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Synthesis and Characterization of Fused Rings from Mannich Bases.
تحضير وتشخيص حلقات مندمجة من قواعد مانخ

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Abstract

In this work , four new compounds of mannich bases were synthesized through reaction of diketone compounds with ammonia or amine derivatives to give enamino ketone as intermediate , which reacts with aldehyde compounds to yield compounds [1-4] .

The structures of all synthesized compounds were characterized by (C.H.N)elementary analysis , ^{1}HNMR spectra and FT-IR spectra.The data obtained gave good support for synthesized compounds [1-4] .

Keyword :mannich base, ring fused ,intermediate.

الخلاصة

تضمن هذا البحث تحضير أربع مركبات جديدة من قواعد مانخ من خلال تفاعل مركبات ثنائية الكيتون مع الأمونيا أو مشتقات الأمين لتعطي مركب وسطي كيتون الأينامين و الذي بدوره يتفاعل مع مشتقات الألديهايد لتنتج المركبات [1-4]شخصت تراكيب المركبات المحضرة بإستخدام تقنية التحليل الكمي الدقيق للعناصر , طيف الرنين النووي المغناطيسي للبروتون و طيف الأشعه تحت الحمراء ,دلت النتائج المستحصلة على صحة تراكيب المركبات المحضرة [1-4].

Introduction

Mannich bases are class of compounds well known for a long time and still continue the object of considerable interest , mainly due to their pharmacological activities[(1-6)] , technological applications in polymer industry specially as paints and surface active reagents and other applications in different fields[(7-11)] .

In recent literature is enriched with progressive findings about the synthesis and biological significance of fused heterocyclic from mannich bases [1-4]which are reported to show biological properties such as antimicrobial ,anti tubercular , anti convuslant, herbicidal pesticidal, anti inflammatory and insecticidal properties[(12-16)] .The activating mathylene group of these intermediates (mannich bases) are react with aldehyde compounds to yield final products of compounds [1-4], this reaction is highly regiospesific and highly product[(17)].

Experimental

-All chemicals used were supplied from Fluka and Merck- chemical companies.
-All measurements were carried out by :
-Melting points :Electro thermal 9300 , melting point Engineering LTD ,U.K .
-FT-IR-spectra: fourrier transform infrared shimadzu (8300) , (FT.IR) , KBr-disc was performed by Qualtitative-Iraq .
-^{1}HNMR-Spectra and(C.H.N) Analysis :
in DMSO as solvent ,Erk, 3380 ,Germany ,carried out in center lab in Jordan.

Synthesis of1,4-dihydro-{4-(N,N-dimethylbenzene)-2,3,5,6-bis (dimethyl cyclohexanone)}-pyridine[1]

A mixture of 5,5–dimethy cyclohexyl–1,3–dione (0.01mole ,5.5 ml) was condensed with *p*-N,N-dimethylbenzaldehyde (0.01mole, 2.8 g) and ammonia (7ml), the precipitate was filtered and recrystallized from absolute ethanol to yield 79% of compound [1] .

Synthesis of 1,4,5,6-Tetra hydro –{5-(methyl phenyl sulphide)-2,8-dimethyl -4,6-di aceto azine[2]

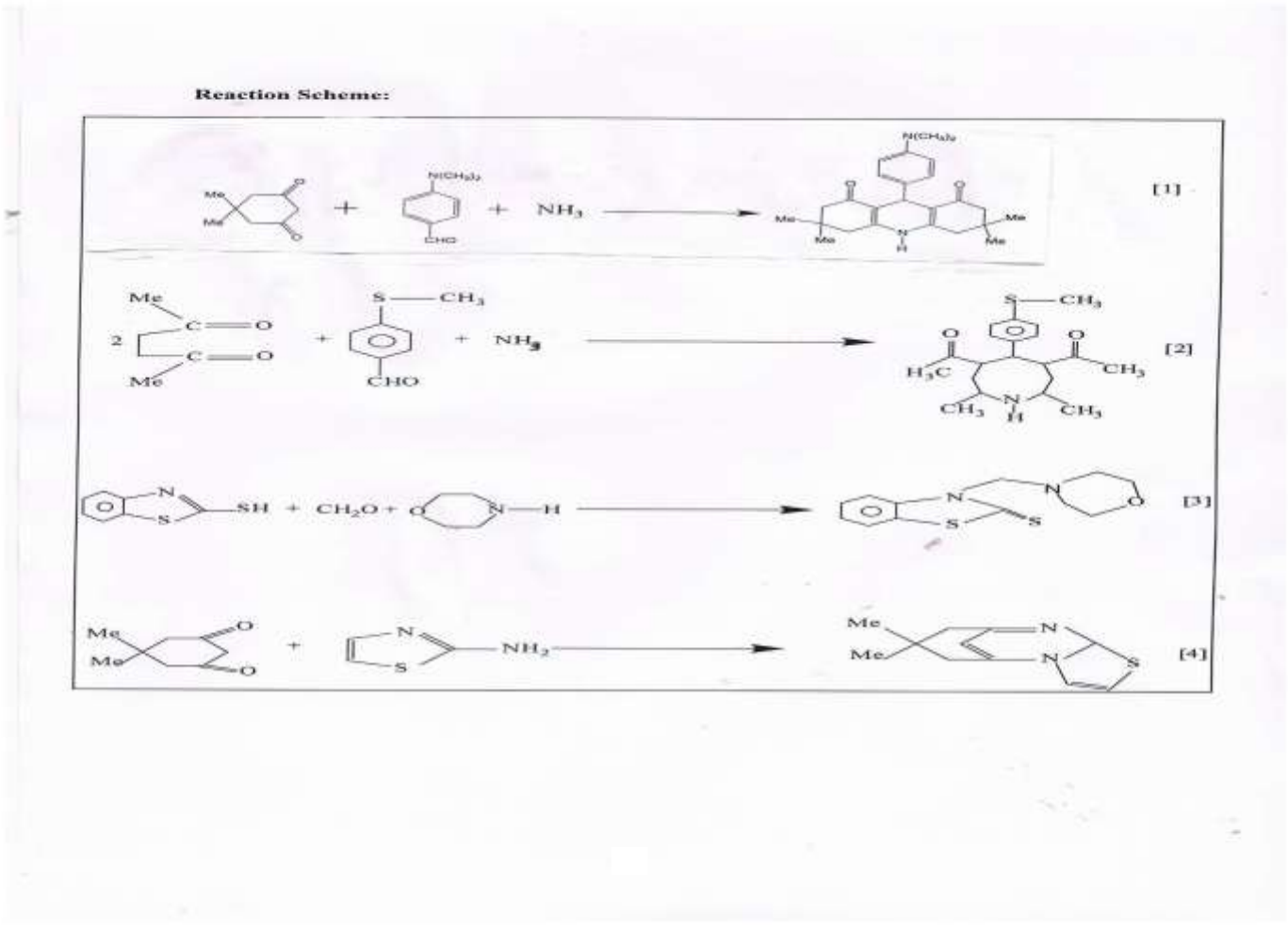
A solution of 2,5–hexane–dione (0.01mole, 5 ml) and *p*- thiomethyl benzaldehyde (0.01mole, 3.4 g) with ammonia (7 ml) was refluxed for (5h) , after cooling, the precipitate was filtered and recrystallized from absolute ethanol to yield 81% of compound [2] .

Synthesis of 3-methylene Morpolone -2-thione –benzothiazole [3]

A solution of 2-mercaptobenzothiazole (0.01mole, 3.4 g) with morpholene (0.01mole ,5 ml) and formaldehyde (0.01mole ,6ml) was refluxed for (4h) in absolute ethanol , the precipitate was filtered and recrystallized from absolute ethanol to yield 85% of compound [3].

Synthesis 1,2-(thiazolino)-4,6-(5,5-dimethyl cyclohexane)-2-hydropyrimidine[4]

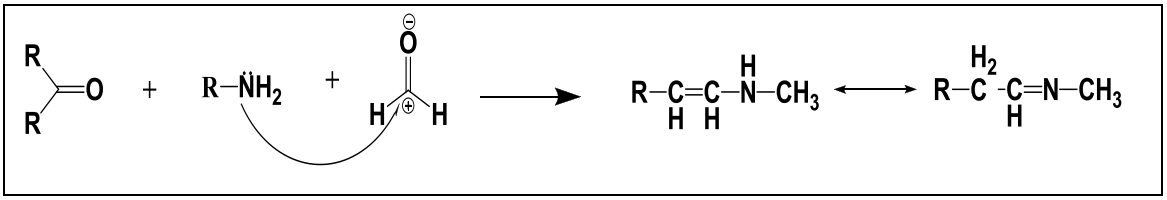
A mixture of 5,5 – dimethyl cyclohexyl -1,3-dione (0.01mole ,6.5ml) was reacted with 2-amino thiazole (0.01mole , 2.3 g) in absolute of ethanol , the precipitate was filtered and recrystallized from absolute ethanol to give 78%of compound[4].



Scheme (1): Reactions pathways

Results and discussion

The mechanism of synthesis of mannich compounds [1-4] proceed through reaction between amine compound and carbonyl of aldehyde compound with ketone, the general mechanism of this reaction was shown in scheme (2)



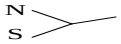
Scheme(2):Mannich reaction mechanism

All synthesized compounds [1-4] have been characterized by (C.H.N) analysis and the spectroscopic methods(FT-IR spectra and ^{1}HNMR spectra):

FT-IR Spectra

In FT-IR spectra ,the formation of mannich comppounds is followed by appearance of absorption band at (3440) cm^{-1} due to (N-H) endo cycle of pyridine , band at(1718) cm^{-1} due to carbonyl of keton (CO) , bands at (1538,1569)cm^{-1} is due to (C-N) endocycle and band at (1373) cm^{-1} is due to
(4-N$(CH_3)_2$) in compound[1] , while compound[2] is appeare absorption band at (3338)cm^{-1} is due to (N-H) endocycle of pyridine , band at (1735) cm^{-1} is due to carbonyl of ketone (CO) ,band at (1587)cm^{-1} is due to (C-N) endocycle[19] ,and band at (1411)cm^{-1} is due to (S-CH_3)group , where as compound [3] appears absorption band at (1537)cm^{-1} is due to (C-N) endo cycle[19] , band at (1230)cm^{-1} is due to (C-O-C) of morfholene cycle & band at (729)cm^{-1} is due to (C-S) endo cycle of thiazole[18] , while compound [4] is appear absorption band at (1577)cm^{-1} is due to (C=N) endocycle[19] of pyrimidine & band at (740)cm^{-1} is due to[18] (C-S) endo cycle of thiazole . And other data of functional groups show in the following , table (1) and figures(1-4) .]

^{1}HNMR Spectra

^{1}HNMR Spectrum of compounds in DMSO as solvent showed : singlet signal at (δ8.87 ,S ,1H) for proton of (N-H) group , signal at (δ 7.26 , for proton of pyridine cycle & signal at (δ 3.99 ,S ,6H) for six proton of dimethyl group (N$(CH_3)_2$) in compounds [1] .
Singlet signal at (δ4.63 ,S, 3H) for protons of methy group[19] (S-CH_3) , doublet Signal at (δ 7.78 ,d ,2H-2H) for 1,4-disubstitute of phenyl (-ph-S-)[18] , and signal at (δ8.69 ,S ,1H) for proton of (N-H) in compound [2] .
Signal at (δ 4.84 ,t ,2H) for protons of (` O-CH_2-CH_2-N) of morpholene cycle and signal at (δ 4.28 ,S ,2H) for protons of methylene group of (N-CH_2-N)[18,19] in compound [3] .
Signal at δ 6.3 for proton of pyrimidine cycle C_4-H and signal at (δ7.82 ,d ,1H) for proton of thiazole () in compound [4] , and other peaks shown in the following , figures (5-8) .

(C.H.N)–Analysis

(C.H.N) analysis , from comparison the calculated data with found data of these compounds , the results were comparable , the data of analysis , M.F and melting points are listed in table (2) .Appearance of (^{1}HNMR , FT-IR , C.H.N) spectra results are strong evidences to synthesized compounds [1-4]

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Table (1) : FT.IR data (cm^{-1}) of compounds [1-4]

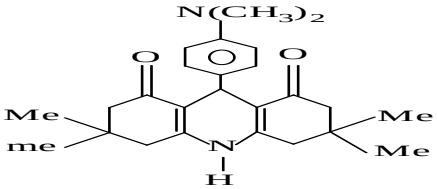
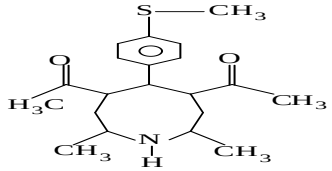
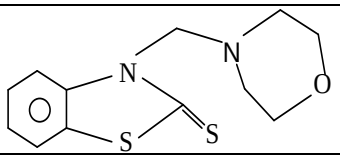
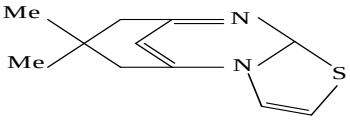
Comp. No.	Structural formula	Name of compounds	Functional groups (Importance groups)
[1]		1,4-dihydro-{4-(N,N-dimethyl phenyl)-2,3,5,6-bis(dimethyl cyclohexanone)}-pyridine.	υ (N-H):3440 m , (-CO-) of ketone : 1718S ,(C-N)endocycle of pyridine :1538,1569S ,4-N(Me)$_2$:Aromatic :1373
[2]		1,4,5,6-Tetra hydro –{5-(methyl phenyl sulphide)-2,8-dimethyl-4,6-di aceto azine .	υ(N-H):3338M , (-CO-)of ketone :1735S, (S-CH_3): 1411S, (C-N)endocycle:1537
[3]		3-methylene Morpolone -2-thione –benzothiazole .	(C-N)endo cycle:1537 (C-S)endocycle of thiazole: 729 ,(C-O-C) of morpholene :1230
[4]		1,2-(thiazolino)-4,6-(5,5-dimethyl cyclo hexane)-2-hydropyrimidine	(C=N) endocycle of pyrimidine : 1577 S, (C-S)endocycle of thiazole : 740 S

Table (2) :melting points ,M.F & Elemental Analysis of compounds [1-4]

Comp. No.	M.F	M.P (°C)	Calc. / Found. C%	H%	N%
[1]	$C_{25}H_{32}N_2O_2$	178	76.530 76.428	8.163 8.113	7.142 7.029
[2]	$C_{20}H_{25}NO_2S$	171	69.970 69.804	7.288 7.113	4.081 4.006
[3]	$C_{12}H_{14}N_2OS_2$	165	54.135 54.037	5.263 5.123	10.526 10.417
[4]	$C_{11}H_{14}N_2S$	157	64.077 63.968	6.796 6.637	13.592 13.387

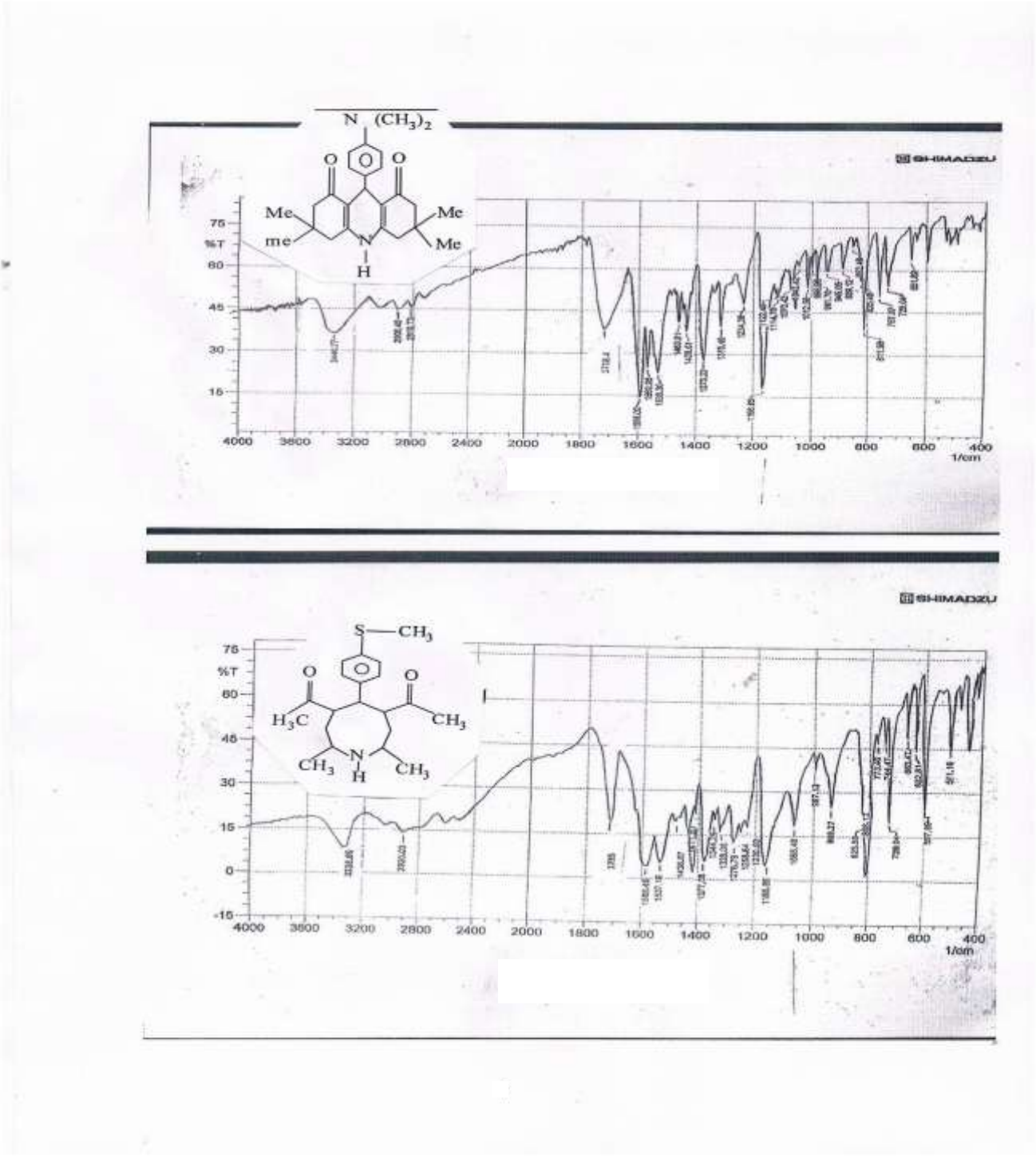


Fig (1):FT.IR spectrum of compound[1,2]

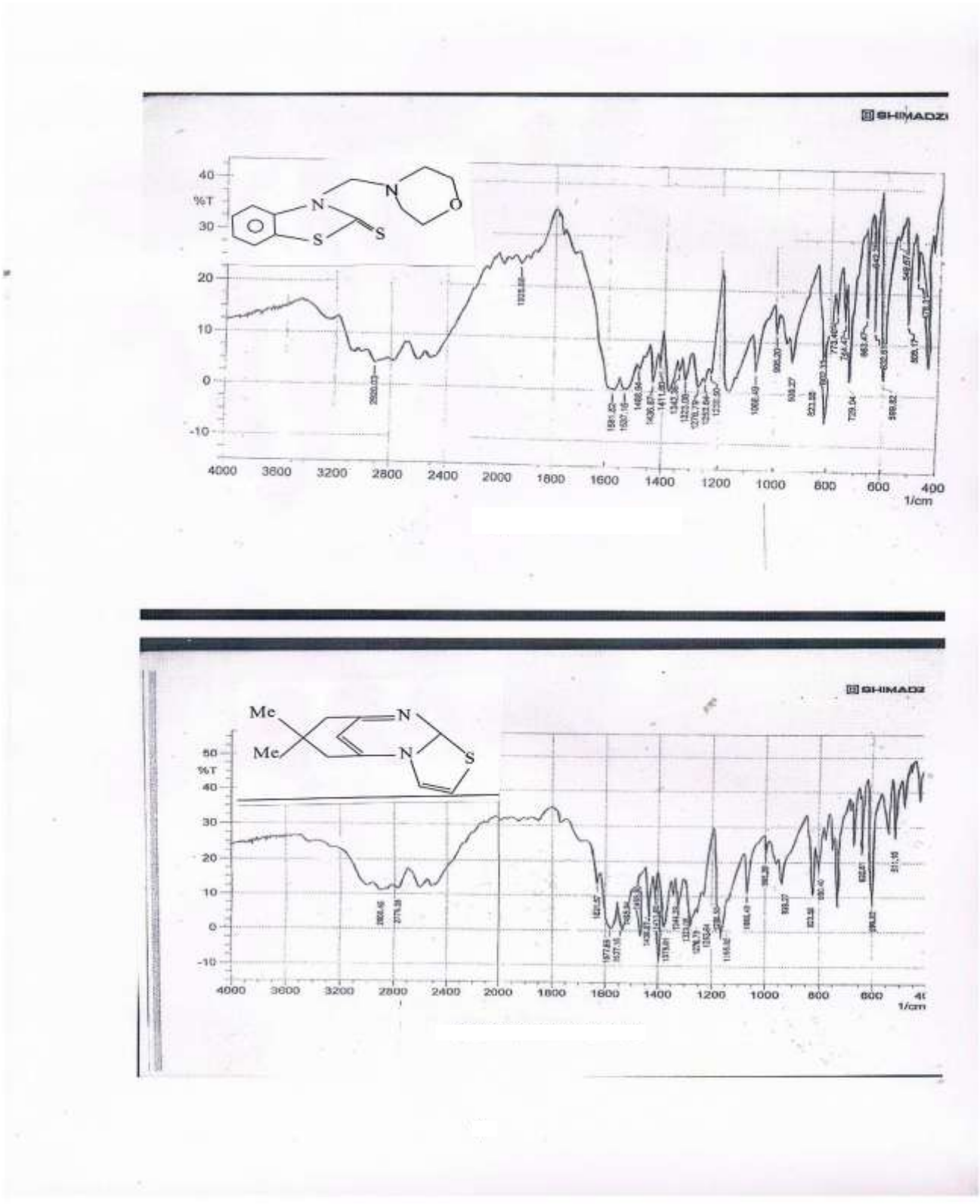


Fig (2):FT.IR spectrum of compound[3 ,4]

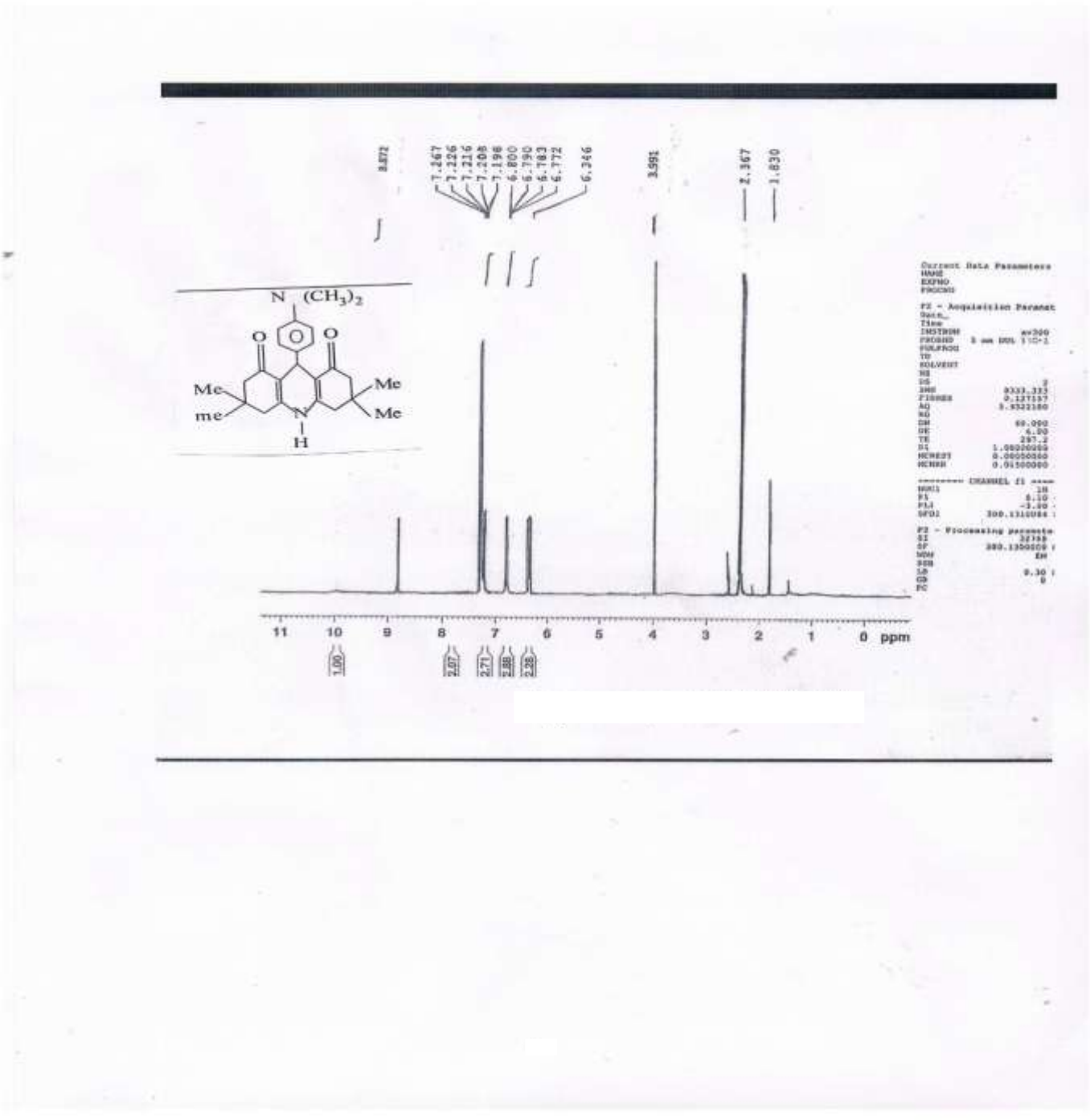


Fig (3):[1]HNMR spectrum of compound[1]

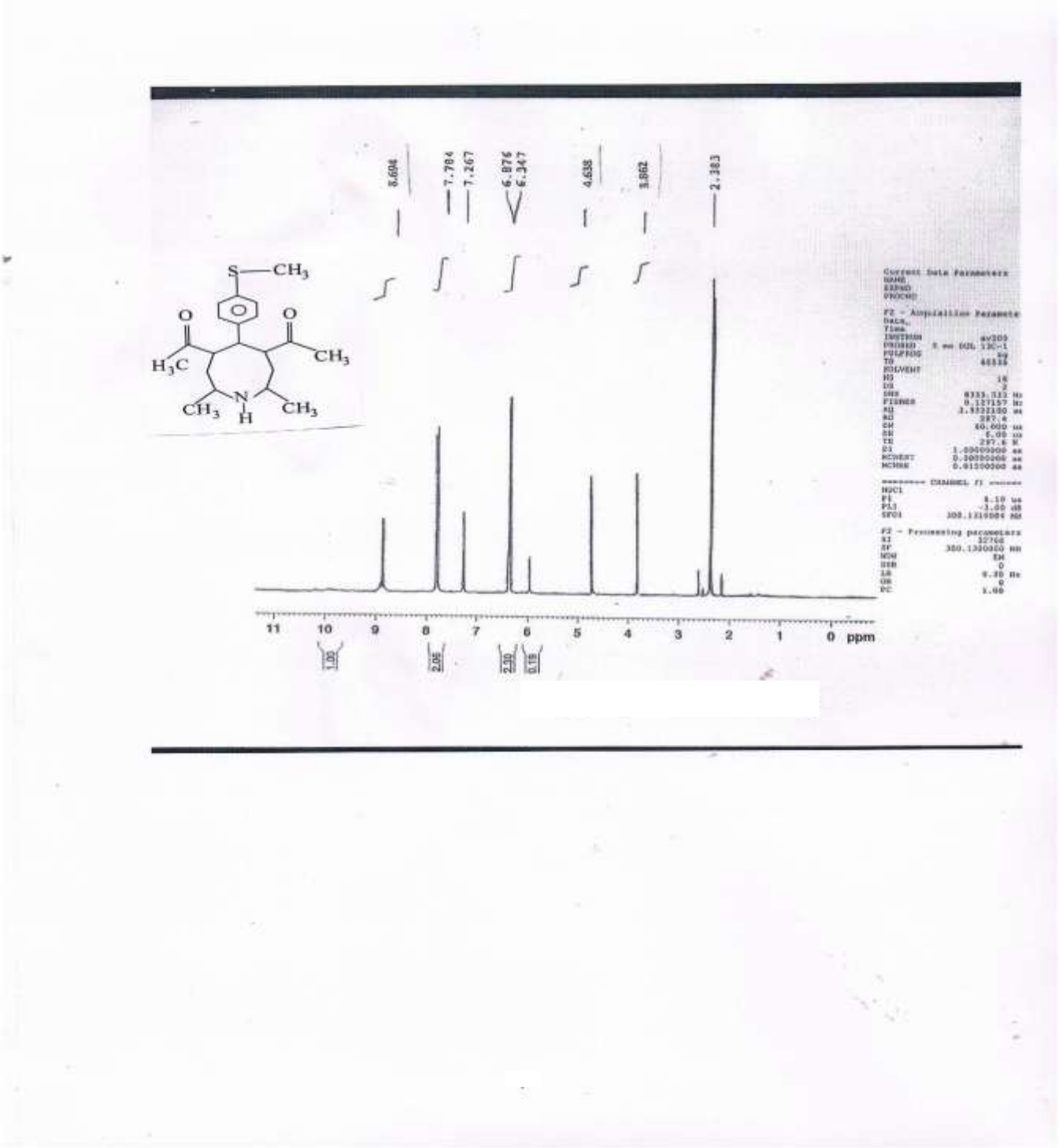


Fig (4):[1]HNMR spectrum of compound[2]

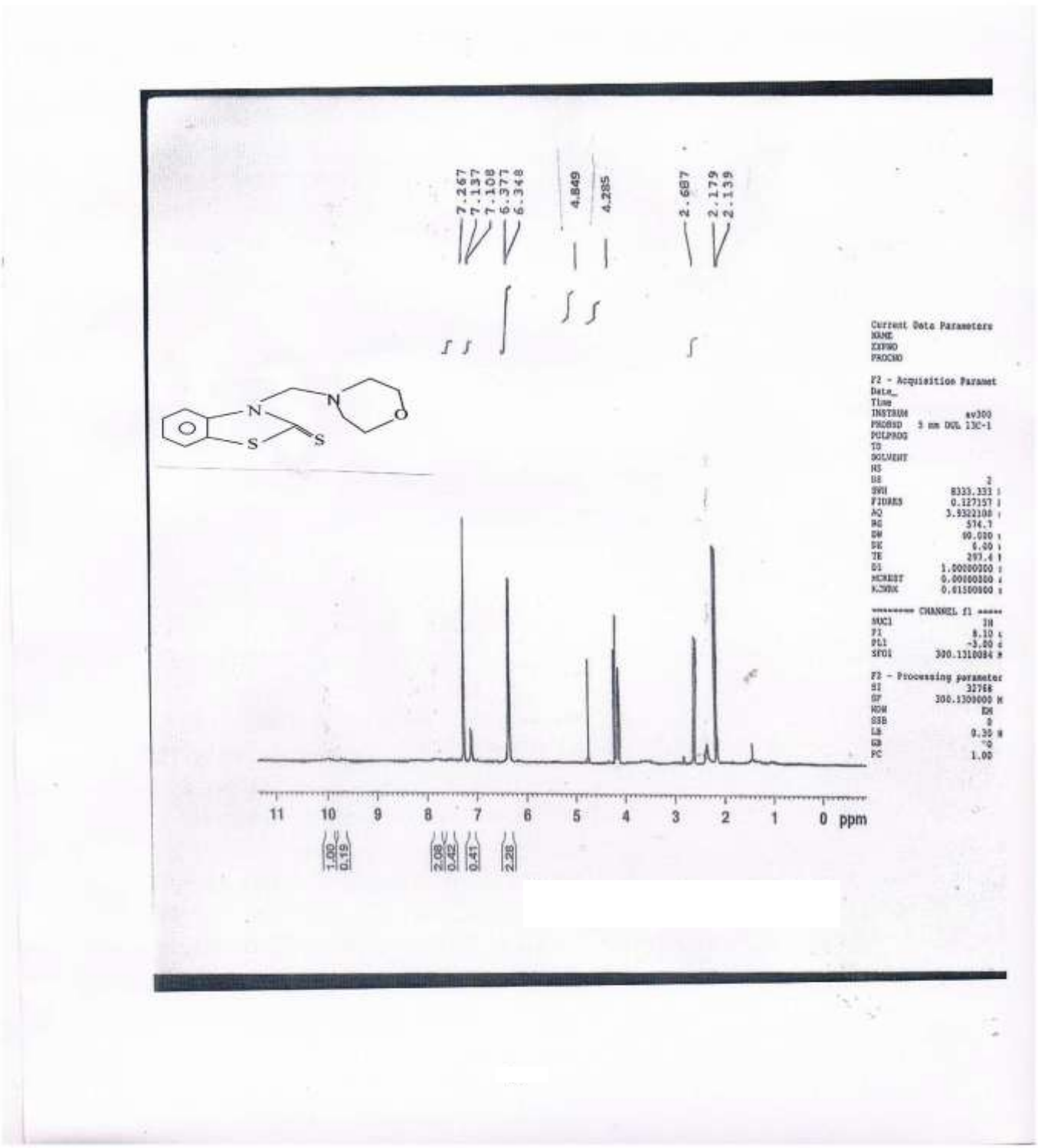


Fig (5):[1]HNMR spectrum of compound[3]

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