UNIVERSITY OF ILLINOIS

May 2 1940

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

JAMES WALTER JANICKA

ENTITLED SYNTHESIS OF 5-HYDROXY-2-METHYLTHIO-

PYRIMIDINE FOR A POTENTIAL [3+2] CYCLOADDITION

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF B.S. BIOCHEMISTRY

Instructor in Charge

APPROVED:

HEAD OF DEPARTMENT OF Chemistry

O-1364

Synthesis of 5-Hydroxy-2-methylthiopyrimidine

for a Potential

[3+2] Cycloaddition

by

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Thesis

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in

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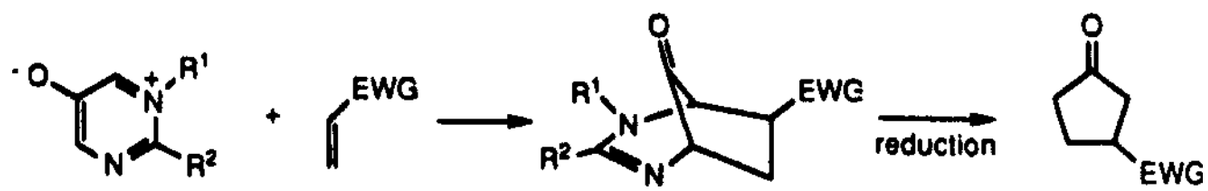
Introduction

Although many advances have been made in synthetic organic chemistry recently, good synthetic methods for forming five-membered carbocyclic rings are still needed. An ideal reaction for this synthesis would be a [3+2] cycloaddition reaction. There has been considerable work done in this area employing 1,3 dipoles which contain the heteroatoms nitrogen, oxygen, and sulfur but these approaches do not form substituted cyclopentane rings.[1] The work described in this thesis is based on a possible use of 5-hydroxypyrimidines or their quaternary salts to produce three carbon analogs for [3+2] cycloaddition reactions. The proposed reaction is shown in Scheme 1.

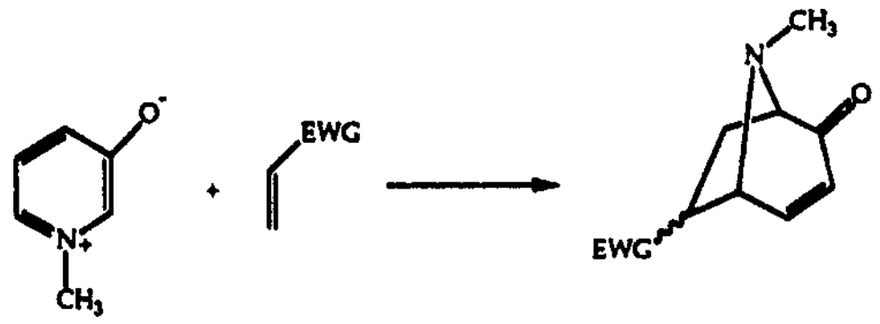
Scheme 1



R^1, R^2=H, alkyl, etc.

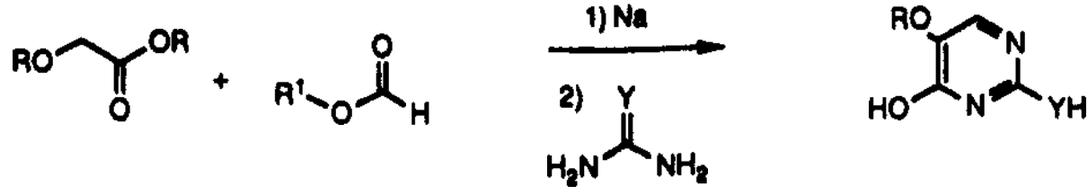
Formation of the (2.3.1) bicyclic system followed by reductive elimination of the nitrogens could provide a potential route to substituted cyclopentanone rings.

The literature provides no reference to the cycloaddition reactions of 5-hydroxypyrimidines or their corresponding quaternary salts. The reactions of 3-hydroxypyridine salts provide a model for the proposed reaction.[1] A typical reaction is:



There are only a handful of references for the synthesis of 5-hydroxypyrimidines. Most of the work in this area of pyrimidine synthesis was performed by J.F.W. McOmie and Z. Budesinsky. Three papers reporting the synthesis of 2,5-dihydroxypyrimidine and some of its derivatives give similar synthetic routes.[2,3,4] The synthetic schemes always begin with a reaction of benzyl benzyloxyacetate (or methyl methoxyacetate), sodium, and ethyl formate (or methyl formate) to form an intermediate that undergoes a nucleophilic ring closing reaction with urea (or thiourea) to form the pyrimidine ring as shown in Scheme 2.

Scheme 2

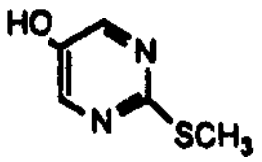


R=CH_3 or benzyl, R^1=CH_3 or CH_3CH_2

Y=S or O

Further transformation of the pyrimidine functional groups result in the desired 2,5-dihydroxypyrimidine or 5-hydroxypyrimidine.

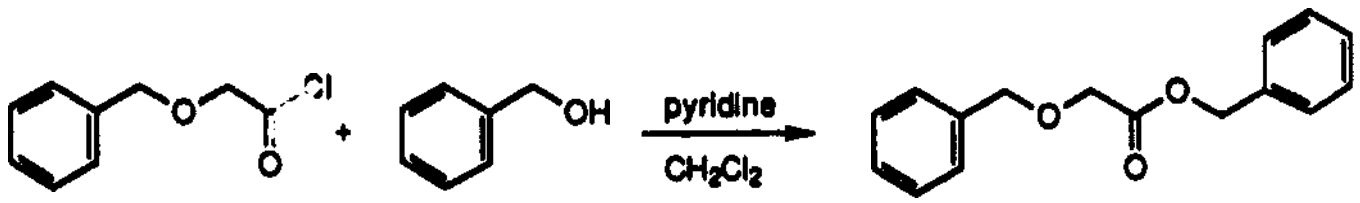
The most easily prepared pyrimidine which could be utilized to test the proposed cycloaddition is 5-hydroxy-2-methylthiopyrimidine (1). Although seemingly straightforward, the synthesis proved to be difficult and many changes had to be made to ensure that the reactions in this multistep synthesis proceeded with good yields and adequate purity.



1

The six step synthetic procedure of McOmie was used as the basis for the synthesis of 1, the desired pyrimidine.[2,3] This first step of this synthetic scheme was replaced with a modern and much more effficient displacement as shown in Scheme 3. By reacting benzyloxyacetyl chloride with benzyl alcohol, the desired benzyl benzyloxyacetate (2), was synthesized in 87% yield.

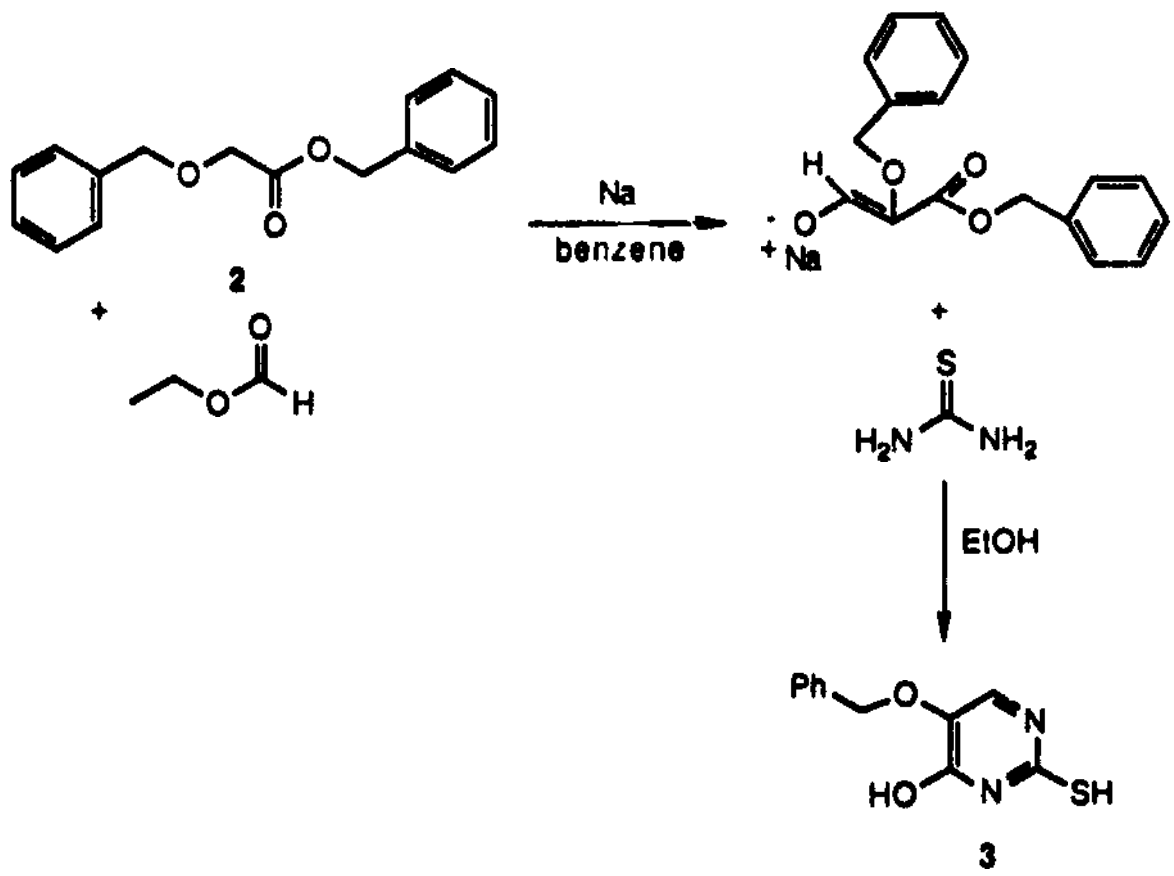
Scheme 3



2

The second step proved to be much more difficult. This step is actually a combination of two different substeps. The first part, consists of deprotonation of the carbon alpha to the carbonyl followed by trapping with ethyl formate as shown in Scheme 4. The reaction provides a viscous solid that is only obtained after removal of the benzene. The solvent for this reaction was changed from toluene to benzene in order to obtain a cleaner reaction mixture. The reaction intermediate undergoes a nucleophilic addition with thiourea followed by an intramolecular nucleophilic ring closing to form 5-benzyloxy-4-hydroxy-2-mercaptopyrimidine (3). The product 3 was obtained in a dissapointing 40-50% crude yield. The isolation of 3 was complicated by its moderate solubility in water.

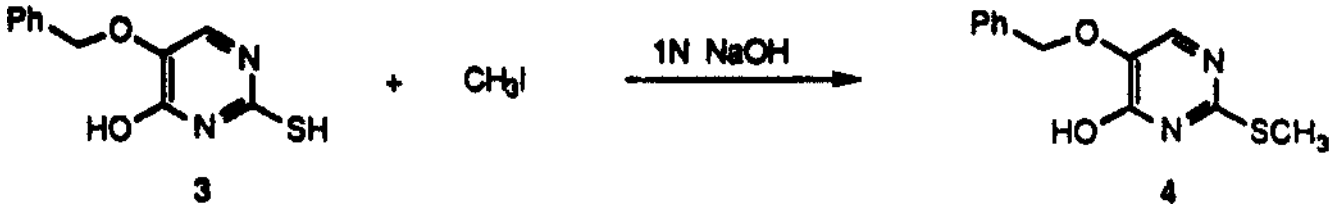
Scheme 4



Another problem encountered in this step was the lack of a good recrystallization solvent. Water could be used to recrystallize a portion of 3 but a large amount of product was unrecovered from the solvent. Since no adequate recrystallization solvents could be found, 3 was taken on to the next step in crude form.

The third step in the synthesis, alkylation of the mercapto group as shown in scheme 5 to give 5-benzyloxy-4-hydroxy-2-methylthiopyrimidine (4), is a very straightforward reaction. Neutralization of the reaction mixture during workup increased the yield of 4, although the true yield was difficult to determine since crude 3 was used as the starting material. Recrystallization in ethanol gave the first *pure* pyrimidine of the synthesis to this point in yields of around 50%.

Scheme 5



3 4

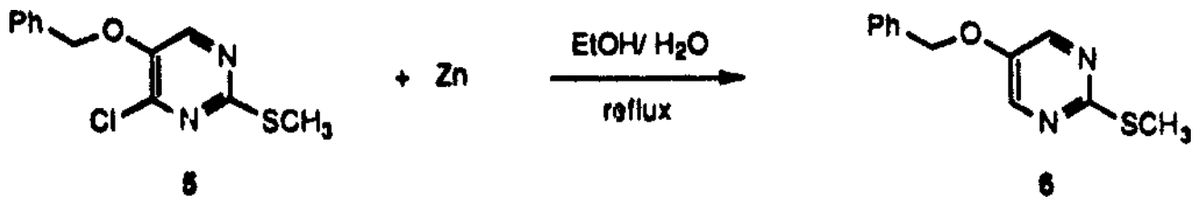
The chlorination reaction with phosphorous oxychloride, the next step as shown in Scheme 6, proved to be a very clean reaction. Replacement of the hydroxyl group of 4 by chlorine gave 5-benzyloxy-4-chloro-2-methylthiopyrimidine (5). Recrystallization in hexane produced extremely pure white needles in about 70% yield.

Scheme 6

4 5

The next step, removal of the chlorine from 5 as shown in Scheme 7 to give 5-benzyloxy-2-methylthiopyrimidine (6), was a difficult problem in the synthesis. This well known dehalogenation reaction with zinc in aqueous ethanol seemed to give excessive decomposition of the pyrimidine ring with prolonged heating.

Scheme 7

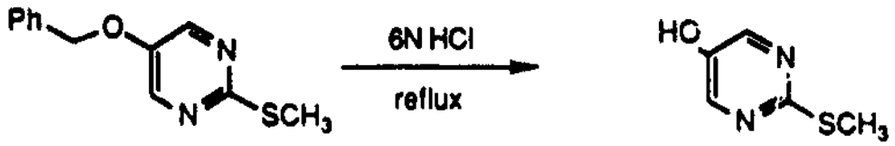


5 6

The yields quoted in the literature were much higher than the yields we observed.[2] The reaction conditions, primarily the time of reflux, was varied to achieve the highest possible yields. Our idea was to stop the reaction before 100% completion so that there is little decomposition of the product. The reaction was checked periodically by thin-layer chromatography with starting material and usually stopped at about 80% completion. Also to limit decomposition of 6, isolation was performed by normal extraction in ethyl ether rather than the continous extraction as stated in the literature.[2] Recrystallization in hexane gave pure 6 in 40-45% yield.

The last step in the synthesis involved deprotecting the alcohol, a step which proved to be the most difficult of the sequence. The most obvious reaction for deprotecting 6 was hydrogenation over a palladium catalyst. This traditional reaction for the removal of benzyl groups usually gives yields better than 90%. Unfortunately the methylthio group on 6 poisons the Pd-C catalyst even with employing one equivalent of catalyst, and the reaction yields only starting material. It has been shown that ethereal boron trifluoride and mercaptoethane can remove aromatic benzyl protecting groups, but unfortunately the reaction of 6 with these reagents gave only starting material and none of the desired 5-hydroxy-2-methylthiopyrimidine (1).[5]

Scheme 8



6 1

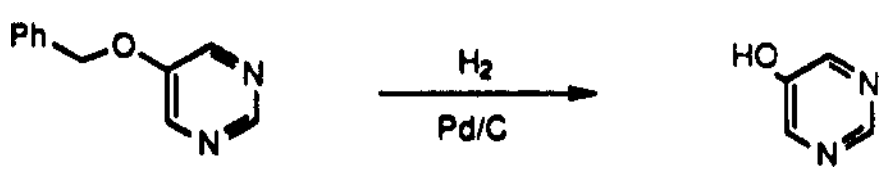
Since mild conditions were unsuccesful in removing the benzyl group, the harsh conditions used in the McOmie synthesis of Scheme 8 had to be utilized, although some changes were made.[2] Heating of 6 at reflux for five hours in 6N hydrochloric acid decomposed about 90-95% of the of the pyrimidine. By changing the reflux time to thirty minutes, 1 was obtained in much higher yields. Another change in the procedure was to isolate the product by normal extraction in ethyl ether rather than continous extraction. This avoids heating the pyrimidine unneccesarily. A recrystallization of 1 using benzene as quoted by McOmie was not succesful.[2] When the solvent was changed to a 40% ethyl acetate/hexane mixture, pale yellow crystals of 1 were obtained in about 50% yield.

Conclusions

Although many obstacles were encountered with the original synthetic scheme, the desired product 5-hydroxy-2-methylthiopyrimidine (1), was obtained in sufficient quantity for future use in the continuation of this research project.

One way to avoid the decomposition of the last steps of the synthesis would be to eliminate the methylation reaction of the third step and subject 3 to the chlorination. Conceivably both the hydroxyl and mercapto functionalities could be removed with $POCl_3$ to give 5-benzyloxypyrimidine (7) and deprotection could be achieved by hydrogenation as shown in Scheme 9, resulting in the formation of 5-hydroxypyrimidine (8). This could also be used as a possible 3-carbon analog in our proposed cycloaddition.

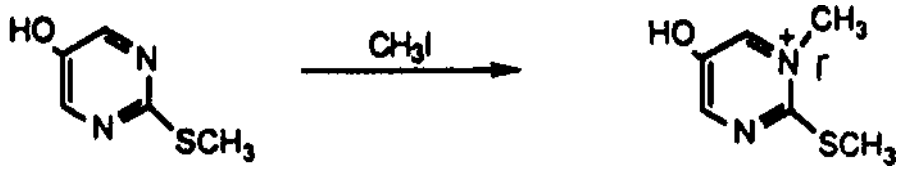
Scheme 9



7 **8**

After synthesizing 1, the next step is to form a quaternary salt which may be used as the three carbon analog in the proposed [3+2] cycloaddition. Quaternary salts have been synthesized using methyl iodide.[6] This last step was not accomplished due to the lack of time available.

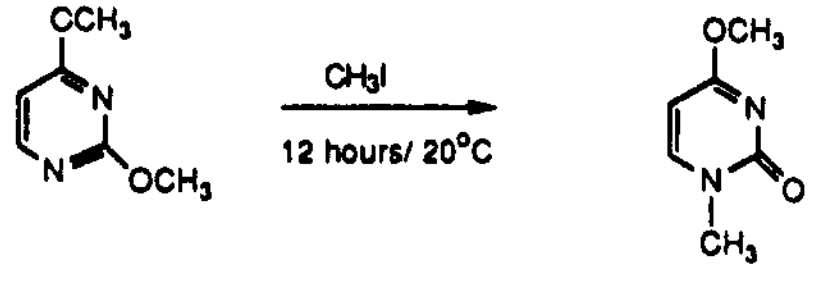
Scheme 10



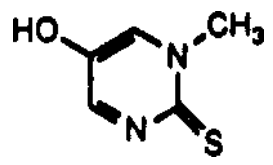
1 9

A possible synthesis for the formation of a quaternary salt 9 from 1 is shown in Scheme 10. It has been shown that a similar pyrimidine, as shown in Scheme 11, undergoes quaternary salt formation followed by decomposition of the salt, resulting in the non-aromatic pyrimidone tautomer.[7]

Scheme 11



If 9 undergoes this decomposition, it would result in an ideal 3-carbon analog for our proposed [3+2] cycloaddition, 5-hydroxy-1-methyl-2-thiopyrimidone (10).



10

General: ^1H NMR spectra were taken on a Varian XL-200 spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard unless otherwise noted. Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS unless otherwise noted. ^{13}C NMR spectra were taken on a General Electric QE-300 FT spectrometer and were proton decoupled in the indicated solvent. Melting points were taken on a Thomas Hoover melting point apparatus and are uncorrected. Gas chromatography/mass spectrometry (GC/MS) analyses were performed on a Hewlett Packard (HP) 5890 gas chromatograph coupled to an HP 5970B mass detector. Flash chromatography was performed with Merck silica gel (0.05 to 0.20mm). Microanalyses were performed by the University of Illinois Microanalytical Service Laboratory.

Materials: Diethyl ether (Et_2O) was distilled from sodium benzophenone. Ethyl Acetate (EtOAc) was distilled from potassium carbonate and hexane from molecular sieves. Methylene chloride (CH_2Cl_2) was distilled from calcium hydride. All other reagents used were obtained from commercial sources.

Benzyl Benzyloxyacetate (2): To 125ml of CH_2Cl_2 was added benzyloxyacetyl chloride (21.4ml, 25g, 135mmol) and pyridine (12ml). Benzyl alcohol (13.9ml, 14.5g, 135mmol) dissolved in 25ml of CH_2Cl_2 was added dropwise to the stirred solution at 0°C over a period of 10 minutes. The mixture was allowed to stir for an additional 15 minutes at 0°C and then for another two hours at room temperature. Workup consisted of concentration *in vacuo* and dilution in 150ml of Et_2O. Subsequent extraction of the ether layer with deionized water (3 x 25ml), 10% NaOH (2 x 25ml), 5% HCl (25ml), and brine (saturated NaCl)(2 x 25ml). The ether layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification was achieved by flash chromatography with 20% EtOAc/Hexane as the eluting solvent to give 30.2g of 2 as an oil, in 87% yield. 1H NMR ($CDCl_3$, 200MHz) δ 4.18 (s, 2H) 4.67 (s,2H) 5.24 (s,2H) 7.40 (s,10H). GC/MS (70eV, EI) m/z *relative intensity* 165 (56), 107 (38), 91 (100), 65(16).

5-benzyloxy-4-hydroxy-2-mercaptopyrimidine (3): To 100ml of benzene was added Na (2.7g, 117mmol). A mixture of 2 (30.2g, 117mmol) and ethyl formate (8.7g, 117mmol) in 25ml of

benzene was added dropwise to the stirred mixture over a period of 10 minutes. The mixture is allowed to stir for an additional 24 hours. Benzene was removed *in vacuo* and the resulting viscous solid was dissolved in 125ml of EtOH. To the stirred reaction flask was added thiourea (9g, 117mmol). The mixture was allowed to stir for one hour at room temperature and then was refluxed for five hours. Workup consisted of concentration *in vacuo*, dissolution in 100ml dionized H_2O, and neutralization to a pH around 6-7 with 6N HCl. The precipitated solid was collected by filtration and dried in the air to give15.6g of 3 in 50% yield. A part of the solid was recrystallized in H_2O yielding yellow crystals, mp 228-230°C *dec.* (lit.[3], 230-232° *dec.*). ^1H NMR (DMSO-d6, 200MHz) δ 3.42 (b, 1H) 4.90 (s,2H) 7.11 (s, 1H) 7.36 (s, 5H) 12.40 (b, 1H). ^{13}C NMR (DMSO-d6, 300 MHz) δ 71.08, 93.70, 123.2, 136.0, 138.6, 157.5, 171.6.

5-benzyloxy-4-hydroxy-2-methylthiopyrimidine (4): To 18.8g (75.8mmol) of 3 dissolved in 80 ml of 1N NaOH, CH_3I (10.0ml, 22.9g, 161 mmol) was added dropwise to a stirred solution over a period of 10 minutes. The reaction was allowed to proceed for another 10 minutes. Workup consisted of neutralization of the solution to a pH of 6-7 using 6N HCl. The precipitated solid was collected by filtration. Purification by recrystallization in EtOH yielded 15.3g of 4 as pale yellow needles in 77% yield, mp 180-182°C (lit.[2], 180-181°). ^1H NMR (DMSO-d6, 200MHz) δ 2.43 (s,3H) 3.33 (b,1H) 5.01 (s, 2H) 7.38 (s, 5H) 7.57 (s, 1H).

5-benzyloxy-4-chloro-2-methylthiopyrimidine (5): To 50ml of phosphorous oxychloride ($POCl_3$) was added dimethylaniline (15ml) and 4 (3.4g, 13.7mmol). The reaction mixture was stirred and refluxed for 1.5 hours. The flask was cooled to 0°C and then *cautiously* poured onto 250ml of ice. After cooling, the mixture was extracted with Et_2O (3 x 50ml). The ether layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification consisted of recrystallization in hexane yielding 2.2g of 5 as white needles in 60% yield, mp 80-82°C (lit.[2] 80-81°). ^1H NMR ($CDCl_3$, 200 MHz) δ 2.53 (s, 3H) 5.19 (s, 2H) 7.41 (s, 5H) 8.14 (s, 1H). GC/MS (70eV, EI) m/z *relative intensity* 266 (M+, 12), 91 (100), 65 (8).

5-benzyloxy-2-methylthiopyrimidine (6): To 2.62g (9.85mmol) of 5 dissolved in a minimum amount of *hot* ethanol was added 175ml of deionized water, and Zn dust (5.4g, 82.6mmol). The stirred solution is refluxed for 2 hours. Workup consisted of *hot* filtration to remove the zinc, cooling and subsequent extraction with Et_2O (3 x 50ml). The ether layers were combined, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification consisted of recrystallization in

hexane, yielding 1.1g of 6 as pale yellow needles in 48% yield, mp 70-71°C (lit.[2], 69-70.5°). ^{1}H NMR ($CDCl_3$, 200MHz) δ 2.54 (s, 3H) 5.10 (s,2H) 7.40 (s, 5H) 8.30 (s, 2H). GC/MS (70eV, EI) m/z *relative intensity* 232 (M+, 23), 91 (100), 65 (9).

5-hydroxy-2-methylthiopyrimidine (1): A mixture of 30ml of 6N HCl and 6 (1.0g, 4.31mmol) was stirred at room temperature for 30 minutes and then refluxed an additional 30 minutes. Workup consisted of extraction with Et_2O (2 x 10ml) followed by neutralization of the aqueous layer with 40% NaOH and re-extraction with Et_2O (3 x 10ml). The ether extracts were combined, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude liquid was placed *in vacuo* at about 1atm overnight. Purification of the precipitated light brown solid consisted of recrystallization in 40% EtOAc/Hexane yielding 250mg of 1 as light yellow crystals in 41% yield, mp 163-164°C (lit.[2], 170.5°). ^{1}H NMR (Acetone-d6, 200MHz) δ 2.48 (s, 3H) 8.26 (s, 2H) 9.07 (s, 1H). ^{13}C NMR (Acetone-d6, 300MHz) δ 14.25, 146.0, 149.4, 162.4. GC/MS (70eV, EI) m/z *relative intensity* 142 (M+, 100), 140 (23), 109 (11), 96(28), 74 (23), 68 (17). Calculated for $C_5H_6N_2SO$ 42.3%C, 4.2%H, 19.7%N, 22.5%S. Found 43.4%C, 4.3%H, 19.3%N, 23.9%S.

References

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5)Budesinsky Z.; Prikryl J.; Svatek E. *Coll. Czech. Chem. Commun.* 1964, *29*, 2980-2990.

6)Ueda T.; Ohtsuka H. *Chem. Pharm. Bull.(Tokyo)* 1973, *21*, 1451.

7)Hilbert G.E.; Johnson T.B. *J. Am. Chem. Soc.* 1930, *52*, 2001.

Spectral Data for Compounds 1–5

...THE HYDROXYL

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SOLVENT ACETON
FILE H

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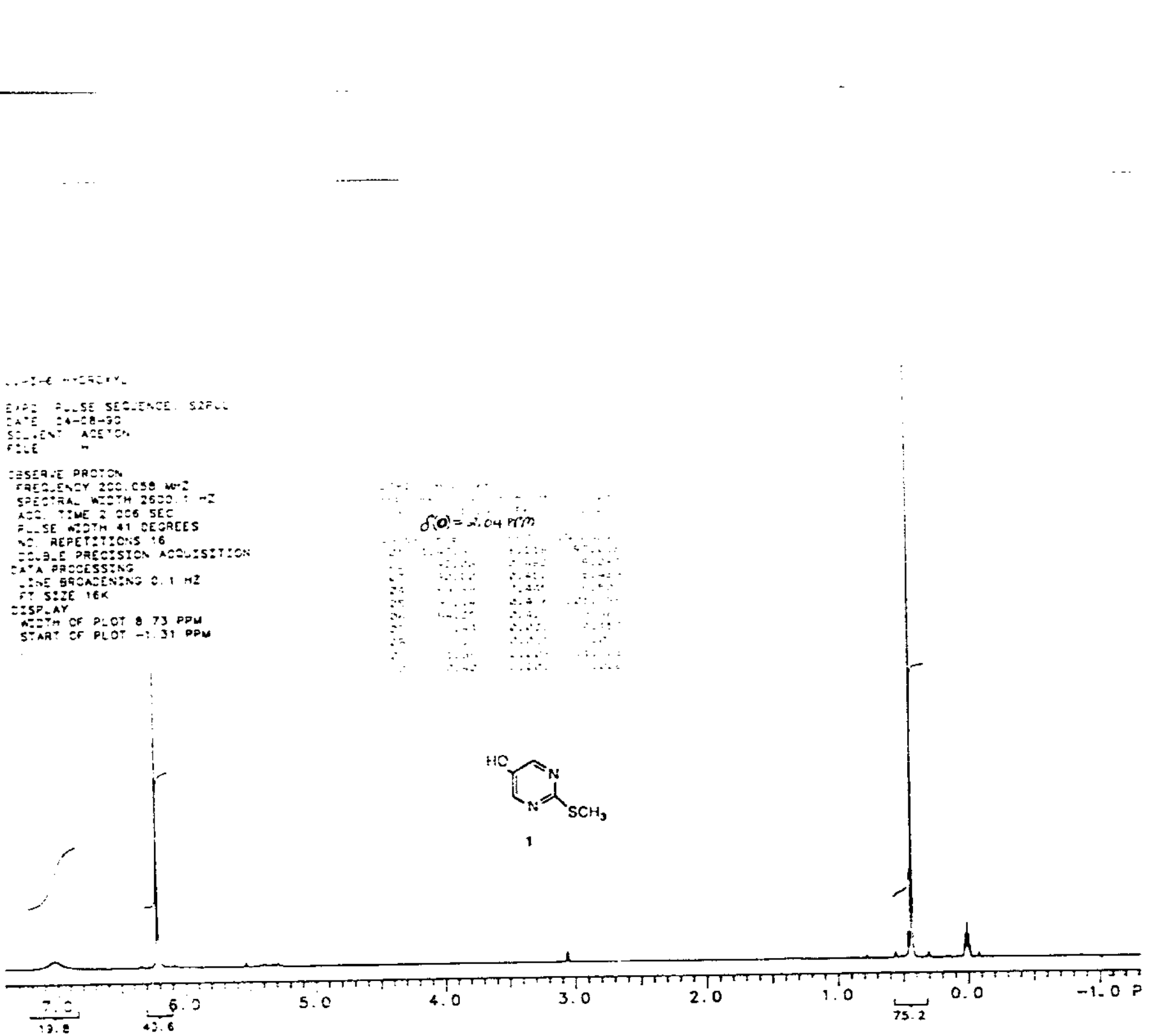

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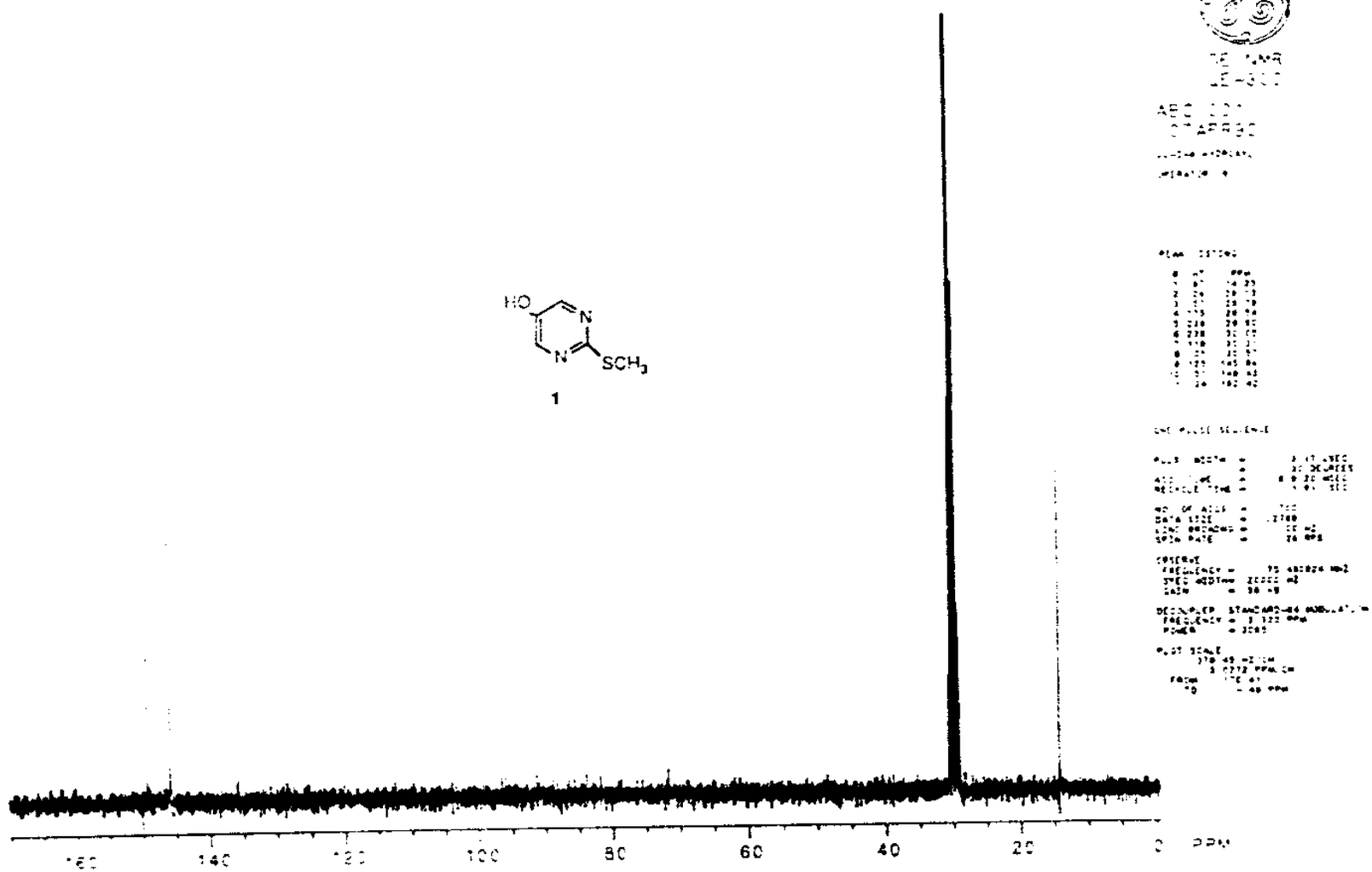
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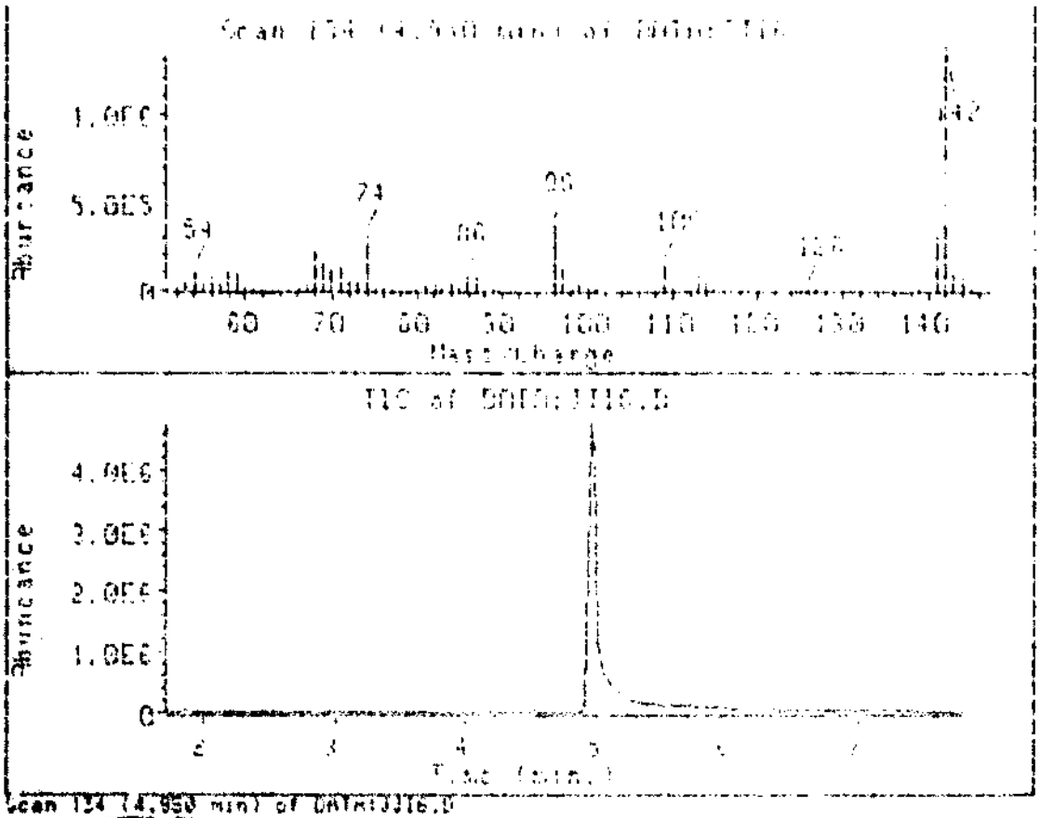

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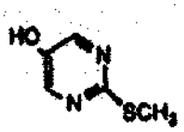

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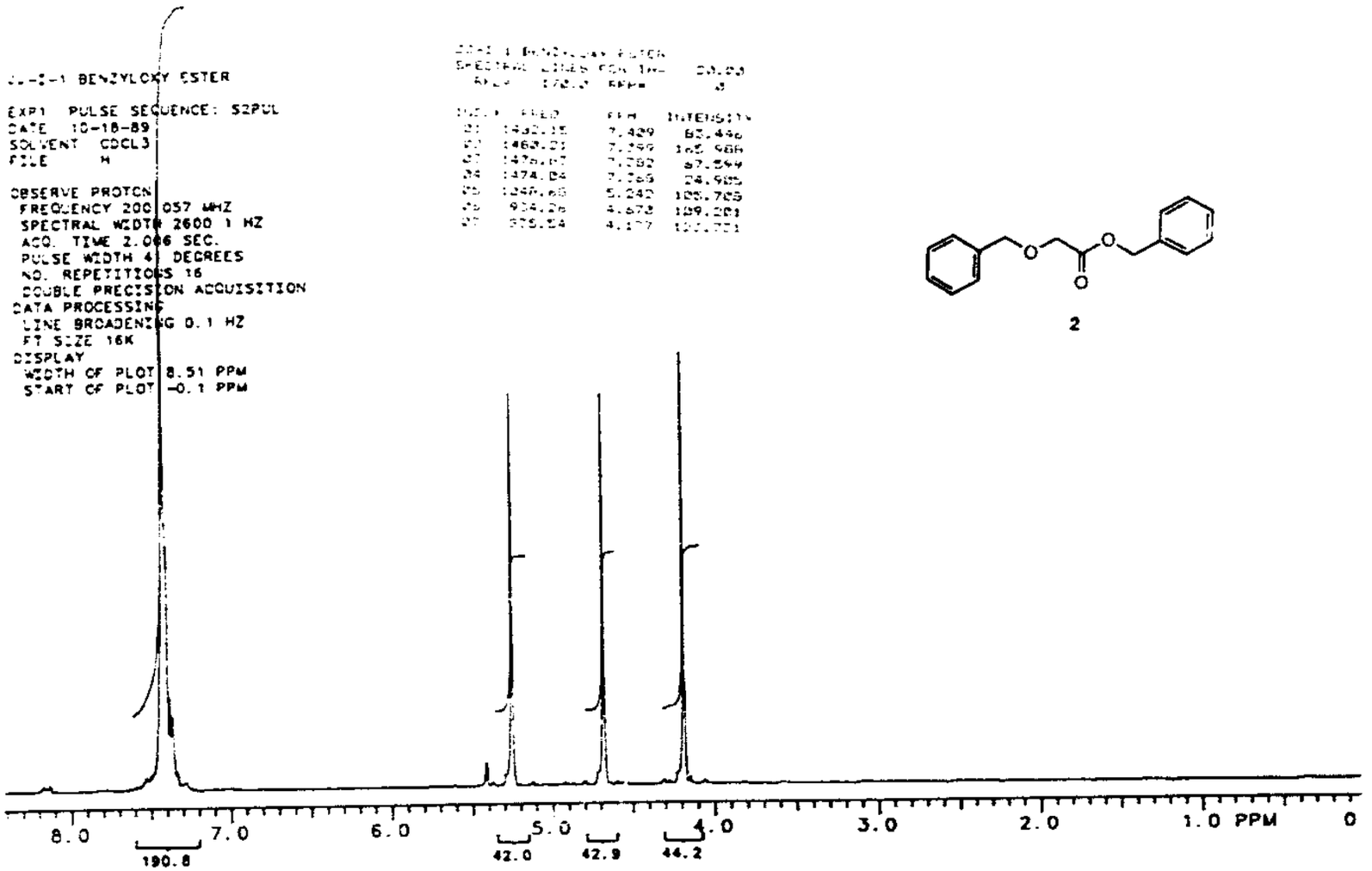
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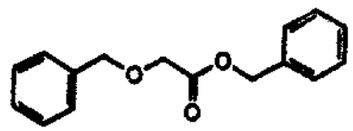

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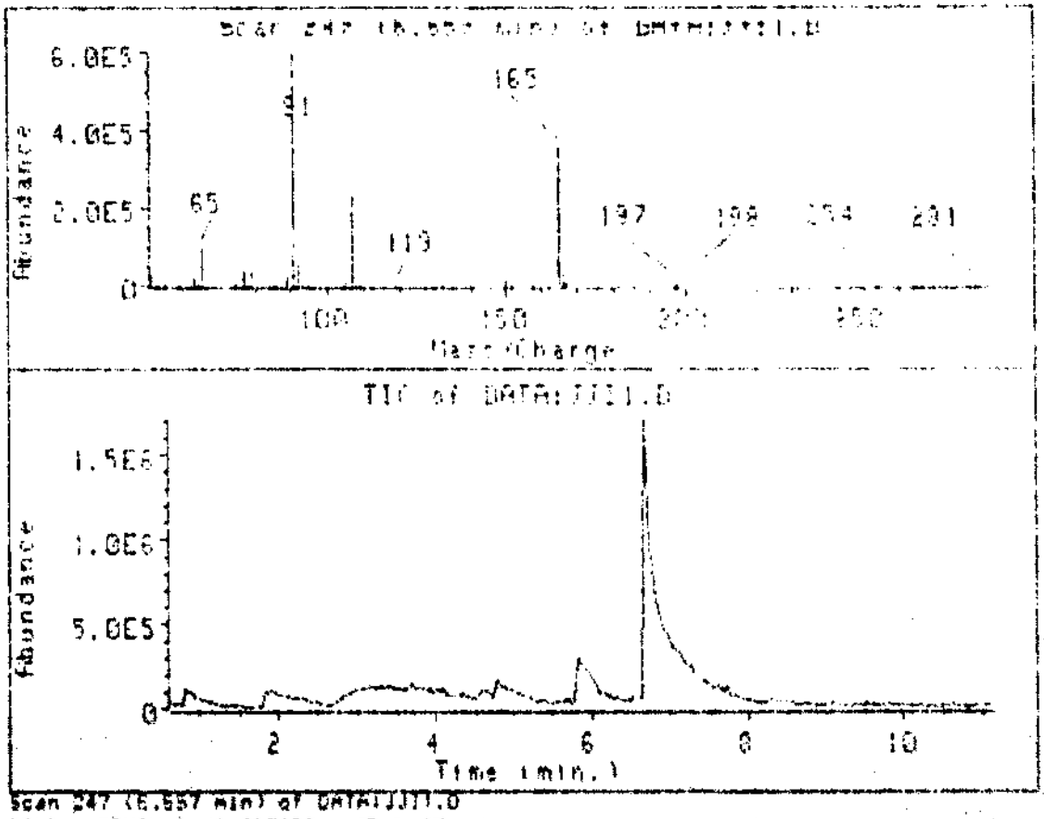
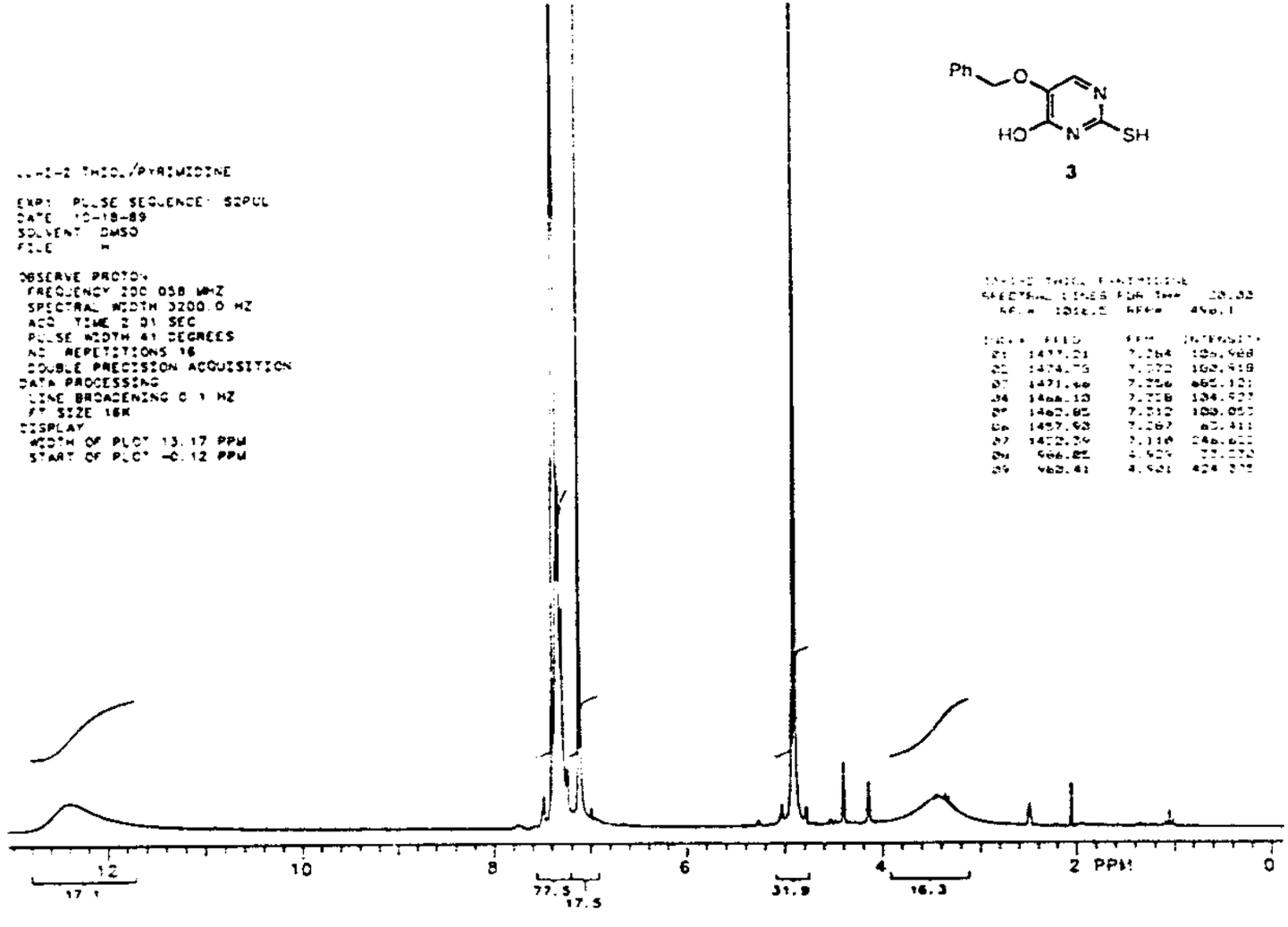


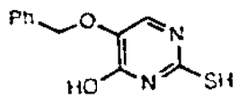
Scan 247 (6.557 min) of DATA:JJJ1.D

BENZYL BENZYLOXYACETATE JJ-I-1

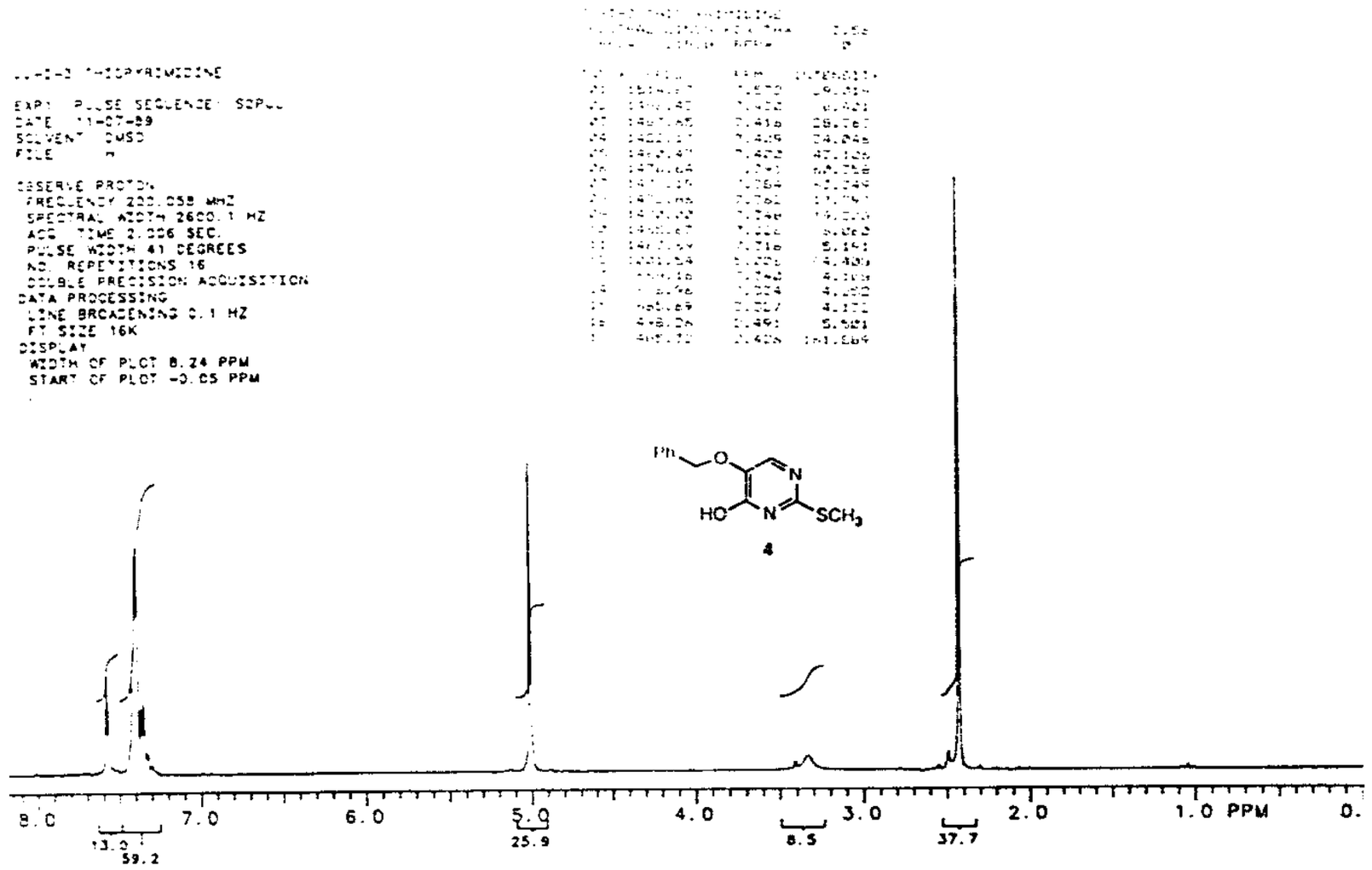
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
51.00	5	65.00	1	91.00	100	150.05	2
52.00	2	77.00	6	92.00	8	165.05	60
52.80	1	78.00	1	105.05	2	166.05	3
63.00	3	79.00	6	107.05	35	167.05	1
64.10	1	89.00	4	108.05	3	197.15	1
65.00	16						

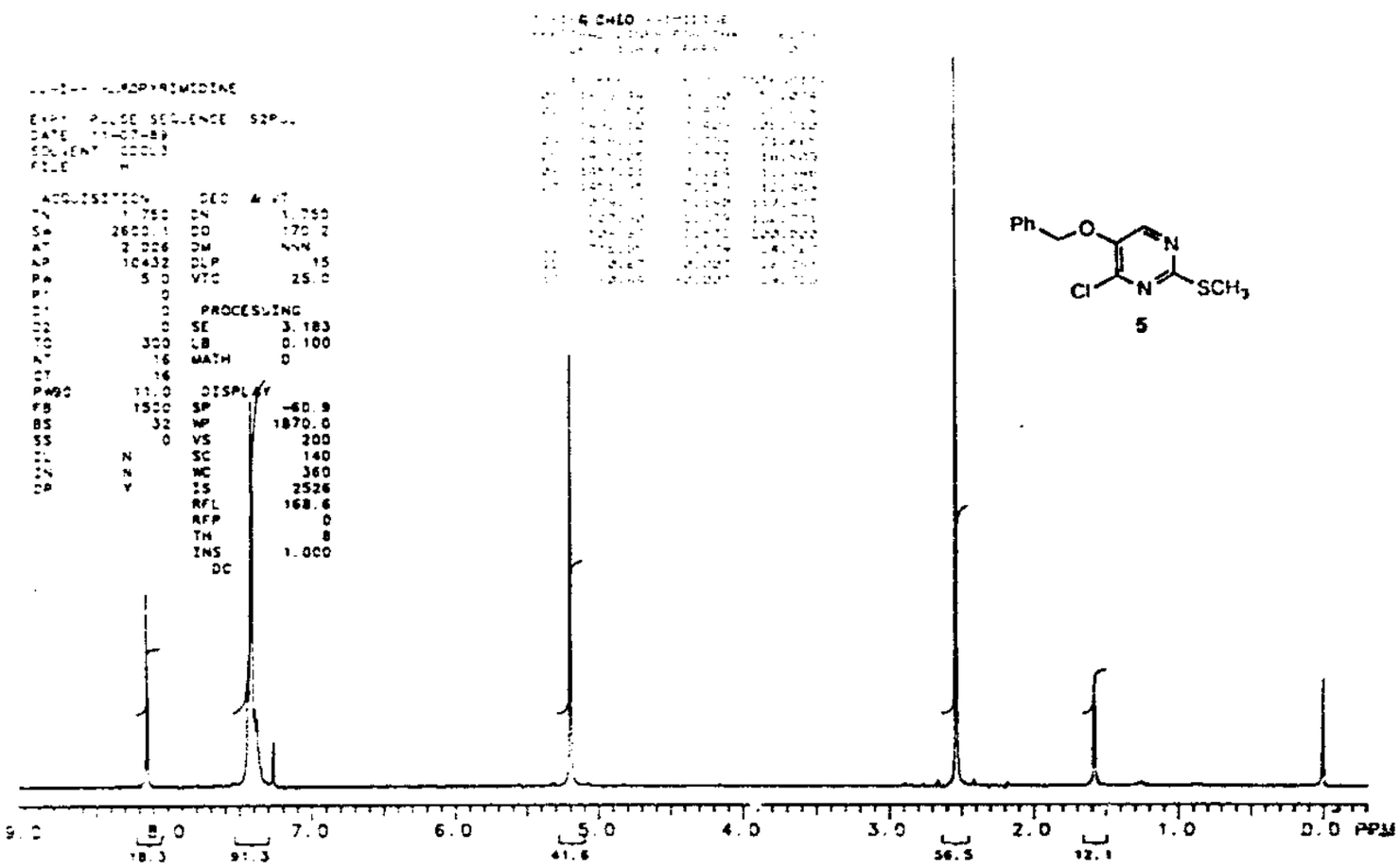

...HI-2 THIOL/PYRIMIDINE
EXPT PULSE SEQUENCE S2PUL
DATE 10-18-89
SOLVENT DMSO
FILE H
OBSERVE PROTON
FREQUENCY 200.058 MHZ
SPECTRAL WIDTH 3200.0 HZ
ACQ TIME 2.01 SEC
PULSE WIDTH 41 DEGREES
NO REPETITIONS 16
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
LINE BROADENING 0.1 HZ
FT SIZE 16K
DISPLAY
WIDTH OF PLOT 13.17 PPM
START OF PLOT -0.12 PPM
Ph
O
N
HO
N
SH
3
12
10
8
6
4
2 PPM
0
17.1
77.5
17.5
31.9
16.3

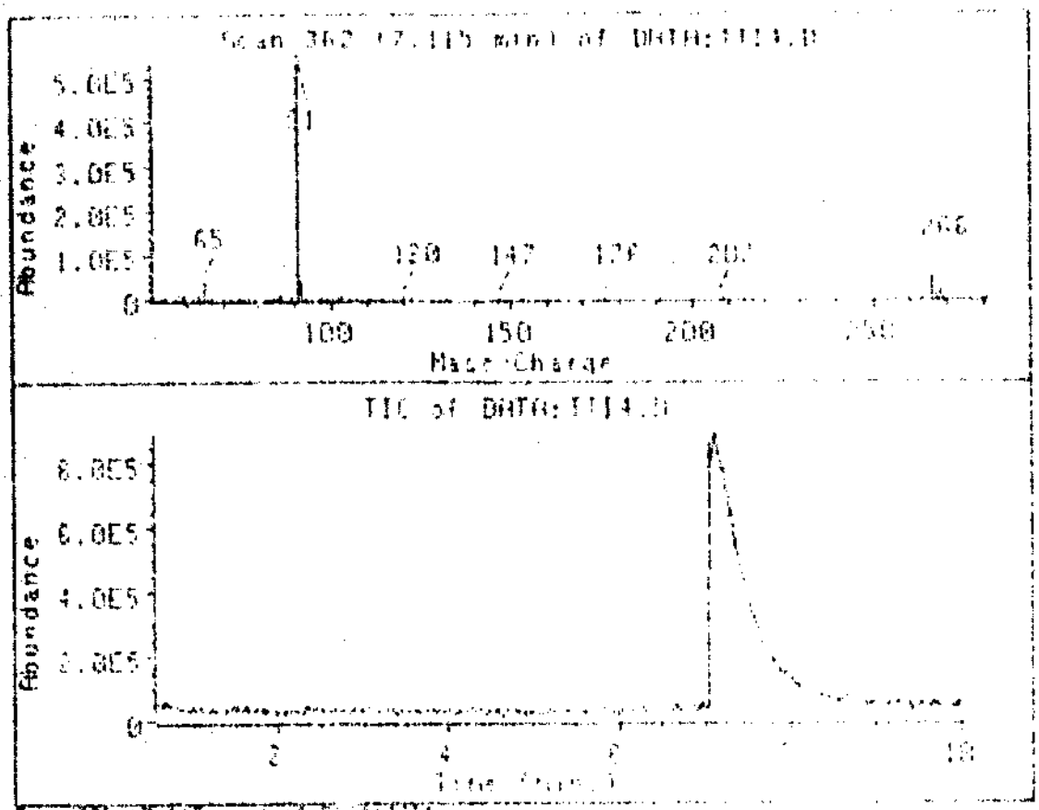
JJ-I-2
DMSO



3

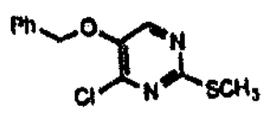

EXP: PULSE SEQUENCE: SCPUL
DATE 11-07-89
SOLVENT DMSO
FILE m
OBSERVE PROTON
FREQUENCY 200.058 MHZ
SPECTRAL WIDTH 2600.1 HZ
ACQ. TIME 2.006 SEC.
PULSE WIDTH 41 DEGREES
NO. REPETITIONS 16
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
LINE BROADENING 0.1 HZ
FT SIZE 16K
DISPLAY
WIDTH OF PLOT 8.24 PPM
START OF PLOT -0.05 PPM
Ph
O
N
HO
N
SCH3
4
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0 PPM
0.
13.0
59.2
25.9
8.5
37.7


Ph
O
N
Cl
N
SCH3
5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0 PPM



Scan 362 (7.115 min) of DHTR:1114.D
4-CHLORO-PYRIMIDINE JJ-1-4

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
51.00	2	65.00	9	80.00	4	114.00	1
51.50	1	66.00	1	84.00	1	122.00	4
55.50	1	70.00	2	91.00	100	237.00	1
56.00	1	71.00	1	92.00	4	240.00	12
59.00	2	74.50	1	102.00	1	269.00	2
62.00	1	76.50	1	104.50	1	304.00	4
62.50	2	77.10	1	114.00	1	305.00	1
63.00	1	64.00	1				

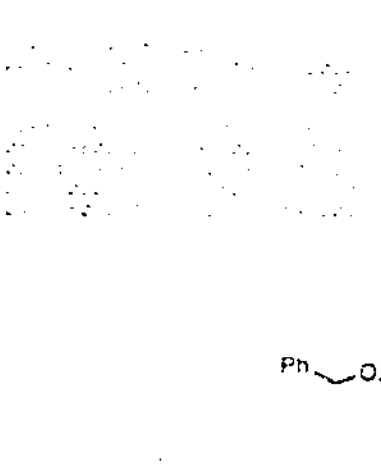


5

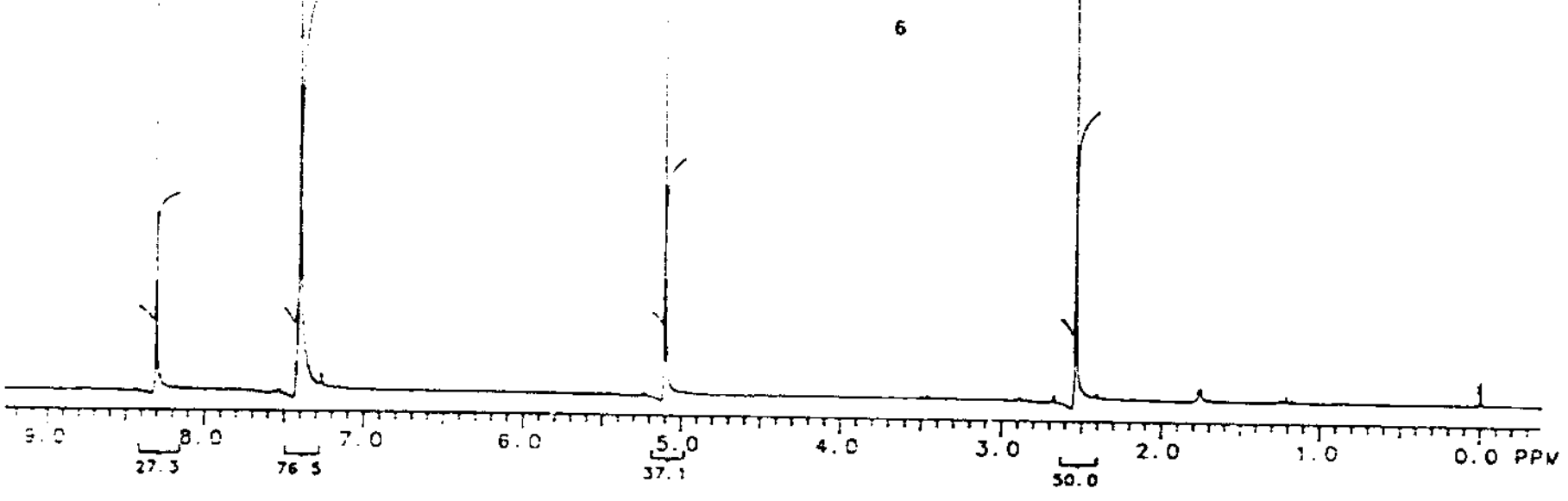
DICHLOROPYRIMIDINE JOT-I-5

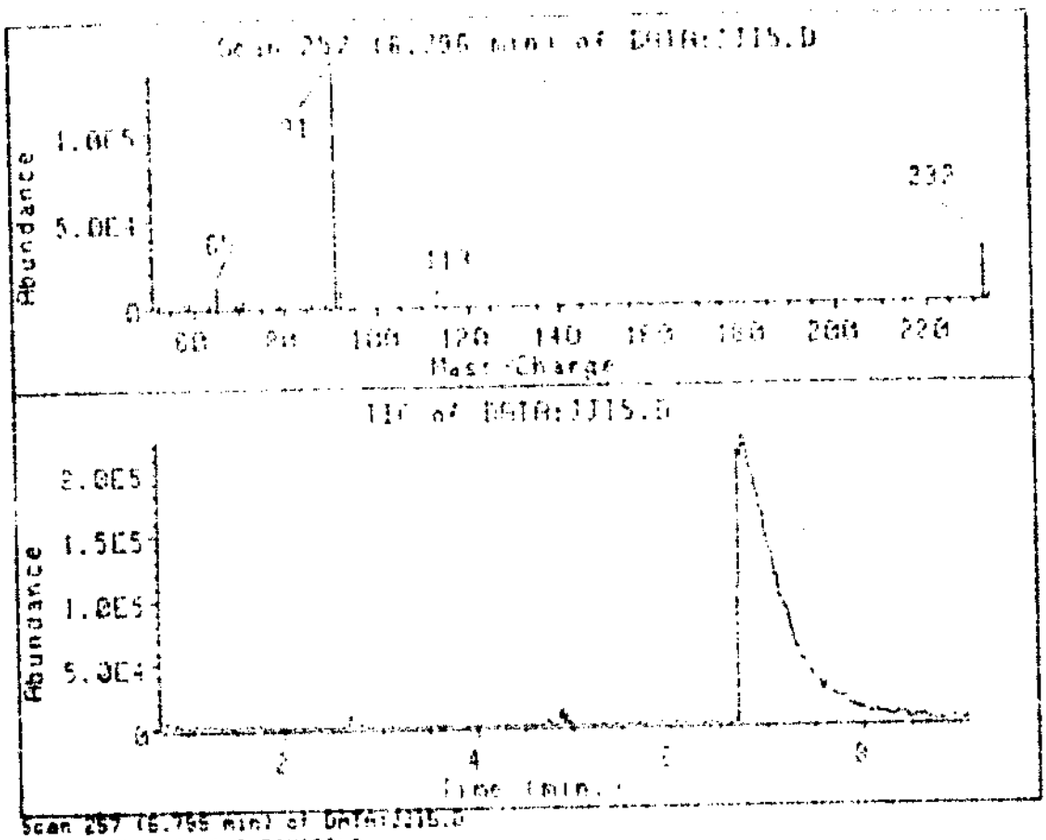
EXP: PULSE SEQUENCE S2PUL
DATE 01-10-90
SOLVENT CDCL3
FILE H

OBSERVE PROTON
FREQUENCY 200.057 MHZ
SPECTRAL WIDTH 2600.1 HZ
ACQ. TIME 2.006 SEC.
PULSE WIDTH 41 DEGREES
NO. REPETITIONS 16
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
LINE BROADENING 0.1 HZ
FT SIZE 16K
DISPLAY
WIDTH OF PLOT 9.65 PPM
START OF PLOT -0.38 PPM



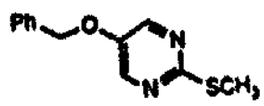
6





Scan 257 (6.755 min) of DATA:JJ15.D
JJ-1-5DEHYDRTHIOLPYRIMIDINE

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
51.15	2	65.05	9	79.05	1	92.05	0
52.05	1	68.15	1	86.05	2	113.05	1
56.05	2	70.05	1	89.05	1	232.05	23
59.05	2	71.05	3	91.05	100	233.15	4
63.15	1						



6