

**The Synthesis and Spectroscopy of a Self-Assembled
Catenane Monolayer**

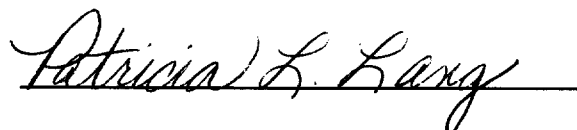
An Honors Thesis (Honrs 499)

By

Deborah L. Pinkstaff

Thesis Advisor

Dr. Patricia L. Lang

A handwritten signature in cursive script that reads "Patricia L. Lang". The signature is written in black ink and is positioned above a horizontal line that extends across the width of the signature.

Ball State University

Muncie, Indiana

December 11, 1998

Expected Graduation: May 1999

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A Brief Introduction

I received an undergraduate honors fellowship to do chemistry research under Dr. Patricia Lang, the fall semester of my junior year. I started my research, and have continued throughout both my junior and senior years here at Ball State University. The basis of my research has been to synthesize and characterize a self-assembled catenane monolayer.

The major goals of my research have been to synthesize both compounds needed to assemble the catenane monolayer and to characterize them using different types of spectroscopy. The types of spectroscopy I have been using include NMR and IR spectroscopy.

The following presentation was given at the Indiana Academy of Science, held on October 30, 1998. The topic of my presentation is the synthesis and characterization of the Bis(thiol)hydroquinone Derivative. This is the first of two compounds needed to form the catenane monolayer. I synthesized the bis(thiol)hydroquinone derivative and characterized it using NMR and IR spectroscopy.

Acknowledgments

I would like to thank the Ball State University Undergraduate Honors Fellowship Program and the Ball State University Summer Research Grant for my funding. I would also like to thank the Ball State University Chemistry Department for the opportunity to participate in research.

I would like to thank Dr. Storhoff for all his help with my research. I appreciate all the ideas he gave us. I would also like to thank him for the use of his equipment. I would also like to thank Dr. Kruger for his help with Chem Windows, and in assigning our NMR peaks.

I would especially like to thank Dr. Patricia Lang for all of her help, guidance and wisdom. I could not have asked for a better mentor. I enjoyed every aspect of my research. It was a wonderful opportunity, and I am grateful for all of her help. The beautiful aroma of thiol will always be with me.

Lastly, I would like to thank my family and friends for all their love and support.

The Synthesis and Spectroscopy of a Self-Assembled Catenane Monolayer

Introduction

A self-assembled monolayer, (SAM), refers to a single layer of organic molecules adsorbed from solution to a metal surface. Self-assembled monolayers have several applications. Some applications include: the study of adhesion, biological interfaces, corrosion, electrochemistry organic surfaces and wettability.

The majority of previous studies have focussed on SAMs of alkanethiols and disulfides on gold surfaces. Less studied have been dithiols. A dithiol allows the monolayer to attach to the gold surface in 2 places. This allows for more control over orientation and conformational structure of the SAM. (See Figure 1)

Previous research was done by Gokel and his co-workers at University of Miami. They synthesized the first surface attached catenane monolayer, and studied it using cyclic voltametry and UV/VIS spectroscopy. The aim of our research is to study the IR spectroscopy of the same catenane monolayer on a gold surface. A catenane monolayer is made up of two interlocking compounds, like a bead and thread. The dithiol threads through the cyclophane and attaches to the gold surface at both ends. Gokel's results are published in the *J. Am. Chem. Soc.*, 1993, 115, 2542-2543. (See Figure 2)

We must first begin with the synthesis because the compounds cannot be purchased.

Procedure

Step 1—Synthesis of the hydroquinone derivative.

The first step of our synthesis is to synthesize the hydroquinone derivative by reacting hydroquinone with 2-(2-Chloroethoxy)ethanol. (See Figure 3)

Reference: Pedersen, C. J., *J. Am. Chem. Soc.*, 1967, 89, pg. 7017-7036

Figure 4 shows the ^{13}C NMR spectrum of the hydroquinone derivative (diol).

The following assignments are made.

^{13}C NMR Spectrum of Diol

Corresponding Carbon on diol	Peak frequency (PPM)
Farthest from ring - <u>C</u> -OH	61.7262
-O- <u>C</u> -C-OH	68.1109
- <u>C</u> -O-C-C-OH	69.7702
-O- <u>C</u> -C-O-C-	72.7293
2C on ring with no H	115.6865
4C on ring with H	153.1001

Figure 5 shows the H NMR spectrum of the hydroquinone derivative.

H NMR Spectrum of Diol

The important features seen on this spectrum are as follows:

4 triplets of equal intensity are seen. These represent the H on the 4 C on the chains off the ring.

Figure 6 shows the infrared spectrum of the hydroquinone derivative. The following assignments are made.

IR Spectrum of Diol

Peak Frequency (cm ⁻¹)	Source of peak
3522.0	v(O-H) non-hydrogen bonded stretch —very characteristic
1515.0	v(C-C) benzene ring stretch
1235.0	v(C-O) "aryl o" stretch
1132.3	v(C-O-C) ether stretch
1056.0	v(CH ₂ -O) ether stretch
824.0	δ out of plane bend—benzene

Step 2—Synthesis of the dichloride.

The second step of our synthesis is to synthesize the dichloride by reacting the hydroquinone derivative with thionyl chloride. (See Figure 3)

Reference: Pedersen, C. J., *J. Am. Chem. Soc.*, 1967, 89, pg. 7017-7036

Figure 7 shows the ¹³C NMR spectrum of the dichloride. The following assignments are made.

¹³C NMR Spectrum of Dichloride

Corresponding Carbon on Dichloride	Peak Frequency (PPM)
Farthest from ring C-Cl	42.8015
-C-C-Cl	68.1874
-C-O-C-C-Cl	69.9766
-O-C-C-O-C	71.5976
2C on ring with no H	115.7171
4C on ring with H	153.1536

Figure 8 shows the H NMR spectrum of the dichloride.

H NMR Spectrum on Dichloride

The proton spectrum is consistent with the Dichloride molecule as well.

Figure 9 shows the infrared spectrum of the dichloride. The following assignments are made.

IR Spectrum of Dichloride

Peak Frequency (cm ⁻¹)	Source of Peak
3441.0	$\nu(\text{O-H})$ H-bonded stretch—residual water
1645.0	Residual water
1513.0	$\nu(\text{C-C})$ benzene ring stretch
1221.7	$\nu(\text{C-O})$ "aryl O" stretch
1129.7	$\nu(\text{C-O-C})$ ether stretch
1076.0	$\nu(\text{CH}_2\text{-O})$ ether stretch
832.0	δ out of plane bend—benzene
668.9	$\nu(\text{C-Cl})$ stretch

We see that the characteristic non-H-bonding stretch is no longer present. The H-bonded stretch is due to residual water.

Step 3—Synthesis of Dithiol—2 steps:

Step 3a—Synthesis of Isothiuronium Salt.

The synthesis of the bis(thiol)hydroquinone derivative is the final step of our procedure. This step is done in two parts. In the first half of this step, we synthesize the isothiuronium salt by reacting the dichloride with thiourea. (See Figure 10)

Reference: Rabjohn, *Organic Synthesis Collective Volume IV*, pg. 401-403

Figure 11 shows the ¹³C NMR spectrum of the isothiuronium salt. The following assignments are made.

¹³C NMR Spectrum of Isothiuronium Salt

Corresponding Carbon on Isothiuronium Salt	Peak Frequency (PPM)
- <u>C</u> -S-C=NH	32.2648
-O- <u>C</u> -C-S-C=NH	67.6751
- <u>C</u> -O-C-C-S-C=NH	69.8237
-O- <u>C</u> -C-O-C-C-S-C=NH	70.1678
2C on ring with no H	115.6330
4C on ring with H	153.0465
-C-S- <u>C</u> =NH	172.4606

Upon expansion, we see another set of three peaks that are consistent with the presence of a compound that has 1 isothiuronium salt end, and 1 chloride end.

We also see a peak at 183.7772 due to residual thiourea.

Using Chem Windows, we were able to compare our peak assignments to the predicted values. The blue values are our actual values, and the red values are the predicted values. From this, we can see that our assignments are correct.

Mistake on overhead: blue 71 should be blue 70. (See Figure 12)

Corresponding Carbon on Isothiuronium Salt	Observed Peak Frequency (PPM)	Predicted Peak Frequency (PPM)
- <u>C</u> -S-C=NH	32.2648	24
-O- <u>C</u> -C-S-C=NH	67.6751	70
- <u>C</u> -O-C-C-S-C=NH	69.8237	73
-O- <u>C</u> -C-O-C-C-S-C=NH	70.1678	74
2C on ring with no H	115.6330	115
4C on ring with H	153.0465	150
-C-S- <u>C</u> =NH	172.4606	164

Figure 13 shows the infrared spectrum of the isothiuronium salt. The following assignments are made.

IR Spectrum of Isothiuronium Salt

Peak Frequency (cm ⁻¹)	Source of peak
3040.0	$\nu(\text{N}=\text{H})$, $\nu(\text{N}-\text{H}_2)$ stretches
1510.8	$\nu(\text{C}-\text{C})$ benzene stretch
1220.0	$\nu(\text{C}-\text{O})$ "aryl O" stretch
1114.2	$\nu(\text{C}-\text{O}-\text{C})$ ether stretch
1034.9	$\nu(\text{CH}_2-\text{O})$ ether stretch

Step 3b—Synthesis of Dithiol.

The final step of our synthesis is to synthesize the bis(thiol)hydroquinone derivative by reacting the isothiuronium salt with KOH. This produces the potassium salt. H_2SO_4 is then added to produce the bis(thiol)hydroquinone derivative. (See Figure10)

Reference: Rabjohn, *Organic Synthesis Collective Volume IV*, pg. 401-403

Figure 14 shows the ^{13}C NMR spectrum of the bis(thiol)hydroquinone derivative.

The following assignments are made.

^{13}C NMR Spectrum of Bis(thiol)hydroquinone derivative

Corresponding Carbon on Dithiol	Peak Frequency (PPM)
- <u>C</u> -SH	24.3891
-O- <u>C</u> -C-SH	68.1033
- <u>C</u> -O-C-C-SH	69.6249
-O- <u>C</u> -C-O-C-C-SH	73.1040
2C on ring with no H	115.7018
4C on ring with H	153.1918

Again, if we expand the spectrum, we see another set of 3 peaks that are consistent with the presence of a compound containing 1 thiol end and 1 chloride end.

Again, using Chem Windows, we were able to compare our observed peak frequencies with those predicted. And again, our predictions were correct.

Mistake on overhead: blue 71 should be blue 73. (See Figure 15)

Corresponding Carbon on Dithiol	Observed Peak Frequency (PPM)	Predicted Peak Frequency (PPM)
-C-SH	24.3891	26
-O-C-C-SH	68.1033	70
-C-O-C-C-SH	69.6249	73
-O-C-C-O-C-C-SH	73.1040	74
2C on ring with no H	115.7018	115
4C on ring with H	153.1918	150

Figure 16 shows the infrared spectrum of the bis(thiol)hydroquinone derivative.

The following assignments are made.

IR Spectrum of Bis(thiol)hydroquinone Derivative

Peak Frequency (cm-1)	Source of Peak
2564.0	ν (S-H) stretch
1508.0	ν (C-C) benzene stretch
1236.6	ν (C-O) "aryl O" stretch
1118.5	ν (C-O-C) ether stretch
1042.6	ν (CH ₂ -O) ether stretch
823.7	δ out of plane bend—benzene
667.1	ν (C-Cl) stretch

The intensity of the C-Cl stretch at 667.2 is greatly reduced.

Future Research

Our next step will be to purify the dithiol and run grazing angle reflectance infrared spectroscopy of the dithiol on a gold surface. Grazing angle reflectance infrared spectroscopy (GAR IR) involves the use of the Perkin Elmer 1760X

FTIR Spectrometer and a grazing angle reflectance accessory. In this system, the IR beam is sent into the monolayer at a grazing angle. Radiation is absorbed by the monolayer, reflected off the gold surface and then absorbed again as the beam passes back through the monolayer.

We will then synthesize the cyclophane, form the monolayer on a piece of gold, and gain GAR IR spectra of the catenane monolayer on a gold surface.

(See Figure 17)

Acknowledgements (See Figure 18)

We would like to thank:

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Ball State University Department of Chemistry Summer Research Program

Ball State University Undergraduate Fellowship Program

Ball State University Summer Research Grant

Dr. Kruger—for his help with our NMR assignments using Chem. Windows

Dr. Storhoff—for all of his help!!

I would especially like to thank Dr. Lang for her help and guidance throughout my research.

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Rabjohn, "Ethanedithiol" *Organic Synthesis Collective Volume IV*, 401-403

Self-Assembled Monolayers

Single layer of molecules adsorbed from solution to metal

Model for: adhesion, membranes, corrosion, etc

Alkanethiols on gold are well studied

Dithiols attach at 2 terminal ends

Previous Research

- Gokel, G. W., et al., *J. Am. Chem. Soc.* **1993**, 115, 2542-2543
- Observed 1st surface attached catenane monolayer

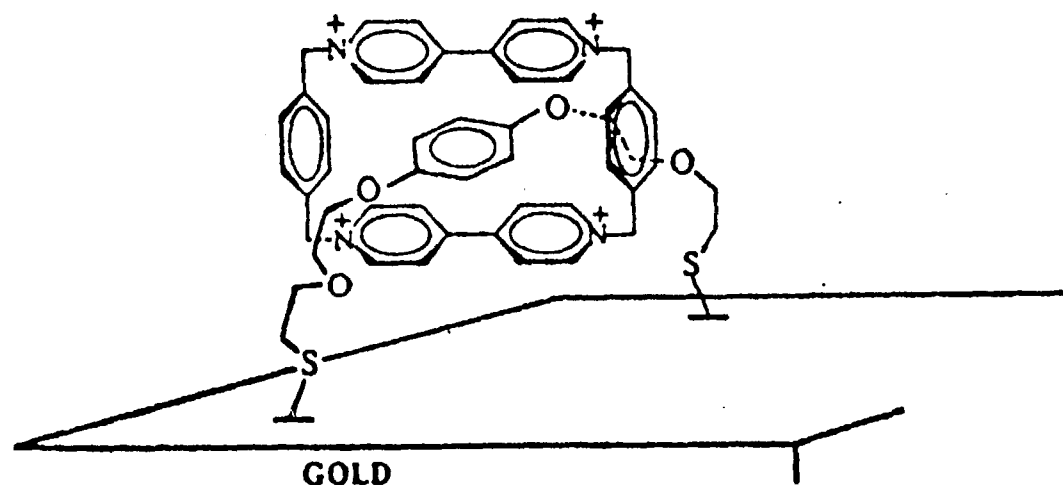
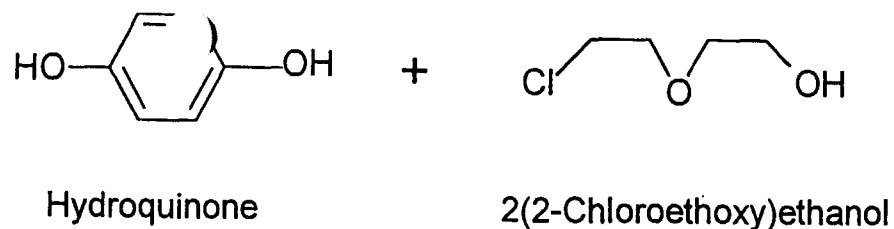
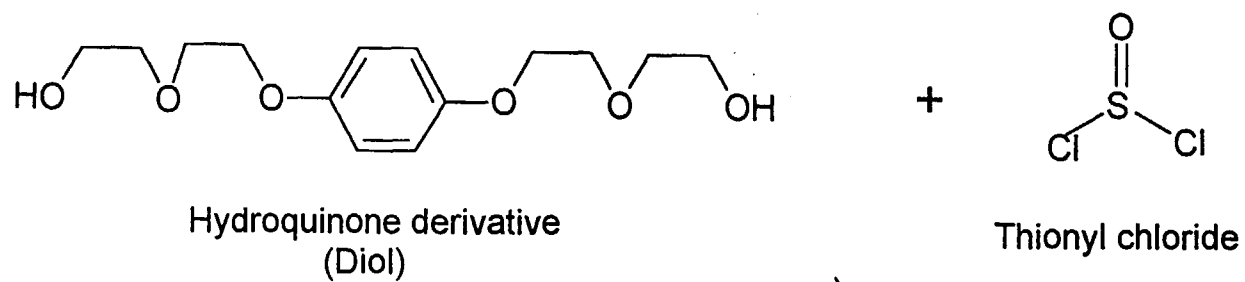


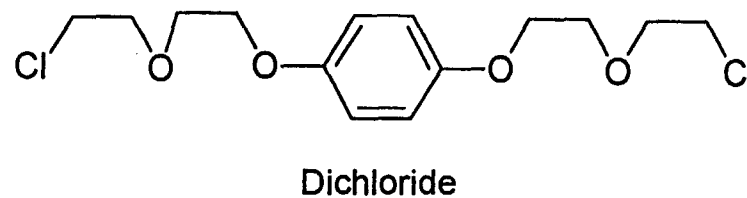
FIGURE 2



NaOH/H₂O
1-Butanol



benzene
pyridine
HCl



Pedersen, C. J., "Cyclic Polyethers and Their Complexes with Metal Salts" *J.*

Am. Chem. Soc. 1967, **89**, 7017-7036

FIGURE 3

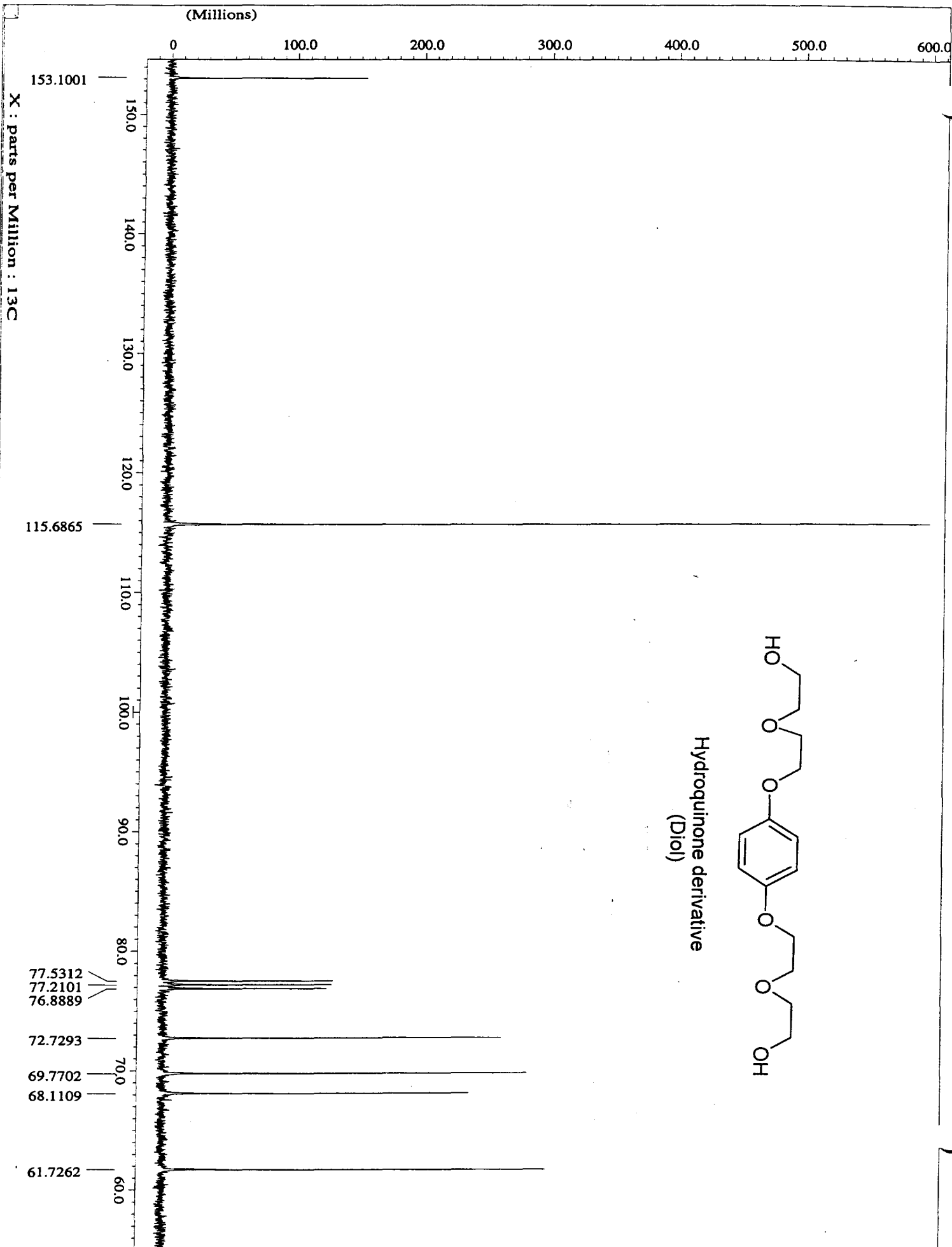
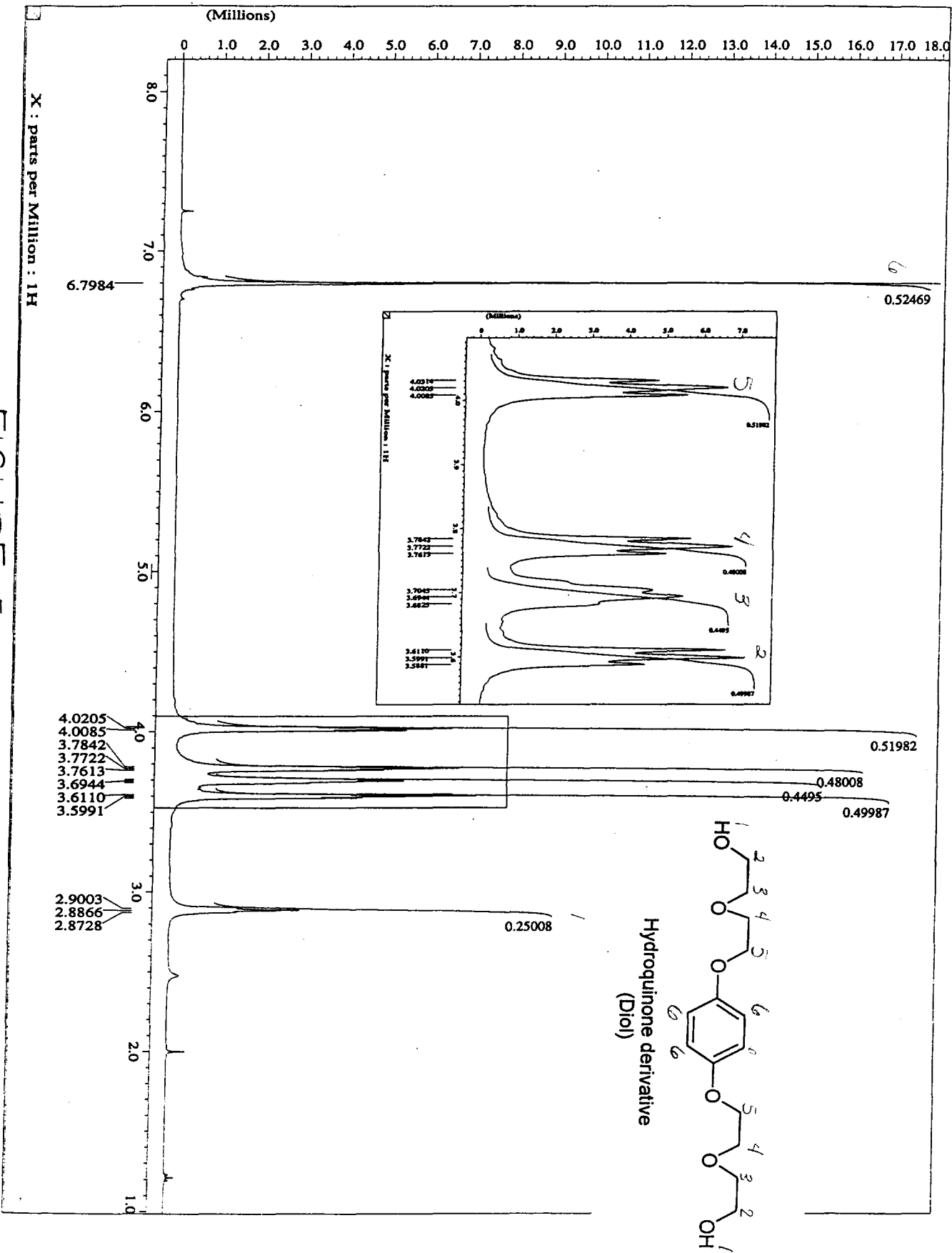


FIGURE 4

FIGURE 5



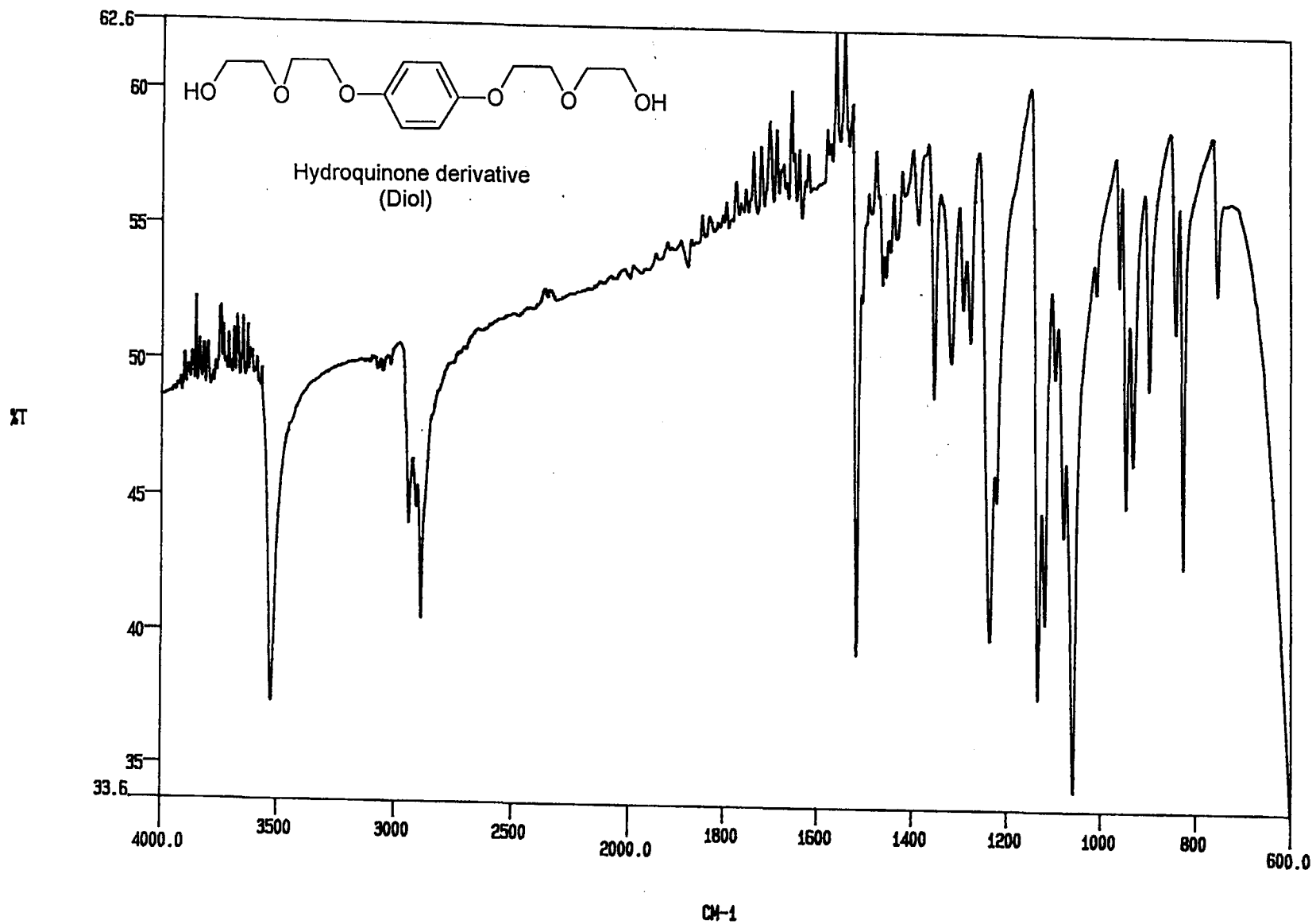
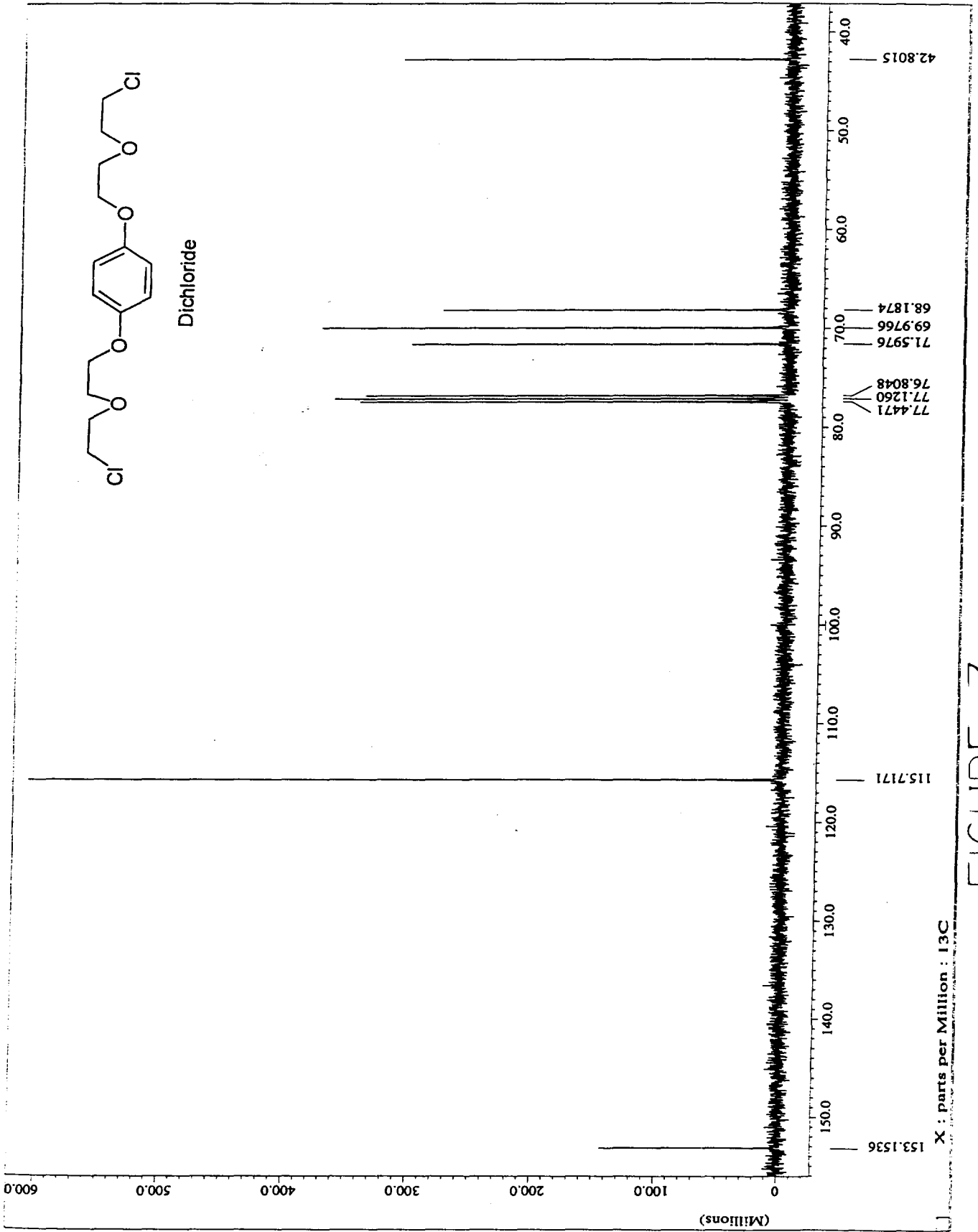


FIGURE 6



X : parts per Million : 13C

FIGURE 7

(Millions)

10.0

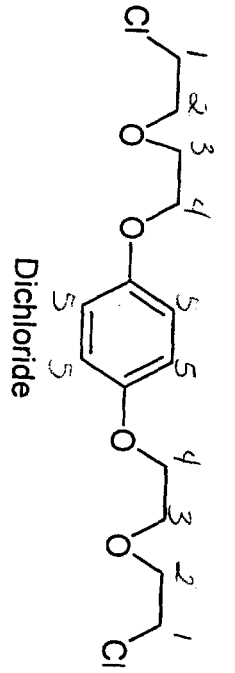
20.0

30.0

6.8387

0.50308

5



7.0

6.0

5.0

4.0763
 4.0644
 3.8409
 3.8290
 3.8254
 3.8107
 3.7961
 3.6431

0.49833

0.50425

(Millions)

0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0

X : parts per Million : 1H

4.1
 4.0882
 4.0763
 4.0644
 3.9
 3.8538
 3.8409
 3.8290
 3.8254
 3.8107
 3.7961
 3.7
 3.6578
 3.6431
 3.6284

3.0

2.0

1.0

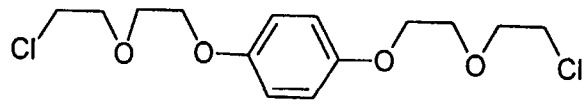
0

X : parts per Million : 1H

FIGURE 8

)

)



Dichloride

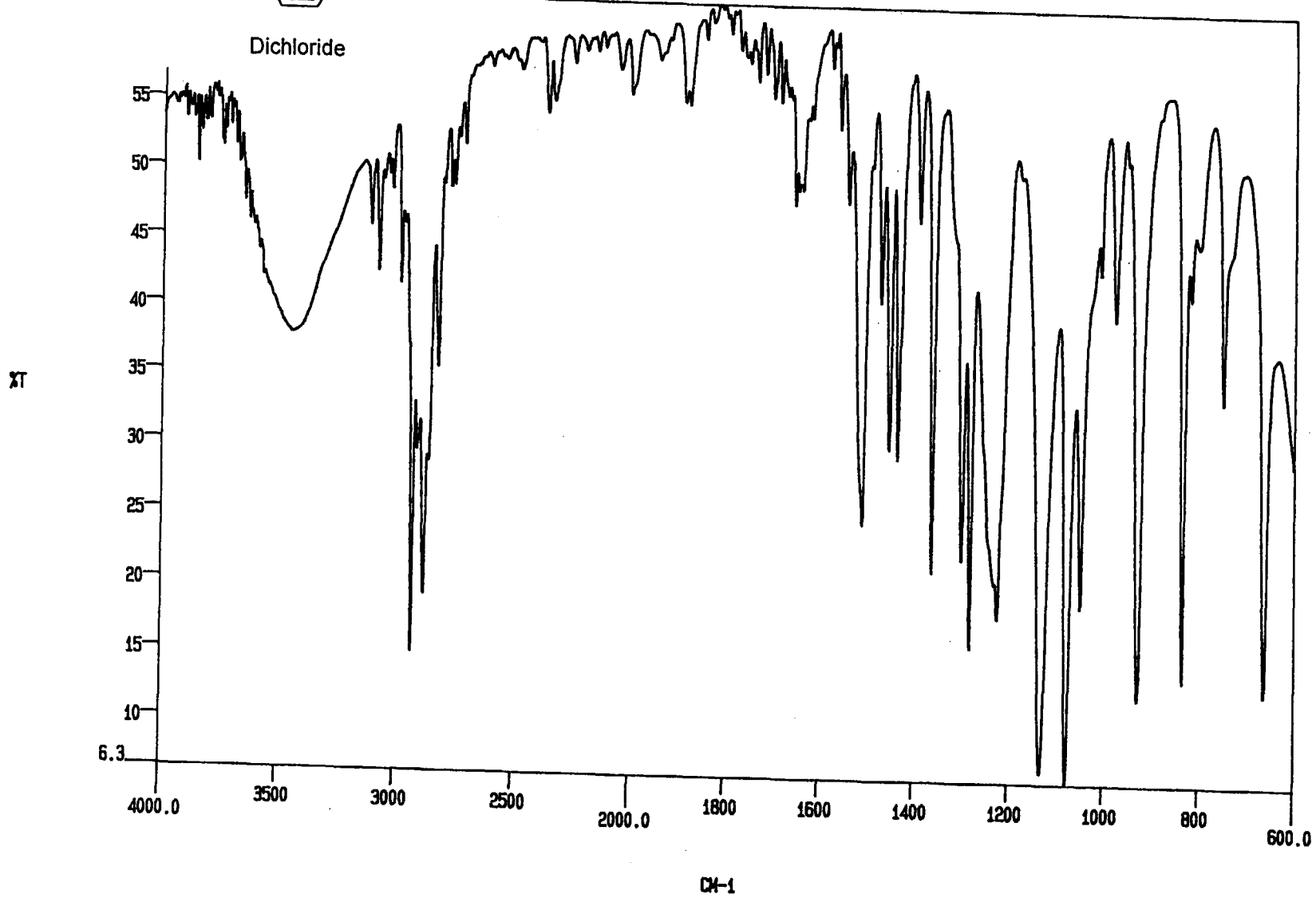
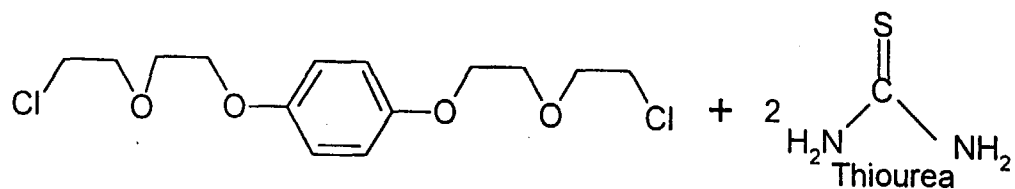
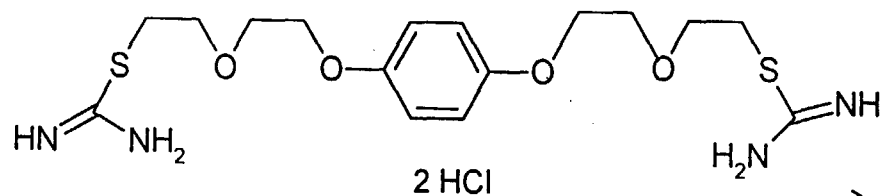


FIGURE 9



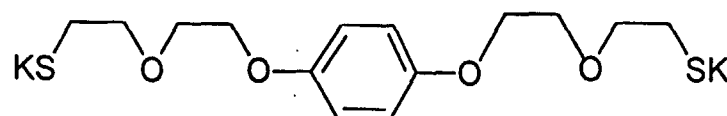
Dichloride

Ethanol

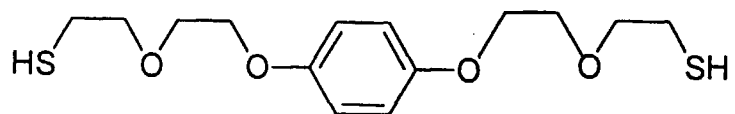


Isothiuronium salt

8 KOH



H_2SO_4/H_2O



Bis(thiol) hydroquinone derivative

+
 $4 NH_3 + 2 K_2CO_3 + 2 KCl + 2 H_2O$

+ K_2SO_4

Rabjohn, "Ethanedithiol" *Organic Synthesis Collective Volume IV*, 401-403

FIGURE 10

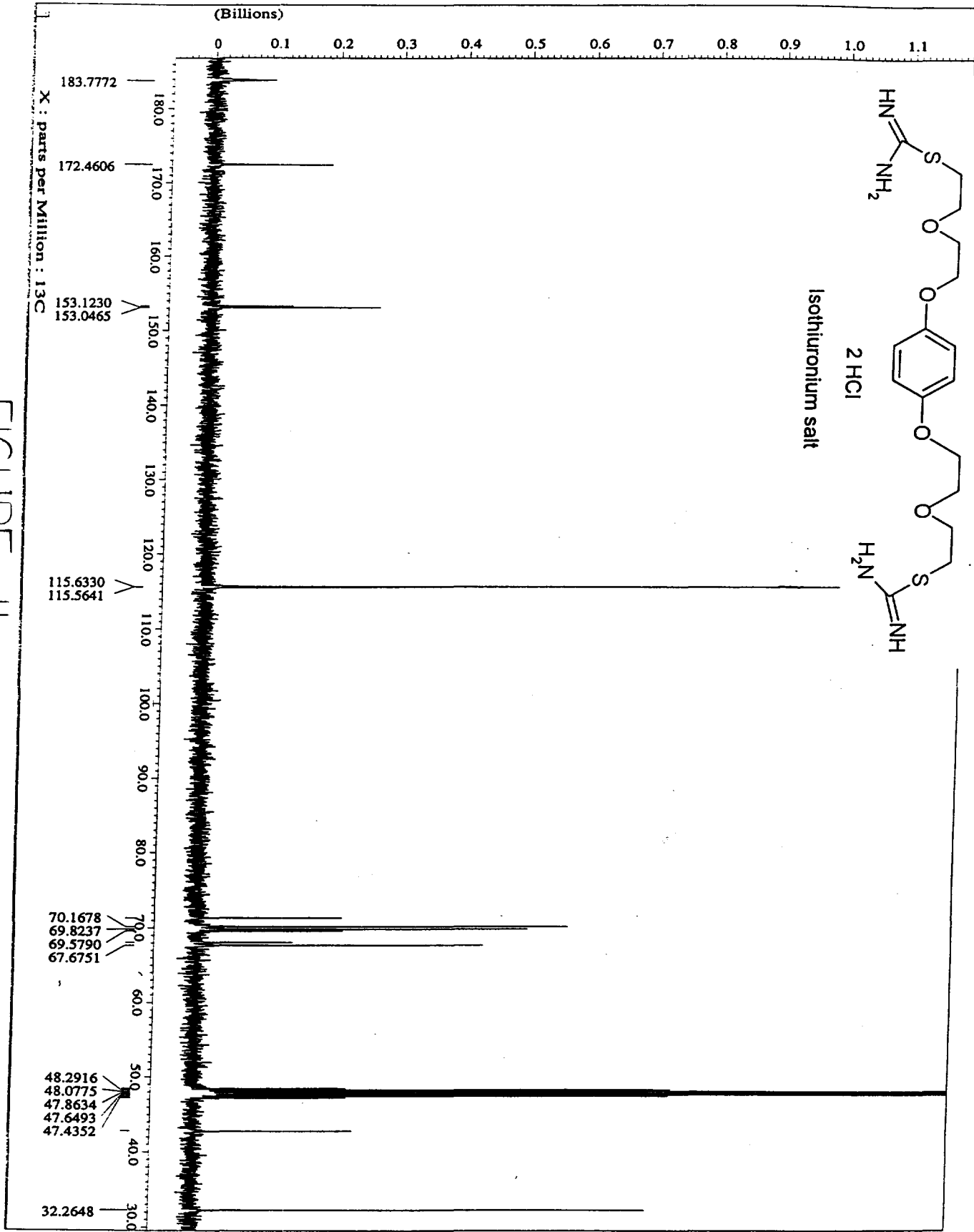


FIGURE 11

^{13}C NMR Spectra

Predicting the spectra chemical shifts from ChemWindows

- Erno Pretch, Andras Furst, Martin Badertscher, Renate Burgin, and Morton Munk, "C13Shift: A Computer Program for the Prediction of ^{13}C -NMR Spectra Based on an Open Set of Additivity Rules" *J. Chem. Inf. Comput. Sci.* 1992, **32**, 291-295.

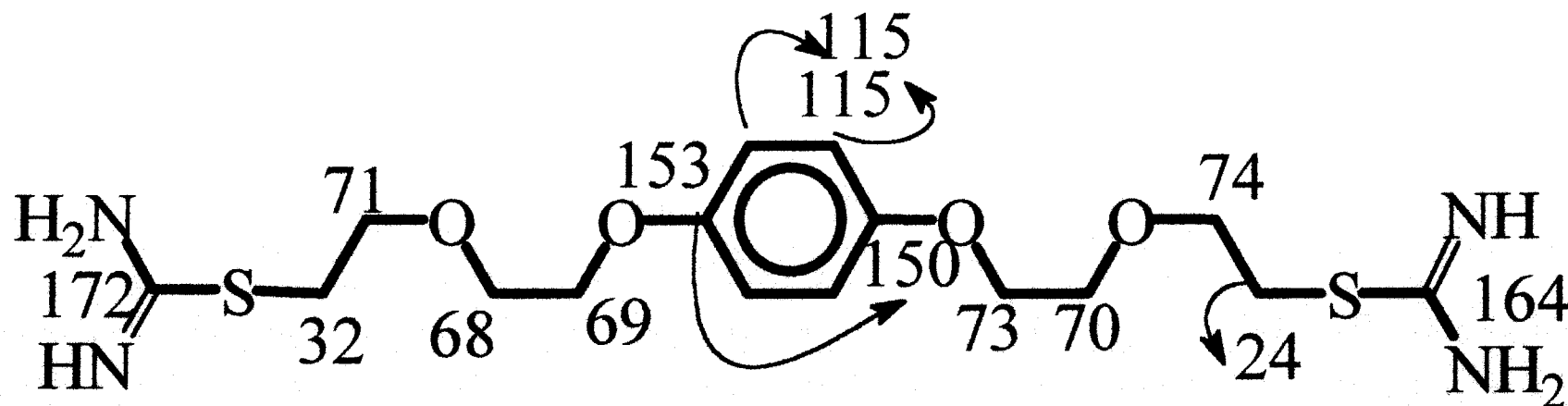


FIGURE 12

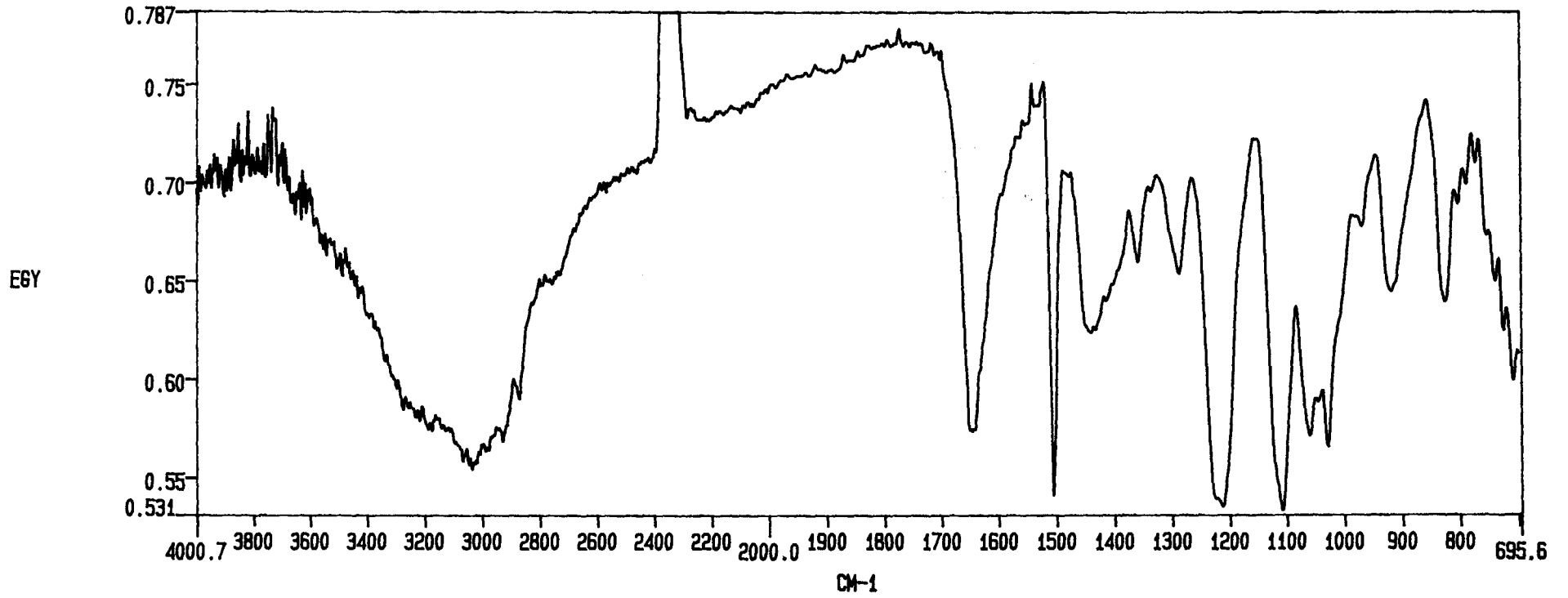
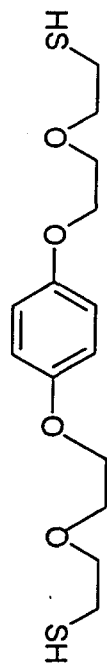


FIGURE 13

(Millions)

0 100.0 200.0 300.0 400.0 500.0 600.0 700.0



Bis(thiol) hydroquinone derivative

153.1918
153.1765

150.0

140.0

130.0

120.0

115.7018
115.6788

110.0

100.0

90.0

80.0

77.4471
77.1260
76.8125
73.1040
71.3759
69.6249
69.5867
68.1033

70.0

60.0

53.5293

50.0

40.0

31.9437

30.0

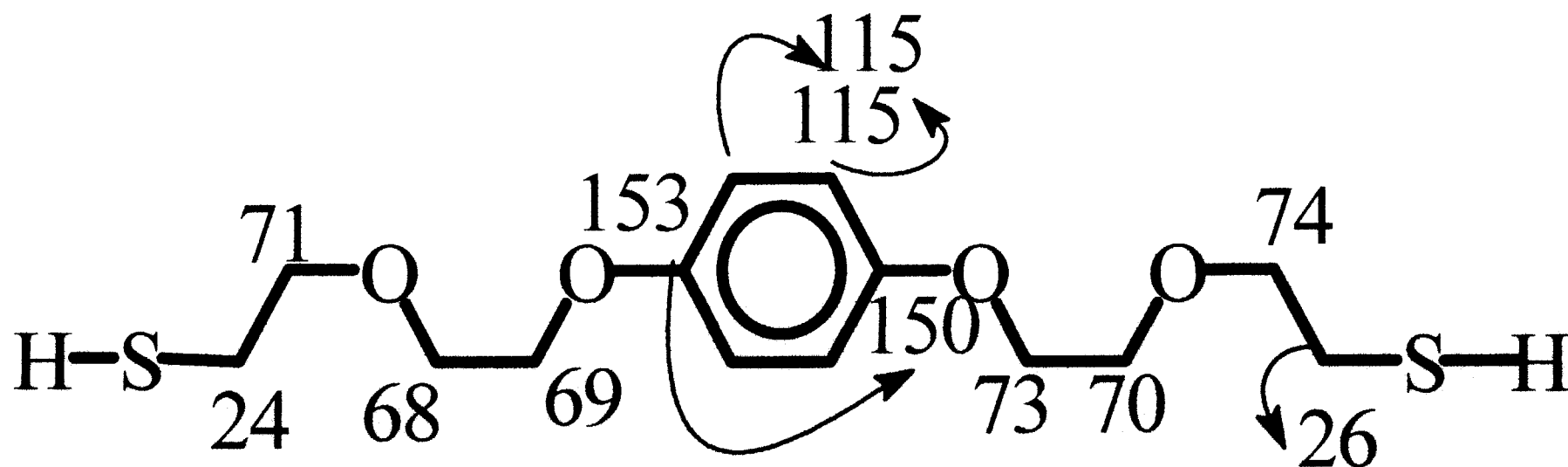
24.3891

X : parts per Million : 13C

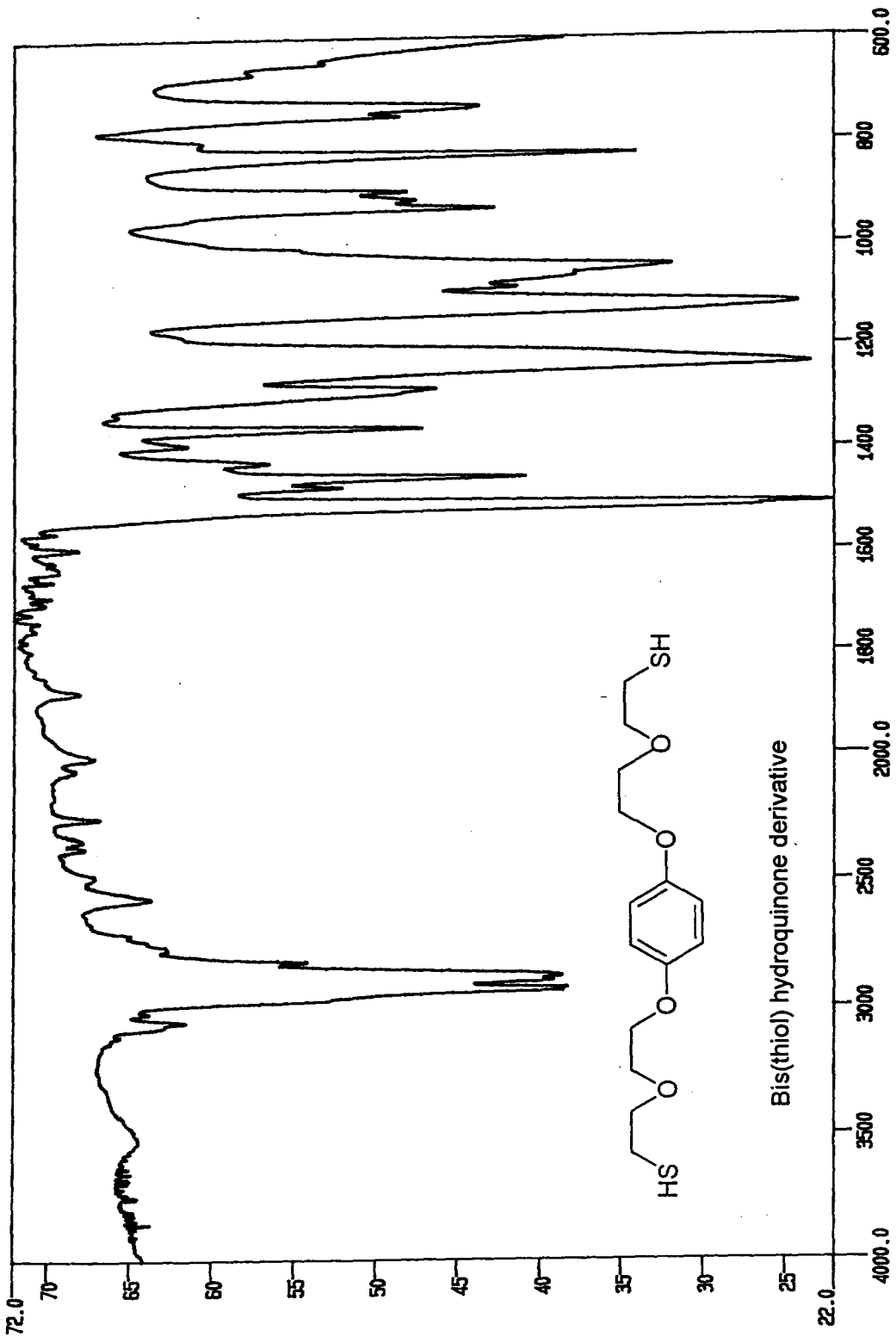
FIGURE 12

Surface Modifier

Dithiols adhere to gold surfaces on both ends.



Bis(thiol) hydroquinone derivative



CM-1

FIGURE 16

Next...

- Grazing Angle Reflectance Infrared (GAR IR) Spectroscopy of dithiol on gold
- Synthesis of Cyclophane
- Form SAM on gold surface
- GAR IR spectroscopy on monolayer

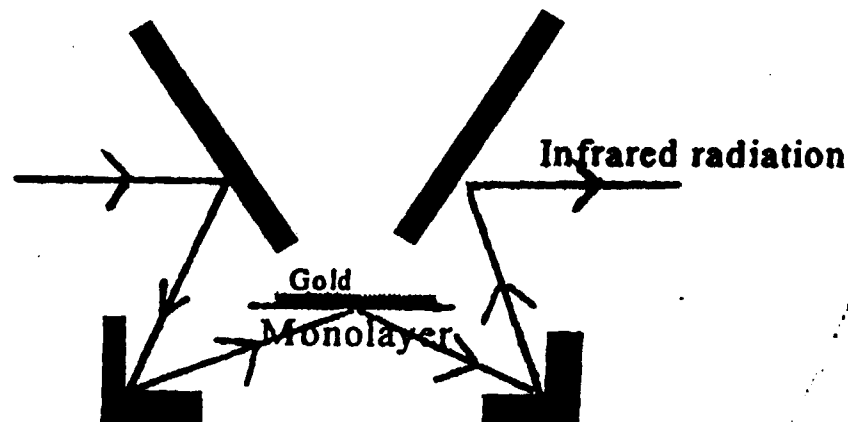


FIGURE 17

Acknowledgements

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Ball State University Summer Research Grant

Dr. Storhoff!!

Dr. Lang

Appendix

This appendix includes other spectral data obtained, but not used in the presentation. Peak assignments can be found directly on the spectra.

Figure 19 shows the ¹H NMR spectrum of the isothiuronium salt.

Figure 20 show the ¹H NMR spectrum of the bis(thiol)hydroquinone derivative.

FIGURE 9

X : parts per Million : 1H

(Millions)

0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0

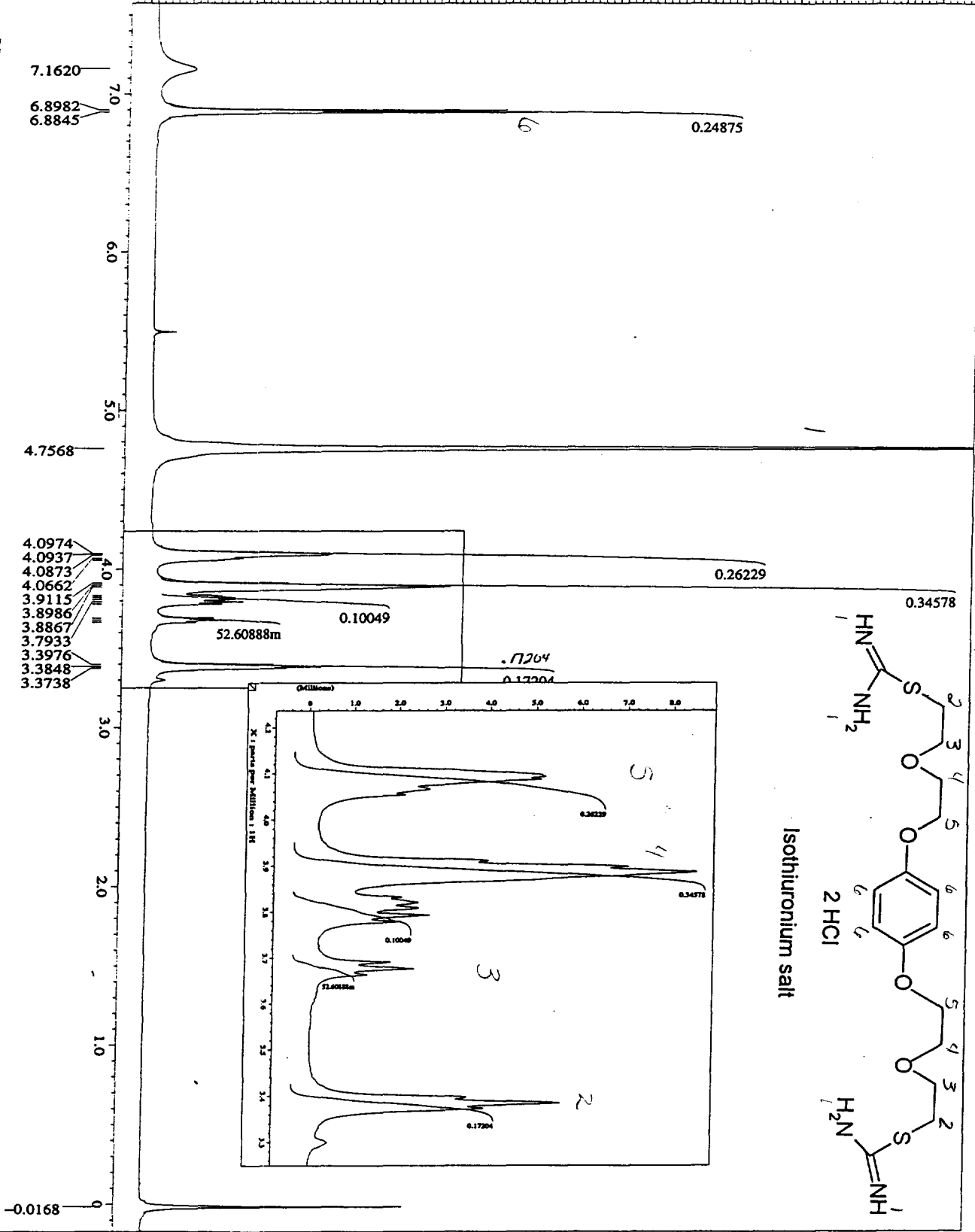
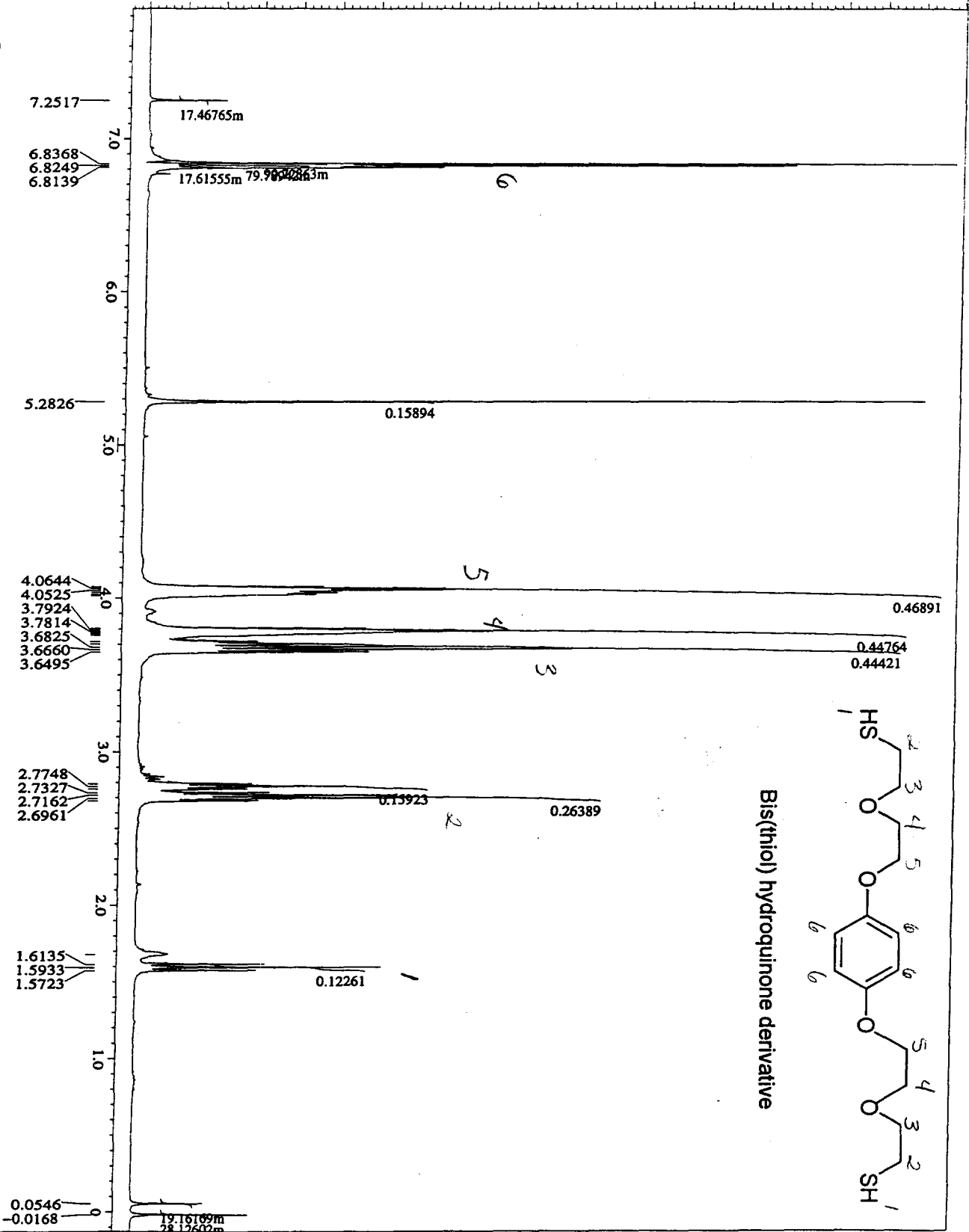


FIGURE 20

X : parts per Million : 1H

(Millions)

0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0



A Brief Reflection

This presentation was the first professional presentation I have ever given. From the time I began preparing for my presentation, until October 30, 1998 when I gave my presentation, I experienced many things I did not expect.

As I began gathering all the information to use for my presentation, I felt very nervous. I also felt very unprepared, with no idea what to expect. I knew very little about the Indiana Academy of Science; what I did know, was based only on the knowledge of other students.

I had given an informal presentation over the summer for the Chemistry department. This is a requirement of the summer research program. That talk helped me determine what kind of audience I would be addressing in October. It also helped me narrow down the types of information to include in my presentation.

Still feeling unprepared, I had a practice run with Dr. Lang the day before I was to give my talk. She helped make corrections in the language I used as well as other little errors I had made. Dr. Lang also explained to me what I could expect at the Indiana Academy of Science. I felt much more prepared and confident going into my presentation.

Overall, I believe that my presentation went very well. I was only asked a few questions, however, the questions that were asked, I was able to answer easily. I feel that my presentation was very informative to the audience. All of my peers agreed that it went very well.

I believe that the decision to do research was a very important one. It was a great experience to actually participate in research. It was an even better experience to present my research at the Indiana Academy of Science. I am very grateful for the opportunity, and I know it has been and will continue to be very beneficial to my career in Chemistry.