Journal of Basrah Researches ((Sciences)) Vol.(40). No.(1) A …… (2014)

Available online at: www.basra-science-journal.org

ISSN -1817 -2695

Uncatalyzed thermal synthesis of new 1,2,3- triazole derivaties

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Received 28-12-2013, Accepted 25-2-2014

Abstract :

Two of new Azide and two of new 1,2,3-triazole compounds were synthesized. The triazole compound was prepared by 1,3-dipolar cycloaddition reaction of azido sulfacetmide and azido sulfamethazin with acetylene dicarboxylic acid in acetone as a solvents under reflux condition without catylest. The reaction mixture was followed by TLC and the yields of products following columgromotography. IR, H-NMR and Mass spectroscopes were used for the identification of prepared compounds.

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

Introduction

The chemistry of azides has thus attracted the attention of many chemists, since many of these compounds play an important role in organic chemistry . One of the most 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 [1]. Azides are considered very important compounds due to both their industrial as well as biological applications[2].

The 1,2,3-triazole ring system has been the subject of considerable research mainly due to its usefulness in synthetic organic chemistry and also because of the pharmacological and Industrial properties shown by some of its derivatives [3] . They have been used as fungicides, herbicides, light stabilizers, fluorescent whiteners, optical brightening agents, and corrosion retardants [4-6]. Moreover 1,2,3-triazole derivatives show significant antimicrobial, cytostatic, virostatic, and anti-inflamatory activities[7].

Huisgen's 1,3-dipolar cycloaddition of an organic azide and an alkyne is an efficacious way for multifarious syntheses of the 1H-1,2,3-triazole ring system. This reaction is by far, the most well-known example of the "Click Chemistry". It was adopted thereafter to synthesize several types of molecules[8].

Experimental :

Melting points were determined with an electronthermal digital point apparatus type Thermo Scientific . IR spectra were obtained using IRAffinity-1 spectrophotometer at laboratories chemistry dept . All the spectra were recoreded as KBr discs.The mass spectra were obtained by using a Agilent technologies 5975c University of Tarbiat Modares Tahran ,Iran ,and ^{1}HNMR were obtained by using Bruker-(400and 250) MHz, Faculty of science, Micro Analytical center TLC is performed on silica gel 60 F_{254} sheet layer (Merck).The materials from Merk , Ridel and Fluka) companies.

Preparation of N-(4-Azido phenyl sufonyl)actamide A1

To a stirred solution of sulfacetmide 0.214 g ,0.001 mol [9] in conc. hydrochloric acid 0.35mL and water 10 ml at 0°C a solution of sodium nitrite 0.078 g, 0.001 mol in water 5 ml, was added dropwise. After 30 minutes a solution of sodium azide0.06 g, 0.001 mol in water 10 ml was added drop wise . The solution was stirred at 0°C for 15 min. and water10 ml was added slowly with cooling. The precipitate was collected by suction filtration and recrystallised from ethenaol to give white needelcrystal with melting point 142.-143°C and yield 98% .

Preparation of 4-Azido-N-(4,6 di metheyle primiden-2-yl)benzene sulfonamide A2

To a stirred solution of azido sulfmethazin 0.278 g ,0.001 mol [9] in conc. hydrochloric acid 0.35ml and water 10 ml at 0°C a solution of sodium nitrite 0.078 g, 0.001 mol in water 5 ml ,was added drop wise. After 30 minutes a solution of sodium azide 0.06 g, 0.001 mol in water 10 ml was added dropwise . 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 chloroform to give white needlecrystal with melting point 140-142°C and yield 60% .

Preparation of 1-(4-N-acytylsulfamoyl)phenyl)-H-1,2,3 trizole-4,5 dicarboxlic acid and 1-(4-(N-(4,6 di methyl pyrimidine-2-yl) sulfamoyl) phenyl)-H-1,2,3 trizole-4,5 dicarboxlic acide T1 &T2

0.240 g ,0.001 mol of azido sulfactamide or 0.304g ,0.001 mole [10] of azido sulfamethazine was dissolved in acetone 10 ml in to 25 ml round bottomed flask and acetylene di carboxylic acid 0.114 gm,0.001 mole in10 ml acetone was added.The mixture was reflexed for 24 hr to 48hr for compounde1and2 respectivly, until the starting material were no more detected at TLC control(2:8 ethanol:chloroform as eluent). The mixture then was evaporated,the crystalline products was crystallized to give triazole compound T_1 and T_2 ,as shown in Table 1.

The phesical properties werw shown in Table 1

Symb.	structure	eluent	Mp ^{0}C	Yield%	color	Time of reaction
A1		2 :8 Ethanole : chloroform	142-143	98	White crystal	-
A2		2 :8 Ethanole : chloroform	140-142	60	nadell crystal	-
T1		2 :8 Ethanole : chloroform	186-188	53	White powder	**24**
T2		2 :8 Ethanole : chloroform	Dec.225	28	White Powder	**48**

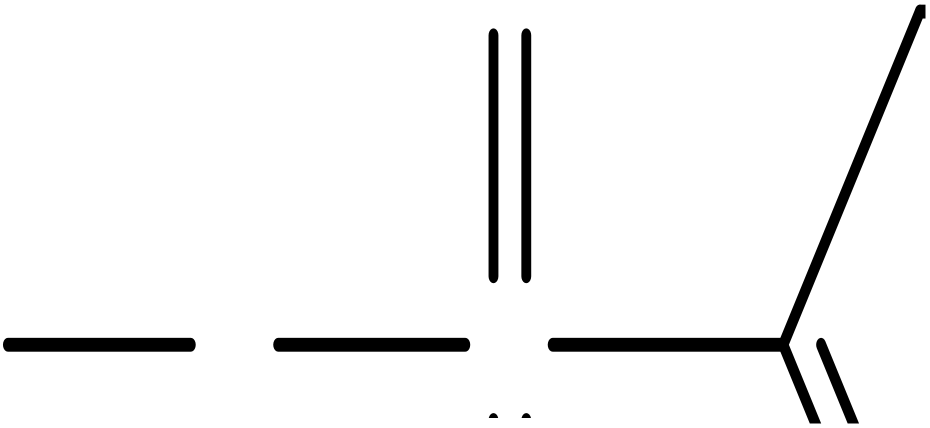
Results and discussion

N-(4-Azido phenyl sufonyl)actamide A1 and 4-Azido-N-(4,6 di metheyle primiden-2-yl)benzene sulfonamide A2 can be prepared from Diazonium salts according to published method [11], as shown in schem 1

.

Schame1

N-(4-Azido phenyl sulfonyl)actamide A1 and 4-Azido N-(4,6 dimethyle pyrimiden-2-yl) benzene sulfonamide A2 react with acetylene dicarboxlic acide compound . by 1,3-dipolar cycloaddition reaction to give 1,2,3-triazole derivatives[12,13] as shown in schem 2



Scheme 2

1- IR spectra [14]

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 spectram of the N-(4-Azido phenyl sufonyl)actamide A1 and4-Azido-N-

(4,6 di metheyle primiden-2-yl)benzene sulfonamide A2
showed the strong absorption band in (2135-2133) cm^{-1} which is characteristic of the (-N_3) stretching , the spectrum showed strong bands due to the (-SO_2) stretching vibration at (1083-1274and 1332) cm^{-1}, while the IR-spectra of Triazole compounds (T_1 and T_2) showed disappear of the of frequency of (-N_3) 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 (1-4). The suggest structures indicate that the reaction was take place the cycloaddition.

Table 2: IR spectra for the prepared compounds

Symb	O-H	N-H	CH$_{arom}$	CH$_{alif}$	N_3	C=O	SO_2	C=C$_{triazole}$ C=C$_{ar}$ N=N$_{triazole}$
A1	-	3305.99	3113	2852	2135	1728	1159-1274	1343-1587
A2		3403	3043	2800	2133		1083-1228	1332-1585
T_1	3423	3423-3350	3126	2868	-	1712	1165-1265	1348-1544
T_2	3441	3441-3300	3143	2865	-	1722	1167-1257	1560-1348

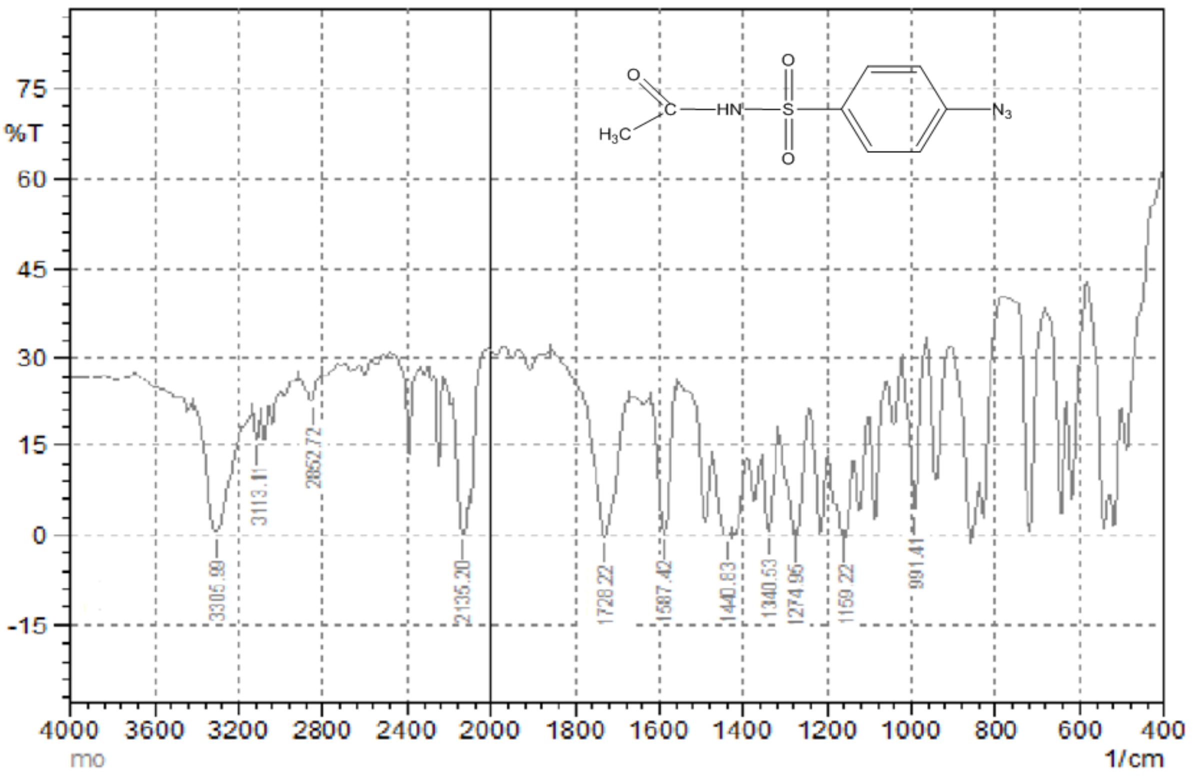


Figure (1-1) IR spectrum of compound A_1

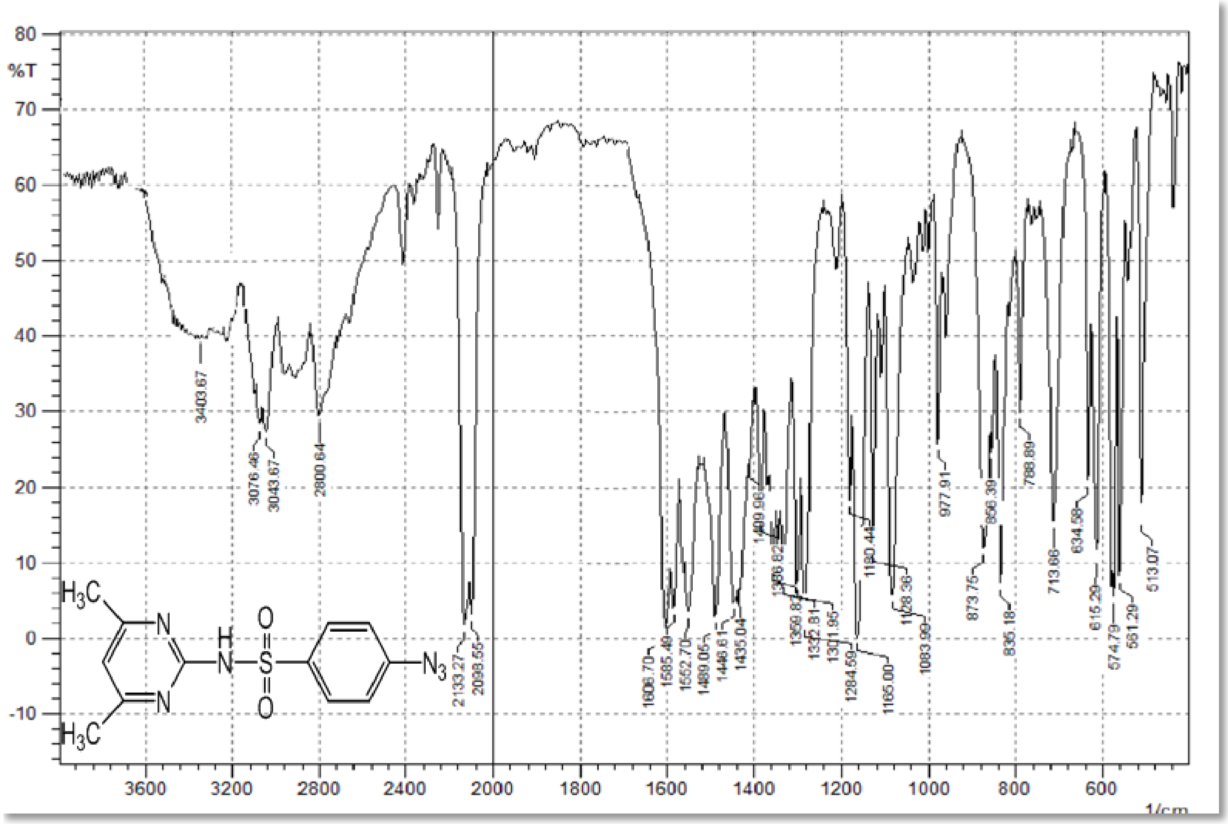


Figure (2-1) IR spectrum of compound A_2

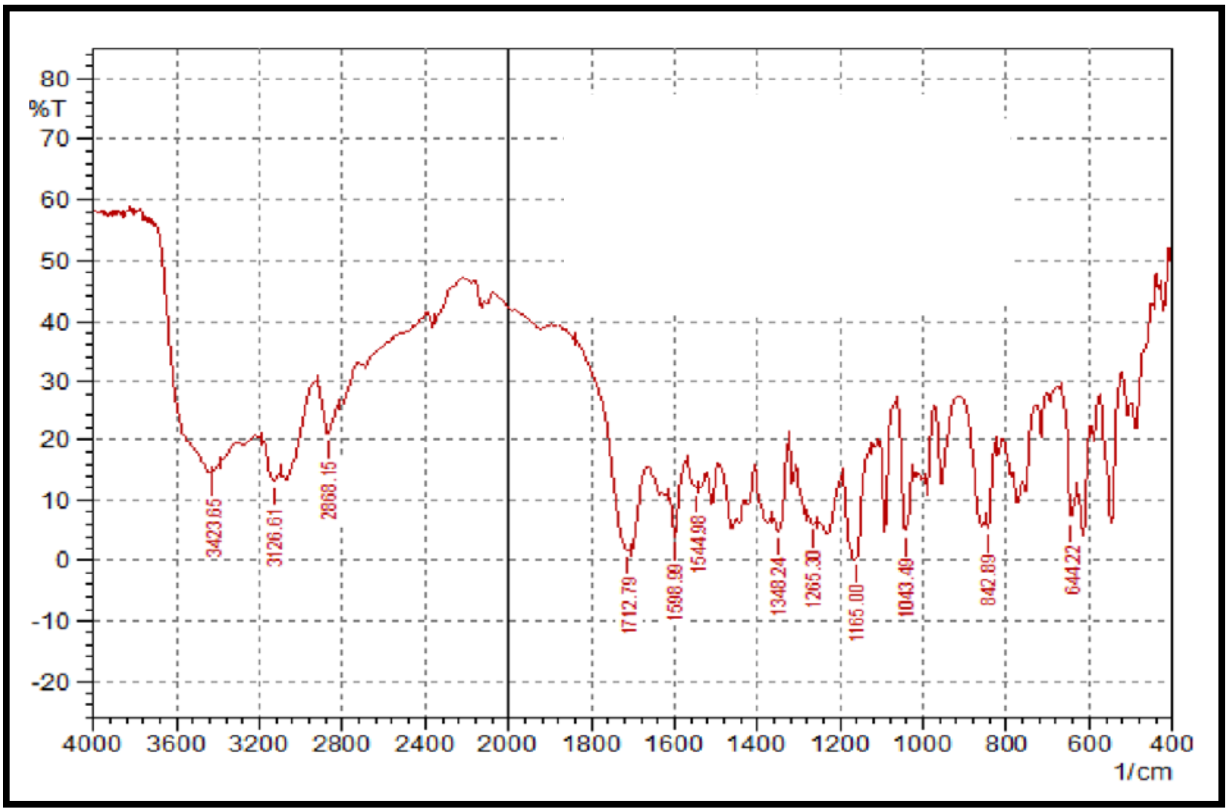


Figure (3-1) IR spectrum of compound T_1

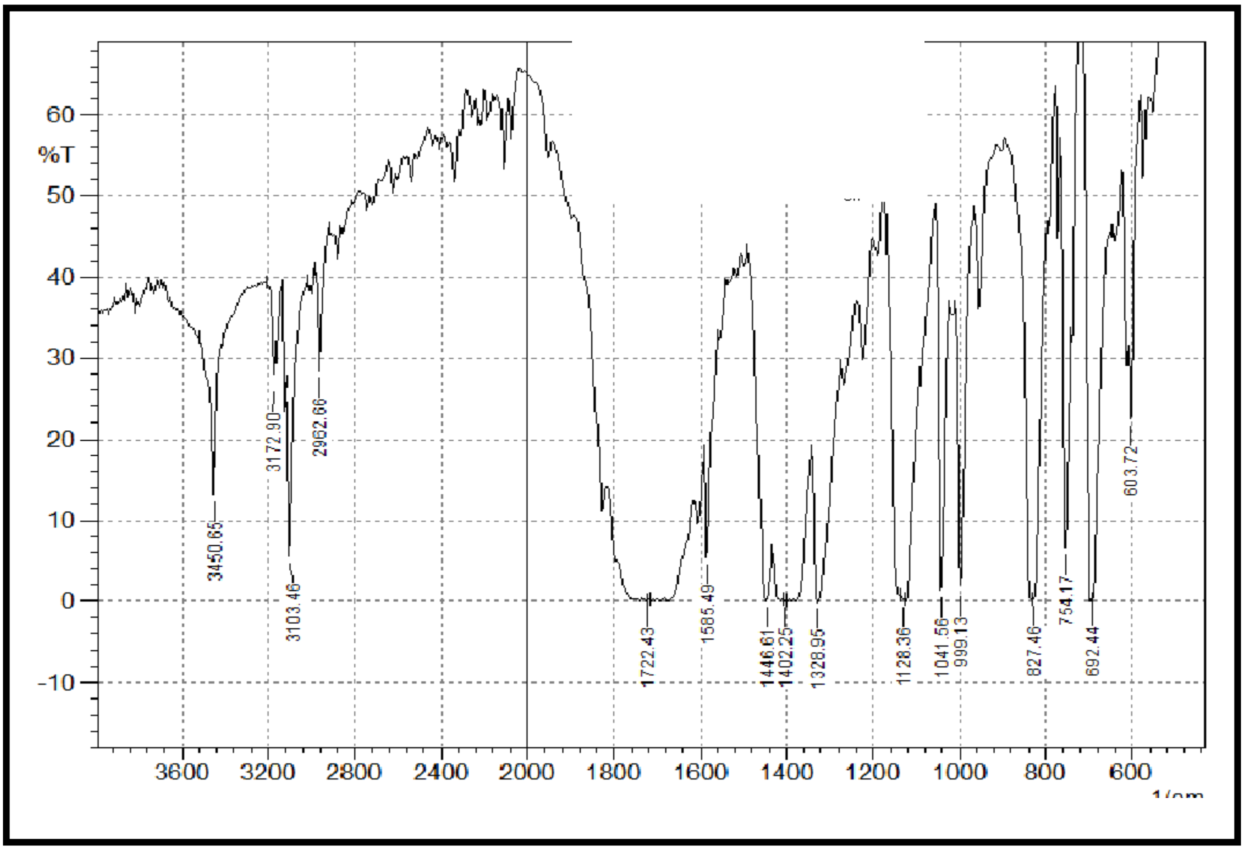


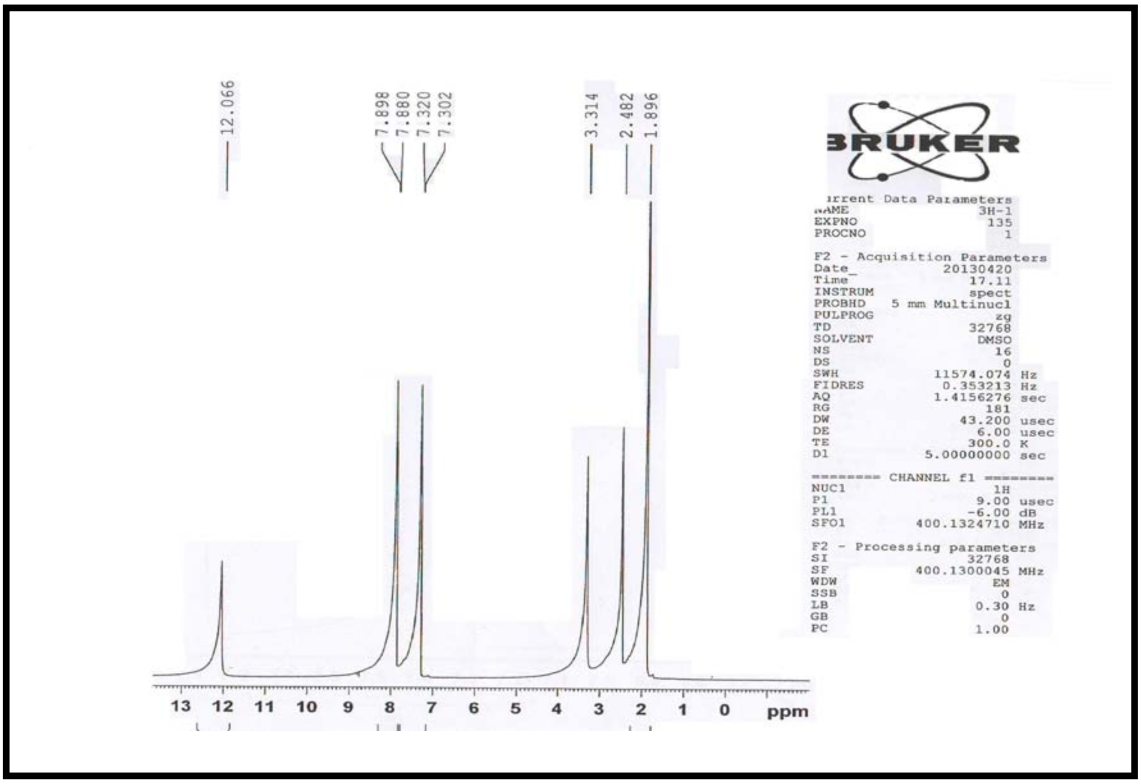
Figure (4-1) IR spectrum of compound T_2

2-^{1} H.NMR Spectra [15]

The ^{1}H-NMR of the investigated compounds are shown in Figures (2-1) – (2-5) and all compounds are dissolved in deuterated di methyl sulphoxide . the spectrum of N-(4-Azido phenyl sufonyl) actamide A1 mainly consist of three groups of signals . for aromatic region , the two doublet signals at (7.302 -7.20) ppm and (7.80-7.898) ppm which attribute to AB-system of aromatic protons,while the singlet signl at high field (12.066) ppm one amino proton.and singlet signl at high field (1.896 ppm) three proton , while the 4-Azido-N-(4,6 di metheyle pyrimidin-2-yl)benzene sulfonamide A2 mainly consist of four groups of signals . for aromatic region , the two doublet signals at (7.300 -7.339) ppm and (8.024-8.050) ppm which attribute to AB-system of aromatic protons, while the singlet signal at high field (9.04) ppm one amino proton .and singlet signal at low field (6.614 ppm) one proton and singlet signal at low field (1.311 ppm) six proton

1,3-Dipolar cycloaddition of of N-(4-Azido phenyl sufonyl) actamide A1 and 4-Azido-N-(4,6 di metheyle primiden-2-yl)benzene sulfonamide A2 to acetylene compounds in aceton respectively , affords one isomer of 1,2,3-triazole derivatives.

Comp.	structure	H.NMR
A1		H_1 (3H, δ=1.896 ppm) , H_2 (1H, δ= 12.066 ppm), $H_{3,3'}$ (2H , δ=7.311 ppm) , $H_{4,4'}$ (2H , δ=7.884 ppm)
A2		$H_{1.1'}$ (6H, =2.311 ppm), H_2 (1H , =6.814 ppm) , H_3 (1H, 9.8 ppm) $H_{4,4'}$ (2H, =7.322 ppm) , $H_{5,5'}$ (2H, = 8 .021ppm)
T1		H_1 (3H , =2.094 ppm) , H_2 (1H = 12.03 ppm) , $H_{3,3'}$ (2H , =8.15 ppm) , $H_{4,4'}$ (2H , =8.042 ppm)
T2		$H_{1,1'}$ (6H , =2.32ppm) , H_2 (1H , =6.80 ppm) , H_3 (1H , =9.53ppm) , $H_{4,4'}$ (2H ,= 7.9 ppm) , $H_{5,5'}$ (2H, = 8 ppm), $H_{6,6'}$ (2H, = 12.8 ppm ,)



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PROCNO                  1

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NS                     16
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FIDRES           0.353213 Hz
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RG                    181
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DE                   6.00 usec
TE                  300.0 K
D1             5.00000000 sec

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P1                   9.00 usec
PL1                 -6.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
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WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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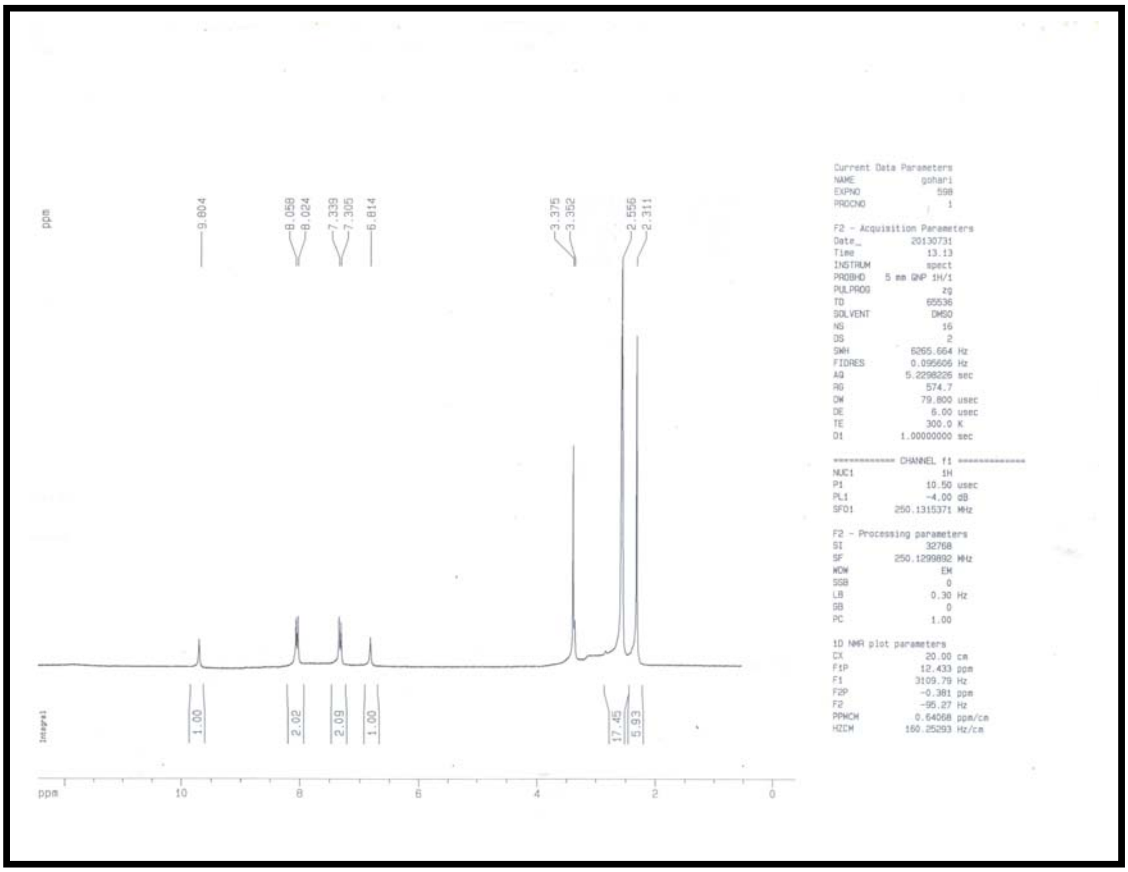
Figure (1-2) HNMR spectrum of compound A_1



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DS                      2
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AQ              5.2298226 sec
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DW                 79.800 usec
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TE                  300.0 K
D1             1.00000000 sec

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P1                  10.50 usec
PL1                 -4.00 dB
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F2 - Processing parameters
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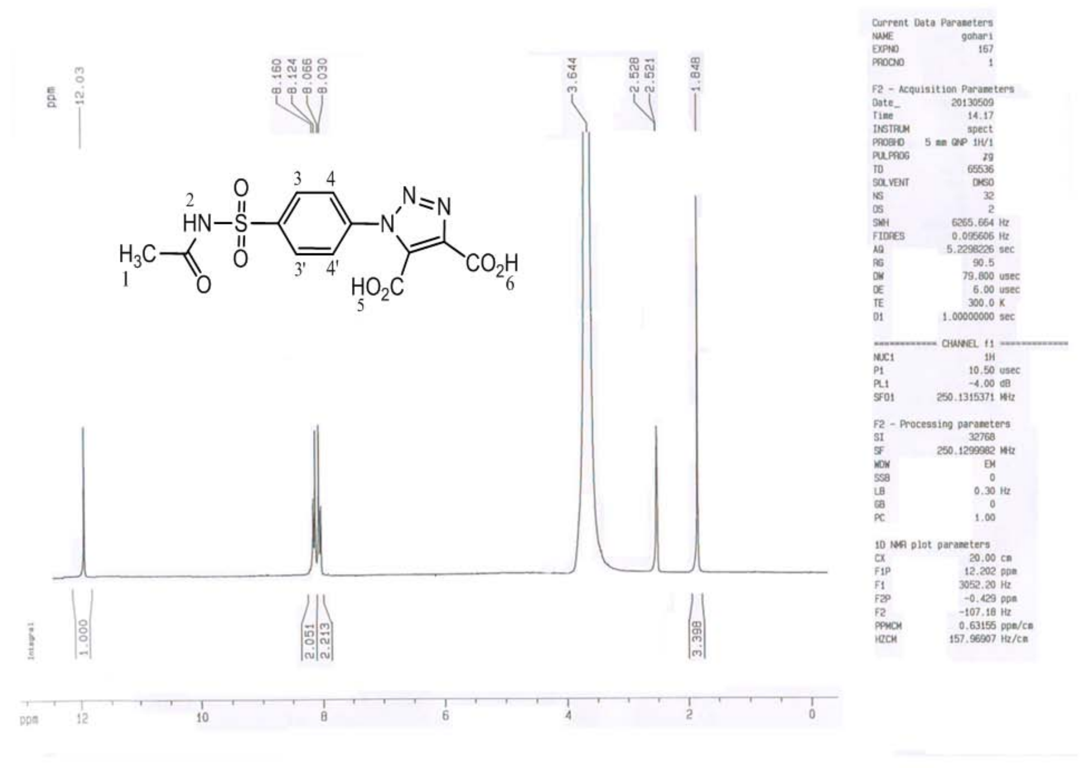
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                12.433 ppm
F1                3109.79 Hz
F2P                -0.381 ppm
F2                 -95.27 Hz
PPMCM             0.64068 ppm/cm
HZCM            160.25293 Hz/cm
```

Figure (2-2) HNMR spectrum of compound A_2



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EXPNO                 167
PROCNO                  1

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PULPROG                zg
TD                  65536
SOLVENT              DMSO
NS                     32
DS                      2
SWH              6265.664 Hz
FIDRES           0.095606 Hz
AQ              5.2298226 sec
RG                   90.5
DW                 79.800 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec

============ CHANNEL f1 ============
NUC1                   1H
P1                  10.50 usec
PL1                 -4.00 dB
SFO1          250.1315371 MHz

F2 - Processing parameters
SI                  32768
SF            250.1299982 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                12.202 ppm
F1                3052.20 Hz
F2P                -0.429 ppm
F2                -107.18 Hz
PPMCM             0.63155 ppm/cm
HZCM            157.96907 Hz/cm
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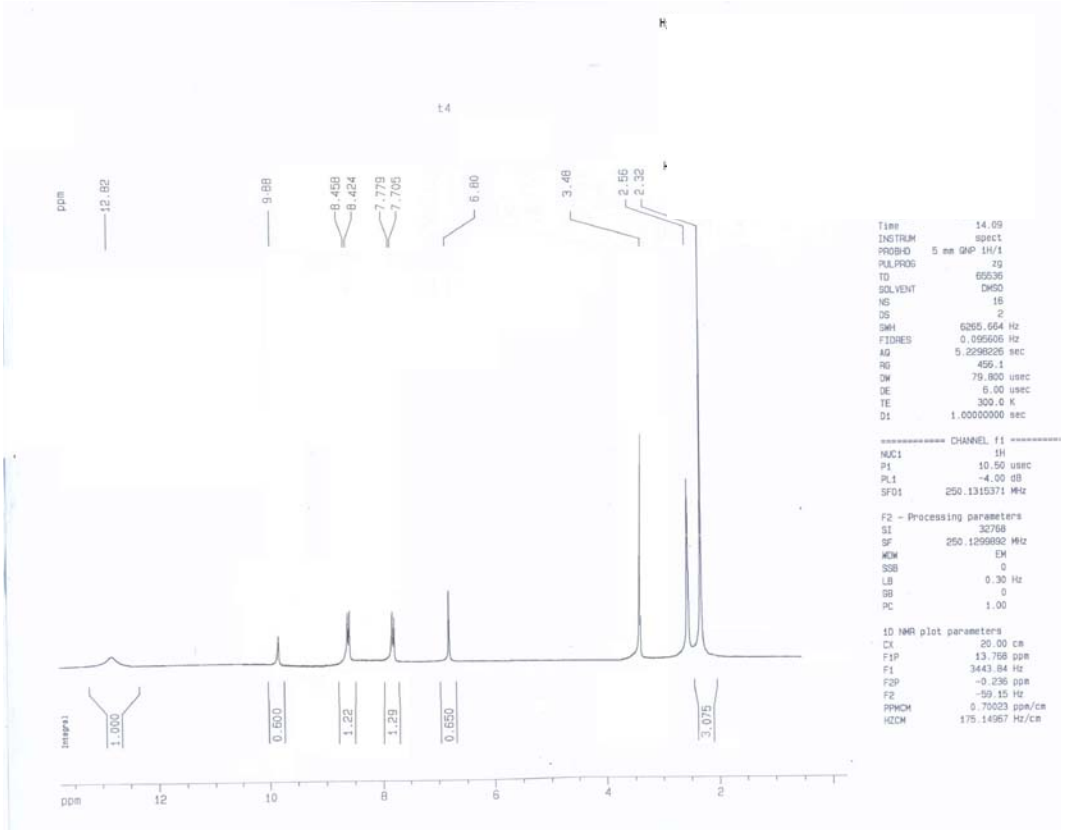
Figure (3-2) HNMR spectrum of compound T_1



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PULPROG                zg
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SOLVENT              DMSO
NS                     16
DS                      2
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FIDRES           0.095606 Hz
AQ              5.2298226 sec
RG                  456.1
DW                 79.800 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec

============ CHANNEL f1 ==========
NUC1                   1H
P1                  10.50 usec
PL1                 -4.00 dB
SFO1          250.1315371 MHz

F2 - Processing parameters
SI                  32768
SF            250.1299892 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                13.768 ppm
F1                3443.84 Hz
F2P                -0.236 ppm
F2                 -59.15 Hz
PPMCM             0.70023 ppm/cm
HZCM            175.14967 Hz/cm
```

Figure (4-2) HNMR compound T2

3- Mass spectra [20,21]

All the compounds exhibit peaks , and the base of beaks of the Triazole compounds are dependent on the derivatives of acetylene.

Symb	m/z					
A1	M+ 240		M- N_2 212	79	83	69
A2	305		276	79	83	69
T1	354	134	3	79	83	69
T2	418		390	79	83	69

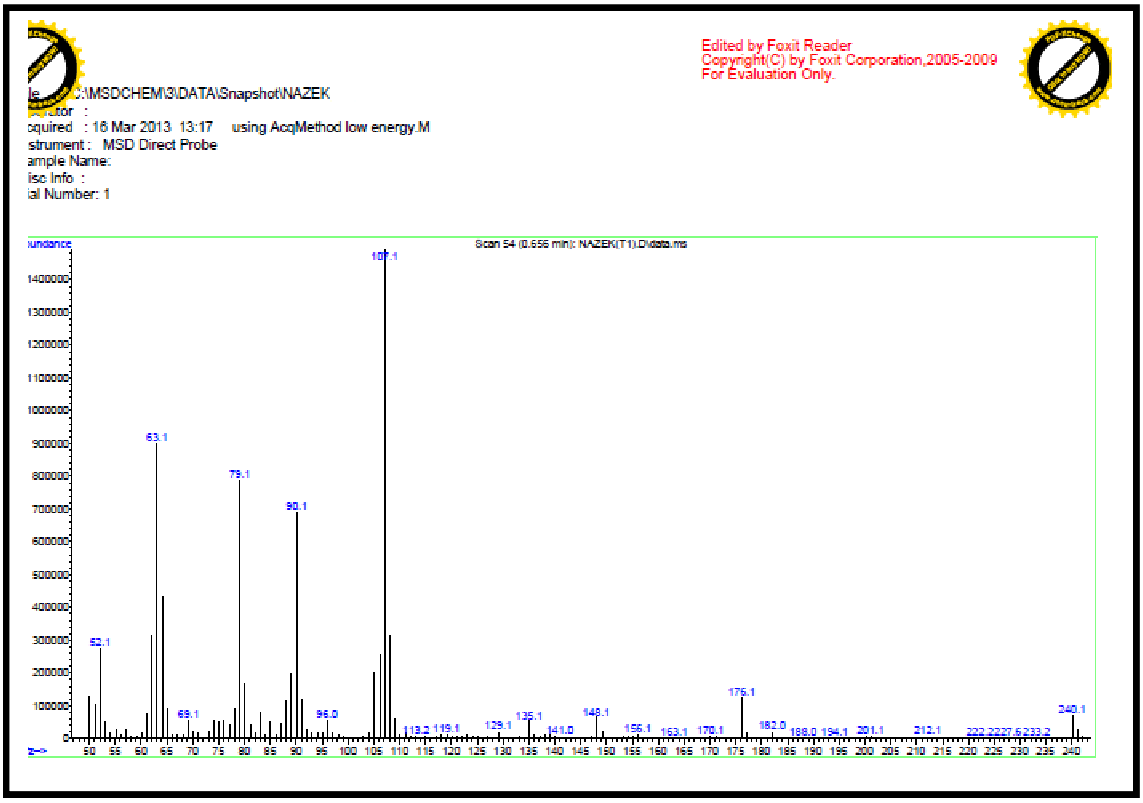

Figure (1-3) Mass spectrum of compound A_1

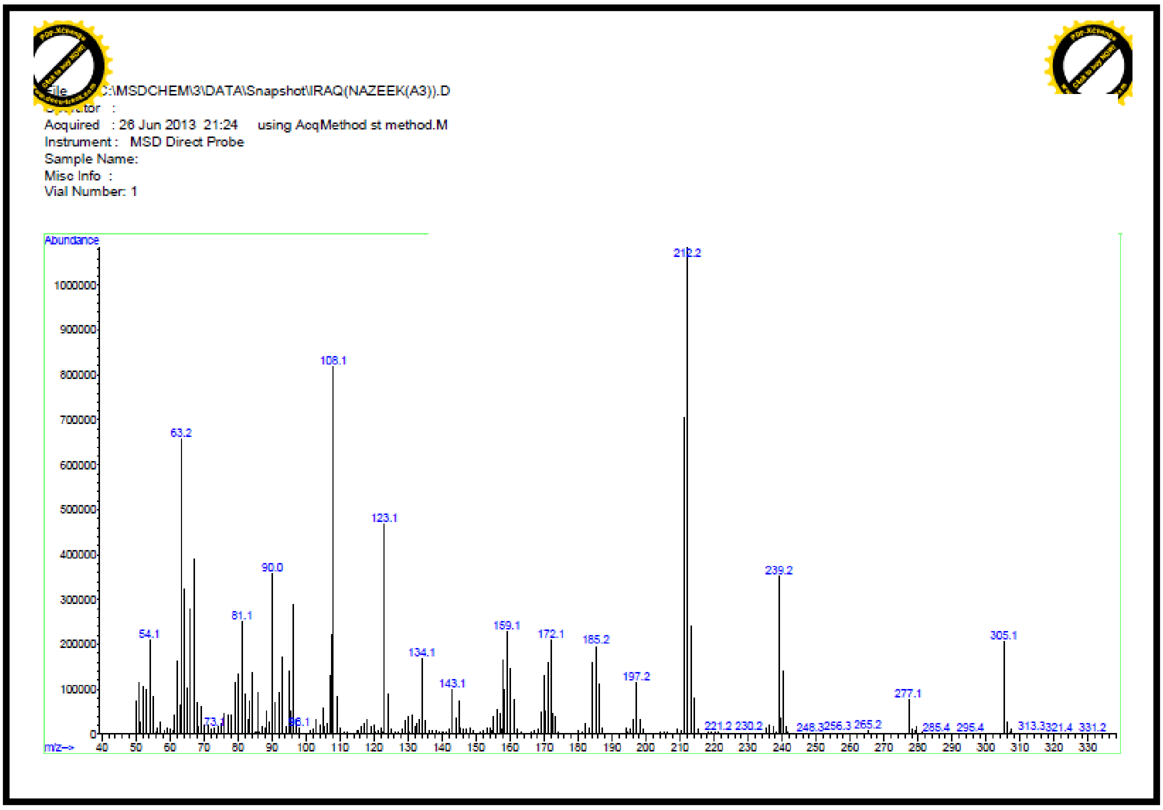

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Figure (2-3) Mass spectrum of compound A2

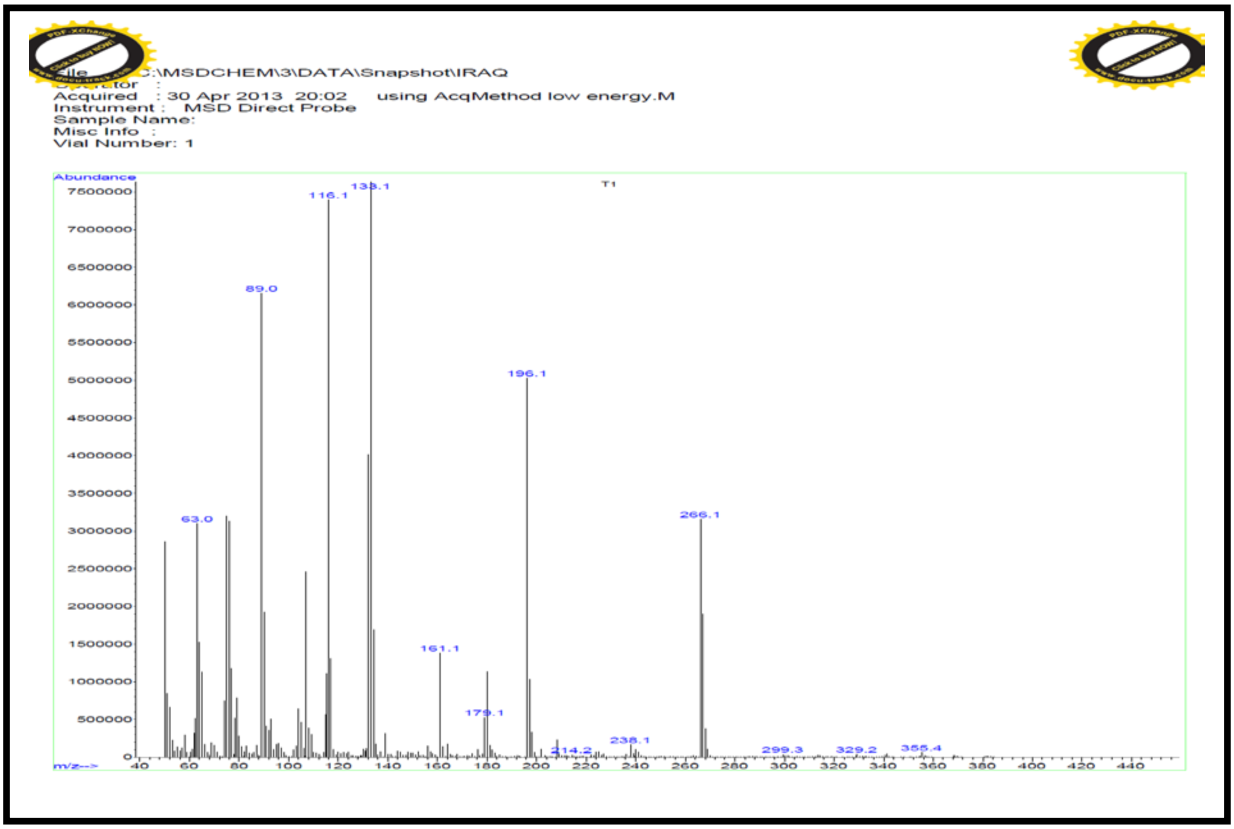

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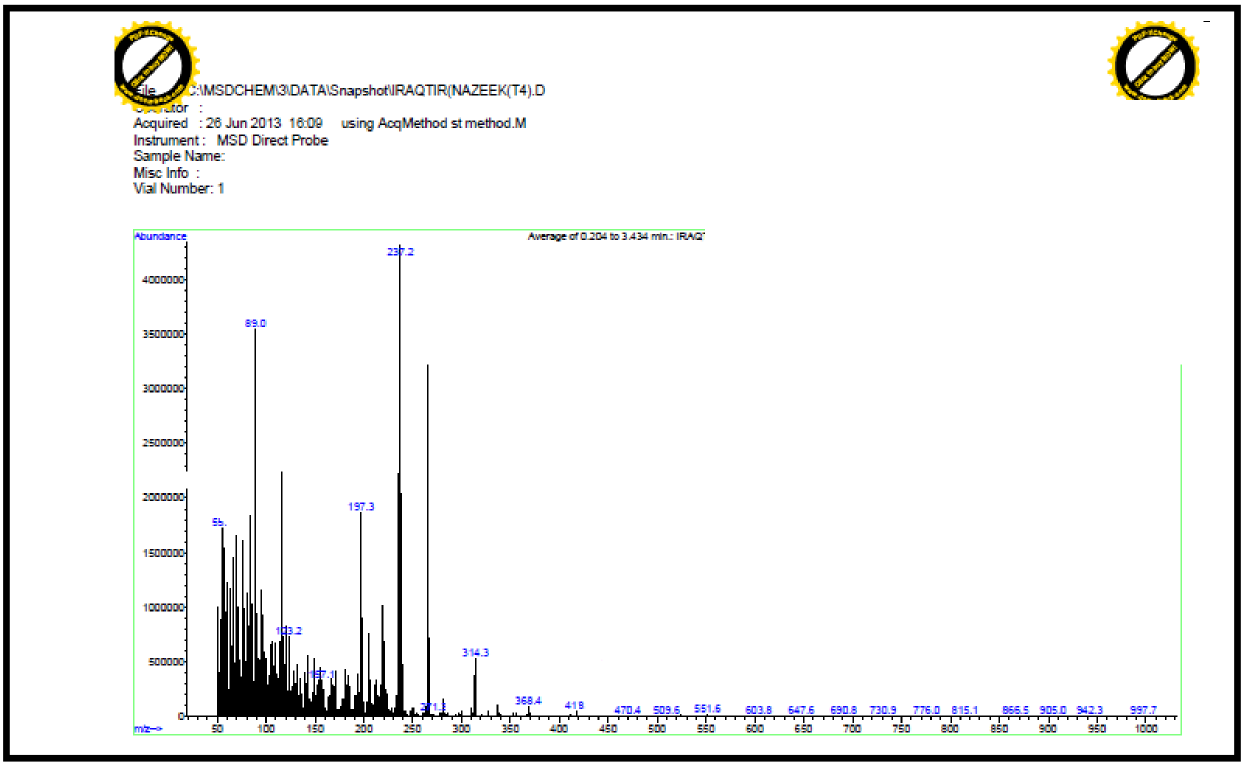
Figure (3-3) Mass spectrum of compound T_1



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Conclusion

1- This study is concerned with synthesis of 1,2,3-triazole compounds and consists of three stages :

2- Synthesis of **N**-(4-Azido phenyl sufonyl)actamide A1 and and 4-AZIDO-N-(4,6 di methyl pyrimidine-2-yl) benzene sulfonamide by diazonium salt.

3- By comparing the IR- Spectra of Azid and 1,2,3-Triazole compounds T1,and T2 We observed that band attributed to the azid ($-N_3$) group disappeared in the spectra of triazole compounds.

4- All the compounds exhibit parent peaks.

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الخلاصة:

تخليق اثنين من مركبات الازايدات و اثنين من مركبات 1،2،3- ترايازول عن طريق الاضافة الحلقية 1،3- ثنائية القطب وذلك بتفاعل ازايدوسلفا استمايد و ازايدو سلفاميثازين مع استلين ثنائي حامض الكاربوكسيلك في الاسيتون كمذيب تحت شروط التصعيد بدون عامل مساعد .

تم متابعة التفاعل بواسطة TLC وشخصت المركبات بمطيافية Mass Spectra,^{1}H.NMR,IR