Iraqi Journal of Science

ISSN: 0067-2904

Synthesis and Characterization of Novel Subs. -1,3,4-Thiadiazolependant on Modified Poly(5-Vinyl Tetrazole-Co-MA).

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Received: 2/6/ 2019 Accepted: 21/ 9/2019

Abstract

New polymers were prepared from a monomer (5-vinyl-1H-tetrazole), which was prepared from acrylonitrile with sodium azide in the presence of ZnCl2.Another monomer (Methyl acrylate) was also used. Co-monomers were polymerized usingBPO as initiator**.** The second step was the preparation of copoly acid hydrazide from the reaction of compound2 with hydrazine hydrate, followed by the reaction with carbon disulphide in the presence of KOH to obtain copoly (5-subs.-2-mercapto-1,3,4-thiadiazole). Next,compound4 was reacted with chloroacetyl chloride to yield compound4 5 which was reacted with (hydrazine hydrate , phenyl hydrazine and 2,4-di nitro phenyl hydrazine) as shown in scheme(1). Physical properties of all the prepared copolymers were characterized by FT-IR and, in certain cases,by1HNMR spectroscopy.

Keywords: Schiff bases, Copolymerization, Acid Hydrazide, 1,3,4-Thiadiazole.

تحضير وتشخيص معوض 4,3,1- ثاياديازول الجديد المتدلي على البوليمر المحور(5- فاينيل تترازول – مشترك – اكريلات المثيل)

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الخلاصة:

تم تحضيرالبوليميرات المشتركة من المونومير (5- فاينيل -H1- تترازول) ، الذي حضر من تفاعل الأكريلونيتريل مع أزيد الصوديوم في وجود $ZnCl_2$ ، كما تم استخدام مونومير آخر أكريلات المثيل. كان المونومرين يستخدمون بعملية بلمرة باستخدام (بنزويل بيروكساید) كبادئ. الخطوة الثانية تم تحضير البوليمرالمشترك حامض الهيدرازايد من تفاعل البوليمر المشترك (5- فاينيل -1 H- تترازول- أكريلات المثيل) مع الهيدرازين المائي ، ثم تفاعله مع ثنائي كبريتيد الكاربون في وجود هيدروكسيد البوتاسيوم KOH للحصول على البوليمر المشترك (5- معوض- 2- ميركبتو- 4,3,1- ثاياديازول) . ثم التفاعل مع كلورو أسيتيل كلوريد لينتج بولي [5- فاينيل -H1- تيترازول- مشترك- {2- (2- ايثانوات كلورو ايثان) -5- فاينيل - 4,3,1- ثاياديازول }]. هذا المركب يتفاعل مع المركبات (الهيدرازين المائي ، فنيل هيدرازين و 4,2- ثنائي نيترو فنيل هيدرازين) لإعطاء مركبات جديدة. تم تشخيص جميع المركبات المحضرة بأطياف FT-IR ، والبعض منها شخصت بال 1H-NMR ودرجات التلين .

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1. Introduction

Five-membered aromatic rings with three heteroatoms are a type of aromatic compounds in which the various heteroatoms contribute very differently to the formation of the aromatic conjugation[1]. 1,3,4-thiadiazole derivatives bearing Schiff base moieties have been reported to display a wide range of biological properties. Heterocyclic compounds are important organic compounds with several applications in electronics, pharmacology, etc. [2]. Thiadiazole is a heterocyclic compound with isomers such as 1,2,3-thiadiazole, 1,2,5-thiadiazole, 1,2,4-thiadiazole, and 1,3,4-thiadiazole. 1,3,4-thiadiazole is the most widely studied isomer. It has been converted into many different derivatives in order to synthesize five-membered heterocyclic compounds with different properties [3, 4]. Its derivatives have several applications in antimicrobial [5], anticancer [6, 7], antipsychotic [8], anti-tubercular [9], antihistamine [10], anticonvulsant [11], anti-inflammatory [12], anti-leishmanial[13], anti-hepatitis B [14], anti-Parkinson [15], and anti-diabetic [16] fields. The existence of the -N=C-S part in the thiadiazole ring induces the mentioned multiple activities. Also, the aromaticity of thiadiazoles contributes to low toxicity and in vivo durability [5]. In the literature, the synthesis of 1,3,4-thiadiazole derivatives has been performed using thiosemicarbazides[17], thiocarbazides[18], dithiocarbazates[19], thioacylhydrazines[20], acylhydrazines[21], and bithioureas[22] as starting materials. Copolymers from free radicals consist of polymerization of two different monomers that have a double bond in structure, with the purpose of improving the properties of the mechanical polymer along with other uses.

Schiff's bases are produced mainly by a condensation process between primary amines and carbonyl compounds. The general formula is RHC=NRI, where R and RI are alkyl, aryl, cycloalkyl, or heterocyclic groups, characterized by the azomethine group[23]. Chemically, a Schiffs base is a nitrogen base of an aldehyde or ketone where the carbonyl group is changed by imine or azomethine group. Schiff's bases also characterized by appear a widely range biological activities(e.l anti-bacterial, anti-fungal, anti-cancer, anti-inflammatory, anti-viral, and anti-pyretic properties)[24,25]. Schiff bases of aliphatic aldehydes are unstable and readily polymerizable, while Schiff bases of aromatic aldehydes with an effective conjugation system are more stable [26].

2.Experimental

1) Preparation of 5-vinyl-1H-tetrazole[27], In a 100 ml round-bottom flask, a mixture of 30 ml distilled water, 0.01 mole(0.53 gm, 0.65 ml) acrylonitrile,0.01 mole(0.72 gm, 0.39 ml) NaN_3 ,and0.01 mole(1.36 gm, 0.47 ml) $ZnCl_2$ was placed. The mixture was refluxed with stirring at 95◦C for 6hrs.The solution was cooled at room temperature, then conc. HCl was added until reaching a pH of 2-3. The reaction mixture was stirred for1hrat room temperature, then the solid precipitate was filtered, washed with 10 ml hot water, and dried in air. The product was purified by re-crystallization from THF. The physical properties are listed in Table-1.

2) Preparation of copoly(5-vinyl-1H-tetrazole-methyl acrylate)[28]: (2)

In a screw-capped polymerization bottle,0.001 mole (0.1 gm) of the pure monomer 5-vinyl-1H-tetrazole and 0.001 mole(0.07 gm, 0.09 ml) of another monomer (methyl acrylate) were dissolved in 1:9 of dry DMSO:THF . An amount equal to 0.02% of the monomers weight of benzoyl peroxide (BPO) was then added. Oxygen was removed from the bottle by pumping an inert gas (nitrogen) for few minutes and the bottle was then firmly stoppered. The clear solution was maintained at 80-90c◦ in a constant temperature oil bath for 7-9 hrs. Then the solution was poured into 10 ml of methanol and the copolymer was precipitated, filtered, washed with water, and dried. The product was purified by dissolving in DMF and precipitated from water. The physical properties are listed in Table-1.

3) General procedure for the preparation of acid hydrazide[29]: (3)

In a 100 ml round-bottom flask,0.01 mole of compound 2 was dissolved in20 ml absolute ethanol, then 4 ml of 99% hydrazine hydrate was added .The mixture was refluxed with stirring at 80◦C for 6 hrs. The solid precipitate was filtered and washed with cooled water. The resulting solid was purified by dissolving in DMSO and re-precipitated from ethanol. The physical properties are listed in Table-1.

4) Preparation of poly (5-vinyl-1H-tetrazole-Co-2-thiol-5-vinyl-1,3,4-thiadiazole) [30] : (4)

Acid hydrazide (0.01 mol) was suspended in absolute ethanol(30 ml) placed in a round-bottom flask(100 ml), then potassium hydroxide (0.01 mol, 0.56 gm) and carbon disulphide (0.01 mol, 0.60 ml) were added respectively with continues stirring. The mixture was stirred under reflux for 1 hr. at room temperature and later at 80ºC for 24 hrs. The solvent was removed and the residue was dissolved in water (100 mL) and acidified with conc. HCl drop by drop. A white-yellowish precipitate was

formed, collected by filtration, and washed with distilled water.The resultingsolid was purified by dissolving in DMSO and re-precipitated from ethanol. The physical properties of compound 4are listed in Table-1.

5) Preparation of poly[5-vinyl-1H-tetrazole-Co-{2-(2-chloroethanethioate)-5-vinyl -1,3,4-thiadiazol}][31]: (5)

Equimolars of compound 4 (0.01mol) with chloroacetyl chloride (0.01 mol) were dissolved in DMF (25ml) in the presence of trace quantities of anhydrous potassium carbonate, then refluxed on a water bath for 14 hrs. The solvent was removed by vacuum and the resulting solid was purified by dissolving in DMSO and re-precipitated from ethanol. The physical properties of compound 5are listed in Table-1.

6) Preparation of poly[5-vinyl-1H-tetrazole-Co-{2-(2- hydrazineylethanethioate)- 5-vinyl -1,3,4-thiadiazol}] [32]: (6)In a 100 ml round-bottom flask, 0.01 mole of compound 5 was dissolved in20 ml of abs.ethanol, then 4 ml of 99% hydrazine hydrate was added. The mixture was refluxed with stirring at 80◦c for 6hrs. The solid precipitate was filtered, washed with cooled water, and dried in air. The resulting solid was purified by dissolving in DMSO and re-precipitated from ethanol. The physical properties of compound 6 are listed in Table- 1.

7) Preparation of schiff bases derivatives [33]: (7-11)

Equimolar quantities of compound 6(0.01mol.),different aromatic aldehydes (0.01mol.) in 25 ml of chloroform, and 3-4 drops of glacial acetic acid were refluxed on a water bath for about 4-5 hrs. at 50◦C. The solvent was removed under reduced pressure to obtain the product. The physical properties of compounds 7-11are listed in Table-1.

8) Preparation of poly(5-vinyl-1H-tetrazole-Co-{2-(2-N-phenyl) hydrazineylethanethioate- 5-vinyl -1,3,4-thiadiazol}][34].

In a 100 ml round-bottom flask,0.01 mole of compound 5 was dissolved in20 ml of abs.ethanol, then 4 ml phenyl hydrazine was added. The mixture was refluxed with stirring at 80◦C for 6hrs. The solid precipitate was filtered, washed with cooled water, and dried in air. The resulting solid was purified by dissolving in DMSO and re-precipitated from ethanol. The physical properties of compound 6 are listed in Table-1.

9) Preparation of compounds 13-17[34]:

Equimolar quantities of compound12(0.01mol.), different aromatic aldehydes (0.01mol) in 25 ml of chloroform, and 3-4 drops of glacial acetic acid were refluxed on a water bath for about 4-5 hr. at 50C. The solvent was removed under reduced pressure to obtain the product. The physical properties of compounds 13-17 are listed in Table-1.

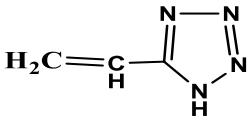
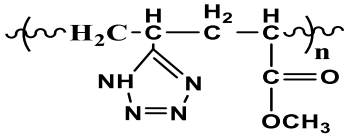
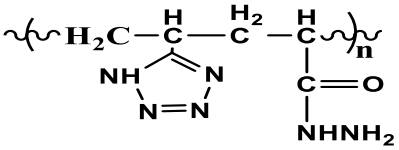
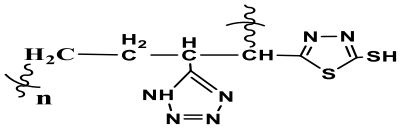
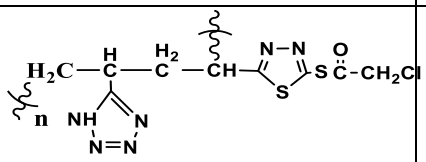
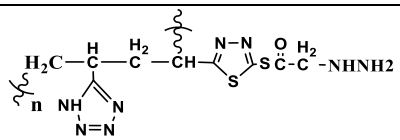
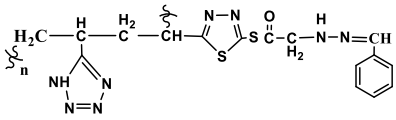
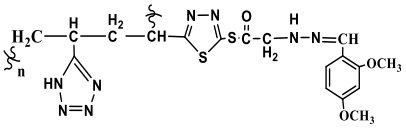
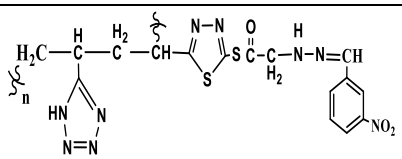
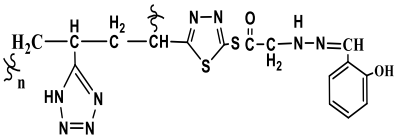
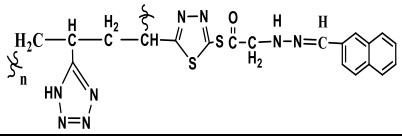
10) Preparation of poly(5-vinyl-1H-tetrazole-Co-{2-(2-N(2,4-initrophenyl)hydrazineyl)ethanethioate-5-vinyl-1,3,4-thiadiazol}] [34]:(18)

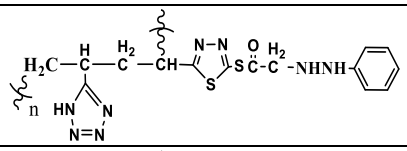
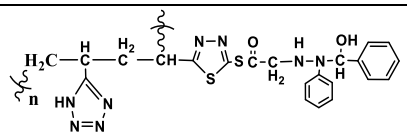
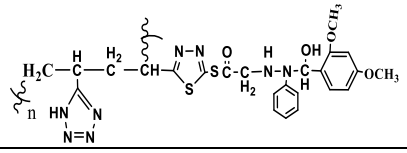
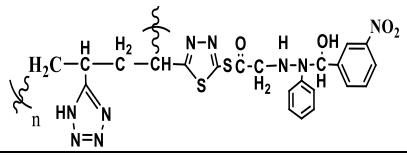
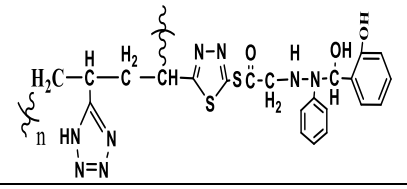
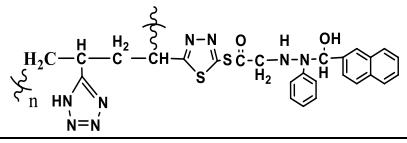
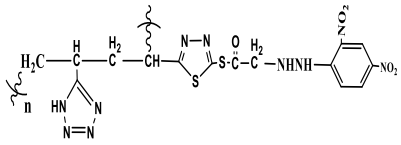
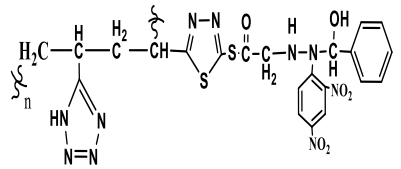
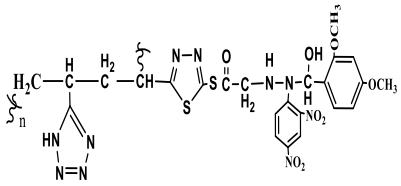
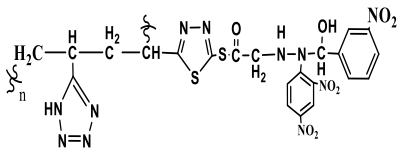
In a 100 ml round-bottom flask, 0.01 mole of compound 5 was dissolved in20 ml abs.ethanol, then 4 ml 2,4-dinitro phenyl hydrazine was added. The mixture was refluxed with stirring at 80◦c for 6hrs. The solid precipitate was filtered, washed with cooled water, and dried in air. The resulting solid was purified by dissolving in DMSO and re-precipitated from ethanol. The physical properties of compound 6are listed in Table-1.

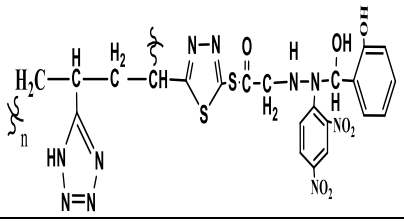
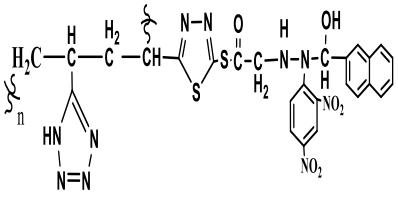
11) Preparation of compounds 19-23[34]:

Equimolar quantities of compound18 0.01mol.,different aromatic aldehydes (0.01mol) in 25 ml of chloroform, and 3-4 drops of glacial acetic acid were refluxed on a water bath for about 4-5 hr. at 50◦C. The solvent was removed under reduced pressure to obtain the product. The physical properties of compounds 19-23 are listed in Table-1.

Table 1-Physical properties of the prepared compounds 1-23

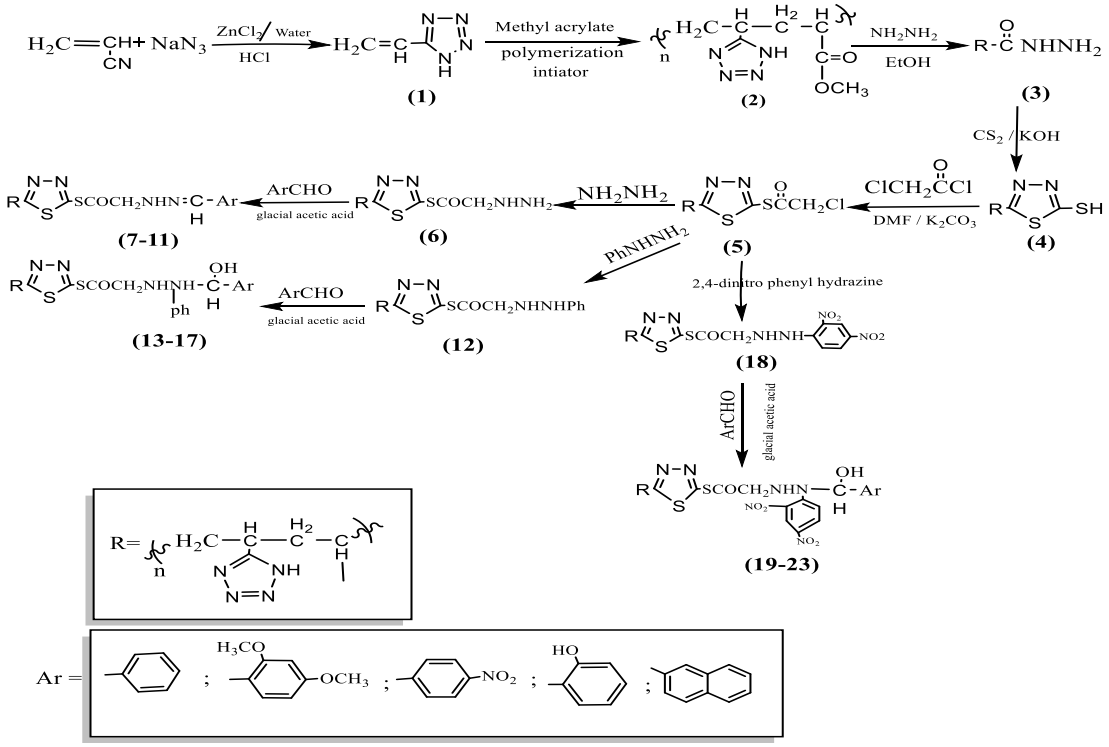
Comp. No.	Structure	Color	Softening point c◦	Conversion %
1		Yellow	210-227	Yield% 65
2		Pale yellow	225-235	85
3		Off white	220-235	87
4		yellow	195-205	67
5		Light yellow	170-180	72
6		Off white	160-150	46
7		yellow	90-100	75
8		Off white	270-285	53
9		Pale yellow	200-210	71
10		Off white	>300	67
11		Pale yellow	>300	77

12		yellow	250-270	90
13		Light brown	>300	87
14		Pale orange	95-110	93
15		yellow	260-275	98
16		Pale yellow	270-285	94
17		Brown - orange	230-245	79
18		orange	200-210	89
19		Dark orange	230-240	95
20		red	250-265	90
21		yellow	270-280	98

22		red	250-260	89
23		orange	270-285	96

3. Results and Discussion

In the current study, the synthesis and characterization of novel subs. -1,3,4-thiadiazole pendant on modified poly(5-vinyl tetrazole-co-methyl acrylate) were obtained by a series of reactions. All products have conversion ratio ranges of46-98 %,softening point ranges of 90-100)-(>300)ºC and other physical properties which are listed in Table-1. The synthesis of compounds 1-23'' are outlined in scheme 1.



Scheme 1-Synthetic routes of compounds 1-23.

Compound 1 was prepared by the reaction of acrylonitrile with sodium azide in the presence ofzncl2 in water for 6 hrs. The yield percentage was 65%,the softening point range was 210-227 c○, while other physical properties are listed in Table-1. FTIR spectrum of this compound shows the appearance of the absorption bands of ʊ N-H, ʊ C=N, and ʊ C=C(olef.)] at 3247 , 1643 , and 1625 cm-1, respectively, while the other absorption bands are listed in Table-2.

Compound 2 was prepared from copolymerization of compound 1 with methyl acrylate(MA) in the presence of benzoyl peroxide (BPO) at 80-90 C○. All physical properties are listed in Table-1. FTIR spectrum of this compound shows the appearance of the absorption bands due to ʊ C=O ester and ʊ C-H aliphatic at 1739 and 2860-2952cm-1, respectively. The other absorption bands are listed in Table-2.

Compound 3 was prepared by the reaction of compound 2 with 99% hydrazine hydrate in ethanol. All physical properties are listed in Table-1. FTIR spectrum of this compound show the appearance of

the absorption bands due to ʊ N-H , ʊ NH2 ,and ʊ C=O amide at 3294 , 3319-3402 , and 1652cm-1, respectively. The other absorption bands are listed in Table-2. 1H-NMR spectrum of this compound showed signals at δ 6.30 ppm of s,1H,NHtetrazole, δ 8.87 ppm ofs,1H,-NH-NH2, δ 4.11 ppm of d,2H,-NH-NH2, δ 2.53 ppm of m,1H,-CH2-CH~-ring, δ 2.50 ppm of m,1H,~H2C-CH-CH2-, δ 1.22 ppm of t,2H,~H2C-CH-CH2-, and δ 1.97 ppm of t,2H,-CH-CH2-CH-.

Compound 4 was prepared by the reaction of compound 3 with carbon disulphide in the presence of KOH in ethanol. The yield percentage was 67%, the softening point range was195-205 c○, and other physical properties are listed in Table-1. FTIR spectrum of this compound show the appearance of the absorption bands of ʊ N-H, ʊ C=N, ʊ C-S, and ʊ S-H at 3280,1652,1244, and 2644 cm-1, respectively, while the other absorption bands are listed in Table-2. 1H-NMR spectrum of this compound showed signals at δ 6.64 ppm of s,1H,NHtetrazole, δ 2.53 ppm of m,1H,-CH2-CH~-ring, δ 2.89 ppm of m,1H,~H2C-CH-CH2-, δ 1.23 ppm of t,2H,~H2C-CH-CH2-, δ 1.91 ppm of t,2H,-CH-CH2-CH-, and δ 13.18 ppm of s,1H.S-H.

Compound 5 was prepared by the reaction of compound 4 with chloroacetyl chloride in the presence of K2CO3 in DMF. The mechanism of this reaction are shown in Scheme**2**[35].

Compound5 was prepared by the reaction of compound 4 with chloroacetyl chloride in the presence of K2CO3 in DMF for 14 hr. The yield percentage was 72%, the softening point range was170-180 c○, and the other physical properties are listed in Table-1. FTIR spectrum of this compound show the appearance of the absorption bands of ʊ N-H, ʊ C=N, ʊ C-S, ʊ C=O, and ʊ C-Cl at 3188,1672,1230,1704, and 719 cm-1, respectively, while the other absorption bands are listed in Table-2. 1H-NMR spectrum of this compound showed signals at δ 6.92 ppm of S,1H,NHtetrazole, δ 2.25 ppm of m,1H,-CH2-CH~-ring, δ 2.11 ppm of m,1H,~H2C-CH-CH2-, δ 1.07 ppm of t,2H,~H2C-CH-CH2-, δ 1.92 ppm of t,2H,-CH-CH2-CH-, and δ 3.47 ppm of S,2H,(C=O)-CH2.

Compounds 6, 12, and 18 were prepared by the reaction of compound 5 with hydrazine and hydrazine derivatives in abs.ethanol for 6 hrs.. All the physical properties of the prepared compounds are listed in Table-1. FTIR spectrum of compounds 6, 12, and 18 showed the appearance of the absorption bands of ʊ C-S at 1190-1284 cm-1,ʊ C=O at 1714-1795 cm-1, and ʊ N-H at 3267-3326 cm-1. The other absorption bands are listed in Table-2. 1H-NMR spectrum of compound18 showed signals at δ 5.05 ppm of S,1H,NHtetrazole, δ 2.95 ppm of m,1H,-CH2-CH~-ring, δ 2.09 ppm of m,1H,~H2C-CH-CH2-, δ 1.05 ppm of t,2H,~H2C-CH-CH2-, δ 1.24 ppm of t,2H,-CH-CH2-CH-, δ 7.67-8.25 ppm of m,3H,Ar-H, δ 3.69 ppm of S,2H,(C=O)-CH2, δ 4.22 ppm of S,1H,CH2-NH-NH-, and δ 6.59 ppm of S,1H,NH-NH-ph.

Compounds 7-11 , 13-17 and 19-23 were prepared by the condensation reaction of compounds 6, 12, and 18 with different aromatic aldehydes in chloroform in the presence of few drops of acetic acid under reflux producing the new derivatives. Compounds 7-11 , 13-17 and 19-23 showed the appearance of the absorption bands of ʊ C-H aromatic at 3004-3100 cm-1, ʊ C=O at 1693-1795 cm-1, and ʊ N-H at 3255-3419 cm-1. Other absorption bands are listed in Table-2. δ 1H-NMR spectrum of compound8 showed signals at δ 6.66 ppm of S,1H,NHtetrazole, δ 2.09 ppm of m,1H,-CH2-CH~-ring, δ 2.03 ppm of m,1H,~H2C-CH-CH2-, δ 1.05 ppm of t,2H,~H2C-CH-CH2-, δ 1.24 ppm of t,2H,-CH-CH2-CH-, δ 7.49-8.27 ppm of m,3H,Ar-H, δ 3.85 ppm of S,2H,(C=O)-CH2, δ 8.85 ppm of S,1H,CH2-NH-N-ph, δ 5.05 ppm of S,1H,N=C-H, and δ 3.89 ppm of S,6H,ph-OCH3.

1H-NMR spectrum of compound14 showed signals at δ 6.67 ppm of S,1H,NHtetrazole, δ 2.90 ppm of m,1H,-CH2-CH~-ring, δ 2.09 ppm of m,1H,~H2C-CH-CH2-, δ 1.03 ppm of t,2H,~H2C-CH-CH2-, δ 1.25 ppm of t,2H,-CH-CH2-CH-, δ 6.70-7.68 ppm of m,8H,Ar-H, δ 3.88 ppm of S,2H,(C=O)-CH2, δ 6.65 ppm of S,1H,CH2-NH-N-ph, δ 5.20 ppm of S,1H,HO-CH-ph, δ 10.19 ppm of S,1H,CH-OH, and δ 3.92 ppm of S,6H,ph-OCH3.

1H-NMR spectrum of compound 19 showed signals at δ 6.50 ppm of S,1H,NHtetrazole, δ 2.53 ppm of m,1H,-CH2-CH~-ring, δ 2.09 ppm of m,1H,~H2C-CH-CH2-, δ 1.07 ppm of t,2H,~H2C-CH-CH2-, δ 1.24 ppm of t,2H,-CH-CH2-CH-, δ 7.50-8.89 ppm of m,8H,Ar-H, δ 3.95 ppm of S,2H,(C=O)-CH2, δ 6.80 ppm of S,1H,CH2-NH-N-ph, δ 4.21 ppm of S,1H,HO-CH-ph, and δ 11.67 ppm of S,1H,CH-OH.

1H-NMR spectrum of compound 23showed signals at δ 6.30 ppm of S,1H,NHtetrazole, δ 2.03 ppm of m,1H,-CH2-CH~-ring, δ 2.09 ppm of m,1H,~H2C-CH-CH2-, δ 1.02 ppm of t,2H,~H2C-CH-CH2-, δ 1.24 ppm of t,2H,-CH-CH2-CH-, δ 7.61-8.89 ppm of m,10H,Ar-H, δ 3.65 ppm of S,2H,(C=O)-CH2, δ 6.85 ppm of S,1H,CH2-NH-N-ph, δ 4.50 ppm of S,1H,HO-CH-ph, and δ 11.77 ppm of S,1H,CH-OH.

Table 2-FTIR spectral data (cm^{-1})for the prepared compounds 1-23.

ComP. NO.	U(N-H) Tetrazole	(C-H)U Aliphatic	(C=N)U (C=N)U imine	(N=N)U	(N-N)U	(C-N)U	(C-S)U	(C=O)U	C=C)U(aromatic	(C-H)U aromatic	Other bands
1	3247	-	1643	1498	1415	1336	-	-	-	-	Olef. 1625U(C=C)
2	3288	2952-2860	1645	1541	1454	1369	-	-	-	-	U(C=O)ester 1739 U(C-O) [1197-1261] U(C-O-C) 1166
3	3294	2920-2850	1631	1539	1465	1375	-	-	-	-	U(NH) 3319 (NH 2) 3380-U3402 U(C=O)Amide 1652
4	3280	2929-2850	1652	1539	1452	1338	1244	-	-	-	U2644 (SH)
5	3188	2954-2875	1672	1541	1461	1375	1230	1704	-	-	U (C-Cl) 719
6	3176	2950-2873	1662	1533	1392	1375	1226	1730	-	-	U(NH) 3267 U(NH 2) 3319-3417
7	3259	2947-2845	1681 - 1649	1541	1490	1305	1211	1718	1623 - 1573	3051	U(NH) 3375
8	3276	2945-2846	1618 - 1598	1517	1454	1330	1213	1712	1517 - 1539	3100	U(NH) 3307 U(C-O)[1168-1272] U(C-O-C)[1076-1107]
9	3168	2952-2894	1681 - 1668	1556	1456	1392	1265	1733	1623 - 1573	3087	U(NH) 3274 U(NO2)[1523-1353]
10	3217	2945-2850	1652 - 1618	1542	1413	1338	1269	1731	1562 - 1573	3041	U(NH) 3296 U(OH) 3427
11	3250	2927-2850	1681 - 1622	1488	1452	1388	1272	1795	1622 - 1573	3043	U(NH) 3384
12	3207	2929-2854	1654 - 1604	1544	1452	1390	1220	1795	1604 - 1558	3056	U(NH) 3313
13	3204	2918-2858	1676 - 1652	1502	1452	1388	1190	1697	1556 - 1523	3016	U(NH) 3305 U(OH) 3463 U(C-O)[1076-1255]

14	3240	2925-2848	1670 - 1602	1502	1469	1334	1215	1764	1602 - 1595	3018	U(NH) 3359 U(OH) 3433 U(C-O)[1101-1265]
15	3176	2931-2860	1676 - 1654	1558	1452	1396	1201	1701	1616 - 1579	3041	U(NH) 3255 U(OH) 3421 U(C-O)[1078-1236] U(NO2)[1353-1535]
16	3282	2931-2889	1654 1637	1492	1442	1398	1272	1720	1620 - 1566	3004	U(NH) 3334 U(OH) 3421 U(C-O)[1080-1220] U(OH)phenolic 3446
17	3203	2931-2848	1652 - 1627	1558	1458	1344	1215	1693	1602 - 1573	3018	U(NH) 3336 U(OH) 3433 U(C-O)[1166-1257]
18	3163	2983-2902	1643 - 1620	1494	1413	1369	1284	1714	1610 - 1575	3099	U(NH) 3326 U(NO2)[1332-1515]
19	3284	2966-2821	1687 - 1614	1548	1419	1328	1270	1708	1614 - 1585	3093	U(NH) 3419 U(OH) 3448 U(C-O)[1085-1220] U(NO2)[1328-1512]
20	3226	2948-2837	1639 - 1610	1525	1415	1305	1207	1735	1544 - 1575	3095	U(NH) 3280 U(OH) 3407 U(C-O)[1029-1269] U(NO2)[1305-1504] U(C-O-C)[1101-1118]
21	3282	2945-2850	1614 - 1587	1587	1423	1379	1282	1703	1614 - 1587	3093	U(NH) 3320 U(OH) 3400 U(C-O)[1093-1222] U(NO2)[1330-1512]
22	3103	2941-2875	1640 - 1618	1488	1417	1392	1272	1710	1618 - 1587	3095	U(NH) 3269 U(OH) 3438 U(C-O)[1087-1203] U(NO2)[1336-1514] U(OH)phenolic 3471
23	3109	2937-2885	1693 - 1647	1550	1419	1332	1265	1706	1618 - 1585	3072	U(NH) 3320 U(OH) 3452 U(C-O)[1134-1218] U(NO2)[1332-1508]

1H-NMR spectra of some prepared compounds.

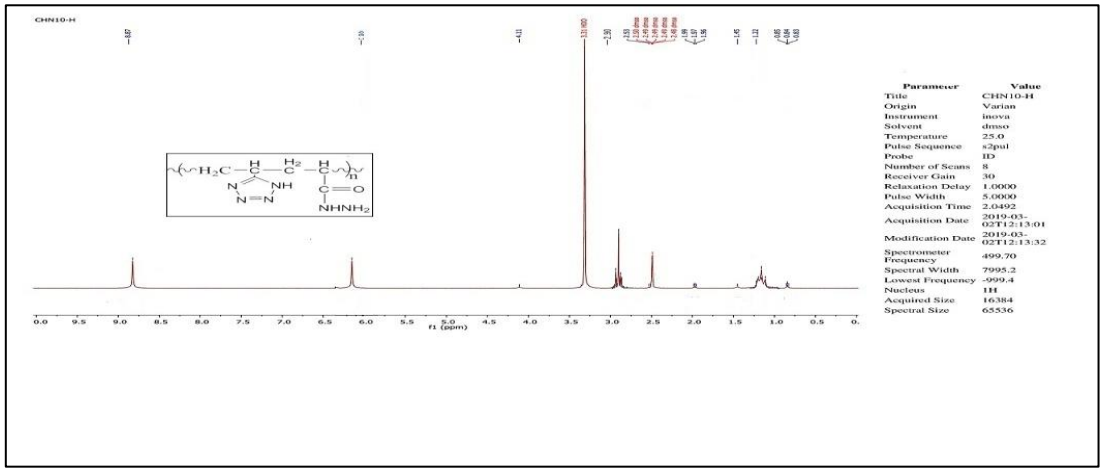


Figure 1-1H-NMR spectrum of compound (3)

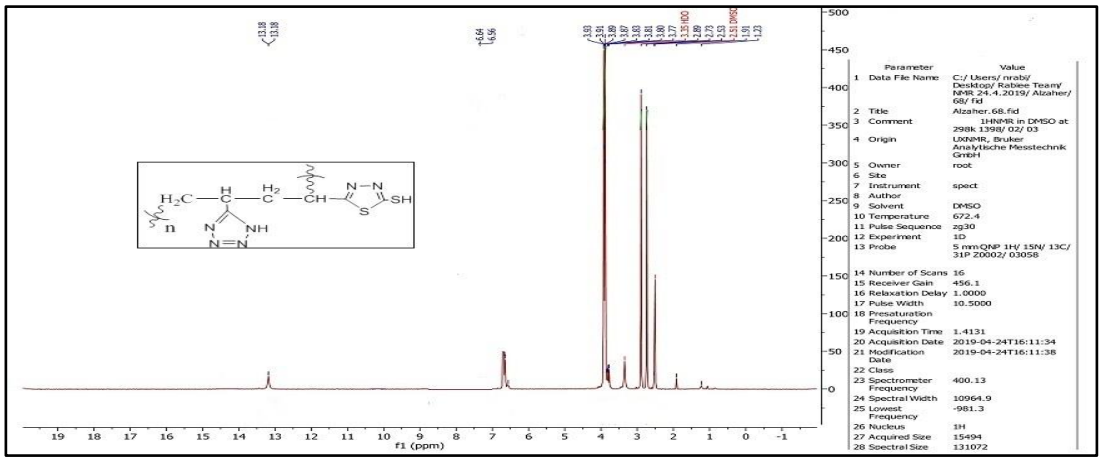


Figure 2- 1H-NMR spectrum of compound 4.

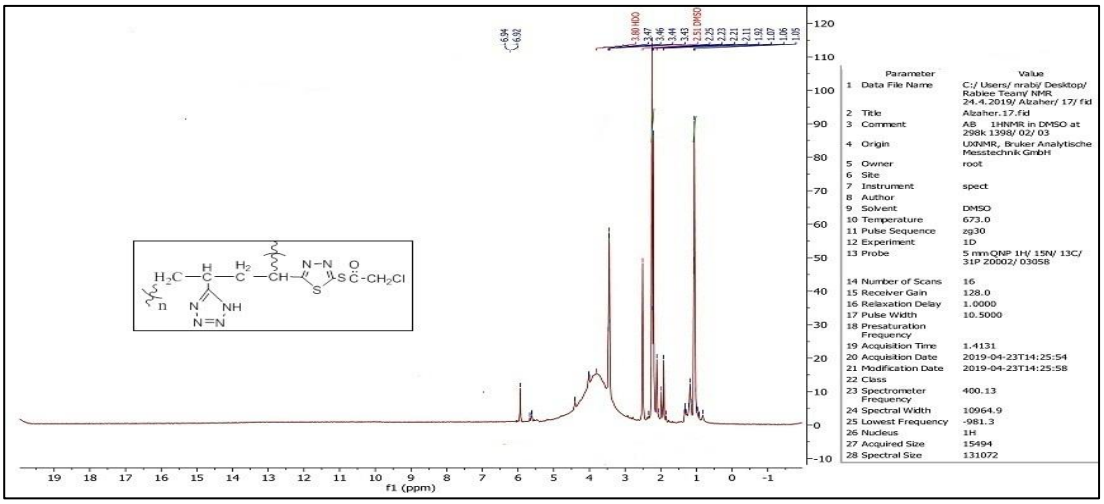


Figure 3-1H-NMR spectrum of compound 5.

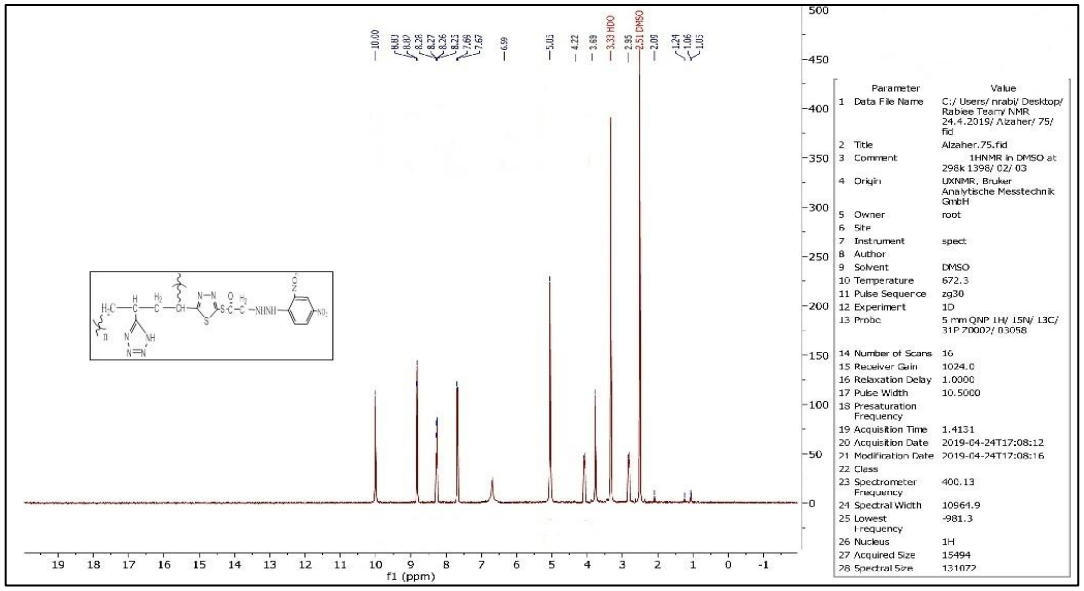


Figure 4-1H-NMR spectrum of compound (18)

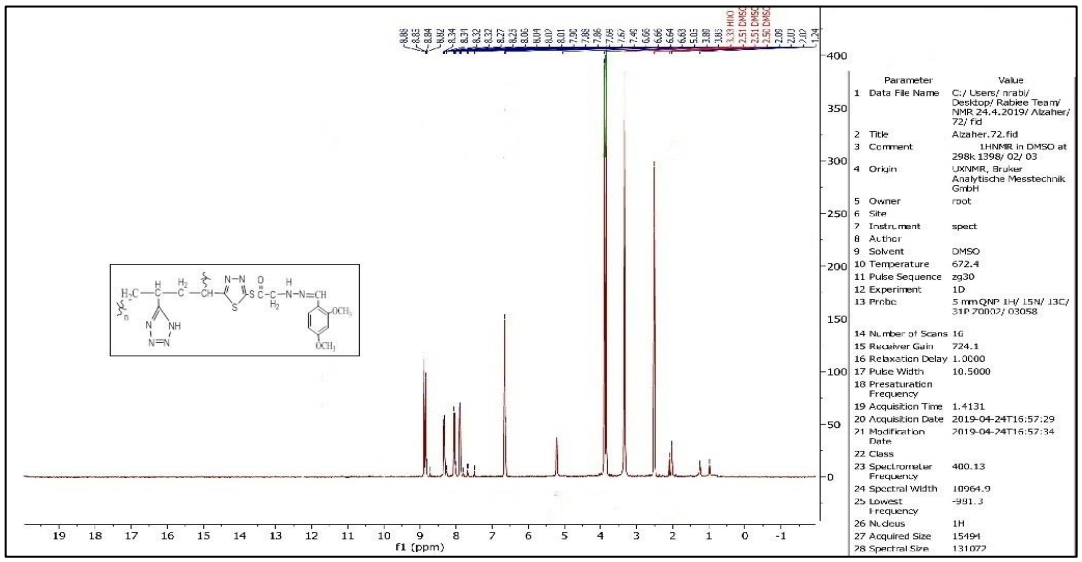


Figure 5- 1H-NMR spectrum of compound 8.

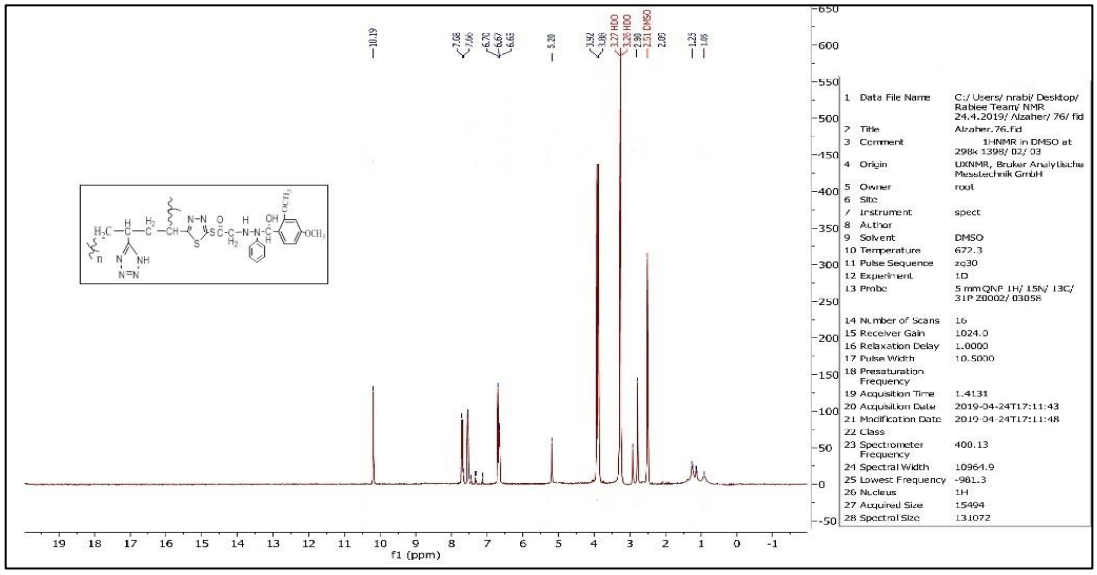


Figure 6-1H-NMR spectrum of compound 14

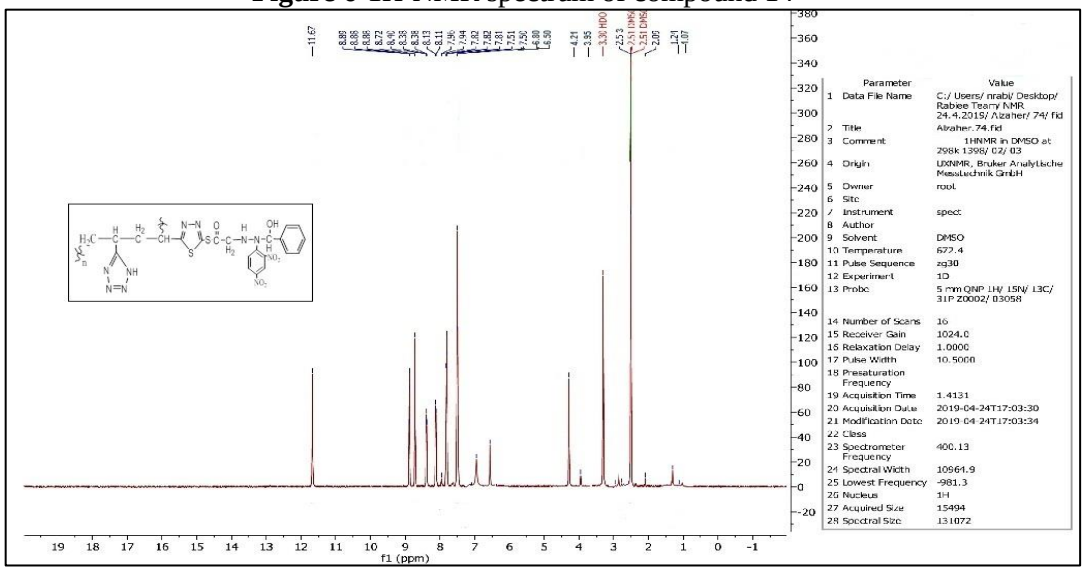


Figure 7- 1H-NMR spectrum of compound 19.

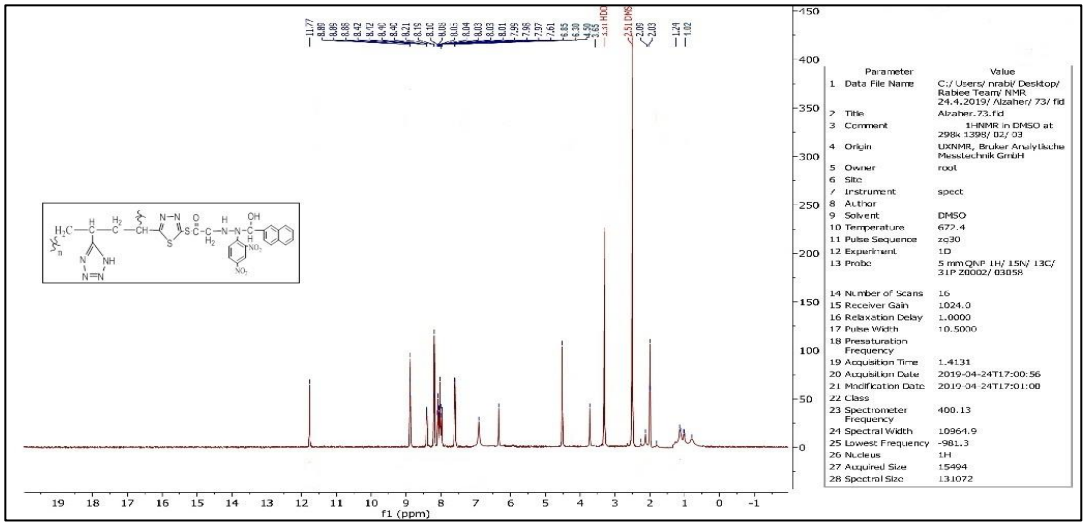


Figure 8- 1H-NMR spectrum of compound 23.

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