

## **1,3-Dipolar Cycloaddition for 4-Azidobenzene Sulfonamide with Acetylenic and Olefinic Compounds**

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### **Abstract**

A series of new 1,2,3-triazole were synthesized by 1,3-dipolar cycloaddition reaction of 4-azido benzene sulfonamide with Acetylenic and olefinic Compounds in acetone and chloroform as a solvents under reflux condition. The reaction mixture was followed by TLC and the yields of products following colum gromotography. IR, H-NMR and Mass spectroscopes were used for identification of these compounds.

**Keywords:** Azides, 1,2,3-triazole, 1,3-dipolar cycloaddition reactions.

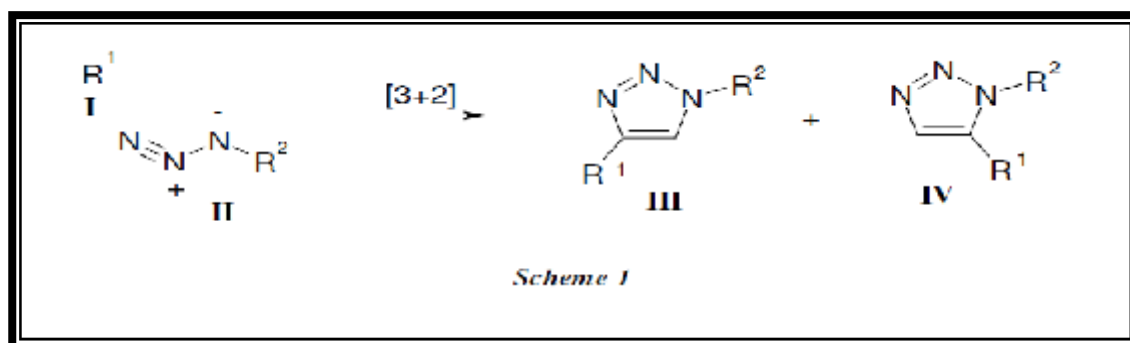
## Introduction

Azides are considered very important compounds due to both their industrial as well as biological applications (Scriven, 1984). Azide derivatives have been used in rubber vulcanization, polymer cross-linking, dyes, tire cored adhesives, foaming of plastics, pharmaceuticals, pesticides and herbicides (Scriven, 1984). Many azide compounds show mutagenic activities (Sander *et al.*, 1977; Nilan *et al.*, 1973).

The chemistry of azides has thus attracted the attention of many chemists, since many of these compounds play an important role in organic chemistry (Scriven and Turnbull, 1983; Patai, 1971, Ridois, 1984). One of the more useful synthetic applications of azides is the preparation of 1,2,3-triazoles via 1,3-dipolar cycloaddition reactions of azides with substituted acetylene compounds (Gilchrist *et al.*, 1974, Purvisis *et al.*, 1984, Patei and Smalley, 1984, Loubinoux *et al.*, 1984).

The chemistry of 1,2,3-triazoles has also received much attention because of their wide range of applications. They have been used as fungicides, herbicides, light stabilizers, fluorescent whiteners, optical brightening agents, and corrosion retardants (Fox *et al.*, 1979, Abdallah, and Abu-Orabi, 1991, Abdulhadi, 1995). Moreover 1,2,3-triazole derivatives show significant antimicrobial, cytostatic, virostatic, and anti-inflammatory activities (Tatsuta, 1981).

The most used approach for the synthesis of 1,2,3-triazoles is the thermal 1,3-dipolar cycloaddition of alkyne to azide compounds described by Huisgen (Scheme 1) (Huisgen, 1984). This reaction is by far, the most well-known example of the "Click Chemistry". It was adopted thereafter to synthesize several types of molecules (Khanetsky. B., Dallinger and Kappe, 2004).



Scheme 1

## Experimental

Melting points were determined with an electronthermal digital point apparatus type Thermo Scientific. IR spectra were obtained using Shimadzu FT-IR8400S spectrophotometer at laboratories petrochemicals. All the spectra were recorded as KBr discs. The mass spectra were obtained by using a Agilent technologies 5975c University of Tarbiat Modares Tehran and  $^1\text{H}$ NMR were obtained by using Bruker-500 MHz, Faculty of science, Micro Analytical center TLC is performed on silica gel 60 F<sub>254</sub> sheet layer (Merck). The materials from Merk, Ridel and Fluka) companies.

## Preparation of 4-azidobenzene sulfonamide (S) (Mekni and Baklouti, 2009):

To a stirred solution of sulfonamide (0.172 g, 0.001 mol) in conc. hydrochloric acid (0.35 mL) and water (10 mL) at 0°C was added drop wise a solution of sodium nitrite (0.078 g, 0.001 mol) in water (5 mL). After 30 minutes a solution of sodium azide (0.06 g, 0.001 mol) in water (10 mL) was added drop wise. The solution was stirred at 0°C for 15 min. and water (10 mL) was added slowly with cooling. The precipitate was collected by suction filtration and recrystallised from hexane to give white

needles with melting point 16-118°C and Triazole compound T<sub>1</sub> and T<sub>2</sub>, as yield 85%. shown in table 1.

**Preparation of N-phenyl maleimide and N-(4-acetyl phenyl) maleimide** (Kurumi *et al.*, 1997).

**Preparation of 1-(4-sulfamoylphenyl)-1H-1,2,3-triazole-4,5-dicarboxylic acid T<sub>1</sub> :And Di Methyl 1-(4-sulfamoylphenyl)-1H-1,2,3-triazole-4,5-dicarboxylate T<sub>2</sub>** (Mohammed *et al.*, 2006; Splitter and Calvin, 1955)

4-Azido benzen sulphanamide (S) (0.198 g, 0.001 mole) was dissolved in acetone (10 ml) into a (25 ml) round bottomed flask and acetylene do carboxylic acid (0.114 gm, 0.001 mole) or di methyl acetylene di carboxylate (0.170 g, 0.001 mole) in (10ml) acetone was added. The solution was refluxed for 6 hrs (comp., 1) and 16 hrs for (comp., 2), until the starting reagents were no more detected at TLC control (3:7 methanol:chloroform as eluent). The solution then was evaporated, the crystalline products was crystallized to

**Preparation of 4-(4,6-dioxo -5-phenyl-4,5,6,6a-tetra hydropyrrolo [ 3,4-d] [1,2,3 ] Triazole -1(3aH) -yl) benzene sulfonamide T3. And 4-(5-(4-acetylphenyl)-4,6-dioxo-4,5,6,6a-tetrahydropyrrolo [3,4-d] [1,2,3] Triazole-1 (3aH) benzene sulfonamide T4** (Smith *et al.*, 1958, , Kurumi *et al.*, 2000).

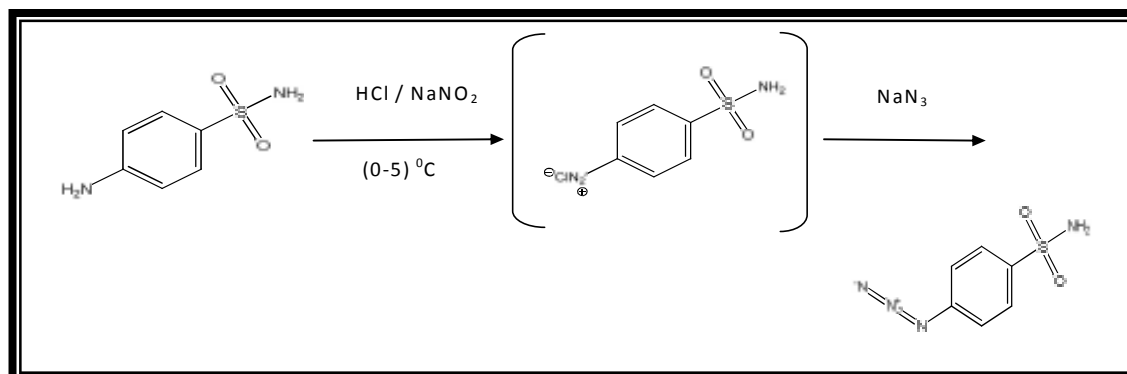
4-azidobenzyen sulfonamide (0.198 g, 0.001 mole) was dissolved in chloroform (10 ml) into a (50 ml) round bottomed flask and N-phenyl maleimid (0.173 g, 0.001 mole) or 4-acetyl-N-maleimid (0.215 g, 0.001 mole) in (10 ml) chloroform was added. The solution was refluxed for 5 h for (3) and (10 h) for (4), until the starting reagents were no more detected at TLC control (7:3 chloroform: acetone for compound 3 and 7:3 toluene: acetone for compound 4) as eluent.

Table (1): Physical properties for the prepared compounds

Symb.	structure	eluent	Mp °C	yield	color	Time of reaction
S		-	116-118	80	crystal White	-
T1		2 : 8 Ethanol : chloroform	160-161	70	powder white	6
T2		2 : 8 Ethanol : chloroform	165-166	55	crystal White	16
T3		3 : 7 Acetone : chloroform	Deco., 210	79	powder white	5
T4		3 : 7 Acetone : toluene	176-177	60	Powder white	10

## Results and discussion

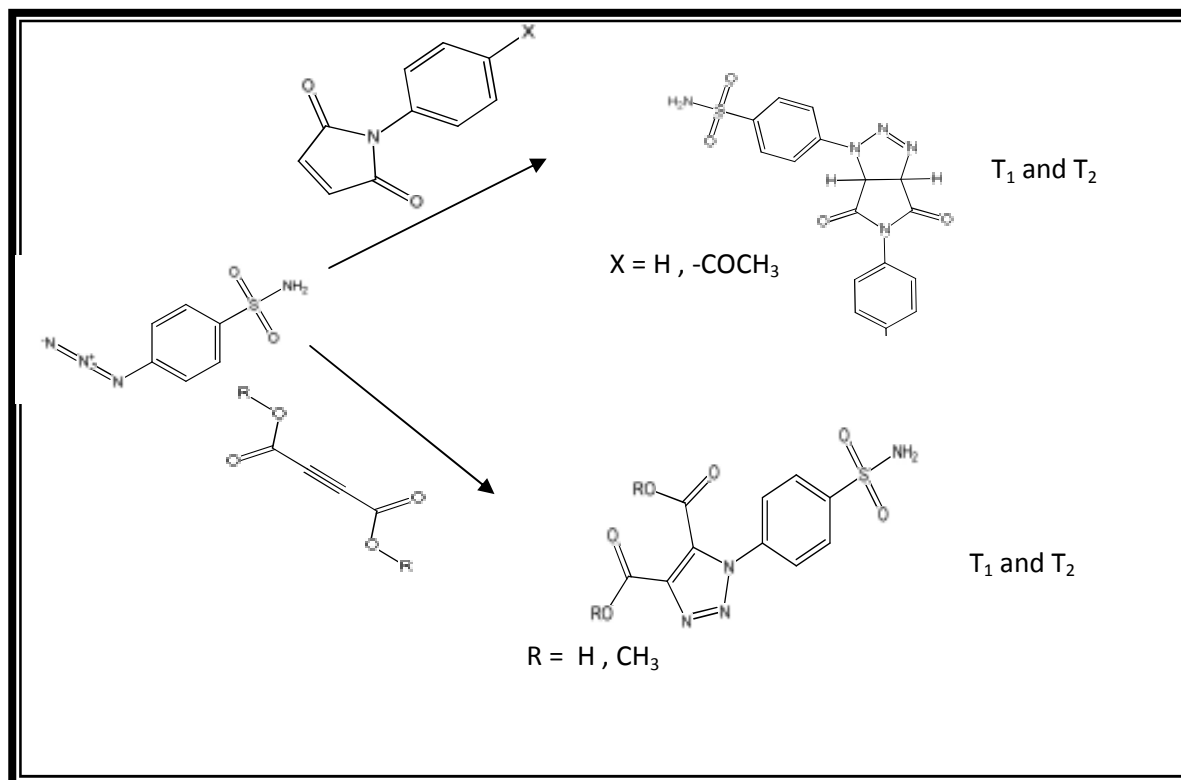
4- Azido benzene sulfonamide can be made from Diazonium salts according to published method as far as possible (Mekni. N. & Baklouti. A., 2009) , as shown in schem 2.



Scheme 2

4- azido benzene sulfonamide react with different olefin and acetylene compounds by 1,3-dipolar cycloaddition reaction to give 1,2,3-

triazole derivatives (Smith *et al.*, 1958; Abood, 1997) , as shown in scheme 3.



**Scheme 3**

### IR spectra (Pavia. D. L, 3<sup>rd</sup> Ed.,)

The IR spectra of all compounds and the study are recorded in the solid state using the KBr disk technique. Selected bands of diagnostic importance are collected in Table(2)

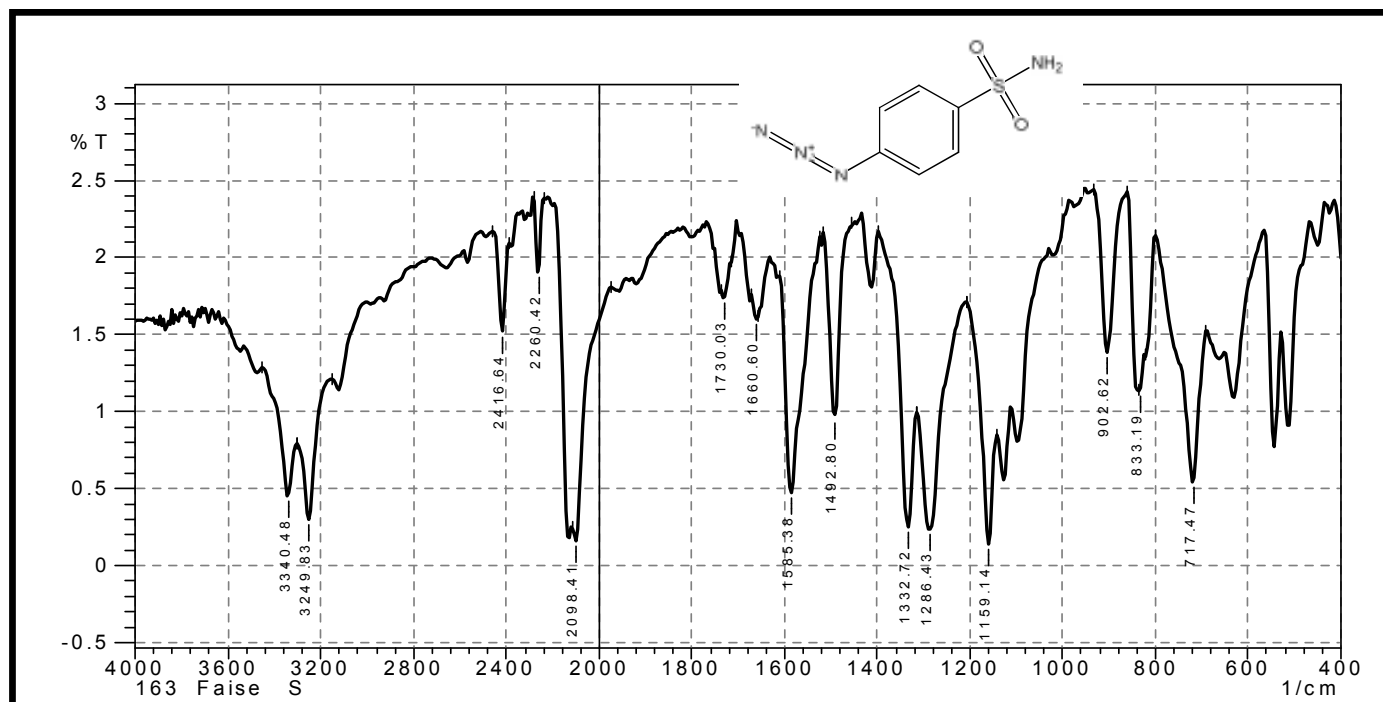
IR spectrum of the 4-azido benzene sulfonamide showed the strong absorption band at 2098  $\text{cm}^{-1}$  that is characteristic of the ( $-\text{N}_3$ ) stretching , the spectrum showed strong bands due to the ( $-\text{SO}_2$ ) stretching vibration at (1286 and 1332)  $\text{cm}^{-1}$ , while the IR-

spectra of Triazole compounds (T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub> and T<sub>4</sub>) showed disappear of the of frequency of (-N<sub>3</sub>) band which related to azide compound and appearance of new absorption bands reacted to Triazole

derivatives as shown in table (2) and figure (1-1) to (1-5). The suggest structures indicate that the reaction was take place the cycloaddition

**Table (2) IR spectral data of of azide and Triazole compounds**

Symb.,	O-H	N-H <sub>2</sub>	CH <sub>arom</sub>	CH <sub>alif</sub>	N <sub>3</sub>	C=O	SO <sub>2</sub>	C=C <sub>triazole</sub> C=C <sub>ar</sub> N=N <sub>triazole</sub>
S	-	3249-3340	3150	-	2098	-	1286-1332	1585
T <sub>1</sub>	3319	3245-3319	3147	-	-	1710	1250-1340	1484-1570
T <sub>2</sub>	-	3236-3344	3097	2962	-	1751	1267-1309	1552-1458
T <sub>3</sub>	-	3280-3434	3107	2920	-	1724	1332-1371	1593-1490
T <sub>4</sub>	-	3253-3369	3107	2995	-	1724	1338-1379	1596-1502



**Figure (1-1): IR spectrum of compound S**

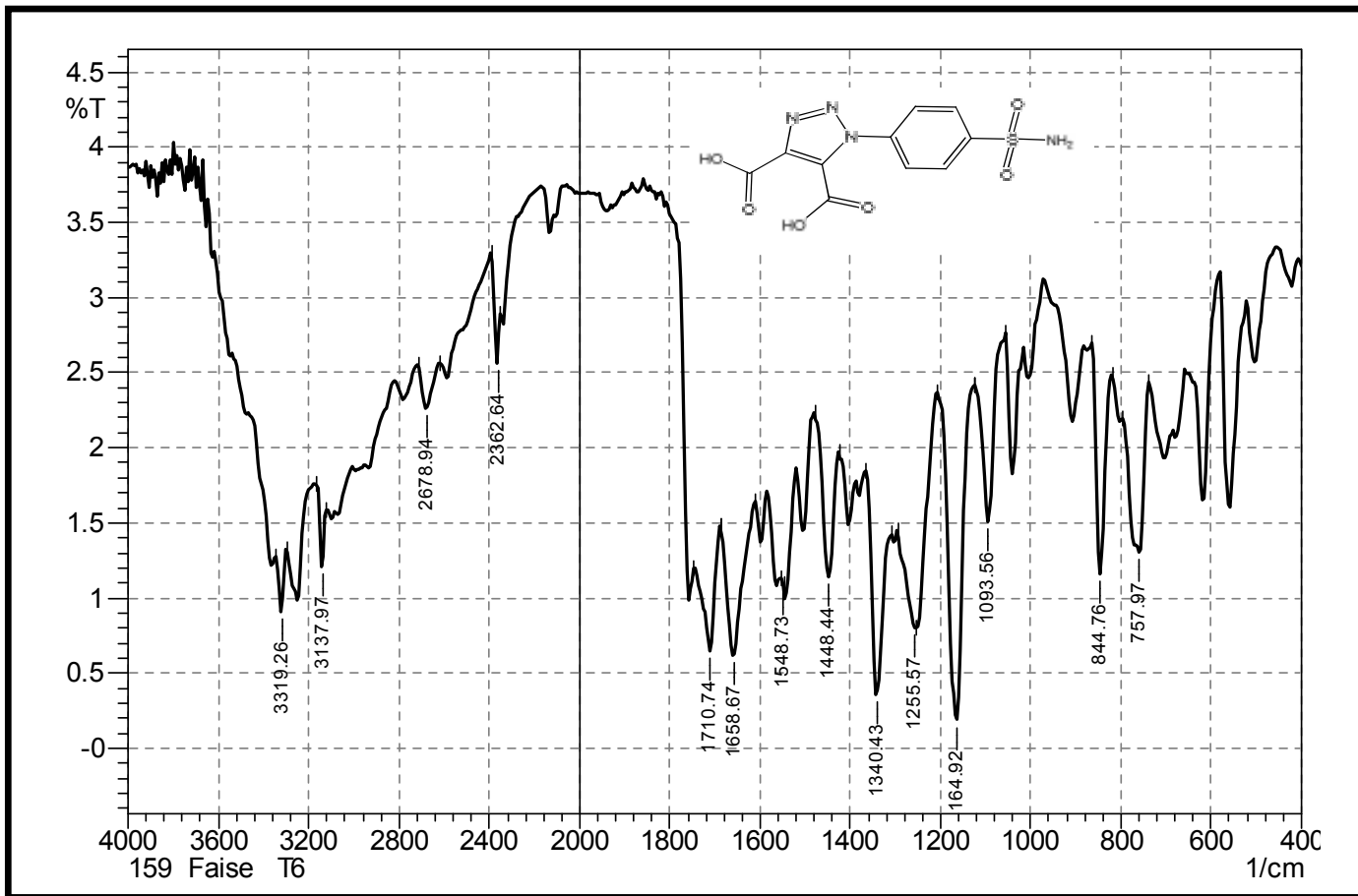


Figure (1-2): IR spectrum of compound T<sub>1</sub>

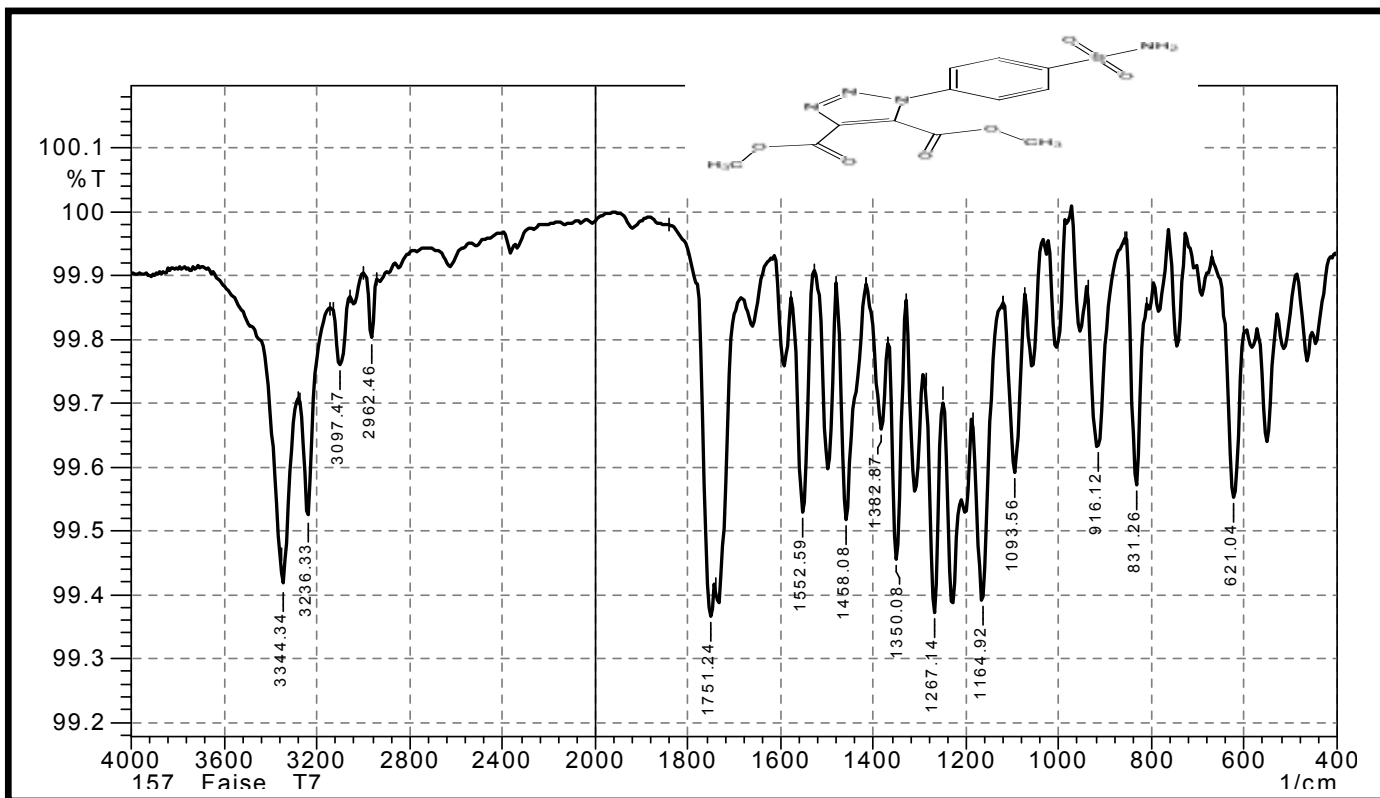


Figure (1-3): IR spectrum of



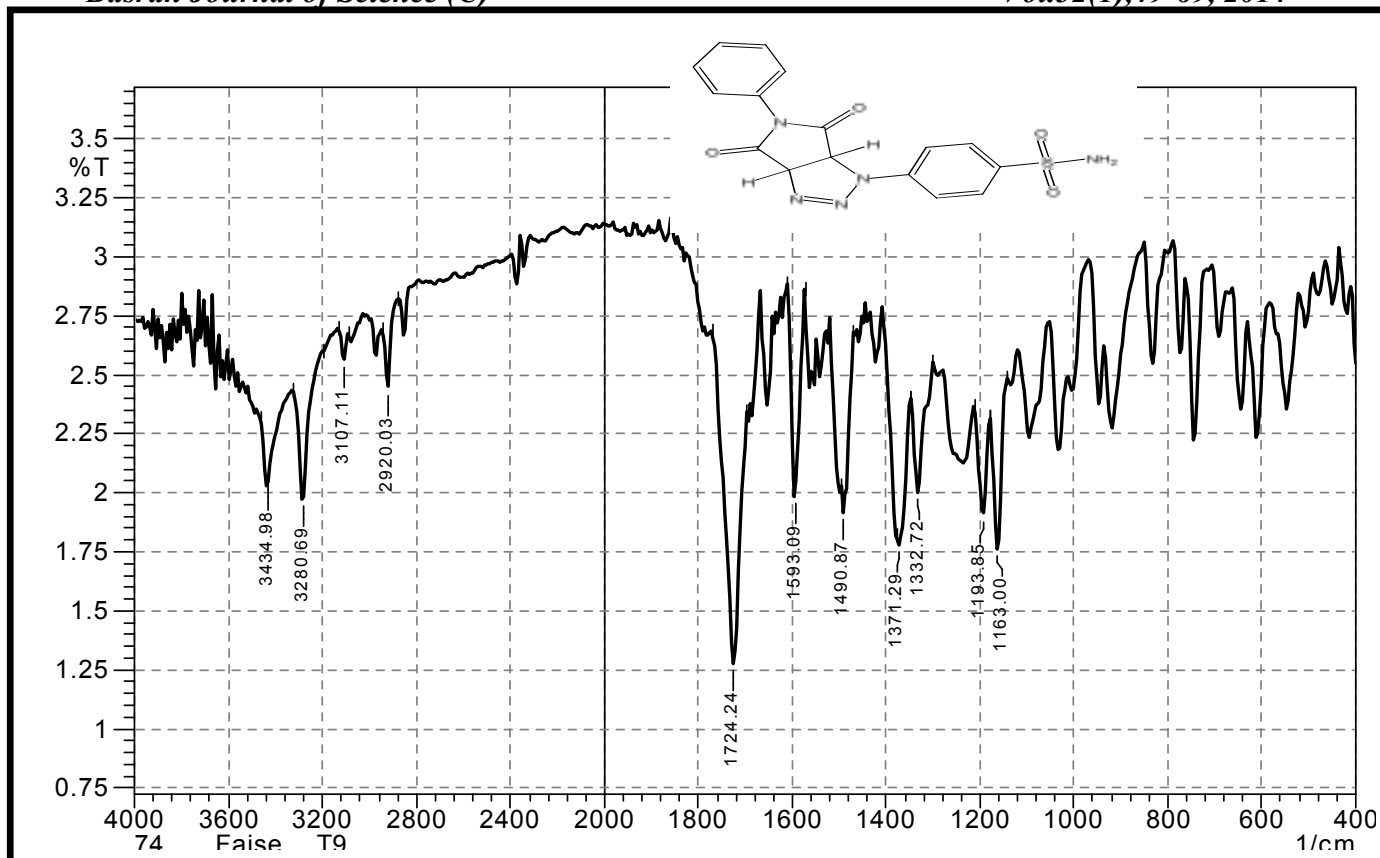


Figure (1-4) IR spectrum of compound T<sub>3</sub>

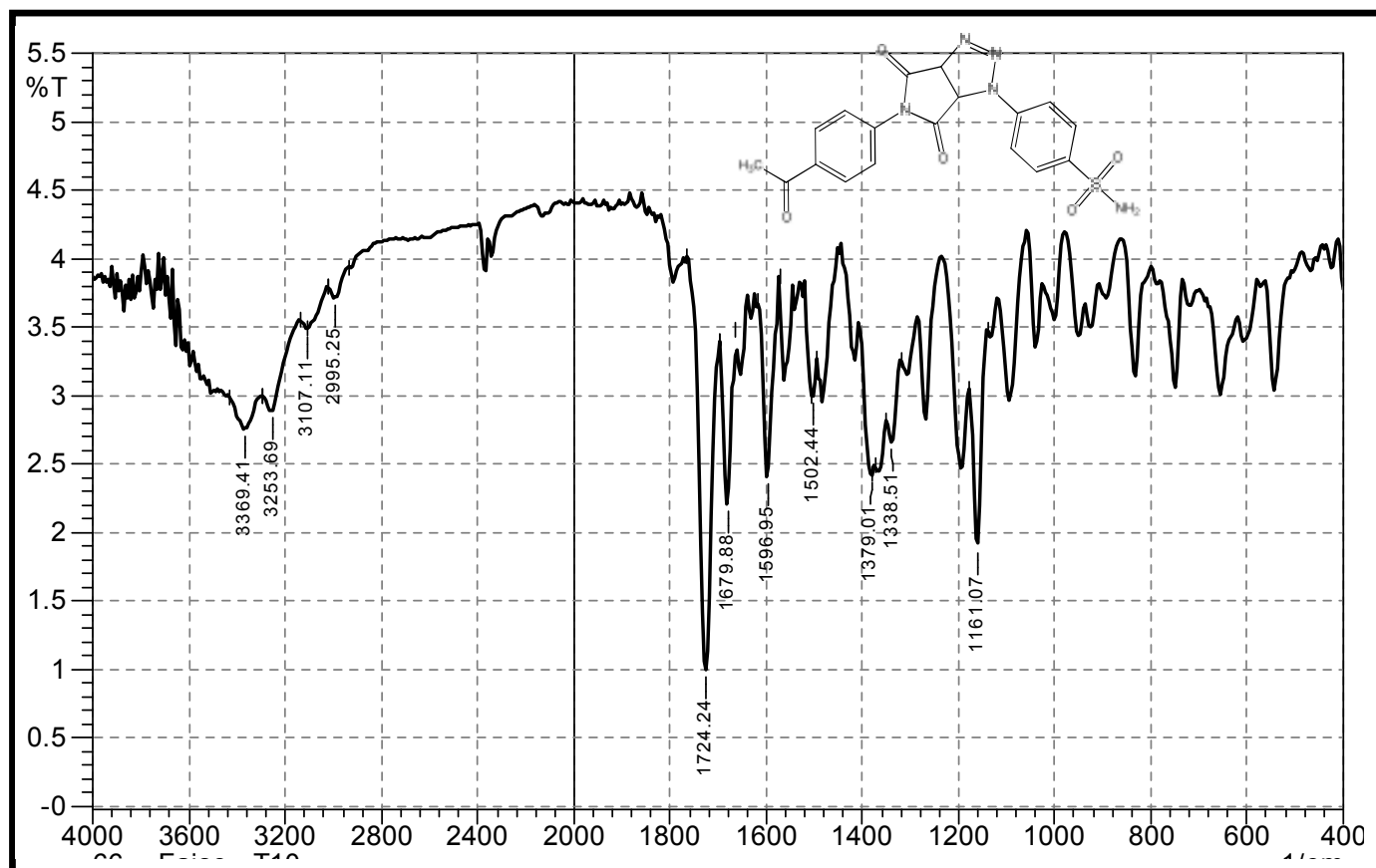


Figure (1-5): IR spectrum of compound

2- <sup>1</sup>H-NMR (Pavia, 3<sup>rd</sup> Ed.,)

The <sup>1</sup>H-NMR of the investigated compounds are shown in figures (2-1) – (2-5) and all compounds are dissolved in deuterated dimethyl sulphoxide. The spectrum of 4-azido benzene sulfonamide (S) mainly consist of three groups of signals. For aromatic region, the two doublet signals at (7.27-7.29) ppm and (7.81-7.83) ppm which attribute to AB-system of aromatic

protons, while the singlet signal at low field (7.36) ppm attribute to two amino proton. 1,3-Dipolar cycloaddition of 4-Azido benzene sulfonamide (S) to olefin and acetylene compounds in chloroform or acetone respectively, affords one isomer of 1,2,3-triazole derivatives.

**Table (3): <sup>1</sup>H-NMR of the azide and triazole compounds**

Comp.	structure	H.NMR
S		H <sub>3,7</sub> (2H, 7.28 ppm, J = 8.6 Hz), H <sub>1</sub> (2H, 7.37 ppm), H <sub>4,6</sub> (2H, 7.82 ppm, J = 8.6 Hz)
T1		H <sub>9</sub> (2H, 7.57 ppm), H <sub>3,5</sub> (2H, 7.79 ppm, J = 8.4 Hz), H <sub>2,6</sub> (2H, 8 ppm, J = 8.4 Hz)
T2		H <sub>22</sub> (3H, 3.88 ppm), H <sub>23</sub> (3H, 3.94 ppm), H <sub>10</sub> (2H, 7.65 ppm), H <sub>4,6</sub> (2H, 7.85 ppm, J = 8.4 Hz), H <sub>3,1</sub> (2H, 8.4 ppm, J = 8.4 Hz)
T3		H <sub>27</sub> (1H, 5.47 ppm, J = 10.7), H <sub>28</sub> (1H, 6.03 ppm, J = 10.7), aromatic protons (5H, 7-7.5 ppm), H <sub>8</sub> (2H, overlap with aromatic proton at 7.4 ppm), H <sub>3,5</sub> (2H, 7.75 ppm, J = 8.85 Hz), H <sub>2,6</sub> (2H, 7.9 ppm, J = 8.85 Hz)
T4		H <sub>28</sub> (3H, 2.6 ppm), H <sub>10</sub> (1H, 5.39 ppm, J = 10.8 Hz), H <sub>11</sub> (1H, 6.05 ppm, J = 10.8 Hz), H <sub>24</sub> (2H, 7.3 ppm), H <sub>18,22</sub> (2H, 7.45 ppm, J = 8.5 Hz), H <sub>3,5</sub> (2H, 7.7 ppm, J = 8.5 Hz), H <sub>2,6</sub> (2H, 7.85 ppm, J = 8.5 Hz), H <sub>19,21</sub> (2H, 8.1 ppm, J = 8.5 Hz)



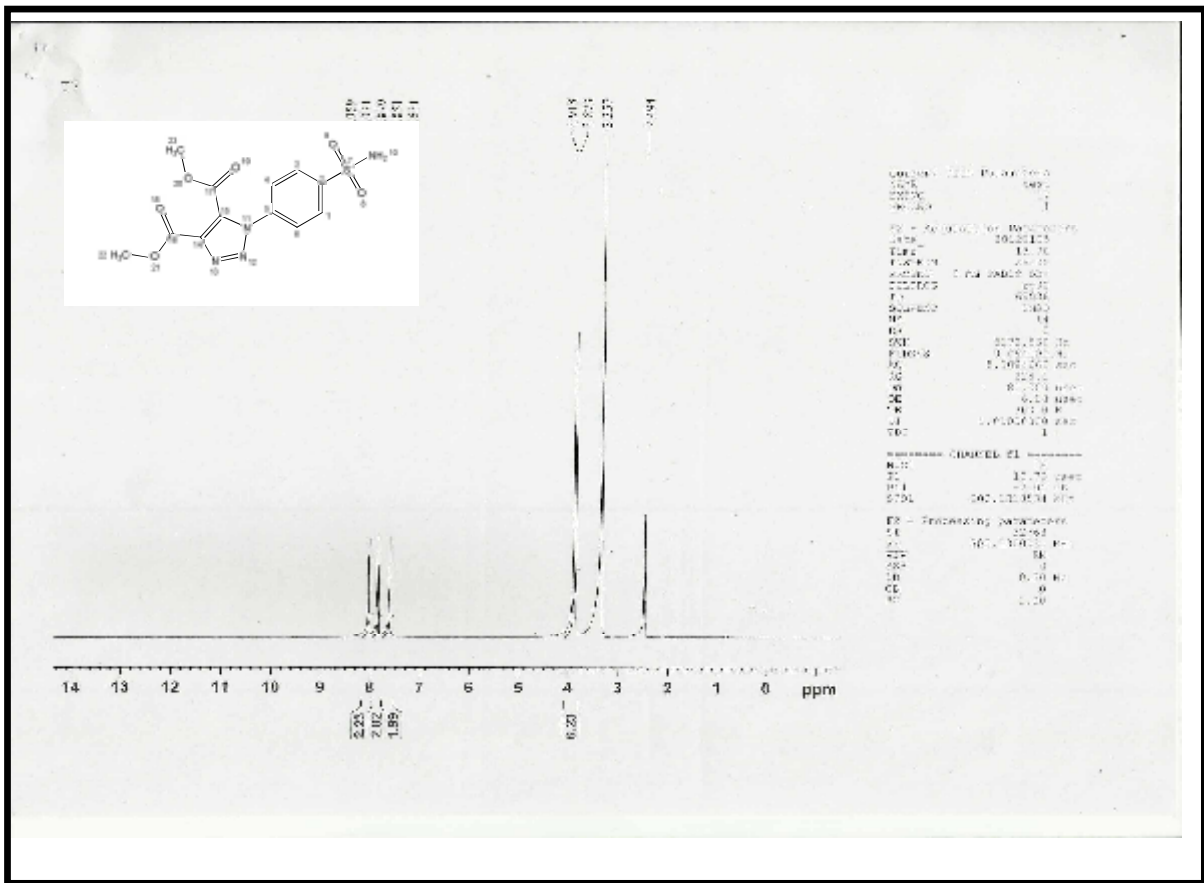


Figure (2-3) HNMR spectrum of compound T<sub>2</sub>

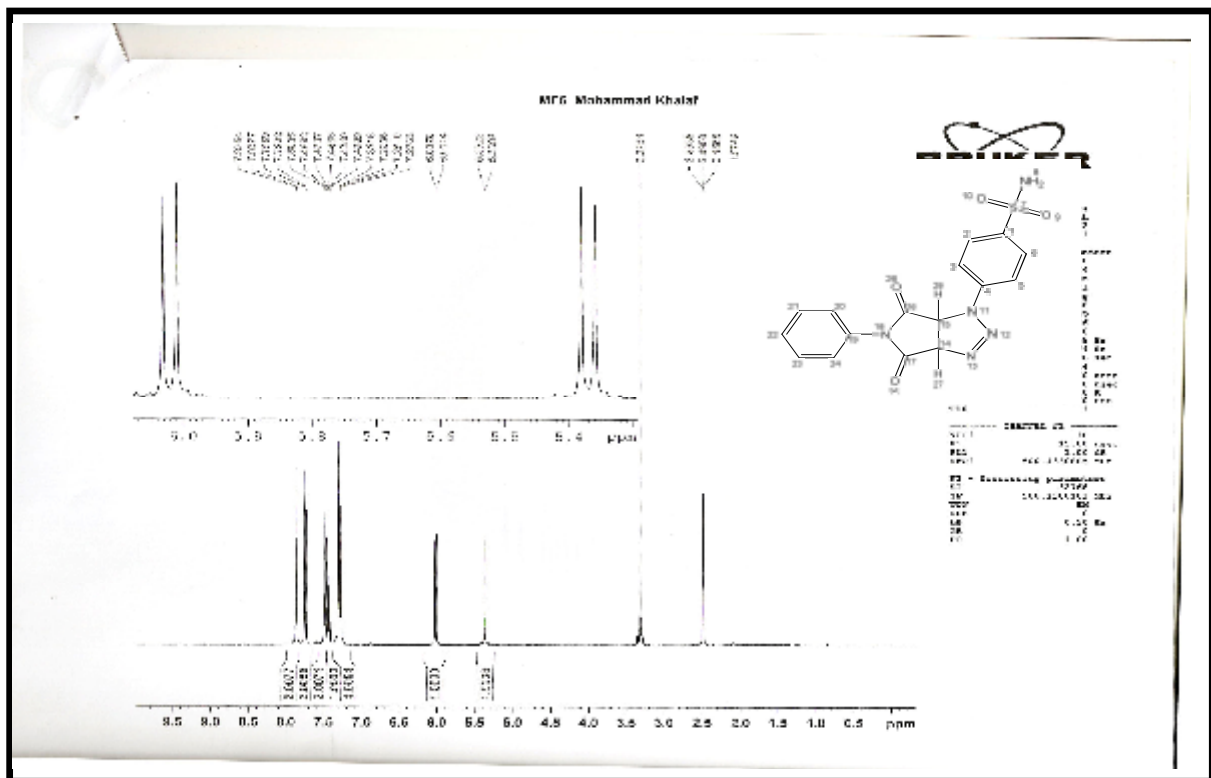


Figure (2-4) HNMR spectrum of compound

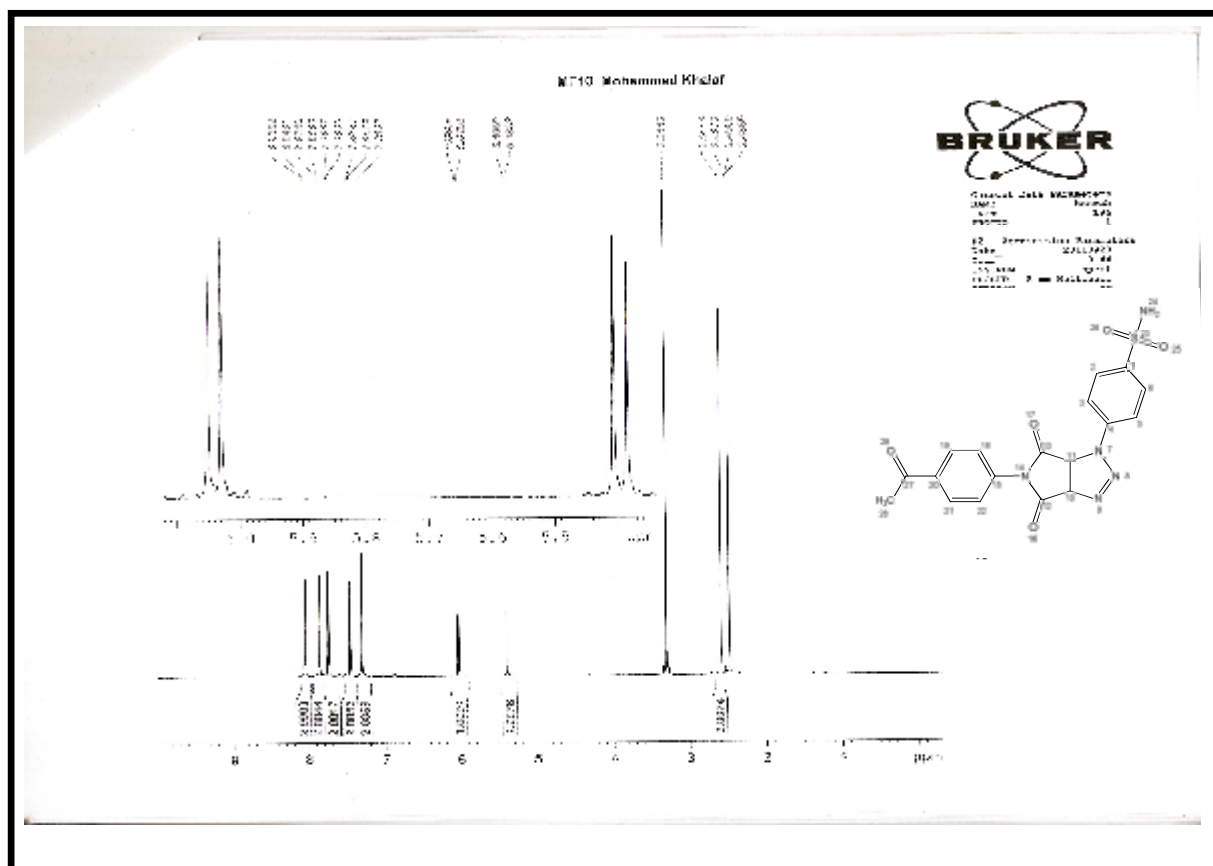
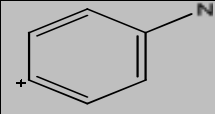
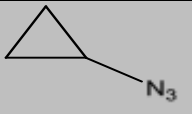
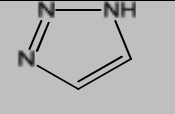
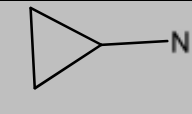


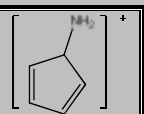
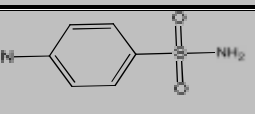
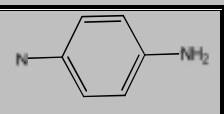
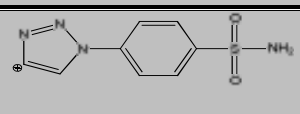
Figure (2-5): <sup>1</sup>H NMR spectrum of compound T<sub>4</sub>

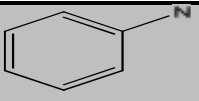

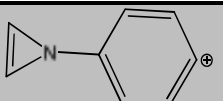
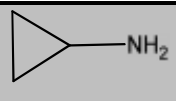
### 3- Mass spectra (Selverstein. R. M., 7<sup>th</sup> Ed)

All the compounds exhibit peaks, and the base of beaks of the Triazole compounds are dependent on the derivatives of olefin or acetylene[V].

Table (4): Import fragments in the mass spectra of prepared compounds

Symb	m/z					
	M <sup>+</sup>	M-N <sub>2</sub>				
S	198	170	-	83	69	55
T1	310	282	-	83	69	55
T4	413	385	90	83	69	55

Symb.	m/z					
	M <sup>+</sup>	M-N <sub>2</sub>				
T2	340	312	80	170	106	223

Symb.	m/z					
	M <sup>+</sup>	M-N <sub>2</sub>				
T3	371	343	91	106	116	57

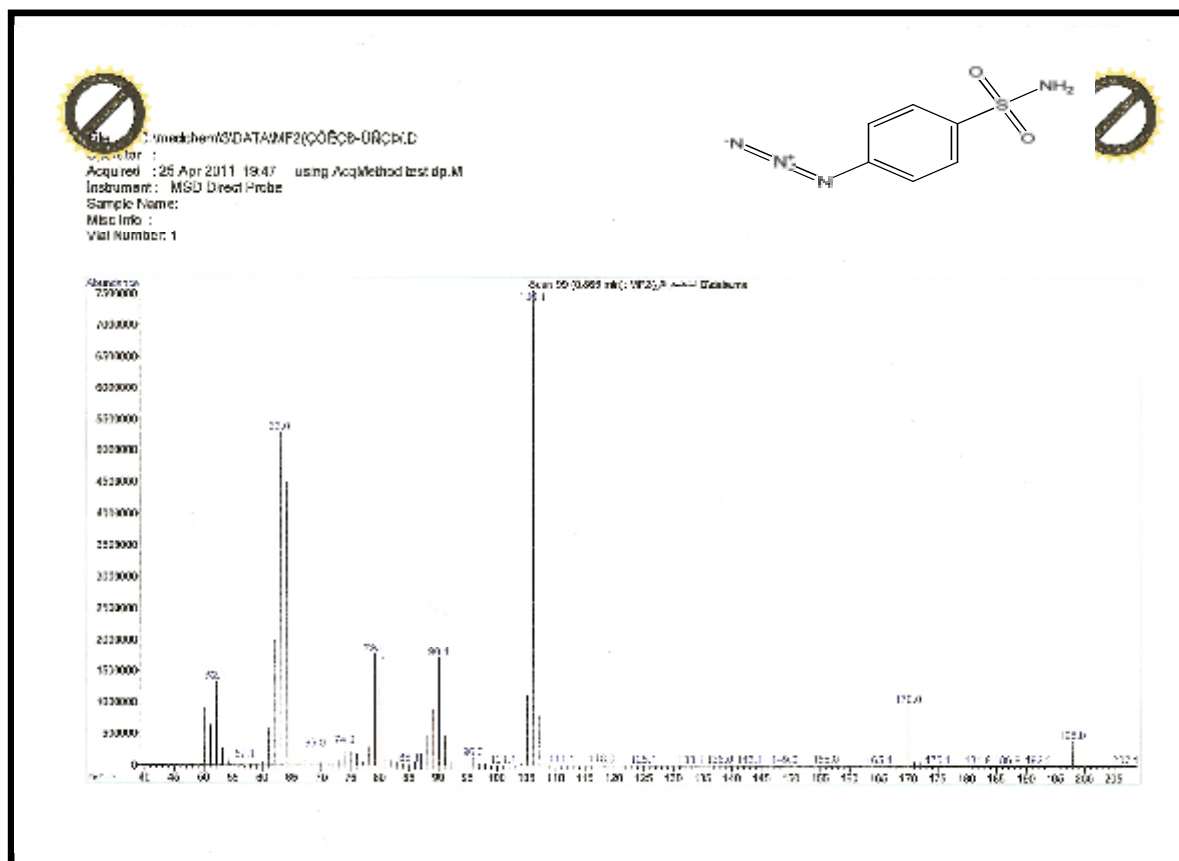


Figure (3-1): Mass spectrum of compound S

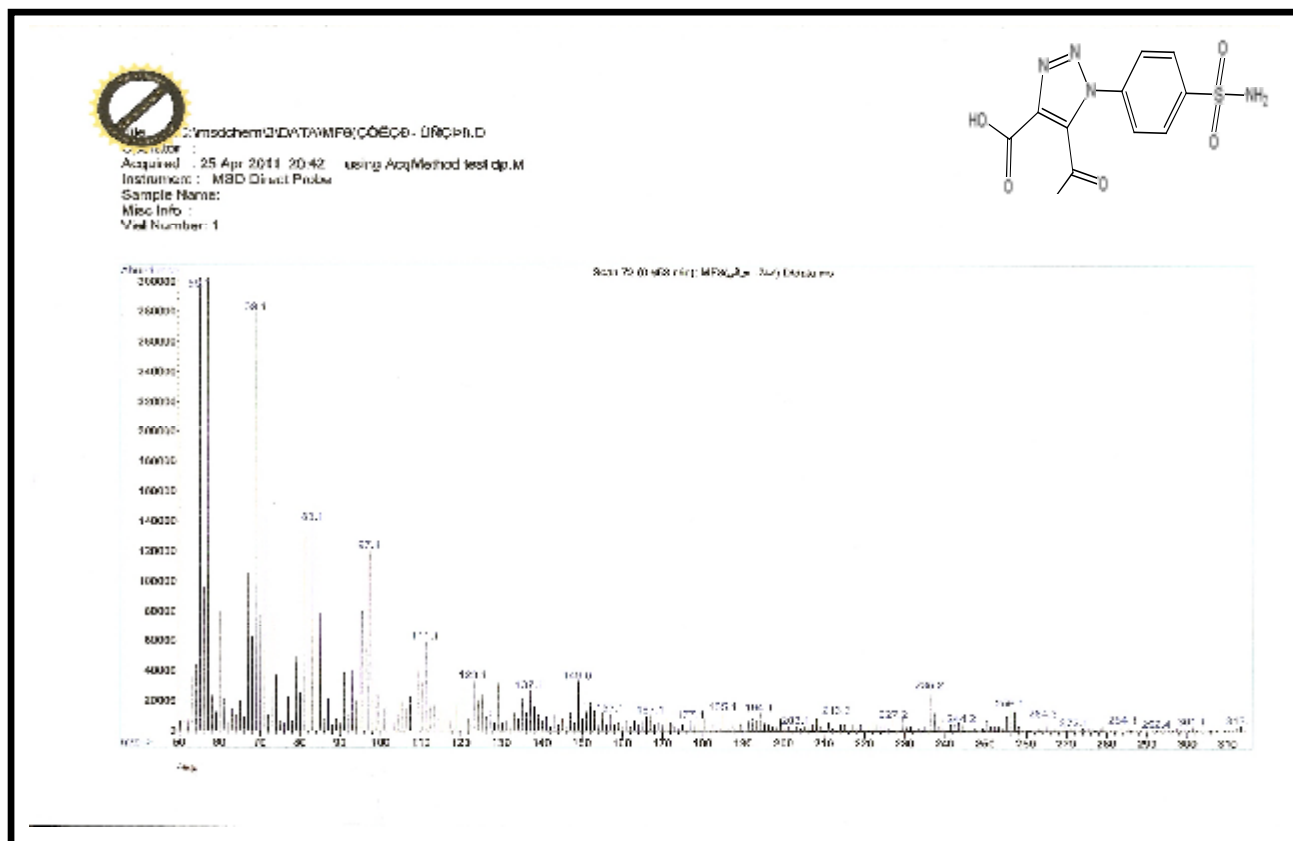


Figure (3-2): Mass spectrum of compound T<sub>1</sub>

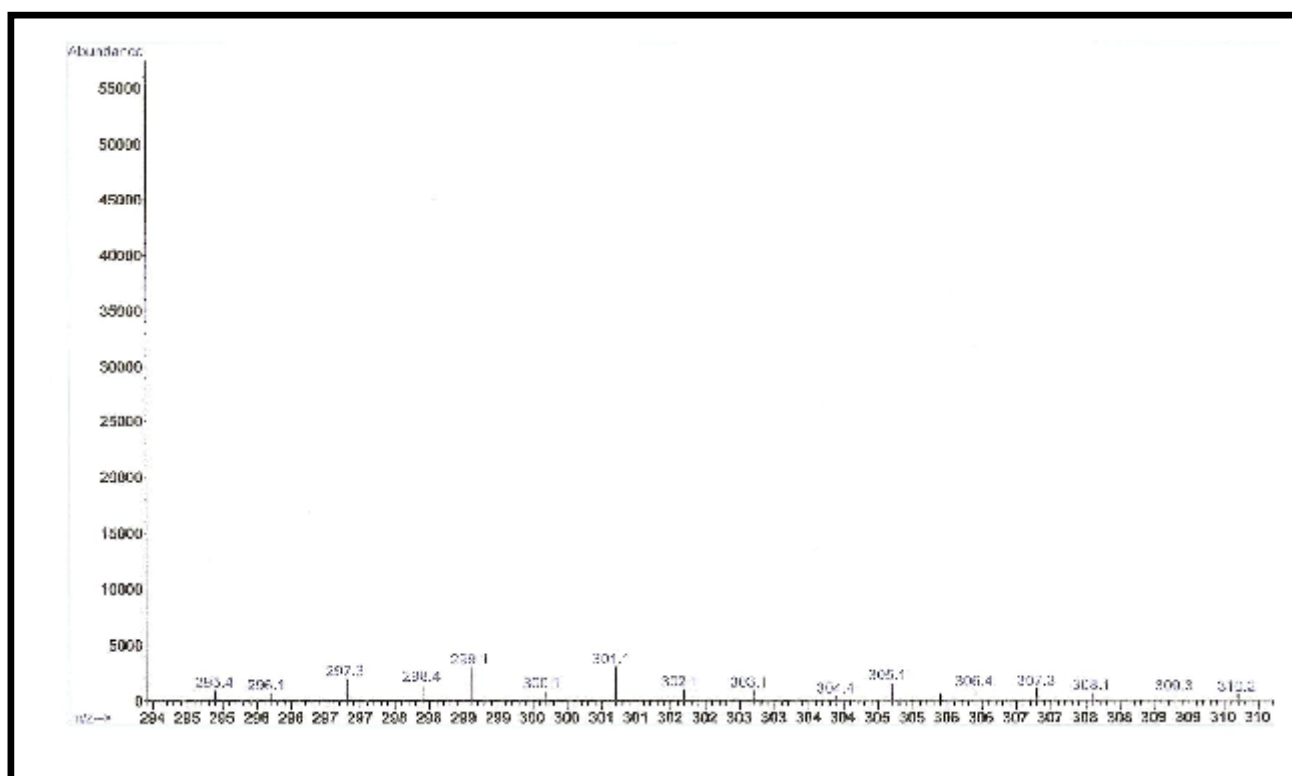


Figure (3-2a): Mass spectrum of compound T<sub>1</sub>

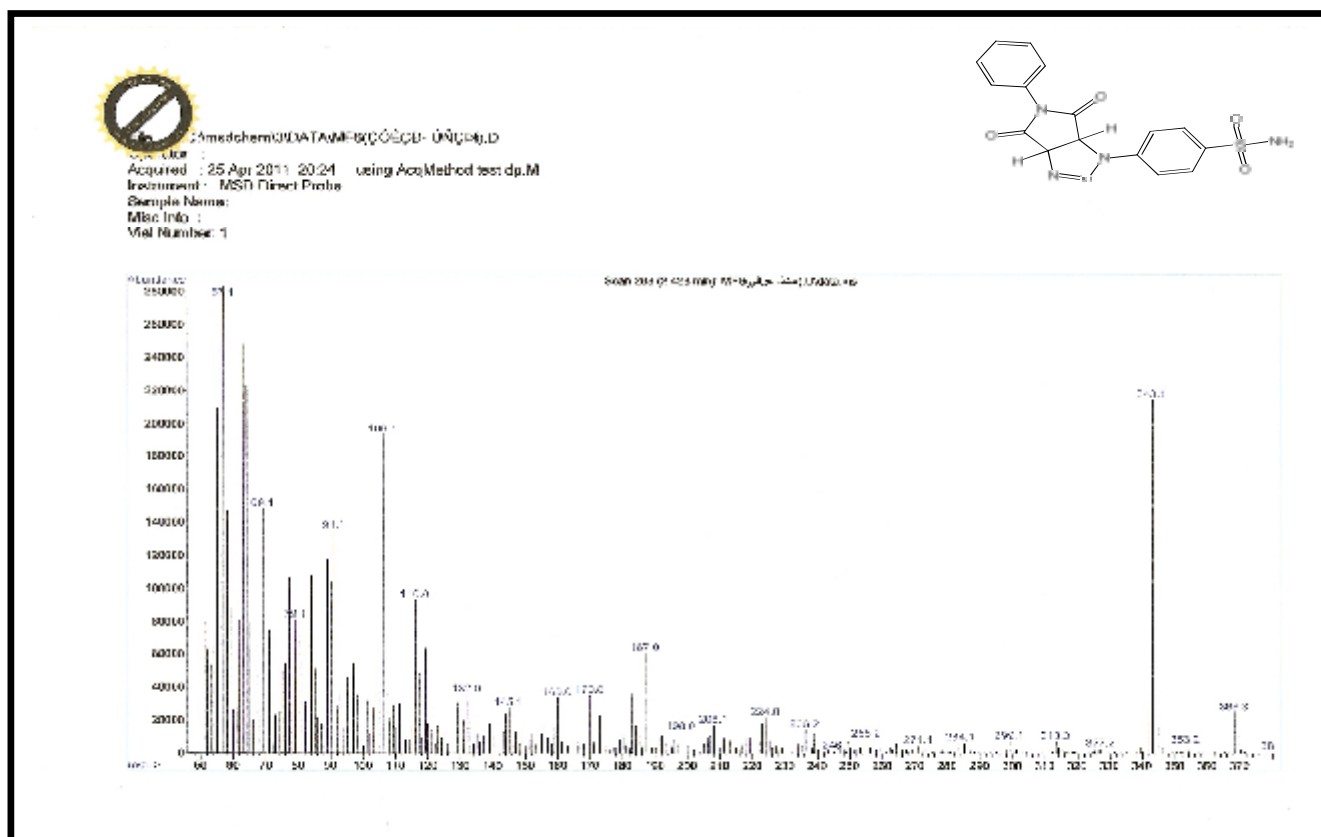


Figure (3-3): Mass spectrum of compound T<sub>2</sub>



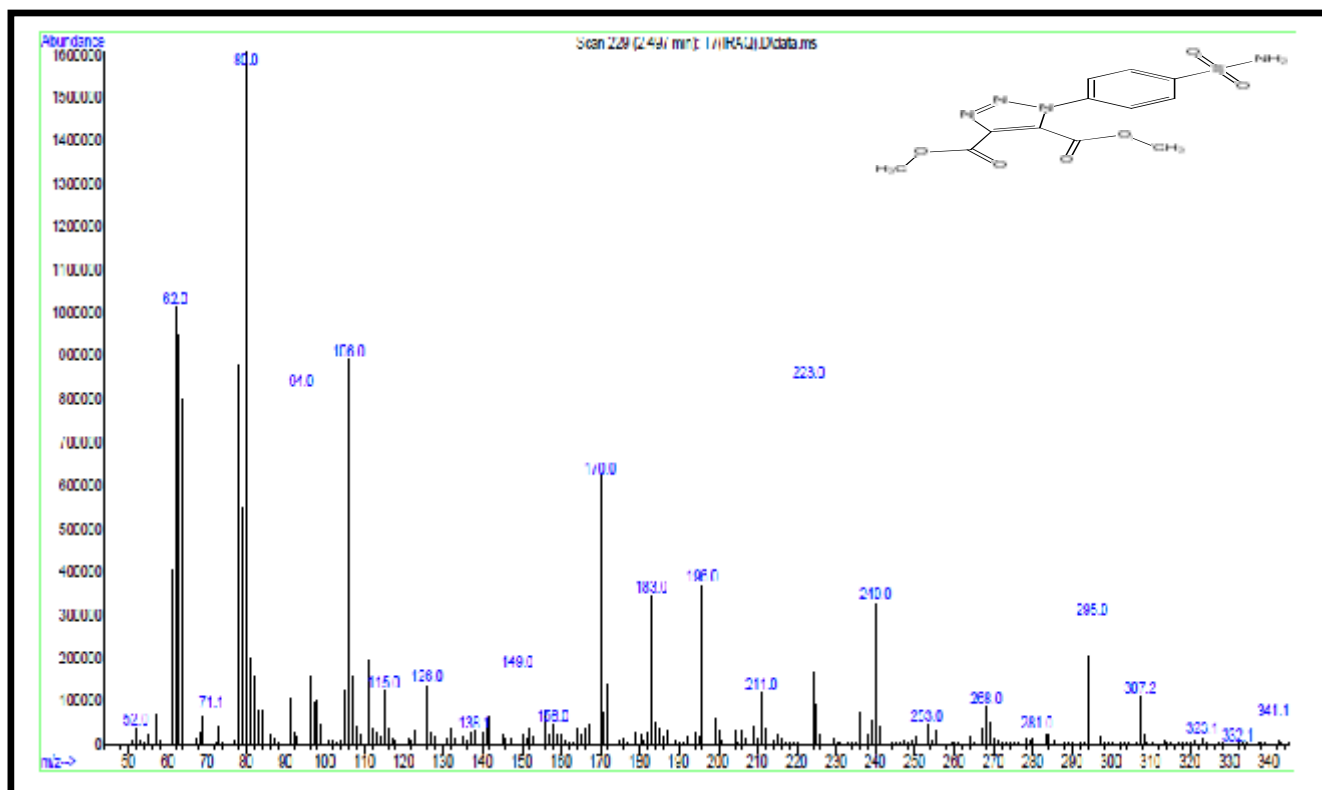


Figure (3-4): Mass spectrum of compound T<sub>3</sub>

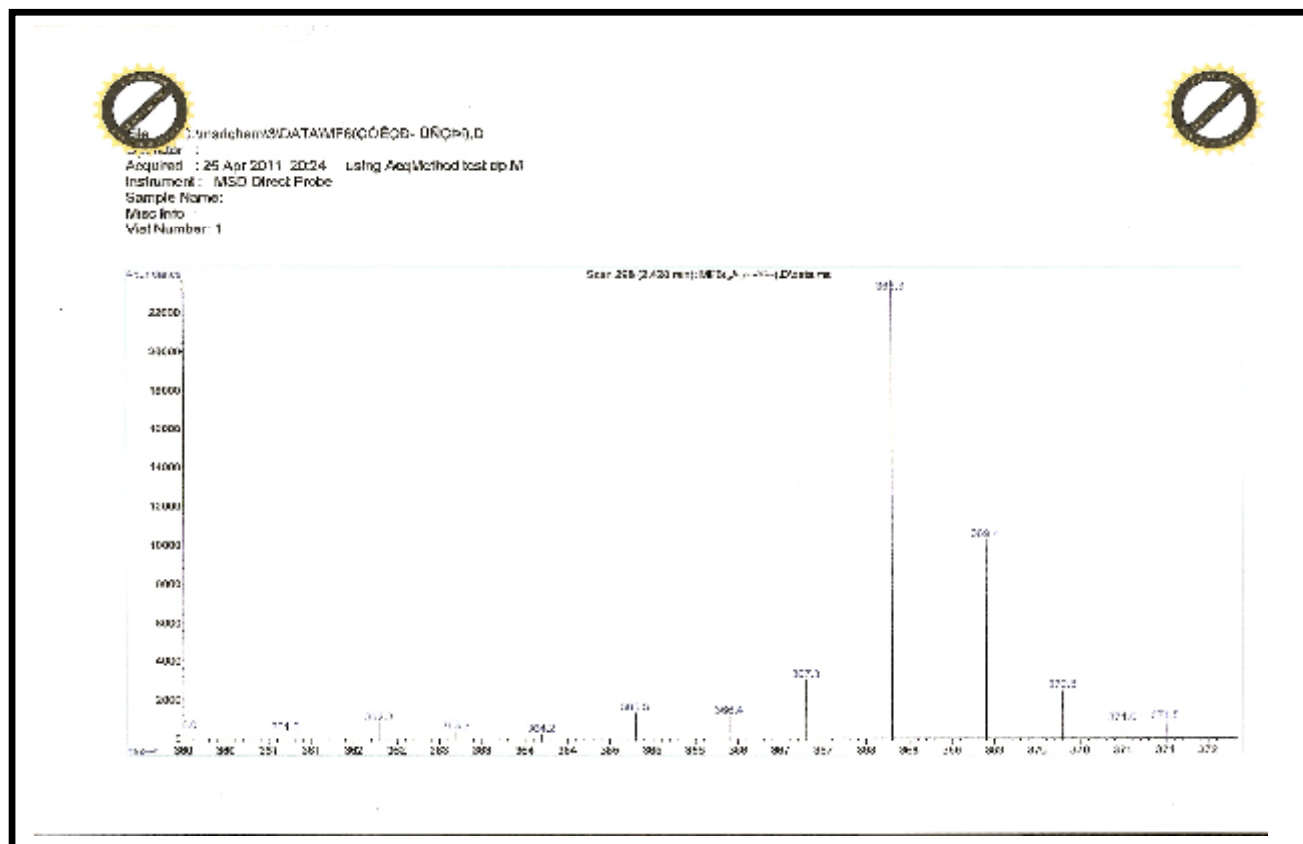


Figure (3-4): Mass spectrum of compound T<sub>3</sub>

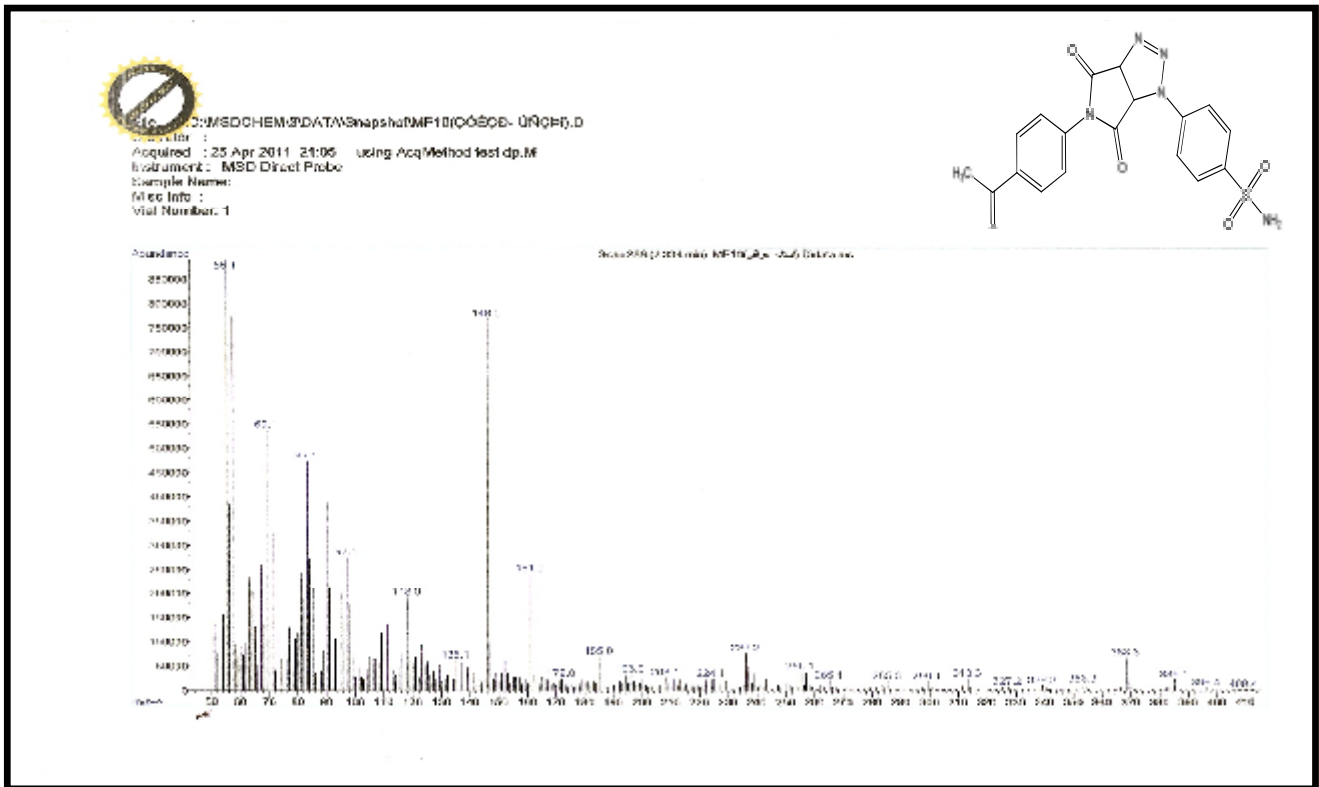


Figure (3-5): Mass spectrum of compound T<sub>4</sub>

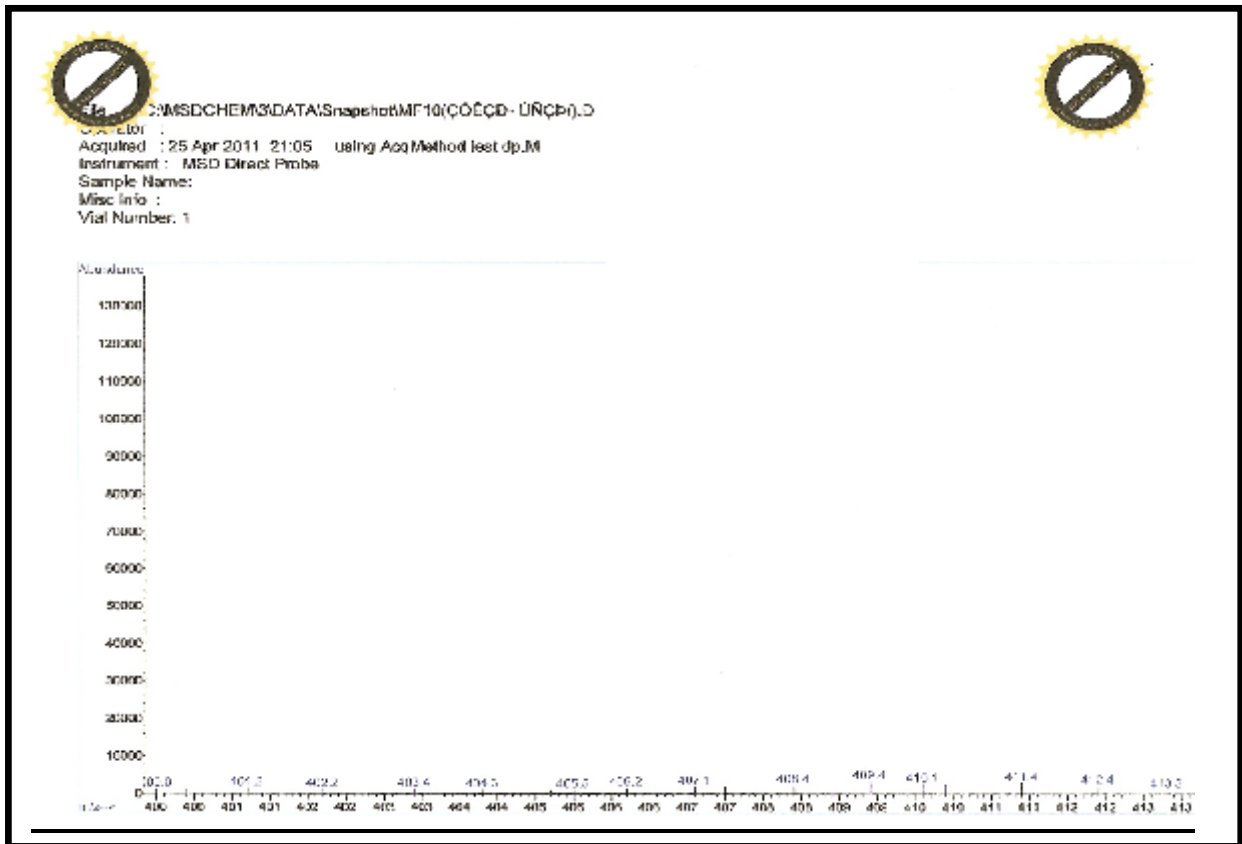


Figure (3-5a): Mass spectrum of compound T<sub>4</sub>

**CONCLUSION**

- 1- This study is concerned with synthesis of 1,2,3-triazole compounds and consists of three stages :
  - a- Synthesis of 4- azido benzene sulfonamide by Diazonium salt.
  - b- Synthesis of N-phenyl maleimide and N- (4-acetyl phenyl) maleimid.
  - c- Dipolar cycloaddition reaction.
- 2- By comparing the IR- Spectra of Azid and 1,2,3-Triazole compounds T1, T2, T3 and T4, We observed that band attributed to the azid (-N<sub>3</sub>) group disappeared in the spectra of triazole compounds.
- 3- All the compounds exhibit parent peaks.

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الإضافة الحلقية 3,1- ثنائية القطب ل-4- ازايذوبنزين سلفوناميد مع مركبات استلينية واوليفينية

فائزة عبد الكريم ناصر المشعل و محمد خلف محمد

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#### الخلاصة

حُضِرَتْ سلسلة من مركبات 3,2,1- ترايازولات عبر تفاعل الأضافة الحلقية 3,1- ثنائية القطب ل-4- ازايذوبنزين سلفوناميد مع مركبات استلينية واوليفينية باستخدام الأستون والكلوروفورم كمذيب للتفاعل وتحت التقطير الإرجاعي. تم متابعة مزيج التفاعل بواسطة كروماتوغرافيا الطبقة الرقيقة TLC ونقي ناتج التفاعل خلال كروماتوغرافيا العمود. استخدمت تقنيات الأشعة تحت الحمراء IR ، الرنين النووي المغناطيسي للبروتون  $^1\text{H-NMR}$  و طيف الكتلة Mass spectroscopes في تشخيص المركبات.