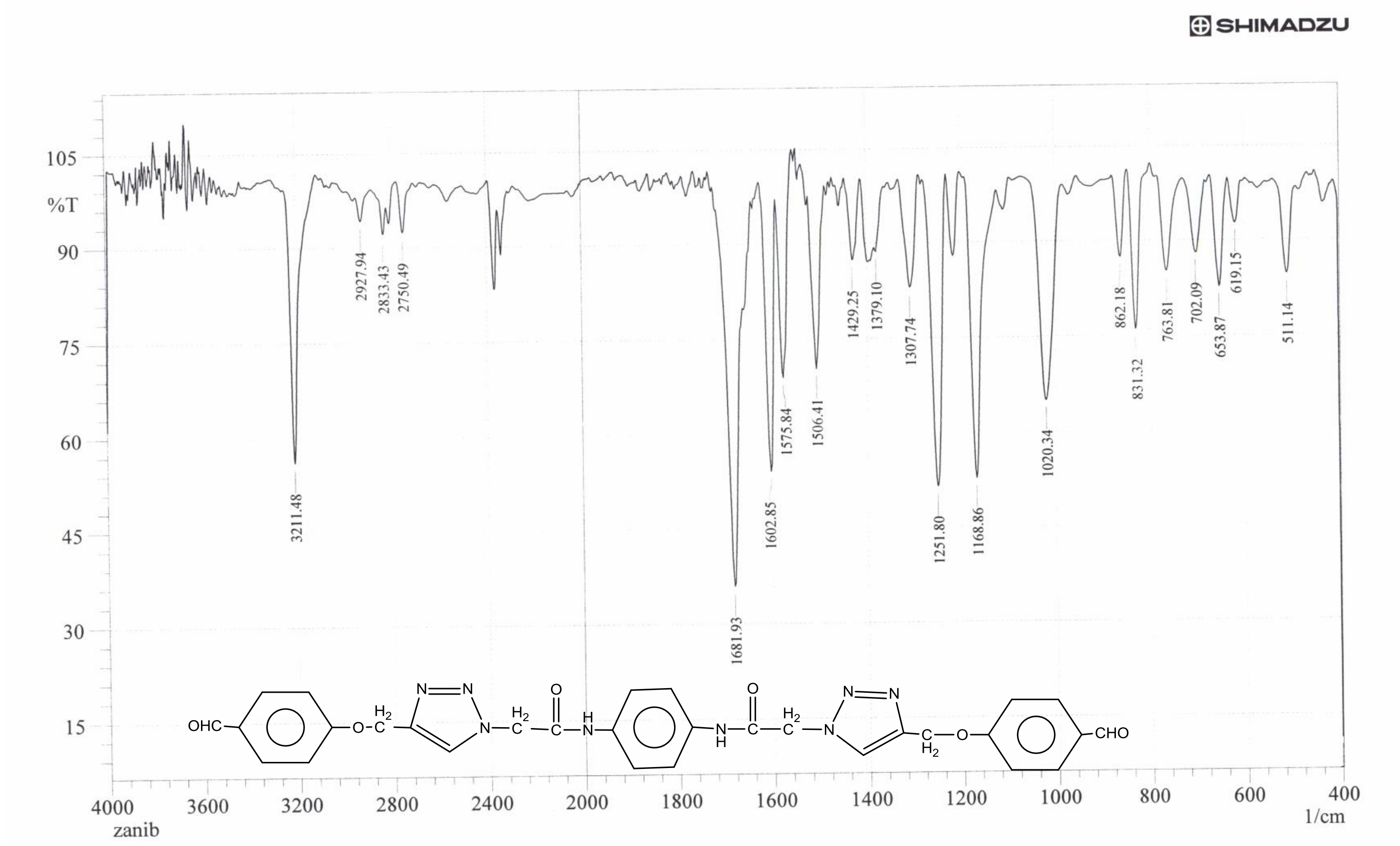


Figure (3-30) FT-IR spectrum for compound[XV]$_b$

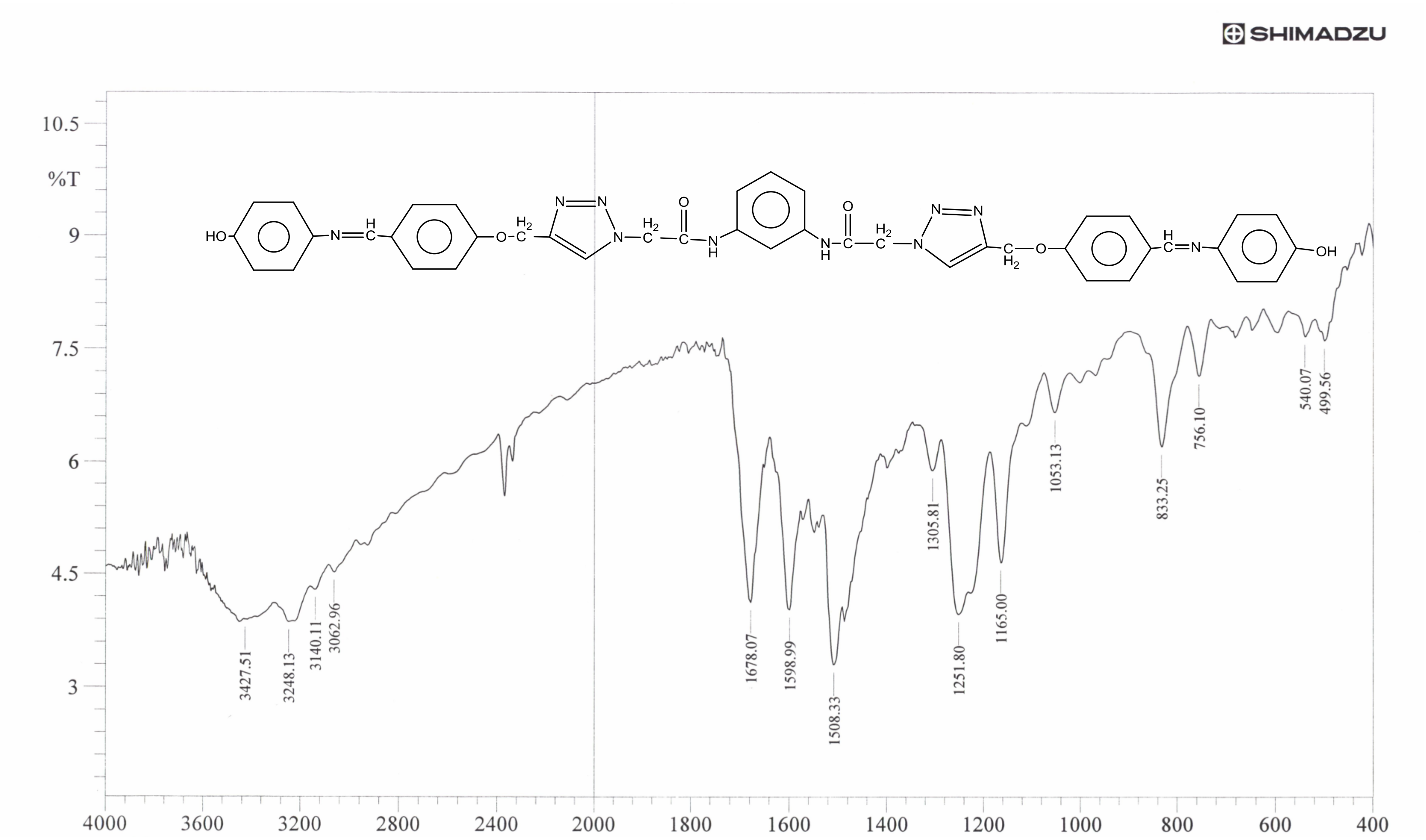


Figure (3-31) FT-IR spectrum for compound[XVI]$_c$

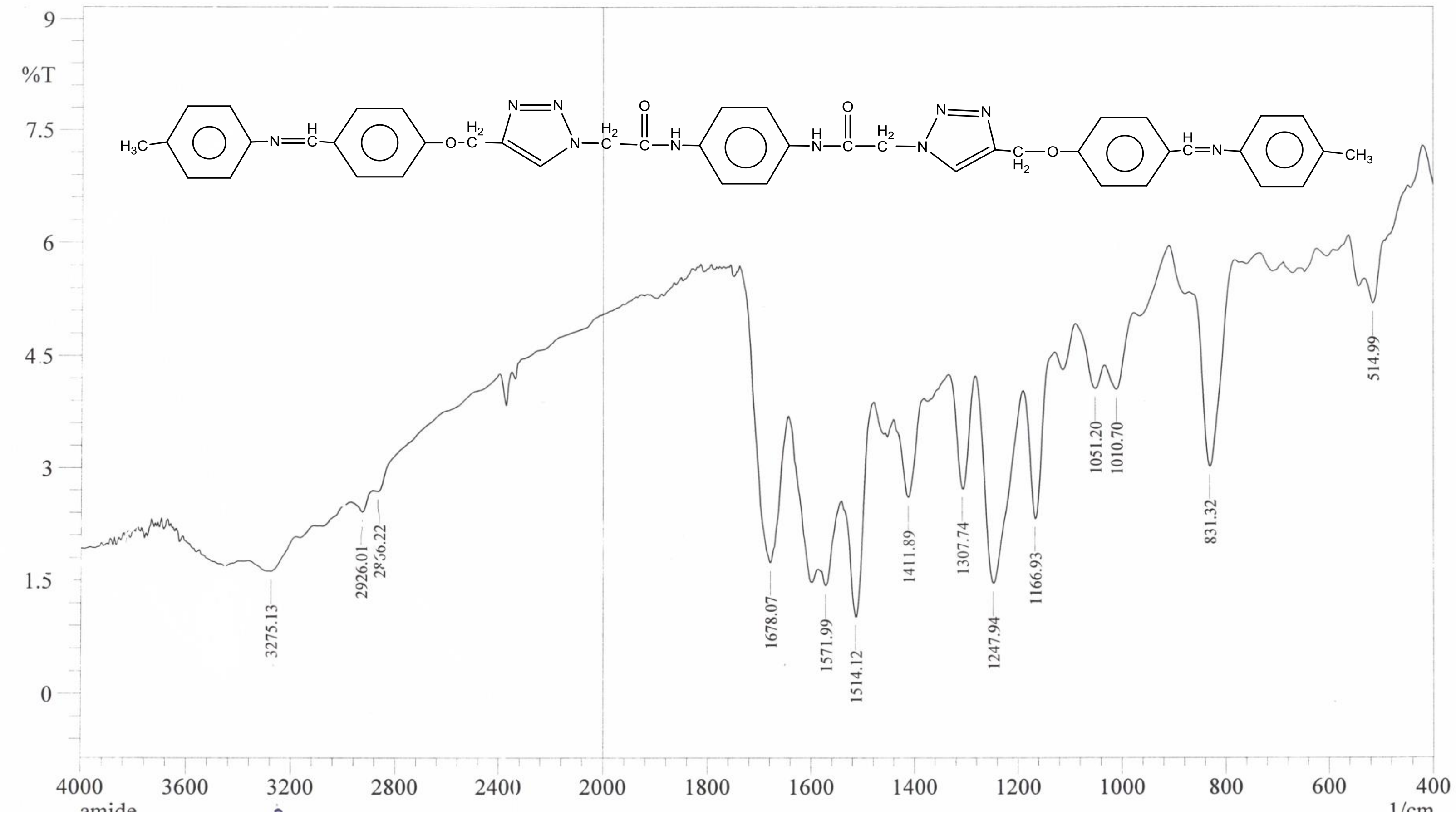


Figure (3-32) FT-IR spectrum for compound[XVII]$_a$

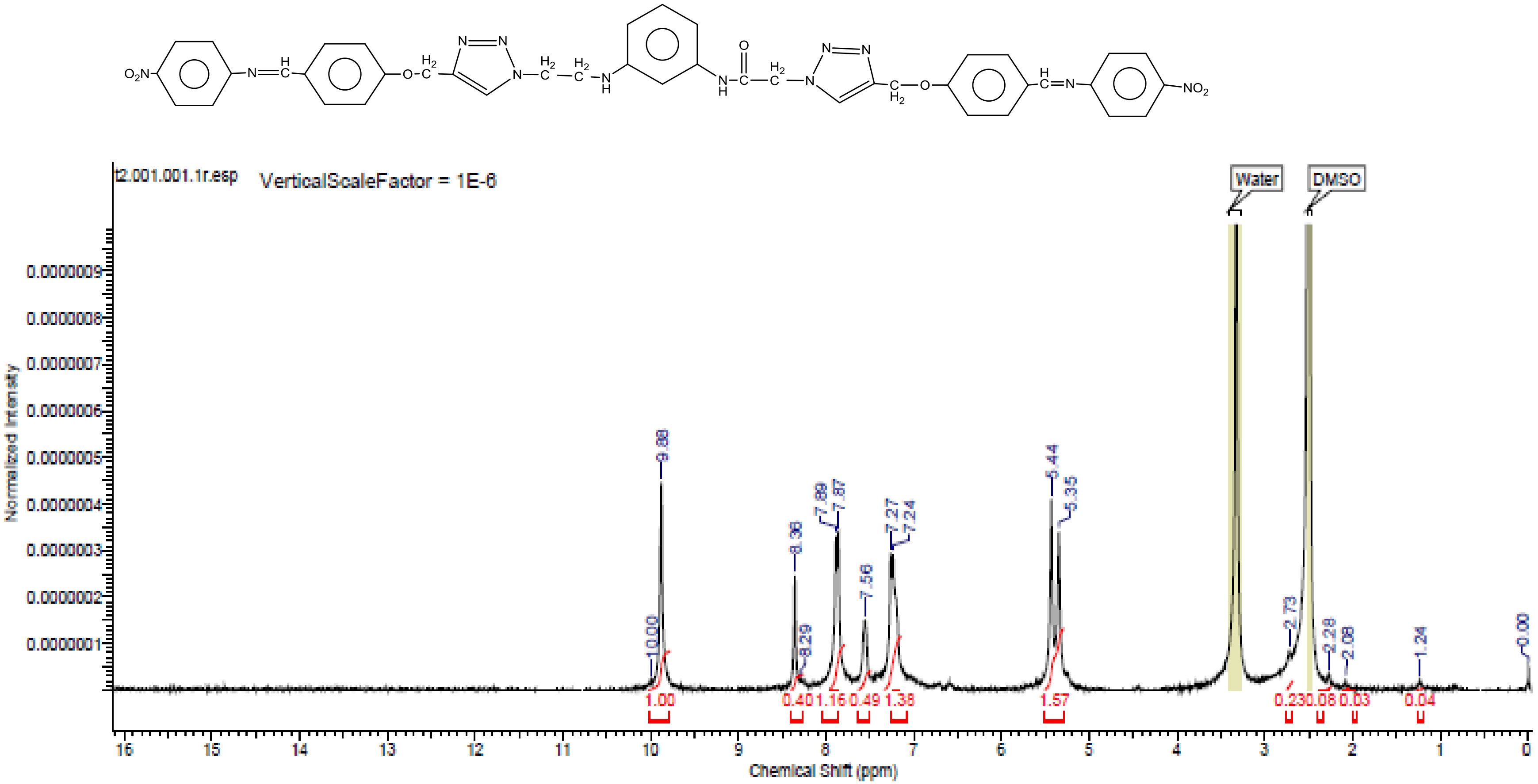


Figure (3-33) ^{1}HNMR spectrum for compound[XVI]$_d$

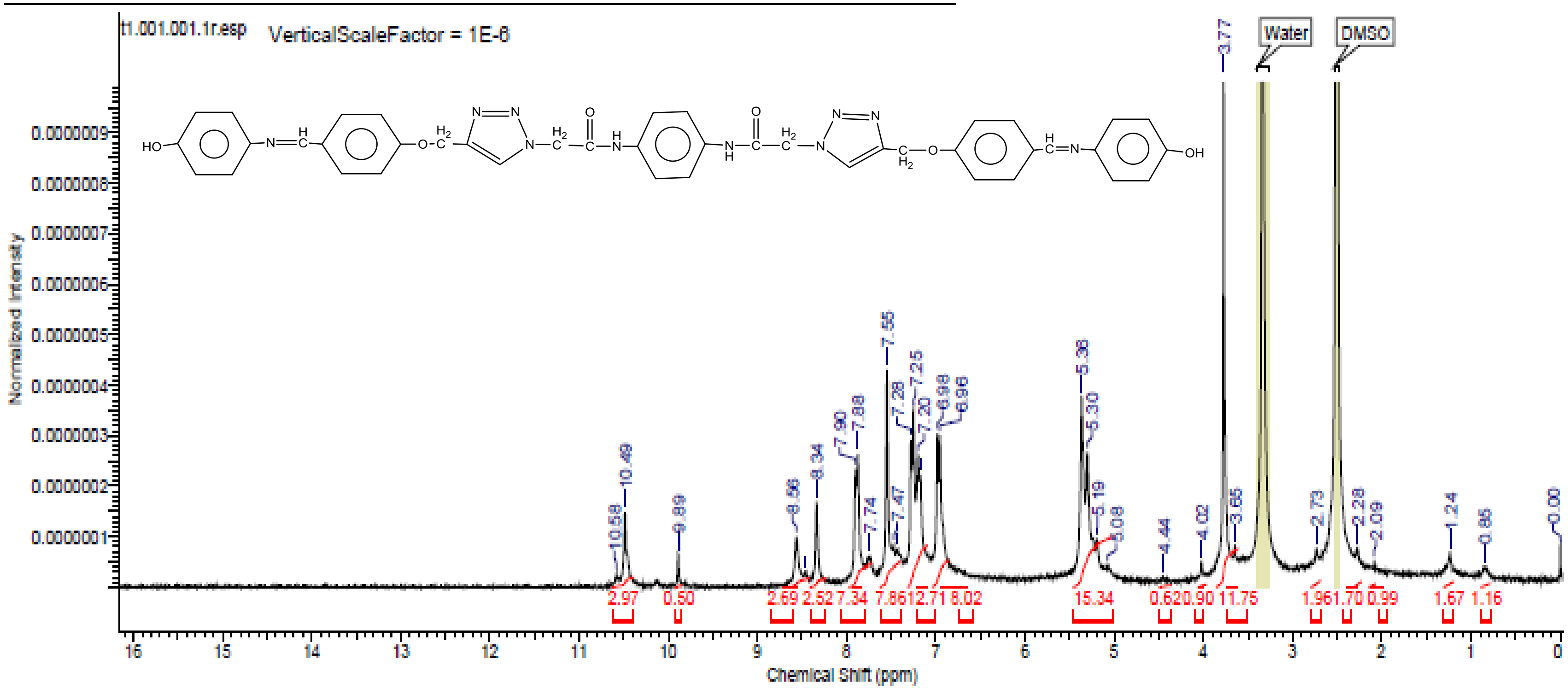


Figure (3-34) ^{1}**HNMR spectrum for compound[XVII]$_{c}$**

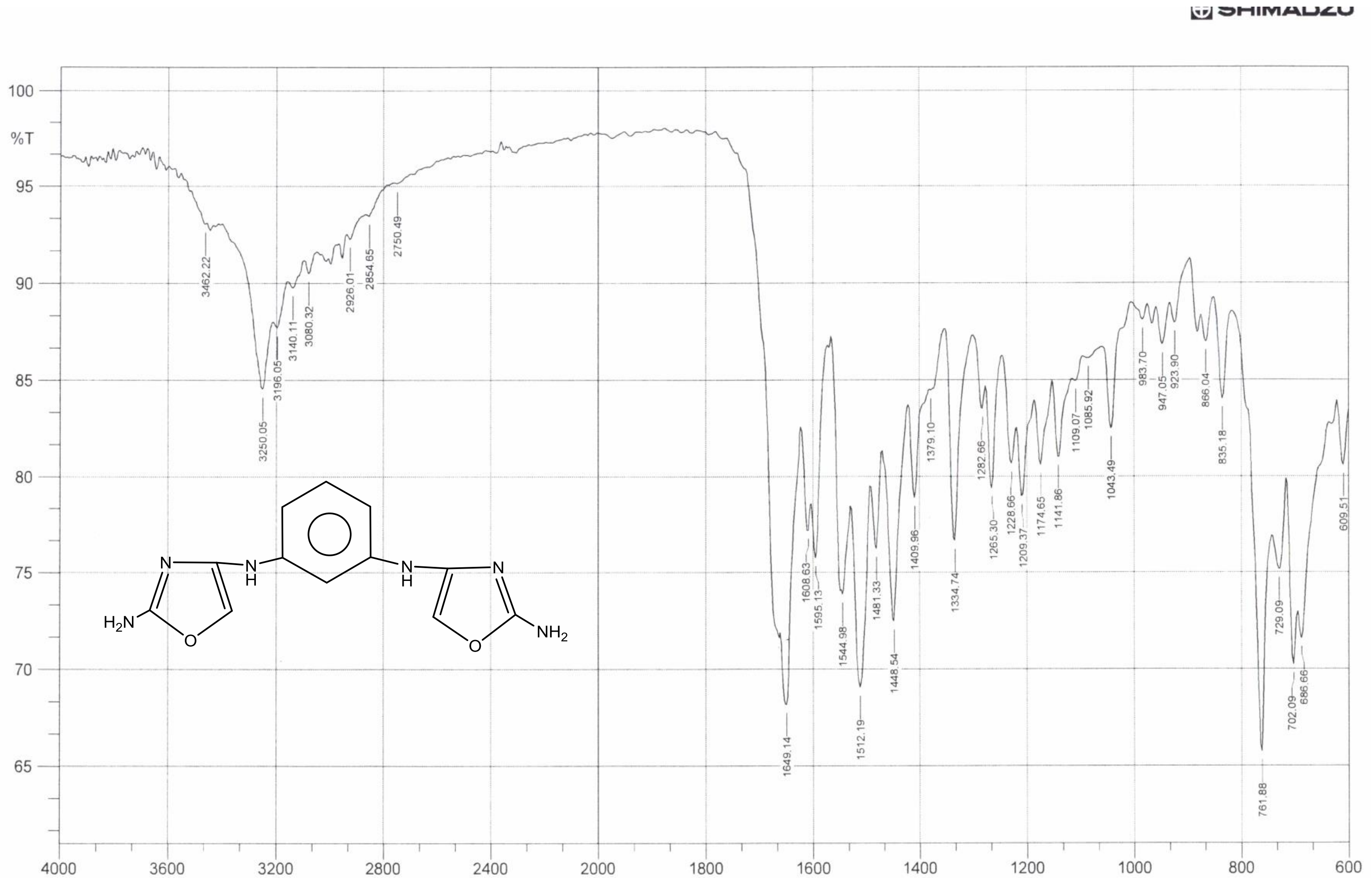


Figure (3-35) FT-IR spectrum for compound[XVIII]$_a$

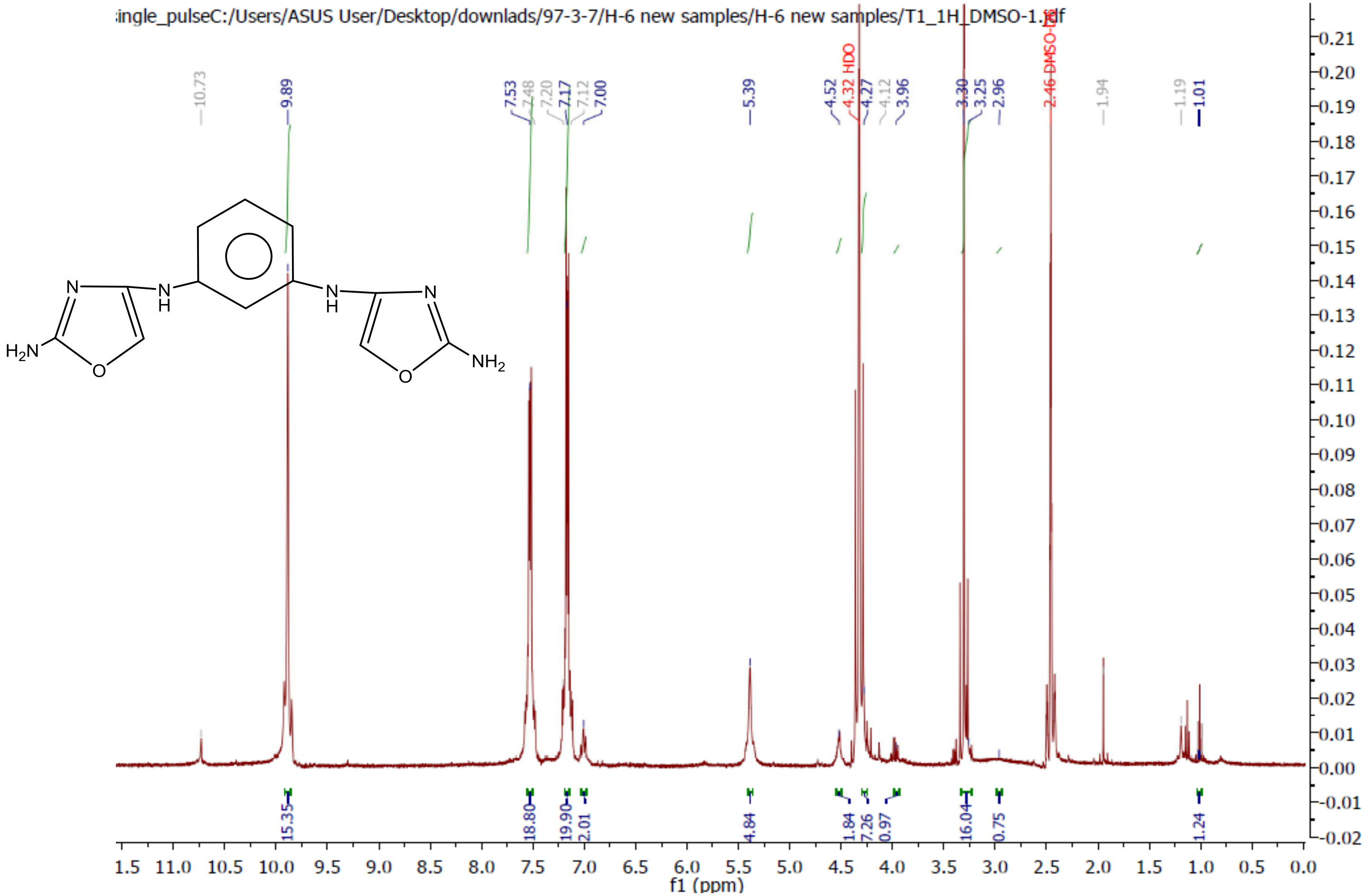


Figure (3-36) ^{1}HNMR spectrum for compound[XVIII]$_a$

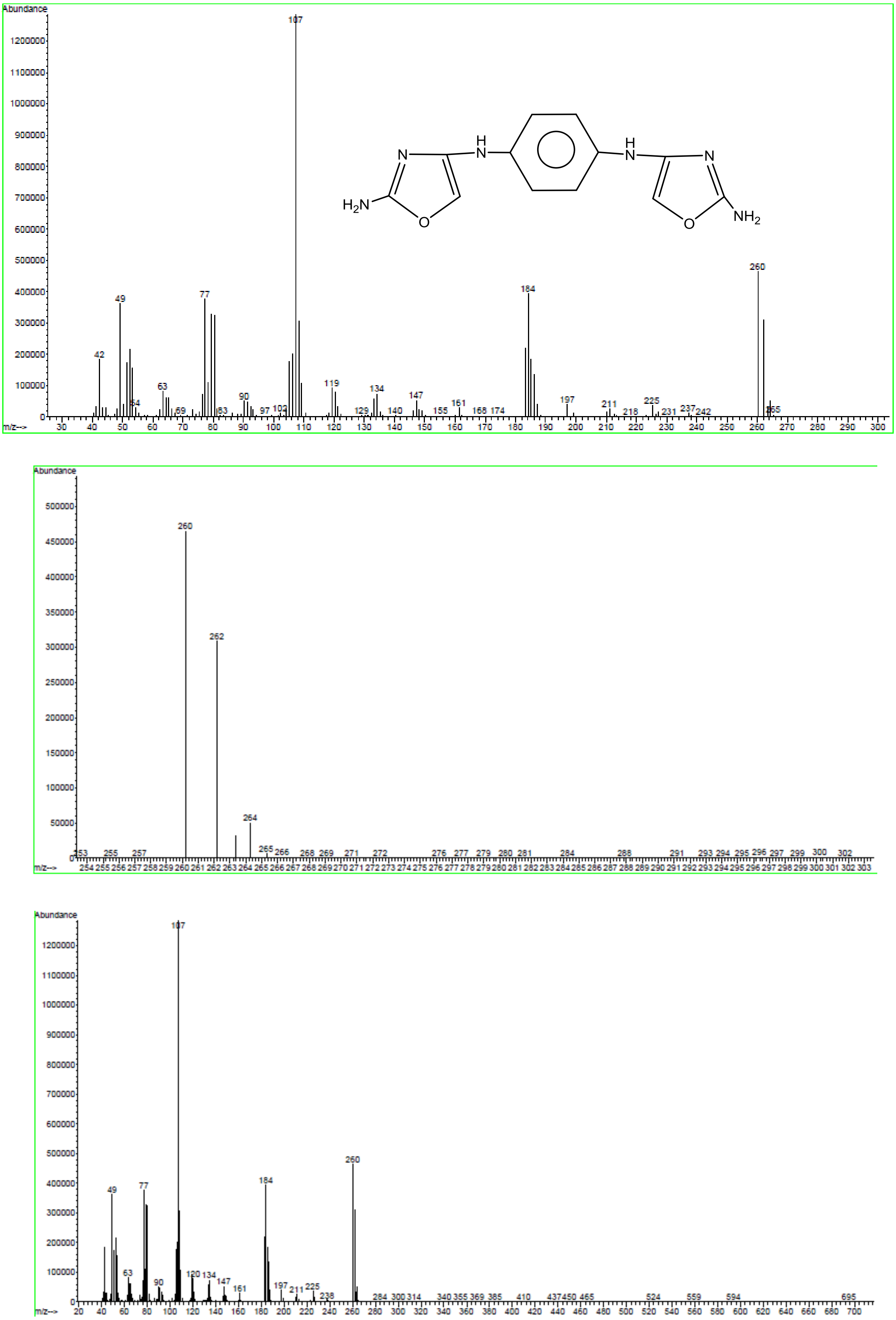


Figure (3-37) Mass spectrum for compound[XVIII]$_b$

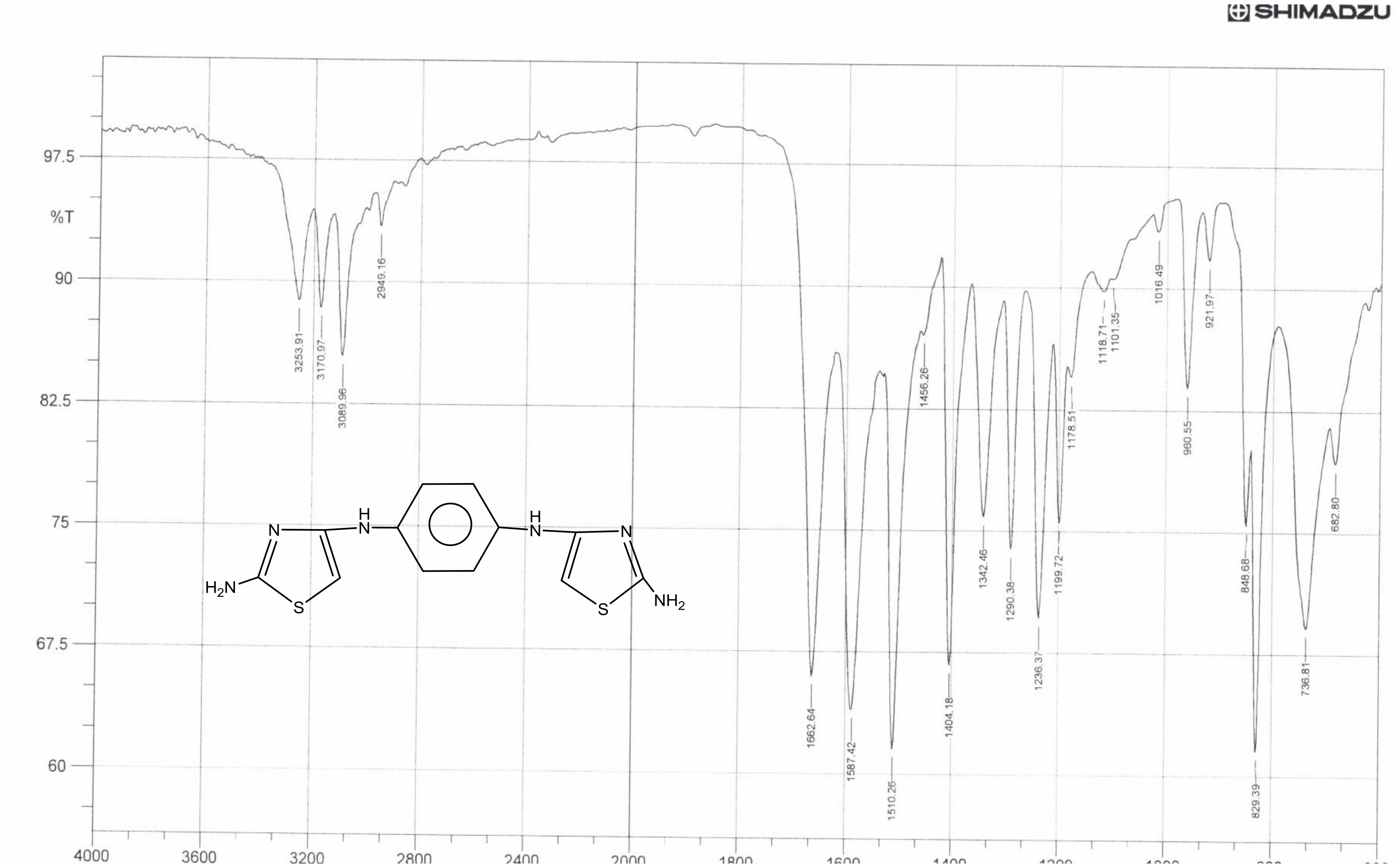


Figure (3-38) FT-IR spectrum for compound[XIX]$_b$

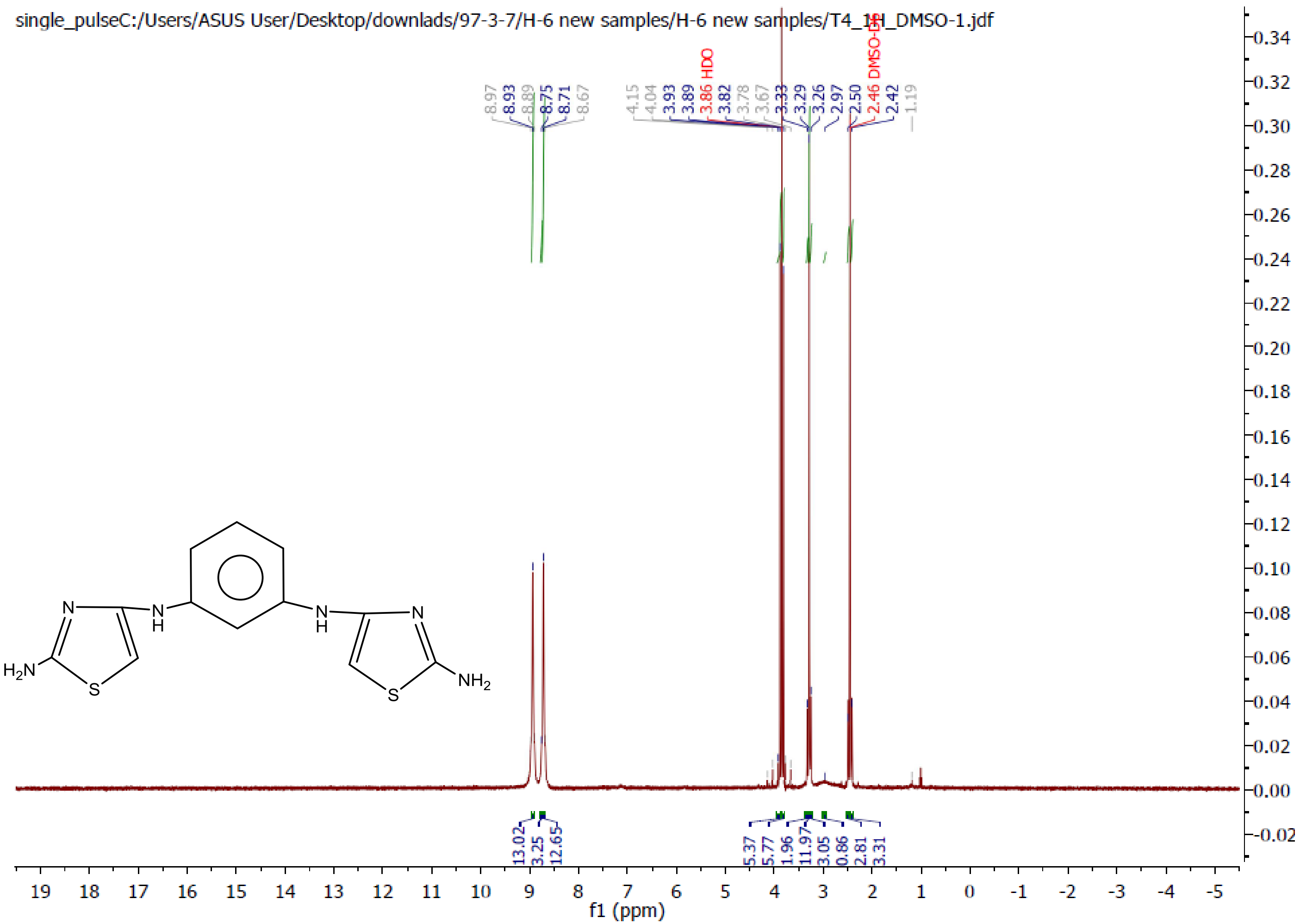


Figure (3-39) ^{1}HNMR spectrum for compound[XIX]$_{a}$

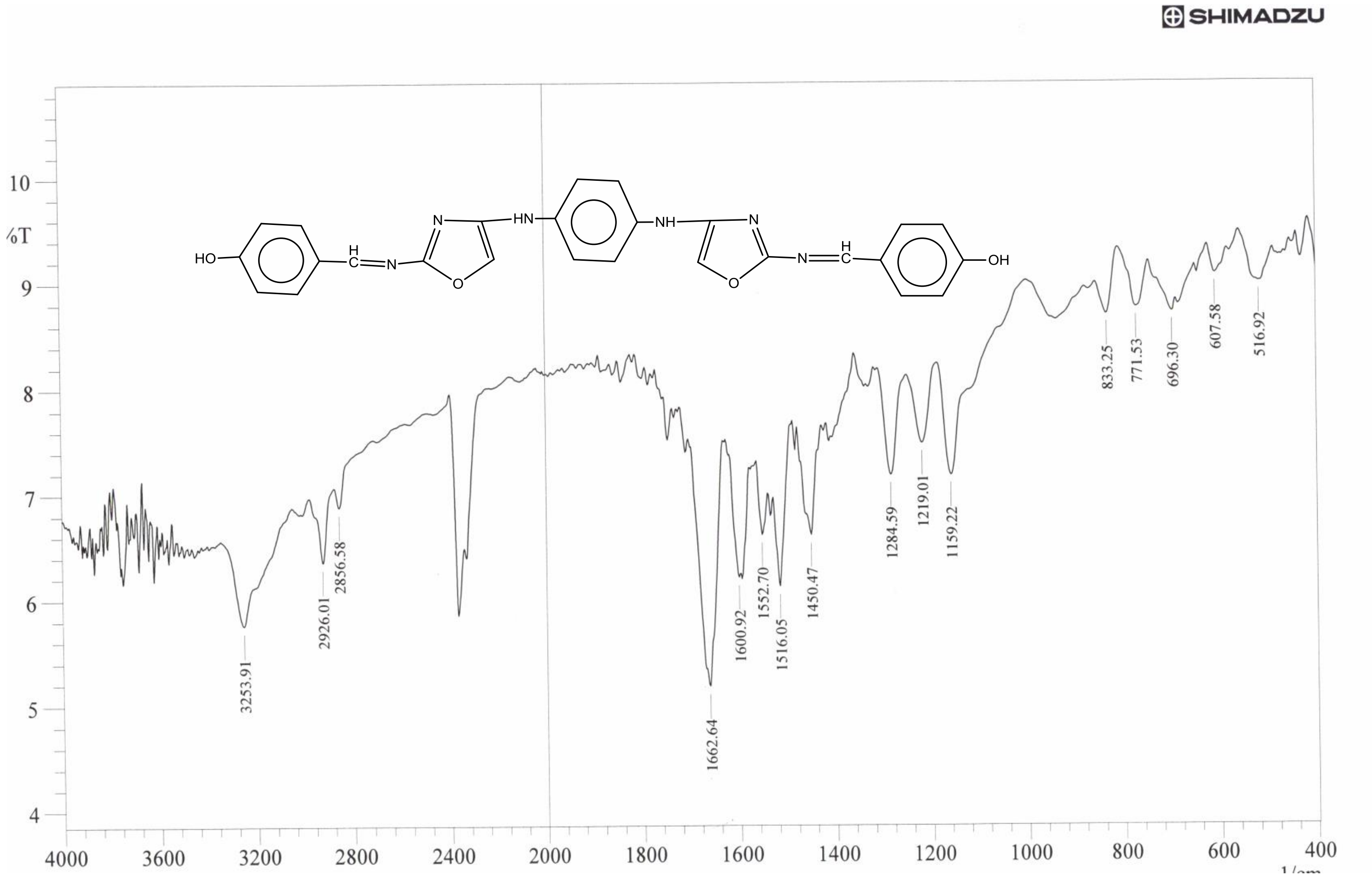


Figure (3-40) FT-IR spectrum for compound[XXI]a

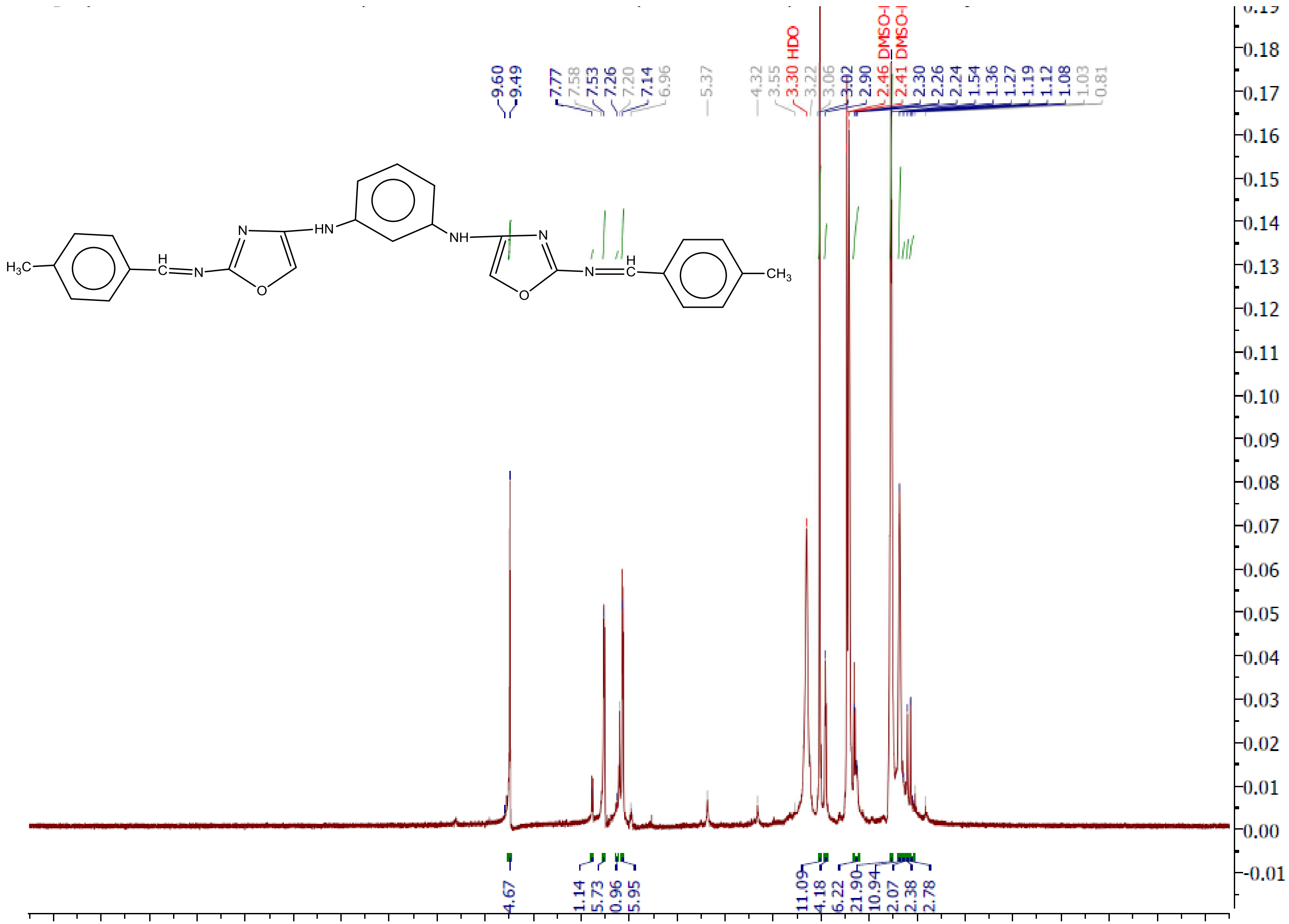


Figure (3-41) ^{1}HNMR spectrum for compound[XX]$_c$

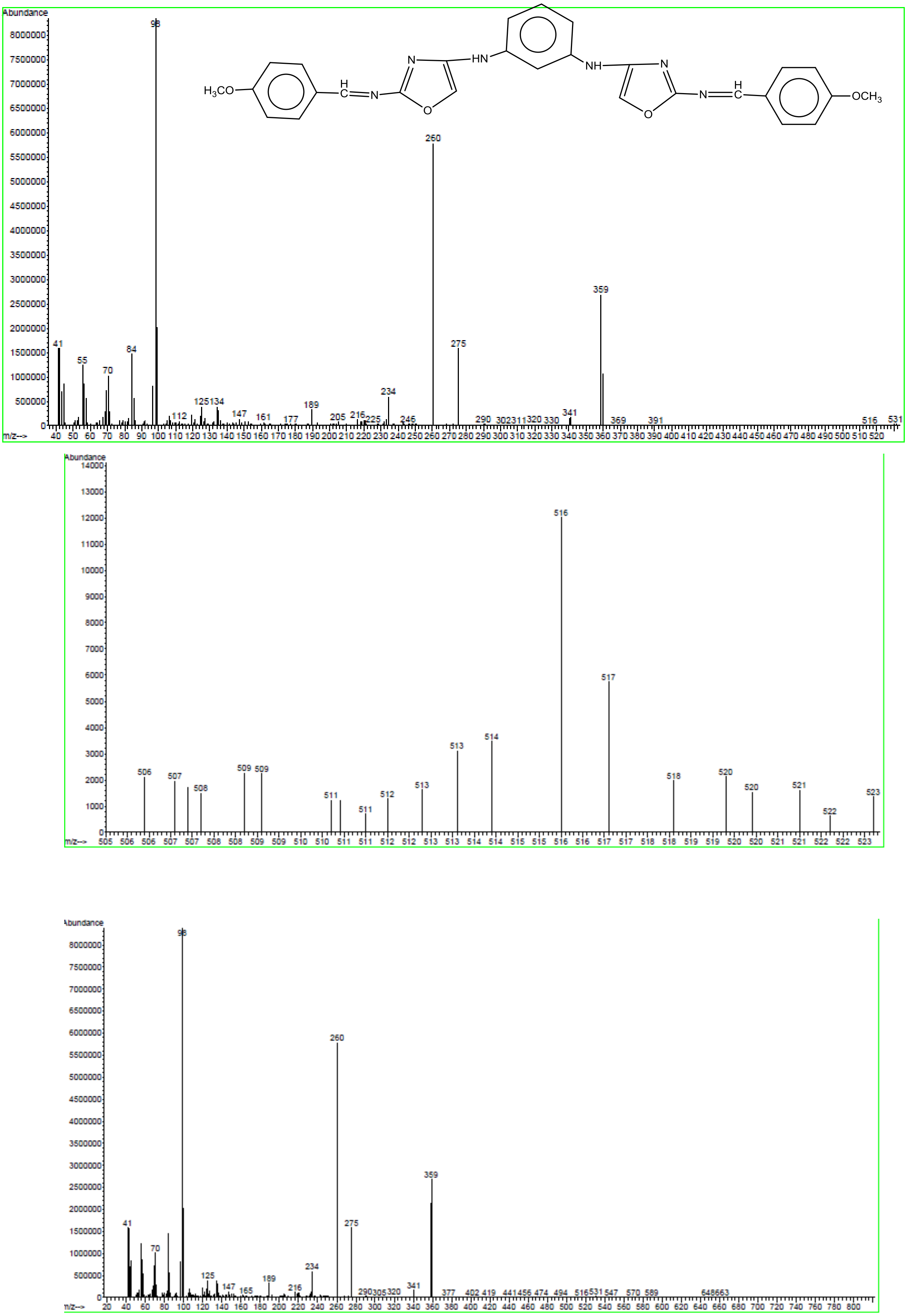


Figure (3-42) Mass spectrum for compound[XX]$_b$

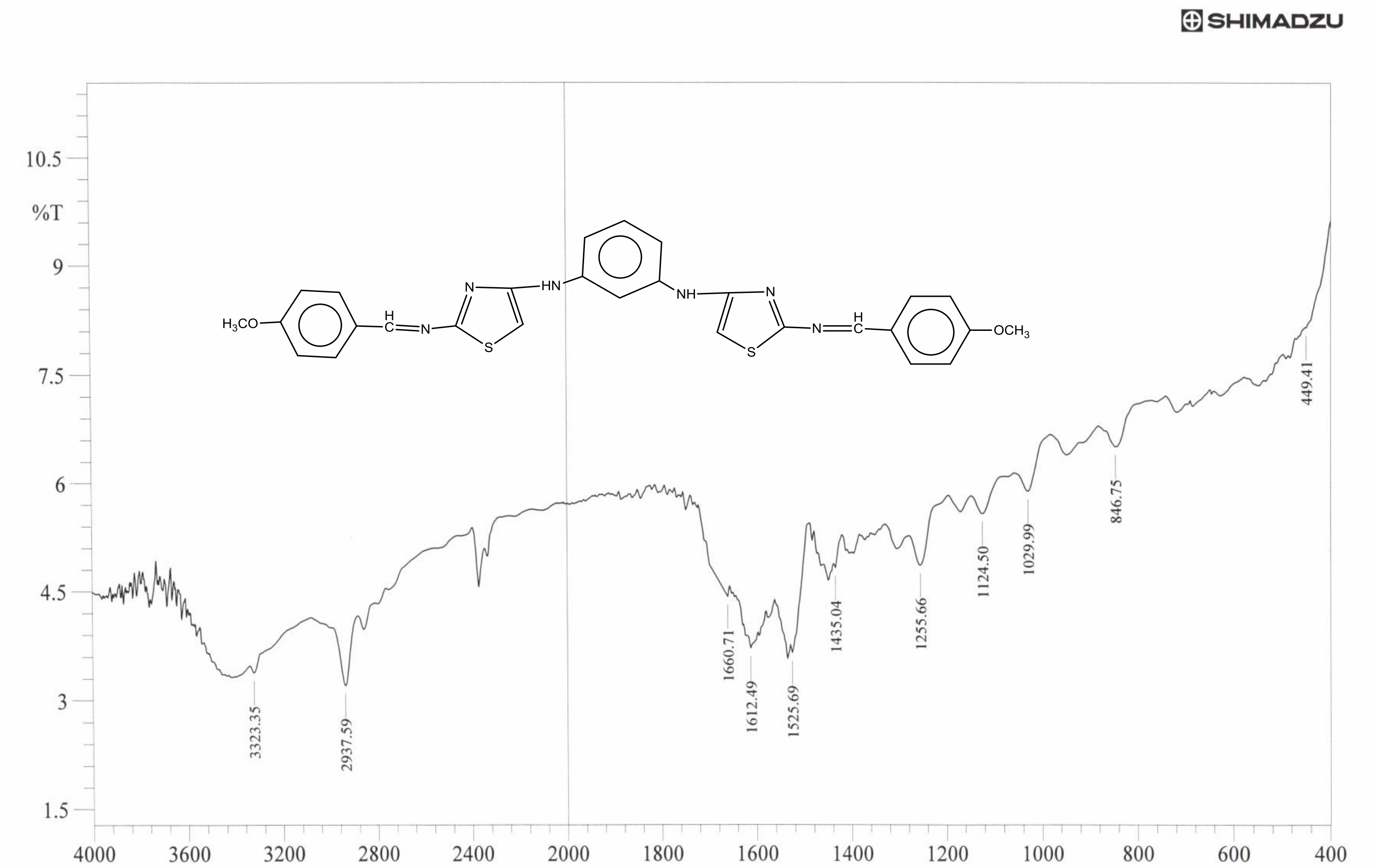


Figure (3-43) FT-IR spectrum for compound[XXII]$_b$

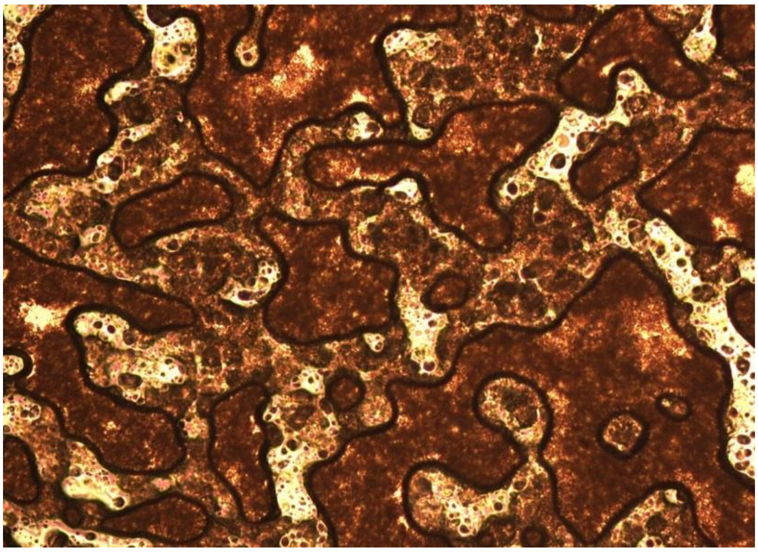


Figure (3-44) Cross polarizing photo micrograph (X200) of compound $[VII]_1$ thread-like texture of the nematic mesophase at 162°C on heating.

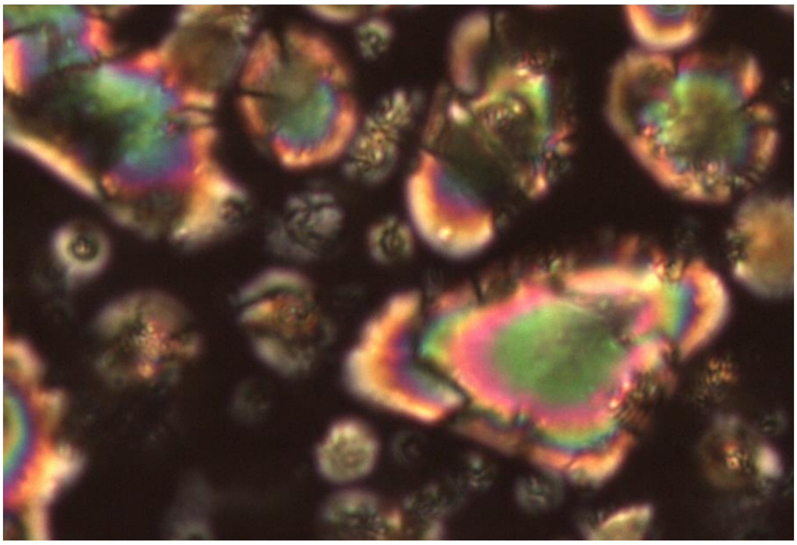


Figure (3-45) Cross polarizing photo micrograph (X200) of compound $[VII]_2$ nematic mesophase at 120°C on heating

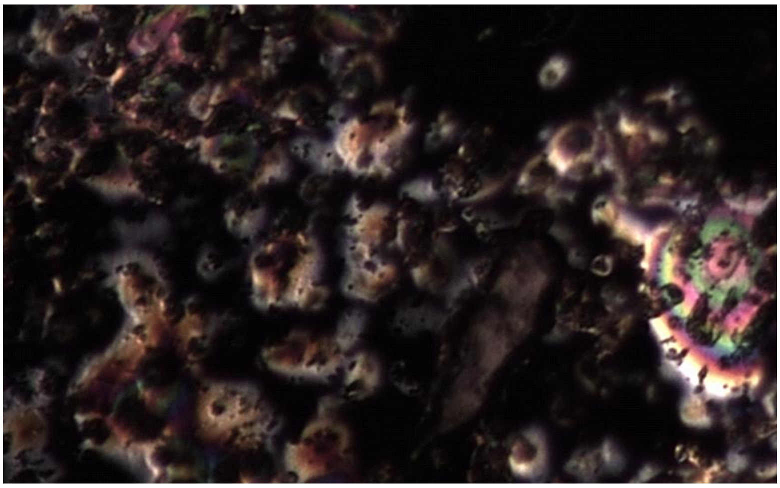


Figure (3-46) Cross polarizing photo micrograph (X200) of compound $[VII]_3$ nematic mesophase at 140°C on heating.

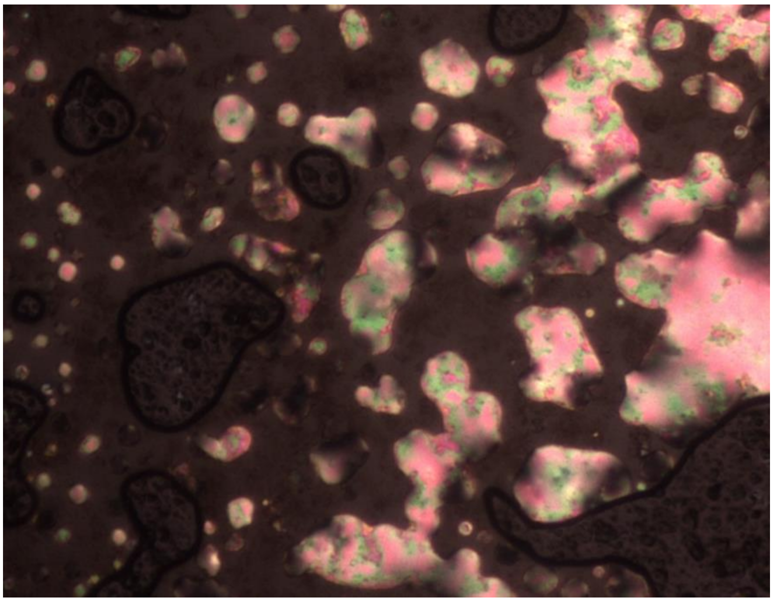


Figure (3-47) Cross polarizing photo micrograph (X200) of compound $[VII]_5$ nematic mesophase at 130°C on heating.

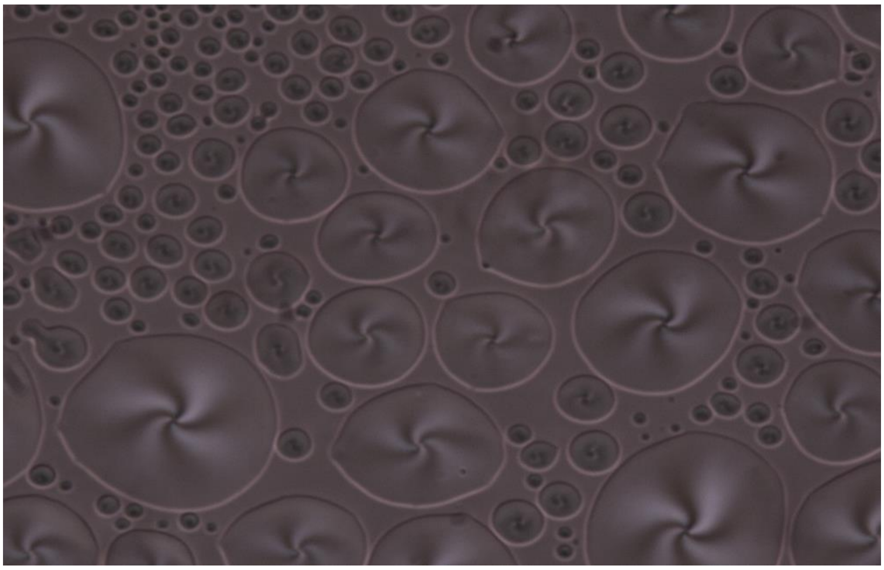


Figure (3-48) Cross polarizing photo micrograph (X200) of compound $[VII]_6$ nematic mesophase at 183°C on heating.

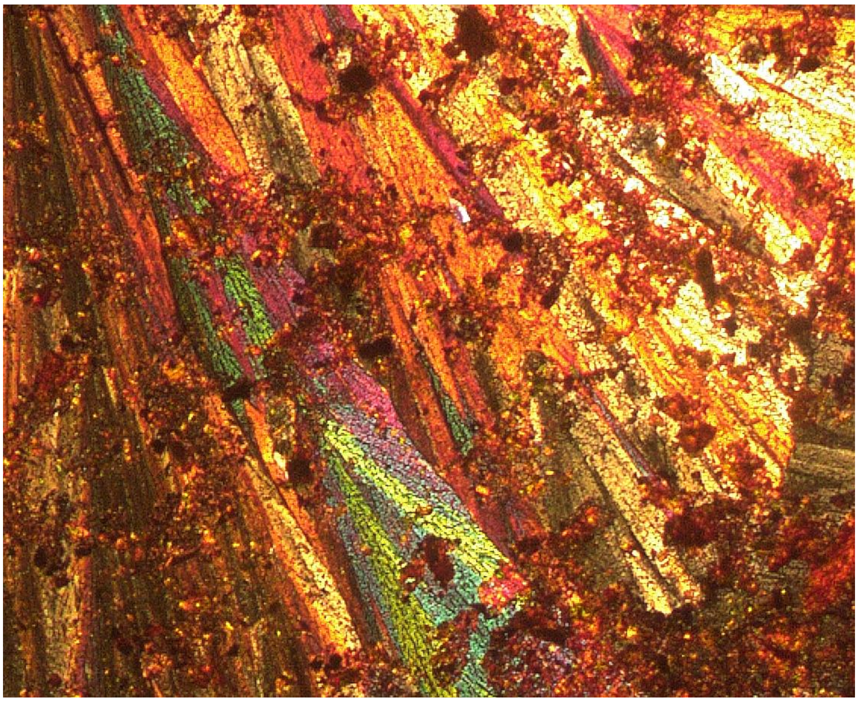


Figure (3-49) Cross polarizing photo micrograph (X200) of compound $[VII]_7$ SmA mesophase at 196°C on heating.

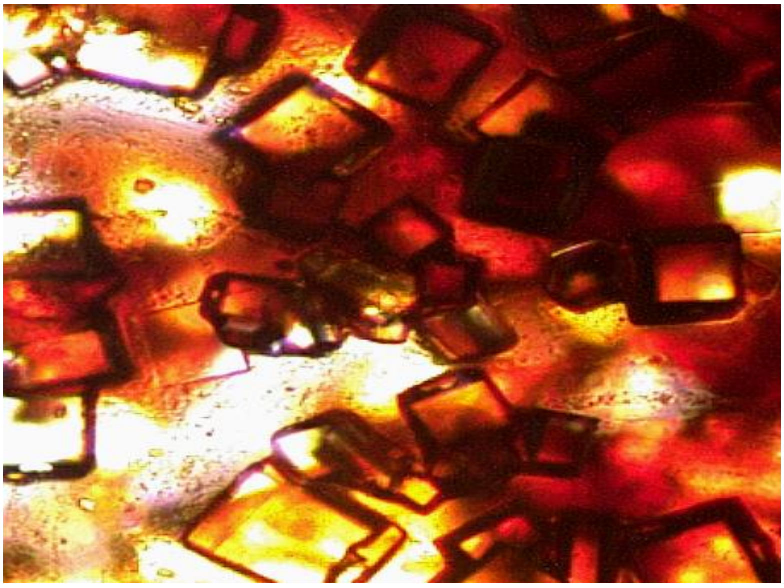


Figure (3-50) Cross polarizing photo micrograph (X200) of compound $[VII]_8$ SmB mesophase at 200°C on heating.

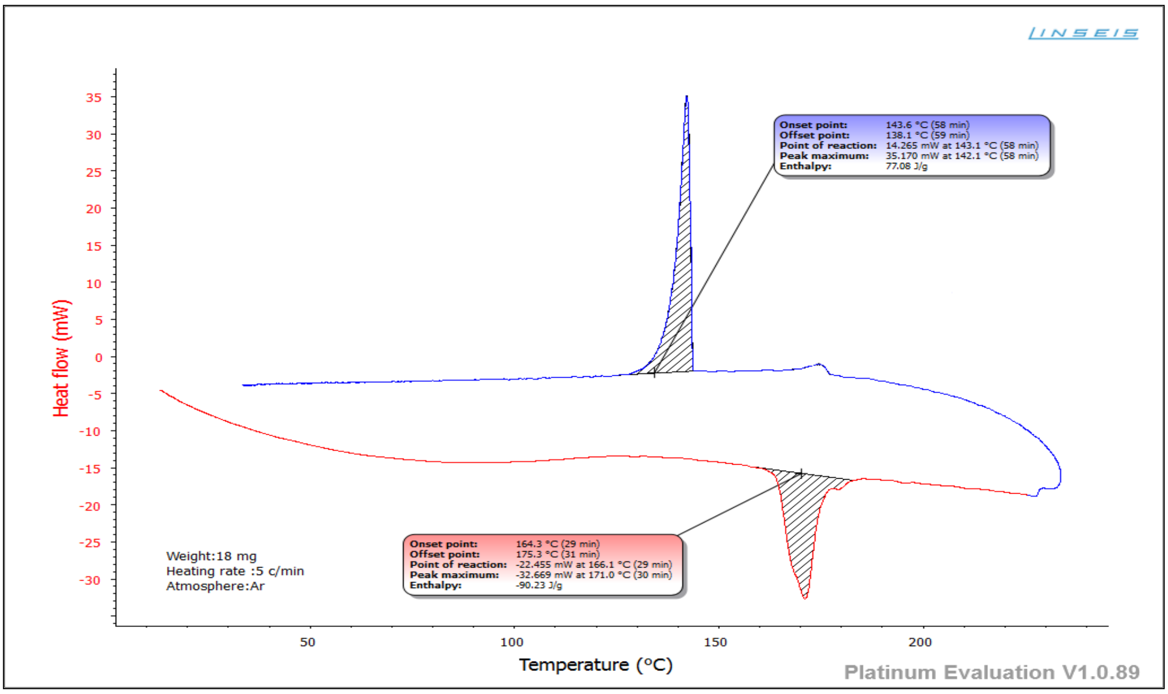
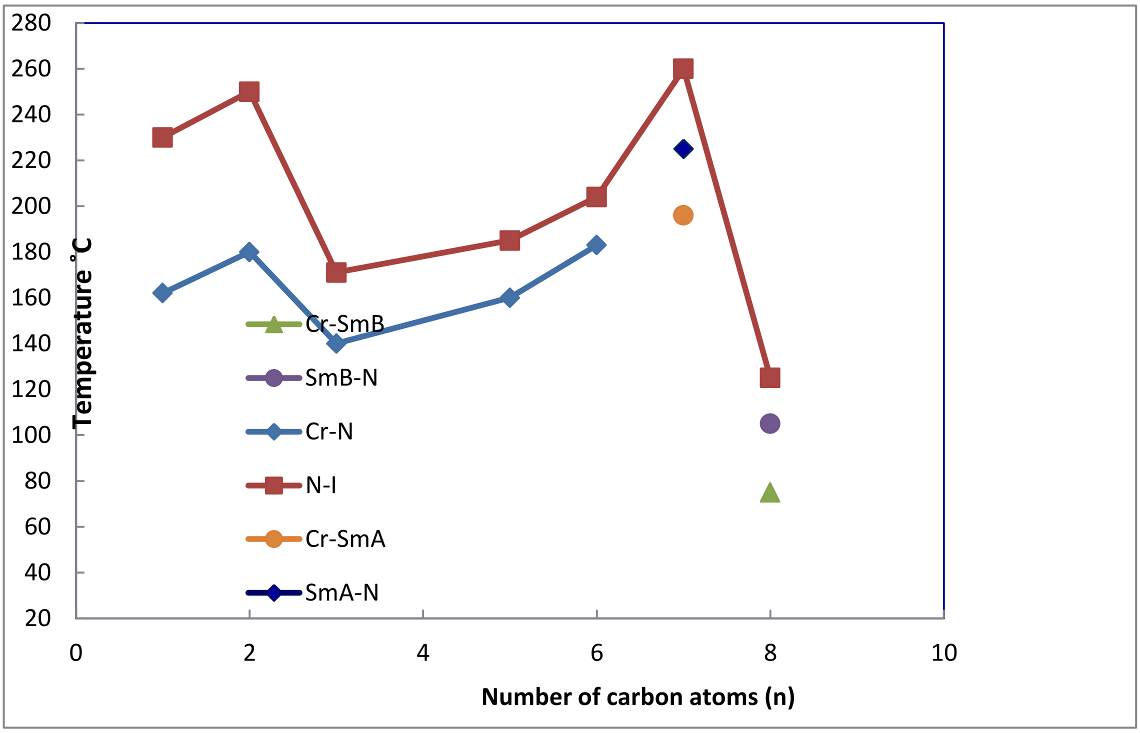


Figure (3-51) : DSC thermogram of compound $[VII]_1$



Figure(3-52): Dependence of transition temperatures on the increasing number of carbon atoms (*n*) in the terminal alkyl chains for the $[VII]_n$ series compounds

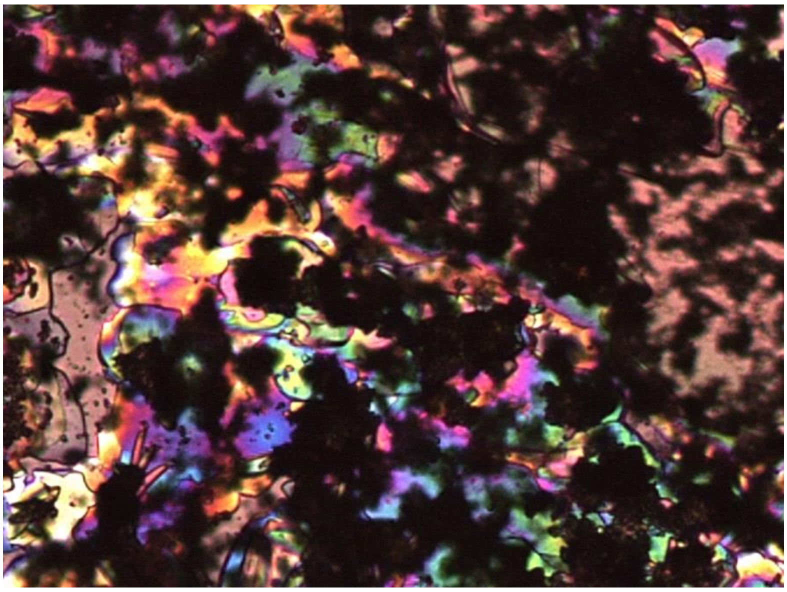


Figure (3-53) Cross polarizing photo micrograph (X200) of compound $[VIII]_2$ nematic mesophase at 135°C on heating.

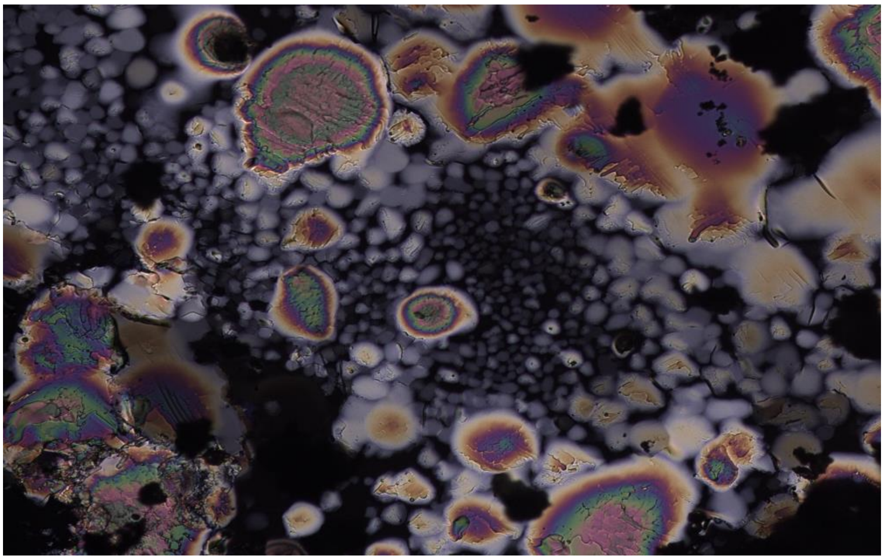


Figure (3-54) Cross polarizing photo micrograph (X200) of compound $[VIII]_3$ nematic mesophase at 160^{o}C on heating.

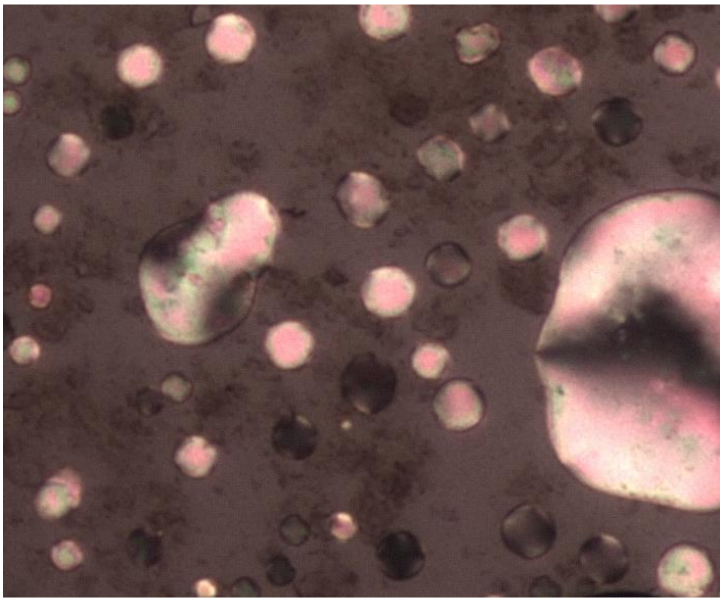


Figure (3-55) Cross polarizing photo micrograph (X200) of compound $[VIII]_5$ droplets of nematic mesophase at 115^{o}C on heating.

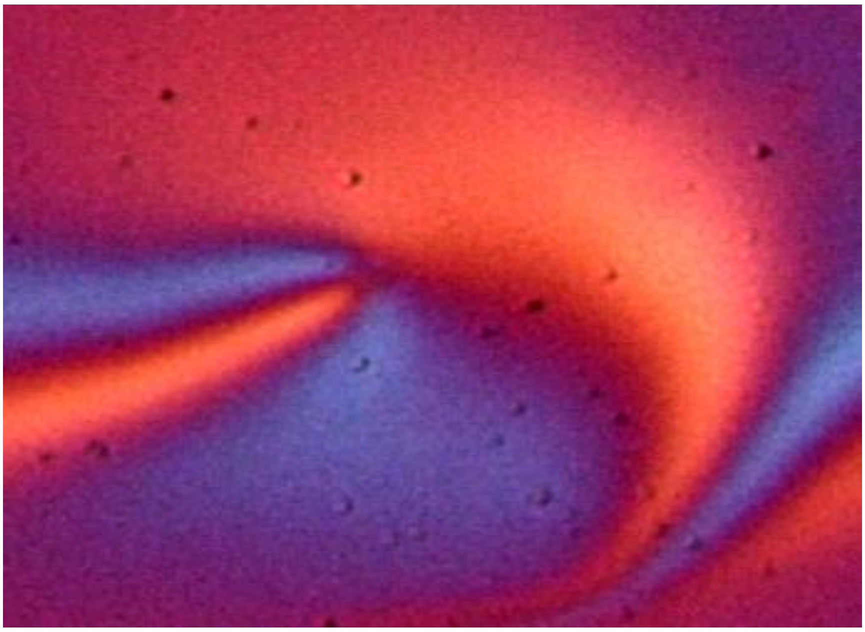


Figure (3-56) Cross polarizing photo micrograph (X200) of compound $[VIII]_6$ Schlieren texture of nematic mesophase at 150^{o}C on heating.

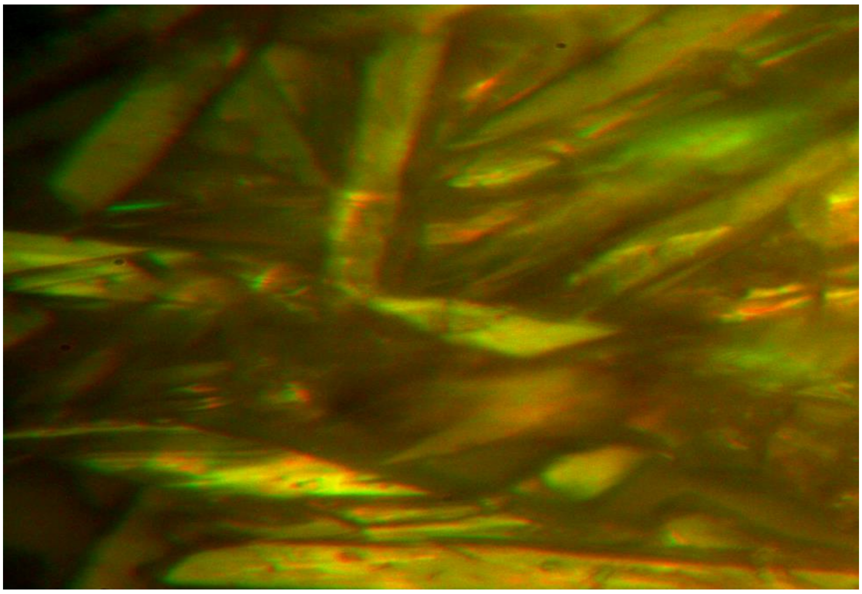


Figure (3-57) Cross polarizing photo micrograph (X200) of compound $[VIII]_7$ SmA mesophase at 190^{o}C on heating.

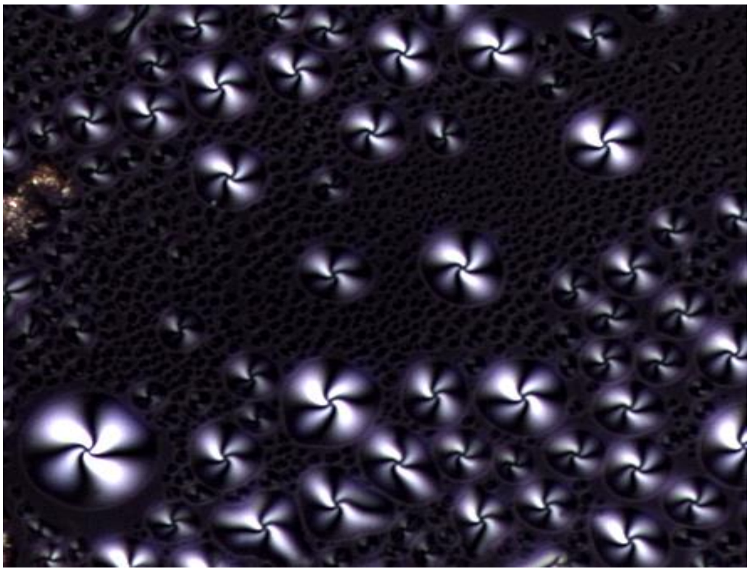


Figure (3-58) Cross polarizing photo micrograph (X200) of compound $[VIII]_8$ nematic mesophase at 209°C on heating.

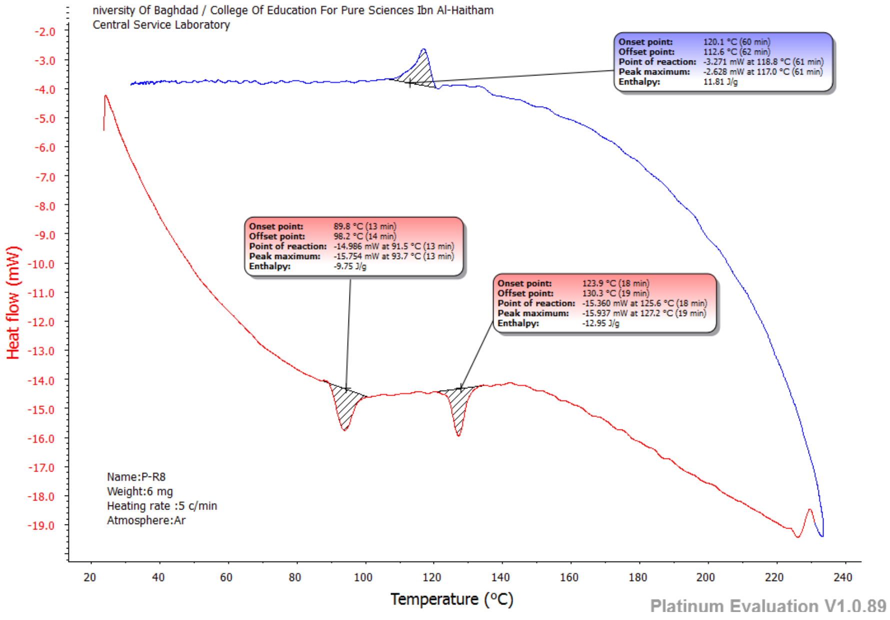
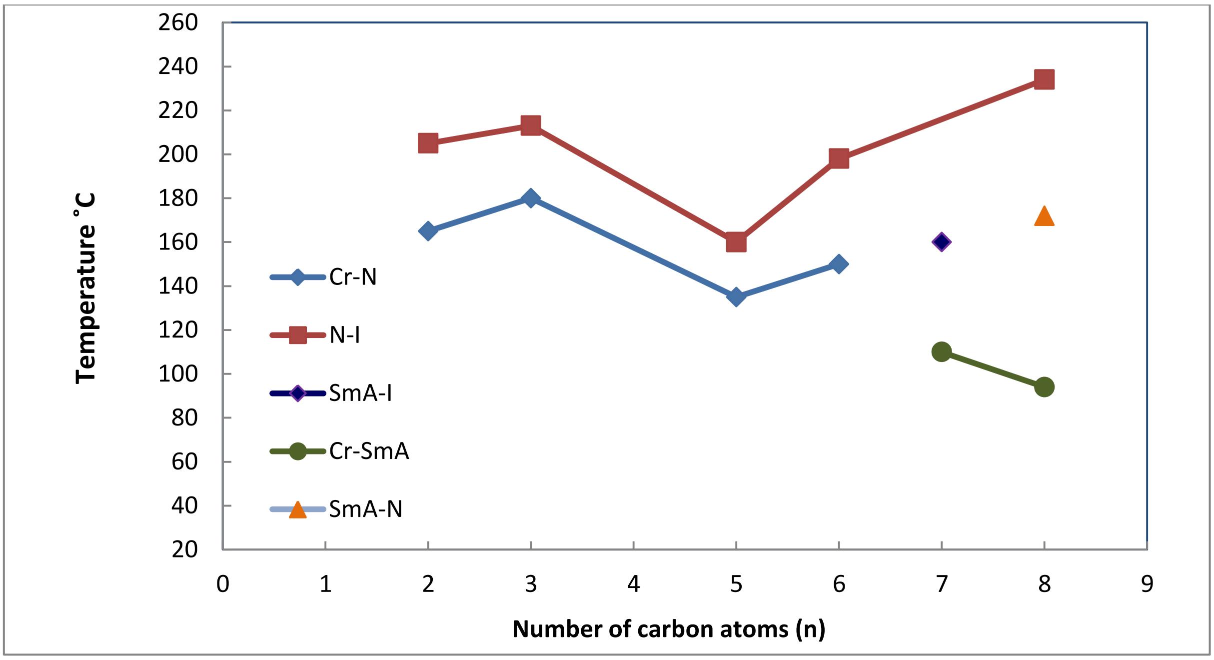


Figure (3-59) : DSC thermogram of compound $[VIII]_8$



Figure(3-60): Dependence of transition temperatures on the increasing number of carbon atoms (*n*) in the terminal alkyl chains for the $[VIII]_n$ series compounds

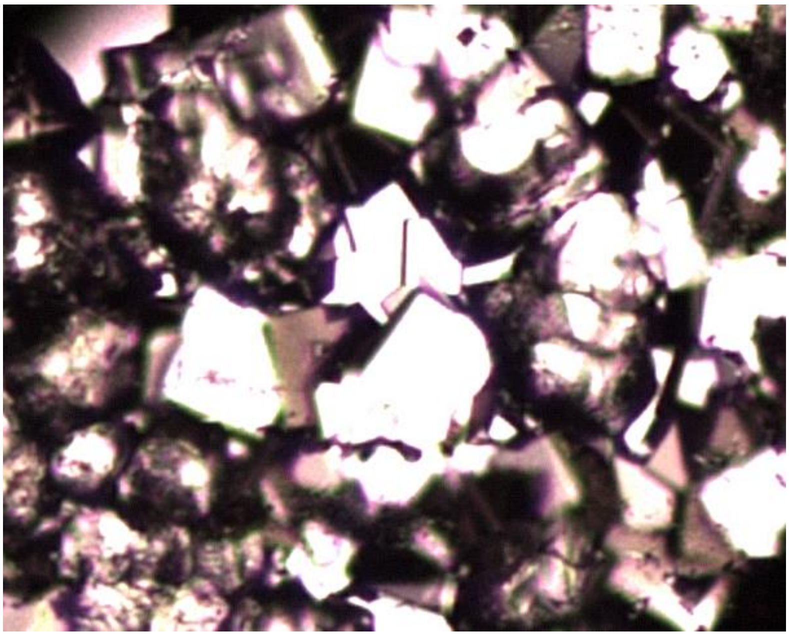


Figure (3-61) Cross polarizing photo micrograph (X200) of compound $[IX]_a$ SmB Mosaic texture mesophase at 194°C on heating.

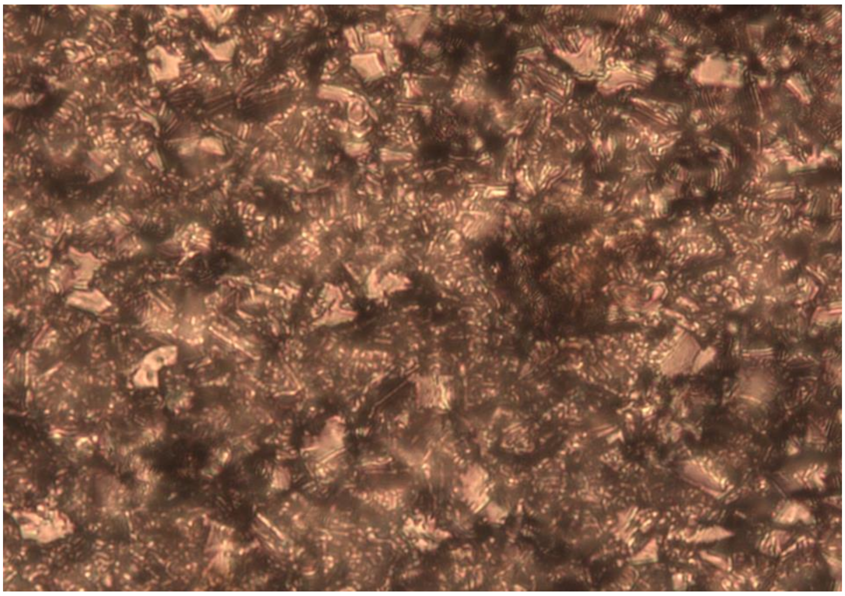


Figure (3-62) Cross polarizing photo micrograph (X200) of compound [IX]$_b$ SmB mesophase at 233^{o}C on heating.

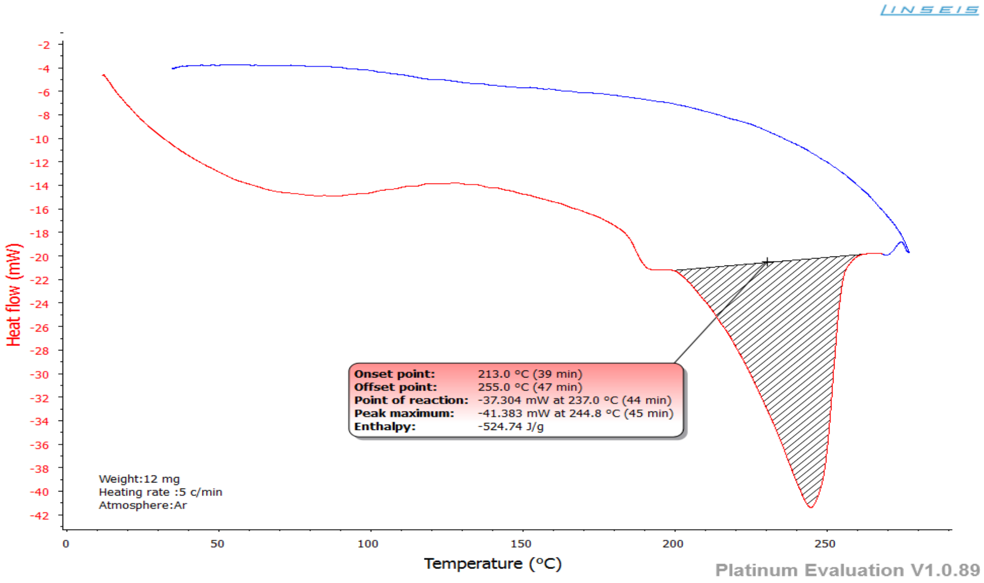


Figure (3-63) : DSC thermogram of compound [[IX]$_b$

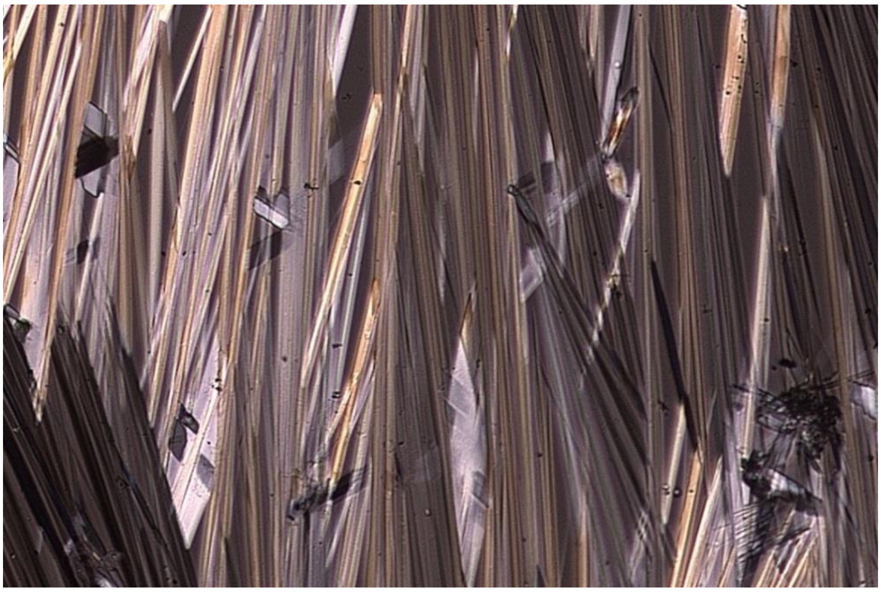


Figure (3-72) Cross polarizing photo micrograph (X200) of compound $[XX]_a$ Fan- shaped texture of SmA mesophase at 240^oC on heating.

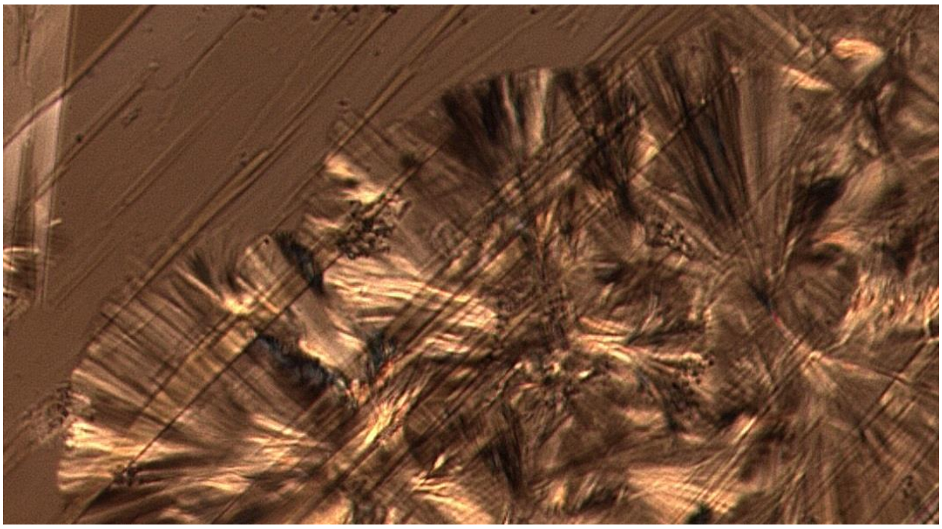


Figure (3-73) Cross polarizing photo micrograph (X200) of compound $[XX]_b$ Focal conic texture of SmA mesophase at 158^oC on heating.

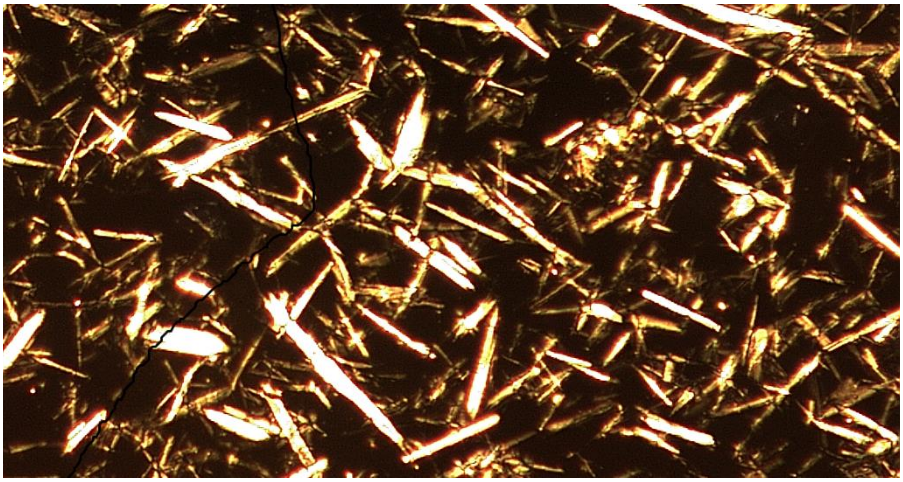


Figure (3-74) Cross polarizing photo micrograph (X200) of compound $[XX]_c$ batonnets texture of SmA mesophase at 188°C on heating.

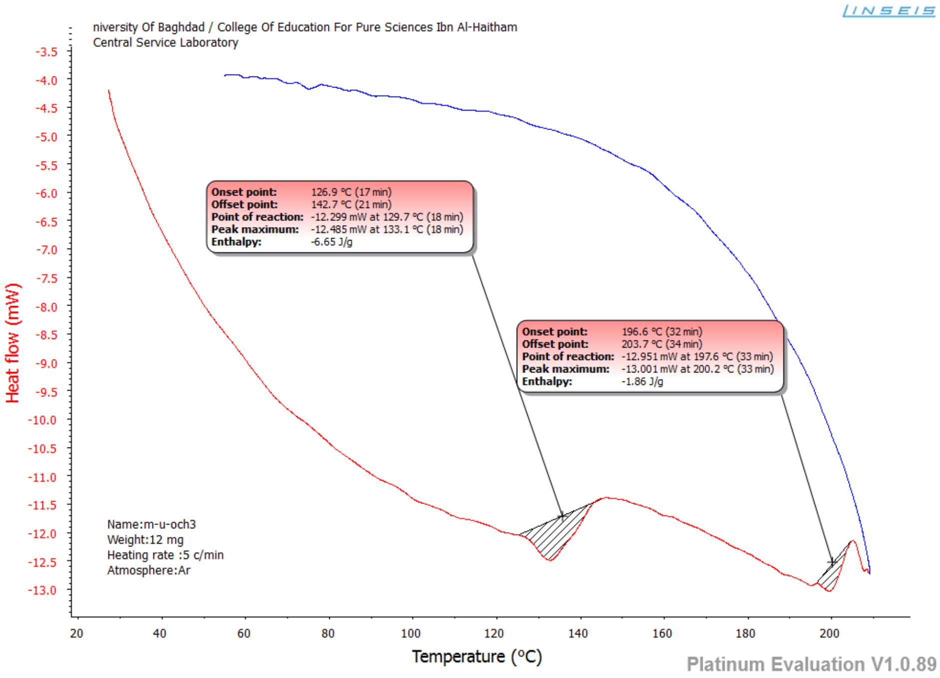


Figure (3-75) : DSC thermogram of compound $[XX]_a$

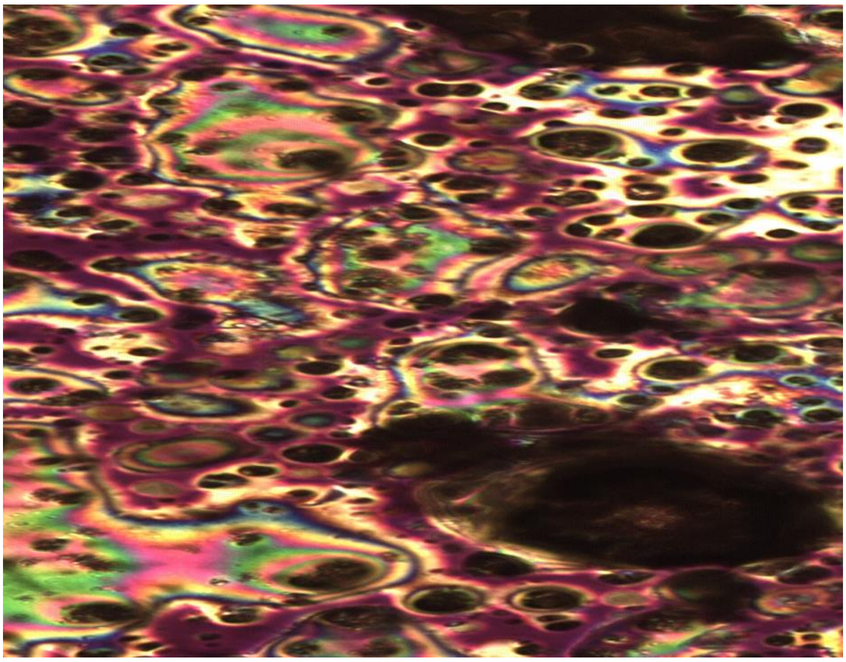


Figure (3-79) Cross polarizing photo micrograph (X200) of compound $[XXII]_a$ nematic mesophase at 219°C on heating.

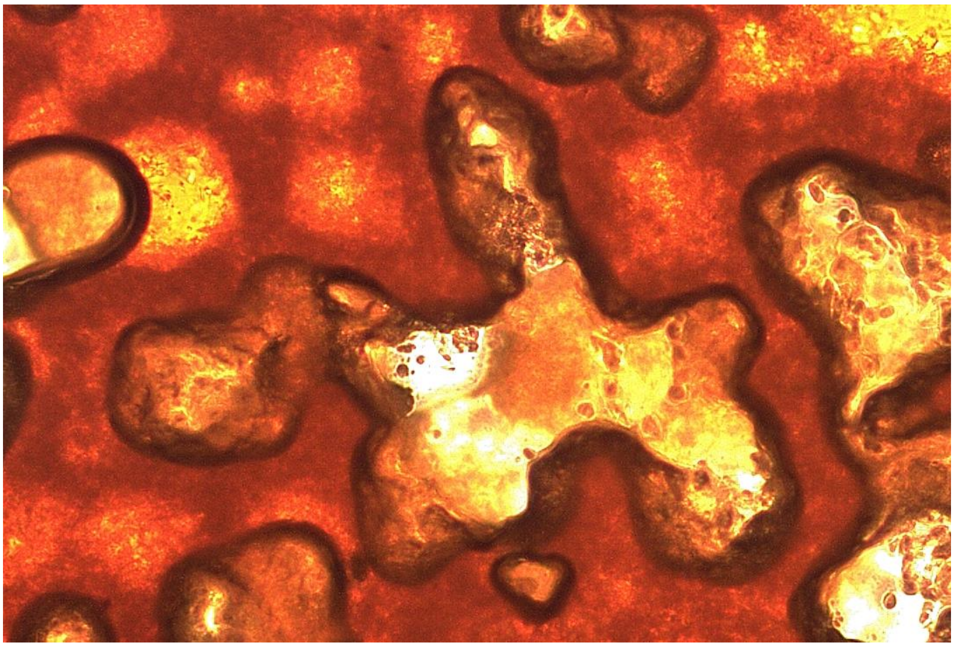


Figure (3-80) Cross polarizing photo micrograph (X200) of compound $[XXII]_c$ thread-like texture of nematic mesophase at 165°C on heating.

Figure (3-81) Cross polarizing photo micrograph (X200) of compound $[XXII]_b$ SmC mesophase at 220^{o}C on heating.

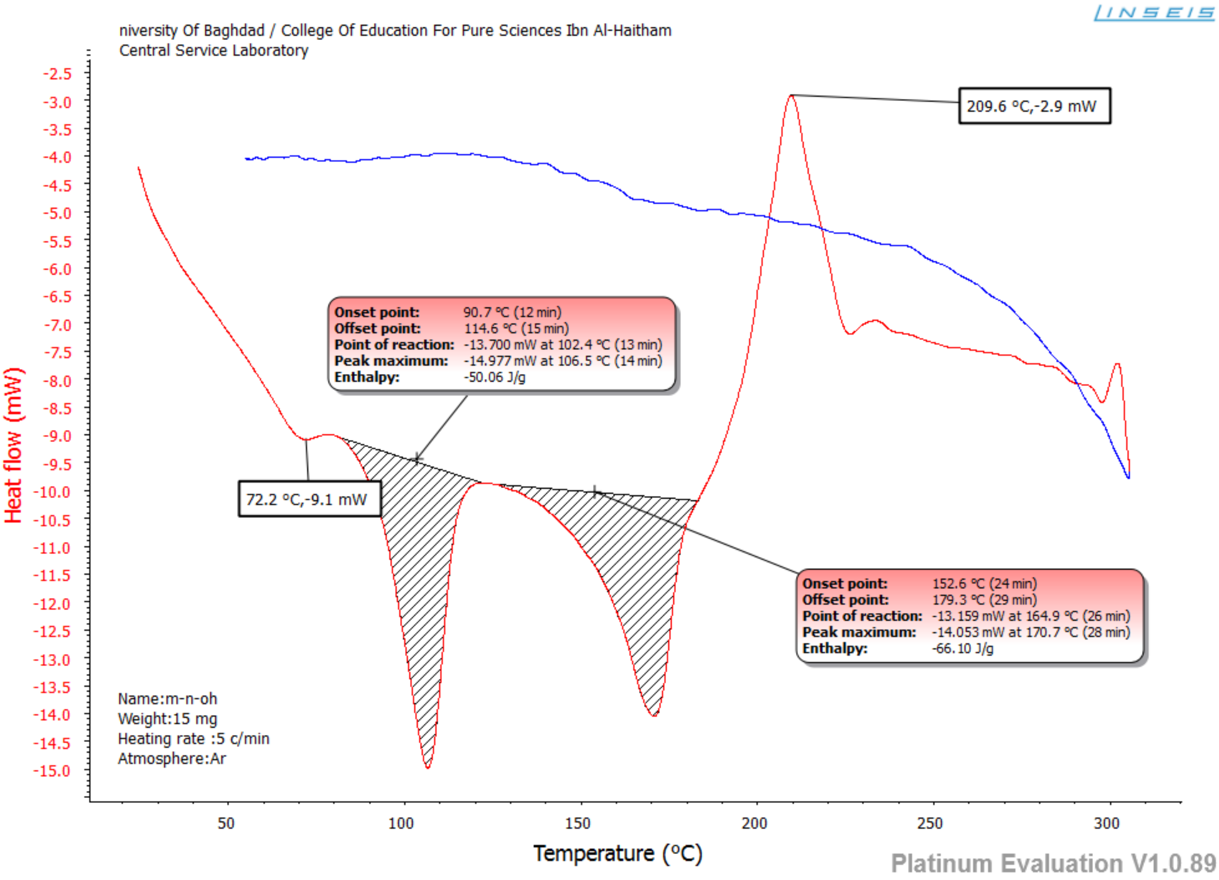


Figure (3-82) : DSC thermogram of compound $[XXII]_b$

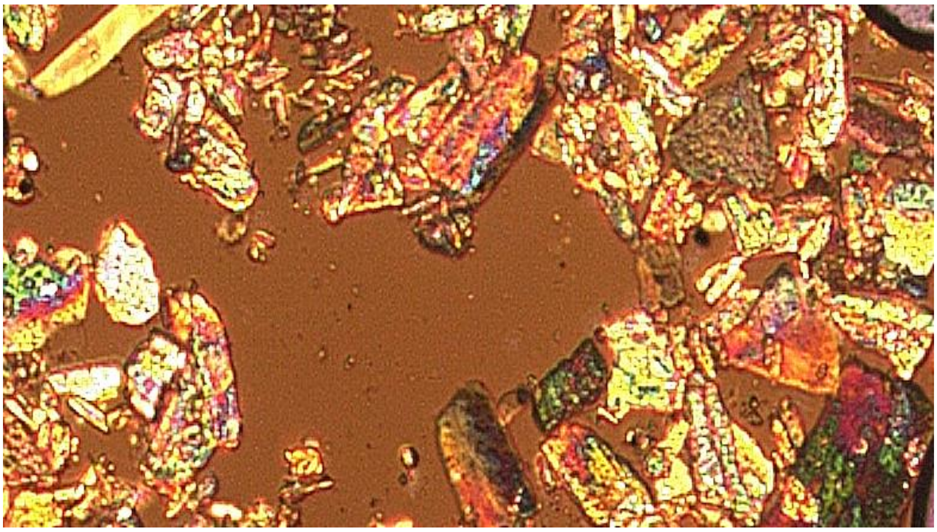


Figure (3-83) Cross polarizing photo micrograph (X200) of compound $[XXIII]_a$ Mosaic texture of SmB mesophase at 185°C on heating.

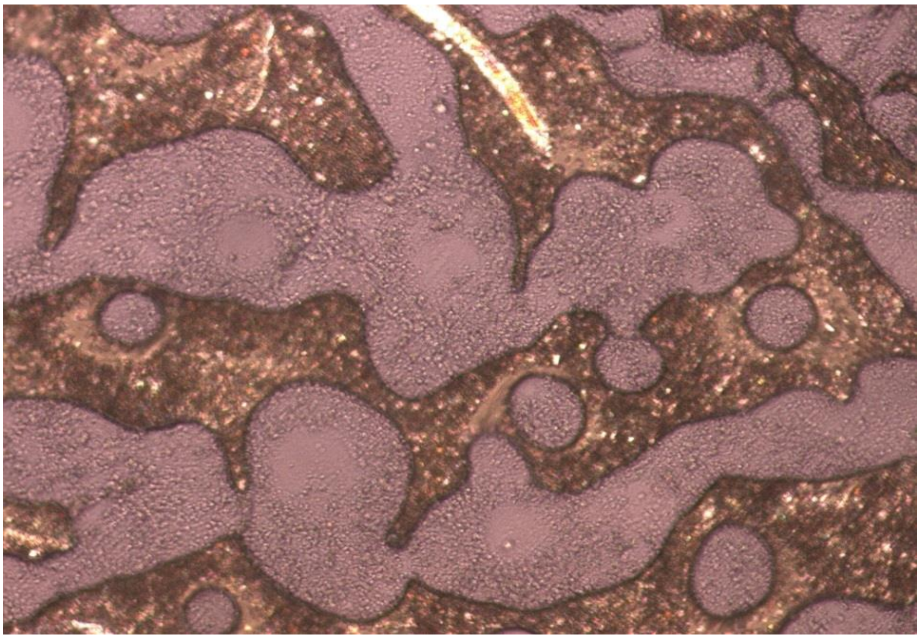


Figure (3-84) Cross polarizing photo micrograph (X200) of compound $[XXIII]_b$ thread-like texture of nematic mesophase at 198°C on heating.

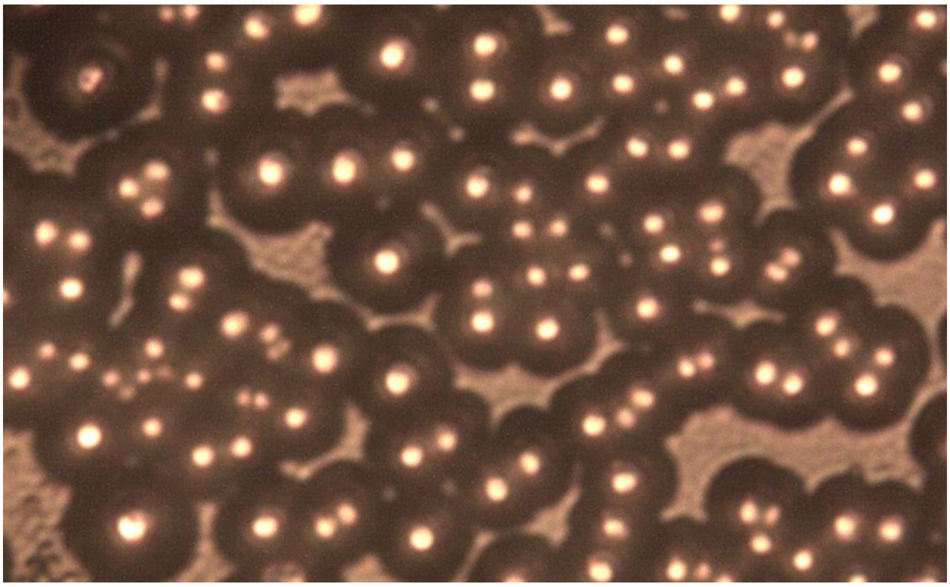


Figure (3-85) Cross polarizing photo micrograph (X200) of compound [XXIII]$_c$ nematic mesophase at 200^{o}C on heating.

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الخلاصة

تضمنت هذه الدراسة تحضير وتشخيص ودراسة السلوك البلوري السائل لبعض المركبات الحلقية غير المتجانسة والمشتقة من مركبات (1و3-فنيلين ثنائي الامين) و(1و4-فنيلين ثنائي الامين) وكالآتي .

يتضمن الجزء الأول تحضير مركبات N,N (3،1او 1 ،4-فنيلين)ثنائي(2- كلورو اسيتامايد) $[I]_{a,b}$ ثم تحويلها الى المركبات المناظرة N,N -(3,1 او 1 ،4-فنيلين)ثنائي(2- أزيدو اسيتامايد) $[II]_{a,b}$ بتفاعلها مع صوديوم أزايد . من مفاعلة المركبات السابقة الذكر مع حامض الأكريلك لتعطي مركبات $[III]_{a,b}$ حيث تتحول الى مركبات الأستر$[IV]_{a,b}$ عند مفاعلتها مع الميثانول بوجود H_2SO_4 ، ايضا نحصل على مركبات الأستر$[IV]_{a,b}$ تتفاعل مع الهيدرازين المائي 80% لتعطي مركبات حامض الهيدرازيد $[V]_{a,b}$.

المركبات ن- الكوكسي بنزالديهايد $[VI]_n$ يحضر من تفاعل 4-هايدروكسي بنزالديهايد مع بروميد الألكيل ، هذه المركبات تتفاعل مع حامض الهيدرازيد لتنتج مركبات قواعد شف $[VII]_n$ و $[VIII]_n$ حيث (n=1,2,3,5,6,7,8) .

أما الجزء الثاني يتضمن تحضير مركبات بنزاميدازول $[IX]_{a,b}$ من تفاعل مركب $[III]_{a,b}$ مع أورثو-فنيلين ثنائي الأمين ، ايضا تحضير مركبات كلوريد الحامض $[X]_{a,b}$ من تفاعل المركب $[III]_{a,b}$ مع كلورايد تالثايونيل إضافة الى ذلك هذه المركبات تتفاعل مع أمينات أروماتية مختلفة لتعطي مركبات الأمايد $[XI]_{a-d}$ و$[XII]_{a-d}$ ، بينما مركبات الثايزوليدين -4-اون $[XIII]_{a,b}$ تحضر من تفاعل مركبات$[I]_{a,b}$ مع الثايوسيانات البوتاسيوم في الأسيتون .

الجزء الثالث يتضمن تحضير مركب4-(بربر-2-ين-1-يلوكسي) بنزالديهايد [XIV] من تفاعل 4-هايدروكسي بنزالديهايد مع بروميد البروبرجيل ، هذا المركب [XIV] يتفاعل مع المركبات $[II]_{a,b}$ لتعطي مركبات 1و2و3- ترايازول $[XV]_{a,b}$ التي تتفاعل مع أمينات أروماتية مختلفة لتنتج مركبات قواعد شف $[XVI]_{a-d}$و $[XVII]_{a-d}$.

أخيرا الجزء الرابع يتضمن تحضير مركبات أوكسازول $[XVIII]_{a,b}$ ومركبات الثايازول $[XIX]_{a,b}$ بواسطة تفاعل مركب $[I]_{a,b}$ مع اليوريا او الثايوريا في الأيثانول المطلق .

بعدها تتفاعل هذه المركبات مع الديهايدات أروماتية مختلفة في البيردين والـ THF لتعطي مركبات الأوكسازول $[XX]_{a-c}$ و $[XXI]_{a-c}$ عند استخدام اليوريا ويعطي مركبات الثايزول $[XXII]_{a-c}$ و $[XXIII]_{a-c}$ عند استعمال الثايوريا

كل المركبات المحضرة شخصت بمطيافية الأشعة تحت الحمراء والرنين النووي المغناطيسي للبروتون وطيف الكتلة (لبعض منها) . درس السلوك البلوري السائل لكل المركبات المحضرة بأستعمال مجهر الضوء المستقطب (OPM) ومسعر المسح التفاضلي DSC (لبعض منها) والنتائج كالآتي :-

كل قواعد شف $[VIII]_n$ and $[VII]_n$ أظهرت السلوك البلوري السائل الأنعكاسي المركبات $[VII]_1$ $[VII]_2$ و$[VII]_3$ و$[VII]_5$ و$[VII]_6$ أظهرت الطور النيماتي الأنعكاسي بينما المركب $[VII]_7$ أظهر الطورين السمكتي A والنيماتي ، بالأضافه الى ذلك أظهر المركب $[VII]_8$ الطورين السمكتي B والنيماتي .

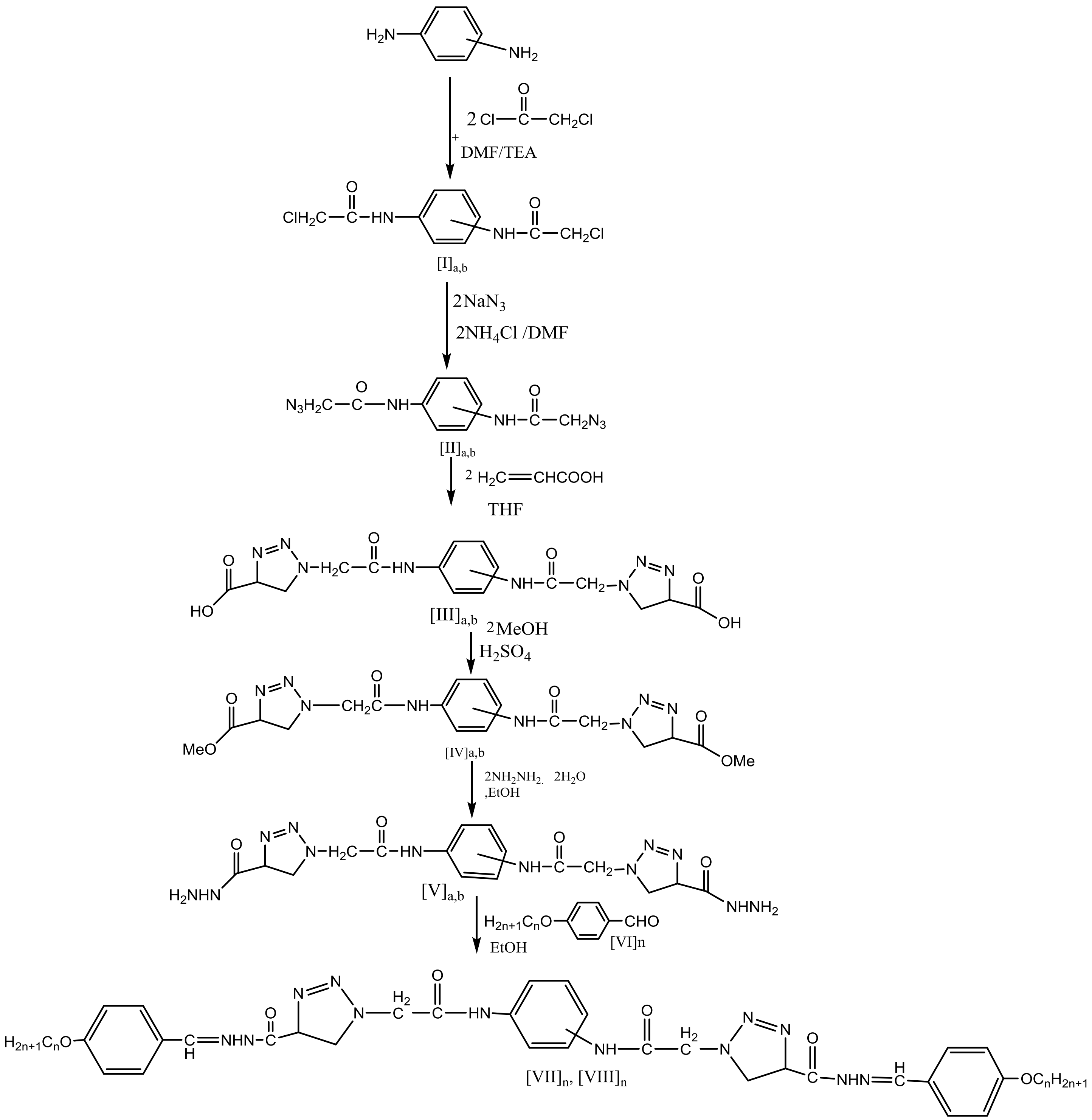
المركب $[VIII]_1$ لم يظهر اي خواص بلورية سائلة بينما المركبات $[VIII]_2$ و$[VIII]_3$ و$[VIII]_5$ و$[VIII]_6$ أظهرت الأطوار النيماتية ، المركب $[VIII]_7$ أظهر فقط الطور السمكتي A . أما المركب $[VIII]_8$ أظهر الطورين الأنعكاسيين السمكتي A والنيماتي .

2- مركبات البنزاميدازول $[IX]_{a,b}$ أظهرت الطور السمكتي ، بينما مركبات الأمايد $[XI]_{a-d}$ و $[XII]_{a-d}$ لم تظهر اي خواص بلورية سائلة فقط أنتقال من الطور البلوري الى الطور الآيزوتروبي ، مركبات الثايازوليدين -4-اون لم تظهر اي خواص بلورية سائلة فقط أنتقال من الطور البلوري الى الطور الآيزوتروبي .

3- المركبات قواعد شف $[XVI]_{a-d}$ و $[XVII]_{a-d}$ لم تظهر أي خواص بلورية سائلة بينما مركبات الأوكسازول $[XX]_{a-c}$ أظرت الطور السمكتي A لكن المركبات $[XXI]_{a-c}$ لم تظهر أي خواص بلورية سائلة .

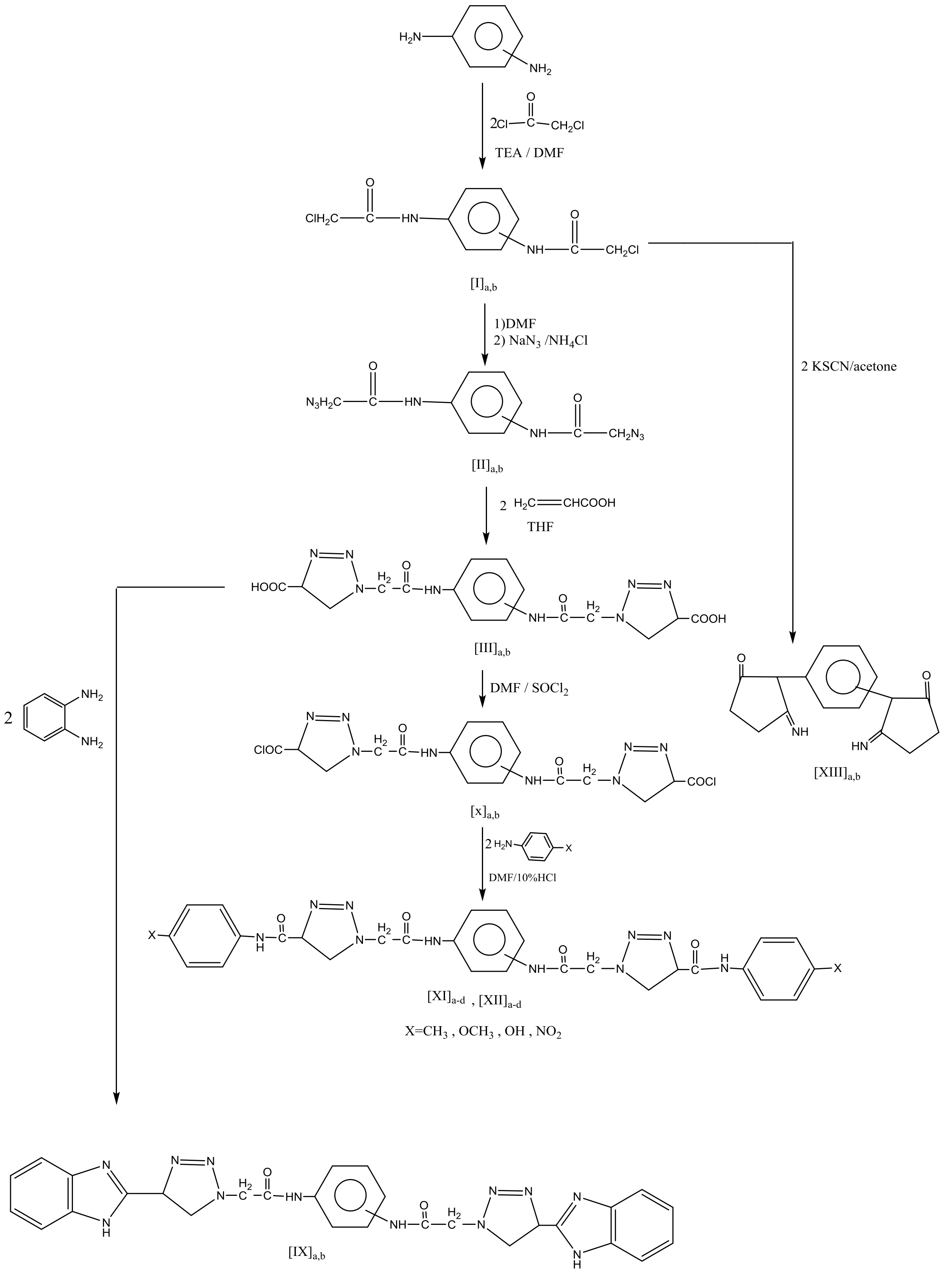
أخيرا قواعد شف لمركبات الثايازول $[XXII]_a$ و$[XXII]_c$ أظهرت الطور النيماتي الأنعكاسي بينما المركب $[XXII]_b$ أظهر الطورالسمكتي C والطور النيماتي ، بينما المركب $[XXIII]_a$ أظهر الطورالأنعكاسي السمكتي B المركبات $[XXIII]_b$ $[XXIII]_c$, أظهرت الاطوار النيماتية الأنعكاسية .

هذا البحث يمكن ان يلخص البحث بالمخططات الآتية (3,2,1، 4)

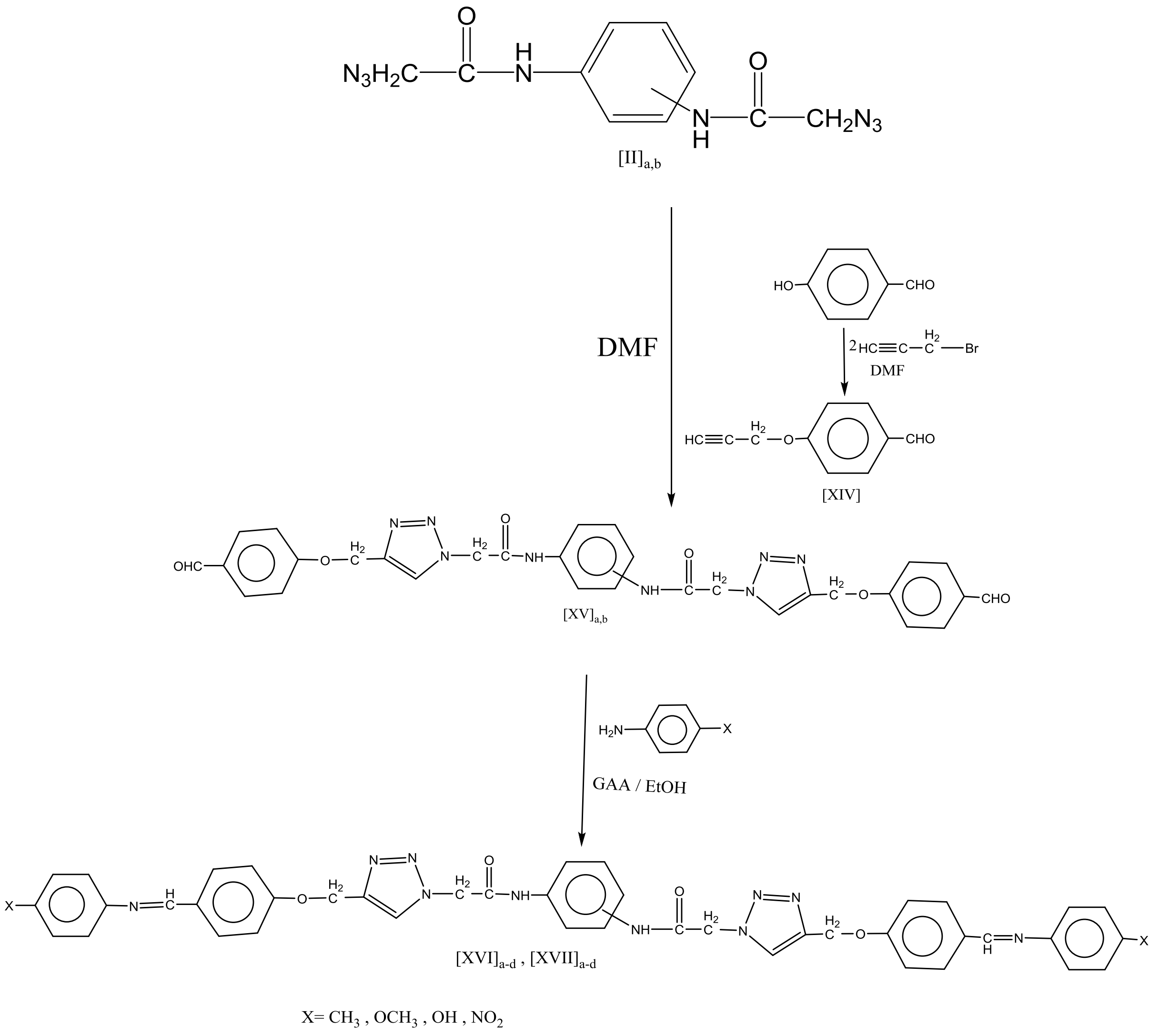


n= 1,2,3,5,6,7,8

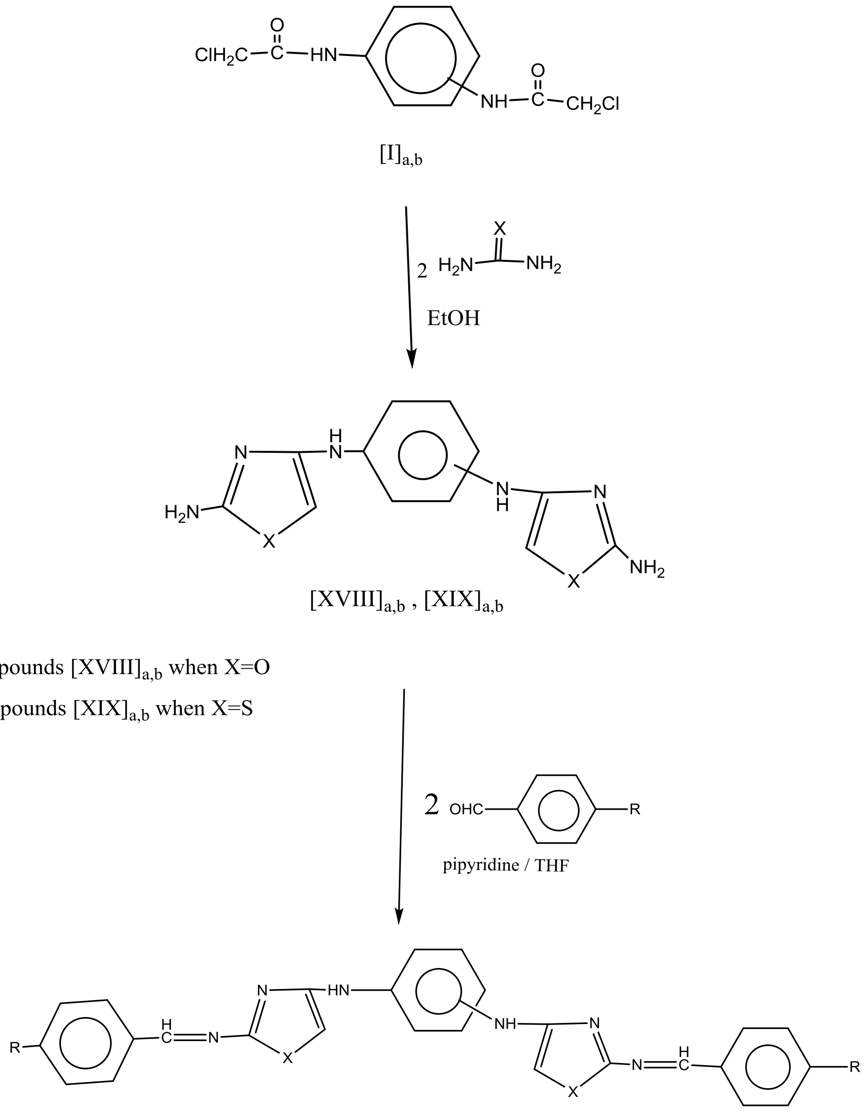
Scheme (1)


2Cl–C(O)–CH2Cl
TEA / DMF
[I]a,b
1)DMF
2) NaN3 /NH4Cl
2 KSCN/acetone
[II]a,b
2 H2C=CHCOOH
THF
[III]a,b
DMF / SOCl2
[XIII]a,b
2
[x]a,b
2 H2N–C6H4–X
DMF/10%HCl
[XI]a-d , [XII]a-d
X=CH3 , OCH3 , OH , NO2
[IX]a,b

Scheme 2


[II]a,b
DMF
HO
CHO
2 HC≡C–CH2–Br
DMF
[XIV]
[XV]a,b
H2N
X
GAA / EtOH
[XVI]a-d , [XVII]a-d
X= CH3 , OCH3 , OH , NO2

Scheme 3



$[I]_{a,b}$

$[XVIII]_{a,b}$, $[XIX]_{a,b}$

The compounds $[XVIII]_{a,b}$ when X=O

The compounds $[XIX]_{a,b}$ when X=S

R =OH, OCH_3 , CH_3

$[XX]_{a\text{-}c}$, $[XXI]_{a\text{-}c}$
$[XXII]_{a\text{-}c}$ $[XXIII]_{a,b}$

The compounds $[XX]_{a\text{-}c}$ and $[XXI]_{a\text{-}c}$ when X=O

The compounds $[XXII]_{a\text{-}c}$ and $[XXIII]_{a\text{-}c}$ when X=S

Scheme4

جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة بغداد

كلية التربية للعلوم الصرفة(ابن الهيثم)

قسم الكيمياء

تحضير , تشخيص ودراسة السلوك الميزوميري لبعض الميزوجينات الجديدة المحتوية على حلقة غير متجانسة

أطروحة مقدمة الى

مجلس كلية التربية للعلوم الصرفة- إبن الهيثم – جامعة بغداد وهي جزء
من متطلبات نيل دكتوراه فلسفة في علوم الكيمياء

من قبل

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بكالوريوس علوم كيمياء / جامعة بغداد 2006

ماجستير علوم كيمياء / جامعة تكريت 2012

بأشراف

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