International Journal of Recent Research and Review, Vol. XII, Issue 1, March 2019
ISSN 2277 – 8322

Synthesis of Some Tetrazole and Thiazolidinone Derivatives From Schiff Bases

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***Abstract*-The present paper involved synthesis of (1) (1-amino-4-methyl-6-phenyl pyrimidine-2-(1H)-thione). The product compound reaction with substitute aromatic aldehyde using glacial acetic acid as catalytic in absolute ethanol to give a new series of Schiff's bases (2a-e). New Thiazolidine-4-one (3a-c) were prepared from reactions Schiff bases (2a-c) with thioglycolic acid on absolute ethanol. Finally the preparation of new tetrazole derivatives (4a-c) by reaction of Schiff bases (2a-c) with sodium azid in THF. The structure of the synthesized compounds are confirmed by I.R. ^{1}H-NMR & ^{13}C-NMR spectra and some physical data.**

***Keywords* - Tetrazole, Thiazolidinone, Schiff Bases, thioglycolic acid.**

I .INTRODUCTION

Schiff bases are used as substrates in the preparation of number of industrial and biologically active compounds via ring closure, (cyclo addition and replacement reaction) [1]. Thiozolidinone derivatives have various pharmacological activities such as antibacterial [2]. antifungal [3]. Anticancer [4], anticonvulsant [5] and herbicidal actions [6], Tetrazoles have been found to exhibit antihistamine [7], antiflammatory properties antifungal [8].

II .EXPERIMENTAL

All reagents and chemicals are from BDH and Fluka, used without purification. Melting points were measured using: Electro thermal melting points apparatus type (not corrected). FT-IR spectra were recorded on Shimadzu FT-IR-8400 Infrared Spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded by Geo. 1400(400 MHz) using acetone-d^6 and $CDCl_3$ as solvent in UK Loughborough.

A. Synthesis of 1-amino-4-Sub.-6-phenyl pyrimidine-2-(1H) thion (1) [9]:

A mixture of (0.01mole) of benzaoyl acetone and (0.01mole) of thiosemicarbazide in (50 ml) absolute ethanol containing a few quantity of pipridine , then reflux for 5hr. the product filtered, the solid recrystallized from ethanol to give pale-yellow product (Yield: 95 %; m.p.160-162°C).

B .Synthesis of Schiff bases (2a-e) [10]:

A mixture of compound (1) (0.01mole) and different aromatic aldehyde (0.01mole) in absolute ethanol (25 ml) containing a few quantity of glacial acetic acid was stirring for 4hr. the solvent was evaporated under vacuum, the solid yield crystallized by methanol .Table 1 involved physical properties.

C. Synthesis of Thiazolidinones derivatives (3a-c)[11-13]:

Mercapto acetic acid (0.002 mole) in absolute ethanol (10 ml) was added slowly to (0.001mole) of Schiff bases (2a-c). refluxed the mixture for 5hrs. then treated with potassium bicarbonate to produce compound. The product filtered and recrystallized by ethanol. Table 2 involved physical properties.

D. Synthesis of Tetrazole derivatives(4a-c)[14]:

Reflux the mixture of compound (2a-c) (0.0004 mole) dissolved in (20 ml) tetrahydrofuran and (0.0006mole) Sodium azid for 16hrs. The product filtered and recrystallized by absolute ethanol. Table 3 involved physical properties.

III. RESULTS AND DISCUSSION

The new Schiff's bases were synthesized from the reaction of [1-amino-4-Sub.-6-phenyl pyrimidine-2-(1H)-thione with different aromatic aldehyde in absolute ethanol and in the catalytic amount of glacial acetic acid. The FT-IR spectra of Schiff's bases compounds (2a-e) showed the absence of peak of

carbonyl groups and the new peaks which appeared at 1580-1606 cm^{-1} which is attributed to the new azomethine (C = N)group as in[15]. Some spectral data are listed in table 4. Thiazolidinoes compounds (3a-c) were prepared from reaction of Schiff's bases (2a-c) with thioglycolic acid in absolute ethanol. FT-IR spectrum showed sharp peaks at (1724-1700) cm^{-1} due to (C=O) imide of thiazolidinoes as in[16]. Some spectral data are listed in table 4. Tetrazole compound (4a-c) were synthesized from the reaction of Schiff bases (2a-c) with sodium azide in THF. The FT-IR absorption peaks at (1580-1599) cm^{-1} show the absence of peak and this give good evidence for the success step of reaction. These absorption bands due to (C=N) imin group stretching frequency. Also FT-IR spectra of tetrazole showed clear absorption peaks at (1441-1499) cm^{-1} due to (N=N). beside this, the FT-IR spectra were evoide of peaks at (2077-2360) cm^{-1} attributed to stretching frequency of azide group [17,18] . Some spectral data are listed in table 4. The ^{1}H-NMR and ^{13}C-NMR spectrum showed the following bands. Compound(1):^{1}H-NMR($CDCl_3$, 400MHz): δ= 7.30 – 7.37(m,5H, Ar-H), 5.96 (s,1H, H-C=C), 3.45-3.40(dd, 2H, NH_2), 2.04 (s, 3H,CH_3). ^{13}C NMR ($CDCl_3$,400MHz): δ= 175.5(C=S),155.4 (C=N), 144.1, 128.7, 128.0, 124.0, 95.3(Ar-H), 55.2(C=C-H),16.1 (CH_3)[19].Compound(2a):^{1}H- NMR (acetone-d^6, 400MHz):δ= 8.61(s,1H,H-C=N),8.5-8.1 (m, 4H, Ar-H), 7.5-7.7(m, 5H, Ar-H), 6.4 (s, 1H,H-C=C). 2.8 (s,3H,CH_3).^{13}C-NMR (aceton -d^6 ,400MHz): δ= 180.2(C=S), 148.9(C=N),140.0,136.4,133.2,130.1,121.3(Ar-H), 28.4(CH_3) [15]. Compound(2c): ^{1}H-NMR(DMSO-d^6, 400MHz): δ= 8.4(s,1H, H-C=N), 8.2-8.1 (m, 4H, Ar-H), 7.4-7.3(m, 4H, Ar-H), 6.4 (s, 1H, H-C=C). 3.3(s,3H,CH_3).^{13}C-NMR (DMSO-d^6 ,400MHz): δ= 179.9 (C=S), 148.1 C=N), 142.1, 140.0, 129.8, 125.5, (phenyl ring), 39.5(CH_3) [15]. Compound(2d): ^{1}H NMR (DMSO-d^6, 400MHz): δ=11.7(s,2H, $2NH_2$), 8.7 (s, 1H, H-C=N),8.3-8.1(m, 4H, Ar-H), 7.6-7.8 (m, 5H,Ar- H),3.3 (s,3H,CH_3).^{13}C-NMR (DMSO -d^6 ,400MHz): δ= 179.7 (C=S), 148.9 (C=N), 140.0, 136.5, 134.1, 131.2, 123.0,121.0(phenyl ring) [15]. Compound(2e): ^{1}H NMR (DMSO-d^6, 400MHz): δ=8.9(s,1H, H-C=N), 8.7 (s, 1H, H-C=C), 8.3-8.0(m, 5H, Ar-H), 7.1-7.7 (m, 5H,Ar- H), 3.8 (s,3H,OCH_3).^{13}C-NMR (DMSO -d^6 ,400MHz): δ= 160.1 (C=S), 150.3 (C=N), 131, 130, 128, 124, 117,115(phenyl ring),59 (OCH_3,55(C=C-H) [15] Compound(3c): ^{1}H NMR ($CDCl_3$, 400MHz): δ= 8.20 – 8.26(m,4H, Ar-H), 7.52-7.87 (m, 5H, Ar-H), 6,98, (S, 1H, H-C-N), 5.77 (s, 1H, H-C=C), 4.40 (br,2H,CH_2),2.34(s, 3H, CH_3) [16].Compound(4a): ^{1}H NMR (DMSO-d^6, 400MHz): δ= 11.6 (s,1H, NH), 8.7 (s, 1H, C=C-H), 8.1-8.4 (m, 4H, Ar-H), 7.2- 7.7(m, 5H, Aar-H), 4.1(s, 1H, H-C-N).3.4(s,3H,CH_3) . ^{13}C-NMR (DMSO-d^6 ,400MHz): δ= 179.1 (C=S), 155(C=N), 149, 140, 135, 134,131,129,128,129,124,122, (phenyl ring), 95(C=C-H), 55 (H-C-N),16 (CH_3) [17],[18].

IV. REFERENCES

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Table I
Physical data for compounds (2a-e)

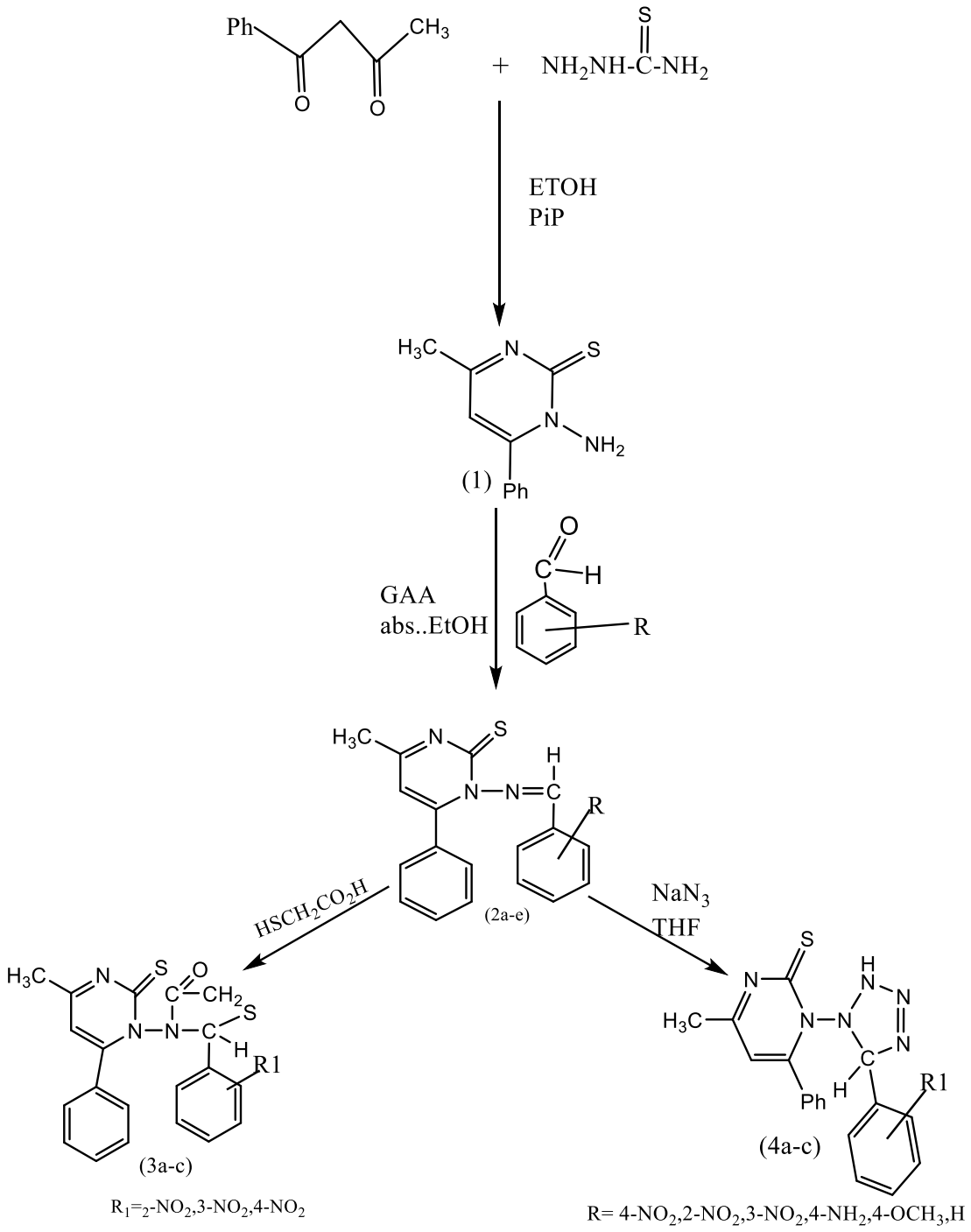
Comp. No	R	M.P.^{0}C	Yield %	Color	Cryst. Solvent
2a	2-NO_2	228-230	74	White	Methanol
2b	3-NO_2	189-190	75	White	Ethanol
2c	4-NO_2	238-240	83	Yellow	Acetone
2d	4-NH_2	99-100	63	Pale Yellow	Methanol
2e	4-OCH_3	148-150	51	Light Brown	Ethanol

Table II
Physical data for compounds (3a-c)

Comp. No	R	M.P.^{0}C	Yield %	Color	Cryst. Solvent
3a	2-NO_2	181-183	62	Green	Ethanol
3b	3-NO_2	186-188	61	White	Methanol
3c	4-NO_2	244-246	86	Yellow	Methanol

Table III
Physical data for compounds (4a-c)

Comp. No	R	M.P.^{0}C	Yield %	Color	Cryst. Solvent
4a	2-NO_2	200-202	51	Light Brown	Ethanol
4b	3-NO_2	228-230	53	Brown	Ethanol
4c	4-NO_2	250-252	75	Yellow	Ethanol



Scheme (1) illustrate the synthesized compounds

Table IV
Some spectral data for synthesized compounds

Comp. No.		V(cm $^{-1}$) IR					
	N-H Tetrazole	Ar C-H	R-CH	C=N Exo	C=S	N-N	Others
1a	…….	3198	2998	1598 Endo	1081	936	3267-3401(NH_2)
2a	…….	3145	2981	1596	1227	1062	NO_2(Asy/sym) 1521-1342
2b	…….	3141	2977	1599	1221	1064	NO_2(Asy/sym) 1542-1346
2c	…….	3089	2986	1580	1270	1085	NO_2(Asy/sym) 1513-1330
2d	…….	3076	2963	1606	1214	1103	(NH_2) 3215-3473
2e	…….	3113	2986	1585	1284	1084	(C-O-C) 1118-1224
3a	…….	3139	2975	…….	1216	1064	(C=O) imide 1700 (C-S-C) 810
3b	…….	3073	2965	…….	1198	1132	(C=O) imide 1703 (C-S-C)762
3c	…….	3024	2982	…….	1207	933	(C=O) imide 1704 (C-S-C)809
4a	3356	3159	2962	…….	1207	911	(N=N) 1447
4b	3423	3160	2966	…….	1211	935	(N=N) 1418
4c	3359	3088	2962	…….	1174	926	(N=N) 1448

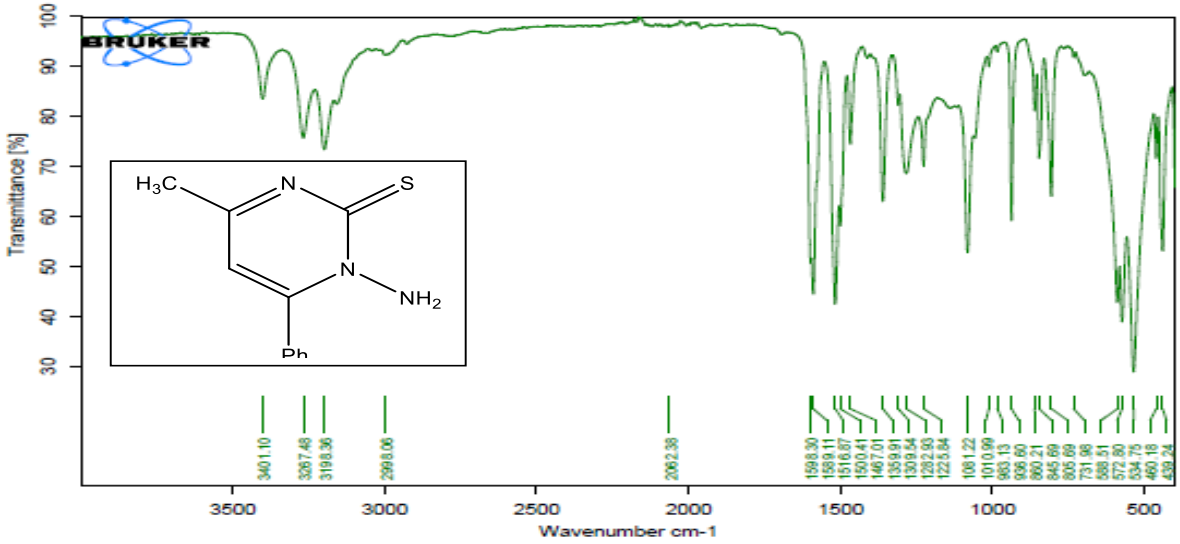


Fig.1. FT-IR for comp.(1a)

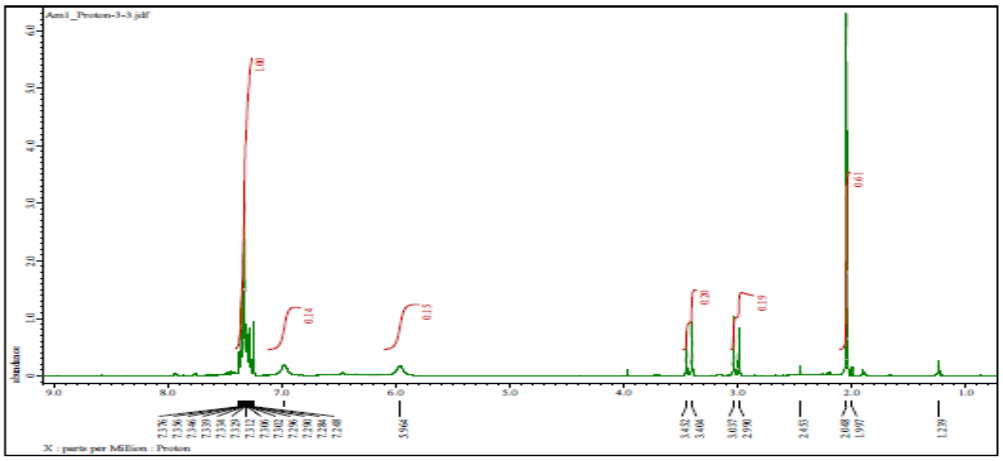


Fig. 2. ^{1}H-NMR for comp (1a)

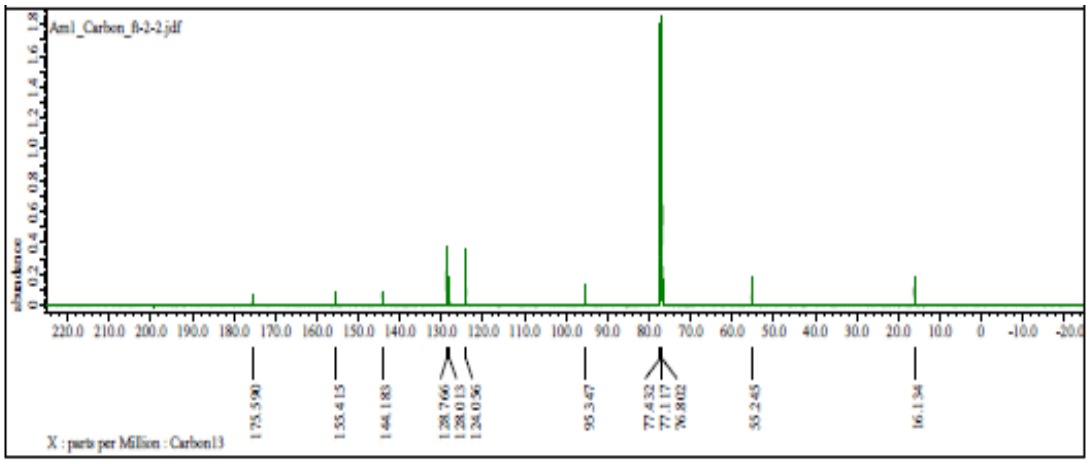


Fig.3. ^{13}C-NMR for comp.(1a)

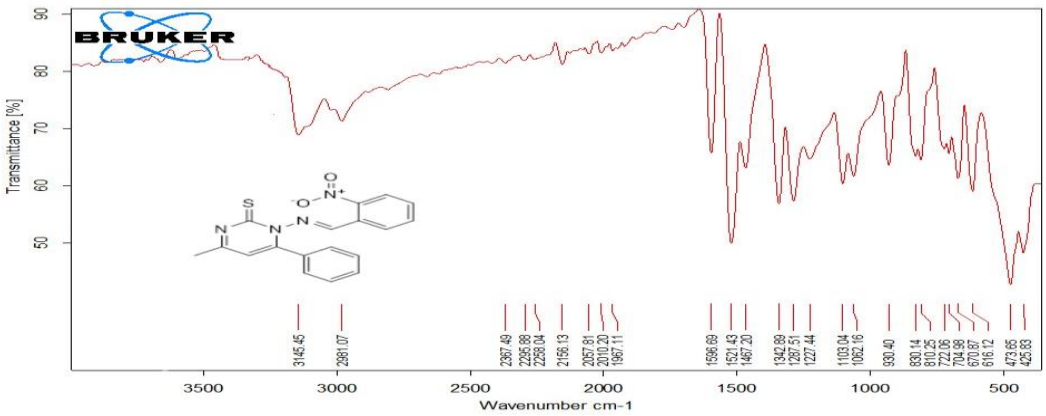


Fig.4. FT-IR for comp.(2a)

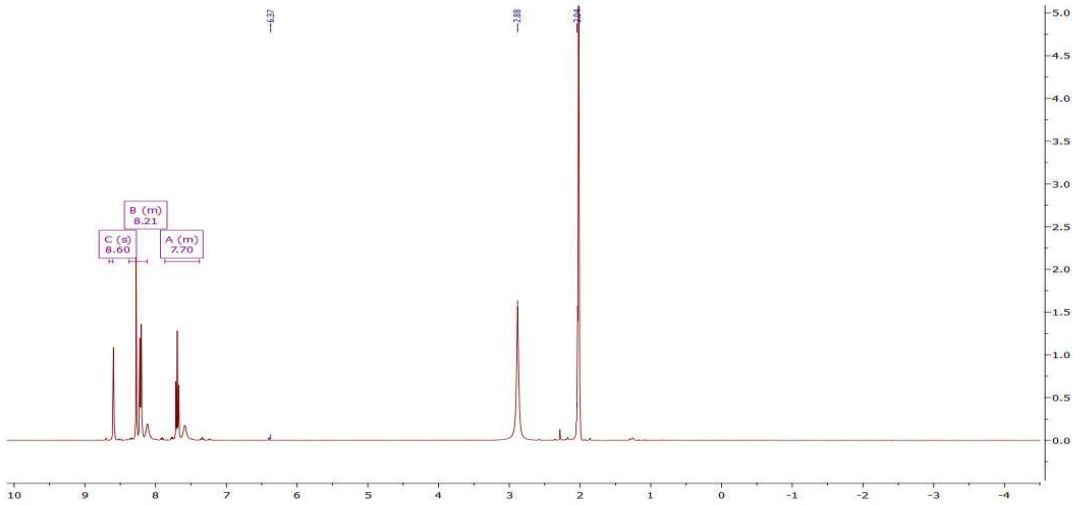


Fig.5. ^{1}H-NMR for comp (2a)

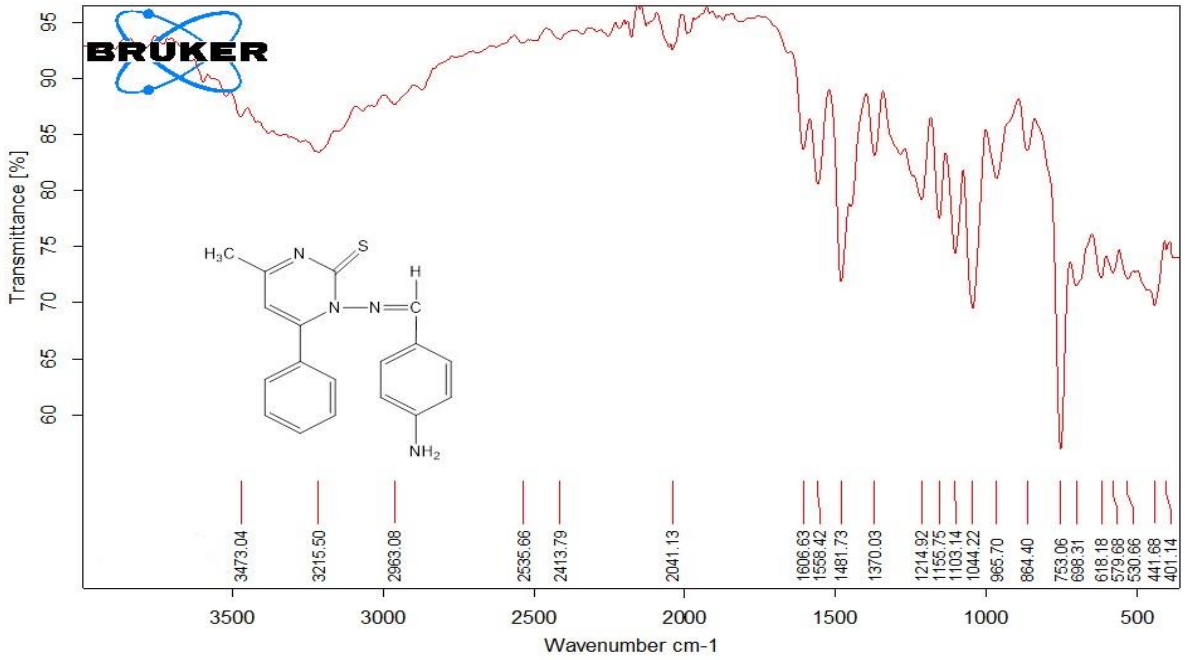


Fig.6. FT-IR for comp.(2d)

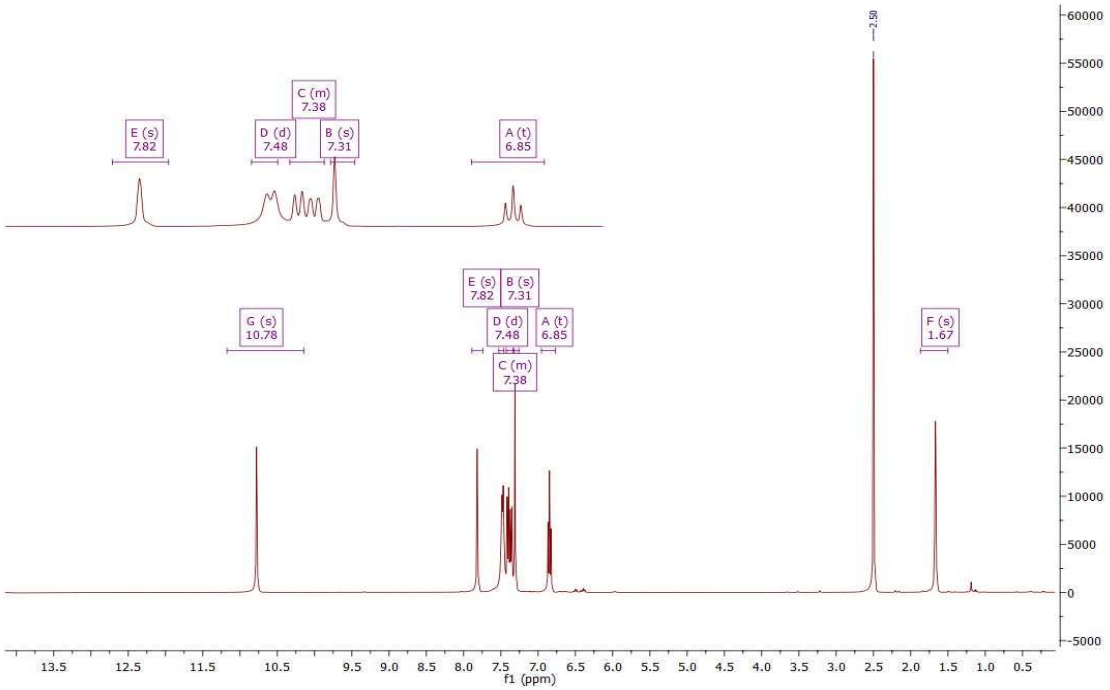


Fig.7. [1]H-NMR: for comp (2d)

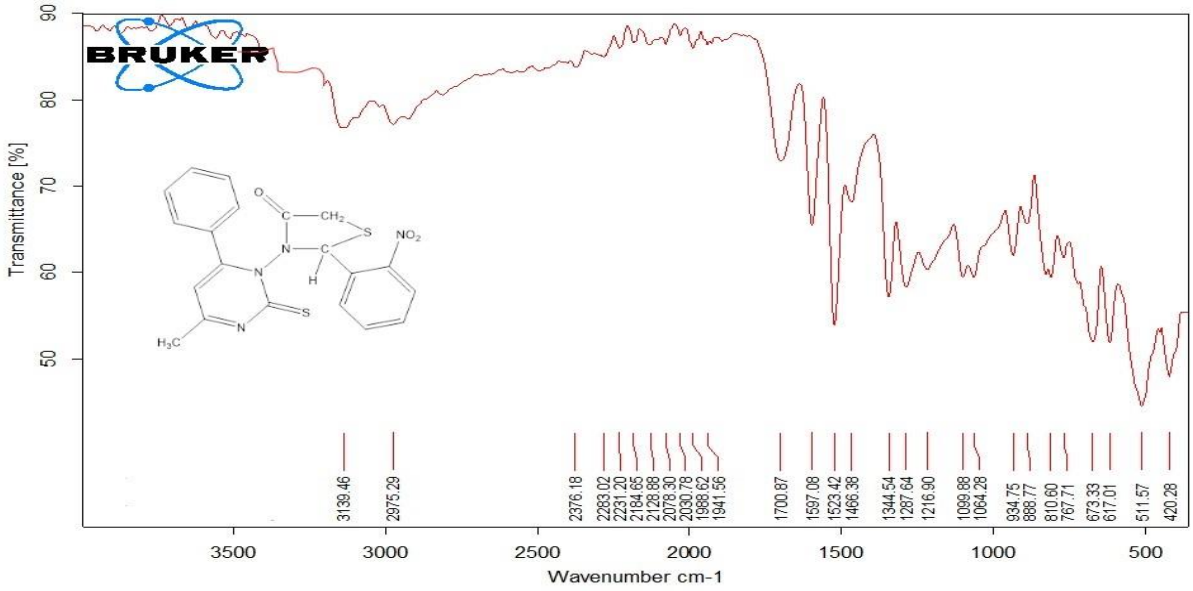


Fig.8. FT-IR for comp.(3a)

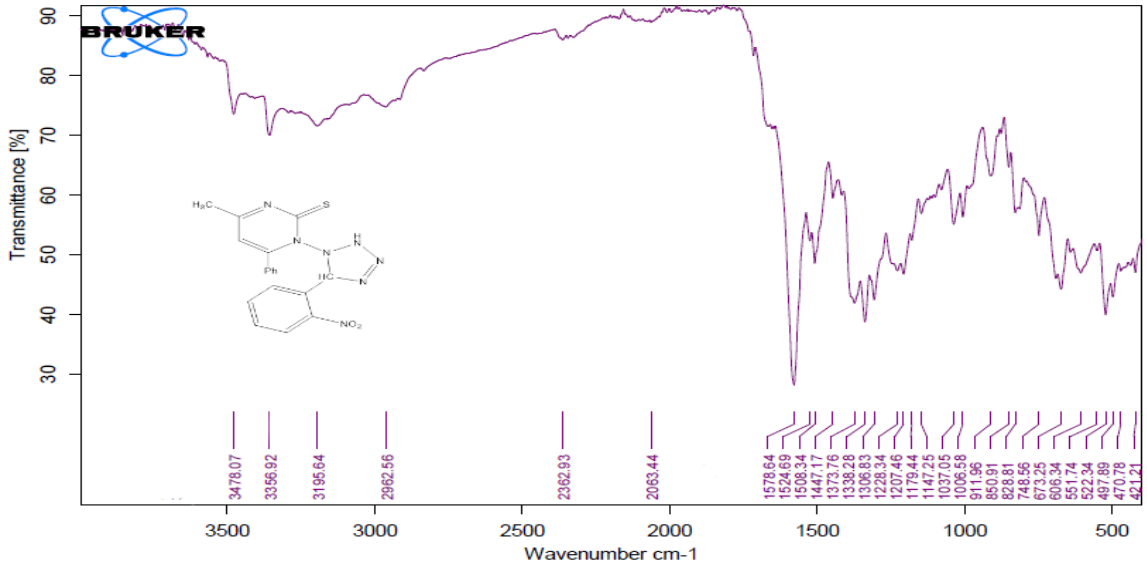


Fig.9. FT-IR for comp.(4a)

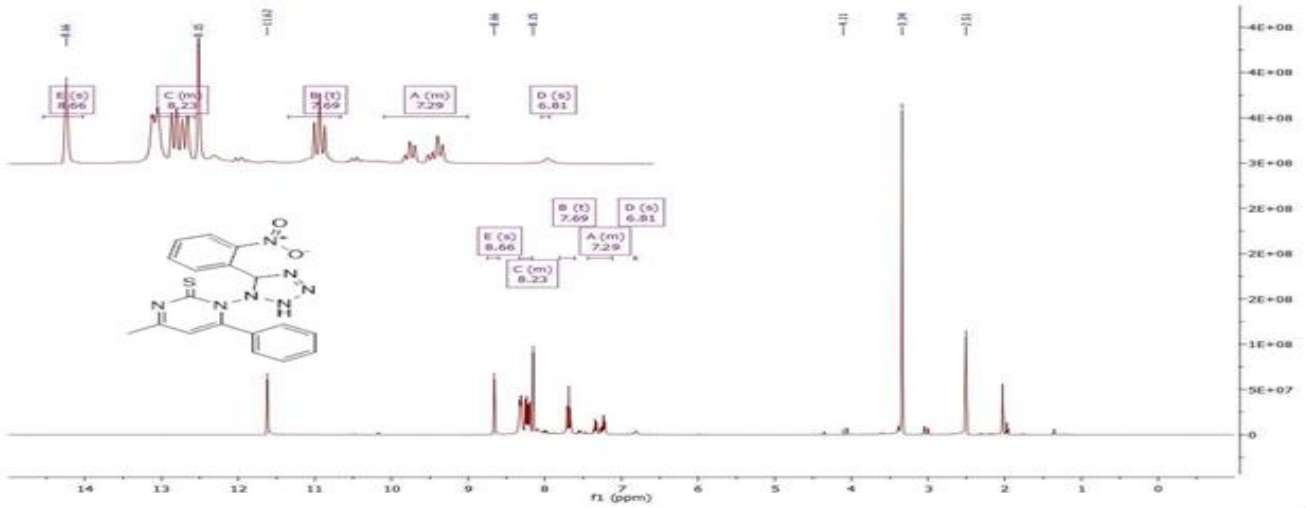


Fig.10. ^{1}H-NMR for comp (4a)