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Research Article
Synthesis and Characterization of Hetero Cyclic Compound Derivatives from (2-amino-5-mercapto-1,3,4-thiadiazole).

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Keywords

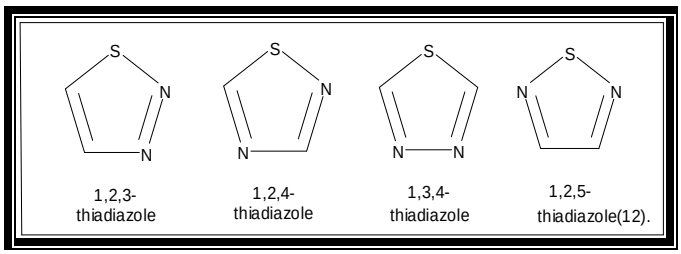
Thiosemicarbazide,
thiadiazole,
Schiff base,
oxazepine,
Biological activity.

Abstract

The research was designed to synthesize chemically -2-amino thiadiazol derivatives and conversion to schiff bases the principle to synthesis of these compound was via two steps : First: by the thermal cyclization of thiosemicarbazide with carbon disulfide in the presence of anhydrous sodium carbonate absolute ethanol to yield 2- amino – 5 – mercapto -1,3,4- thiadiazole. Second: schiffs base formation by reflux of aldehyde or keton with 2- amino-5-mercapto -1,3,4- thiadiazole in the presence of ethanol. The chemical structures of all prepared compounds were confirmed by spectral data(FT-IR and H.NMR) .The synthesized compounds were evaluated for their antimicrobial activity against two bacteria (Gram-positive), two bacteria(Gram-negative) .some of compounds showed good antimicrobial activity.

Introduction

Thiadiazole is one of a class of Organic heterocyclic compounds containing a five member di unsaturated ring structure composed of two nitrogen atom at posit ion (3and4) and one sulfur atom at position1[(1)]. The synthesis of 1,3,4-thiadiazole derivatives which were vestigated for antibacterial [(2),]antifungal [(3)] antitubercular [(4)] anti- flammatory[(5)] anticonvulsant([(6)] antioxidant[(7)] anticancer [(8)] controlling blood pressure [(9)] and can affect central nervous system[(10)] Anumber of methods for the preparation have been developed many synthesis of 1,3,4-thiadiazole proced from thiosemicarbazide or substituted thiosemicarbazid [(11)] there are several isomers of thiadiazole (Fig.1) that is



Scheme (1):structures of thiadiazole isomers

Experimental :

Synthesis of Compound (A1)
According to procedure([12])

A mixture of (2g,0.02mol)of thiosemicarbazide and(2.33g,0.02mol)anhydrous sodium carbonate was dissolved in 25ml ethanol abs. to this solution (3.2g,0.04mol)of carbon disulphide was added . the solution mixture was heated under reflux for 7 hrs . the reaction mixture was then allowed to cooldown to room temperature .Most of solvent was remoned under reduced pressure and the residue was dissolved in distilled water 200ml. carefully axidified with cold conc . Hydro chloric acid to give pale yellow precipitation .The crude product was filtered and washed with cold water, recrystallized from ethanol to give the desired product as yellow needles yield (1.6g,67%), m.p(228-230), reported lit (230-231).

Synthesis of Compound(A2)

Synthesis of schiff bases (A2)from 2-amino-5-mercapto-1,3,4-thiadiazol according to general procedure[(12)] ,a mixture of

compound (A1)(1mol) ethanol abs and appropriate ketone acetyl acetone (1mol)in acidic condition(3)drops of acetic acid was refluxed in water bath for(4-5)hrs .The reaction mixture was then allowed to cool at room temperature , and the precipitate was filtered and dried , recrystallized from ethanol 50% to give colored crystal.

Synthesis of Compound(A3)

A mixture of (0.02mol) of imine compound(schiff bases)and(o.o4mol)of maleic anhydride were refluxed for(7h)with stirrer in presence of benzene after cooled the precipitate filtered and dried , recrystallized to produce 52% of seven - membered of oxazepine named compound (A3).

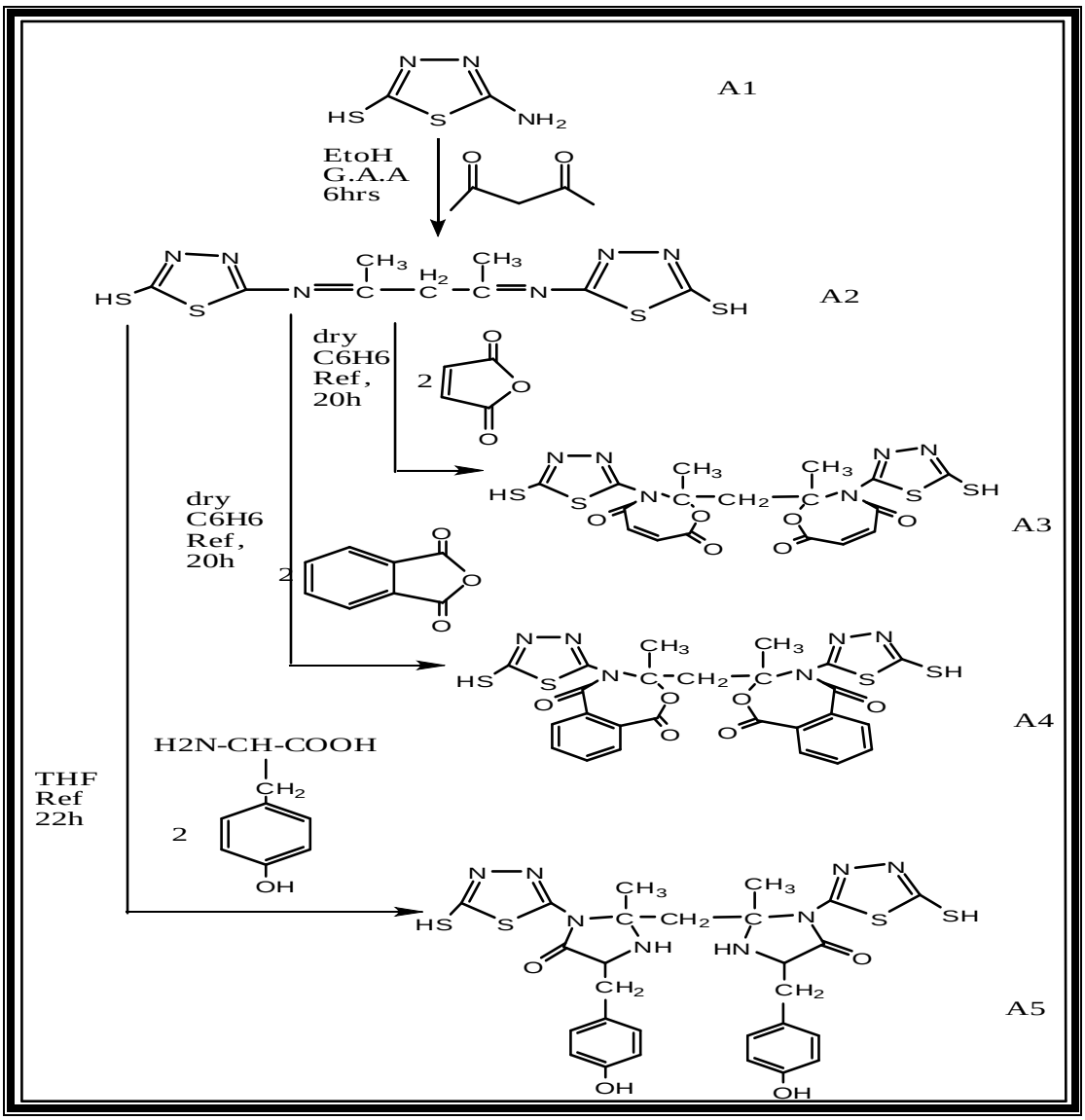
Synthesis of Compound(A4)

A mixture of(0.02mol)of imine comppund (schiff bases)and(0.04mol)of phthalic anhydride were refluxed for (7h) with stirrer in preseuce of benzene after cooled the precipitate filtered and dried ,recrystallized to product 60% of seven- membered of oxazepin named compound (A4)

Synthesis of Compound(A5)

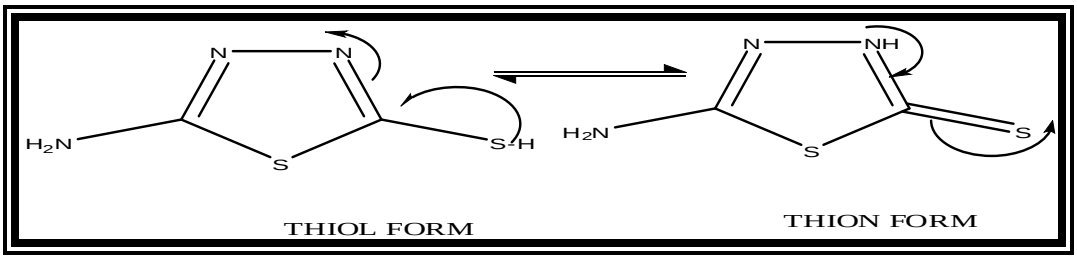
A mixture of(0.02mol)of imine compounds (schiff bases)and(0.04mol)of amino acid tyrosin were refluxed for(8h)with stirrer in presence of THF after cooled the precipitate filtered and dried , recrystallized to product 67% of Imidazolidine named compound (A5).

Scheme(2):synthesis of compounds



Results and Discussion

Compound(A1) 2-amino-5-mercapto -1,3,4-thiadiazole was identified by its melting point and FT-IR spectroscopy . The FT- IR spectrum of compound (A1) show the following characteristic bands , two bands at 3396cm^{-1} and 3278cm^{-1} were due to asymmetric and symmetric stretching vibration of (-NH_2) group respectively ,an absorption band at 3093cm^{-1} was due to the (N-H) stretching (tautomeric) form the (-SH) stretching band found as very weak shoulder at 2775cm^{-1} , a band at 1600 cm^{-1} was due to (C=N) stretching of the thiadiazole ring moiety . The sharp band at 1535cm^{-1} and 1383cm^{-1} are due to the (N-H) bending and (C-N) stretching vibration respectively .Also ,the absorption band at 1062cm^{-1} for the (C=S) group which gives an evidence that compound (A) can exist in two tautomeric forms thiol and thion form in Scheme (3).



Scheme (3) : thiadiazole forms

Other data of other compounds in Tables(1-3) and Figures(1-5)

Table (1) FT.IR data (cm-1) of compound (A2)

Comp. No.	Imine υ (C=N)	Thiadiazole υ (C=N)	Alphatic υ (C-H)	Thiadiazole υ (C-S)
A2	1604	1521	2960	1053

Table (2) FT.IR data (cm-1) of compounds (A3-A4)

Comp No.	Lactone υ (C=O)	Lactam υ (C=O)	Endocyclic υ (C=N)	Lactone υ (C-O)	Alkene υ (C=C)
A3	1720	1639	1604	1280	1523
A4	1724	1645	1604	1253	1523

Table (3) FT.IR data(cm-1) of compound (A5)

Comp No.	Keton υ (C=O)	Amine υ (N-H)	Aliphatic υ (C-H)	Aromatic υ (C-H)	Thiadiazole υ (C=N)	OH
A5	1699	3205	2953	3122	1523	3423

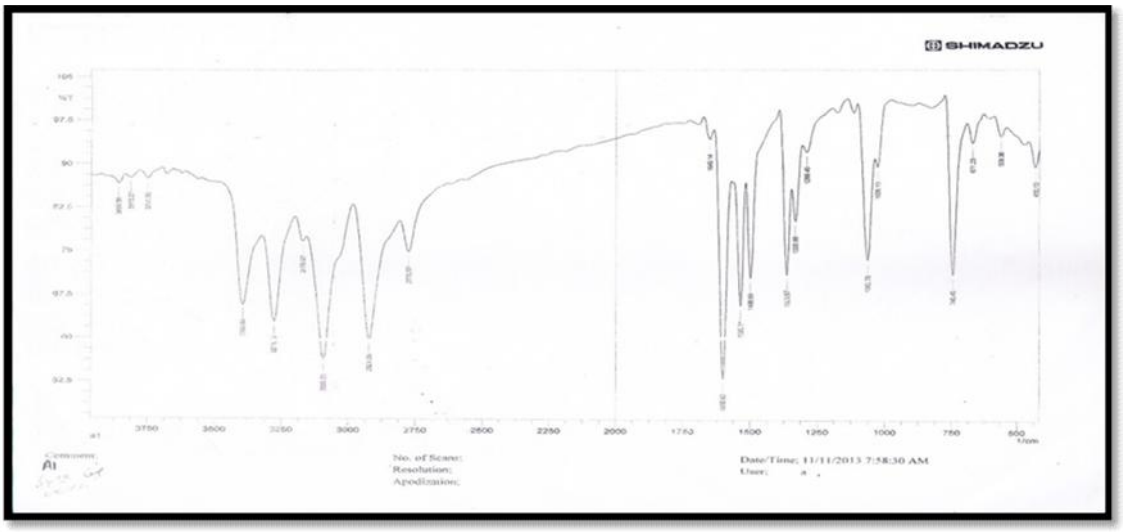


Fig (1) FT-IR Spectrum of compound (A1)

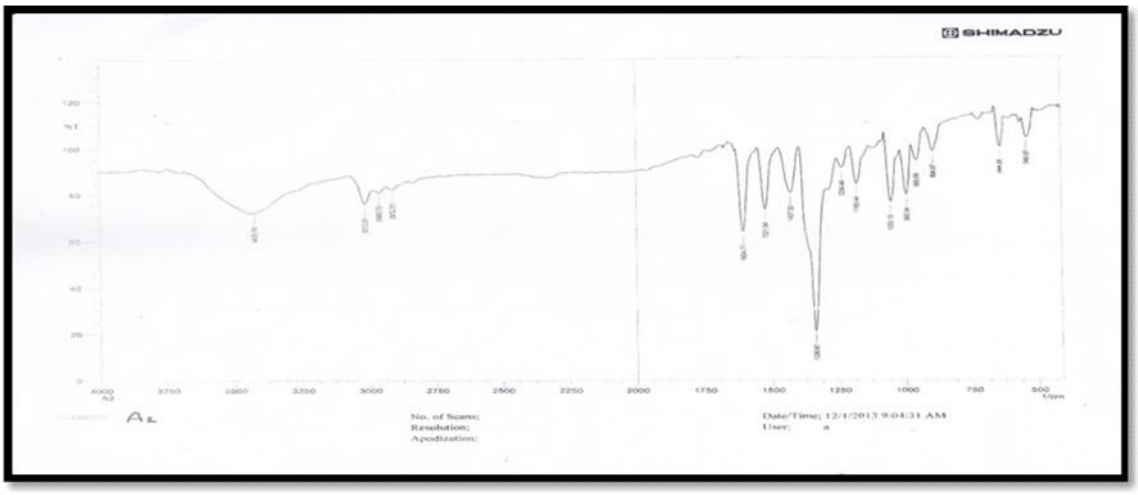


Fig (2) FT-IR Spectrum of compound (A2)

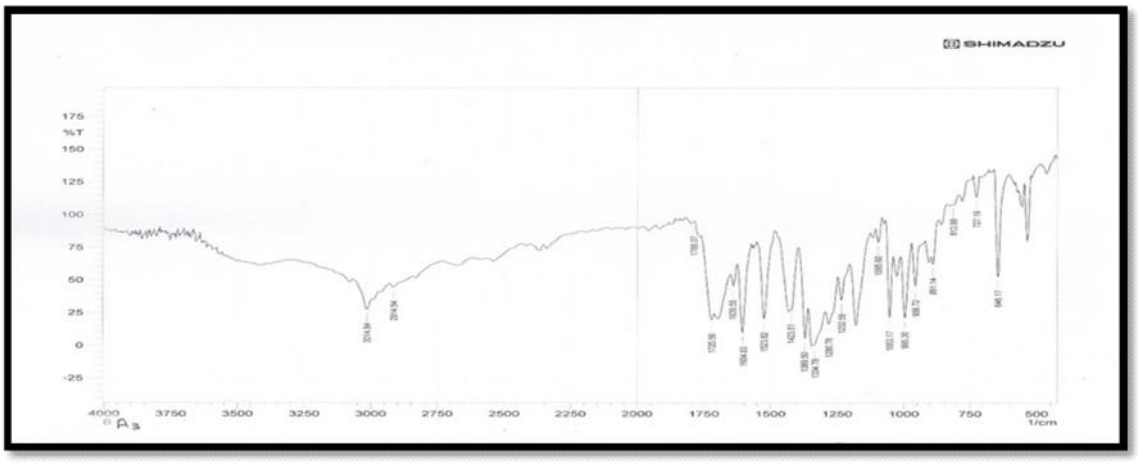


Fig (3) FT-IR Spectrum of compound (A3)

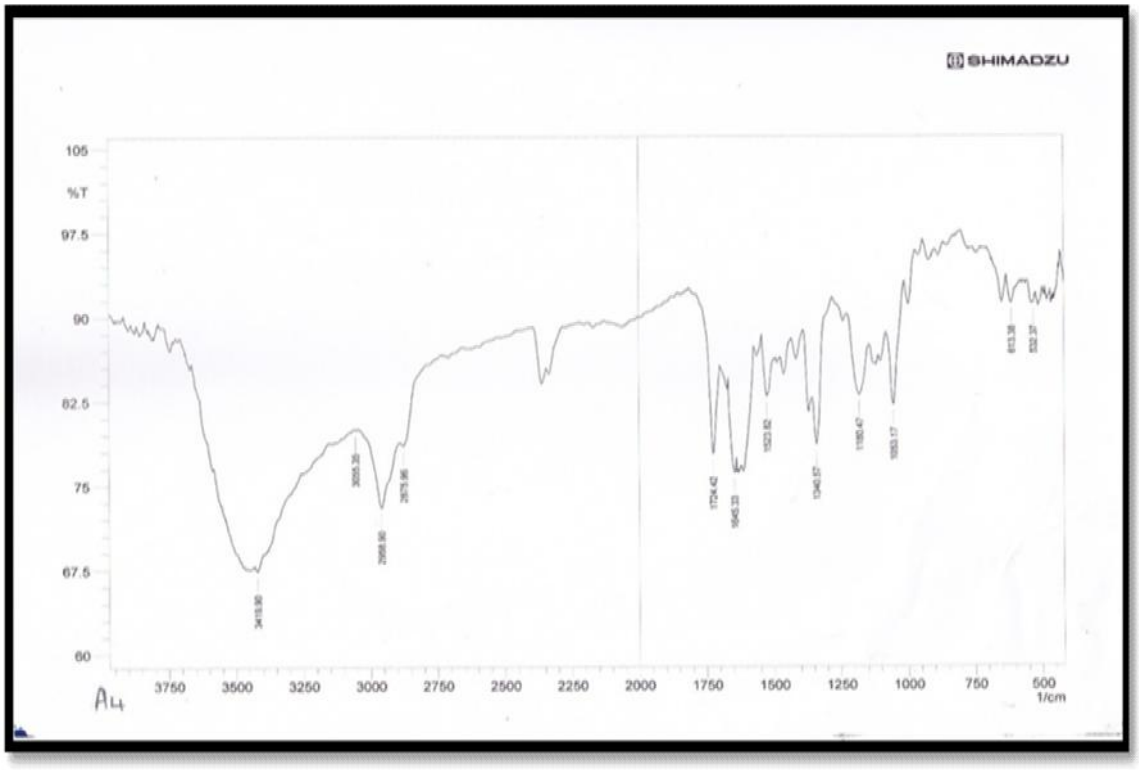


Fig (4) FT-IR Spectrum of compound (A4)

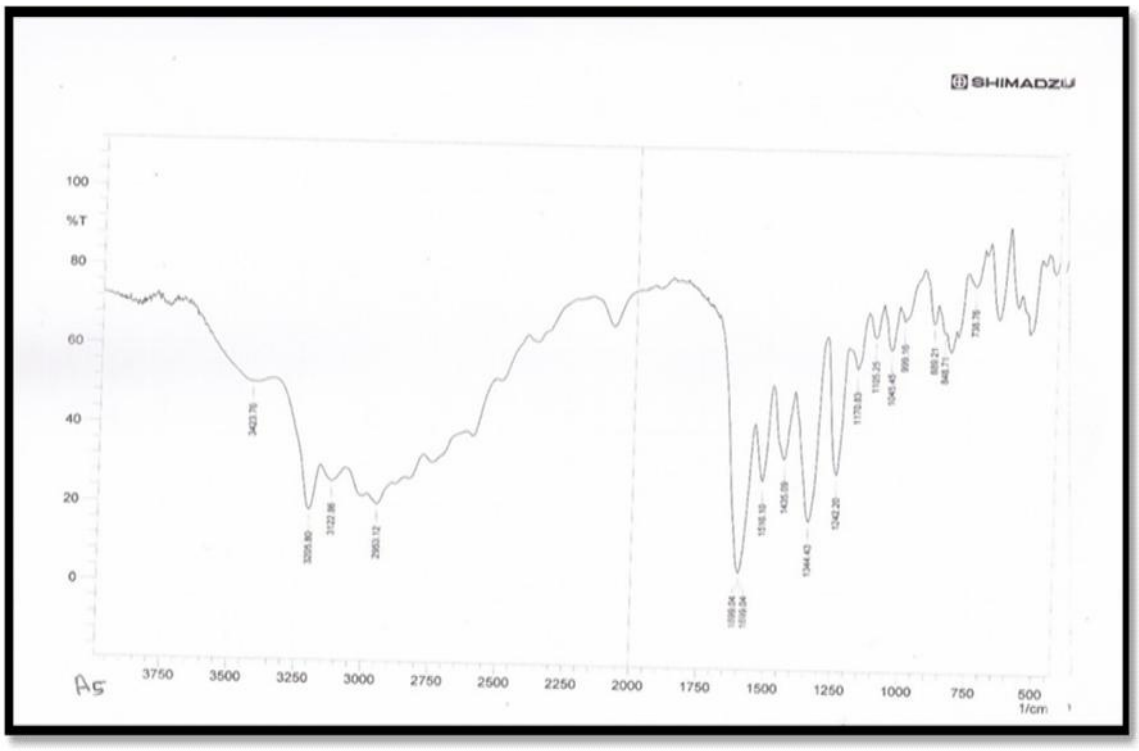
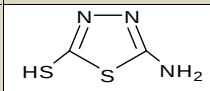
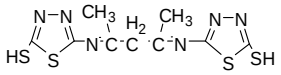
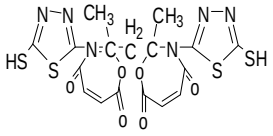
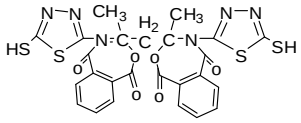
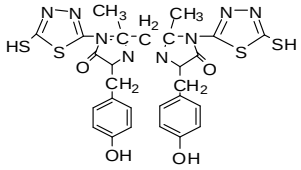


Fig (5) FT-IR Spectrum of compound (A5)

Other data (physical properties) , melting points ,structure , molecular weight , R.F , yield % of all compounds in Table (2).

Table (2): show the physical properties of synthesized compounds.

Comp No.	Formula	Molecular Formula	M.WT	M.P	Yield	R.F
A1		**$C_2H_3N_3S_2$**	**133**	**228-230**	**60%**	**0.6**
A2		**$C_9H_{10}N_6S_4$**	**330**	**124-126**	**75%**	**0.7**
A3		**$C_{17}H_{14}N_6O_6S_4$**	**526**	**160-162**	**52%**	**0.6**
A4		**$C_{25}H_{18}N_6O_6S_4$**	**608**	**120-122**	**66%**	**0.50**
A5		**$C_{27}H_{28}N_8O_4S_4$**	**656**	**220-222**	**67%**	**0.66**

Their H.NMR–spectrum signal at δ 13.16 due to (NH_2) amine group[14] in compound [1], which disappeared and other band appeared such as (-CH=CH-) at δ (6.02 , 6.08) protons of alkene of cycle in compound [3] . The proton of (SH) appeared at δ (3.39–3.58) due to protons of thiadiazole ring in compounds [1-5] , and other signals shown in figures (6 -8).

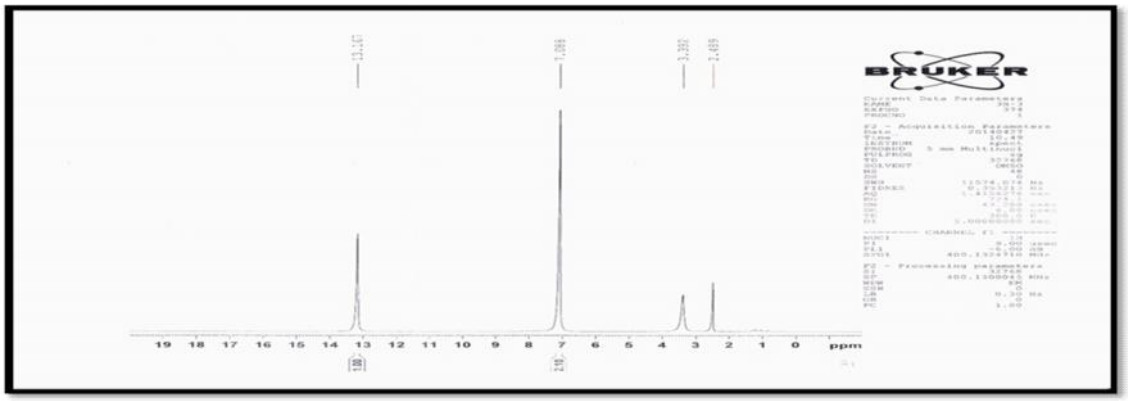


Fig (6): ^{1}H.NMR Spectrum of compound (A1)

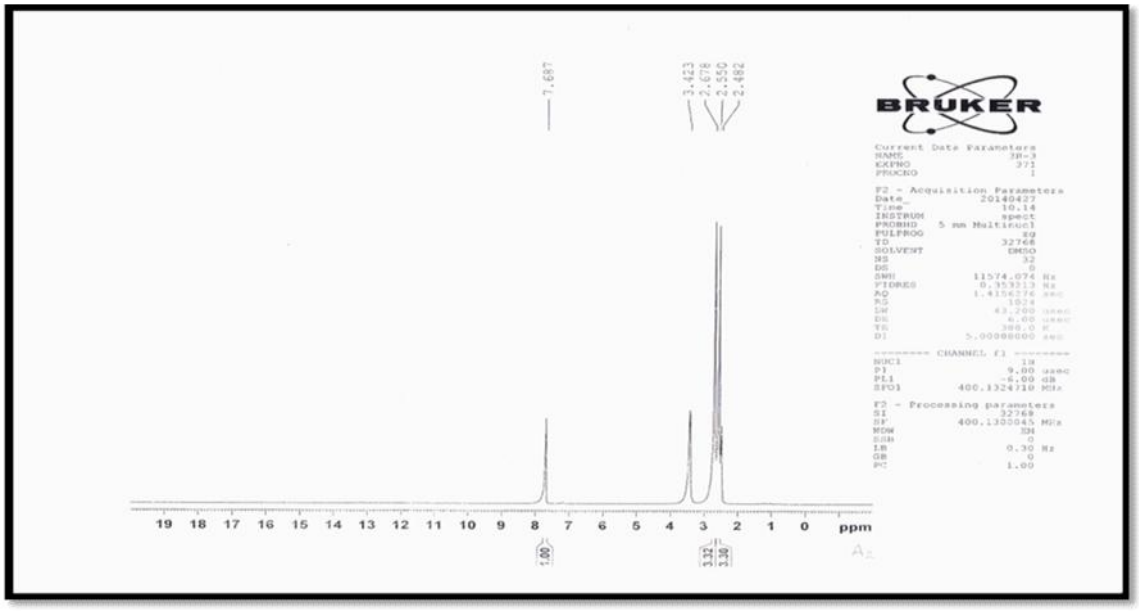


Fig (7): ^{1}H.NMR Spectrum of compound (A2)

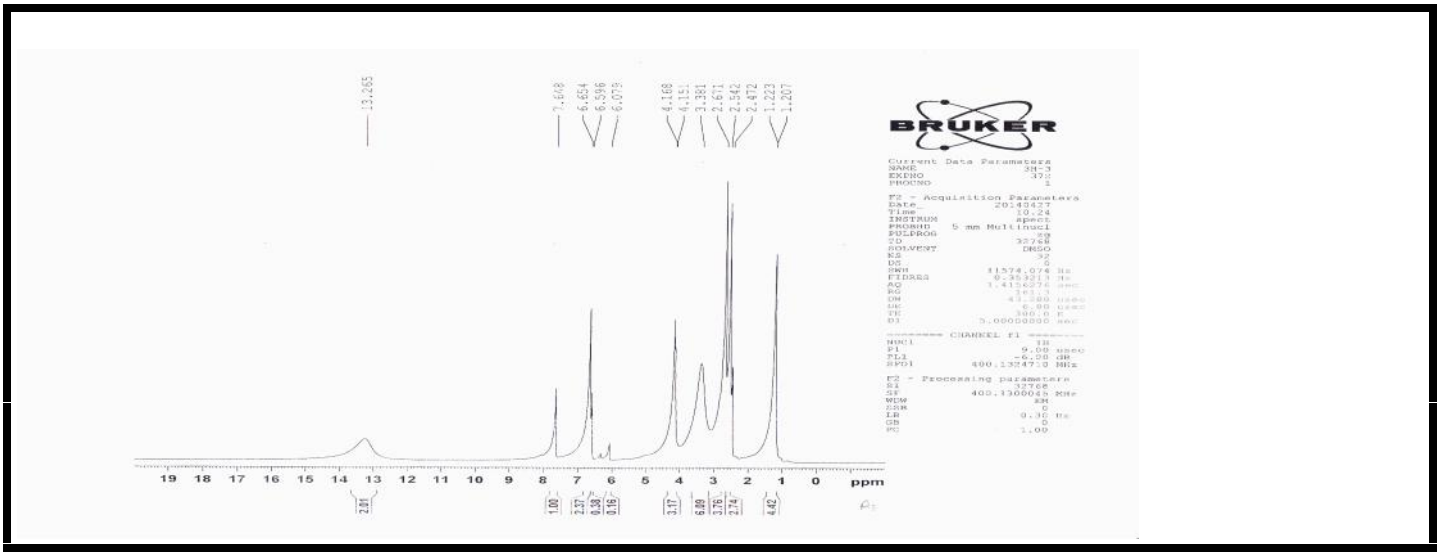


Fig (8): ^{1}H.NMR Spectrum of compound (A3)

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