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Synthesis and characterization of substituted 1, 2,4-triazole and their derivatives on poly ethylene

Rana Abid Ali [1], Zainab Amer [1] Entesar O. Al-Tamimi[1]
Department of Chemistry, College of Science, University of Baghdad
Jadiriya , Baghdad, Iraq

Abstract

New derivatives of 1,2,4- triazole , 1,2,4-triazole -3-one and 1,2,4-triazole-3-thione were obtained through this research. Acid hydrazide derivative was present from reaction of poly acryloyl chloride with hydrazine hydrate in presence of DMF as a solvent then reacted with benzonitrile and its derivatives to give 1,2,4-triazole derivatives. After that reaction of poly acryloyl chloride with semicarbazide and semithiocarbazide to form semicarbazone and semithiocarbazone derivatives respectively. Finally, closing of semicarbazone and semithiocarbazone derivatives with 2% NaOH gave 1,2,4-triazole -3-one and 1,2,4-triazole-4-thione derivatives respectively. These new synthesized products have been characterized by infrared, ^{1}H-nuclear magnetic resonance and ^{13}C-nuclear magnetic resonance for some of them and their physical properties were measured.

Keywords: 1,2,4-triazole, 1,2,4-triazole-3-one, 1,2,4-triazole-3-thione

INTRODUCTION

Non-homogeneous ring chemistry is one of the branched organic chemistry that has a future prospects and long history. 1,2,4-Triazole are heterogeneous aromatic rings containing five-membered ring of two carbon atoms and three nitrogen atoms[(1)]. 1,2,4-Triazole derivatives have attracted scientists interest in having broad chemical properties, pharmalogical activities and synthetic versatility such as antifungal antbacterial[(2)], antimicrobial [(3)], anti-inflammatory, anti cancer and analgestic[(4)]. Cyano-acid hydrazide derivatives are intermediate compounds for the preparation of a large and varied number of heterogeneous ring compounds. The beta functional nitrile moiety of the molecules a favorable unit to add followed by closure by cycloaddition with multiple reagent to give heterocyclic compound of various ring sizes with one or multiple heteroatoms that are interesting as dyes, as herbicides and as pharmaceutical[(5-8)]. 1,2,4-Triazole-3-one and 1,2,4-triazole-3-thione derivatives are prepared in several methods. One of the most popular ways to prepare these compounds includes cyclodehydration of semicarbazides and semithiocarbazide with a diversity of basic reagents, such as sodium carbonate, sodium hydroxide, triethyl amine, potassium hydroxide, ……etc.[(9)]. These compounds have been reported to possess antifungal, antitubercular and antimicrobial properties[(10)].

MATERIAL AND METHOD

All used chemicals in this article were purchased from Sigma-aldrich unless otherwise stated. Fourier transform infrared radiation spectra were recorded on SHIMADZU FTIR - 8400 Fourier Transform Infrared spectrophotometer as KBr disc. ^{1}H-nuclear magnetic resonance and ^{13}C nuclear magnetic reasonance spectra were recorded on Bruker spectrospin ultra shield magnets 400 MHz instrument in Ahl-Albate University in Jordan. Softening point were determined on thermal microscope Riecherthermover.

Polymerization of acryloyl chloride [1][(11)]

This combination was synthesized according to the literature's procedure [(11)].

Preparation of acid hydrazide derivative [2] [(12)]

A mixture of poly acryloyl chloride and hydrazine hydrate (0.05 mole) in 15 ml of DMF was refluxed for 7 hrs. The content was concentrated, cooled and fitltered. The separated precipitate was purified by dissolved in DMF and reprecipitate from acetone.

Preparation of 1,2,4-triazole derivatives [3-5] [(13)]

A mixture of (0.01 mole) of acid hydrazide derivative [2] and benzonitrile derivatives (0.01) mole in presence of DMF as a solvent was refluxed for 3 hrs. The separated precipitate was cooled, filtered and purified by dissolved in DMF and reprecipitate from acetone.

Preparation of semicarbazone[6] and semithiocarbazone [7] [(14)]

(0.03 mole) of poly acryloyl chloride [1] in 10 ml of DMF was added to (0.018 mole) of semicarbazide and semithiocarbazide then refluxed for 3 hrs. The separated precipitate was cooled, filtered and purified by dissolved in DMF and reprecipitate from acetone.

Preparation of 1,2,4-triazole -3-one [8] and 1,2,4-triazole -3-thione[9] [(15)]

(0.003) mole of semicarbazide derivative [6] and semithiocarbazide derivative [7] was placed in a round bottomed flask equipped with 40 ml of 2 % NaOH and refluxed for 5 hrs. The solution was cooled and naturalized with dil. HCl. The separated precipitate was cooled, filtered and purified by dissolved in DMF and reprecipitate from acetone.

Physical properties of synthesized polymers [2-9] are listed in Table (1).

FT-IR spectral data of synthesized polymers [2-9] are listed in table (2).

^{1}H-NMR and ^{13}C-NMR spectral data of some prepared polymers (3,8 and 9) are listed in Table (3,4).

RESULT AND DISCUSSION

This research was carried out in several steps , which were carried out in schemes (1) and (2).

The acid hydrazide derivative [2] was synthesized from the reaction of polyacryloyl chloride with hydrazine hydrate in presence of DMF as a solvent. FTIR spectrum of compound [2] (figure 7) showed the appearance of some bands at [(3440 asy - 3421 sym), 3227, 1680 and 2900] cm^{-1} belong to ν(-NH_2), ν(-NH), ν(C=O) amide and ν(C-H) aliphatic respectively. The infrared indicated disappearance band of ν(C-Cl) recorded in table (2).

Then acid hydrazide derivative [2] reacted with acetonitrile and its derivatives to form 1,2,4-triazole derivatives [3-5]. FTIR specral of 1,2,4-triazole derivatives [3-5] showed disapperance of band of ν(-NH_2) and appearance of the bands at (1646-1650) cm^{-1} belong to ν(C=N), and of [(3319-3385), (1570-1590), (3010-3080), (2250-2314)] cm^{-1} belong to ν(-NH), ν(C=C) aromatic, ν(C-H) aromatic and ν(CN) respectively

^{1}H-NMR spectrum data of compound [3] δ ppm in (DMSO+TFA) showed singlet signal of δ = 7.9 ppm due to (-NH) proton, singlet weak signal δ = (0.8-1.1) ppm due to (C-H) aliphatic protons and signal of δ = (7.5-7.7) due to aromatic protons, table (3) figure (1). ^{13}C-NMR : 109-132 (aromatic carbon), 15 (C-H), 10 (C-H_2), 157 (C=N) table (4) figure (2).

On the other hand FTIR spectrum of compound [6] (figure 8) showed the following bands at [(3471 asym, 3428sym), 3371, 1700 and (2900-2980)] cm^{-1} belong to ν(-NH_2), ν(-NH), ν(C=O) and ν(C-H) aliphatic respectively. FTIR specrum of compound [7] showed the following bands at [(3470 asym, 3430sym), 3370, 1290 and (2850-2900)] cm^{-1} belong to ν(-NH_2), ν(-NH), ν(C=S) and ν(C-H) aliphatic. FTIR of compound [8] showed the characteristic apperance of absorption bands at [1570, 1690, 3372, 2855] cm^{-1} belong to ν(N=N), ν(C=O), ν(-NH) and aliphatic ν(C-H) mentioned in table (2).

^{1}H-NMR specta of compound [8] δ ppm showed singlet signal of δ = 8 ppm due to (N-H) proton, singlet signal δ = (1.2-2.3) ppm due to (C-H) aliphatic, table (3) figure (3). ^{13}C-NMR specta of compound [8] 163 (C=O), 38 (C-H), 20 (C-H_2) table (4) figure (4).

FTIR of compound [9] showed the characteristic apperance of absorption bands at [1560, 1298, 3370 and 2850] cm^{-1} belong to ν(N=N), ν(C=S) thiocarbonyl group, ν(-NH) and aliphatic ν(C-H), Table (2).

^{1}H-NMR specta of compound [9] δ ppm showed singlet signal of δ = 8.5 ppm due to (N-H) proton, singlet signal δ = (1.5-2.1) ppm due to (C-H) aliphatic, table (3) figure (5). ^{13}C-NMR specta of compound [9] 183 (C=O), 38 (C-H), 20 (CH_2) table (4) figure (6).

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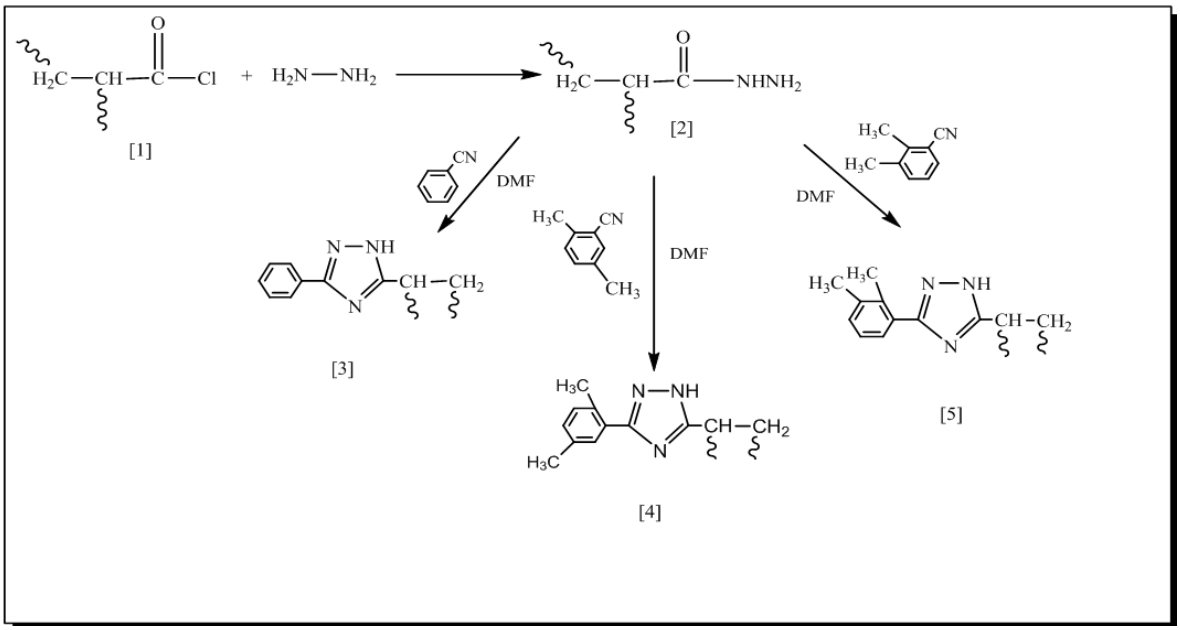
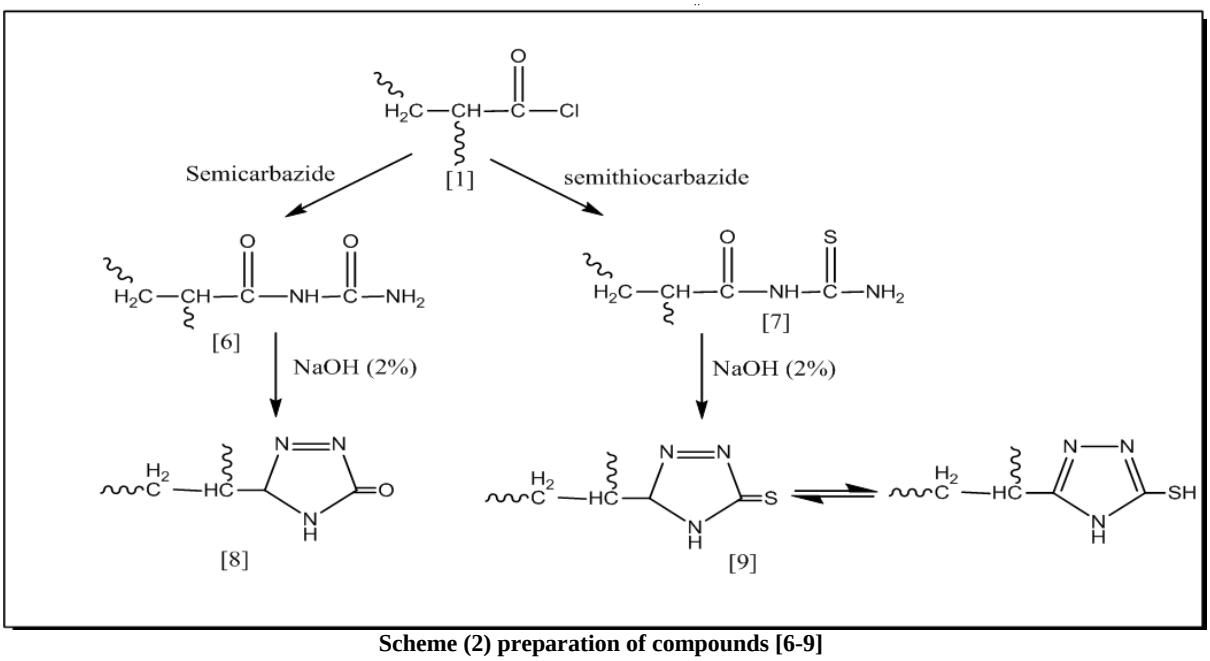


Scheme (1) preparation of compounds [2-5]



Scheme (2) preparation of compounds [6-9]

Table (1) physical properties of the prepared compounds [2-8]

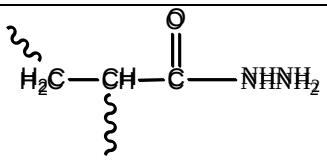
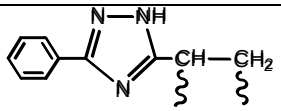
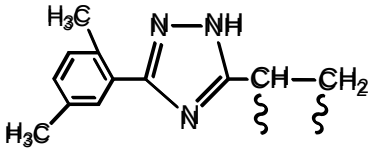
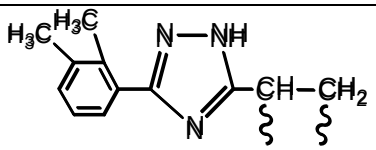
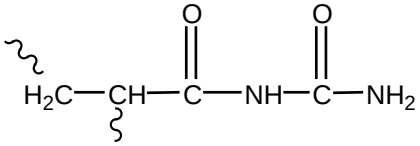
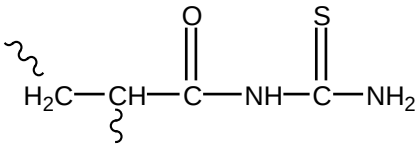
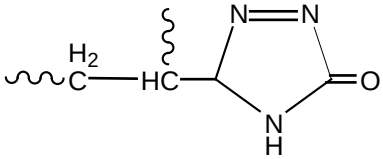
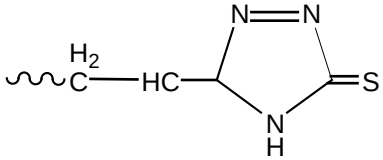
Compound No.	Compound Structure	s.p C^0	color	% Yield
2		220-240	White	94
3		180-205	White	96
4		210-230	White	78
5		170-185	White	75
6		120-138	White	80
7		220-230	Green	70
8		225-236	White	75
9		248-260	Off White	60

Table (2) FTIR spectral data of the prepared compounds [2-8]

Compound No.	N=N	C=N	N-H	N-H2	C=O Amide	C=C aromatic	C=S	C-H aliphatic	C-H aromatic	C≡N
2	----	---	3227	3440 asym 3421 sym	1680	---	-----	2890-2900	---	---
3	----	1650	3350	---	---	1580	------	2880-2900	3010	2250
4	----	1646	3319	---	--	1570	------	2837-2880	3050	2314
5	----	1647	3385	---	---	1590	------	2900-2972	3080	2310
6	---	---	3371	3471 asym 3428 sym	1700	---	----	2900-2980	----	---
7	---	----	3370	3470 asym 3430 sym	---	---	1290	2850-2900	----	---
8	1570	----	3372	---	1690	----	----	2855-2910	---	---
9	1560	----	3370	---	---	---	1298	2850-2900	---	---

Table (3) H-NMR specrtal data of some of the prepared compounds [3,8 and 9]

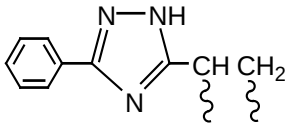
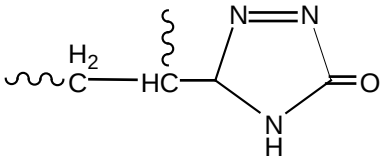
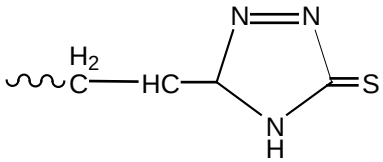
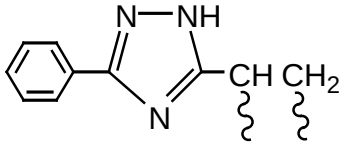
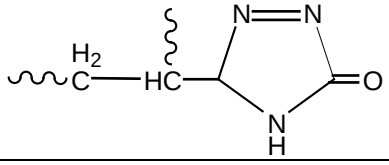
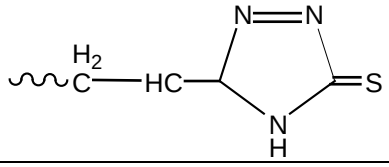
Compound No.	Compound structure	H-NMR spectral data δ ppm
3		7.5-7.7(m , 5H) aromatic , 7.9(s, N-H) , 1.1 (CH), 0,8 (CH2)
8		8 (s, N-H), 2.3 (t, CH), 1.2(d,CH2)
9		8.5 (s, N-H), 2.1 (t, CH), 1.5(d,CH2)

Table (4) ^{13}C-NMR specrtal data of some of the prepared compounds [3,8 and 9]

Compound No.	Compound structure	^{13}C-NMR spectral data δ ppm
3		109-132 (aromatic carbon), 15 (C-H), 10 (C-H2), 157 (C=N)
8		163 (C=O),38 (C-H), 20(CH2)
9		183 (C=S), 38 (C-H), 20(CH2)

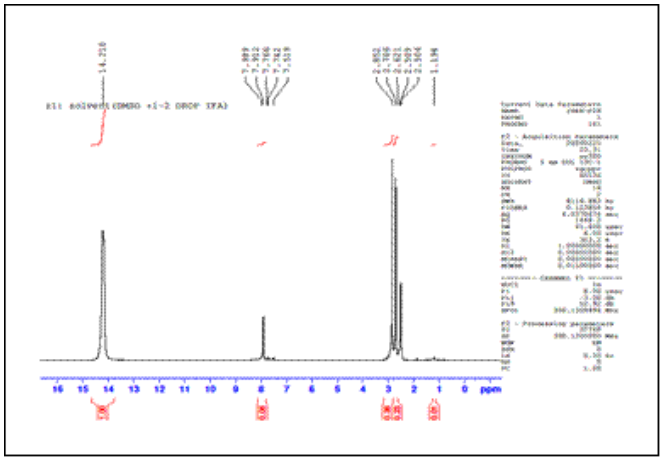


Figure (1) HNMR spectum of compound [3]

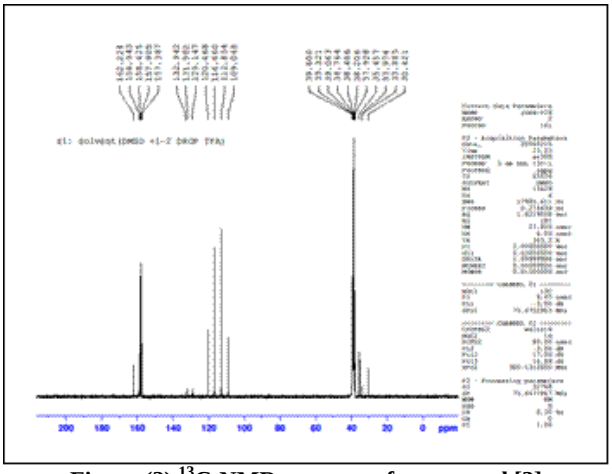


Figure (2) ^{13}C-NMR spectum of compound [3]

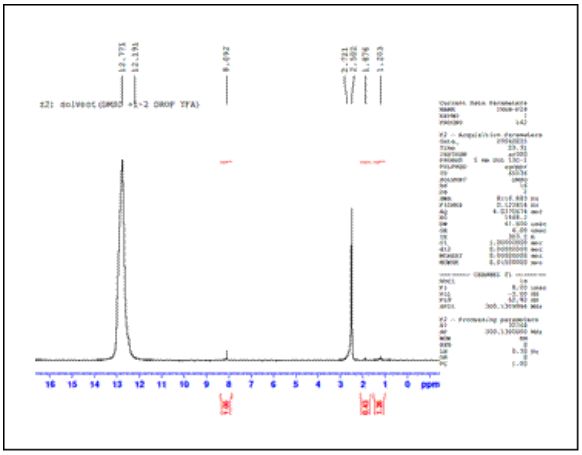


Figure (3) HNMR spectum of compound [8]

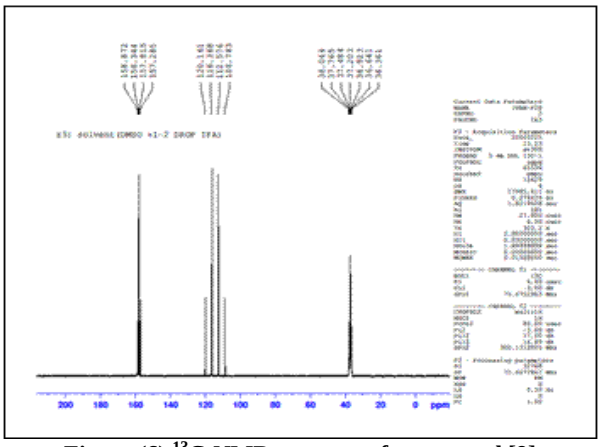


Figure (6) ^{13}C-NMR spectum of compound [9]

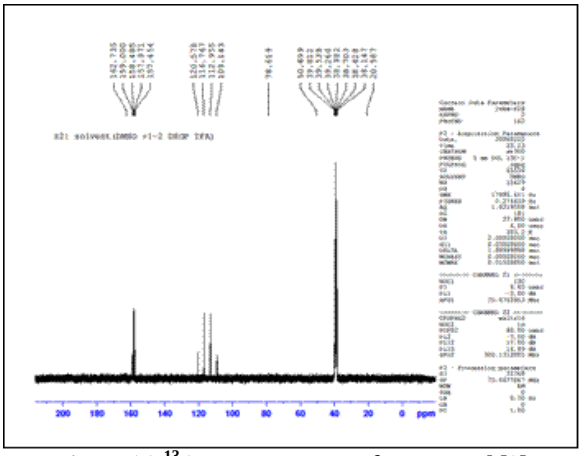


Figure (4) ^{13}C-NMR spectum of compound [8]

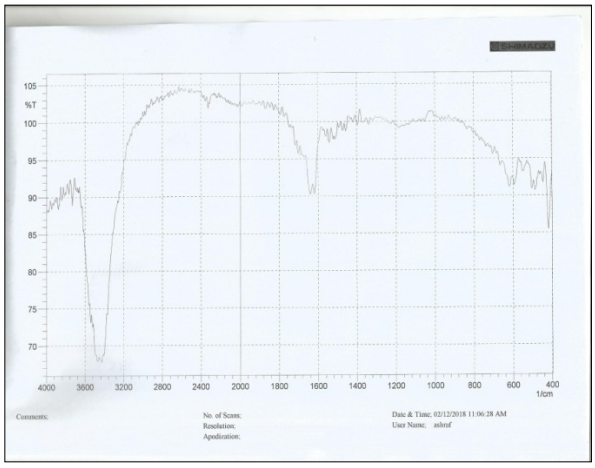


Figure (7)FTIR of compound [2]

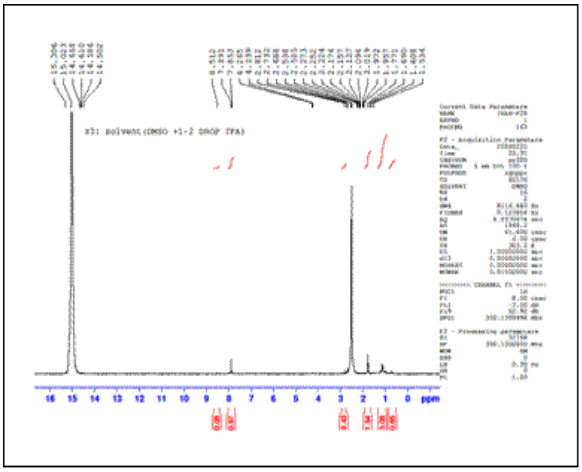


Figure (5) HNMR spectum of compound [9]

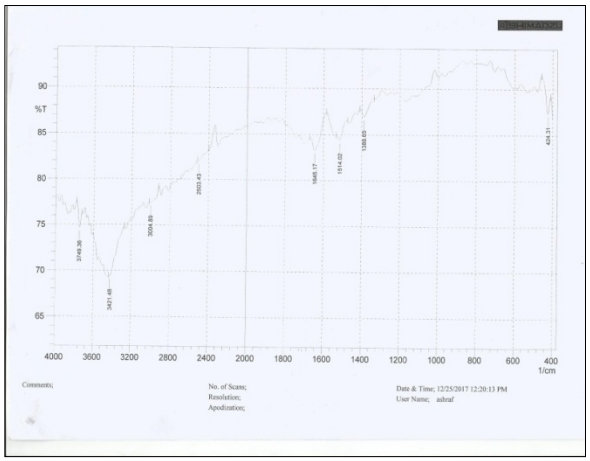


Figure (8)FTIR of compound [6]

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