DOT/FAA/AR-07/25

Air Traffic Organization
Operations Planning
Office of Aviation Research
and Development
Washington, DC 20591

Development and Testing of Flame Retardant Additives and Polymers

April 2007

Final Report

U.S. Department of Transportation
Federal Aviation Administration

NOTICE

Technical Report Documentation Page

1. Report No. DOT/FAA/AR-07/25	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle DEVELOPMENT AND TESTING OF FLAME RETARDANT ADDITIVES AND POLYMERS		5. Report Date April 2007 6. Performing Organization Code
7. Author(s) Joshua L. Jurs		8. Performing Organization Report No.
9. Performing Organization Name and Address Rice University 6100 Main Street Houston, TX 77005		10. Work Unit No. (TRAIS) 11. Contract or Grant No.
12. Sponsoring Agency Name and Address U.S. Department of Transportation Federal Aviation Administration Air Traffic Organization Operations Planning Office of Aviation Research and Development Washington, DC 20591		13. Type of Report and Period Covered Final Report 14. Sponsoring Agency Code ANM-100

15. Supplementary Notes

The Federal Aviation Administration Airport and Aircraft Safety R&D Division COTR was Dr. Richard Lyon.

16. Abstract

Novel flame-retardant chemical additives and polymers were synthesized and their flammability measured in the Underwriters Laboratory test for flammability of plastics (UL94). Self-extinguishing (V-0) compositions were obtained for poly (acrylonitrile-butadiene-styrene) and high-impact polystyrene by adding as little as 10 weight percent of boronic acid derivatives or halogen-containing bisphenylethenes (BPH). Self-extinguishing (V-2) compositions were obtained for polyethylene by adding as little as 10 weight percent BPH. The efficacy of BPH additives as flame-retardants suggested incorporating these moieties directly into the polymer to further reduce flammability. Polymers and copolymers were synthesized having BPH backbone and pendant groups, including backbone copolymers containing acetylene and phosphineoxide. The thermal combustion properties of polymers containing a BPH backbone or pendant groups were measured by microscale combustion calorimetry and found to be among the lowest values ever recorded, suggesting that aircraft cabin materials made from these polymers would be ultra-fire-resistant.

17. Key Words Polymer, Copolymer, Fire, Flammability, Flame resistance, Heat release rate, Heat release capacity, Char, Boron, Halogen, Phosphorus		18. Distribution Statement This document is available to the public through the National Technical Information Service (NTIS) Springfield, Virginia 22161.	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 303	22. Price

Acknowledgements

My graduate career would not have been made possible if it were not for some important people in my life. I have purposely waited until the end of this thesis to remember the people that have helped me over the last five years. I want to talk a little about me and my graduate experience at Rice University and the University of South Carolina.

After college (Assumption College, Worcester Massachusetts, Class of 1995) I pursued several part time jobs until I landed my first fulltime job at a local biotech firm. I was bounced around to several departments within the company working in manufacturing, PNA synthesis, and finally quality control. It was because of this experience that I knew I had to go back to school to get an advanced degree in chemistry. I learned a lot while working there and it was because of these lessons that I decided to do more with my life. It was during this time that I met my wife and a couple of good friends.

In the spring of 1998 I started researching different graduate schools both in and out of New England. After seeing the facilities and meeting the faculty at the University of South Carolina, I knew that this was the place for me. I started my graduate career in the summer of August, 1998. It was a difficult move for me; I had never really left New England for an extended period of time. I grew up in Connecticut and my undergraduate college was a short two hour drive to Massachusetts. It was a hard decision to leave my family and friends, but I knew staying in the Boston area was not going to help my career. I arrived in Columbia, SC and proceeded to move in with my new roommate Kenneth Brown. It was there in that hot South Carolina summer that I met many new people; some I consider to be lifelong friends. The first year of graduate school was a difficult year for me. I had been out of college for three years and it was tough getting back into the academic mind set. In addition, organic chemistry was the specialty area I chose and it had been five years since my last organic class. If it was not for the help of my fellow first year graduate students, Kenneth Brown, Shawn Dirk, and Burjor Captain, I do not think I would have survived the first year. It was also in this first year that I met my advisor, James Tour. I was amazed by his charisma, research, and his success as a professor. I knew after meeting with him and learning about flame retardant polymer additives that this was what I wanted to do for my graduate research. After I joined the group, I learned that he was moving to Rice University in Houston, Texas and was taking all of his graduate students who wanted to continue their research with him. I had no permanent ties to Columbia, SC and had no problems moving to Houston, Texas. The relocation of an entire academic lab to another state is another experience I will never forget. It was during these times, that I became close with some of my lab mates, Shawn Dirk, Aaron Engel, David Price, and Adam Rawlett. Setting up the lab from the beginning was hard but exciting work and I learned a lot about how to design and run a laboratory that summer. My research continued at Rice University for the next four years. I have been through many experiences and seen many people leave and join the Tour group. It is these people that I want to acknowledge.

I would like to acknowledge the friendship of three important people that I became close to in these past five years. In particular, I would like to thank Shawn Dirk. I really appreciate your friendship and help you gave me with my chemistry. We have been through some tough years in the Tour group and it was your support and care-free outlook on life that made this place tolerable. I thank you for the memories.

The next person who made an impact on my life would be David Price. It was your "Iron Man" work ethic and sense of humor that I will miss most. I really appreciate all the help you have given me over the years, and I will never forget some of the memorable southern clichés that always made me laugh.

The last person I would like to acknowledge is Aaron Engel. I really appreciate your help, wit and the various "Engelism" that have also made me smile. I would like to thank you for your intellect and support on many issues, including chemistry and life.

In addition there are other people I would like acknowledge that have made an impact on me from the Tour group. They are listed here in no particular order: Jeffrey Bahr, Stephanie Chanteau, Jake Ciszek, Chris Dyke, Jarred Hudson, Dustin James, Francisco "Pancho" Maya, Edward Mickelson, Alex Morgan, Adam Rawlett, Lionel Saudan, David Skyler, Jason Stephenson and Michael Stewart. Thank you all for your help, support and "Chemical Conversation".

The last person I would like to thank and acknowledge is my advisor and mentor James Tour. It has been a long and sometimes difficult relationship between the two of us, but I thank you for never giving up on me. I only hope that I can accomplish a small amount of success and wisdom that you have achieved throughout your life. I thank you for your no "BS" attitude and willingness to accept only the best from your students. I am forever indebted to you and the degree that you have bestowed on me.

At this time I would like to acknowledge some very important people in my life that have been through this with me and made all of this possible.

I would like to thank my family and in particular my mother and father, Joanne and Kenneth Jurs. I thank you for the love, help and support over the years. The importance of school was something that you have instilled in me since I can remember. You have always been there for me in everything I do, and I am glad to have had your guidance over the years.

The values that you have taught me have made me the man I am. Also, your attitude that I can do anything that I put my mind to has made this possible. I would also like to acknowledge the rest of my family that have been there for me, including my grandparents, Violet and Ernest Jurs and my sister Amy Jurs. I would like to thank you for all of your love and support over the years. It would not have been possible without it.

Another important person who was there every day over the last five years is my wife Monica. I would like to thank you for the love and support you have given me throughout these last five years of graduate school. My graduate career has been a difficult ride at times, and it has been your voice, compassion and love that have seen me through this to the end. I am glad that we have made the journey together and I look forward to enjoying the rest of my life with you. "My love to you always."

In addition, there are some important friends and family in my life that have also supported me through the years and I would like to thank you for your friendship and support: Gregory and Meredith Bornstein, Eugene Byrnes, Marcus Hayes, Helen Krieble, Ryan Luscatova, Ram and Sashi Prabhu, Albert and Janis Sapia, Peter and Cindy Walsh, Erik White, Jim and Carrie White, David Whitston, Matthew Zabrosky. I would like to give a special thank you to the Vernon K. Krieble Foundation for their belief in me and for support in my undergraduate studies. In addition as not to forget anyone else, I would like to thank everyone who has made some impact on my life.

TABLE OF CONTENTS

EXECUTIVE SUMMARY

Novel flame-retardant chemical additives and polymers were synthesized and their flammability measured. Self-extinguishing compositions were obtained for poly (acrylonitrile-butadiene-styrene) and high-impact polystyrene by adding as little as 10 weight percent of boronic acid derivatives or halogen-containing bisphenylethenes (BPH). Self-extinguishing compositions were obtained for polyethylene by adding as little as 10 weight percent BPH. The efficacy of BPH additives as flame-retardants suggested incorporating these moieties directly into the polymer to further reduce flammability. Consequently, polymers and copolymers were synthesized having BPH backbone and pendant groups, including backbone copolymers containing acetylene and phosphineoxide. The thermal combustion properties of polymers containing a BPH backbone or pendant groups were measured by microscale combustion calorimetry and found to be among the lowest values ever recorded, suggesting that aircraft cabin materials made from these polymers would be ultra-fire resistant.

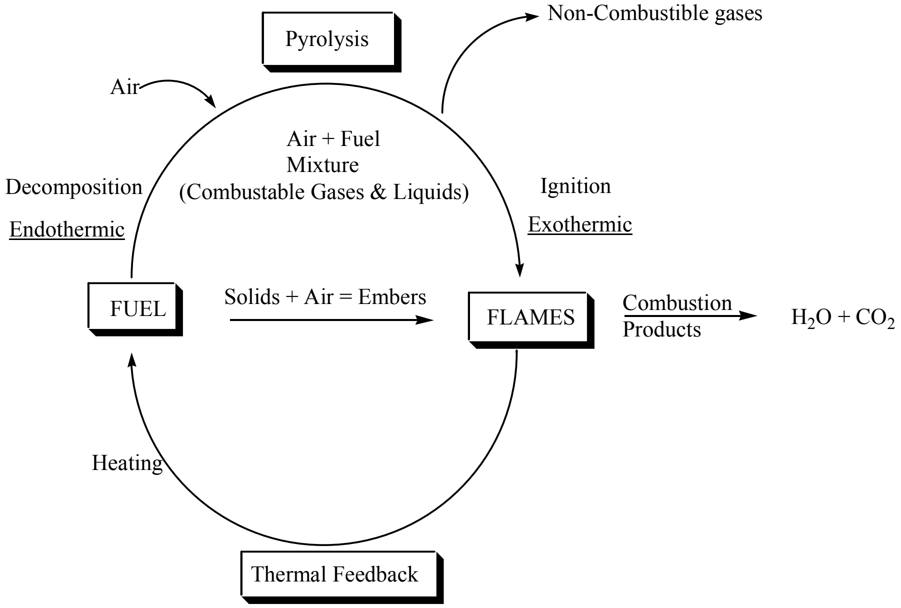
Introduction to Fire and Flame Retardants

There is an old saying that goes, "never scream 'fire' in a crowded theater." The reason for this is that the word 'fire' has been known for centuries to cause fear and panic amongst people who have witnessed its destructive power. Some of the worst tragedies on record have been caused by the devastating power of fire. In spite of its destructive nature, the energy and power given off in a fire, also known as the combustion process, have been used and harnessed by mankind since the first meal was cooked in a fire pit. The chemistry of the combustion process, or more correctly the combustion cycle, has been well studied. The reason we have electricity, heat, and automobiles is due to the extensive research and knowledge into how the combustion cycle can be used for energy.

Combustion Cycle

In order to discuss the combustion cycle, it is important to mention that there are two distinct flames: 1. premixed flame where gas and fuel source are kept constant (i.e. oxygen acetylene torch) and 2. diffusion flame where the oxygen diffuses into the fuel mixture from the surrounding atmosphere (i.e. candle).[1] The burning or combustion process of any type of fuel source, either wood or polymer constitutes a cycle with three steps that need to occur in this order: 1. heating of the fuel source. 2. decomposition of the fuel source into combustible and non-combustible materials. 3. ignition of the combustible fuel and air mixture to produce a flame.[1] The decomposition of the fuel source, i.e. breaking the chemical bonds into high energy free radicals, is initially done by an external ignition source that starts the cycle. Once the combustion process is started and the fuel/air mixture remains constant, the heat generated by the exothermic ignition of the fuel is enough to keep the combustion cycle going (Figure 1).

Figure 1



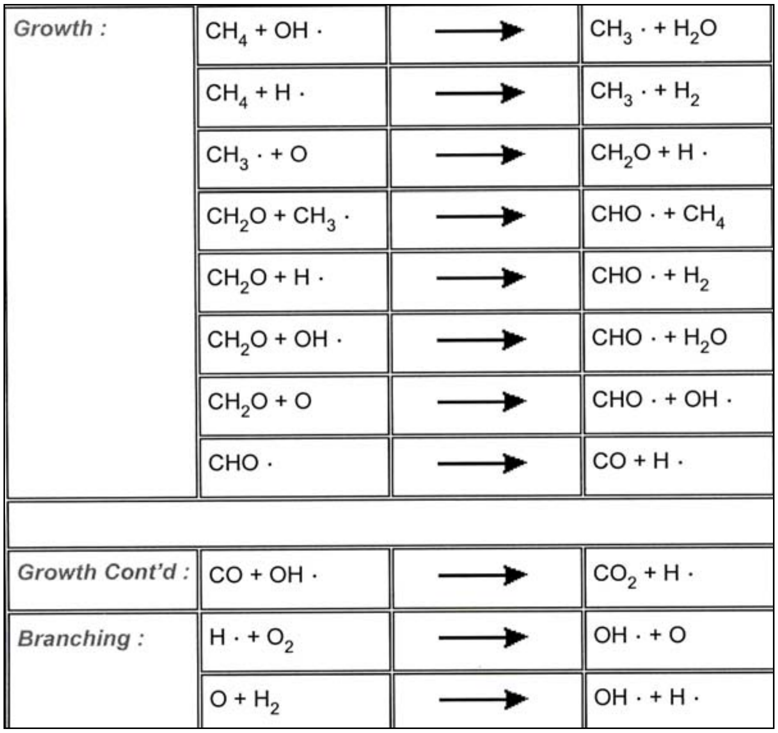
The mass transfer of the fuel/air mixture into the pyrolysis zone and energy transfer back to the fuel source are crucial to sustain the combustion cycle. The fuel source and oxygen diffuse to the flame as a result of temperature and concentration gradients caused by the flame.[1] The energy transfers to the fuel source (condensed phase) by thermal conduction through the solid fuel. Radiant heat from the flame decomposes the fuel into high energy free radicals.[1] This flame combustion process takes place only in the gas phase (vapor phase).[1]

Combustion Chemistry

It is important to discuss the chemistry of the combustion process and what occurs in the both the condensed and vapor phases. It is through the understanding of the chemistry in these two phases that helps us design and develop ways to extinguish a fire and hence stop the combustion cycle. The chemistry of combustion process is well-studied, but the exact mechanism of producing some of the products is still not completely understood. The decomposition process of a simple organic molecule such as methane is known to involve a free radical mechanism. When methane combined with oxygen is burned in a flame, the final products are carbon dioxide water, and heat. The free radical process to form these two byproducts is quite extensive. (Figure 2).

Figure 2

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{Heat}$$



Growth :	$CH_4 + OH\cdot$	→	$CH_3\cdot + H_2O$
	$CH_4 + H\cdot$	→	$CH_3\cdot + H_2$
	$CH_3\cdot + O$	→	$CH_2O + H\cdot$
	$CH_2O + CH_3\cdot$	→	$CHO\cdot + CH_4$
	$CH_2O + H\cdot$	→	$CHO\cdot + H_2$
	$CH_2O + OH\cdot$	→	$CHO\cdot + H_2O$
	$CH_2O + O$	→	$CHO\cdot + OH\cdot$
	$CHO\cdot$	→	$CO + H\cdot$
Growth Cont'd :	$CO + OH\cdot$	→	$CO_2 + H\cdot$
Branching :	$H\cdot + O_2$	→	$OH\cdot + O$
	$O + H_2$	→	$OH\cdot + H\cdot$

Troitzsch, J.; International Plastics Flammability Handbook, 2nd ed. New York; Hanser Publishers 1990. p 18.

Figure 2 shows that the combustion of a simple hydrocarbon such as methane has intricate steps. The OH· and H· radicals that form from the chain branching steps are considered high energy species that contribute their energy, sometimes explosively, to the flame.[1] The formation of water ($\Delta_f H$ = -57.75 kJ/mol; ΔG = -56.69 kcal/mol) and carbon dioxide ($\Delta_f H$ = -93.99 kcal/mol; ΔG = -94.254 kcal/mol) are exothermic reactions that feed energy back into the system.[2] This energy leads to further breakdown of the fuel source to continue the combustion cycle.

Flame Retardant-Background

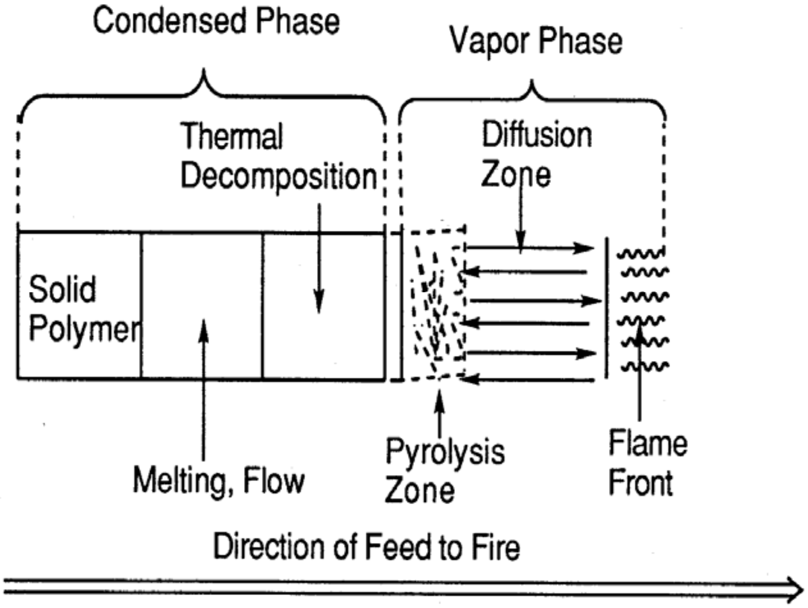
Flame retardants and methods for making flammable materials resistant to fires have been around since the beginning of recorded history. Vinegar and Alum (potassium aluminum sulfate $KAl(SO_4)_2{\cdot}12H_2O$ or an ammonium aluminum sulfate $NH_4Al(SO_4)_2{\cdot}12H_2O$) were used as paints or coatings for wood to help impart some flame resistance. Over time, different types of clays, gypsum, borax, and asbestos have been used to make canvas and clothing impervious to flames. Inorganic salts and materials have been the staple of flame retardants and are still used today.

It was not until the early part of the 20th century that William Henry Perkins[1] developed the ground work for the flame retardant theory. He was the first person to study the mechanism of flame retardancy on wood, cotton, paper and plastics.[1] Inorganic salts, acids and clays were the main ingredients of his flame retardant mixtures. World War II was another dominant milestone in the creation of flame retardants. Troops slept in canvas tents made flame retardant and waterproof by the use of chlorinated paraffin, antimony oxide and a binding agent.[3] In the 1950's, the polymer industry was starting to grow into a big market. During this period the majority of commodity plastics (e.g. polystyrene, polyurethane, polyethylene) were developed on a widespread and economically favorable scale and were preferred over other materials such as wood and metal alloys. It was not until the mid-1960s before the government created federal laws to mandate that plastics be made less flammable. The government also established guidelines for fire safe materials in fabrics and transportation materials, particularly airplanes.[3] To satisfy the laws, the development of flame retardants became a multibillion dollar industry.

Combustion Process

In order to stop materials, and in particular plastics, from burning, the combustion cycle has to be stopped. When a polymer breaks down there are many pathways in which the polymer can decompose or “unzip” to form the high energy free radicals. There have been numerous strategies for combating the fire chemically and physically in both the vapor phase and condensed phase. Figure 3 illustrates that a burning piece of plastic has two distinct phases: a vapor phase and a condensed phase.[4] In the condensed phase, two methods were utilized to stop the combustion: formation of char, which adds a protective layer between the flame front and the polymer fuel, and dilution of solid fuel with inorganic fillers that decompose to dilute the flame.[1]

Figure 3



Stevens, M.P.; *Polymer Chemistry: An Introduction*, 3rd ed.; Oxford University Press: Oxford, 1999.

In the vapor phase, the combustion cycle can be stopped by physically diluting the flame with non-combustible gases and chemically capping the high energy free radicals with halogens.[1] Attacking the flame in both the condensed and vapor phase has historically proven to be the best strategy in stopping a fire.

Flame retardant polymers can be divided into two distinct classes: additives and inherently flame retardant polymers. The additives, as the name implies, are various organic and/or inorganic compounds that are added to commercial polymers in conjunction with a synergist to make a flammable polymer, such as ABS (acrylonitrile-butadiene-styrene) or polystyrene, flame retardant. Additives make up the majority of the flame retardant market due to lower costs for processing these commodity materials into flame retardant polymers. Additives work well for most flame retardant applications but they also have a few drawbacks. Flame retardant additives leach out of the plastics over time, making the polymer less flame resistant and polluting the environment. Another drawback to the approach of using flame retardants additives is their tendency to degrade the physical properties such as tensile strength or impact resistance of the native polymer.

Inherently flame retardant plastics are more complicated since these polymers have flame resistant moieties incorporated either in the backbone of the polymer or as a pendant group. Flame retardant polymers represent a smaller class of compounds usually referred to as high-resistant engineering plastics. They tend to be expensive due to the high cost of processing these materials and their smaller sales volumes. These polymers are usually found in specialty applications where cost is not as important a factor.

Flame Retardant Additives

The most successful flame retardant additives on the market today are halogenated flame retardant additives. These compounds are used in conjunction with a synergist to help increase flame retardancy with lower loadings. The halogenated flame retardant retard the flame efficiently by acting quickly as a radical trap. The halogen radicals, in particular chlorine and bromine, catalytically stop the fire by capping the high energy free radicals HO· and H· in the vapor phase, therefore stopping the combustion cycle and extinguishing the flame (Figure 4).[1]

Figure 4

$$H\bullet + HX \rightarrow H_2 + X\bullet$$

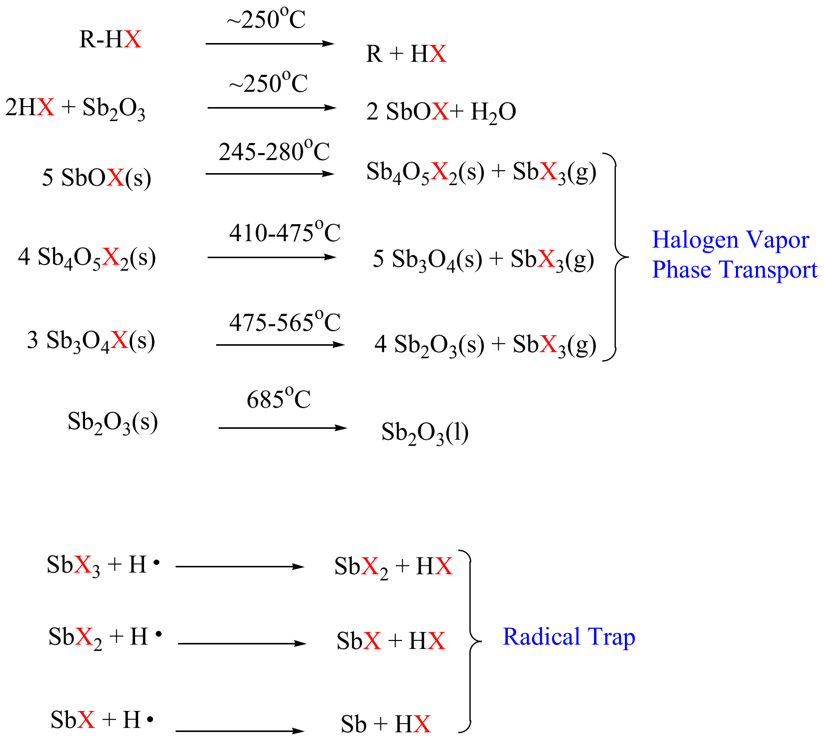
$$HO\bullet + HX \rightarrow X\bullet + H_2O$$

$$X\bullet + RH \rightarrow HX + R\bullet$$

$$X = Cl \text{ or } Br$$

In addition, these halogen radicals dilute the flame with a non-flammable gas such as HBr or HCl while creating a protective layer on the condensed phase to stop further combustion of the polymer.[1] Bromine and chlorine are two reactive halogens that have worked well for flame retardant purposes. Organofluorine compounds have not been as effective because its bond energy is so high that energy needed to break the carbon fluorine bond is not produced at the temperature at which these halogenated flame retardants work.[3] Conversely, the iodine-carbon bond is so weak that it is easily cleaved by light, and can leach out of the plastics, therefore making it unusable for this application.[3] The halogen radicals themselves work effectively as a flame retardants enhanced by the addition of a synergist, in particular antimony oxide (Sb_2O_3). The synergist acts to improve the activity of the additive in the polymer, thus lowering the amount of halogenated additive needed. Antimony oxide acts as a halogen shuttle bringing SbX_3 into the vapor phase (Figure 5).[1,3]

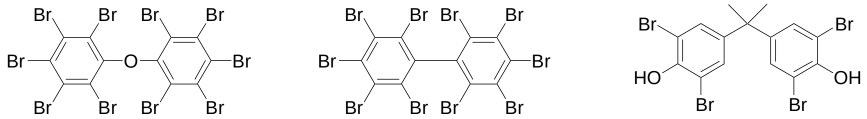
Figure 5



Khanna, Y. P., Pearce, E. M., Synergism and Flame Retardancy, Vol. 2. New York; Plenum Press 1978. p. 110.

Halogen containing flame retardants have developed into a billion dollar per year enterprise, keeping plastics safe from combustion. The majority of these halogenated additives are similar poly brominated biphenyls (PBB) as seen in figure 6**,** have long been used in commercial polymers to impart flame retardancy.

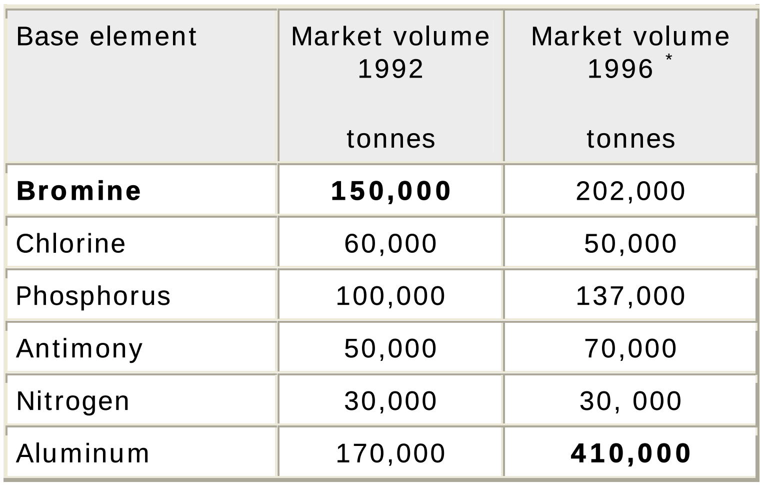
Figure 6



Decabromodiphenlyether (DBDE) Decabromobipheyl (DBB) Tetrabromobisphenol A (TBBPA)

Halogenated compounds can have negative environmental and toxicological impacts which have deterred many countries from using them in commercial products.[5] The European Union is trying to remove halogenated compounds from all plastics due to environmental concerns. Leaching additives can end up in drinking water. Additionally, halogenated organic compounds are considered Persistent Organic Pollutants (POPs) which are not easily broken down or oxidized by the environment. Another problem is the use of antimony oxide, which carries with it heavy metal concerns and it is a possible link to Sudden Infant Death Syndrome (SIDS).[6] Figure 7 shows world consumption of classes of flame retardants with the brominated class of flame retardants having the highest consumption in 1992. Aluminum containing flame retardant materials overtook brominated flame retardant materials in 1996, possibly due to the formerly discussed environmental concerns.

Figure 7



Base element	Market volume 1992 tonnes	Market volume 1996 * tonnes
Bromine	**150,000**	202,000
Chlorine	60,000	50,000
Phosphorus	100,000	137,000
Antimony	50,000	70,000
Nitrogen	30,000	30, 000
Aluminum	170,000	**410,000**

Other	50,000	55,000
Total	610,000	924,000

* Includes USA, W.Europe, Asia

Source: http://www.mst.dk/udgiv/Publications/1999/87-7909-416-3/html/kap01_eng.htm#kap1.3

Inorganic flame retardants make up a large part of the market encompassing various aluminum, nitrogen, phosphorous, and boron compounds. These widely used low cost materials have been around for centuries, proven to be effective flame retardants in fibers in clothing and fillers for textiles. The majority of these inorganic flame retardants work by diluting both the condensed and vapor phase of the polymer with non-flammable salts, acids and by-products such as water and alumina (Al_2O_3).[1] The synergistic effect of phosphorous and nitrogen has been proven to be an effective method for flame retarding cellulose materials.[3] Nitrogen decomposes in the vapor phase to form non-flammable gases such as HNO_2 and HNO_3 and also prevents the phosphorous compounds from being pyrolyzed in the vapor phase.[1] Phosphorous acts to dehydrate the cellulose to form a layer of non-flammable phosphoric acid which forms char that insulates the condensed phase.[1] Phosphorous has also been used as a component in the formulation of intumescent flame retardant materials. When intumescent flame retardants are subjected to a flame, they foam up by producing non-volatile gases and a flame resistant coating to protect the surface.[1,3] Intumescent flame retardant materials are used as coatings for wood and metal products where fire resistance is needed.

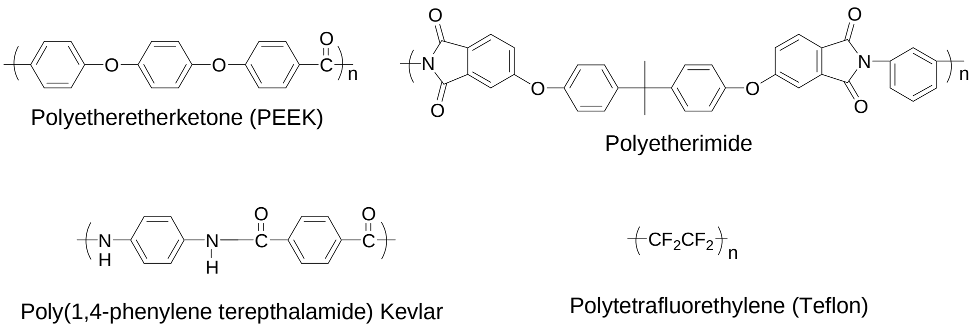
In addition to the flame retardant compounds mentioned above, several other inorganic compounds have been tried over the years, but have limited use in specialty applications. Flame retardant additives make up the majority of the flame retardant compounds sold. Little needs to be done or altered to a polymer production line when it comes to adding these flame retardant additives making them an attractive option. Commercial polymers, such as polystyrene or polyethylene, are continuous batch processes that require the addition of fillers and plasticizers to make the final product. Introduction of a flame retardant additive to a polymer processing line requires minor production modification. To produce specialty flame retardant polymers that require rigorous or high temperature production methods entails altering an expensive production line or even developing a new production line. Cost concerns will always be the deciding factor for determining the success of any product.

Flame Retardant Polymers

The market for flame retardant polymers is considerably smaller than for additives. Most of the products that fit the criteria for being a flame retardant polymer are usually marketed as heat-resistant materials, meaning these polymers do not burn but rather decompose at elevated temperatures. There are five main principles that have to be considered while developing heat resistant polymers.[7] 1. Compounds with strong covalent bonds should be used. 2. There should be no easy pathway for the molecular rearrangements. 3. Resonance stabilization of aromatic polymer rings should be used to maximize the bonding energy. 4. All of the rings in the structure should have normal bond angles, i.e. no bond strain or weak points. 5. Multiple bonding to several centers should be utilized, i.e. ladder polymer would be the most stable.[7] These are idealized goals for heat resistant polymers and no material utilizes all of these qualities to their maximum efficiency. Rather, they are guidelines to be used when designing a polymer. In reviewing the several types of polymer made with these heat-resistant properties, key observations can be made about what makes a good material. Polymer chains that use para-linkages between rings have shown to be the most stable, unfortunately this also results in poor processibility and insolubility in most solvents.[7] Adding aliphatic branching only provides additional fuel for a fire and makes the polymer more prone to oxidation.[7] Flexible linker groups that have worked the best and have negligible impact on the polymer's stability include: -CO-, -COO-, -CONH-, -S-, -SO_2-, -O-, -[CF_2]-, -[$C(CF_3)_2$]-.[7]

There have been many polymers that have been developed over the years as heat-resistant or flame retardant polymers, but few have ever achieved commercial success. A few polymers have emerged as economically feasible, most notably Kevlar, polyether imides, polyetheretherketone (PEEK), and Teflon (Figure 8).

Figure 8



Polyetheretherketone (PEEK)

Polyetherimide

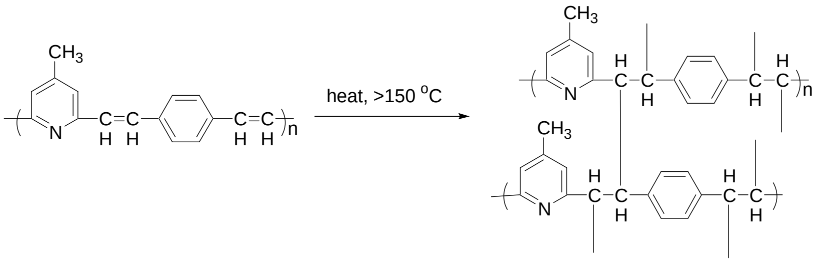
Poly(1,4-phenylene terepthalamide) Kevlar

Polytetrafluorethylene (Teflon)

Polymers such as Kevlar and Teflon are common place in today's market but still command a high price tag due to the cost of making them and their low sales volume. While these materials are non-combustible, they are not flame extinguishing. The decomposition byproducts from these types of polymers are important indicators as to how well they will perform when exposed to a flame. Some of these byproducts are quite harmful and toxic. The decomposition of Teflon in air, under 650 °C produces carbonyl difluoride ($O=CF_2$), carbon monoxide and carbon dioxide. It is these non-flammable decomposition products that help impart heat-resistance and in some cases flame retardancy.

Another important feature in some of these polymers is having unsaturation in the polymer backbone or various leaving groups, which will crosslink in a fire to form char, i.e. poly (styryl pyridine) or PSP (Figure 9).

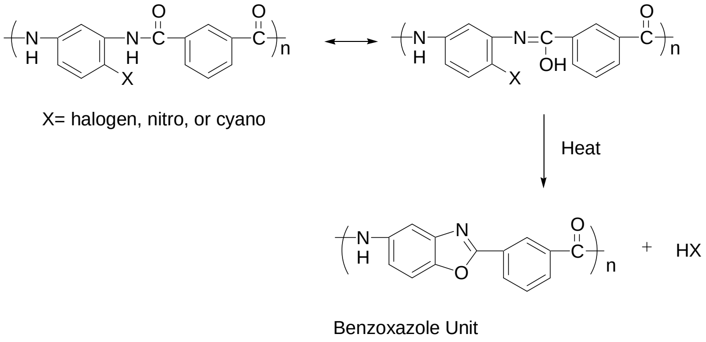
Figure 9



Critchley, J.P., Knight, G. J., Wright, W. W., Heat-Resistant Polymers, New York, Plenum Press, 1983, pg. 74.

The final way in which these polymers can form char during the burning process is to form additional rings either by Claisen-Cope or Diels Alder rearrangement. The following polyamide, similar to Dupont's Nomex, forms a more stable benzoxazole structure on heating (Figure 10).[5]

Figure 10



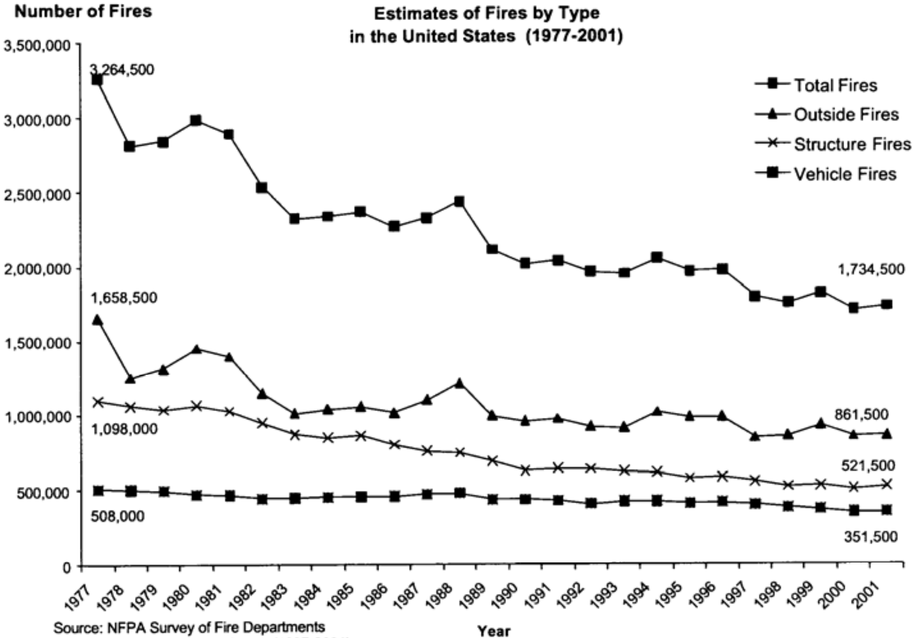
Pearce,E. M., Weil, E. D., Barnov. *Fire and Polymers Materials and Solutions for Hazard Prevention*; ACS Symposium Series: 797: Washington D.C., 2001.

Heat-resistant polymers are a growing market. These products are becoming more common every day. Research in this area is ongoing and the goal of a low cost, easily processible, flame retardant polymer is well within reach.

Fire Statistics

The National Fire Protection Association (NFPA)'s 2001 annual report on fire statistics reports 1,734,500 fires were responded to by public fire departments.[8] Vehicles fires (cars, airplanes, trains, etc...) were 351,500 of these incidents.[8] The property loss is immense with any kind of structure fire and in 2001 resulted in $8.9 billion of damage (an additional amount of $33.4 billion has been attributed to the events of 9/11/01)[8] The civilian loss due to fire was 6,196 fatalities (2,452 are a result of 9/11/01) and 21,000 casualties (800 are a result of 9/11/01). This is a significant number and one of the main reasons government agencies want to reduce the amount of fires and casualties that are a result of burning or combustible materials. In figure 11, it can be seen that the number of fires is decreasing over the years due to better fire safe materials, better public awareness and tighter regulations building and construction materials.

Figure 11



Estimates of Fires by Type in the United States (1977-2001)

Source: NFPA Survey of Fire Departments for U.S. Fire Experience, (1997-2001)

Fire Loss In the U.S., 11/02 4 NFPA Fire Analysis and Research, Quincy, MA

Conclusion

The field of flame retardants is a constantly developing area that encompasses a multitude of regulations and fire codes with volumes of government and local city ordinances that deal with hundreds of regulations and fire safety procedures. Using the tools of chemistry and physics we continue to allow these codes and regulations to be improved to make houses, materials, and vehicles safer every year.

It is my hope that the following thesis will contribute a small part to this ever growing field of flame retardant polymers. Using all the background information and data from the literature and various groups, I have developed several flame retardant additives and polymers that I hope will make an impact on the flame retardant polymer market. There have been many goals throughout my graduate career, but the most important objective is and has always been to save lives.

References

(1) Troitzsch, J. *International Plastics Flammability Handbook*; 2nd Ed. ed.; Hanser Publishing: New York, 1990.

(2) Lide, D. R. In *Handbook of Chemistry and Physics*; 71 ed.; Lide, D. R., Ed.; CRC Press Inc.: Boca Raton, 1991.

(3) Lyons, J. W. *The Chemistry and Uses of Fire Retardants*; John Wiley and Sons Inc.: New York, 1970.

(4) Stevens, M. P. *Polymer Chemistry: An Introduction*; Oxford University Press: Oxford. New York, 1999.

(5) Pearce, E. M.; Weil, E. D.; Barinov, V. Y. In *Fire and Polymers Materials and Solutions for Hazard Prevention*; Nelson, G. L., Wilkie, C. A., Eds.; American Chemical Society.: Washington D.C., 2001.

(6) Cullen, A.; Kiberd, B.; Devaney, D.; Gillan, J.; Kelehan, P.; Matthews, T. G.; Mayne, P.; Murphy, N.; O'Regan, M.; Shannon, W.; Thorton, L. *Arch Dis Child* 2000, *82*, 244-247.

(7) Critchley, J. P.; Knight, G. J.; Wright, W. W. *Heat-Resistant Polymers*; Plenum Press: New York, 1986.

(8) Karter, M. J. "Fire Loss in the United States During 2001," National Fire Protection Association, 2002.

Chapter 1

Novel Flame Retardant Additives

Boronic Acid Flame Retarding Polymer Additives

1.1 Introduction- Boronic Acid Flame Retarding Polymer Additives

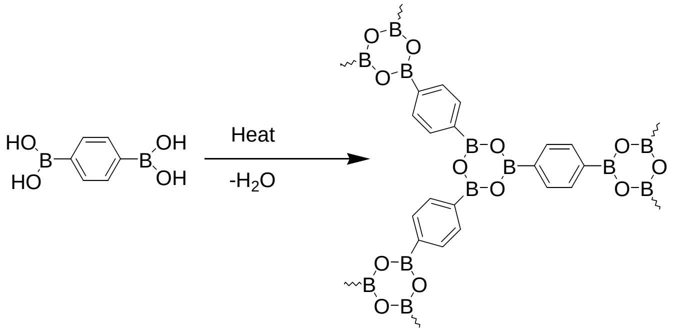
The development of synthetic polymers and plastics in the twentieth century has created a giant and growing industry. Due to their low cost, ease of manufacturing, and physical properties they have taken over where other materials such as wood and steel have become outdated. Furthermore, new products have emerged that could not have been fabricated from any other material, such as aircraft engine parts, seals, and reentry panels for the shuttle.

Polymers are commonly made from highly flammable hydrocarbons that burn quite readily upon ignition. Hence, making polymers resistant to burning is of great importance to their safe use in today's society. One way to make polymers flame retardant is by blending in additives. The development of flame retarding additives has been a subject of serious investigation for many years. Companies such as Great Lakes, Inc. and Albemarle, Inc. have done a great deal of research in the development of flame retardants. Our work has been to synthesize and test new flame retarding additives that could be used by industry to make flammable polymers flame resistant, and in some cases even stop a fire that is already burning.

Flame retardancy can be achieved using any of three different approaches: (1) causing "char" formation in the pyrolysis zone, (2) adding material that decomposes to produce nonflammable gases or endothermically cools the pyrolysis zone, and (3) prohibiting the combustion process in the vapor phase.[1] Many flame retardants have been developed to combat the thermal break down of polymers. The combustion of polymers has been shown to take place by a free radical process with several distinct steps. It is these free radicals that aid combustion in both the pyrolysis zone and vapor phase.[2] When used with antimony oxide, halogenated flame retarding additives have been shown to be good radical traps, thus stopping free radical production in the pyrolysis zone and quenching the combustion of the "polymer fuel". The halogenated additives also help in making the free radicals less active in the vapor phase.[2] One of the problems with halogenated and inorganic flame retarding additives is that the smoke generated during the burning is more toxic, due to the halogenated and heavy metal additives.

The goal of this project is to develop novel ways of producing flame retardant polymer additives that are less hazardous when burned. The use of boron materials has been investigated by Morgan *et al.* It is believed that during combustion boronates undergo crosslinking to form a boronate glass and produce char that inhibits flame growth in the pyrolysis zone(figure 1).[3,4]

Figure 1



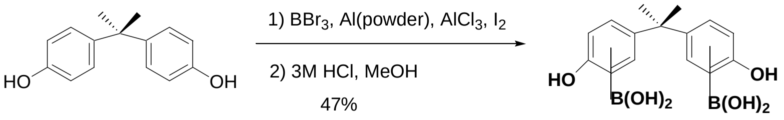
Morgan, A.B. Doctoral Dissertation, Univ. of South Carolina, 1998.

The boronate glass network also acts as a thermal insulator to protect the remaining unburned plastic from thermal degradation.[3,4] The main goal of Morgan's flame retardant research was to use available halogenated raw materials to synthesize new boron flame retardants. It was assumed that the use of available materials would make the resulting products more commercially viable. We therefore designed synthesis of monomers containing boronic acid moieties to extend Morgan's approach.

1.2 Results and Discussion- Boronic Acid Flame Retarding Polymer Additives

The synthesis of the diboronic bisphenol A (**1**) was performed using a modified version of the traditional Friedel-Crafts alkylation.[5] We used neat boron tribromide (BBr_3) to produce a direct boronation of the aromatic rings, since Morgan observed that using BBr_3 in dichlorobenzene does not yield the desired product. After the boronation of bisphenol A, the reaction mixture was treated with 3M HCl to form the boronic acid **1** **(**Reaction 1).

Reaction 1

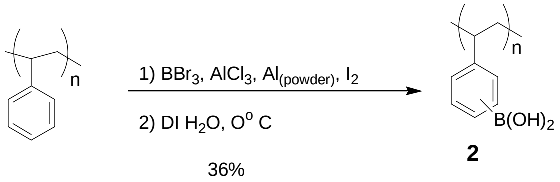


1

The highly reactive nature of the BBr_3 gives rise to possible side reactions, such as bromonation or decomposition of the bisphenol A moiety. The product was blended into ABS (Acrylonitrile co-Butadiene, co-Styrene) and summarized in Table 1.

The boronation of low molecular weight polystyrene (Polyscience low M_w polystyrene, 800-5000 M_w; Lot # 461855) was the next approach. The first step was as above, a direct boronation of the polystyrene in neat boron tribromide to make a boronic acid polystyrene **2** (Reaction 2).

Reaction 2

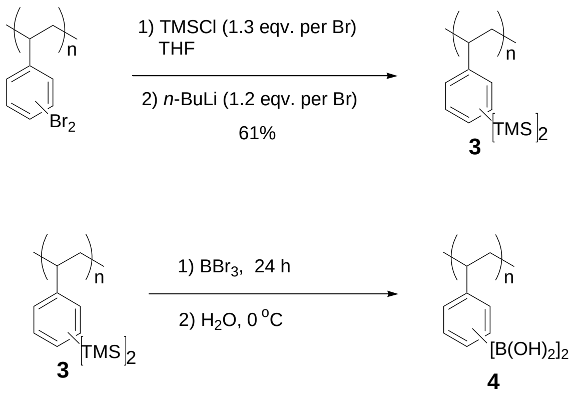


2

The poor solubility of **2** in most common solvents limited the characterization of this product. The boronic acid functional groups may have increased the water solubility of the product such that it becomes water soluble, making the isolation difficult.

A different synthetic path to the product was designed to afford the boronated polystyrene. Dibromopolystyrene was subjected to lithium halogen exchange conditions and capped with trimethylsilyl group. Trimethylsilyl chloride (TMSCl) was added first so that an excess of TMSCl would be present when *n*-butyllithium was added dropwise. As the rapid lithium-halogen exchange took place, it was expected that TMSCl would quench the reaction immediately to give the desired silylated polystyrene **3** (Reaction 3 and 4). The next step was to take **3** and convert the two TMS groups into boronic acid functional groups to make a diboronic acid polystyrene **4** (Reaction 3 and 4).[6]

Reaction 3 and 4

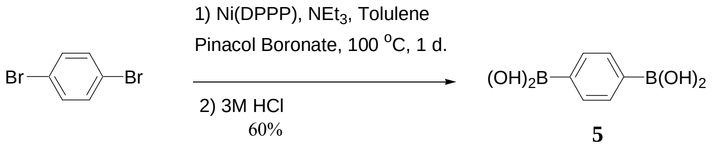


The excessive yield in the second reaction is due to the production of boric acid from the excess boron tribromide. The poor solubility of **4** in organic solvents made the purification from the boric acid quite difficult. Likewise, characterization of **4** is also difficult. The burn results for these polymers are summarized in Table 1.

The next thrust of my research was two-fold. First, Morgan discovered that the use of 1,4-benzene diboronic acid as an additive in polycarbonate gave a V-0 rating (0.1 wt % PTFE, 5 wt % 1,4-benzene diboronic acid). Morgan found that using the 1,4-benzene diboronic acid in ABS produced long burn times, with very high char formation. These high char yields are important because it shows that the 1,4-benzenediboronic does crosslink in ABS but does not act as an adequate flame retardant. My work focused on the use of Cloisite® clays as a synergist with **5** to help extinguish the flame in ABS. The problem with these clays is that they have poor melt blendability. The burn results for these polymer and clay mixtures are summarized in Table 1.

The second part of my boronate work focused on obtaining physical characteristics of **5** including thermal analysis, elemental analysis, and X-ray powder diffraction data since we discovered a novel synthetic route to making 1,4-benzenediboronic acid using Ni-catalyzed cross coupling step (Reaction 5).[3,4]

Reaction 5



The burn results for the boronic acid additives are summarized in Table 1.

Table 1. HVUL-94 Burn Results.

Additive	First Ignition[a] (sec)	Observed Dripping[b]	Second Ignition[a] (sec)	Observed Dripping[b]	UL-94 Rating
10 wt% **1**, ABS	385, 352	No, No	<1[d], <1[d]	No, No	?, ?
10 wt% **2**, 1wt% PTFE, ABS	312, 350	Yes, Yes	<1[d],<1[d]	No, No	?, ?
10wt% **4**;1wt% PTFE; ABS	292, 248	Yes, Yes[c]	<1[d],<1[d]	No, No	?, ?
10 wt% **5**; 10 wt% Cloisite 6A, ABS	351, 357	No, No	<1[d], <1[d]	No, No	?, ?
10wt% **5**; Cloisite 10A, 5wt%; 1wt% PTFE; ABS	372, 374	No, No	<1[d],<1[d]	No, No	?, ?
10wt% **5**; Cloisite 15A, 5wt%; 1wt% PTFE; ABS	302, 256	No, No	<1[d],<1[d]	No, No	?, ?
10wt% **5**; Cloisite 20A, 5wt%; 1wt% PTFE; ABS	314, 314	No, No	7, 8	No, No	?, ?

10wt% **5**; Cloisite 25A, 5w%; 1wt% PTFE; ABS	269, 307	No, No	9, 5	No, No	?, ?
10wt% **5**; Melamine, 10wt%; 1wt% PTFE; ABS	384, 373	Yes, No	<1[d],<1[d]	No, No	?, ?
10wt% **5**; Polyvinyl Alcohol, 10wt%; PTFE, 10wt%; ABS	300	No	<1[d]	No	?, ?
10wt% **5**; Cloisite 30B, 5wt%; PTFE, 1wt%; ABS	361, 364	No, No	3, <1[d]	No, No	?, ?
10wt% **5**; 10wt% Polyacrylic Acid, 10wt% PTFE ; ABS	248	No	<1[d]	No	?
10wt% **5**; Sb2O3, 5wt%; PTFE, 1wt%; ABS	93, 236	Yes[c], Yes[c]	<1[d],<1[d]	No, No	?, ?
10wt% **5**; ABS, 30wt%; PTFE, 0.1wt%; PC	100, 25	Yes[c], Yes[c]	<1[d], 14	No, No	?,?

a Time to self-extinguishing in seconds after 1st, 2nd, 3rd 10 sec ignition. **b** Indicates that molten ABS did (Y) or did not (N) drip on to cotton patch underneath ignited bar during UL-94 test. **c** Indicates ignition of cotton patch underneath ignited bar of plastic. **d** Indicates time that only glowing, not flame occurred after re-application of flame. X indicates not enough bar remaining for 2nd ignition. * Wt % based on halogen content

The boronic acids did not show flame retardant properties in ABS, but resulted in extended burn times. The extended burn times are a result of high char formation in these polymer blends. Even with the addition of the different clays a V-0 result was not achieved. As a result of the data we obtained from these polymer blends, we did not pursue boron flame retardant additives.

1.3 Experimental

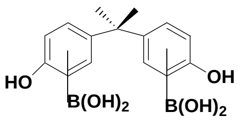
General Procedures: All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Silica TLC plates were 250 μm thick, 40 F254 grade from EM

Science. Silica gel was grade 60 (230-400 mesh) from EM Science. ^{1}H NMR spectra were observed at 400 MHz and ^{13}C NMR spectra were observed at 100 MHz on a Brüker Avance 400 spectrometer. ^{1}H chemical shifts (δ) are reported in ppm downfield from tetramethysilane. IR spectra were obtained on a Nicolet Avatar 360 FTIR. Gas chromatography experiments were performed on a Hewlett-Packard GC model 5890A. Thermal gravimetric analysis (TGA) was performed with a Perkin Elmer TGA7 from 30 - 900 °C at 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) was performed with a Perkin Elmer DSC7 using a 30 - 450 °C scanning window at 10 °C/min. under nitrogen. Polymer blending/extrusion were done with a Custom Scientific Instruments CSI-183MMX Mini-Max Blender/Extruder or with a Brabender Prep-Center using a type 6/2 mixer head. An Atlas Electric HVUL-94 flame test station was used for the UL-94 flame tests. Melting points were obtained using a Büchi melting point apparatus. Reagent grade tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. Dry benzene, toluene, methylene chloride, and triethylamine were distilled over calcium hydride and under nitrogen. Unless otherwise stated, all other reagents were used as received. Mass spectrometry work was obtained from the Rice University Mass Spectrometry Laboratory.

General Procedure for Blending Boron Containing Flame Retardant Additives and Plastic (ABS or PC) in Brabender 30 ml Type 6/2 Mixing bowl – Prep Center.[7] The additive and plastic were weighed out in their respective amounts according to the wt % of additive: 25.41g batch (PC), 22.05 g batch (ABS). Heating temperatures for the blending bowl varied depending on the material involved. The processing temperatures used during the blending were: ABS 225 °C. PC: 270 °C. After the bowl had been heated to the necessary processing temperature, the sample was poured quickly through the top opening of the Brabender while the blades were rotating at 50 RPM. The opening was then closed with the weighted handles and the sample was blended according to the type of flame retardant added. If a melt-blendable additive was used, the plastic and additives were blended for 10 min at 100 RPM. If a non-melt blendable additive was used, the plastic and additive were blended for 10-30 min at 150 RPM. If fibrillare PTFE (Dupont PTFE 30, 60 % PTFE in an aqueous suspension; density = 1.3 g/mL) was used as an anti-drip additive, the resin and the PTFE[7] were blended first for 10 min at 150 RPM. The flame-retardant additives were added and the mixture was blended again for 10 min at 150 RPM. After the blending was complete and the blades were stopped, the bowl was opened and the molten blend was removed with a bronze spatula. The plastic was then further blended in the CSI-183MMX blender and extruded to give bars for the UL-94 test.

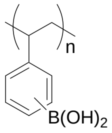
General Procedure for Extruding Plastic in the UL-94 Test Bars.[7] The cooled polymer blend removed from the Brabender mixing center was broken into smaller pieces and inserted into the heated cup of the CSI-183MMX blender until the cup was full. The plastic and additives were heated until molten and extruded into a heated 1/8” thick × ½” wide × 3” long rectangular bar mold. Heating temperatures for the blend cup and the extrusion mold varied depending on the material involved. The general processing temperature for the plastics used are as follows: mold temperature: 40-90 °C. PC: blending cup temperature: 270 ^{o}C, mold temperature 71-93 °C, ABS: blending cup temperature 225-230 °C.

General Procedure for the Modified HVUL-94 Burn Test.[7] Two 1/8” thick × ½” wide × 3” long plastic (polymer + additive) rectangular bars were used for this test. The setting on the methane tank pressure regulator was set to 23 psi. The pressure regulator on the HVUL-94 test station was set to 5 psi. The Bunsen Burner flame height was 125 mm, and the height from the top of the Bunsen Burner to the bottom of the test bar was 70 mm. All test bars underwent two trials, each trial consisting of moving the Bunsen Burner flame under the sample for 10 seconds, followed by flame removal. Self extinguishing times and dripping were recorded.



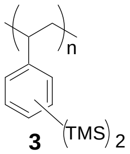
1

Diboronic Bisphenol A. (1).[7] To a 500 mL round bottom flask equipped with a stir bar and flushed with nitrogen was added Bisphenol A (5.25 g, 23 mmol), aluminum powder (6.21 g, 230 mmol), aluminum trichloride (0.821 g, 5.75 mmol), and iodine (trace). The flask was equipped with a West reflux condenser and sealed under nitrogen atmosphere with a rubber septum. Boron tribromide (21.74 mL, 230 mmol) was added via syringe drop-wise to the sealed flask. Bubbling was observed and the solution turned to a dark brown color. The reaction was heated to reflux at approximately 90 °C for 2 d. Upon completion of the reaction the dark brown solution was quenched with deionized water and ice at 0 °C. The resulting mixture was extracted three times with diethyl ether. The combined organic layers were dried with anhydrous magnesium sulfate and filtered through celite. The solution was then concentrated on the rotary evaporator and the residue was subjected to hydrolysis with methanol and 3M HCl. A dark brown powder was achieved in 47% yield after filtration. FTIR (KBr) 3210, 1385, 1297, 1150, 1128, 825, 759, 646. ^{1}H NMR(400MHz, CD_3OD) δ 7.56- 7.60 (m), 7.28 (m), 7.27 (m), 7.25 (m), 6.6-6.8 (m), 5.51 (m), 1.17-1.21 (m).



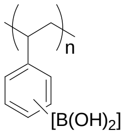
2

Styrene Boronic Acid (2).[7] To a 25 ml round bottom flask equipped with a stir bar and flushed with nitrogen was added polystyrene (219 mg, 2 mmol), aluminum powder (45 mg, 20mmol), aluminum trichloride (6.6 mg, 0.25 mmol), and iodine (trace). The flask was equipped with a West reflux condenser and sealed under nitrogen atmosphere, with a rubber septum. Boron tribromide (1.9 mL, 20 mmol) was added via syringe drop-wise to the sealed flask and condenser. Bubbling was observed and the mixture turned a dark reddish-brown color. The reaction was heated to reflux approximately 90 °C for 2 d. Upon completion of the reaction the dark brown mixture was poured into deionized water and ice at 0 °C. After the reaction was quenched with deionized water and ice, the mixture was stirred for 30 min. The slurry was then filtered through celite and the filter cake was rinsed with copious amounts of water (1500-1600 mL). The filter cake was then extracted with THF (5×), acetone (5×), and methylene chloride (5×). The combined organic filtrates were concentrated via a rotary evaporator to give a dark brown sticky residue. The residue was taken up in 400 ml of methylene chloride and the mixture was stirred overnight. The solution was then filtered through celite and the filter cake was rinsed with methylene chloride (3×). Solvent was removed from the combined filtrates using a rotary evaporator. The residue and then dried *in vacuo* for 24 h. The celite that still contained products was mixed with acetone the slurry was stirred for 6 h. The slurry was filtered through fresh celite to give a light brown filtrate. The filtrate was concentrated via the rotary evaporator and dried 24 h *in vacuo*. This second portion of the product was redissolved in acetone. The solution was stirred for 2 h and then filtered through a fritted funnel to obtain a white powder. The fritted funnel was put in the vacuum oven for 2 days at 60 °C. FTIR (KBr) 3215, 1377, 1188, 1108, 753, 702, 644. ^{1}H NMR(300MHz, CD_2Cl_2) δ 7.25 (s), 6.97-7.20 (bm), 3.80-3.88 (bm), 3.43-3.47 (bm), δ 3.74(s), 1.95 (bs), 1.72 (bs), 1.43 (s), 1.38 (s), 1.25 (s), .875-.967(bm).



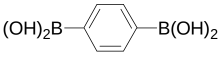
3

Poly(bistrimethylsilyl)styrene (3).[6] To a 1 L three neck round bottom flask, equipped with a mechanical stirrer and flushed with nitrogen was added dibromopolystyrene (5.28 g, 20 mmol). The reaction flask was sealed with a septum, evacuated, and backfilled with nitrogen (3×). Dry THF (500 mL) was added to the reaction flask via a cannula. Nitrogen purged, TMSCl (6.59 mL, 52 mmol) was added via syringe and the reaction mixture was cooled to –77 °C. n-butyllithium/hexane (30.3 mL/48 mmol) was added drop-wise, with a syringe pump. The solution was stirred overnight and allowed to warm to room temperature. The reaction was quenched with water and then diluted with methylene chloride. After separation of the aqueous layer, the organic layer was washed with brine (3×). The aqueous layers were combined and extracted with methylene chloride (3×). The organic layers were combined, dried with anhydrous magnesium sulfate, and filtered through celite. Solvent was then removed from the filtrate, via a rotary evaporation, and the sample was allowed to dry continuously *in vacuo* for 24 h. The solid was dissolved in methylene chloride and pipetted into a stirring solution of methanol (800 mL) which caused the polymer to precipitate. The precipitate was then filtered and dried *in vacuo* for 24 h. FTIR (KBr) 2955, 1572, 1452, 1251, 1122, 1040, 838, 757, 691, 455. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.8-6.6(m), 0.5-0(m).



4

Polystyrene diboronic acid (4).[7] To a 500 mL three neck round bottom flask equipped with a stir bar and flushed with nitrogen was added poly(bistrimethylsilyl)styrene (3.06 g, 12.24 mmol). The reaction flask was sealed with a septum, evacuated, and then backfilled with nitrogen (3×). Dry methylene chloride (37 mL) was added *via* syringe. The reaction was cooled to –78 °C and a solution of boron tribromide in methylene chloride (24.5 mL, 24.5 mmol, 1 M) was added drop-wise. The mixture was stirred and allowed to warm to room temperature overnight. The reaction was then heated at reflux for 24 h and the mixture was removed from the heat and allowed to cool to room temperature, followed by quenching with ice water. The two-phase mixture was stirred for 4 h. The solvent and water were removed by rotoevaporation then dried *in vacuo* for 24 h. FTIR (KBr) 3223, 2924, 2854, 1449, 1249, 1191, 1120, 1040, 837, 759, 647, 543, 476. ^{1}H NMR (400 MHz, DMSO) δ 8.13 (bs), 6.50 (bs), 3.32 (bs).



5

1,4-Benzene diboronic acid (5).[3,4] To a 250 mL round bottom flask equipped with a magnetic stir bar and reflux condensor was added 1,4-dibromobenzene and Ni(dppp)Cl_2 (6 mol%). The flask was sealed with a septa under nitrogen and toluene (35 mL), triethylamine (8 equivalents), and pinacol borane (2.6 equivalents) was added dropwise *via* syringe. The mixture was then heated to 100 °C for 24 h and then was allowed to cool to room temperature. A saturated solution of ammonium chloride (NH_4Cl) was added slowly to the flask to quench the reaction. Diethylether was then added to dilute the mixture and the two layers were separated. The organic layer was washed with ammonium chloride (3×) and dried with magnesium sulfate (Mg_2SO_4) and filtered through celite. The solvent was removed *via* rotary evaporation. The product was hydrolyzed to the acid by heating in MeOH (150 mL) and HCl (3 M; 150 mL) until the product was dissolved. The solution was then allowed to cool slowly to room temperature and then refrigerated for 12 h to form crystals. The crystals were isolated by filtering through a buchner funnel and drying in the vacuum oven for 16 h at 50 °C. ^1H NMR (400MHz, CD_3OD, DCl in D_2O) δ 7.6 (s, 4 H), 5.5 (s, 4 H).

1.4 References

(1) Stevens, M. P. *Polymer Chemistry: An Introduction*; Oxford University Press: New York, 1999.

(2) Nelson, G. L. *Chemistry* **1978**, *51*, 22-27.

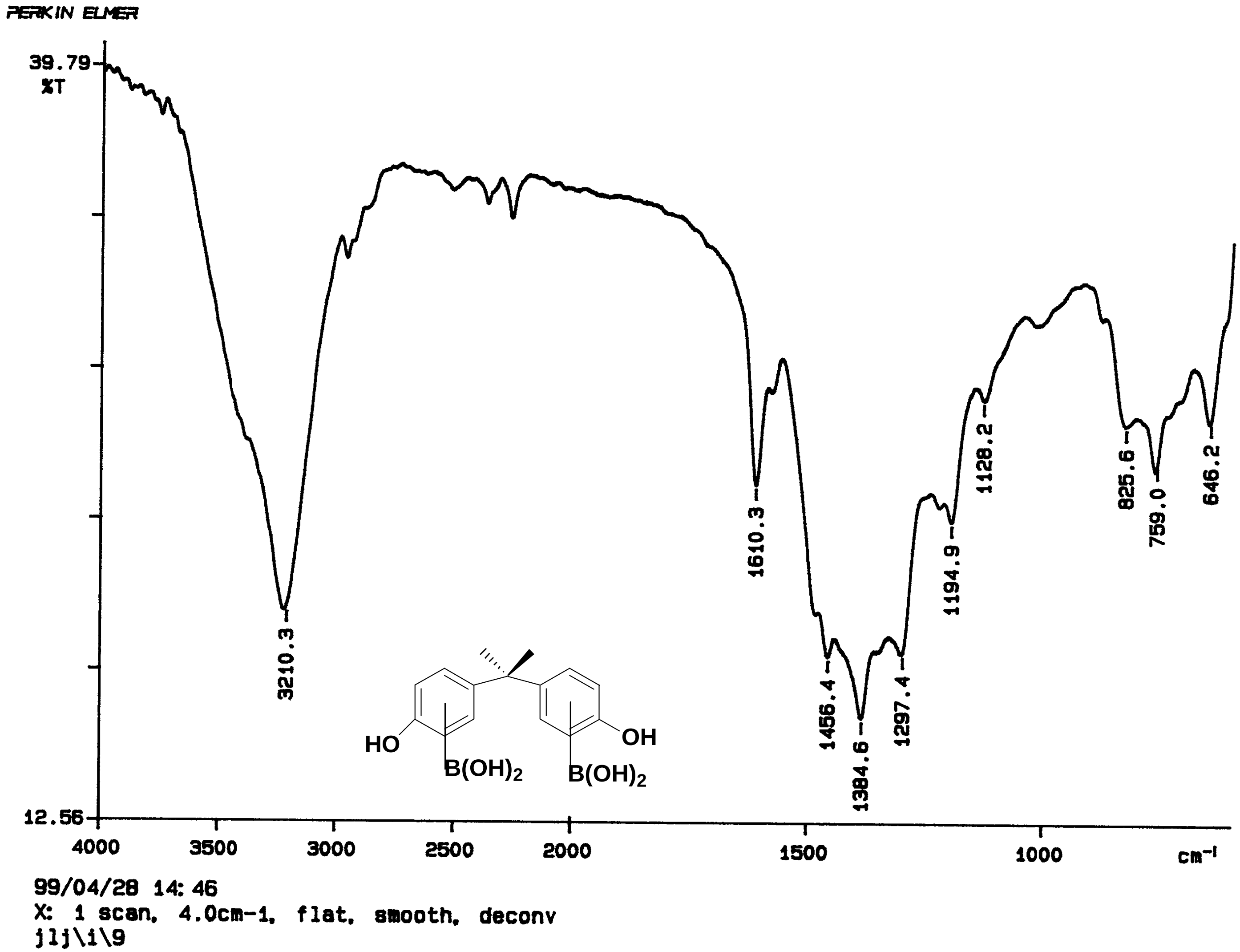
(3) Morgan, A. B.; Jurs, J. L.; Tour, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem)* **1999**, *40*, 553-554.

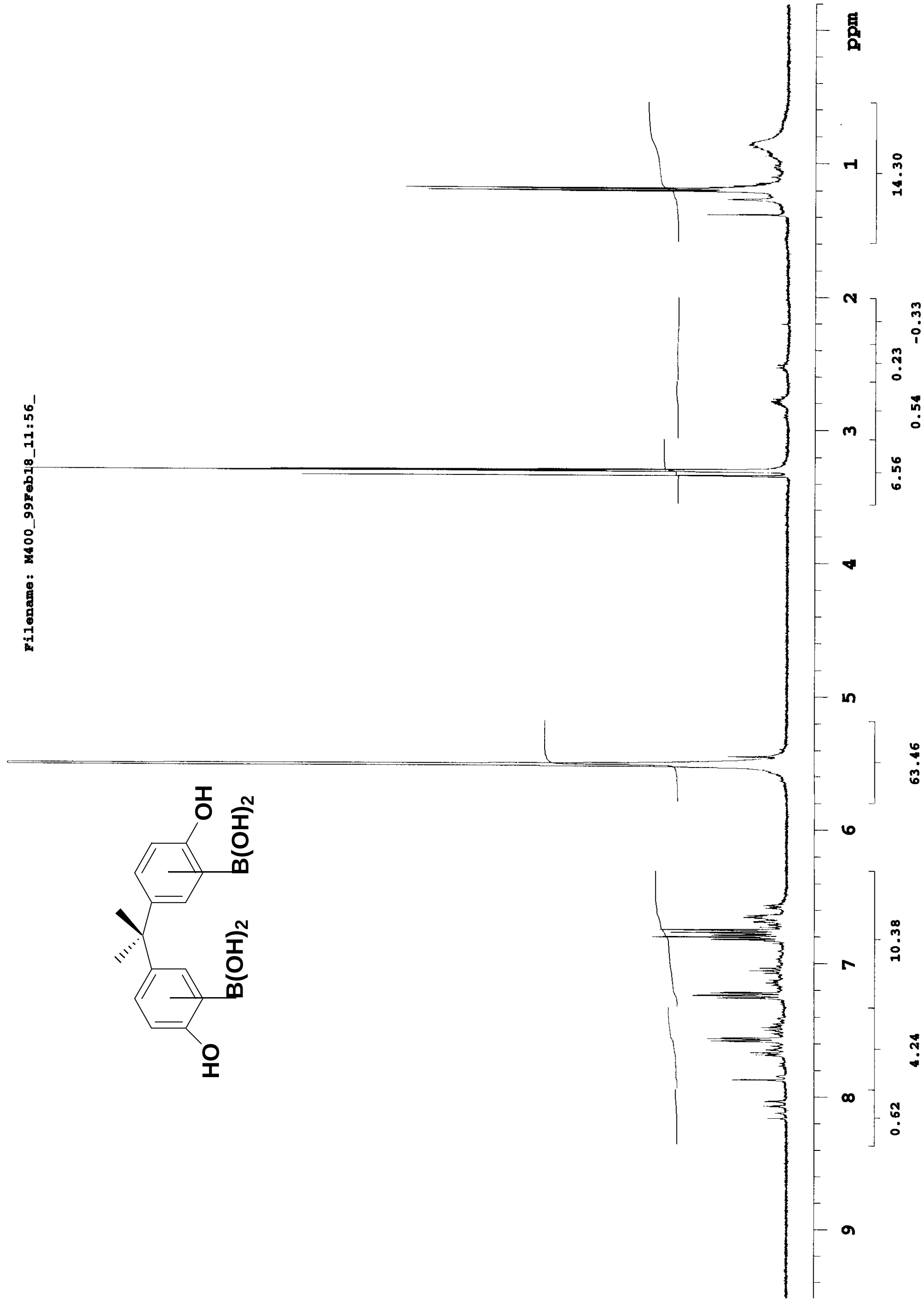
(4) Morgan, A. B.; Jurs, J. L.; Tour, J. M. *J. of Applied Poly. Sci.* **2000**, *76*, 1257-1268.

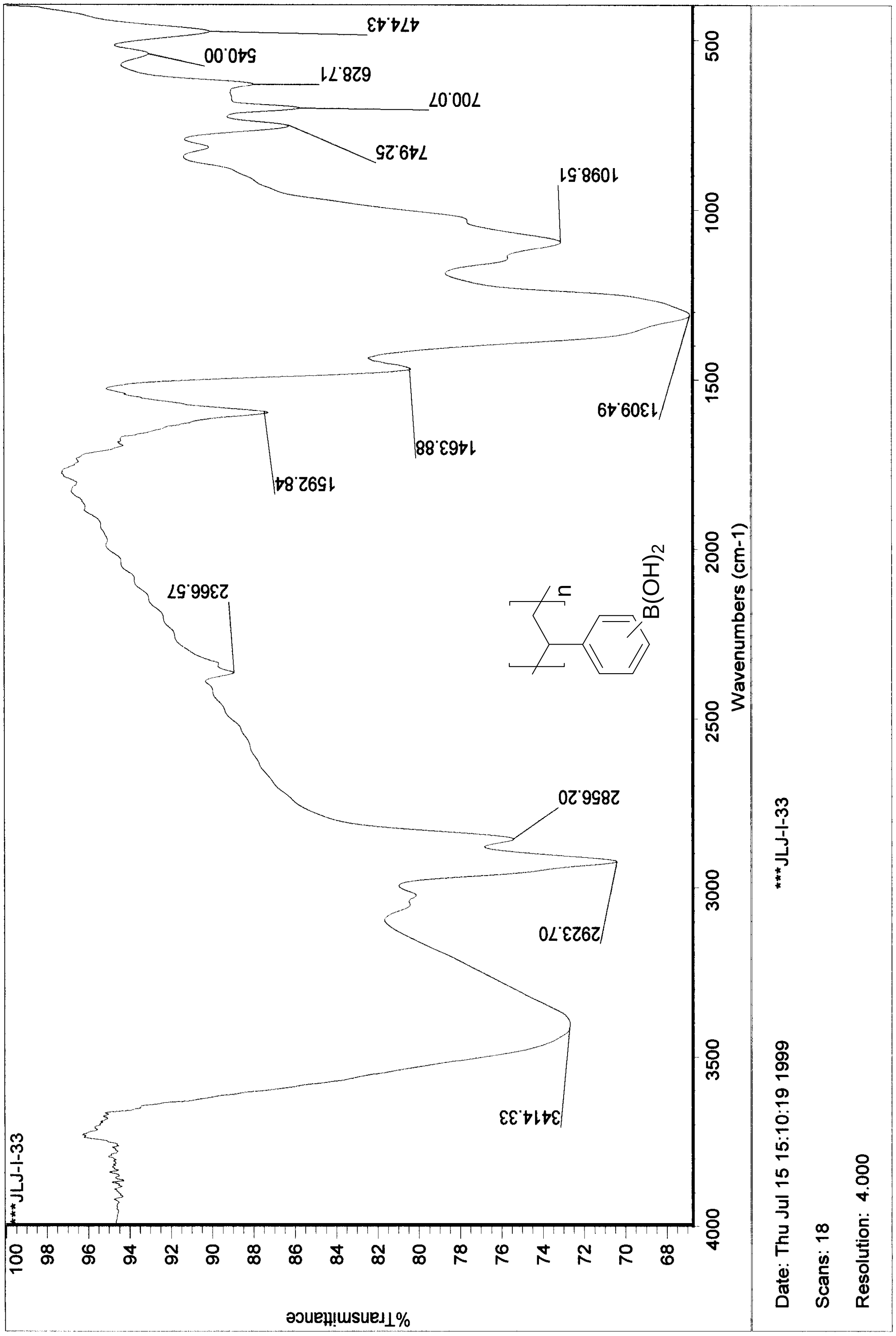
(5) Smith, M. B. *Organic Synthesis*; 3rd ed.; McGraw-Hill, Inc.: New York, 1994.

(6) Murray, M. M.; Karzynski, D. A.; Chang, W.; Dougherty, D. A. *J. Am. Chem. Soc.* **1994**, *116*, 8152-8161.

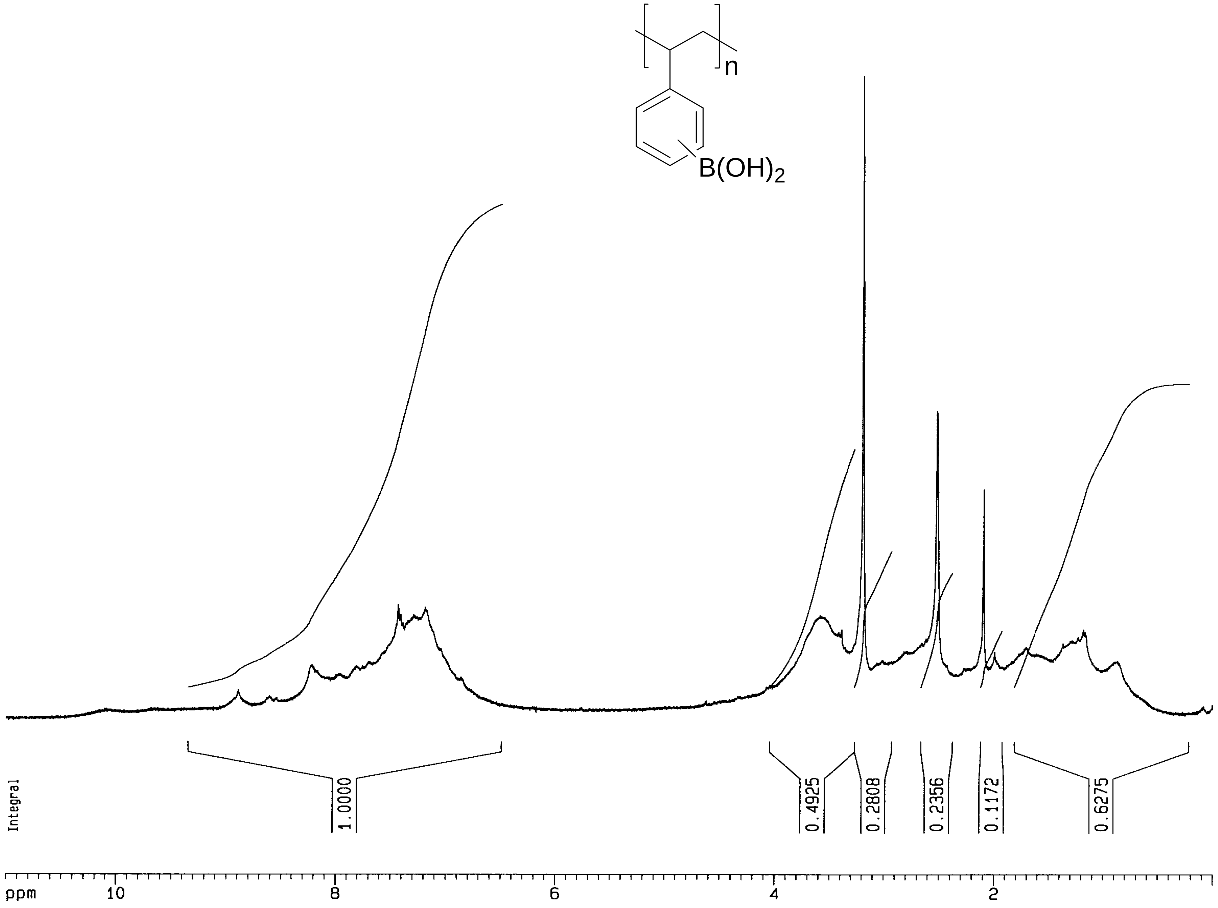
(7) Morgan, A. B., Ph.D. Thesis, University of South Carolina: Columbia, **1998**.


PERKIN ELMER
39.79
%T
12.56
4000
3500
3000
2500
2000
1500
1000
cm⁻¹
3210.3
1610.3
1456.4
1384.6
1297.4
1194.9
1128.2
825.6
759.0
646.2
HO
OH
B(OH)2
B(OH)2
99/04/28 14:46
X: 1 scan, 4.0cm-1, flat, smooth, deconv
jlj\i\9

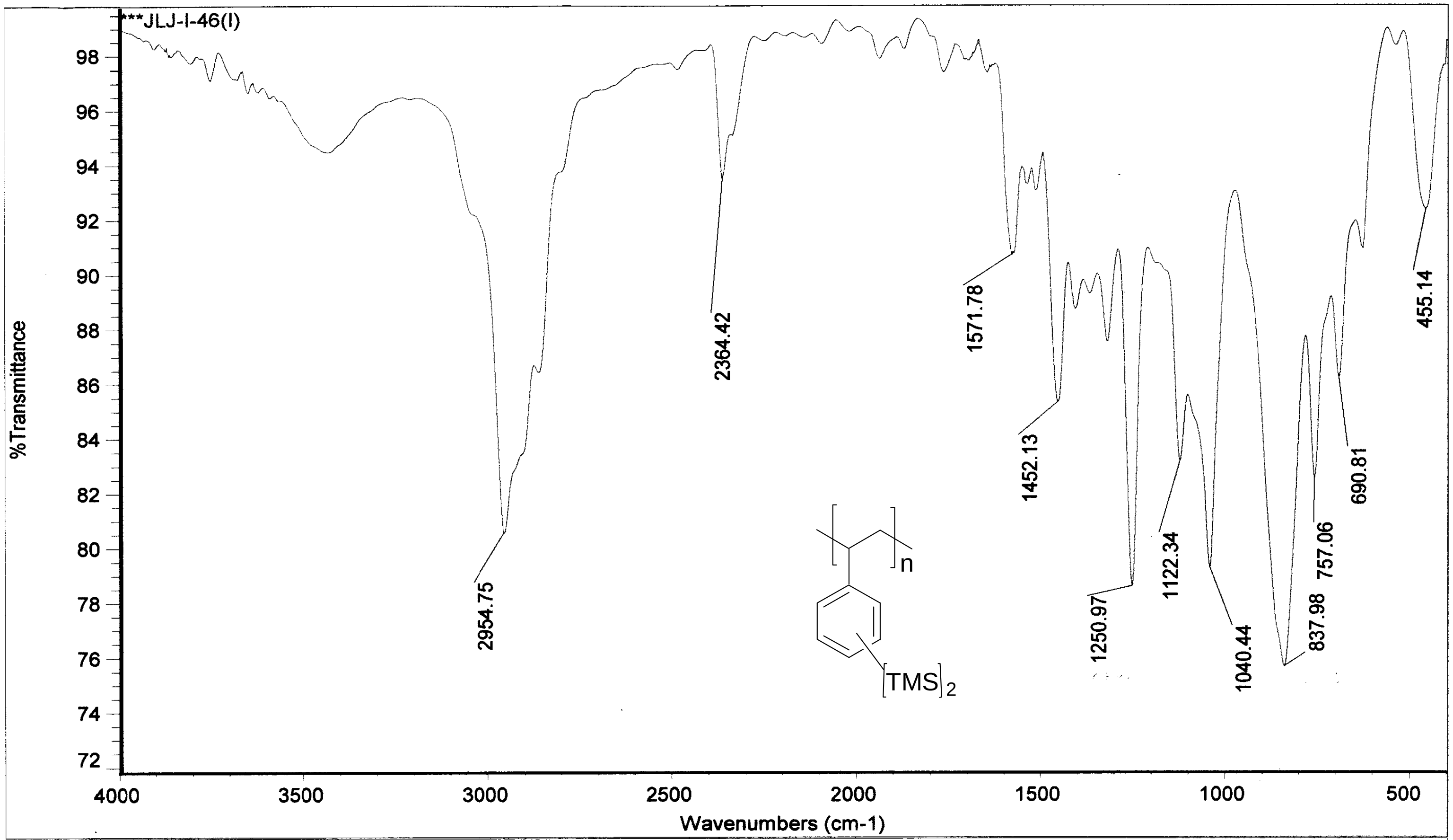

Filename: M400_99Feb18_11:56_
HO
OH
B(OH)2
B(OH)2
ppm
9
8
7
6
5
4
3
2
1
0.62
4.24
10.38
63.46
6.56
0.54
0.23
-0.33
14.30


***JLJ-I-33
%Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
3414.33
2923.70
2856.20
2366.57
1592.84
1463.88
1309.49
1098.51
749.25
700.07
628.71
540.00
474.43
n
B(OH)2
Date: Thu Jul 15 15:10:19 1999
***JLJ-I-33
Scans: 18
Resolution: 4.000

JLJ-I-330RGANICS
IN DMSO



```
Current Data Parameters
NAME        JLJ-I-330RG
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_            990726
Time              14.18
INSTRUM           spect
PROBHD    5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                  181
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P              11.000 ppm
F1              4401.43 Hz
F2P               0.000 ppm
F2                 0.00 Hz
PPMCM           0.55000 ppm/cm
HZCM          220.07150 Hz/cm
```

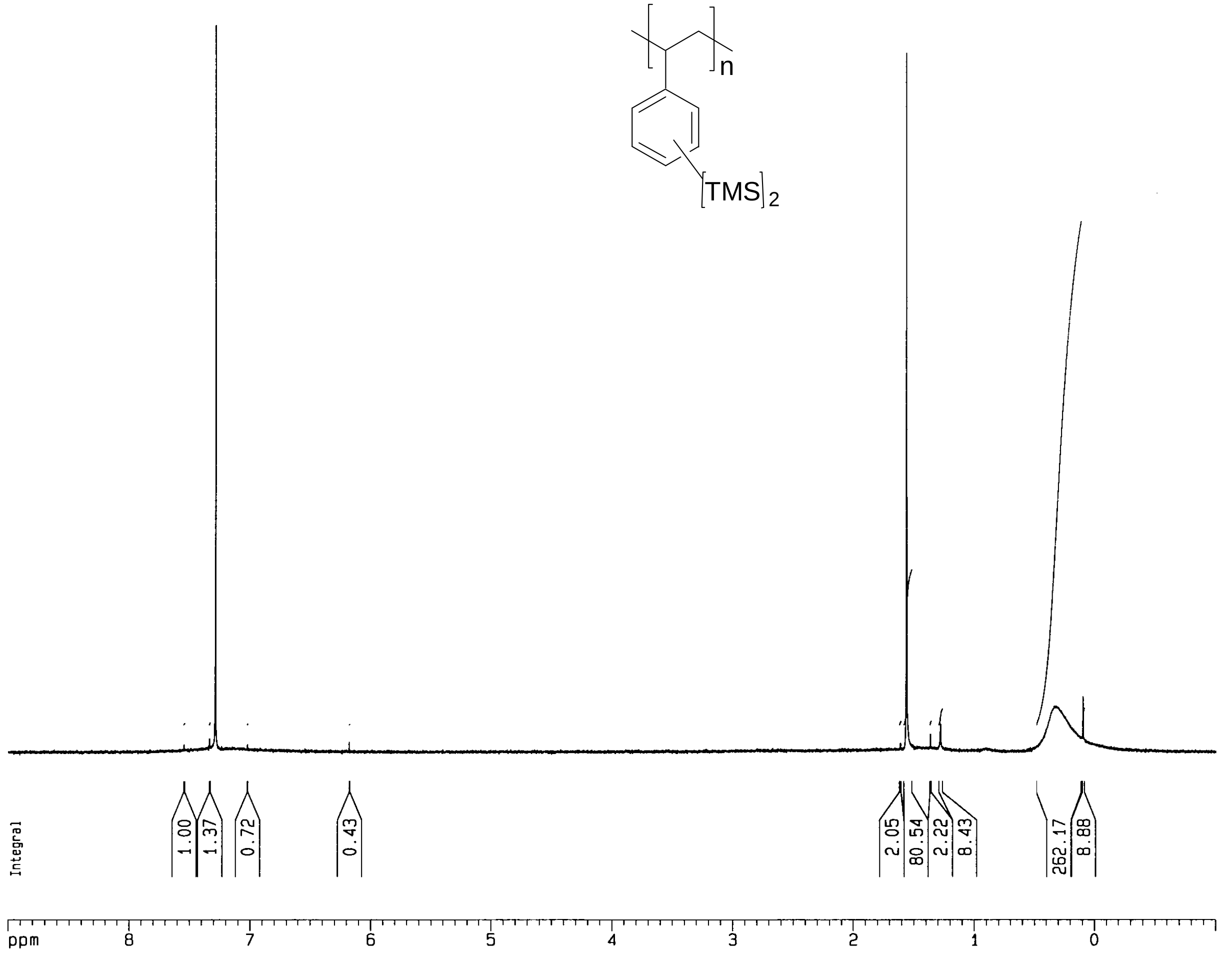


Date: Mon Aug 16 11:08:25 1999 ***JLJ-I-46(I)

Scans: 18

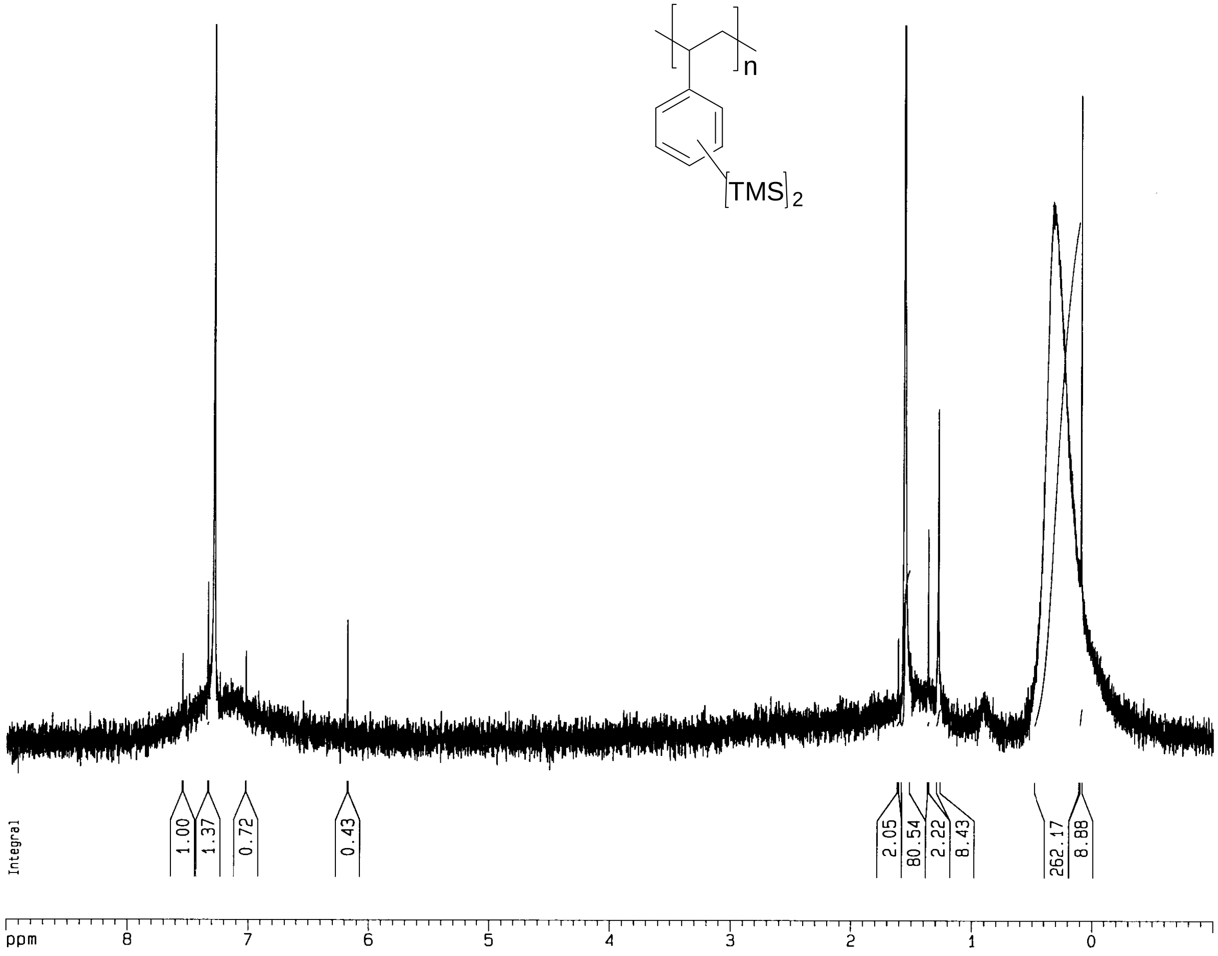
Resolution: 4.000

JLJ-I-46
PRECIPITATED (CONC.)

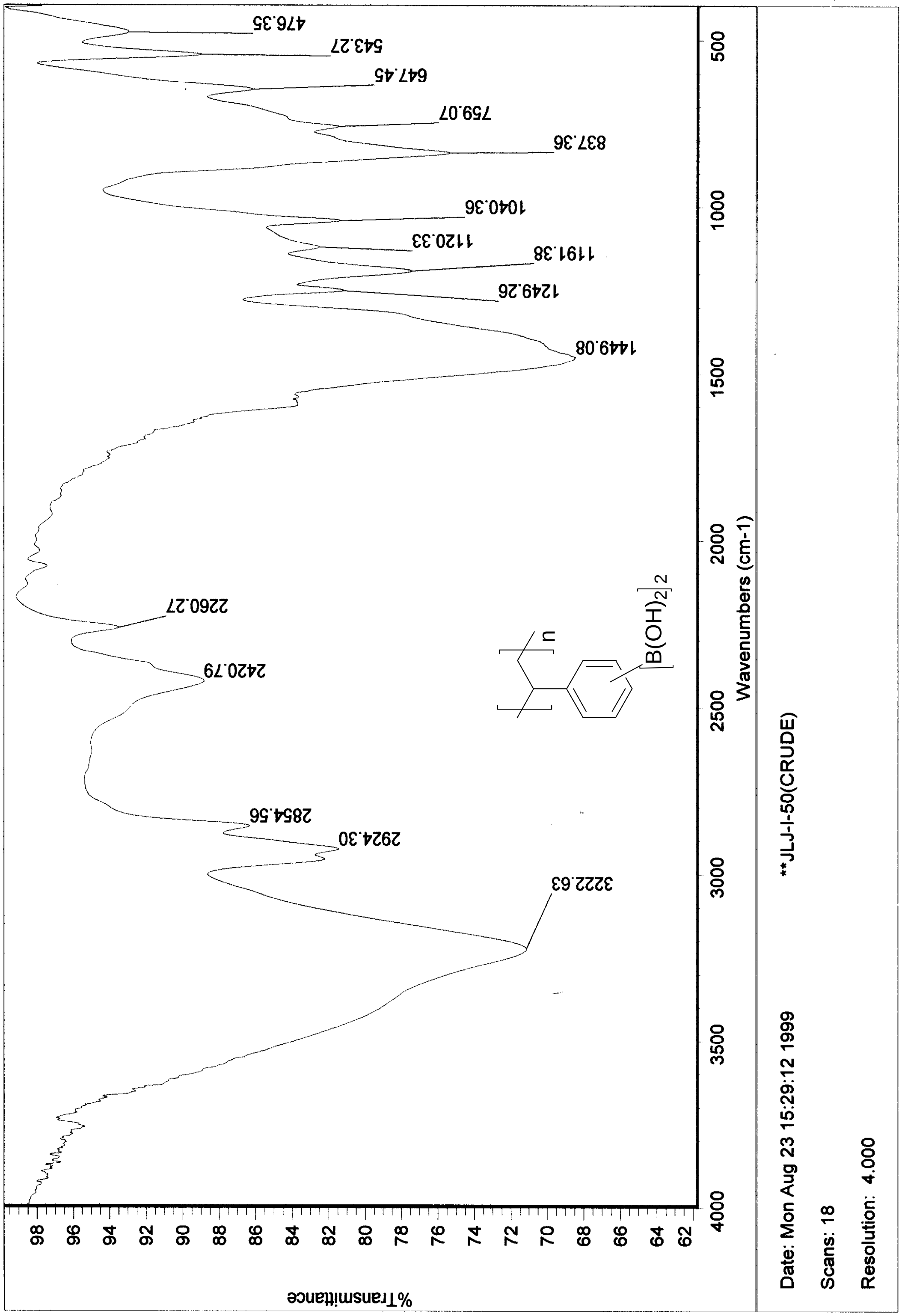


```
Current Data Parameters
NAME      JLJ-I-46precip
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_             990817
Time               11.31
INSTRUM            spect
PROBHD    5 mm BBO BB-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 574.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06500 Hz/cm
```

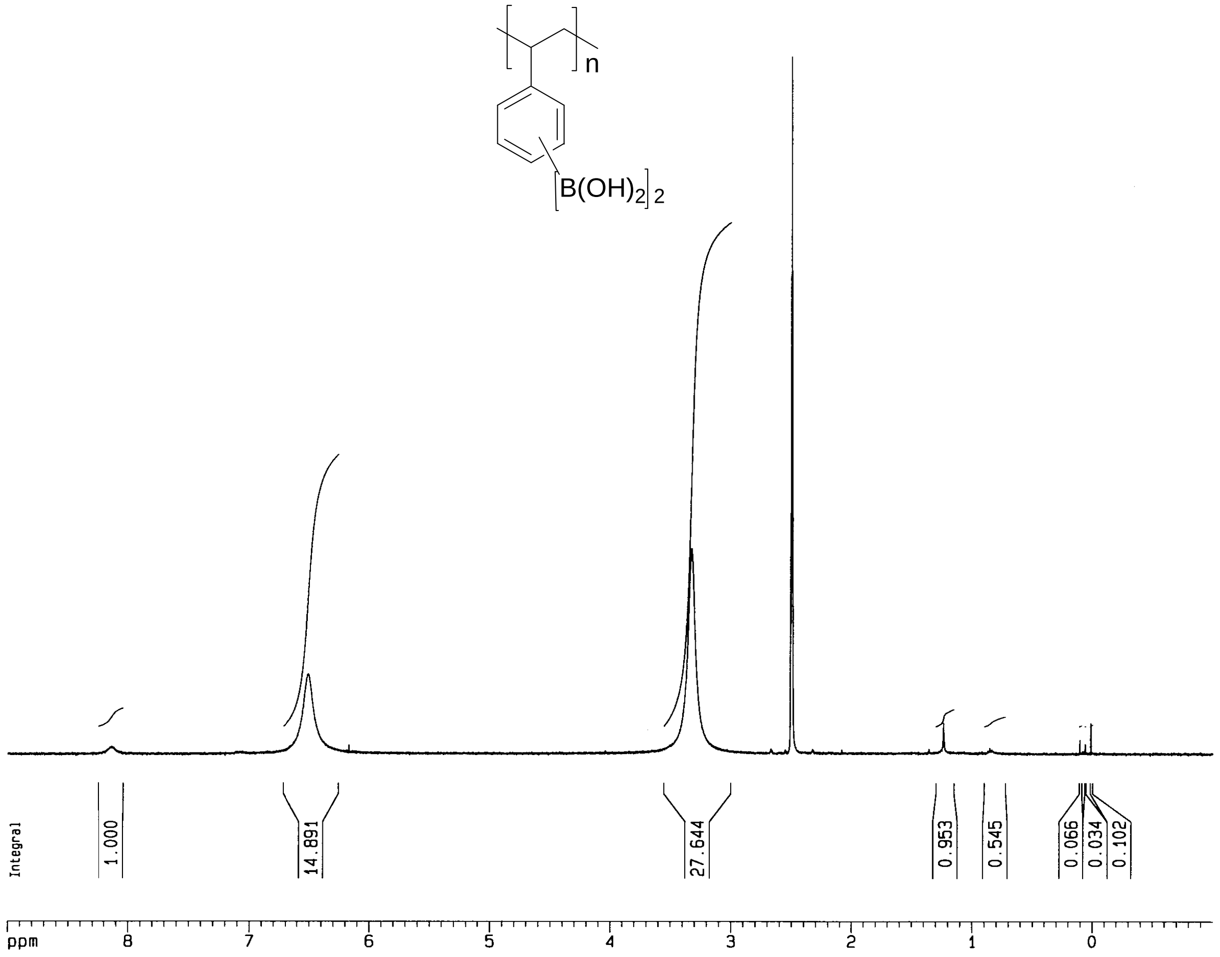
JLJ-I-46
PRECIPITATED (CONC.)



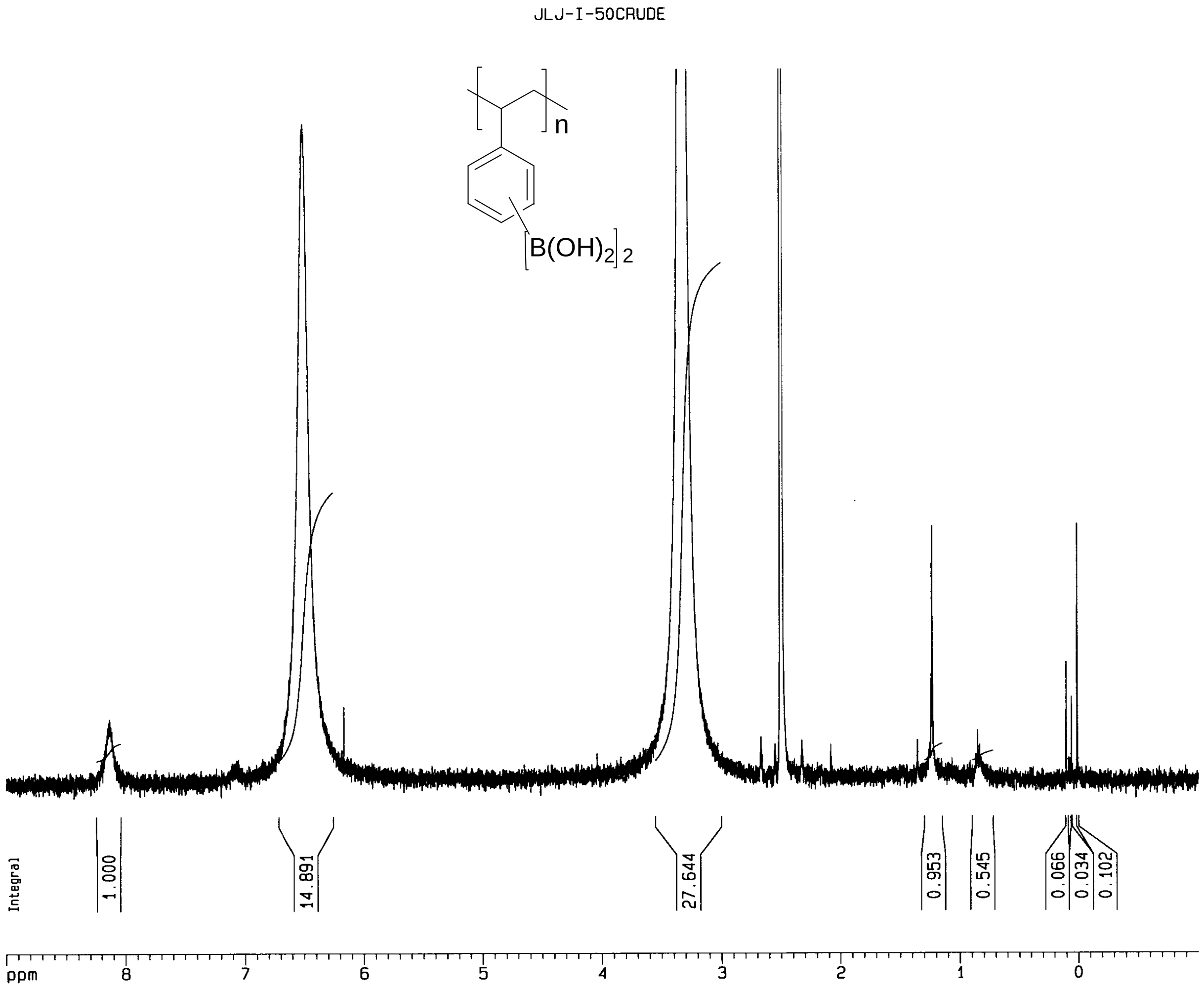
```
Current Data Parameters
NAME      JLJ-I-46precip
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_             990817
Time               11.31
INSTRUM            spect
PROBHD    5 mm BBO BB-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 574.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06500 Hz/cm
```


%Transmittance
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
3222.63
2924.30
2854.56
2420.79
2260.27
1449.08
1249.26
1191.38
1120.33
1040.36
837.36
759.07
647.45
543.27
476.35
n
B(OH)2
2
Date: Mon Aug 23 15:29:12 1999
Scans: 18
Resolution: 4.000
**JLJ-I-50(CRUDE)

JLJ-I-50CRUDE

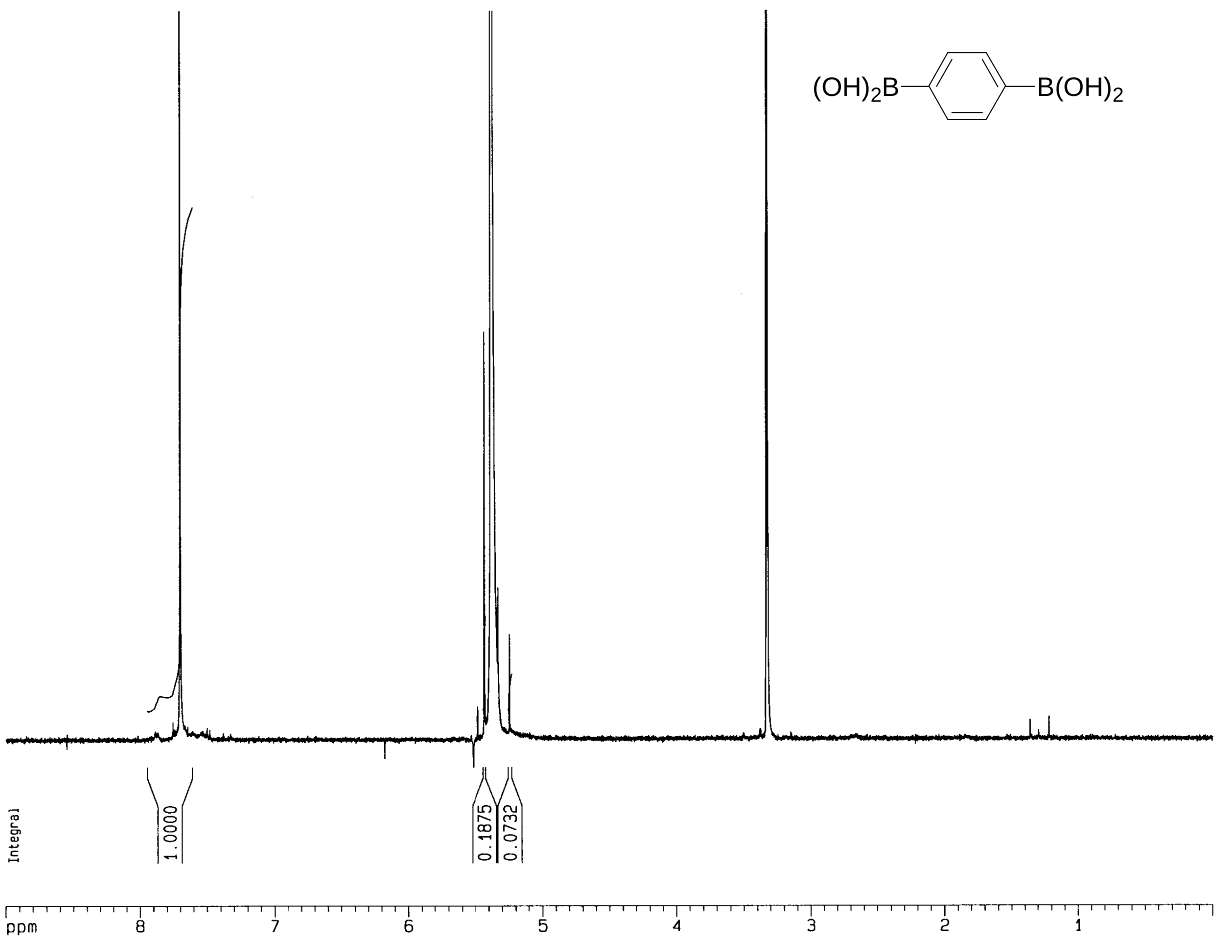


```
Current Data Parameters
NAME             JLJ-I-50
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_              990823
Time                14.21
INSTRUM             spect
PROBHD   5 mm BBO BB-1
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     32
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  912.3
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 ========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300026 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 9.000 ppm
F1                3601.17 Hz
F2P                -1.000 ppm
F2                -400.13 Hz
PPMCM             0.50000 ppm/cm
HZCM            200.06499 Hz/cm
```



```
Current Data Parameters
NAME             JLJ-I-50
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_              990823
Time                14.21
INSTRUM             spect
PROBHD    5 mm BBO BB-1
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     32
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  912.3
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 ========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300026 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 9.000 ppm
F1                3601.17 Hz
F2P                -1.000 ppm
F2                -400.13 Hz
PPMCM             0.50000 ppm/cm
HZCM            200.06499 Hz/cm
```

JLJ-I-41 RECRYSTALYZED
(X1)



```
Current Data Parameters
NAME        JLJ-I-41rec
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_            990817
Time              15.24
INSTRUM           spect
PROBHD    5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT            MeOH
NS                    9
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                456.1
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 =========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P               0.000 ppm
F2                 0.00 Hz
PPMCM           0.45000 ppm/cm
HZCM        180.05850 Hz/cm
```

Chapter 2

Novel Flame Retardant Additives

Halogenated Flame Retardant Additives

2.1 Introduction-Halogenated Flame Retarding Additives

1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane is the IUPAC name for an organochlorine species more commonly known as dichlorodiphenyltrichloroethane, or simply, DDT. While DDT was first synthesized in 1873, it was not until 1939 that P. Muller discovered its insect-killing properties.[1] The efficiency with which DDT was able to control insect populations, along with its low degree of acute toxicity towards mammalian species (particularly human) and the low cost with which it could be produced, led to its ever-increasing use by agribusinesses. The amounts commonly applied to agricultural fields were 80 kg per acre.[2] Furthermore, it had become the mainstay of the World Health Organization's malaria control program and has, no doubt, saved millions of lives as a result.[1]

Beginning in the 1960's, a burgeoning environmental movement began to raise concerns about the effects DDT might be having on the environment, particularly on the reproductive cycle of birds.[3] Several studies indicated that DDT had a deleterious effect on the shell integrity of certain species of bird eggs, making them thinner.[4] As a result, DDT was banned from use as a pesticide in the United States in 1972.[1]

While the effects of DDT on wildlife remain controversial to this day, there is still no conclusive evidence that DDT possesses any more than a low degree of toxicity towards or is carcinogenic to humans.[1,5] And while newer pesticides have been developed that are both more efficient and less persistent in the environment, DDT continues to serve a role in Third World countries (particularly in the battle against malaria) because it remains an effective insecticide that can be produced at low cost.[1,2]

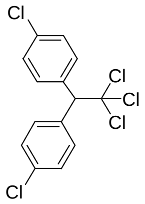
Irrespective of DDT's actual or perceived harm to the environment, an alternative use exists for this chemical. We show here that the brominated compounds that are generally used in polymer blends to impart flame retardancy can be replaced with the chlorinated compound DDT and its thermal degradation product, 2,2-bis(4-chlorophenyl)-1,1-dichloroethylene (DDE). DDT and DDE were used in amounts that would provide a halogen content comparable to that provided by the brominated compounds we were seeking to replace. It was speculated that these compounds would be good flame retarding additives based on their high halogen content. Additionally, they both have melting points (107-110 °C for DDT and 88-90 °C for DDE) that are amenable to blending. DDT and DDE were blended (along with Sb_2O_3 and polytetrafluoroethylene (PTFE), which are used along with brominated compounds in commercial plastics with ABS (acrylonitrile/butadiene/styrene) polymer and HIPS (high-impact polystyrene) and subjected each to the industry standard UL-94 flame test.

2.2 Results and Discussion- Halogenated Flame Retarding Additives

10 wt % (based on the weight percent of halogen) of DDT with 4 wt % antimony oxide and 1 wt % of an anti-drip additive (PTFE) gave a UL-94 V-0 result in ABS and HIPS. DDT also gave promising results in polyethylene, but due to excessive dripping a V-0 result could not be obtained. Unfortunately the public stigma of associated with the use of DDT in applications with environmental exposure would severely hinder its commercialization in any flame retardant blends. Thus, a major focus of the research here has been the synthesis of new analogs of DDT and (DDE) (Table1).

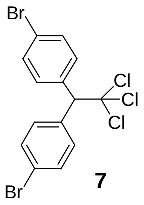
Table 1

DDT and Analogs



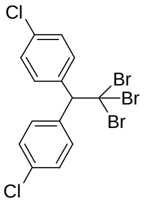
1

1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane



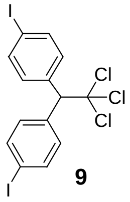
7

1,1-Bis(4-bromophenyl)-2,2,2-trichloroethane



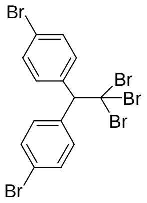
3

1,1-Bis(4-chlorophenyl)-2,2,2-tribromoethane



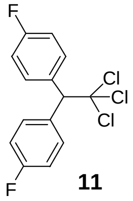
9

1,1-Bis(4-iodophenyl)-2,2,2-trichloroethane



5

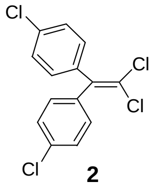
1,1-Bis(4-bromophenyl)-2,2,2-tribromoethane



11

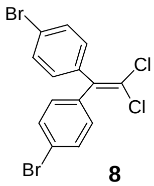
1,1-Bis(4-fluorophenyl)-2,2,2-trichloroethane

DDE and Analogs



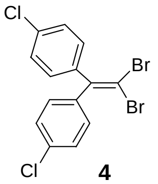
2

2,2-Bis(4-chlorophenyl)-1,1-dichloroethylene



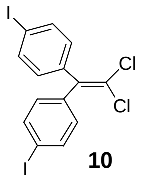
8

2,2-Bis(4-bromophenyl)-1,1-dichloroethylene



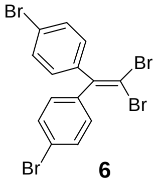
4

2,2-Bis(4-chlorophenyl)-1,1-dibromoethylene



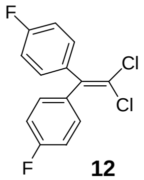
10

2,2-Bis(4-iododphenyl)-1,1-dichloroethylene



6

2,2-Bis(4-bromophenyl)-1,1-dibromoethylene

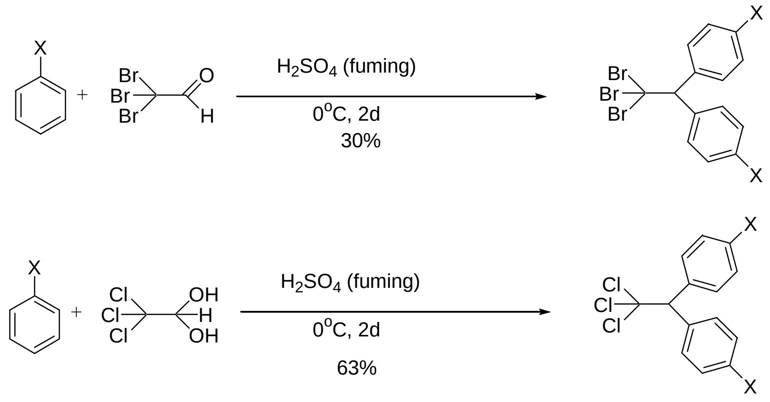


12

2,2-Bis(4-fluorophenyl)-1,1-dichloroethylene

The brominated and chlorinated versions of DDT and DDE were synthesized by a condensation reaction of tribromoacetylaldehyde (bromal) or trichloroethanediol (chloral hydrate) with a mono halogenated benzene in the presence of fuming sulfuric acid (Reactions 1 & 2).[6]

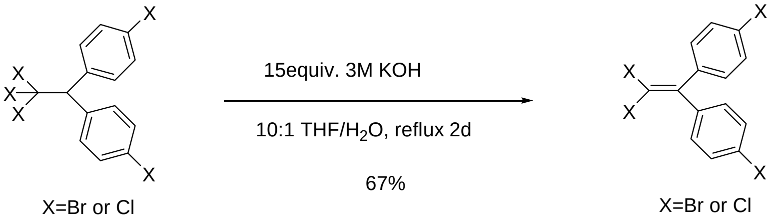
Reactions 1 & 2



X=Br, Cl, F, I

Burn results from all of the DDT analogs in both ABS and HIPS gave a V-0 rating. Each DDT analog was converted into its corresponding DDE analog. Via dehydrohalogenation by in the presence of 15 equivalents of a 3 M potassium hydroxide and methanol for 2 days. (Reaction 3).

Reaction 3



Although poor UL-94 results were obtained with DDE, the brominated DDE derivatives gave V-0 results in both ABS and HIPS.

Working with the bromo DDE core **8,** other polymers and large molecules have been tested. The first system being made by a palladium copper cross coupling reaction with phenylacetylene to give 2,2-bis(*p*-phenylene ethynylene)-1,1-dichloroethlyene **13** (Reaction 4). Burn results for this compound were not good. Alkynes are known to crosslink in a fire and create char, but this process is exothermic and contributes its energy to the fire, which and caused this compound to have extended burn times in ABS plastic.[7]

Reaction 4

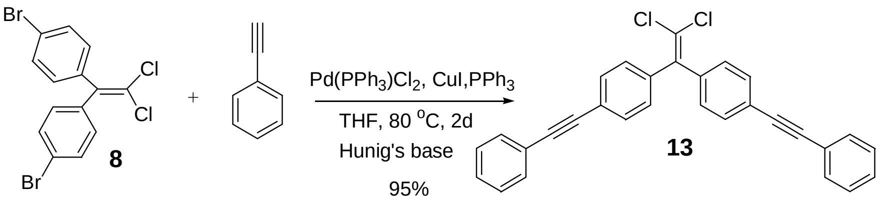


Table 2. HVUL-94 Burn Results for DDT and DDE additives.

Additive	First Ignition[a] (sec)	Observed Dripping[b]	Second Ignition[a] (sec)	Observed Dripping[b]	UL-94 Rating
1, 10wt%; Sb_2O_3, 4wt%; ClPE, 10wt%; ABS	202, 0	No, No	24, 177	No, No	?, ?
1, 23.6wt%; Sb_2O_3, 4wt%; ClPE, 10wt%; ABS	2, 4	No, No	2, <1[d]	No, No	V-0, V-0
1, 23.6wt%; Sb_2O_3, 4wt%; PTFE, 1.0wt%; ABS	0,0	No, No	<1[d], 3	No, No	V-0, V-0
1, 23.6wt%; Sb_2O_3, 4wt%; PTFE, 1wt%; HIPS	3, 0	No, No	4, 8	No, No	V-0, V-0
1, 23.6wt%; PTFE, 1wt%; ABS	274, 100	Yes[c], Yes[c]	49, 98	No, No	?, ?
1, 20wt%; Sb_2O_3, 4wt%; PTFE, 1wt%; ABS	0, 1	No, No	<1[d], 2	No, No	V-0, V-0

1, 20wt%; Sb_2O_3, 1wt%; PTFE, 1wt%; ABS	56, 9	No, No	83, 42	Yes^d,Yes^d	?, ?
1, 20wt%, Sb_2O_3, 2wt%, PTFE, 1wt%; ABS	2, 2	No, No	1, 1	No, No	V-0, V-0
1, 3wt%; Sb_2O_3, 1wt%; BDBA, 10wt%; PTFE, 1wt%; ABS	45, 75	Yes^c, Yes^c	123, 85	No, No	?, ?
1, 20wt%; Sb_2O_3, 4wt%; PTFE, 1wt%; HIPS	0, 0	No, No	8, 10	No, No	V-0, V-0
1, 20wt%; Sb_2O_3, 4wt%; PTFE, 1wt%; PE	2, 2, 3	Yes^c, No, Yes^c	2, <1^d, 2	Yes, Yes^d, Yes	?, ?, ?
1, 10wt%*; Sb_2O_3, 2wt%; CaCO3, 14wt%; PE	3, 2	Yes^c, Yes^c	0, 18	Yes, Yes	V-2, V-2
2, 22.2wt%; Sb_2O_3, 4wt%; ABS	1, 265	No, No	23, 23	Yes^d, No	?, ?
3, 10wt%*; Sb_2O_3, 2wt%; PTFE, 1wt%; ABS	0, 0	No, No	1, 0	No, No	V-0, V-0
3, 10wt%*; Sb_2O_3, 2wt%; PTFE, 1wt%; HIPS	0, 1	No, No	0, 0	No, No	V-0, V-0
4, 10wt%*; Sb_2O_3, 4wt%; PTFE, 1wt%; ABS	0,0	No, No	1, 0	No, No	V-0, V-0
4, 10wt%*; Sb_2O_3, 4wt%; PTFE, 1wt%; HIPS	<1, <1	No, No	1,1	No, No	V-0, V-0
5, 10wt%*; Sb_2O_3, 2wt%; PTFE, 1wt%; ABS	1, 0	No, No	0, 0	No, No	V-0, V-0
5, 10wt%*; Sb_2O_3, 2wt%; PTFE, 1wt%; HIPS	0, 1	No, No	0, 0	No, No	V-0, V-0

6, 10wt%*; Sb_2O_3, 4wt%; PTFE, 1wt%; ABS	0,0	No, No	1,1	No, No	V-0, V-0
6, 10wt%*; Sb_2O_3, 4wt%; PTFE, 1wt%; HIPS	1,0	No, No	2,1	No, No	V-0, V-0
7, 10wt%*; Sb_2O_3, 2wt%; PTFE, 1wt%; ABS	0, 0	No, No	1, 1	No, No	V-0, V-0
7, 10wt%*; Sb_2O_3, 2wt%; PTFE, 1wt%; HIPS	9, 1, 0	No, No, No	50, 0, 0	Yes ,No, No	?, V-0, V-0
8, 10wt%*; Sb_2O_3, 4wt%; PTFE, 1wt%; ABS	0,1	No, No	0,1	No, No	V-0, V-0
8, 10wt%*; Sb_2O_3, 4wt%; PTFE, 1wt%; HIPS	38, 0, 10	No, No, No	0, 2, 1	No, No, No	V-1, V-0, V-0
13, 10wt%*; Sb_2O_3, 4wt%; PTFE, 1wt%; ABS	189, 322	No, No	13, 0	No, No	?,?

a Time to self-extinguishing in seconds after 1st, 2nd, 3rd 10 sec ignition. **b** Indicates that molten ABS did (Y) or did not (N) drip on to cotton patch underneath ignited bar during UL-94 test. **c** Indicates ignition of cotton patch underneath ignited bar of plastic. **d** Indicates time that only glowing, not flame occurred after re-application of flame. X indicates not enough bar remaining for 2nd ignition. * Wt % based on halogen content.

Blending these DDT and DDE analogs with antimony oxide and an anti-drip with thermoplastic polymers like ABS and HIPS, have imparted flame retardancy to what are otherwise flammable plastics. The results above show that all of the analogs, except **2**, give a V-0 result in the UL-94 test for flammability, in both ABS and HIPS. DDT worked well in polyethylene by quickly putting out the flame, but due to excessive dripping and ignition of the cotton patch did not result in a V-0 rating.

While Sb_2O_3/halogen-compound additive systems are currently used to produce flame-resistant commercial plastics, most employ brominated compounds as the halogen source. In this study, we have opted for a chlorine-containing halogen source. The novelty in this lies in the types of chlorinated compounds used (chloral and its derivatives) and the fact that chlorine containing halogen sources had previously been thought to be inferior, in flame retarding ability, to brominated sources. Despite this, we have created polymer blends that contain more than 75 wt % commercial polymers and still rate as V-0 in the industry-standard UL-94 flame test. This, coupled with the low cost of chlorinated species, may yield a promising new class of flame-retarding materials.

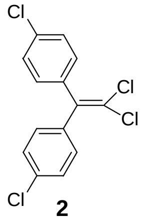
2.3 Experimental

General Procedures: All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Silica TLC plates were 250 μm thick, 40 F254 grade from EM Science. Silica gel was grade 60 (230-400 mesh) from EM Science. ^{1}H NMR spectra were observed at 400 MHz and ^{13}C NMR spectra were observed at 100 MHz on a Brüker Avance 400 spectrometer. ^{1}H chemical shifts (δ) are reported in ppm downfield from tetramethysilane. IR spectra were obtained on a Nicolet Avatar 360 FTIR. Gas chromatography experiments were performed on a Hewlett-Packard GC model 5890A. Thermal gravimetric analysis (TGA) was performed with a Perkin Elmer TGA7 30 - 900 °C at 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) was performed with a Perkin Elmer DSC7 using a 30 - 450 °C scanning window at 10 °C/min. under nitrogen. Polymer blending/extrusion was done with a Custom Scientific Instruments CSI-183MMX Mini-Max Blender/Extruder or with a Brabender Prep-Center using a type 6/2 mixer. An Atlas Electric HVUL-94 flame test station was used for the UL-94 flame tests. Melting points were obtained using a Büchi melting point apparatus. Reagent grade tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. Dry benzene, toluene, methylene chloride, and triethylamine were distilled over calcium hydride and under nitrogen. Unless otherwise stated, all other reagents were used as received. Mass spectrometry work was obtained from the Rice University Mass Spectrometry Laboratory.

General Procedure for Blending Flame Retardant Additives and Plastic (ABS or PC) in Brabender 30 ml Type 6/2 Mixing bowl – Prep Center.[7] The additive and plastic were weighed out in their respective amounts according to the wt % of additive: 25.41g batch (PC), 22.05 g batch (ABS). Heating temperatures for the blending bowl varied depending on the material involved. The processing temperatures used during the blending were: ABS 225 °C. PC: 270 °C. After the bowl had heated to the necessary processing temperature, the sample was poured quickly through the top opening of the Brabender while the blades were rotating at 50 RPM. The opening was then closed with the weighted handles and the sample was blended according to the type of flame retardant added. If a melt-blendable additive was used, the plastic and additives were blended for 10 min at 100 RPM. If a non-melt blendable additive was used, the plastic and additive were blended for 10-30 min at 150 RPM. If fibrillare PTFE (Dupont PTFE 30, 60 % PTFE in an aqueous suspension; density = 1.3 g/mL) was used as an anti-drip additive, the resin and the PTFE[7] were blended first for 10 min at 150 RPM. The flame-retardant additives were added and the plastic was blended again for 10 min at 150 RPM. After the blending was complete and the blades were stopped, the bowl was opened and molten plastic with the additives was removed with a bronze spatula. The plastic was then blended in the CSI-183MMX blender and extruded to give bars for the UL-94 test.

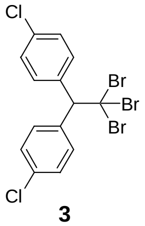
General Procedure for Extruding Plastic in the UL-94 Test Bars.[7] The plastic removed from the Brabender mixing center was then broken into smaller pieces and inserted into the heated cup of the CSI-183MMX blender until the cup was full. The plastic and additives were heated until molten and extruded into a heated 1/8” thick × ½” wide × 3” long rectangular bar mold. Heating temperatures for the blend cup and the extrusion mold varied depending on the material involved. The general processing temperature for the plastics used are as follows: mold temperature: 40-90 °C. PC: blending cup temperature: 270 °C, mold temperature 71-93 °C, ABS: blending cup temperature 225-230 °C.

General Procedure for the Modified HVUL-94 Burn Test.[7] Two 1/8” thick × ½” wide × 3” long plastic (polymer + additive) rectangular bars were used for this test. All flame tests were done in an Atlas Electric HVUL-94 flame test station. The setting on the methane tank pressure regulator was set to 23 psi. The pressure regulator HVUL-94 test station was set to 5 psi. The Bunsen Burner flame height was 125 mm, and the height from the top of the Bunsen Burner to the bottom of the test bar was 70 mm. All test bars underwent two trials, each trial consisting of ignition for 10 seconds, followed by flame removal and self extinguishing times were recorded.



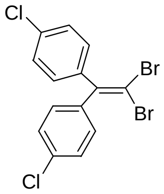
2

2,2-Bis(4-chlorophenyl)-1,1-dichloroethylene (2).[8] To a 250 mL round bottom flask, equipped with a stir bar and purged with nitrogen, was added DDT, **6** (3.54 g/10 mmol) and the flask was sealed under nitrogen with a septum. THF (50 mL) was added via syringe. A nitrogen sparged KOH solution (10 mL, 30mmol, 3M) was added drop-wise via syringe. The reaction was then heated slightly (~50 °C) and stirred for 24 h. The reaction mixture was then diluted with methylene chloride. The organic layer was washed with water (3×). Aqueous washes were then extracted with methylene chloride (3×). The combined organic extracts were dried over magnesium sulfate and filtered through celite. Solvent was then removed from the filtrate via rotary evaporation and dried *in vacuo* for 24 h. MP 87-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dt, J = 8.7, 2 Hz, 4 H), 7.20 (dt, J = 8.7, 2 Hz, 4 H).



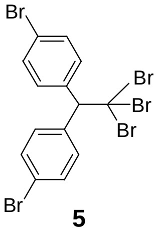
3

1,1-Bis(4-chlorophenyl)-2,2,2-tribromoethane (3).[6] A 250 mL round bottom flask was equipped with a stir bar, an addition funnel, purged with nitrogen, and sealed with a septum. Tribromoacetylaldehyde (1.89 mL, 18 mmol) and nitrogen sparged chlorobenzene (29 mL, 285 mmol) were added via syringe. The reaction was cooled to 2 °C and fuming sulfuric acid was added, via the addition funnel, drop-wise over a period of 1h. The reaction mixture was stirred and the temperature was kept below 6 °C for 24 h. The reaction mixture was then quenched with ice water and then extracted with ether (3×). The combined organic layers were washed with a dilute solution of sodium bicarbonate (3×). The organic solution was dried over magnesium sulfate and filtered through celite. Solvent was then removed from the filtrate via rotary evaporation and the residue was dried for 24 h *in vacuo* with slight heating to 50 °C to remove any excess chlorobenzene. MP 106-108 °C. FTIR (KBr) 2919, 1484, 1402, 1091, 1008, 828, 735, 694, 637, 573, 511. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6 (dt, *J* = 8.5, 2 Hz, 4 H), 7.3 (dt, *J* = 8.7, 2 Hz, 4 H), 5.2 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 134.2, 131.2, 128.5, 71.5, 45.4. HRMS calc'd for $C_{14}H_9Br_3Cl_2$: 487.758856; Found: 487.758364; 1.01 ppm error.

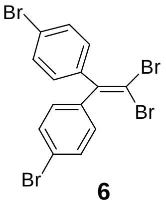


4

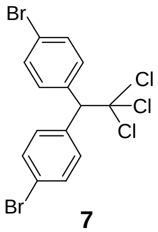
2,2-Bis(4-chlorophenyl)-1,1-dibromoethylene (4).[6] To a 250 mL round bottom flask, equipped with a stir bar and a reflux condensor and purged with nitrogen, was added **3**. The flask was then sealed under nitrogen with a septum. THF/H_2O (10:1 solution) was added via syringe. A nitrogen sparged KOH solution (15 equivalents, 3 M) was added drop-wise via syringe. The reaction was heated to reflux and stirred for 2 d. After this period of time, the reaction mixture was diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was then extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was removed from the filtrate via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. MP 106-108 °C. FTIR (KBr) 3053, 2355, 1903, 1585, 1482, 1391, 1254, 1090, 1008, 831, 778, 640, 512. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dt, *J* =8.56, 2.20 Hz, 4 H), 7.21 (dt, *J* =8.66, 2.20, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 139.2, 134.2, 130.2, 128.7, 91.4. HRMS calc'd for $C_{14}H_8Br_2Cl_2$: 405.8358; Found: 405.8348; 2.5 ppm error.


5

1,1-Bis(4-bromophenyl)-2,2,2-tribromoethane (5).[6] A 500 mL three neck round bottom flask was equipped with a mechanical stirrer and an addition funnel, purged with nitrogen, and sealed with a septum. Tribromoacetylaldehyde (3.8 mL, 36 mmol) and nitrogen sparged bromobenzene (60.02 mL, 570 mmol) were added *via* syringe. The reaction was cooled to 0 °C and fuming sulfuric acid (81.8 mL, 570 mmol) was added, via the addition funnel, drop-wise over a period of 1h. The reaction mixture was stirred and kept at 0 °C for 2 d. The reaction mixture was then quenched with ice water and diluted with CH_2Cl_2. The organic layer was washed with a dilute solution of sodium bicarbonate (3×) and the aqueous layer was extracted with ether (3×). Organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed from the filtrate via rotary evaporation and the resulting solid was dried for 24 h *in vacuo* with slight heating to 50 °C to remove any excess bromobenzene. MP 164-169 °C. FTIR (KBr) 1898, 1587, 1483, 1398, 1071, 1007, 820, 716, 617, 571, 488. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dt, *J* = 8.61, 2.18 Hz, 4 H), 7.48 (dt, *J* = 8.79, 2.22 Hz, 4H), 5.17 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 131.5, 122.5, 71.6, 45.0. HRMS calc'd for $C_{14}H_9Br_5$: 575.6582; Found: 575.6677; 1.1 ppm error.

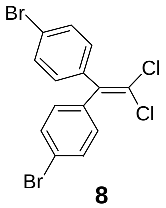

6

2,2-Bis(4-bromophenyl)-1,1-dibromoethylene (6).[6] To a 250 mL round bottom flask, equipped with a stir bar, and reflux condensor, and purged with nitrogen, was added **5**. The flask was then sealed under nitrogen with a septum. THF/H_2O (10:1 solution) was added via syringe. A nitrogen sparged KOH solution (15 equivalents, 3M) was added drop-wise *via* syringe. The reaction was then heated to reflux and stirred for 2 d. After this period of time the reaction mixture was then diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was then extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was removed, via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. MP 119-121 °C. FTIR (KBr) 2920, 1903, 1578, 1477, 1387, 1064, 1004, 825, 773, 716, 634, 481. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (dt, *J* =8.58, 2.18, 4 H), 7.52 (dt, *J* =8.60, 2.17, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 139.7, 131.7, 130.5, 122.5, 91.3. HRMS calc'd for $C_{14}H_8Br_4$: 495.7321; Found: 495.7312; 1.8 ppm error.



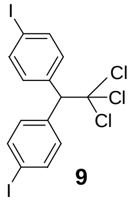
7

1,1-Bis(4-bromophenyl)-2,2,2-trichloroethane (7).[6] A 500 mL three neck round bottom flask was equipped with a mechanical stirrer and an addition funnel, purged with nitrogen, and sealed with a septum. Trichloroethanediol (5.95 g, 36 mmol) and nitrogen sparged bromobenzene (60 mL, 570 mmol) were added via syringe. The reaction was cooled to 0 °C and fuming sulfuric acid (81.8 mL, 570 mmol) was added, via the addition funnel, drop-wise over a period of 1h. The reaction mixture was stirred and kept at 0 °C for 2 d. The reaction mixture was then quenched with ice water and diluted with CH_2Cl_2. The organic layer was washed with a dilute solution of sodium bicarbonate (3×) and the aqueous layer was extracted with ether (3×). Organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed from the filtrate via rotary evaporation and the resulting solid was dried for 24 h *in vacuo* with slight heating to 50 °C to remove any excess bromobenzene. MP 142-143 °C. FTIR (KBr) 1583, 1487, 1403, 1076, 1010, 849, 776, 761, 672, 612, 492. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dt, *J* = 8.82, 2.85 Hz, 4 H), 7.44 (dt, *J* =8.75, 2.63 Hz, 4 H), 5.75 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 131.6, 122.6, 100.5, 69.7. HRMS calc'd for $C_{14}H_9Br_2Cl_3$: 439.8137; Found: 439.8140; 0.67 ppm error.



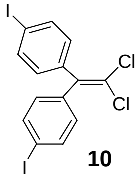
8

2,2-Bis(4-bromophenyl)-1,1-dichloroethylene (8).[6] To a 250 mL round bottom flask, equipped with a stir bar, reflux condensor, and purged with nitrogen, was added **7**. The flask was then sealed under nitrogen with a septum. THF/H_2O (10:1 solution) was added via syringe. A nitrogen sparged KOH solution (15 equivalents, 3M) was added drop-wise via syringe. The reaction was then heated to reflux and stirred for 2 d. After this period of time the reaction mixture was diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was then extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed from the filtrate via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. MP 121-123 °C. FTIR (KBr) 2362, 1902, 1582, 1484, 1391, 1070, 1010, 970, 857, 822, 788, 716, 668, 489. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dt, *J* =8.59, 2.25 Hz, 4 H), 7.14 (dt, *J* =8.66, 2.23 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.8, 131.6, 131.0, 122.51, 120.5. HRMS calc'd for $C_{14}H_8Br_2Cl_2$: 405.8348. Found: 405.8347; 0.32 ppm error.



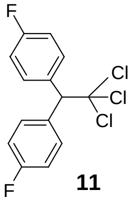
9

1,1-Bis(4-iodophenyl)-2,2,2-trichloroethane (9).[9] A 500 mL three neck round bottom flask was equipped with a mechanical stirrer and an addition funnel, purged with nitrogen, and sealed with a septum. Trichloroethanediol (5.95 g, 36 mmol) and nitrogen sparged iodobenzene (60.02 mL, 570 mmol) were added via syringe. The reaction was cooled to 0 °C and fuming sulfuric acid(81.8 mL, 570 mmol) was added, via the addition funnel, drop-wise over a period of 1h. The reaction mixture was stirred and kept at 0 °C for 2 d. The reaction mixture was then quenched with ice water and then diluted with CH_2Cl_2. The organic layer was washed with a dilute solution of sodium bicarbonate (3×) and the aqueous layer was extracted with ether (3×). Organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed from the filtrate via rotary evaporation and the resulting solid was dried for 24 h *in vacuo* with slight heating (50 °C) to remove any excess iodobenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6 (dt, *J* = 8.5, 2.2 Hz, 4H), 7.3 (dt, *J* = 8.5, 2.1 Hz, 4H), 5.0 (s, 1H).



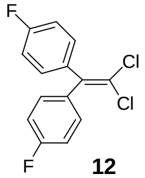
10

2,2-Bis(4-iodophenyl)-1,1-dichloroethylene (10). To a 250 mL round bottom flask, equipped with a stir bar, reflux condensor, and purged with nitrogen, was added **9**. The flask was then sealed under nitrogen with a septum. THF/H_2O (10:1 solution) was added via syringe. A nitrogen sparged KOH solution (15 equivalents, 3M) was added drop-wise via syringe. The reaction was then heated to reflux and stirred for 2 d. After this period of time the reaction mixture was diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was then extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed from the filtrate via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. MP 144 –145 °C. FTIR (KBr) 3051, 1901, 1575, 1475, 1381, 1248, 1055, 1001, 851, 816, 781, 711, 654, 478. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6 (dt, *J* = 8.5, 2.2 Hz, 4H), 7.0 (dt, *J* = 8.5, 2.1 Hz, 4H).). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.6, 137.8, 131.3, 120.6, 94.5. HRMS calc'd for $C_{14}H_8I_2Cl_2$: 499.8092. Found: 499.8094; 0.40 ppm error.



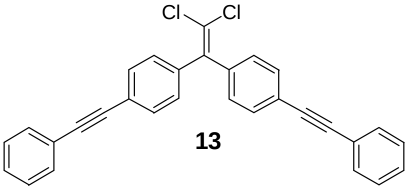
11

1,1-Bis(4-fluorophenyl)-2,2,2-trichloroethane (11).[10] A 500 mL three neck round bottom flask was equipped with a mechanical stirrer and an addition funnel, purged with nitrogen, and sealed with a septum. Trichloroethanediol (5.95 g, 36 mmol) and nitrogen sparged iodobenzene (60.02 mL, 570 mmol) were added via syringe. The reaction was cooled to 0 °C and fuming sulfuric acid (81.8 mL, 570 mmol) was added, via the addition funnel, drop-wise over a period of 1h. The reaction mixture was stirred and kept at 0 °C for 2 d. The reaction mixture was then quenched with ice water and then diluted with CH_2Cl_2. The organic layer was washed with a dilute solution of sodium bicarbonate (3×) and the aqueous layer was extracted with ether (3×). Organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed from the filtrate via rotary evaporation and the resulting solid was dried for 24 h *in vacuo* with slight heating (50 °C) to remove any excess fluorobenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5 (q, *J* = 4.6 Hz, 4H), 7.0 (t, *J* = 8.6 Hz, 4H), 5.0 (s, 1H).



12

2,2-Bis(4-fluorophenyl)-1,1-dichloroethylene (12). To a 250 mL round bottom flask, equipped with a stir bar, reflux condensor, and purged with nitrogen, was added **11**. The flask was then sealed under nitrogen with a septum. THF/H_2O (10:1 solution) was added via syringe. A nitrogen sparged KOH solution (15 equivalents, 3M) was added drop-wise via syringe. The reaction was then heated to reflux and stirred for 2 d. After this period of time the reaction mixture was diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was then extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. FTIR (KBr) 3440, 3057, 1896, 1594, 1504, 1299, 1233, 1157, 1233, 1157, 1095, 1015, 969, 828, 766, 581, 539. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (q, *J* = 4.7 Hz, 4H), 7.0 (t, *J* = 8.7 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 161.3, 138.5, 135.2, 135.1, 131.3, 131.2, 120.0, 115.5, 115.3. HRMS calc'd for $C_{14}H_8F_2Cl_2$: 293.9971. Found: 283.9973; 0.75 ppm error.



13

2,2-Bis(*p*-phenyleneethynylene)-1,1-dichloroethlyene (13). To a 250 mL round bottom flask, equipped with a stir bar and reflux condensor, was **8**, (4.06 g/ 10 mmol), Copper Iodide (0.190 g/ 1mmol), bistriphenylphosphine palladium(II) dichloride (0.351 g/ 0.5 mmol), and triphenylphosphine (0.262 g/1 mmol). The flask was then sealed with a septum, evacuated, and backfilled with nitrogen (3×). Benzene (92 mL), Hunig's base (10.45 mL/60 mmol), and phenylacetylene (3.3 mL/30 mmol) were added via syringe. The reaction was heated to reflux for 2 d. The reaction mixture was diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was removed from the filtrate via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. MP 128-131 °C. FTIR (KBr) 3414, 1600, 1505, 1440, 1400, 1105, 1020, 971, 863, 785, 755, 688, 576, 516. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.48 (m), 7.36-7.32 (m), 7.27(dt, *J* =8.37, 1.81 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.9, 131.5, 131.5, 129.5, 128.5, 128.4, 123.2, 123.0, 96.4, 88.9. HRMS calc'd for $C_{30}H_{18}Cl_2$: 448.0786. Found: 448.0787; 0.26 ppm error.

2.4 References

(1) Green, M. B.; Hartley, G. S.; West, T. F. In *Chemicals for Crop Improvement and Pest Management*; 3rd Editon ed.; Pergamon Press: Oxford, 1987, pp 70-83.

(2) Hileman, B. *Chem. & Eng. News* **1999**, *77*, 41.

(3) Hall, R. J.; Marco, G. J.; Hollingworth, R. M.; Durham, W. In *Silent Spring Revisited*; American Chemical Society: Washington, 1987.

(4) Brown, A. W. A. In *Ecology of Pesticides*; J. Wilely and Sons: New York, 1978, pp 248-269.

(5) Ames, B. N.; Gold, L. S. *Angew. Chem Int. Ed. Engl.* **1990**, *29*, 1197.

(6) Cristol, S. J.; Haller, H. L. *J. Am. Chem. Soc.* **1946**, *68*, 140-141.

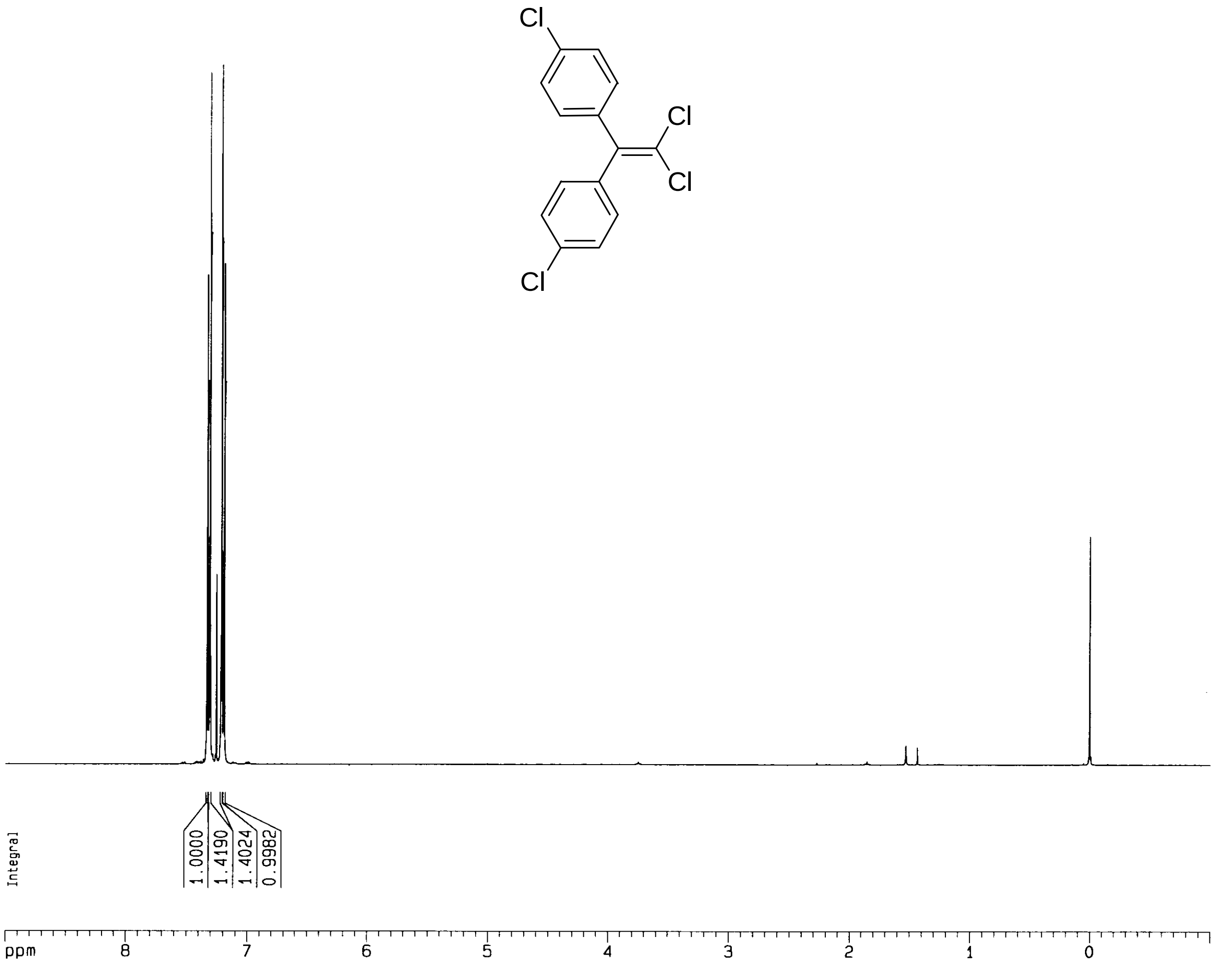
(7) Morgan, A. B., Ph.D. Thesis, University of South Carolina: Columbia, **1998**.

(8) Forrest, J.; Stephenson, O.; Waters, W. *J. Chem. Soc.* **1946**, 333-343

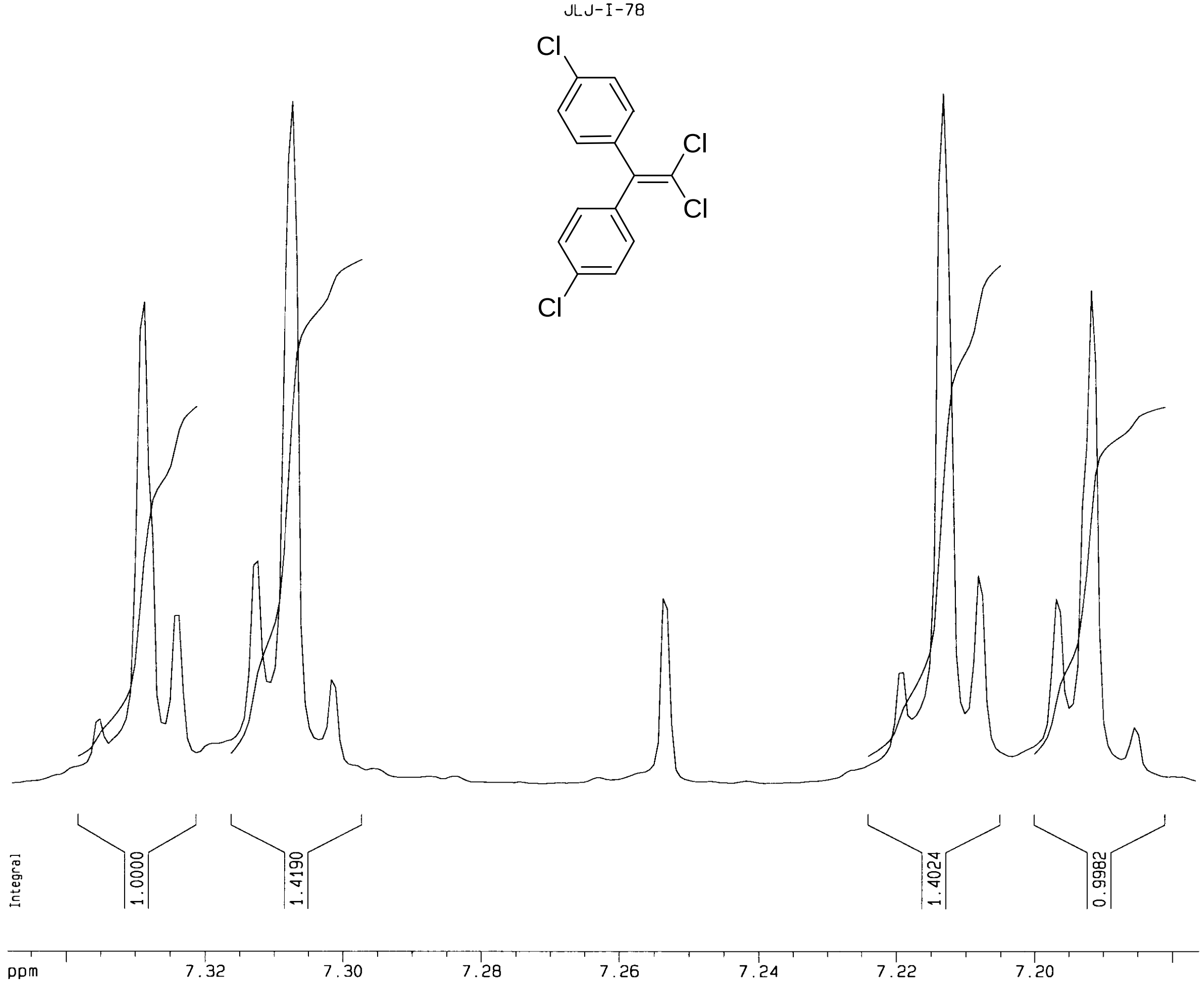
(9) Schneider, M.; Fankuchen, I. *J. Am. Chem. Soc.* **1946**, *68*, 2669-2670.

(10) Bradlow, L. H.; VanderWerf, C. A. *J. Am. Chem. Soc.* **1947**, *69*, 662-664.

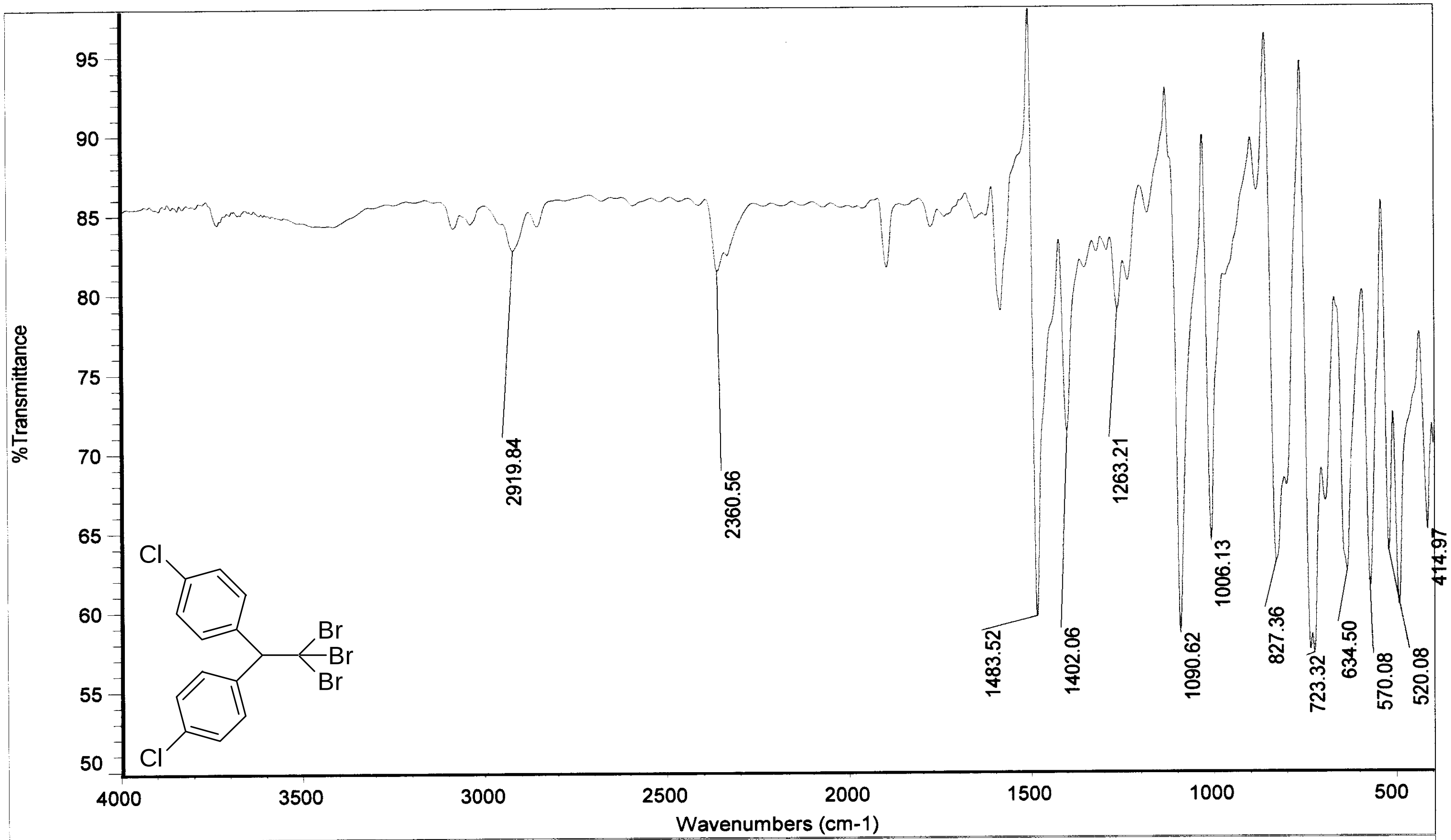
JLJ-I-78



```
Current Data Parameters
NAME             JLJ-I-78
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_              991004
Time                16.20
INSTRUM             spect
PROBHD    5 mm BBO BB-1
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      9
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  456.1
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 =========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300121 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 9.000 ppm
F1                3601.17 Hz
F2P                -1.000 ppm
F2                -400.13 Hz
PPMCM             0.50000 ppm/cm
HZCM            200.06500 Hz/cm
```



```
Current Data Parameters
NAME            JLJ-I-78
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_             991004
Time               16.20
INSTRUM            spect
PROBHD    5 mm BBO BB-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     9
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 456.1
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300121 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.348 ppm
F1               2940.33 Hz
F2P                7.176 ppm
F2               2871.42 Hz
PPMCM            0.00861 ppm/cm
HZCM             3.44581 Hz/cm
```

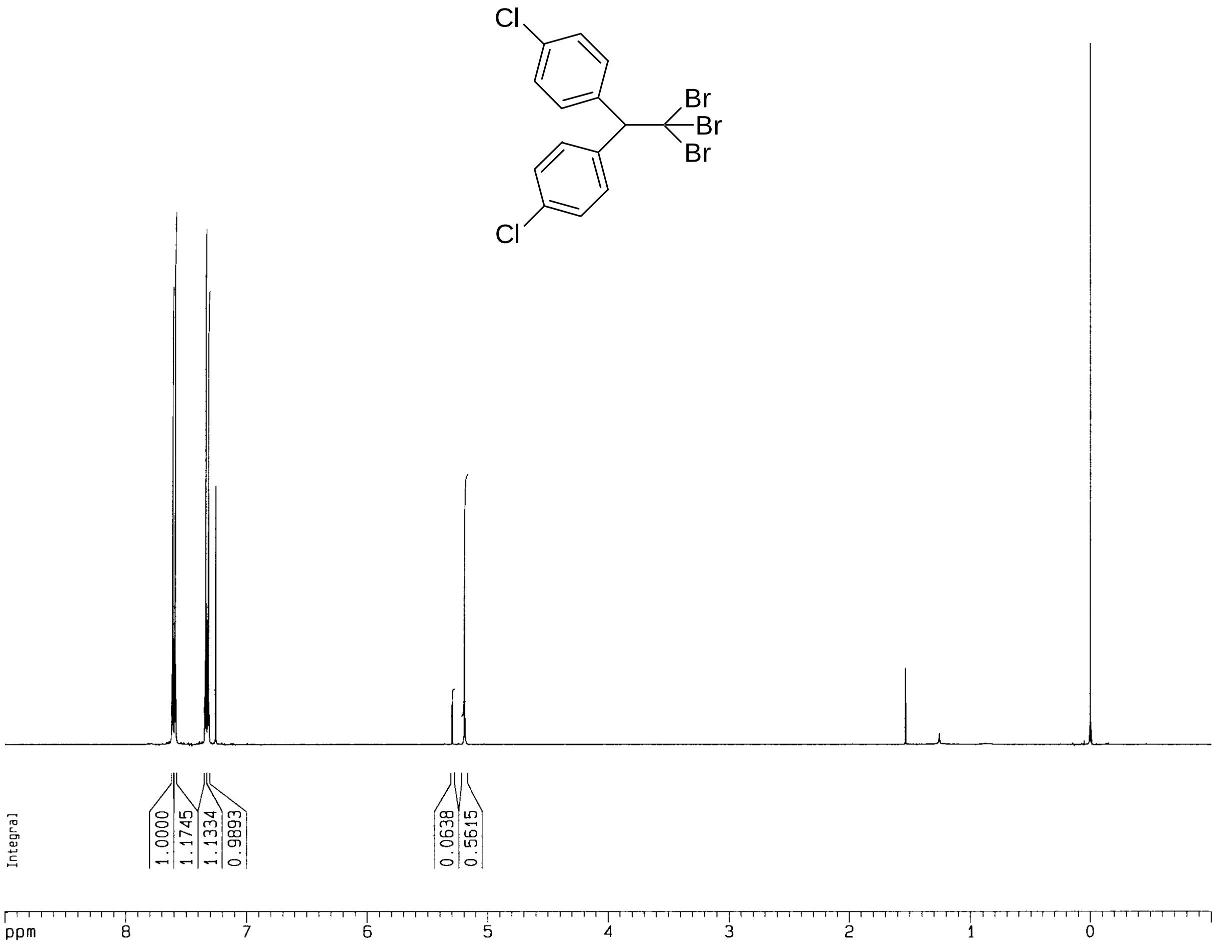


Date: Wed Jan 26 14:56:12 2000 ***JLJ-I-127 col. 3; frac 2&3

Scans: 18

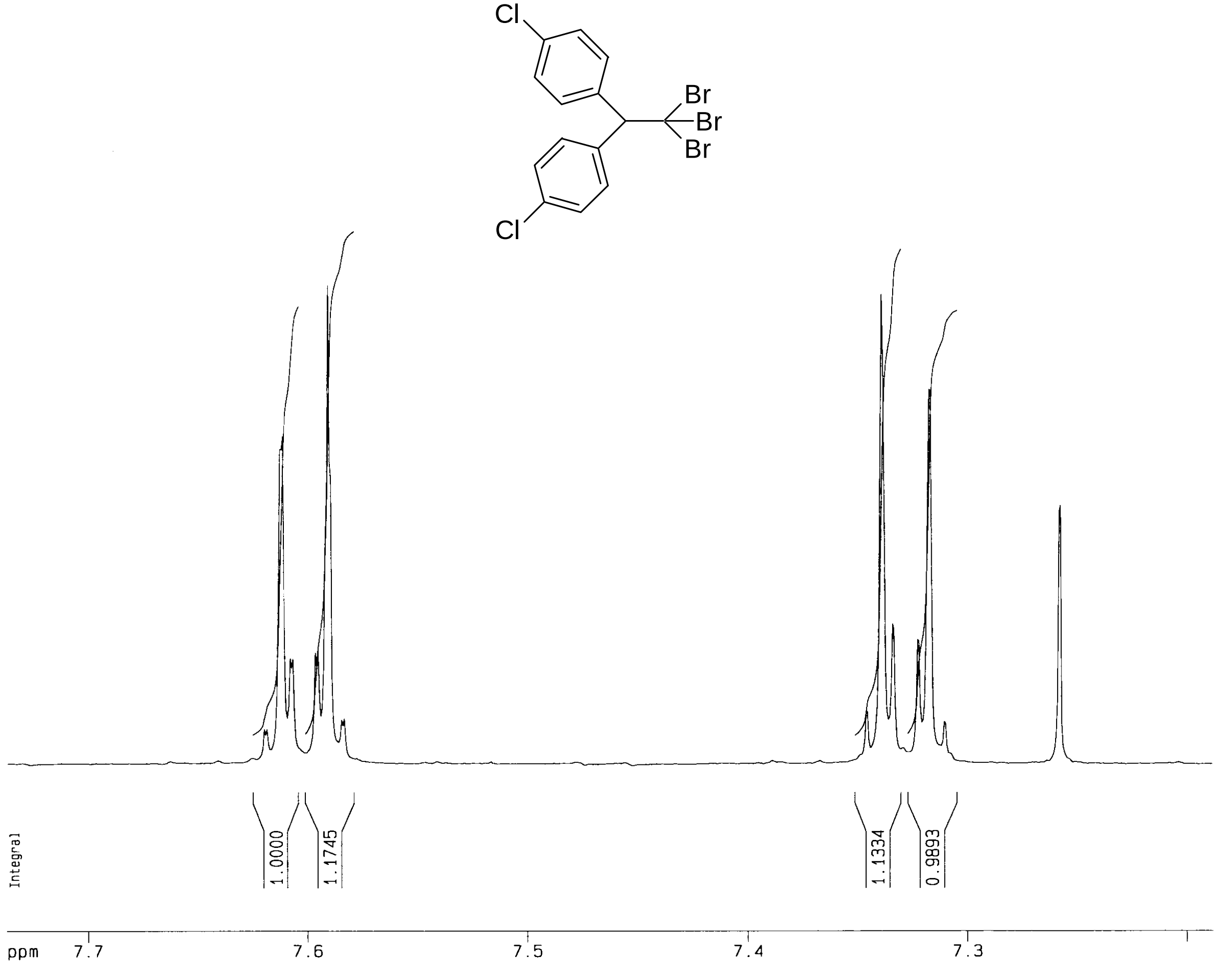
Resolution: 4.000

JLJ-I-127
col. 3, frac.1



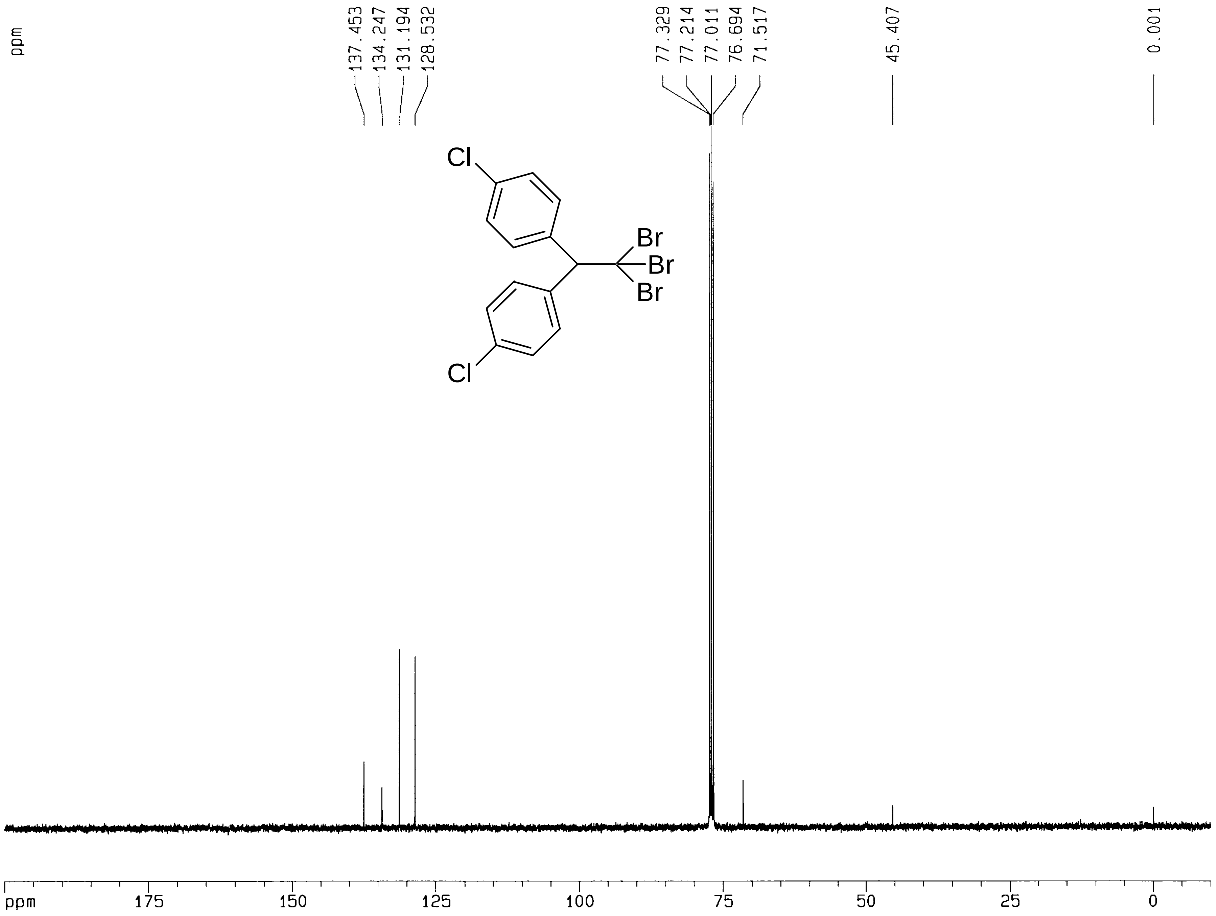
```
Current Data Parameters
NAME          JLJ-I-127
EXPNO                 8
PROCNO                1

F2 - Acquisition Parameters
Date_          20000126
Time              14.09
INSTRUM           spect
PROBHD   5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                645.1
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300101 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -1.000 ppm
F2              -400.13 Hz
PPMCM           0.50000 ppm/cm
HZCM          200.06500 Hz/cm
```

JLJ-I-127
col. 3, frac.1



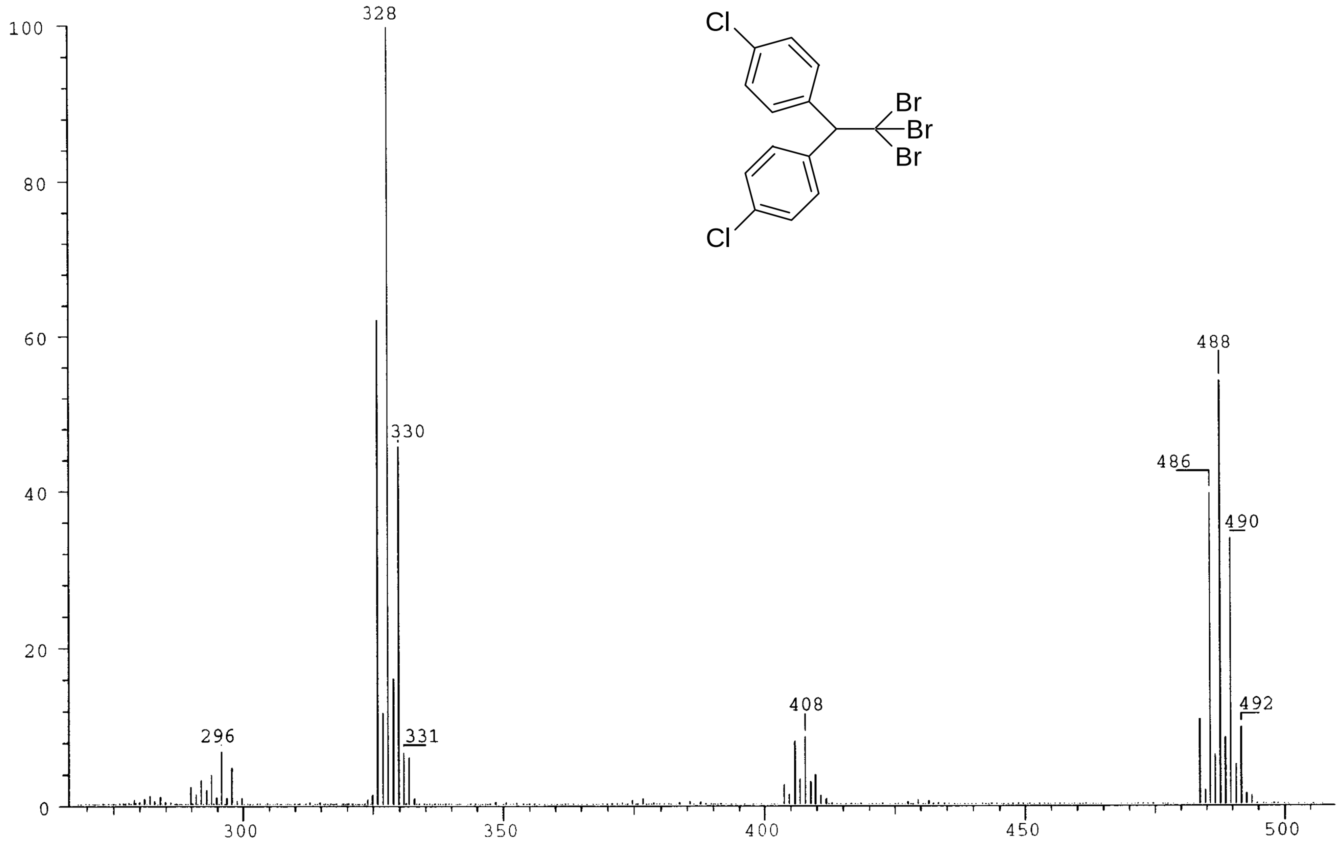
```
Current Data Parameters
NAME            JLJ-I-127
EXPNO                   8
PROCNO                  1

F2 - Acquisition Parameters
Date_            20000126
Time                14.09
INSTRUM             spect
PROBHD   5 mm BBO BB-1
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  645.1
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 ========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300101 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 7.737 ppm
F1                3095.63 Hz
F2P                 7.188 ppm
F2                2876.28 Hz
PPMCM             0.02741 ppm/cm
HZCM             10.96717 Hz/cm
```

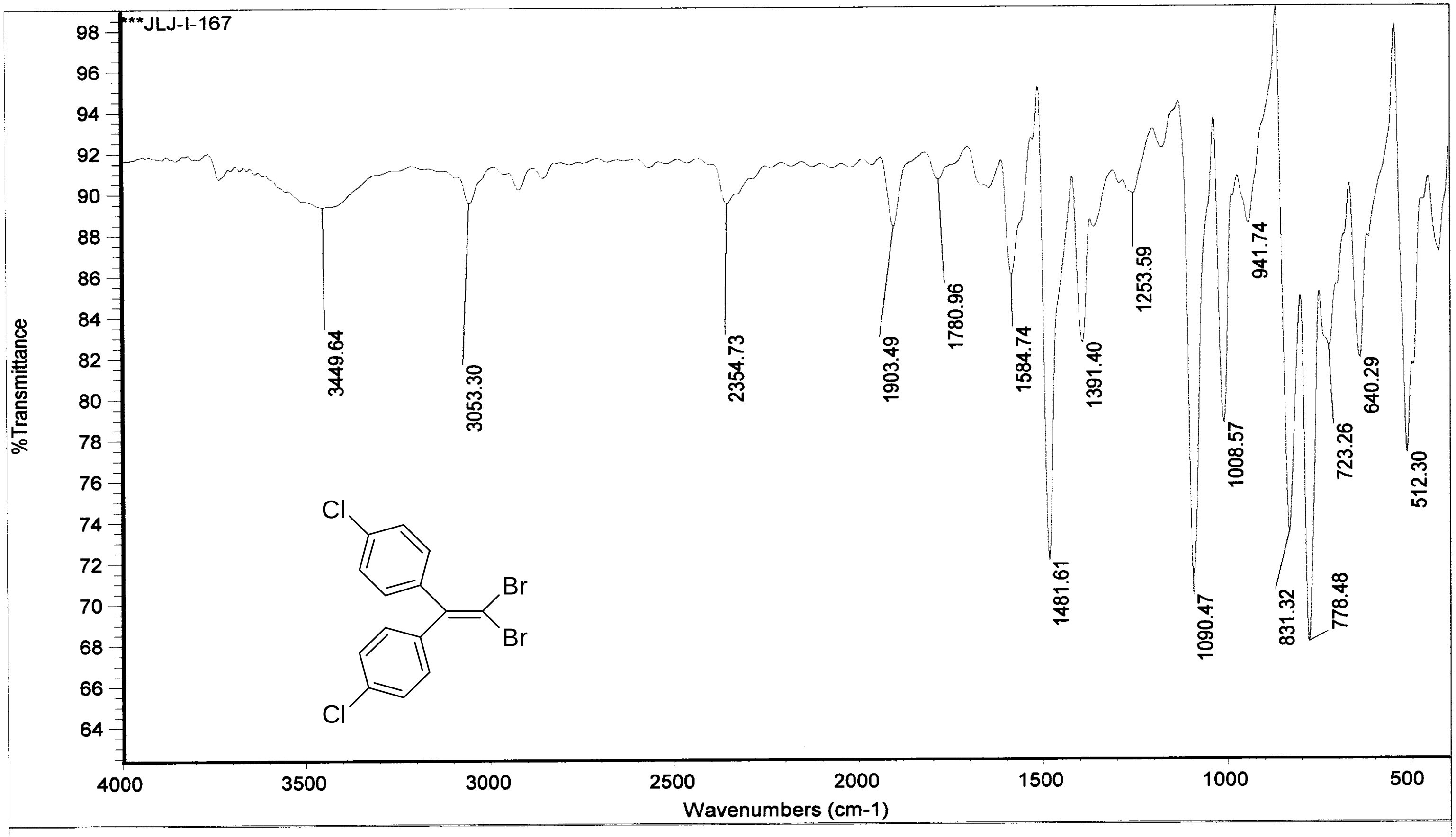
JLJ-I-127
frac. 2&3



```
Current Data Parameters
NAME           JLJ-I-127
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20000205
Time               12.00
INSTRUM            spect
PROBHD    5 mm BBO BB-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     0
SWH            25125.629 Hz
FIDRES          0.383387 Hz
AQ             1.3042164 sec
RG                 16384
DW                19.900 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                 13C
P1                  8.30 usec
PL1                 0.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 ============
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                11.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127697 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              200.000 ppm
F1              20122.55 Hz
F2P              -10.000 ppm
F2              -1006.13 Hz
PPMCM           10.50000 ppm/cm
HZCM          1056.43408 Hz/cm
```

```
SPEC: jlji127fr1.dat (11-Feb-00 10:39:42)                       Scans:   1 > 84
Samp: JLJ-I-127 Frac.#1  C14 H9 Br3 Cl2  487
Oper: TDM                    Study:  EI +                        Client:  JLJ/JMT
Base: 234.92                 Masses:  50.00 > 600.00             #Peaks:  1160
Peak:    1.0 amu             Intensity:   24512768               RIC: 132553487
Scan 67 @ 3.93 min (EI +VE +LMR  BSCAN (EXP) UP HR NRM)                   1.5E+06
```



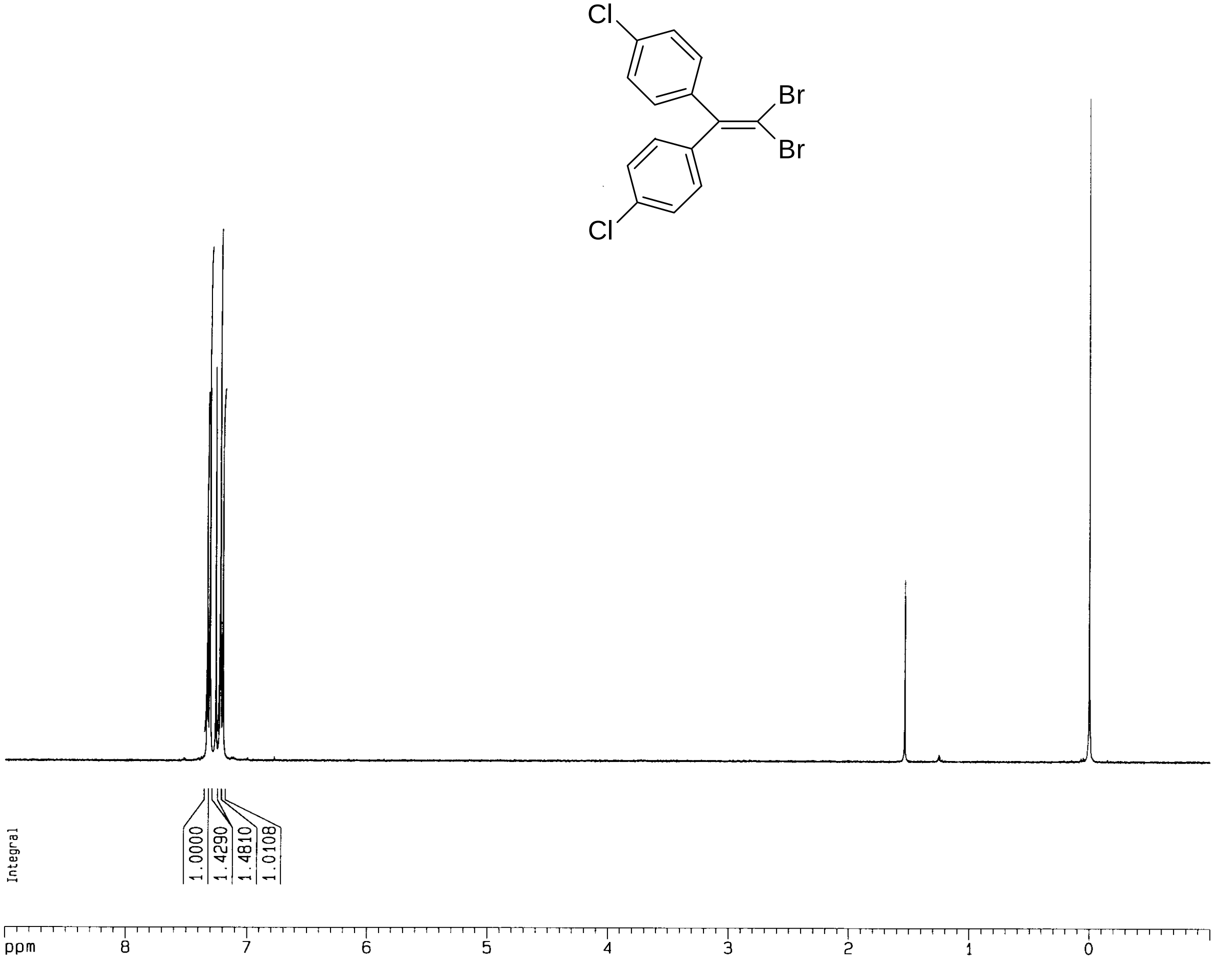


Date: Thu May 11 18:04:06 2000 ***JLJ-I-167

Scans: 20

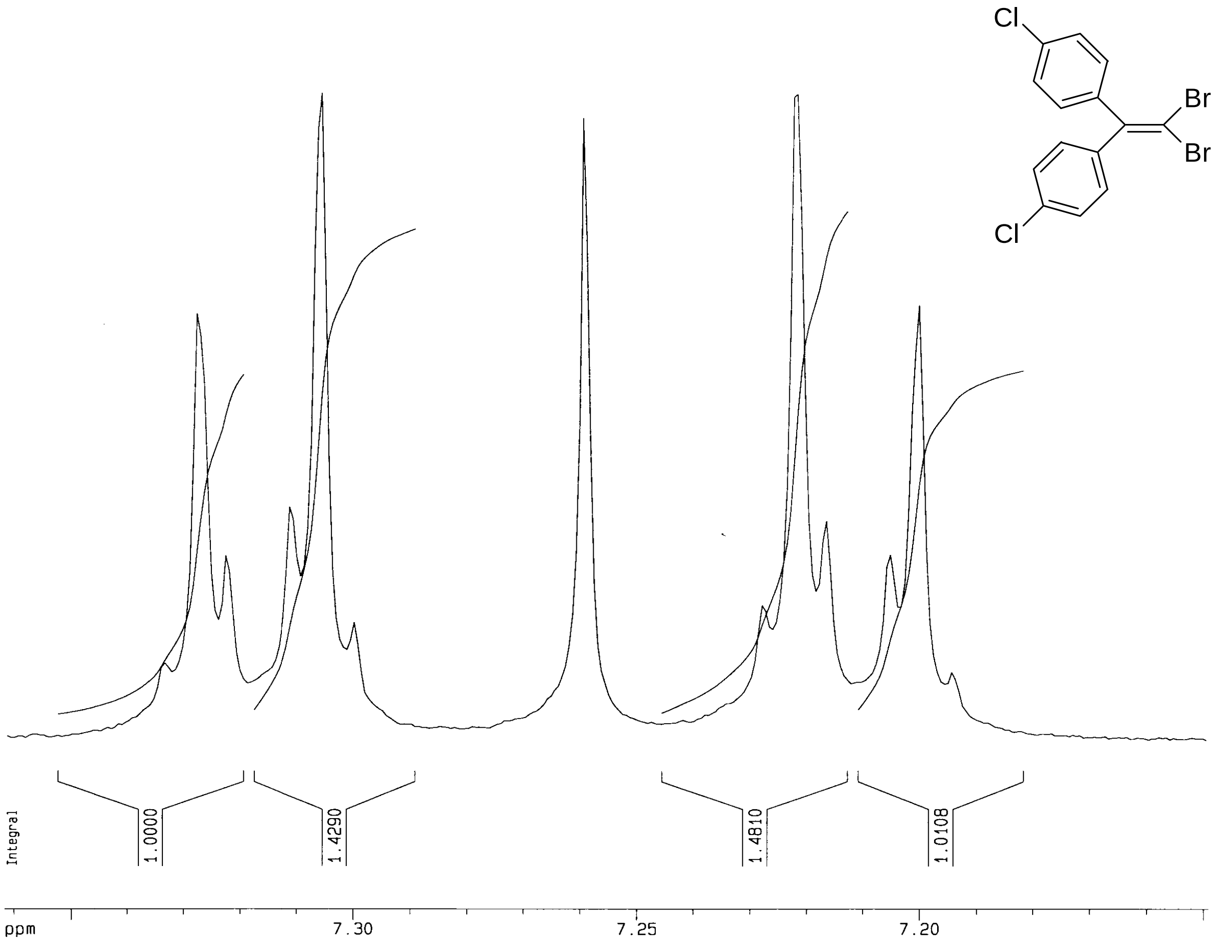
Resolution: 4.000

JLJ-I-167
recrystillized



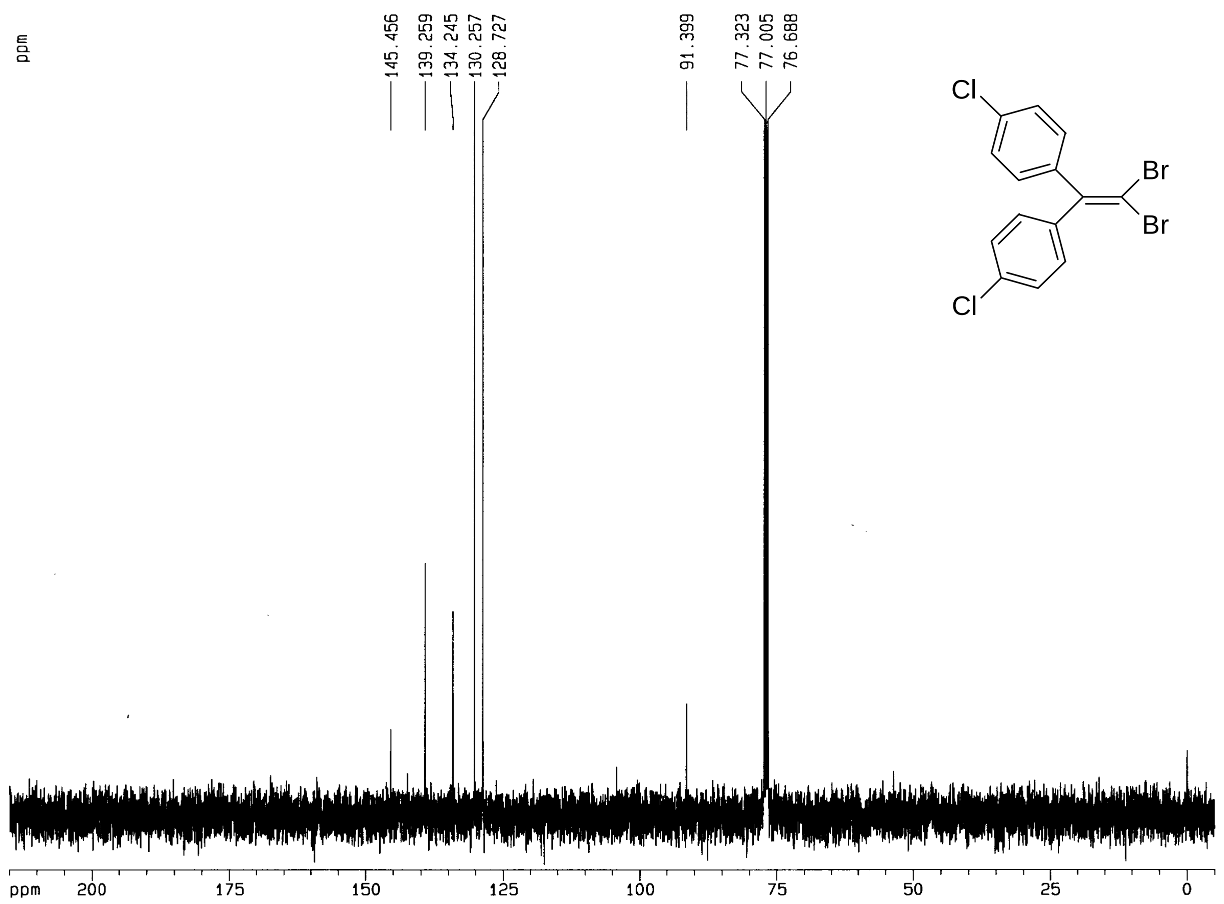
```
Current Data Parameters
NAME             JLJ-I-167
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20000331
Time                 11.00
INSTRUM              spect
PROBHD    5 mm BBO BB-1
PULPROG               zg30
TD                   65536
SOLVENT              CDC13
NS                       8
DS                       0
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                   912.3
DW                  60.400 usec
DE                    6.00 usec
TE                   300.0 K
D1              3.00000000 sec

============ CHANNEL f1 =========
NUC1                    1H
P1                   12.50 usec
PL1                   0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF             400.1300099 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                  9.000 ppm
F1                 3601.17 Hz
F2P                 -1.000 ppm
F2                 -400.13 Hz
PPMCM              0.50000 ppm/cm
HZCM             200.06500 Hz/cm
```

JLJ-I-167
recrystillized



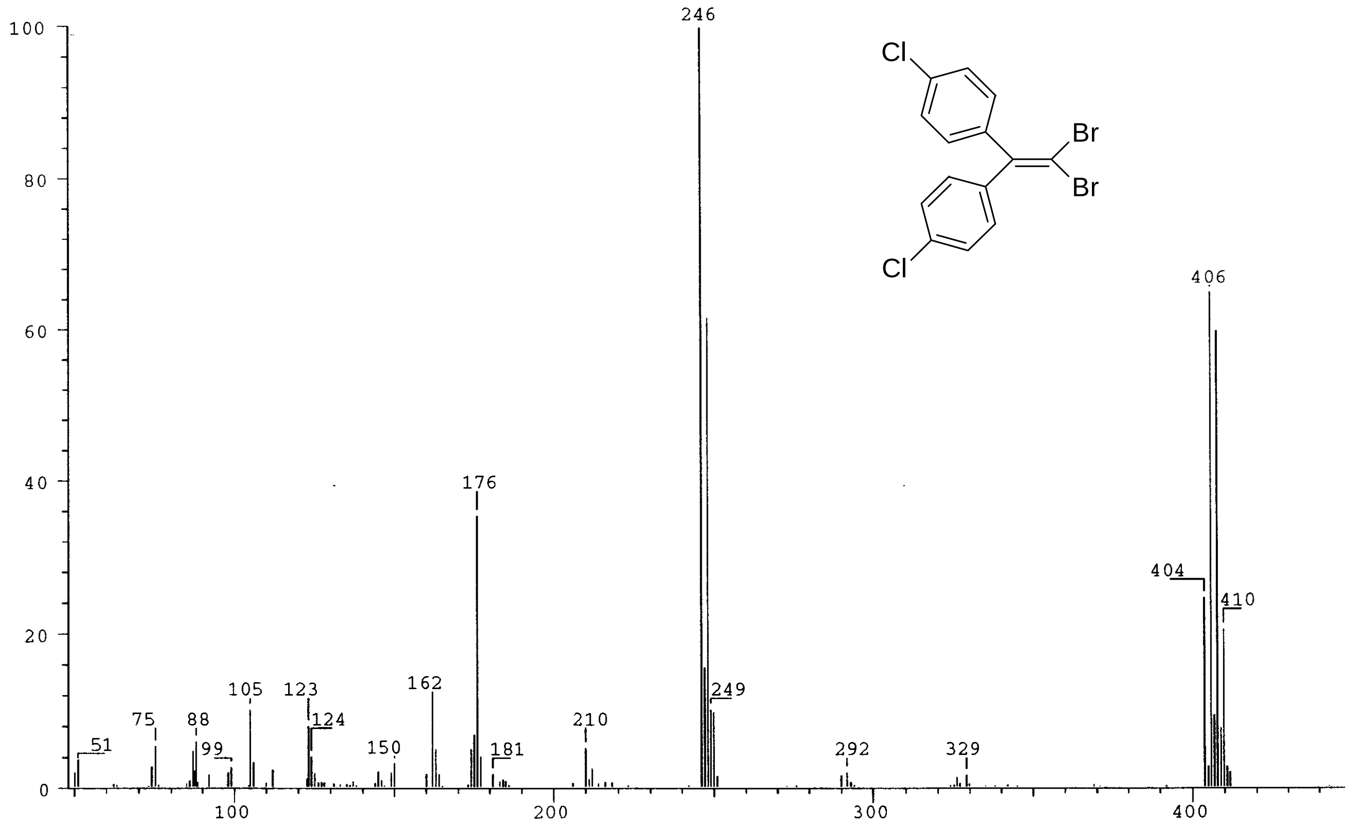
```
Current Data Parameters
NAME          JLJ-I-167
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20000331
Time              11.00
INSTRUM           spect
PROBHD   5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                912.3
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300099 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               7.362 ppm
F1              2945.61 Hz
F2P               7.149 ppm
F2              2860.59 Hz
PPMCM        0.01062 ppm/cm
HZCM         4.25082 Hz/cm
```

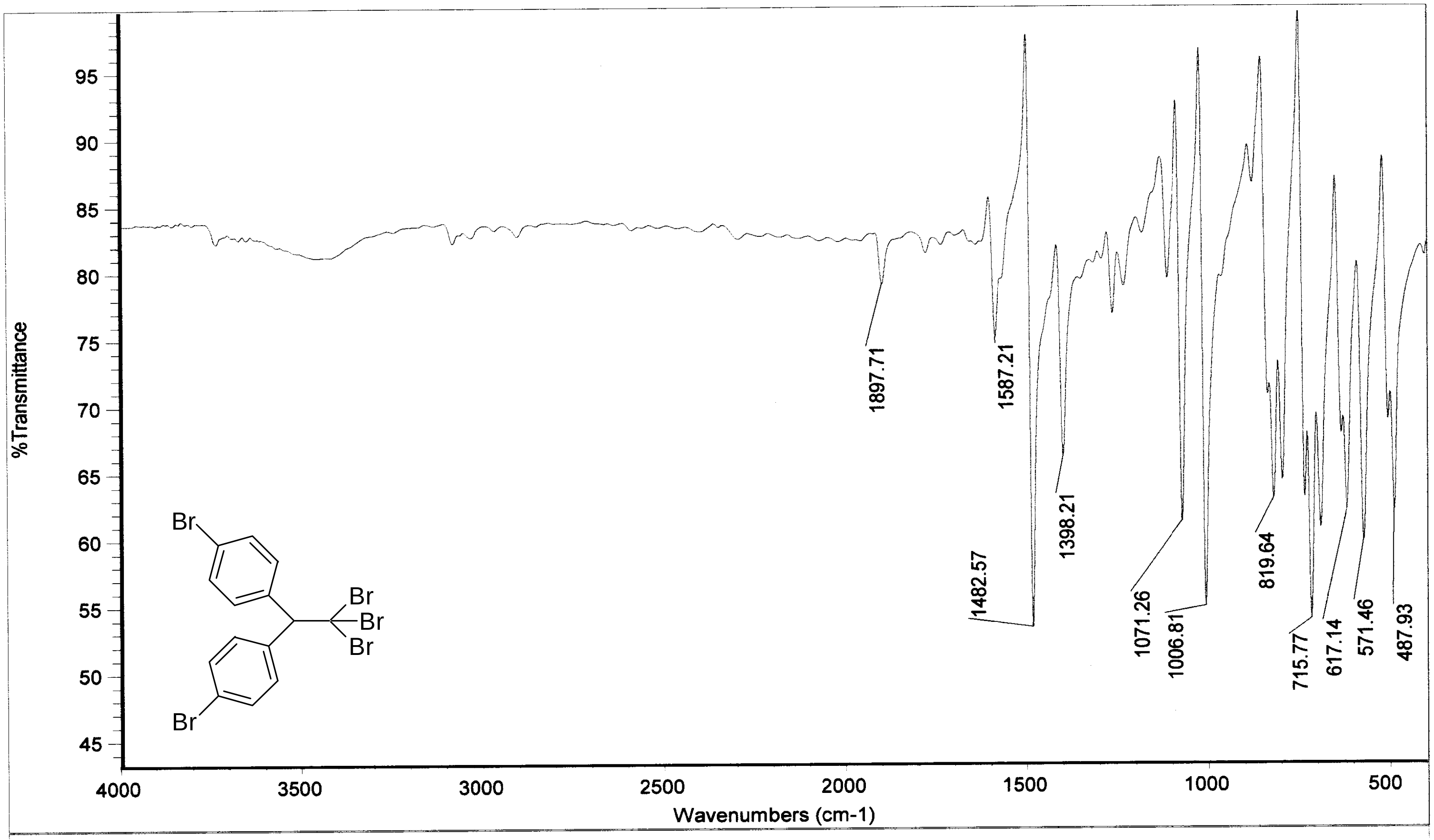
JLJ-I-167



```
Current Data Parameters
NAME             JLJ-I-167
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20000511
Time                 18.44
INSTRUM              spect
PROBHD    5 mm BBO BB-1
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     256
DS                       0
SWH              25125.629 Hz
FIDRES            0.383387 Hz
AQ               1.3042164 sec
RG                   322.5
DW                  19.900 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
d12             0.00002000 sec

============ CHANNEL f1 ============
NUC1                   13C
P1                    8.30 usec
PL1                  -3.00 dB
SFO1           100.6237959 MHz

============ CHANNEL f2 ============
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 18.00 dB
PL13                 18.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF             100.6127705 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                215.000 ppm
F1                21631.74 Hz
F2P                 -5.000 ppm
F2                 -503.07 Hz
PPMCM             11.00000 ppm/cm
HZCM            1106.74048 Hz/cm
```

```
SPEC: jlji167 (05-Apr-00 11:57:58)                              Scans:  1 > 92
Samp: JLJ-I-167 C14 H8 Br2 Cl2  403.837002
Oper: TDM                  Study: EI + HR                       Client: JLJ/JMT
Base: 245.96               Masses: 50.00 > 600.00               #Peaks: 107
Peak: 1000.0 mmu           Intensity:  1050504                  RIC: 5885246
REG #9 @ 12.47 min (EI +VE +LMR  BSCAN (EXP) UP HR NRM) (+50-20)        1.1E+06
```

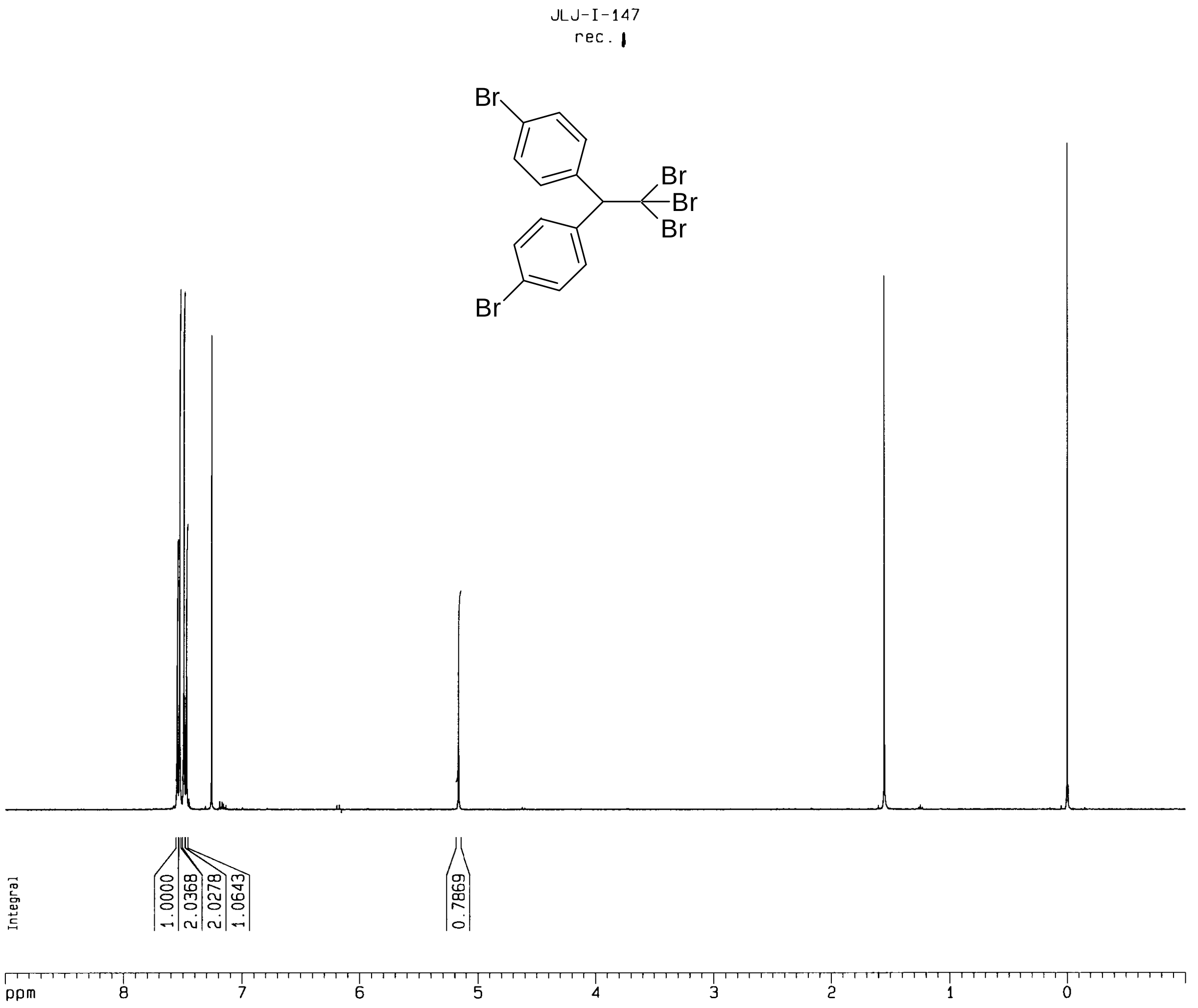




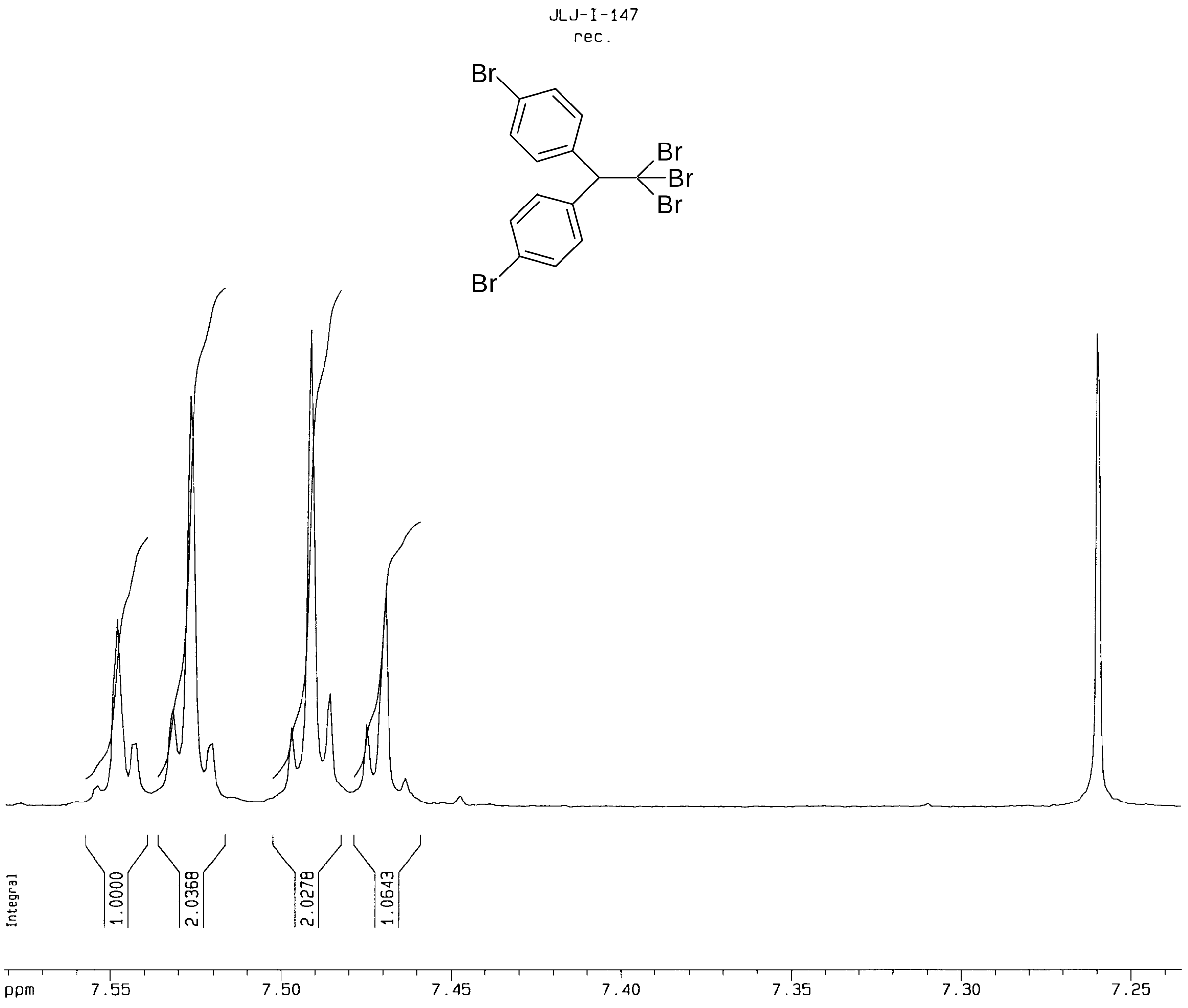
Date: Wed Feb 23 13:58:05 2000 ****JLJ-I-141

Scans: 20

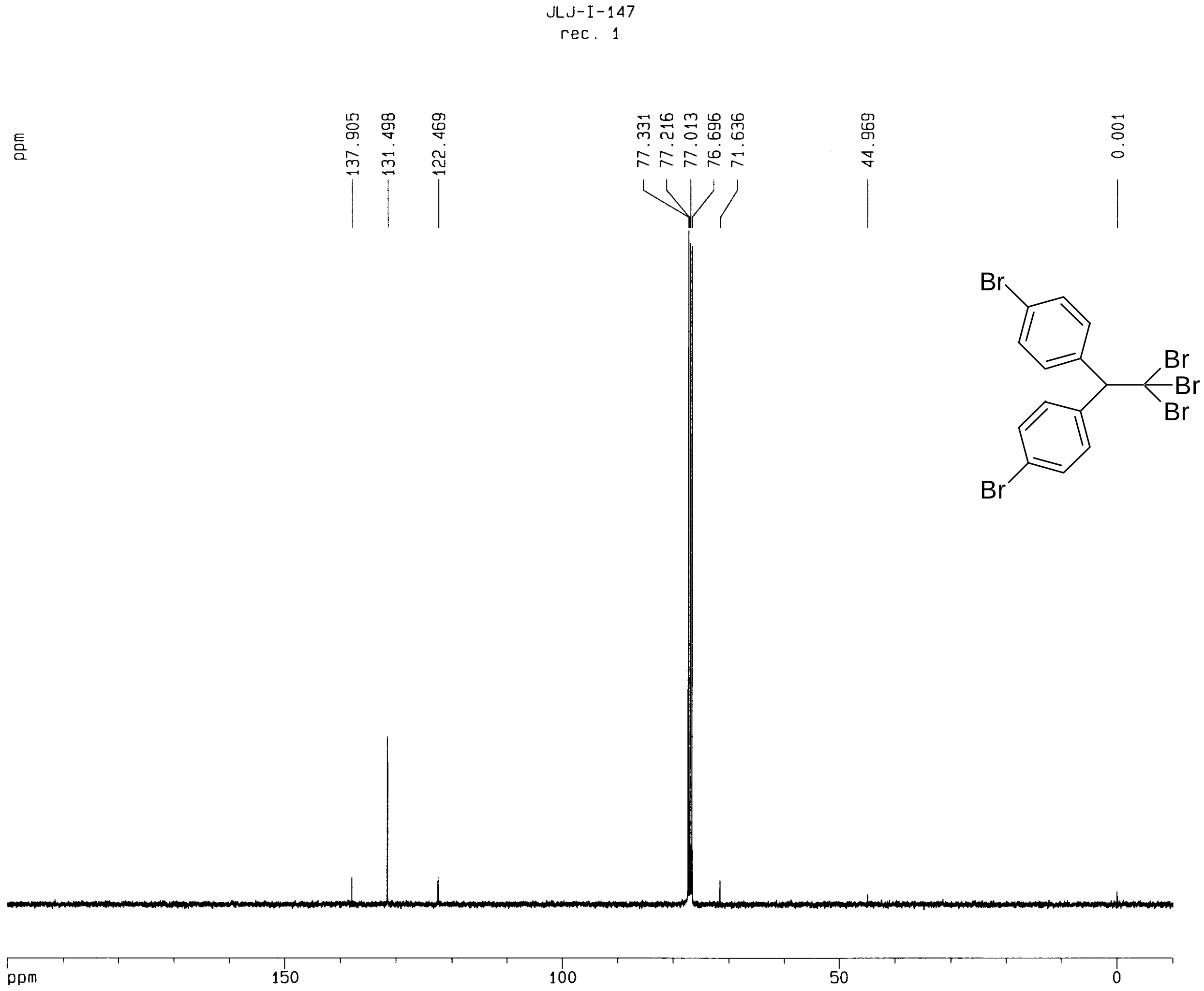
Resolution: 4.000



```
Current Data Parameters
NAME           JLJ-I-147
EXPNO                  9
PROCNO                 1

F2 - Acquisition Parameters
Date_           20000307
Time               14.04
INSTRUM            spect
PROBHD   5 mm BBO BB-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 574.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1           3.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SF01         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300096 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06500 Hz/cm
```



```
Current Data Parameters
NAME          JLJ-I-147
EXPNO                 9
PROCNO                1

F2 - Acquisition Parameters
Date_          20000307
Time              14.04
INSTRUM           spect
PROBHD    5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                574.7
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300096 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               7.581 ppm
F1              3033.45 Hz
F2P               7.235 ppm
F2              2895.01 Hz
PPMCM           0.01730 ppm/cm
HZCM            6.92202 Hz/cm
```

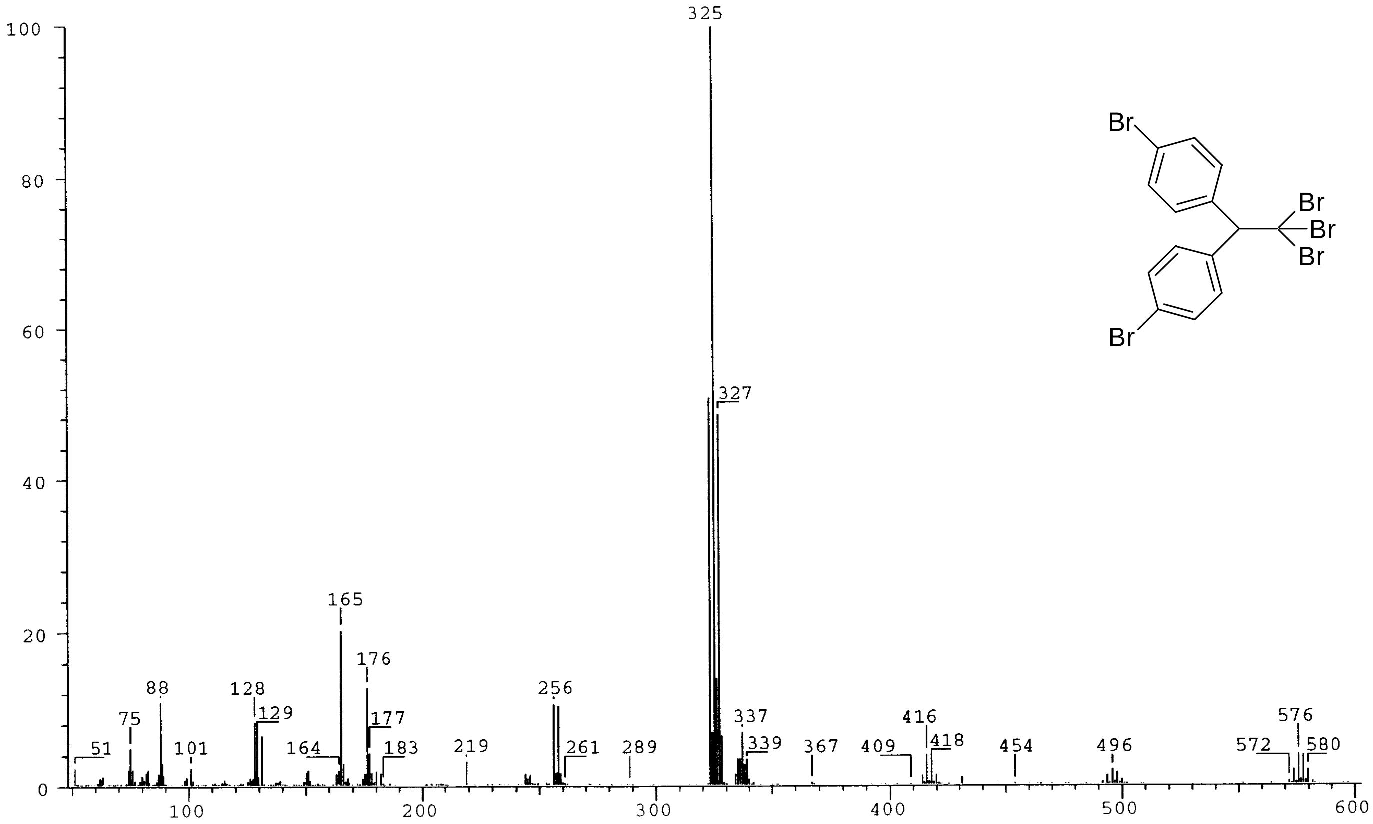


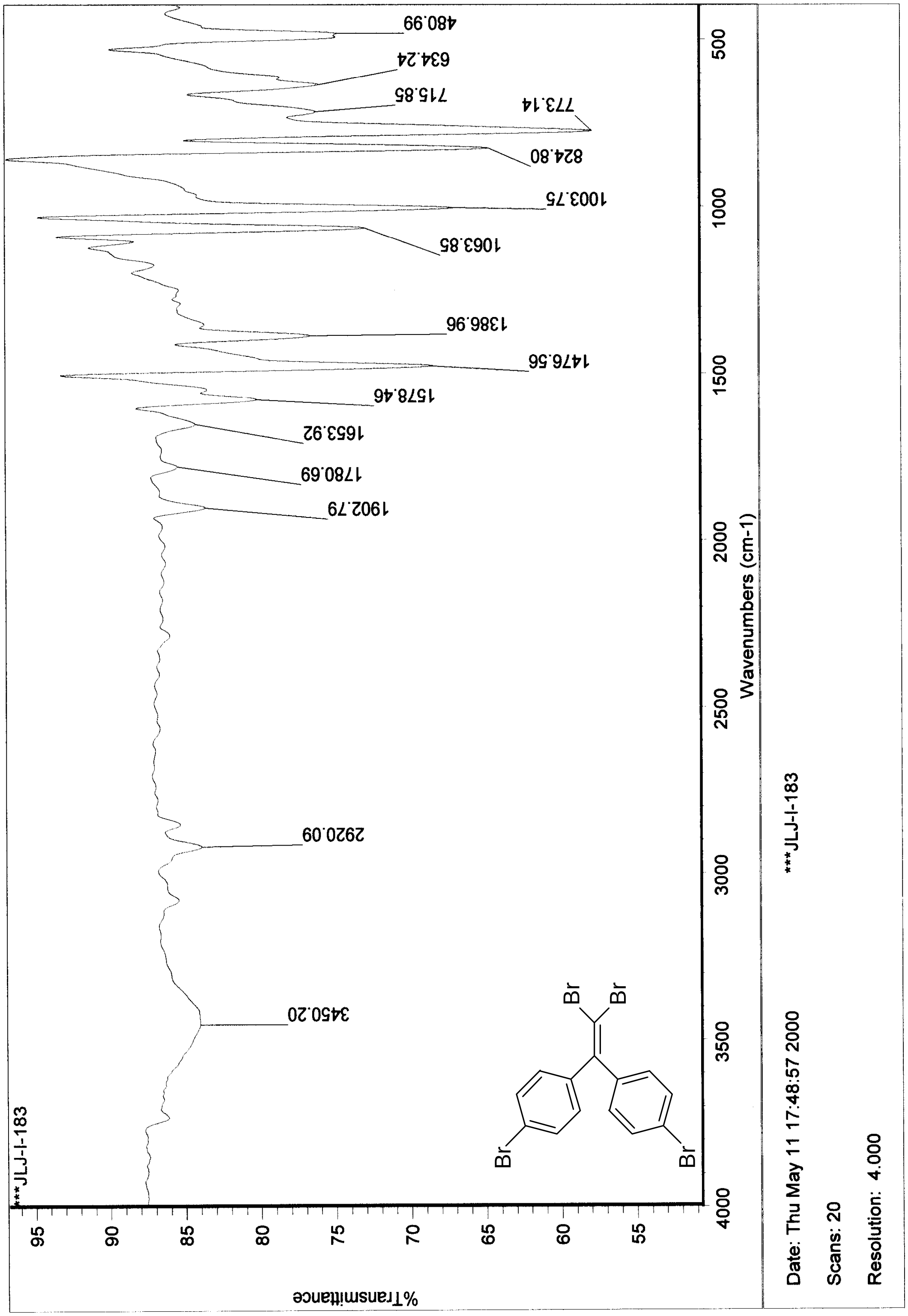
```
Current Data Parameters
NAME          JLJ-I-147
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20000307
Time              20.01
INSTRUM           spect
PROBHD   5 mm BBO BB-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    0
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ            1.3042164 sec
RG               1625.5
DW               19.900 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

============ CHANNEL f1 ============
NUC1                13C
P1                 8.30 usec
PL1                0.00 dB
SFO1        100.6237959 MHz

============ CHANNEL f2 ============
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               11.00 dB
PL12              18.00 dB
PL13              18.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127697 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P             200.000 ppm
F1             20122.55 Hz
F2P             -10.000 ppm
F2             -1006.13 Hz
PPMCM          10.50000 ppm/cm
HZCM         1056.43408 Hz/cm
```

SPEC: jlji147 (02-Mar-00 16:53:59)
Samp: JLJ-I-147 C14 H9 Br5 575.658184
Oper: TDM Study: EI +
Base: 324.90 Masses: 50.00 > 650.00
Peak: 1000.0 mmu Intensity: 4281146
REG #9 @ 8.43 min (EI +VE +HMR BSCAN (EXP) UP HR NRM) (+33-65)

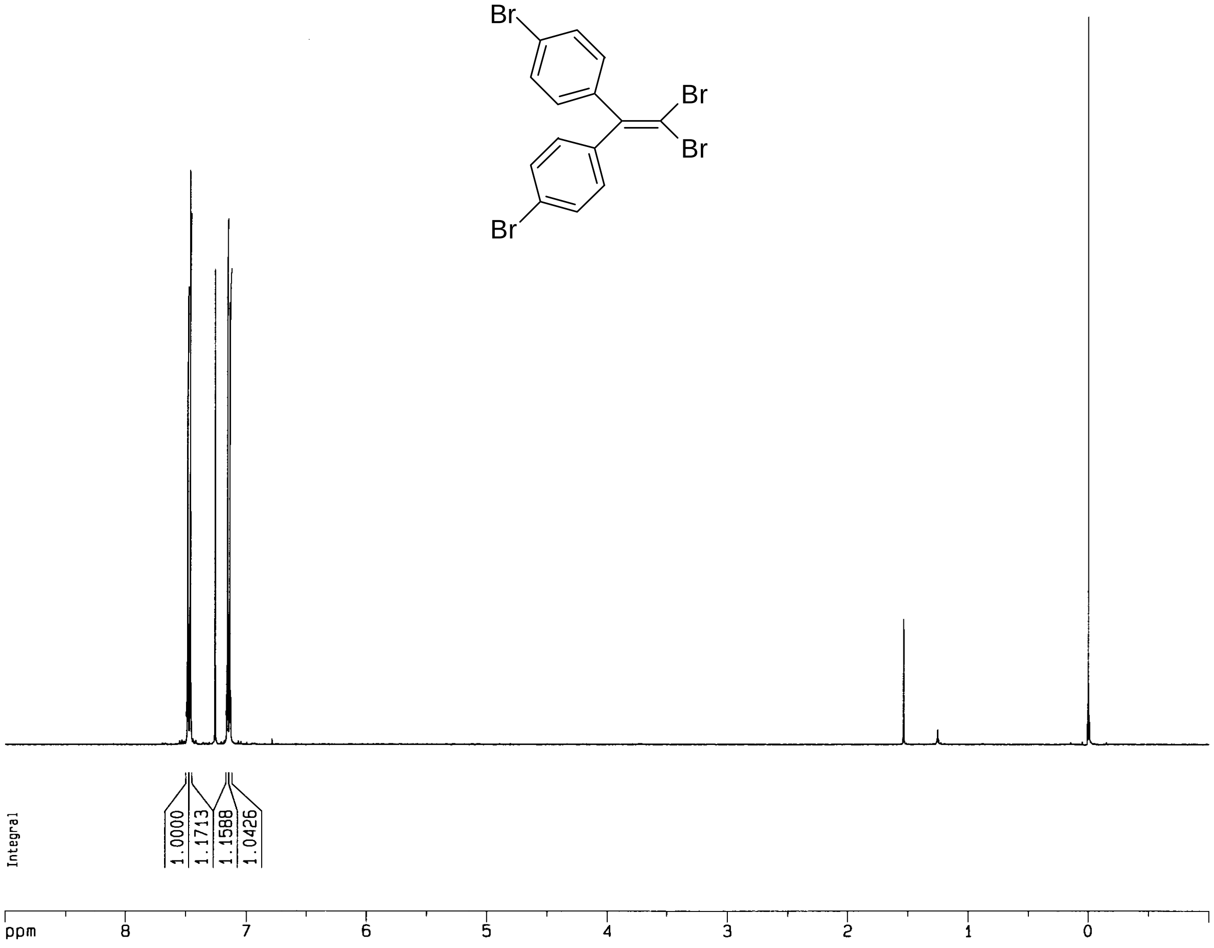
Scans: 1 > 71
Client: JLJ/JMT
#Peaks: 307
RIC: 19201777

4.3E+06

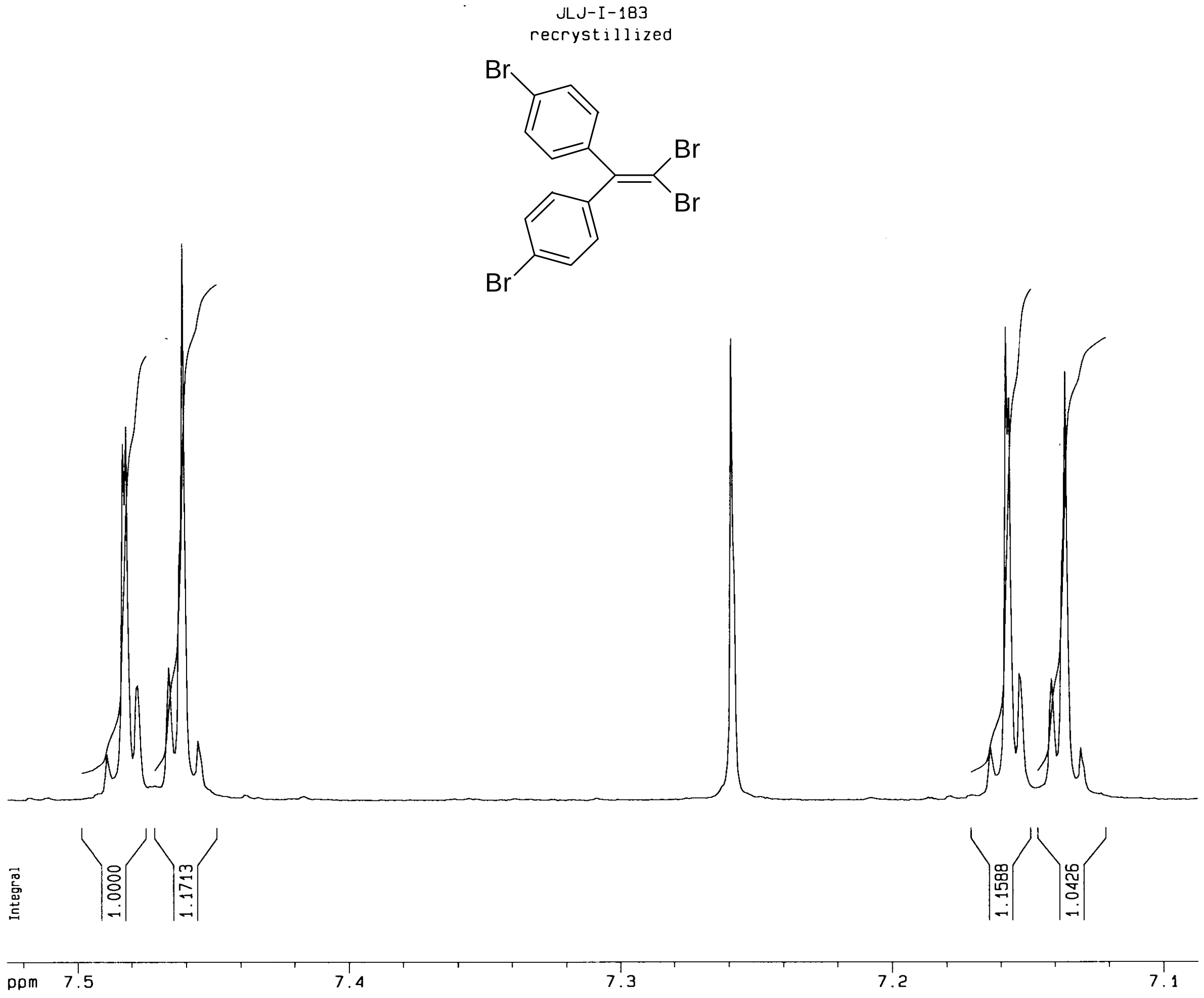



***JLJ-I-183
%Transmittance
95
90
85
80
75
70
65
60
55
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
3450.20
2920.09
1902.79
1780.69
1653.92
1578.46
1476.56
1386.96
1063.85
1003.75
824.80
773.14
715.85
634.24
480.99
Br
Br
Br
Br
Date: Thu May 11 17:48:57 2000
Scans: 20
Resolution: 4.000
***JLJ-I-183

JLJ-I-183
recrystillized

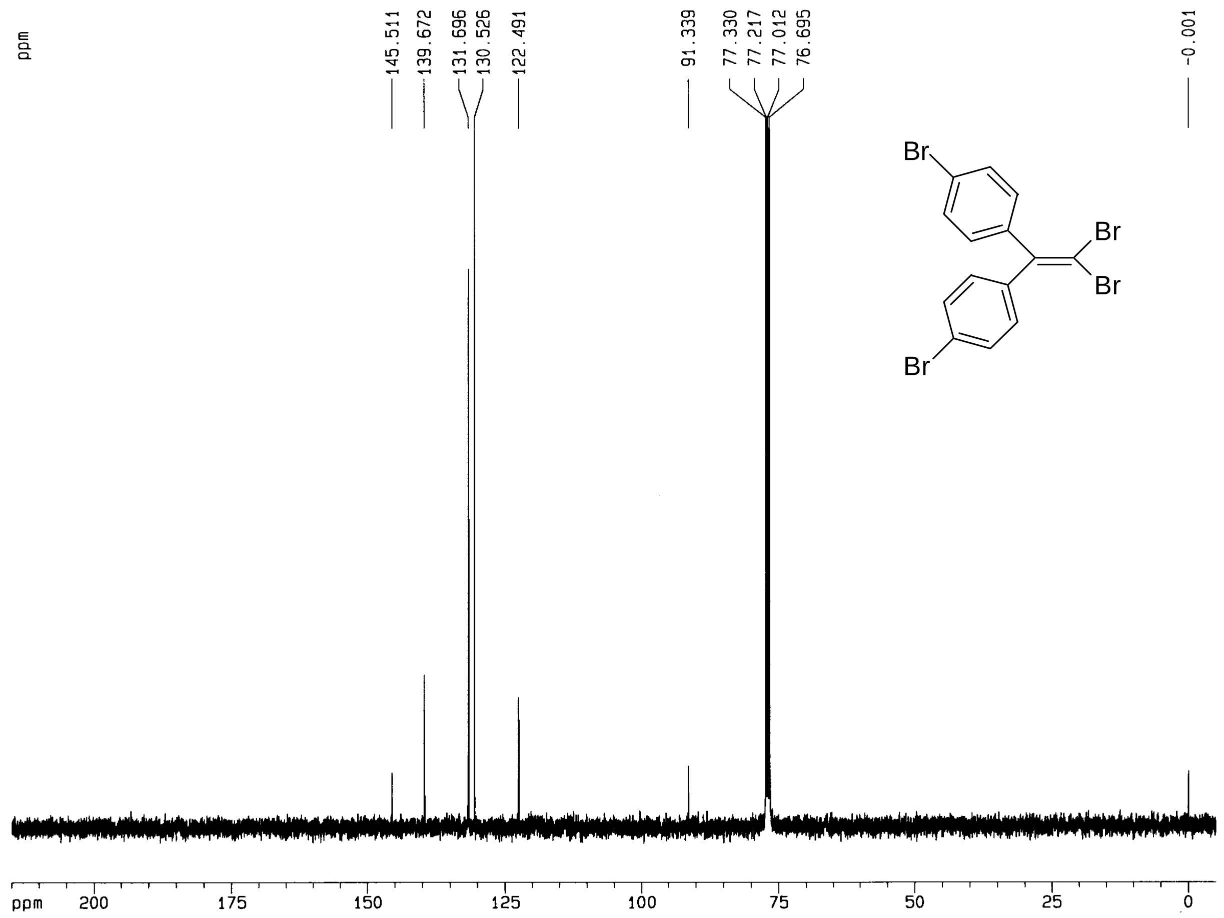


```
Current Data Parameters
NAME              JLJ-I-183
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_             20000508
Time                 15.19
INSTRUM              spect
PROBHD     5 mm BBO BB-1
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                   724.1
DW                  60.400 usec
DE                    6.00 usec
TE                   300.0 K
D1              3.00000000 sec

============ CHANNEL f1 ========
NUC1                    1H
P1                   12.50 usec
PL1                   0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF             400.1300099 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                  9.000 ppm
F1                 3601.17 Hz
F2P                 -1.000 ppm
F2                 -400.13 Hz
PPMCM              0.50000 ppm/cm
HZCM             200.06500 Hz/cm
```



```
Current Data Parameters
NAME            JLJ-I-183
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20000508
Time                15.19
INSTRUM             spect
PROBHD    5 mm BBO BB-1
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  724.1
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 ========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300099 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 7.526 ppm
F1                3011.40 Hz
F2P                 7.088 ppm
F2                2835.92 Hz
PPMCM             0.02193 ppm/cm
HZCM              8.77369 Hz/cm
```

JLJ-I-183



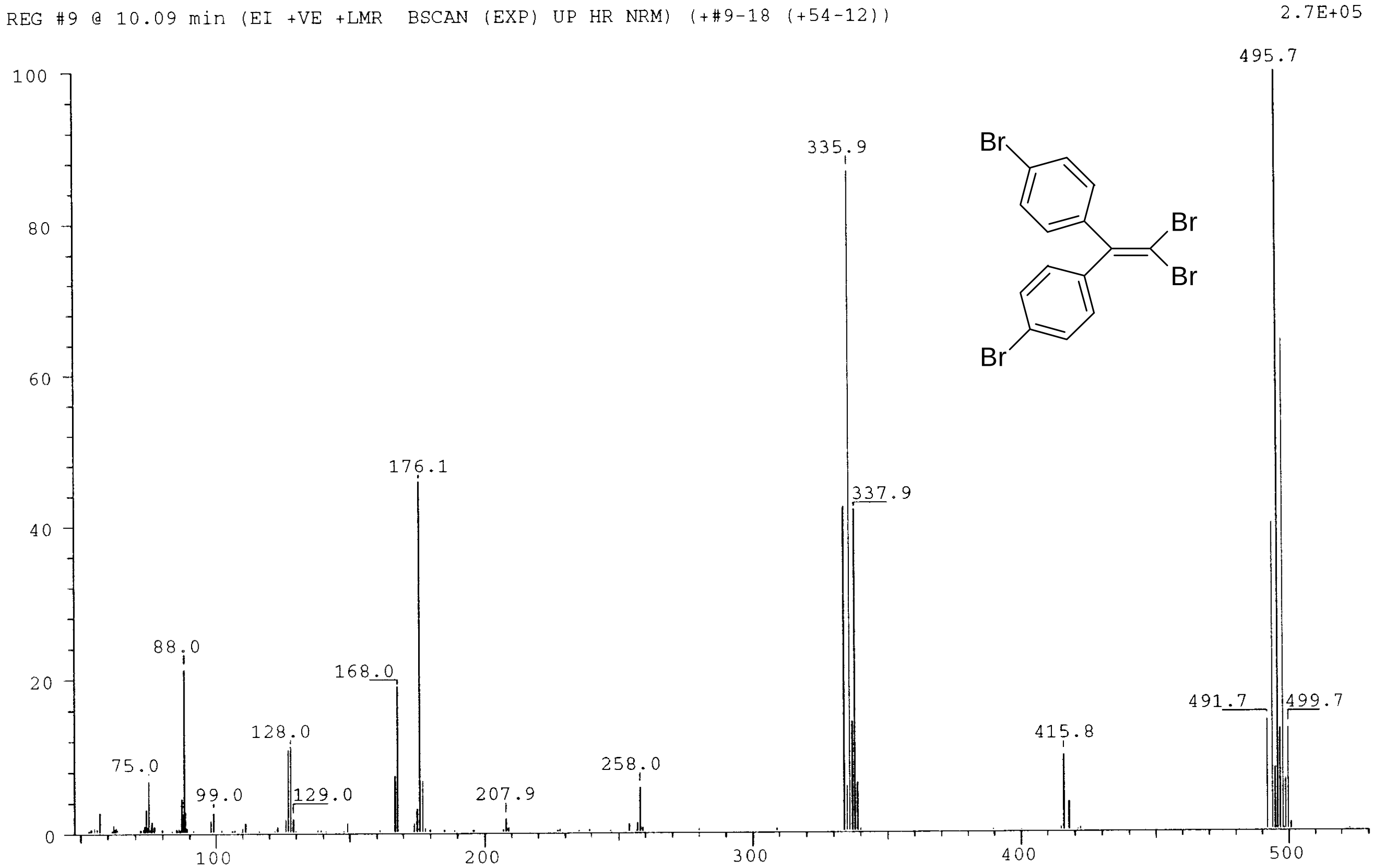
```
Current Data Parameters
NAME          JLJ-I-183
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20000511
Time              18.31
INSTRUM           spect
PROBHD   5 mm BBO BB-1
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 765
DS                   0
SWH          25125.629 Hz
FIDRES        0.383387 Hz
AQ           1.3042164 sec
RG               16384
DW              19.900 usec
DE                6.00 usec
TE               300.0 K
D1          5.00000000 sec
d11         0.03000000 sec
d12         0.00002000 sec

============ CHANNEL f1 ===========
NUC1               13C
P1                8.30 usec
PL1              -3.00 dB
SFO1       100.6237959 MHz

============ CHANNEL f2 ===========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             18.00 dB
PL13             18.00 dB
SFO2       400.1316005 MHz

F2 - Processing parameters
SI               32768
SF         100.6127705 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40

1D NMR plot parameters
CX               20.00 cm
F1P            215.000 ppm
F1            21631.75 Hz
F2P             -5.000 ppm
F2             -503.06 Hz
PPMCM         11.00000 ppm/cm
HZCM        1106.74048 Hz/cm
```

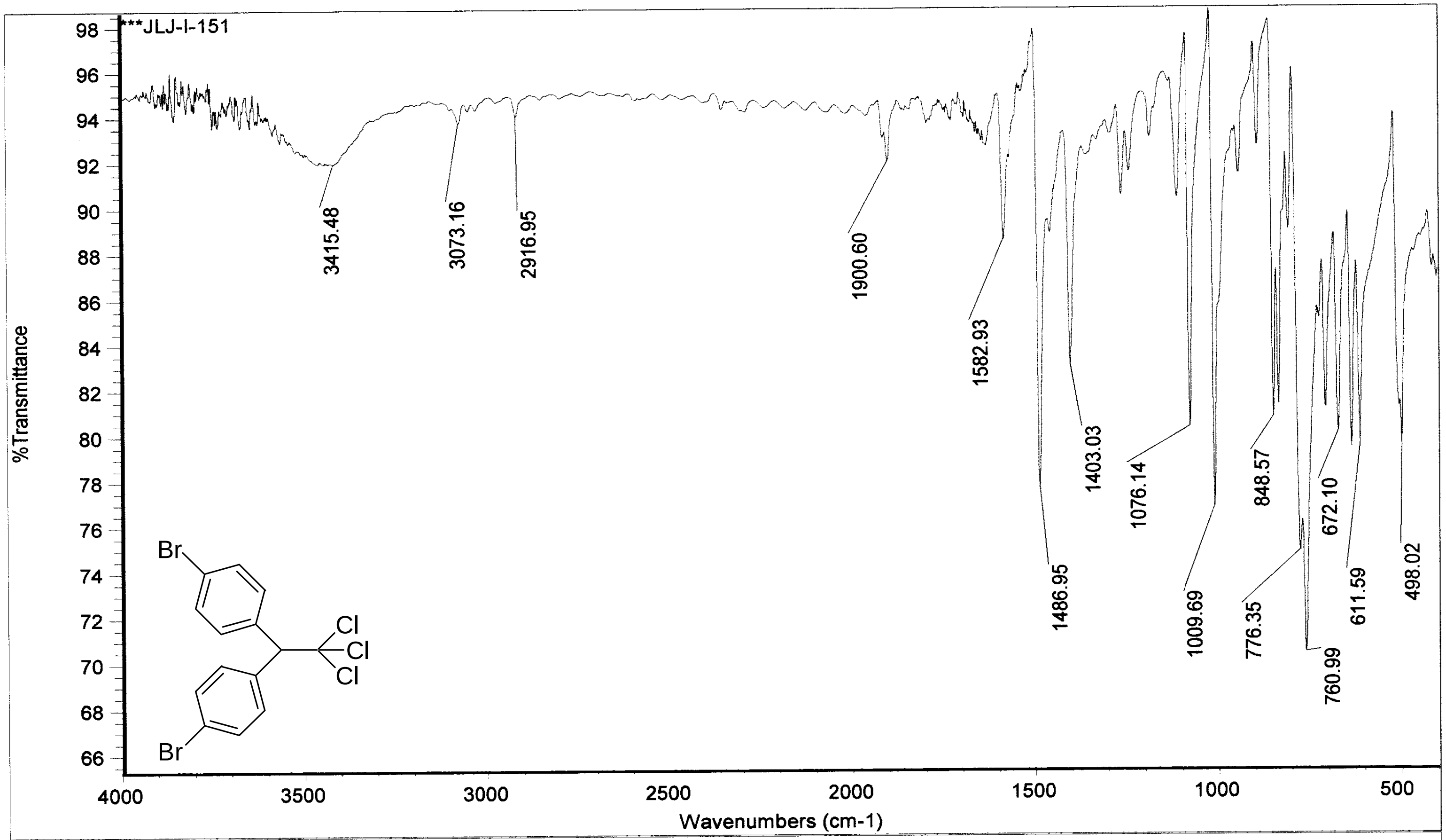
SPEC: jlji183 (15-May-00 17:25:19)
Samp: JLJ-I-183 C14 H8 Br4 495.732064
Oper: TDM Study: EI + HR
Base: 495.74 Masses: 50.00 > 600.00
Peak: 1000.0 mmu Intensity: 265245

Scans: 1 > 95

Client: JLJ/JMT
#Peaks: 110
RIC: 1738489

REG #9 @ 10.09 min (EI +VE +LMR BSCAN (EXP) UP HR NRM) (+#9-18 (+54-12))



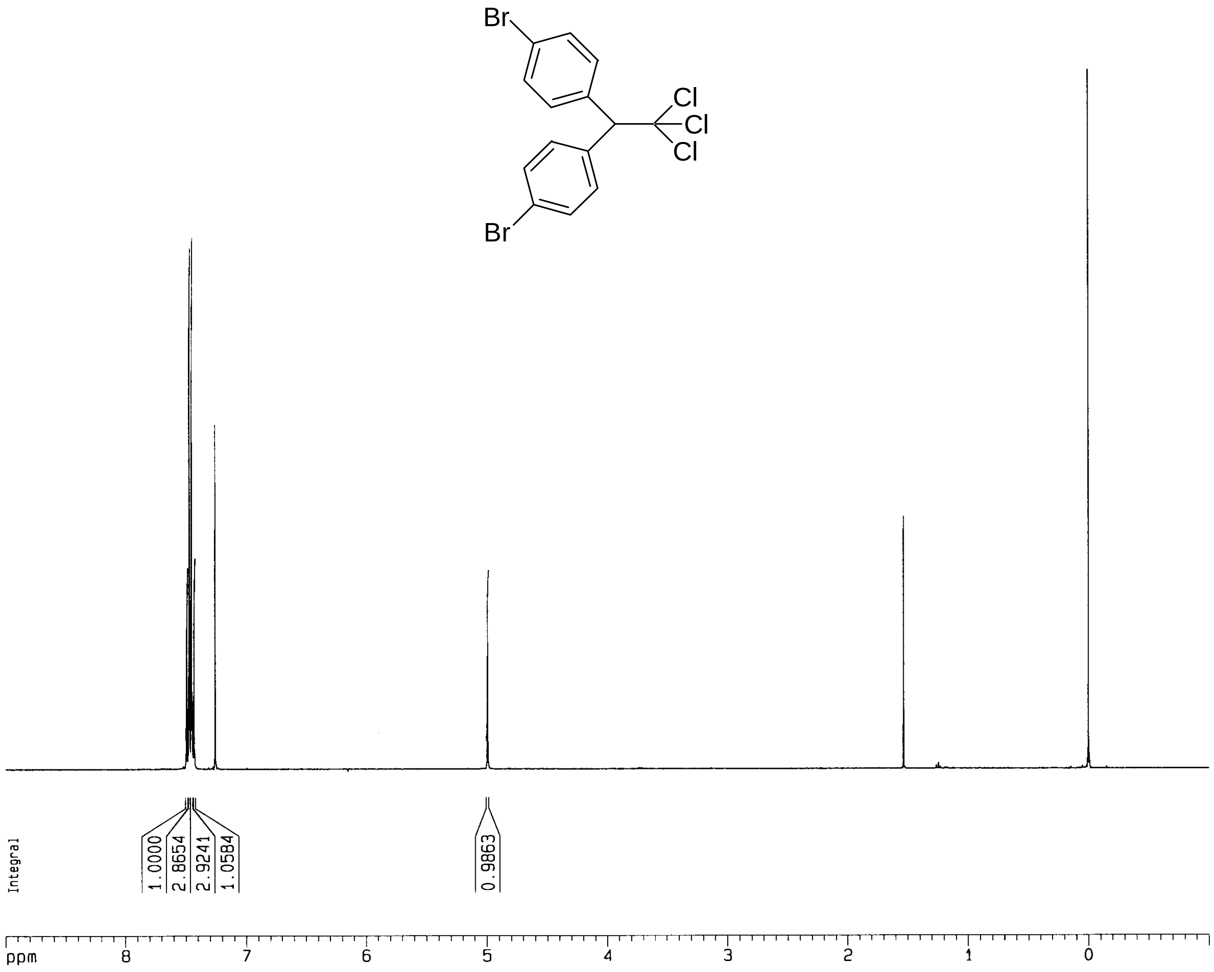


Date: Wed Mar 15 15:11:01 2000 ***JLJ-I-151

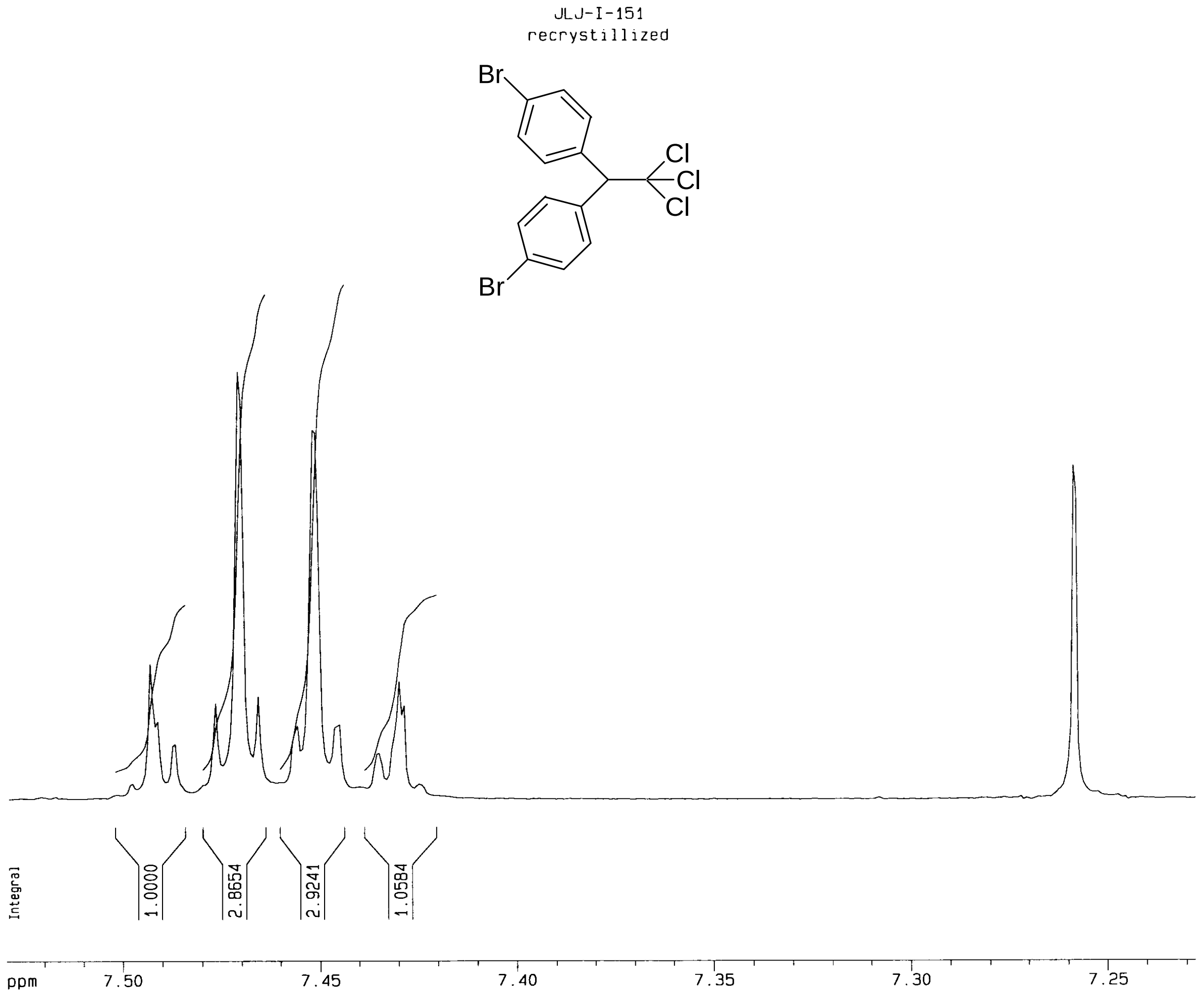
Scans: 20

Resolution: 2.000

JLJ-I-151
recrystillized

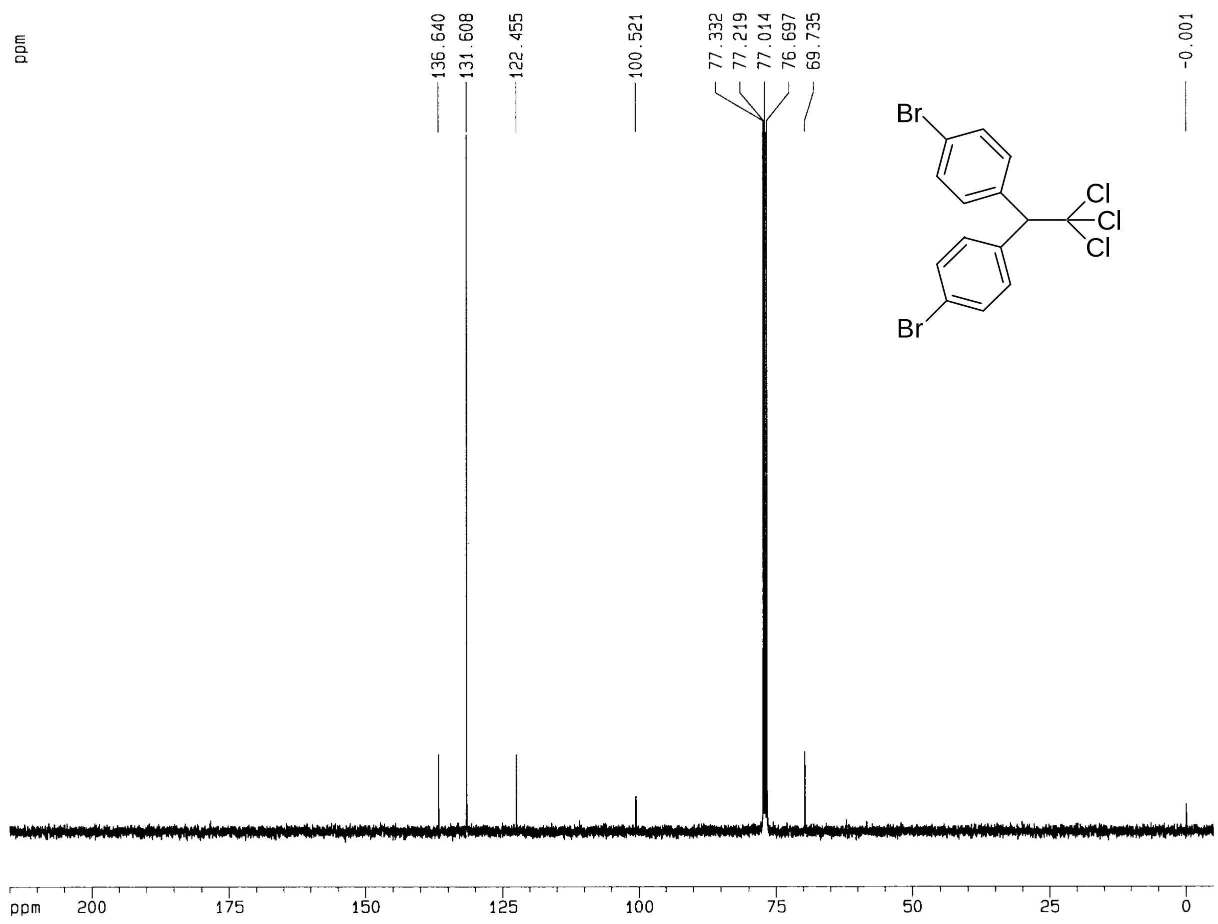


```
Current Data Parameters
NAME          JLJ-I-151
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20000310
Time              10.40
INSTRUM           spect
PROBHD    5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                912.3
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300101 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -1.000 ppm
F2              -400.13 Hz
PPMCM           0.50000 ppm/cm
HZCM          200.06500 Hz/cm
```



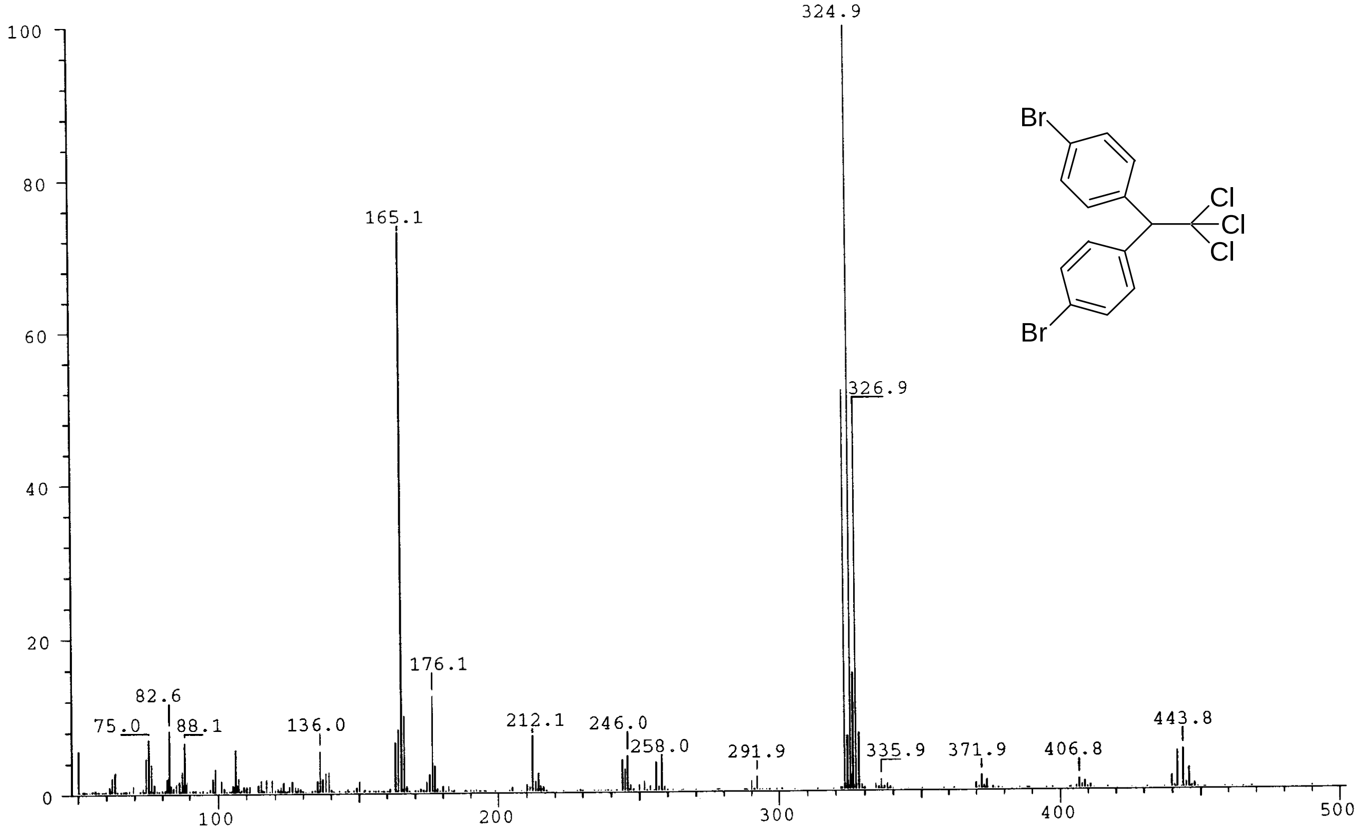
```
Current Data Parameters
NAME          JLJ-I-151
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20000310
Time              10.40
INSTRUM           spect
PROBHD   5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                912.3
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300101 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               7.530 ppm
F1              3012.84 Hz
F2P               7.228 ppm
F2              2892.08 Hz
PPMCM           0.01509 ppm/cm
HZCM            6.03789 Hz/cm
```

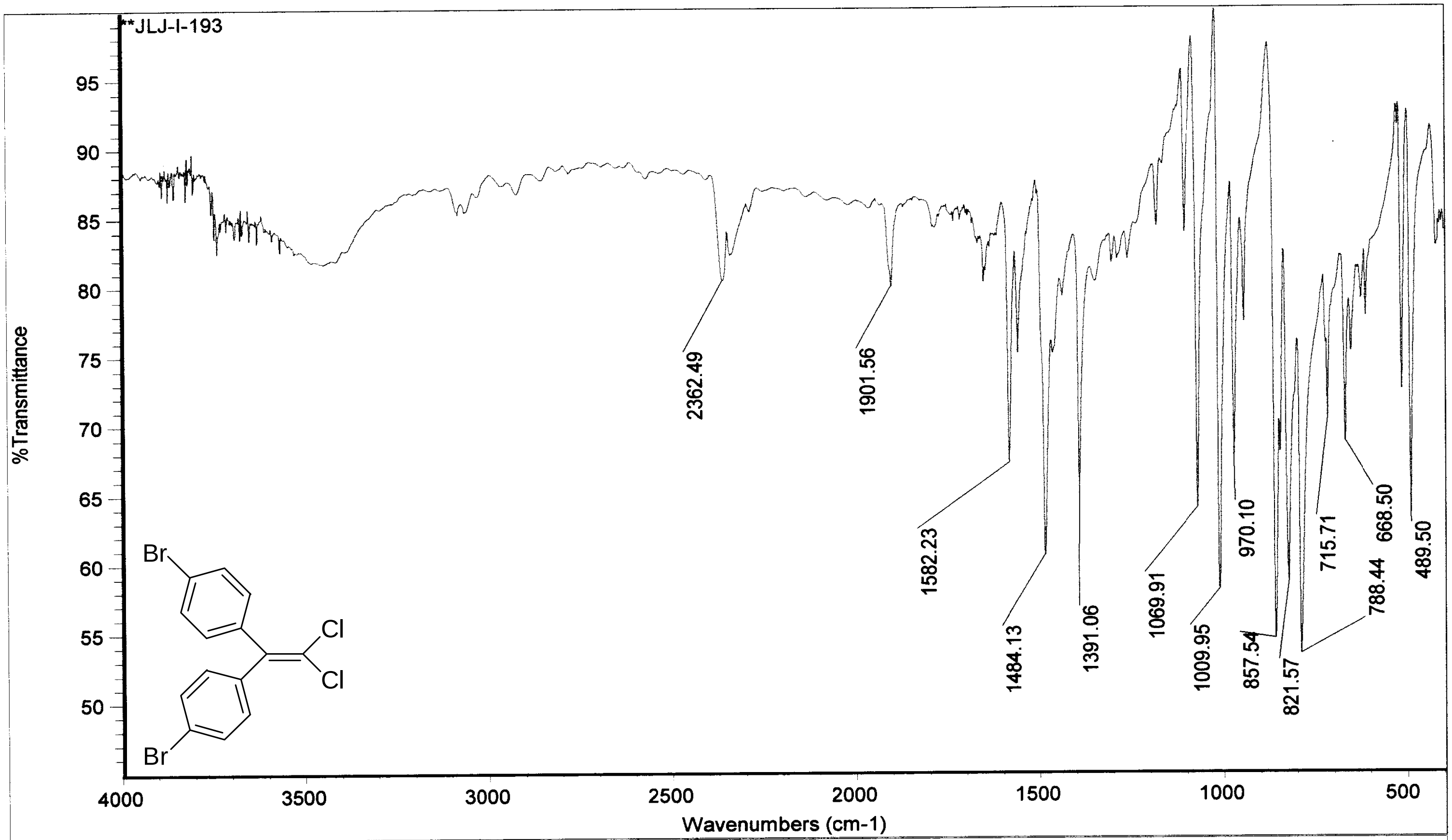
JLJ-I-151
recrystillized



```
Current Data Parameters
NAME          JLJ-I-151
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20000329
Time              17.47
INSTRUM           spect
PROBHD   5 mm BBO BB-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    0
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ            1.3042164 sec
RG                 8192
DW               19.900 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

============ CHANNEL f1 ============
NUC1                13C
P1                 8.30 usec
PL1                0.00 dB
SFO1        100.6237959 MHz

============ CHANNEL f2 ============
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              18.00 dB
PL13              18.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127697 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P             215.000 ppm
F1             21631.75 Hz
F2P              -5.000 ppm
F2              -503.06 Hz
PPMCM          11.00000 ppm/cm
HZCM         1106.74048 Hz/cm
```

```
SPEC: jlji151 (17-Mar-00 15:38:45)                                Scans:   1 > 92
Samp: JLJ-I-151 C14 H9 Br2 Cl3  443.809019
Oper: TDM                         Study:  EI + HR                 Client:  JLJ/JMT
Base: 324.90                      Masses:  50.00 > 500.00         #Peaks:  339
Peak: 1000.0 mmu                  Intensity:   2181704            RIC: 11788641
REG #9 @ 15.23 min (EI +VE +HMR  BSCAN (EXP) UP HR NRM) (+43-25)            2.2E+06
```

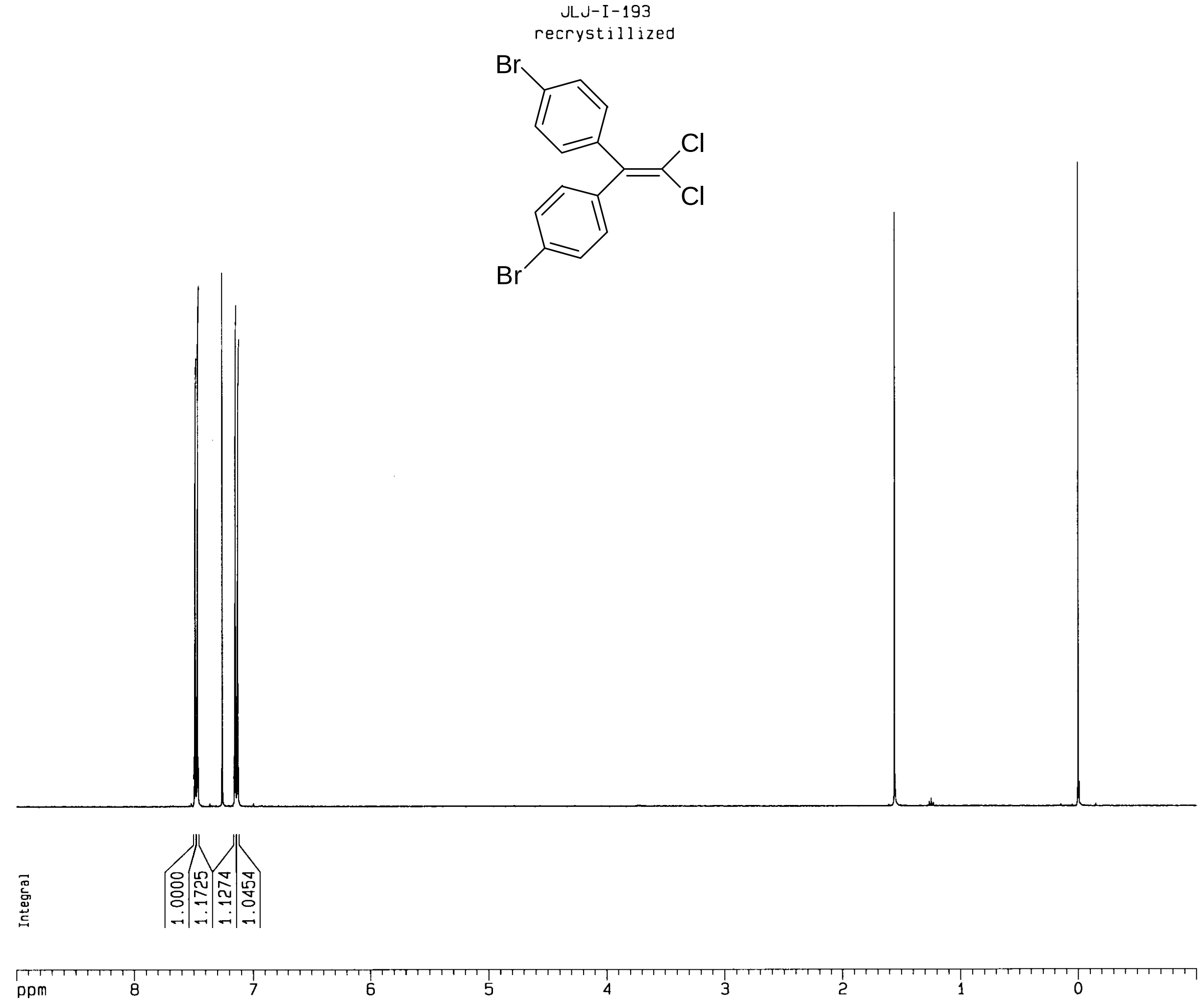




Date: Fri Jun 09 11:48:19 2000 **JLJ-I-193

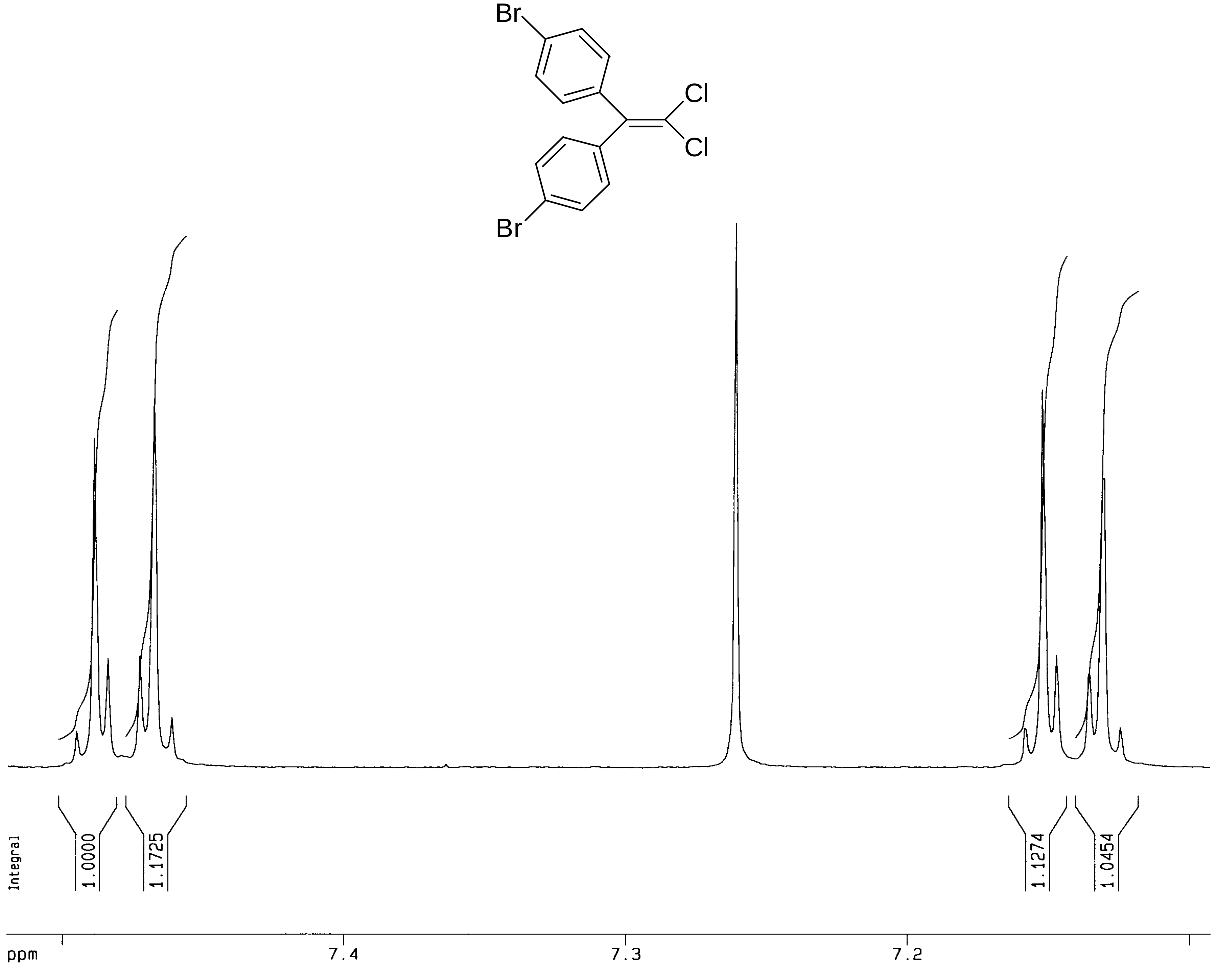
Scans: 20

Resolution: 4.000

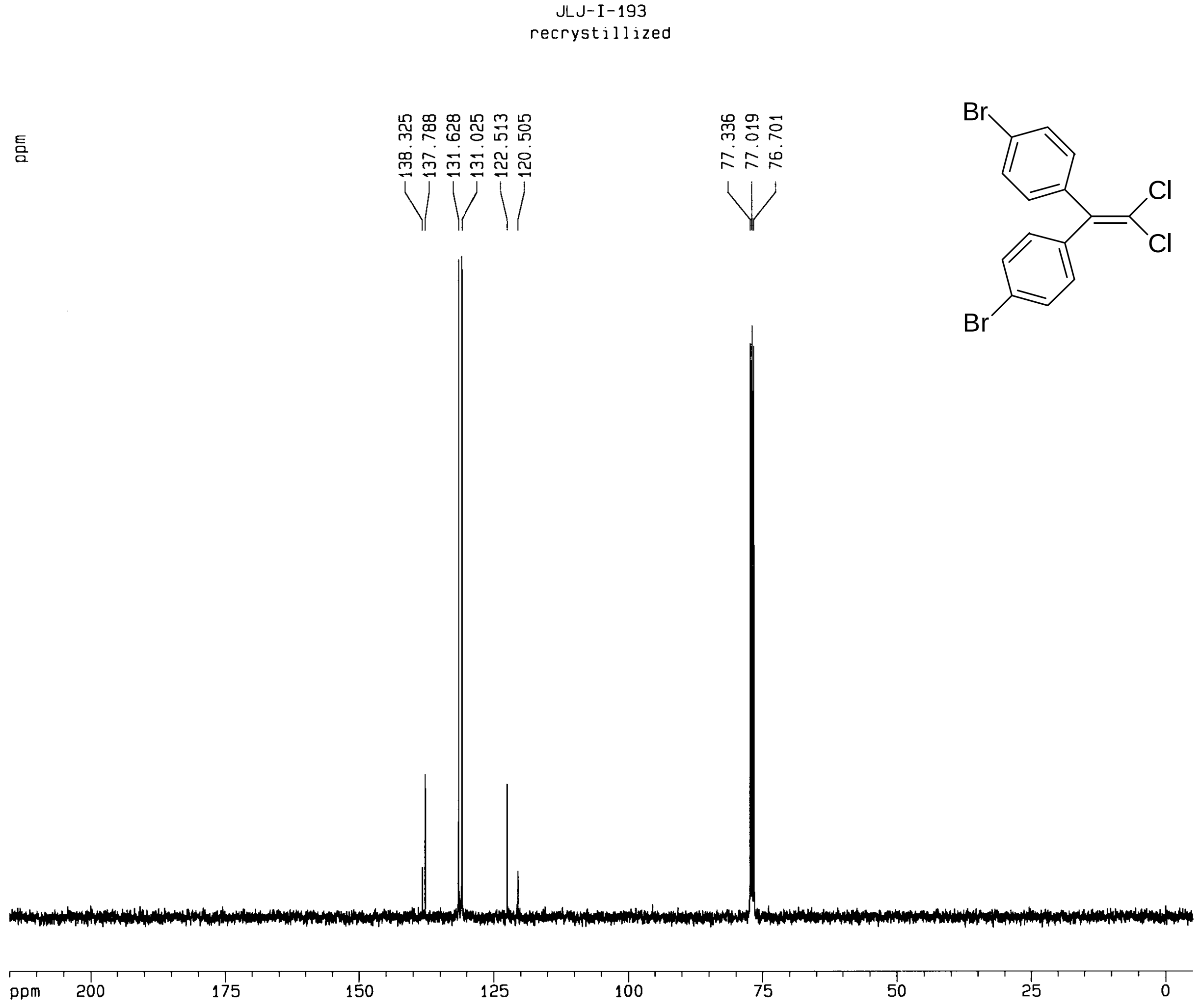


```
Current Data Parameters
NAME          JLJ-I-193
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20000526
Time               8.52
INSTRUM           spect
PROBHD    5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                574.7
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 =========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300091 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -1.000 ppm
F2              -400.13 Hz
PPMCM           0.50000 ppm/cm
HZCM          200.06500 Hz/cm
```

JLJ-I-193
recrystillized

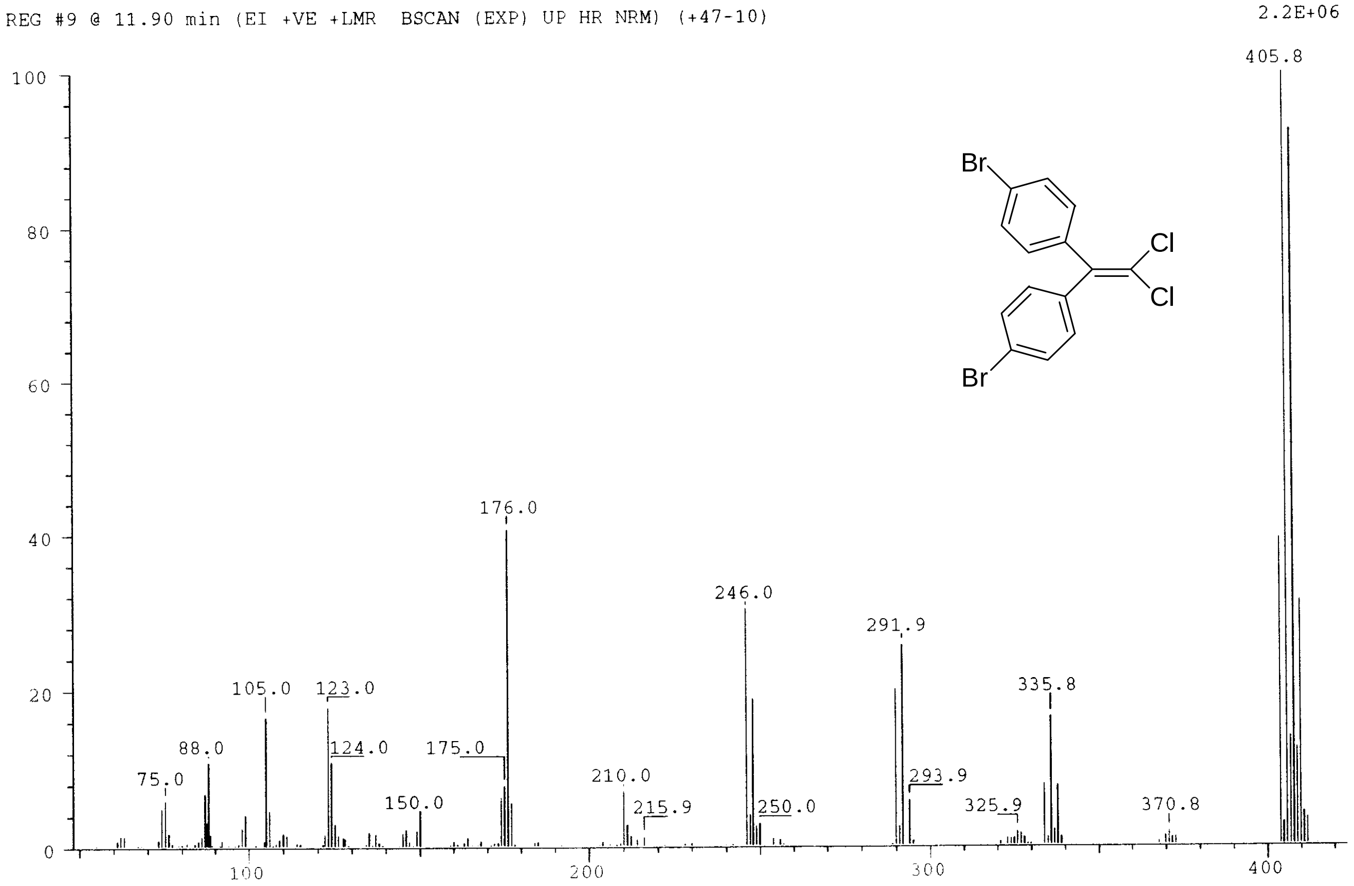


```
Current Data Parameters
NAME          JLJ-I-193
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20000526
Time               8.52
INSTRUM           spect
PROBHD    5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                574.7
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 =========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300091 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               7.519 ppm
F1              3008.76 Hz
F2P               7.093 ppm
F2              2837.93 Hz
PPMCM           0.02135 ppm/cm
HZCM            8.54155 Hz/cm
```

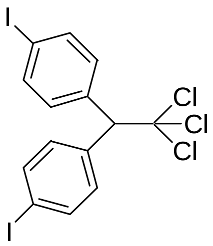


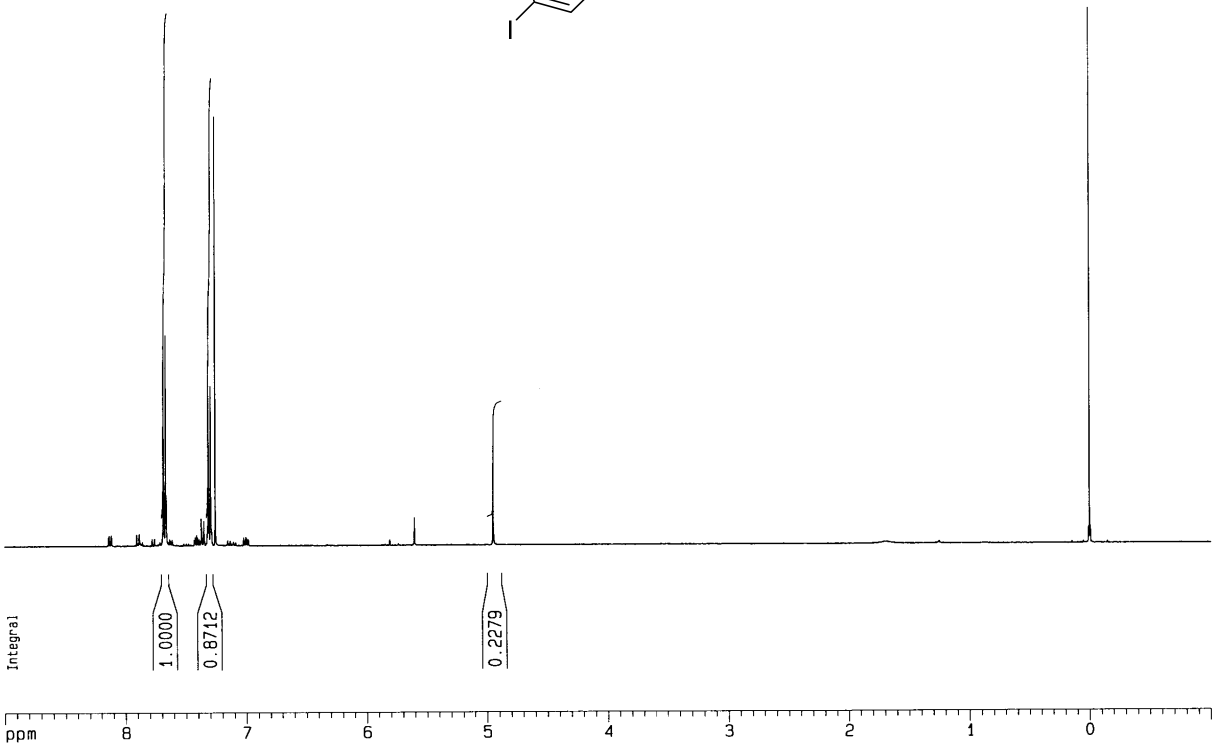
```
Current Data Parameters
NAME          JLJ-I-193
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20000616
Time              16.50
INSTRUM           spect
PROBHD   5 mm BBO BB-1
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 256
DS                   0
SWH          25125.629 Hz
FIDRES        0.383387 Hz
AQ           1.3042164 sec
RG              7298.2
DW              19.900 usec
DE                6.00 usec
TE               300.0 K
D1          2.00000000 sec
d11         0.03000000 sec
d12         0.00002000 sec

============ CHANNEL f1 ===========
NUC1               13C
P1                8.30 usec
PL1              -3.00 dB
SFO1       100.6237959 MHz

============ CHANNEL f2 ===========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             18.00 dB
PL13             18.00 dB
SFO2       400.1316005 MHz

F2 - Processing parameters
SI               32768
SF         100.6127705 MHz
WDW                 EM
SSB                  0
LB                2.00 Hz
GB                   0
PC                1.40

1D NMR plot parameters
CX               20.00 cm
F1P            215.000 ppm
F1            21631.75 Hz
F2P             -5.000 ppm
F2             -503.06 Hz
PPMCM         11.00000 ppm/cm
HZCM        1106.74048 Hz/cm
```

```
SPEC: jlji193 (02-Jun-00 12:50:02)                                Scans:   1 > 98
Samp: JLJ-I-193  C14 H8 Br2 Cl2   405.834782
Oper: TDM                        Study:  EI + HR                  Client:  JLJ/JMT
Base: 405.79                     Masses:  50.00 > 650.00          #Peaks:  147
Peak: 1000.0 mmu                 Intensity:   2192474             RIC: 14570813
REG #9 @ 11.90 min (EI +VE +LMR  BSCAN (EXP) UP HR NRM) (+47-10)
```



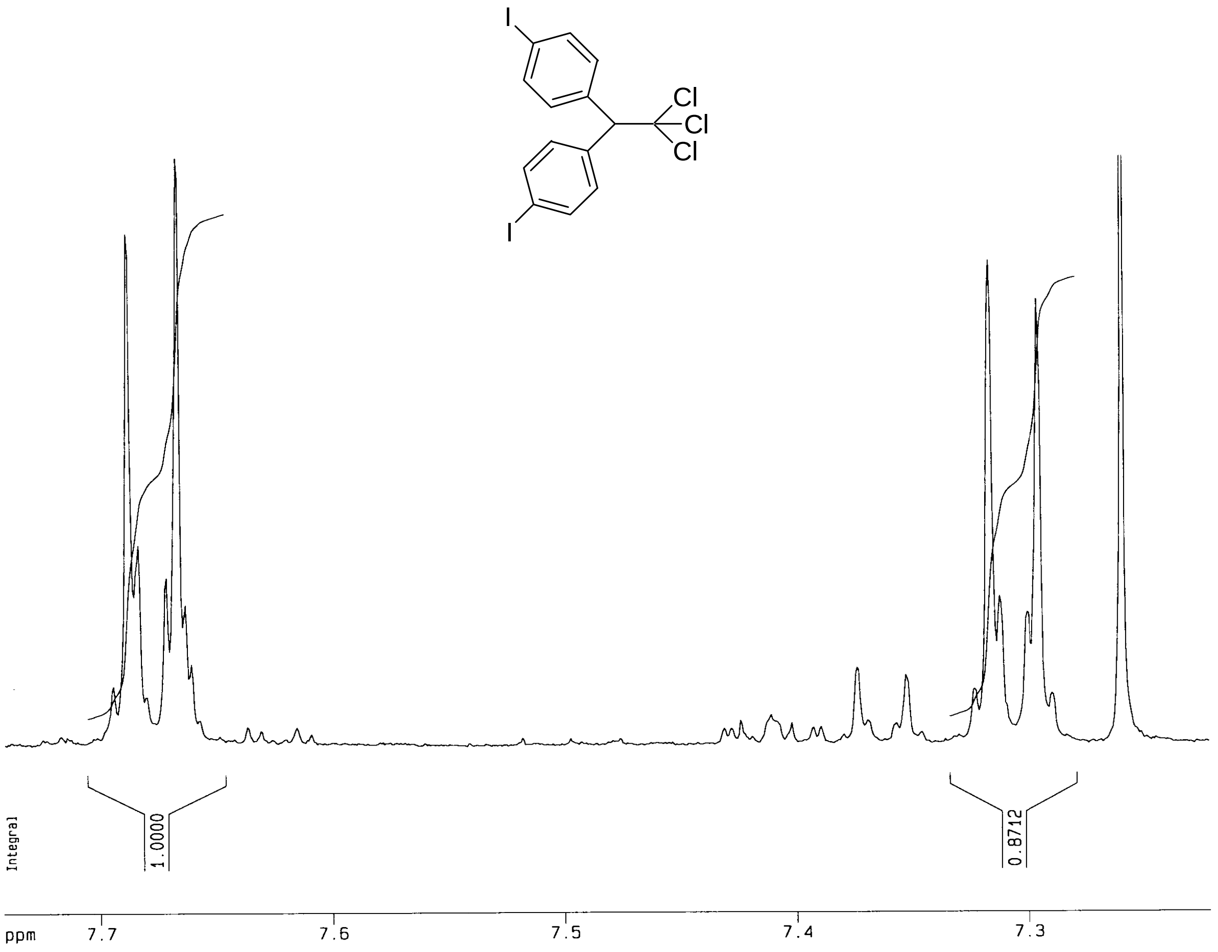
JLJ-II-77
ev vacuo 24h





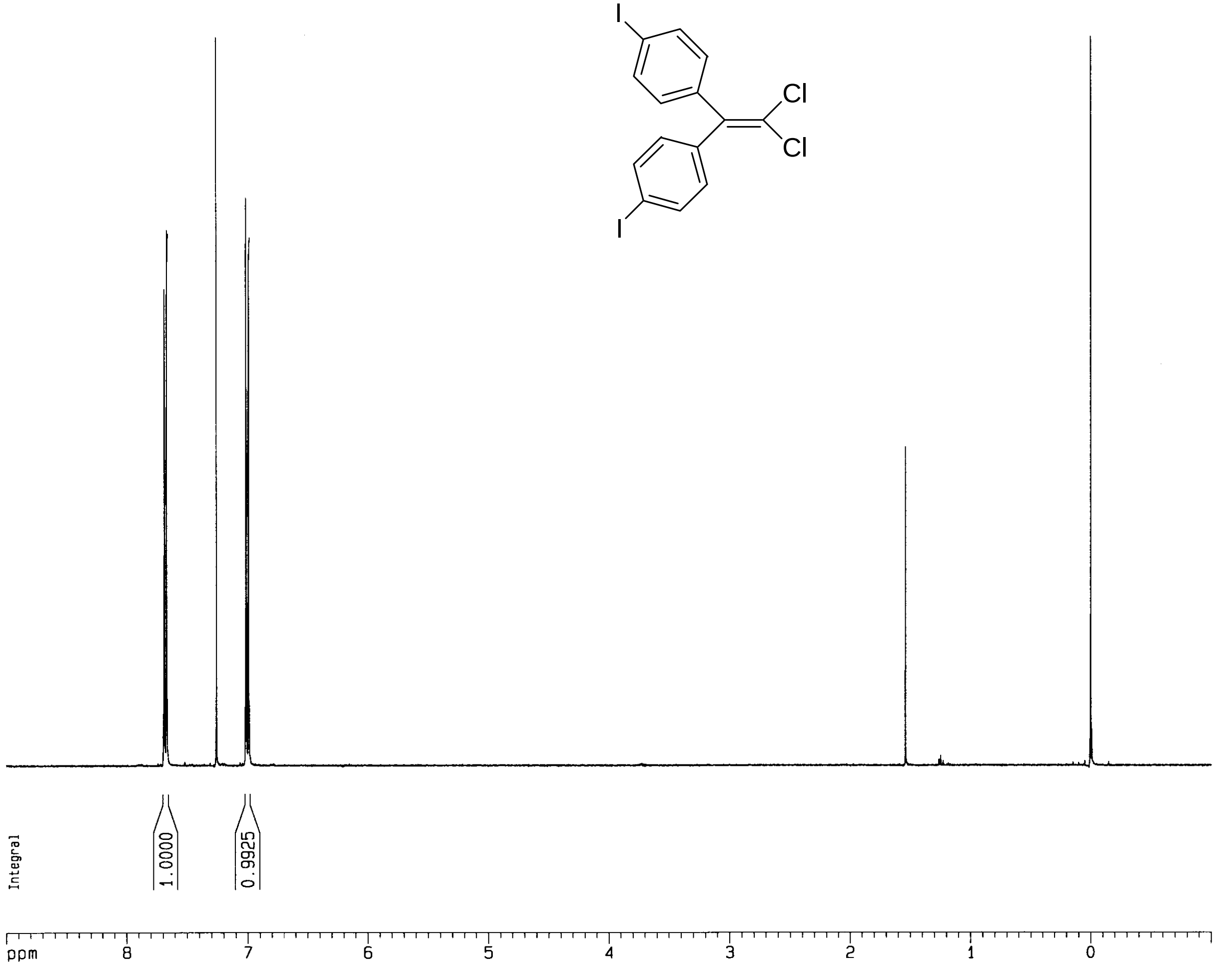
```
Current Data Parameters
NAME          JLJ-II-77
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20010426
Time              14.37
INSTRUM           spect
PROBHD    5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                812.7
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300109 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -1.000 ppm
F2              -400.13 Hz
PPMCM           0.50000 ppm/cm
HZCM          200.06500 Hz/cm
```

JLJ-II-77
ev vacuo 24h

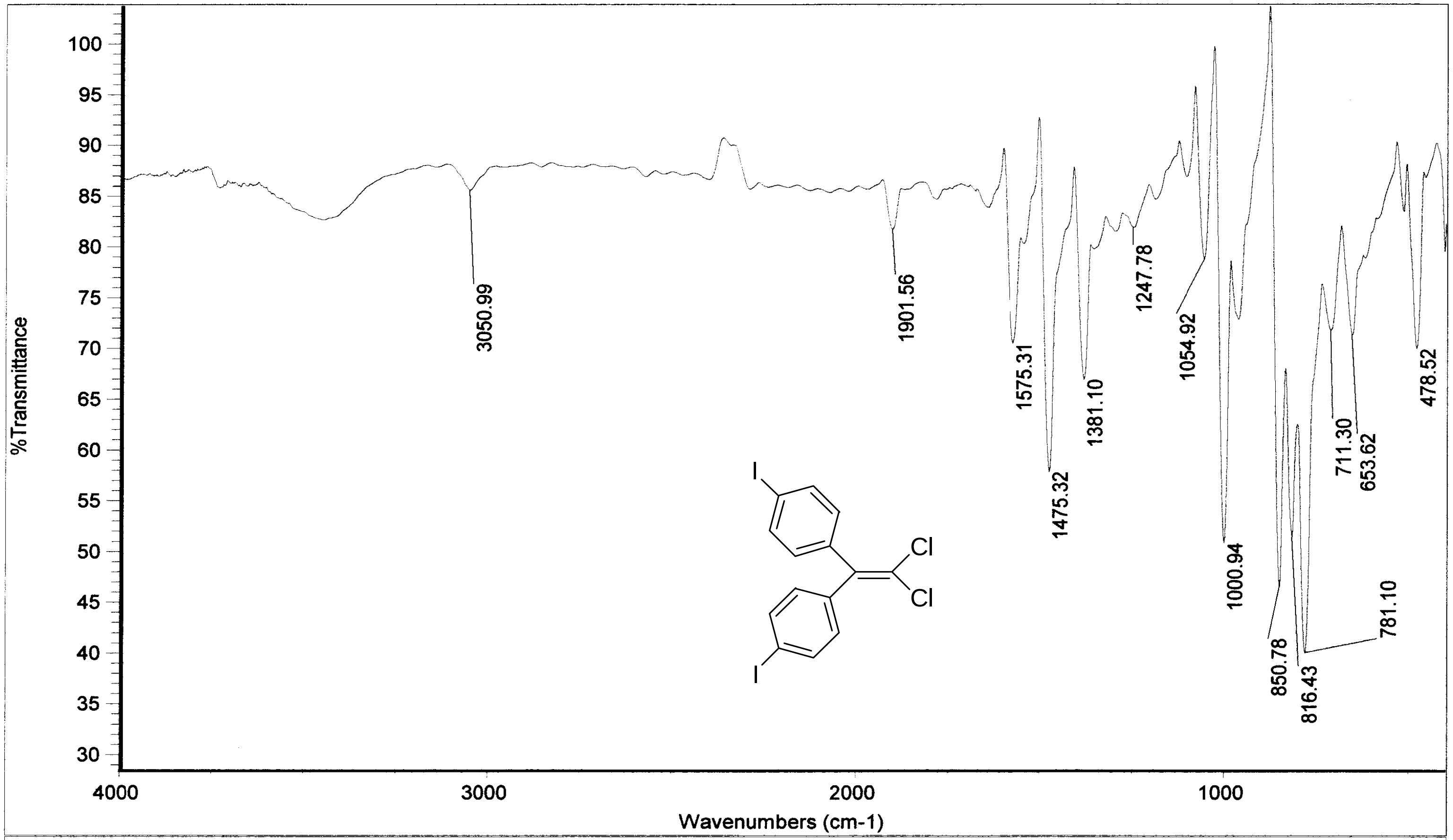


```
Current Data Parameters
NAME           JLJ-II-77
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20010426
Time               14.37
INSTRUM            spect
PROBHD    5 mm BBO BB-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 812.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300109 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.742 ppm
F1               3097.68 Hz
F2P                7.222 ppm
F2               2889.59 Hz
PPMCM            0.02600 ppm/cm
HZCM            10.40452 Hz/cm
```

JLJ-II-78
rec.1



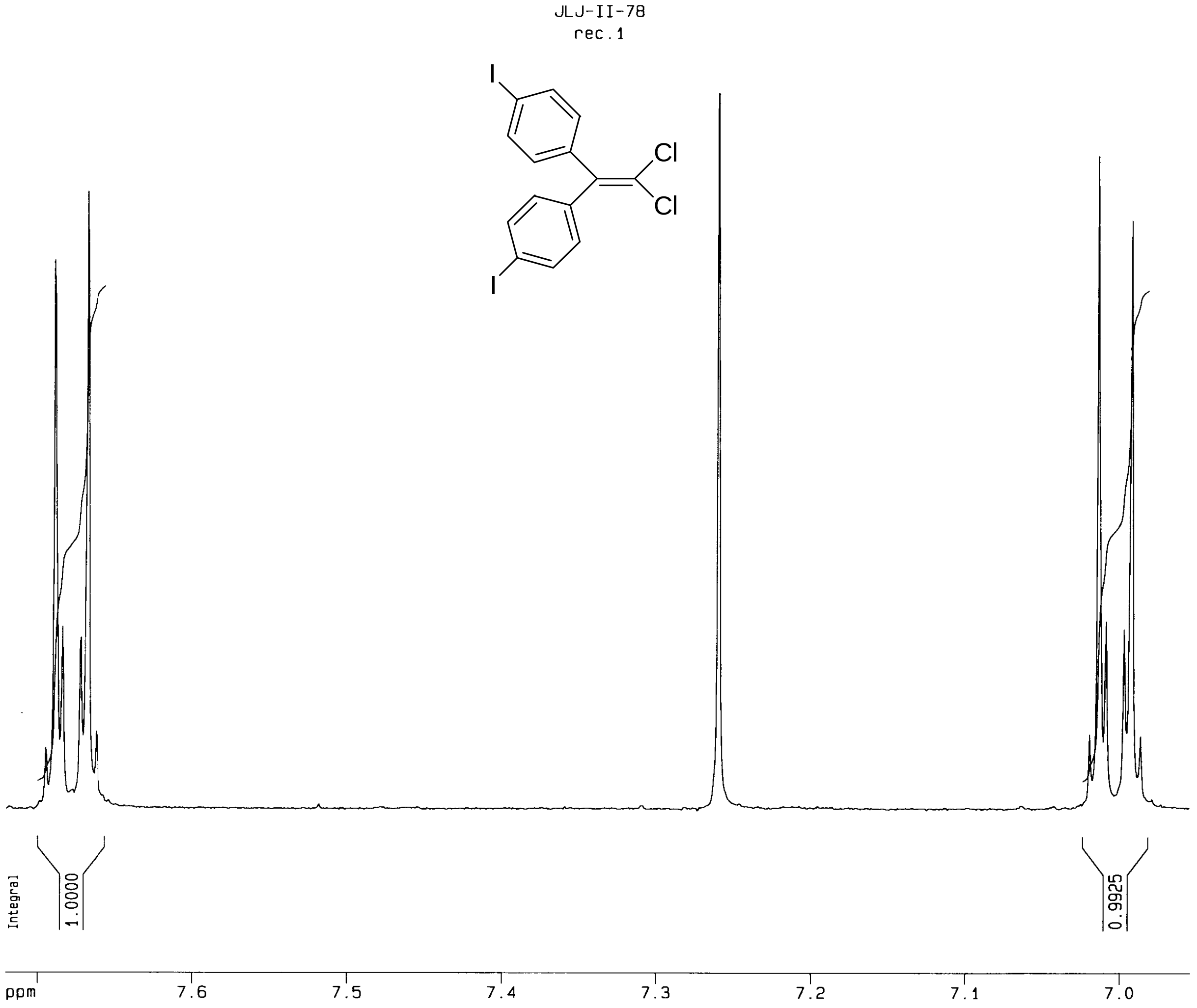
```
Current Data Parameters
NAME          JLJ-II-78
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20010502
Time              17.27
INSTRUM           spect
PROBHD    5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                724.1
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300096 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -1.000 ppm
F2              -400.13 Hz
PPMCM           0.50000 ppm/cm
HZCM          200.06500 Hz/cm
```



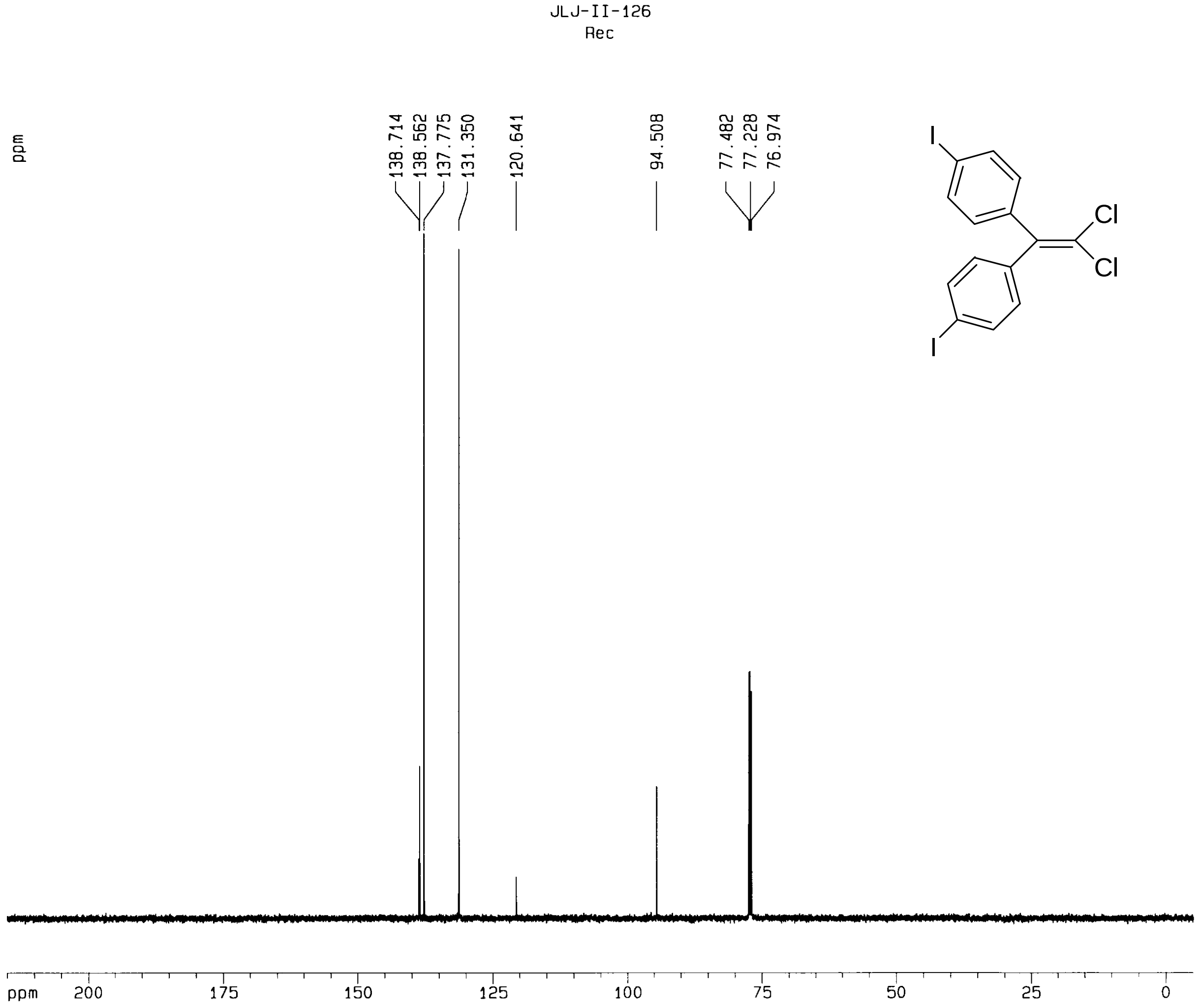
Date: Wed Jul 16 15:34:55 2003 ***JLJ-II-126

Scans: 18

Resolution: 4.000

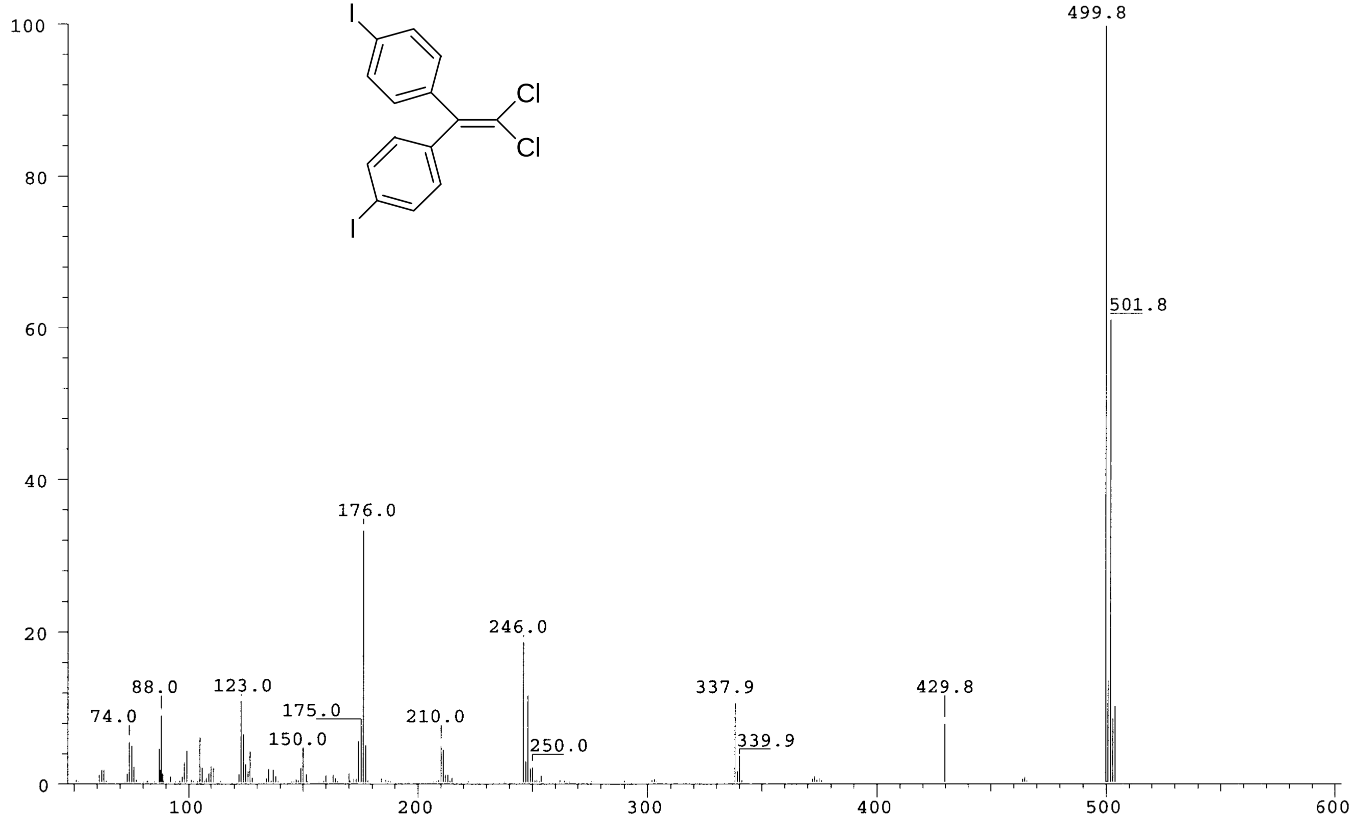


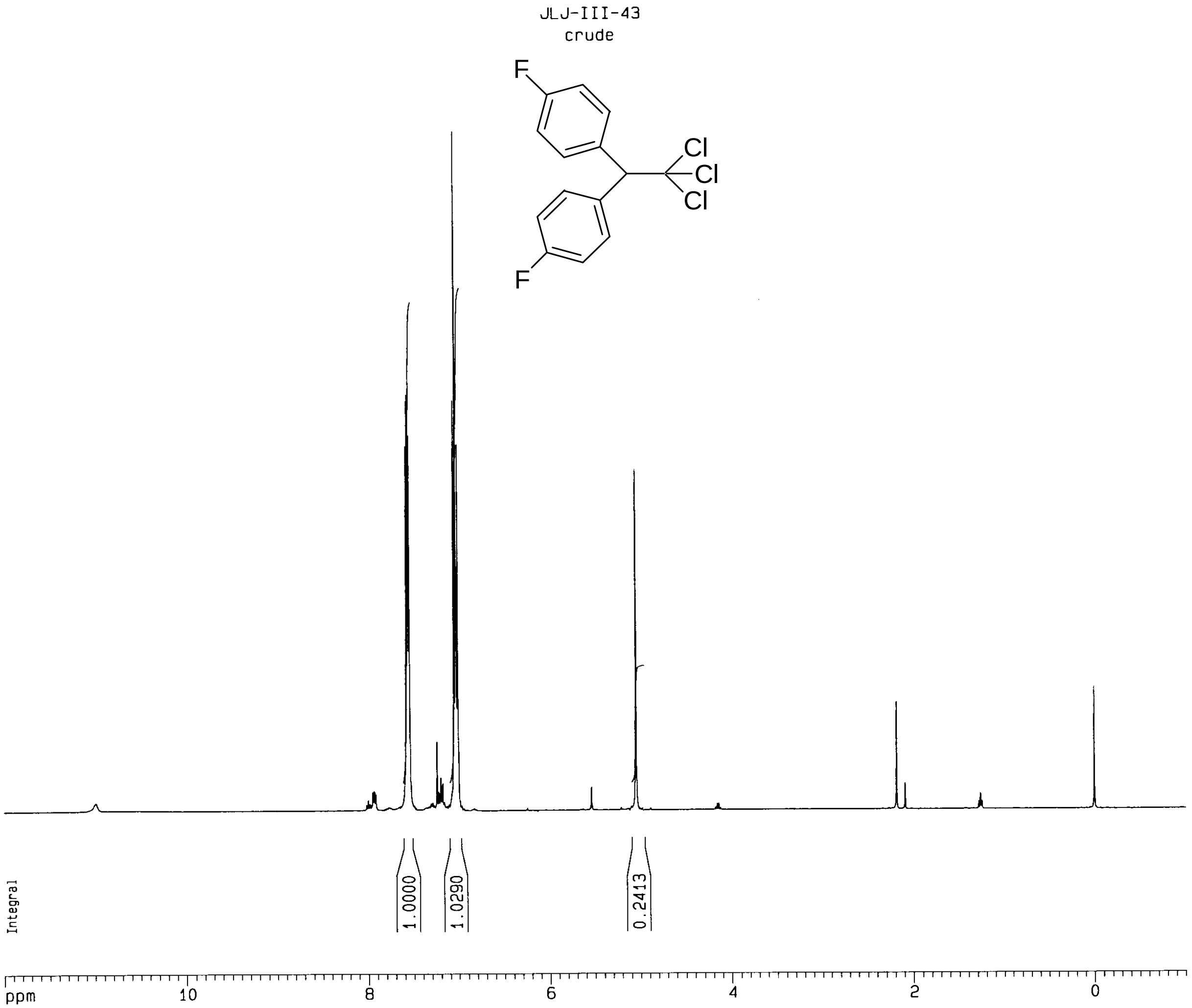
```
Current Data Parameters
NAME            JLJ-II-78
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20010502
Time                17.27
INSTRUM             spect
PROBHD     5 mm BBO BB-1
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  724.1
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 =========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SF01          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300096 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 7.720 ppm
F1                3089.19 Hz
F2P                 6.955 ppm
F2                2782.74 Hz
PPMCM             0.03829 ppm/cm
HZCM             15.32275 Hz/cm
```



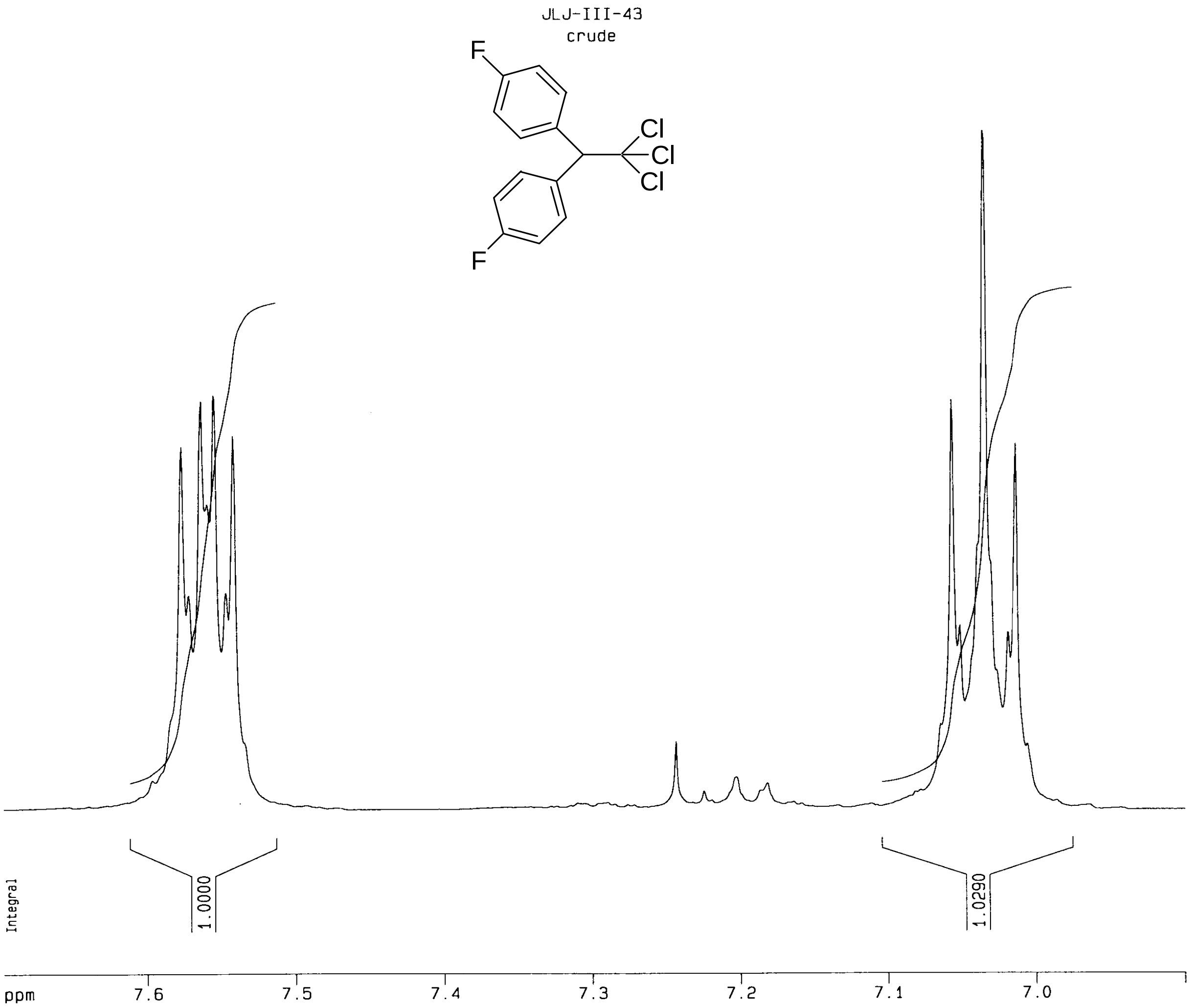
```
Current Data Parameters
NAME             jljii126
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20030717
Time                13.59
INSTRUM             spect
PROBHD   5 mm BBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     81
DS                      0
SWH             31446.541 Hz
FIDRES           0.479836 Hz
AQ              1.0420724 sec
RG                  16384
DW                 15.900 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec

============ CHANNEL f1 ============
NUC1                  13C
P1                   5.80 usec
PL1                  0.00 dB
SFO1          125.7715719 MHz

============ CHANNEL f2 ============
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -1.00 dB
PL12                22.60 dB
PL13                22.60 dB
SFO2          500.1320005 MHz

F2 - Processing parameters
SI                  32768
SF            125.7577685 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
F1P               215.000 ppm
F1               27037.92 Hz
F2P                -5.000 ppm
F2                -628.79 Hz
PPMCM            11.00000 ppm/cm
HZCM           1383.33545 Hz/cm
```

```
SPEC: jlj-ii-126 (03-Aug-03 16:29:45)                                        Scans:   1 > 80
Samp: C14H8Cl2I2 mw=500.93
Oper: Xiao                     Study:  EI +                                  Client:  Jurs/Tour
Base: 499.76                   Masses:  50.00 > 600.00                       #Peaks:  159
Peak: 1000.0 mmu               Intensity:   20742144                         RIC: 88434786
REG #9 @ 10.35 min (EI +VE +LMR  BSCAN (EXP) UP HR NRM) (+#9-10 (+56-5))                2.1E+07
```

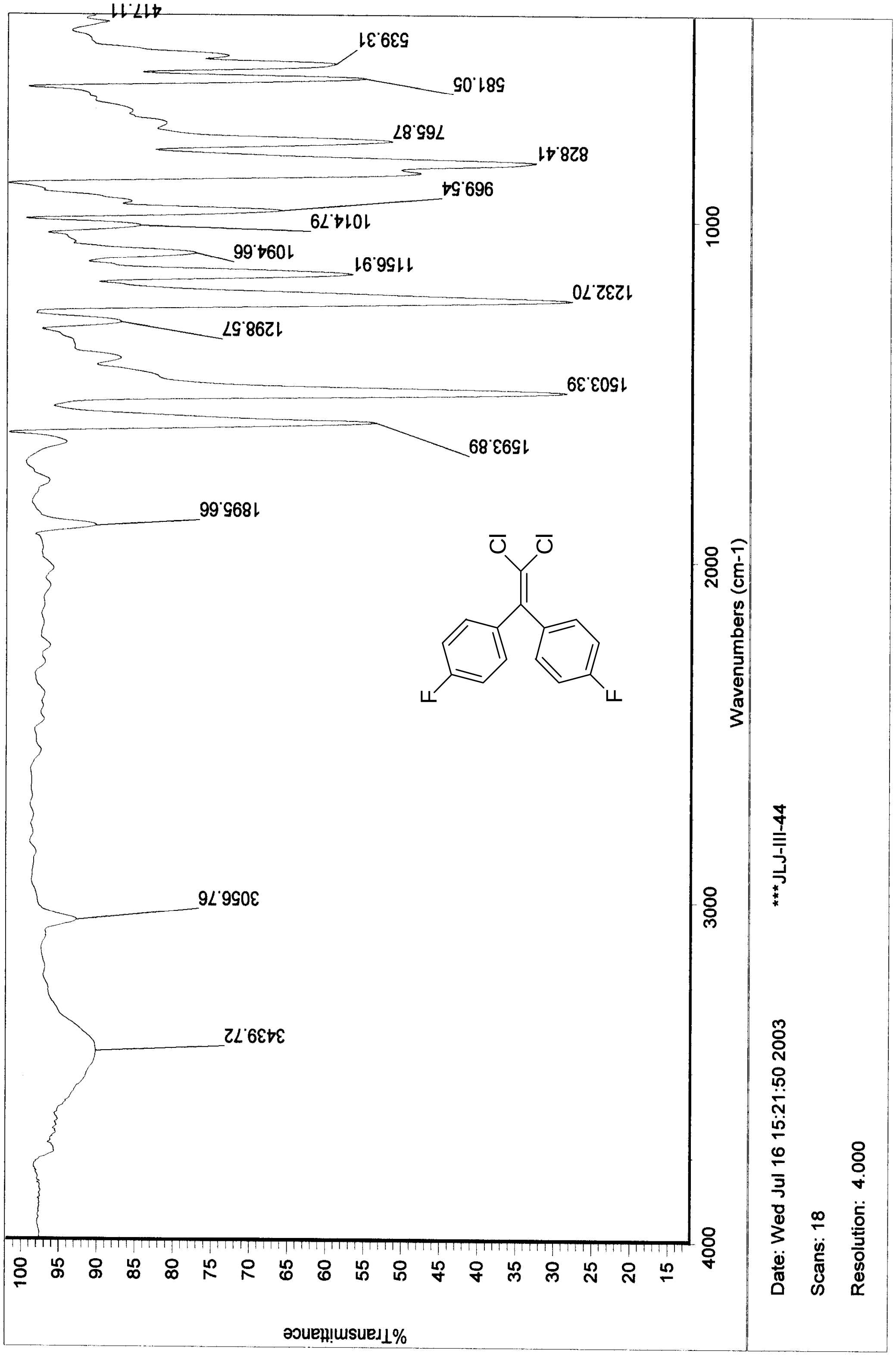


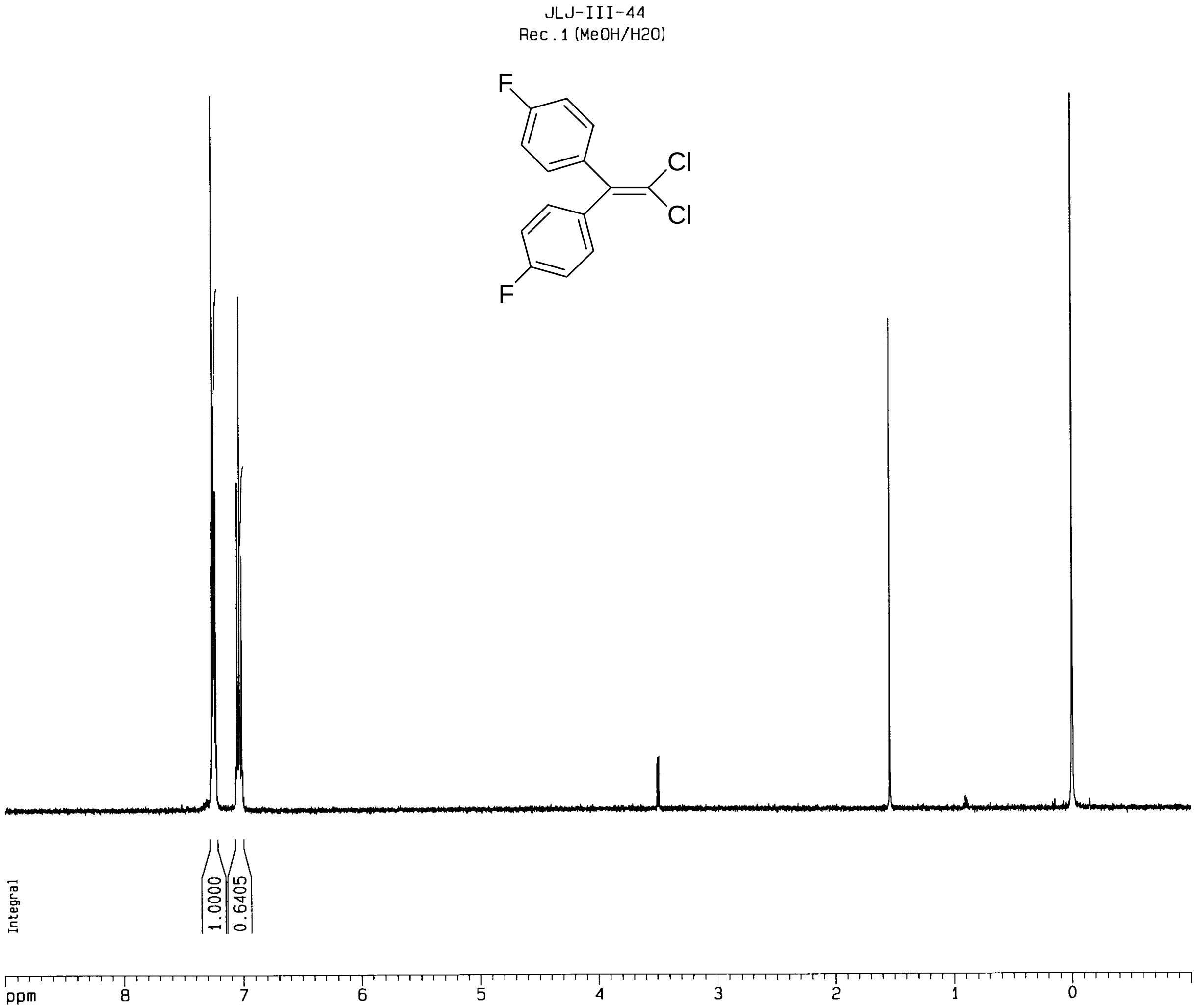

JLJ-III-43
crude

```
Current Data Parameters
NAME              JLJiii43
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20020212
Time                 16.30
INSTRUM              spect
PROBHD     5 mm BBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                   203.2
DW                  60.400 usec
DE                    6.00 usec
TE                   300.0 K
D1              3.00000000 sec

============ CHANNEL f1 =========
NUC1                    1H
P1                   12.50 usec
PL1                   0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF             400.1300162 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                 12.000 ppm
F1                 4801.56 Hz
F2P                 -1.000 ppm
F2                 -400.13 Hz
PPMCM              0.65000 ppm/cm
HZCM             260.08450 Hz/cm
```



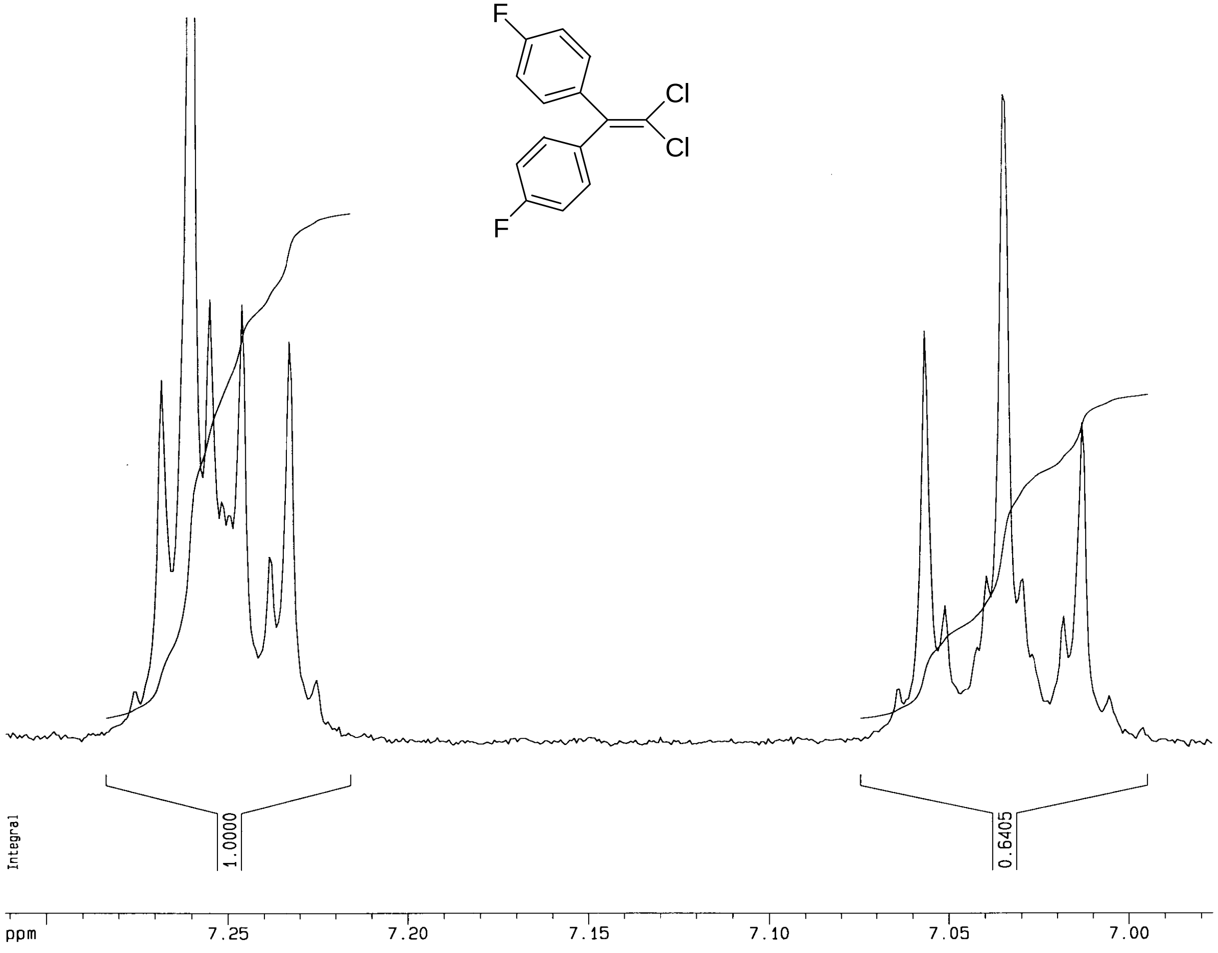
```
Current Data Parameters
NAME            JLJiii43
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20020212
Time               16.30
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 203.2
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300162 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.697 ppm
F1               3079.83 Hz
F2P                6.900 ppm
F2               2760.85 Hz
PPMCM            0.03986 ppm/cm
HZCM            15.94912 Hz/cm
```


%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
4000
3000
2000
1000
Wavenumbers (cm-1)
3439.72
3056.76
1895.66
1593.89
1503.39
1298.57
1232.70
1156.91
1094.66
1014.79
969.54
828.41
765.87
581.05
539.31
417.11
F
F
Cl
Cl
Date: Wed Jul 16 15:21:50 2003
***JLJ-III-44
Scans: 18
Resolution: 4.000



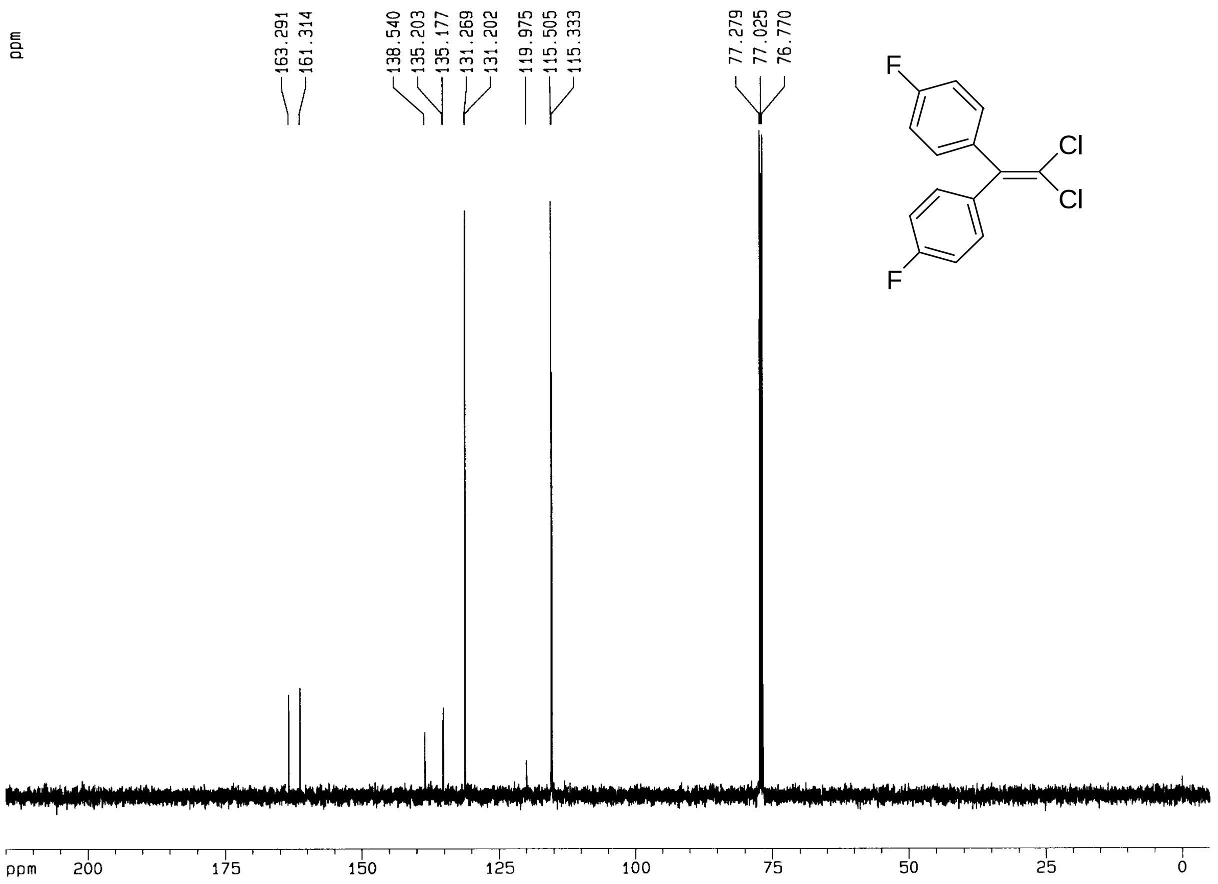
```
Current Data Parameters
NAME             jljiii44
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20020312
Time                10.54
INSTRUM             spect
PROBHD     5 mm BBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  724.1
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 ========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300094 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 9.000 ppm
F1                3601.17 Hz
F2P                -1.000 ppm
F2                -400.13 Hz
PPMCM             0.50000 ppm/cm
HZCM            200.06500 Hz/cm
```

JLJ-III-44
Rec.1 (MeOH/H2O)



```
Current Data Parameters
NAME             jljiii44
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20020312
Time                10.54
INSTRUM             spect
PROBHD     5 mm BBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  724.1
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 ========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300094 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 7.311 ppm
F1                2925.47 Hz
F2P                 6.977 ppm
F2                2791.65 Hz
PPMCM             0.01672 ppm/cm
HZCM              6.69110 Hz/cm
```

JLJ-III-44
Rec



```
Current Data Parameters
NAME             jljiii44
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20030717
Time                14.11
INSTRUM             spect
PROBHD     5 mm BBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    81
DS                     0
SWH            31446.541 Hz
FIDRES          0.479836 Hz
AQ             1.0420724 sec
RG                 16384
DW                15.900 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                 13C
P1                  5.80 usec
PL1                 0.00 dB
SFO1         125.7715719 MHz

============ CHANNEL f2 ============
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -1.00 dB
PL12               22.60 dB
PL13               22.60 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577891 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              215.000 ppm
F1              27037.93 Hz
F2P               -5.000 ppm
F2               -628.79 Hz
PPMCM           11.00000 ppm/cm
HZCM          1383.33569 Hz/cm
```

SPEC: jlj-iii-44 (03-Aug-03 16:48:21)
Samp: C14H4Cl2F2 mw=285.12
Oper: Xiao
Base: 214.04
Peak: 1000.0 mmu

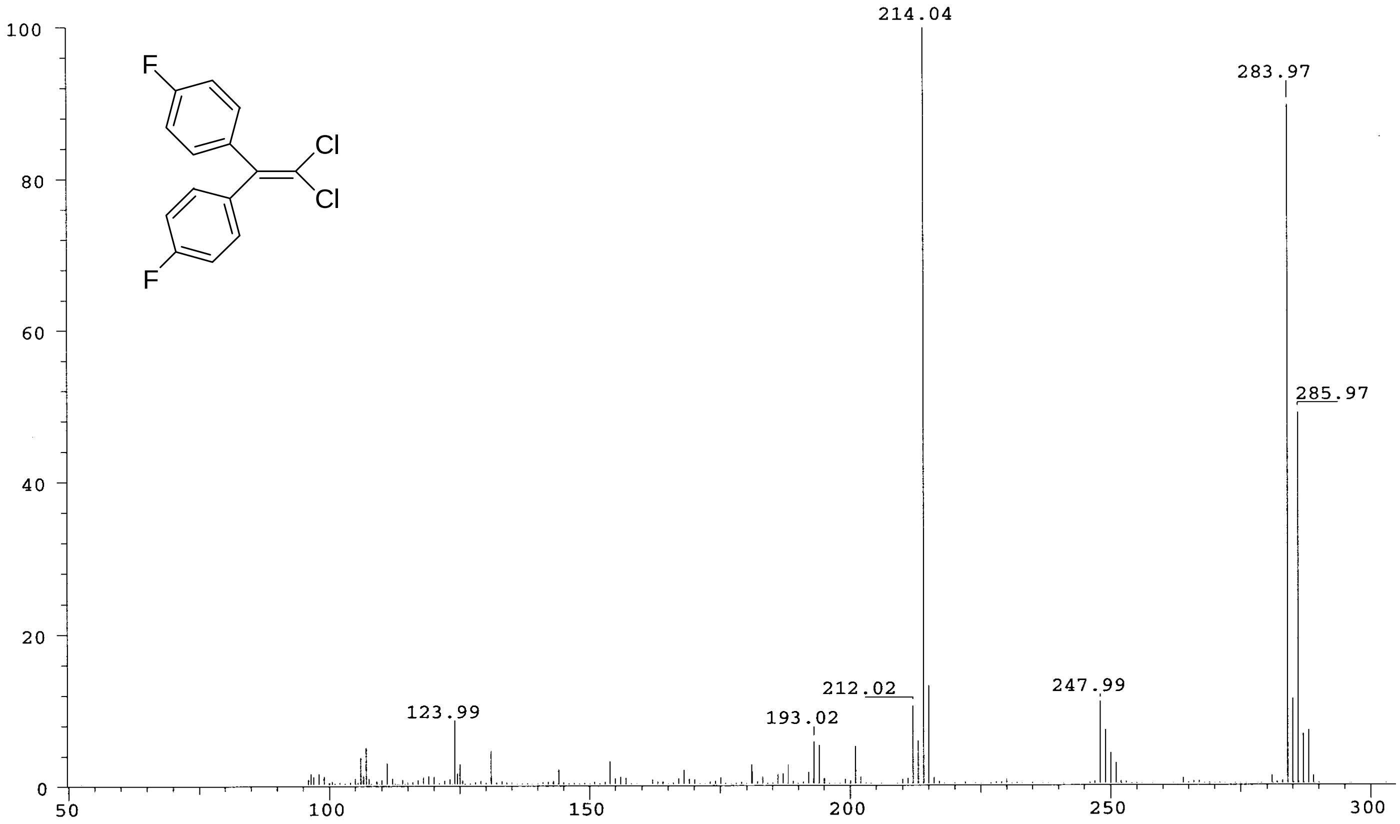
Study: EI +
Masses: 50.00 > 600.00
Intensity: 88525160

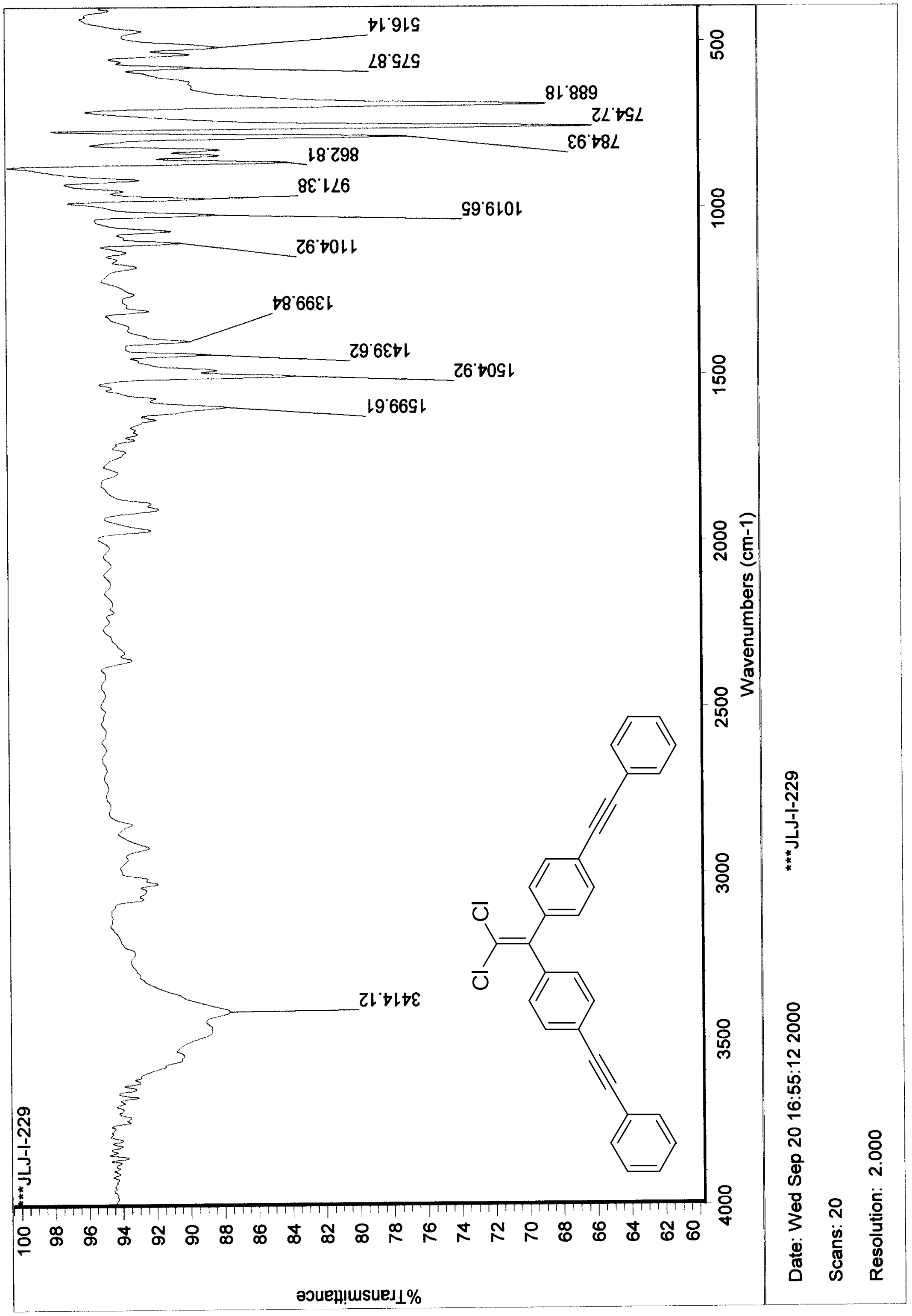
Scans: 1 > 54

Client: Jurs/Tour
#Peaks: 508
RIC: 384112586

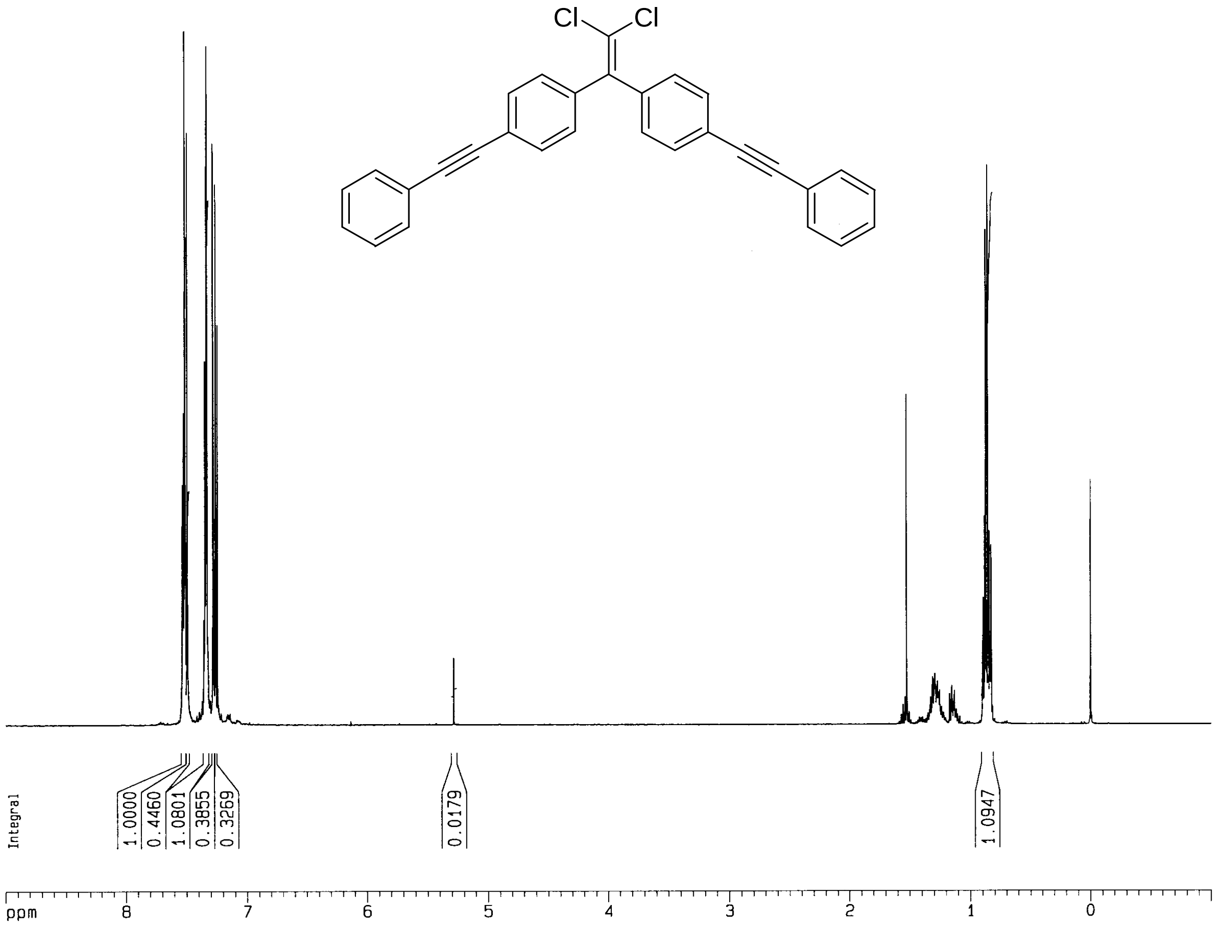
REG #9 @ 6.98 min (EI +VE +LMR BSCAN (EXP) UP HR NRM) (+37-11)

8.9E+07

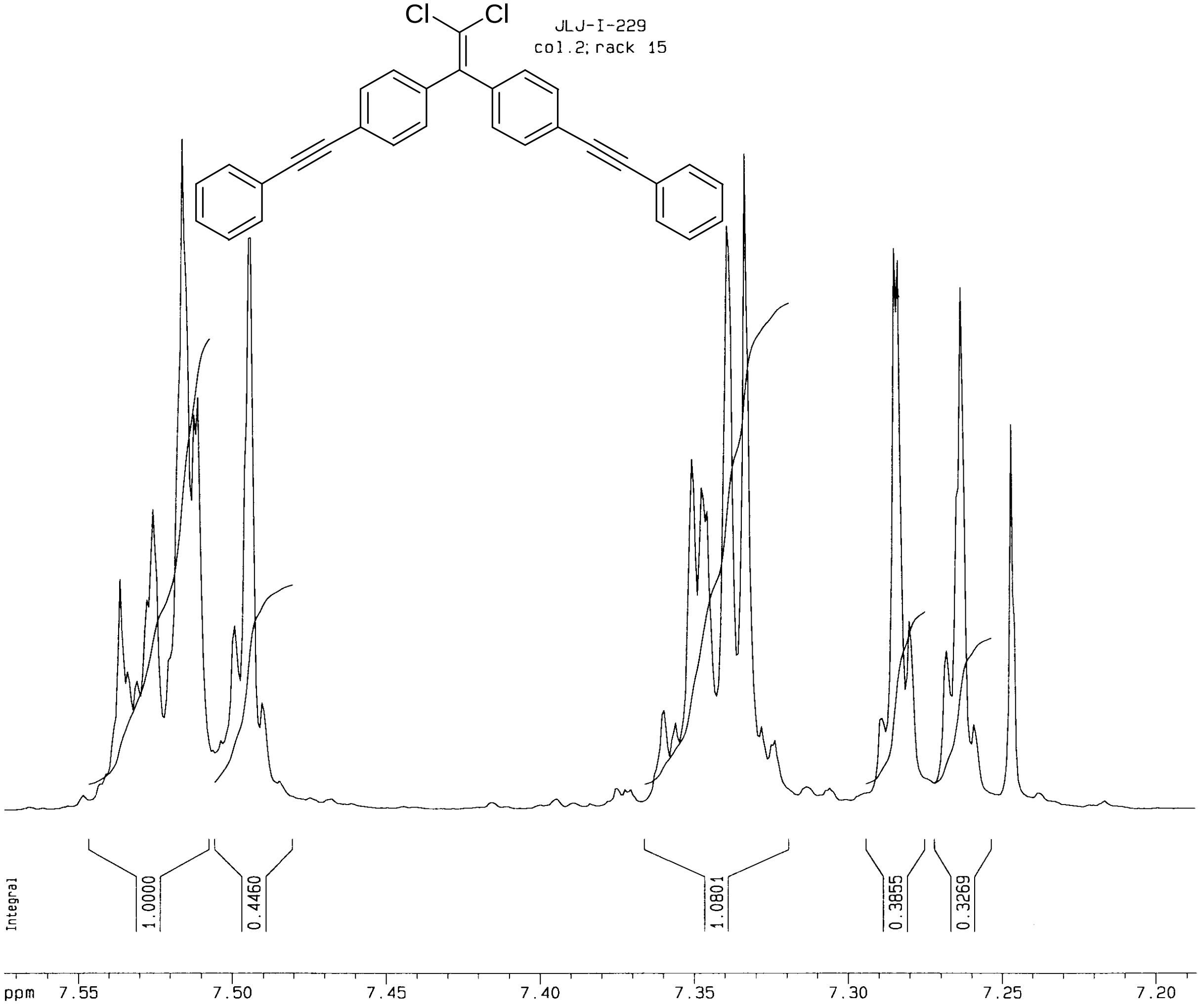



***JLJ-I-229
%Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
3414.12
1599.61
1504.92
1439.62
1399.84
1104.92
1019.65
971.38
862.81
784.93
754.72
688.18
575.87
516.14
Cl
Cl
Date: Wed Sep 20 16:55:12 2000
***JLJ-I-229
Scans: 20
Resolution: 2.000

JLJ-I-229
col.2; rack 15

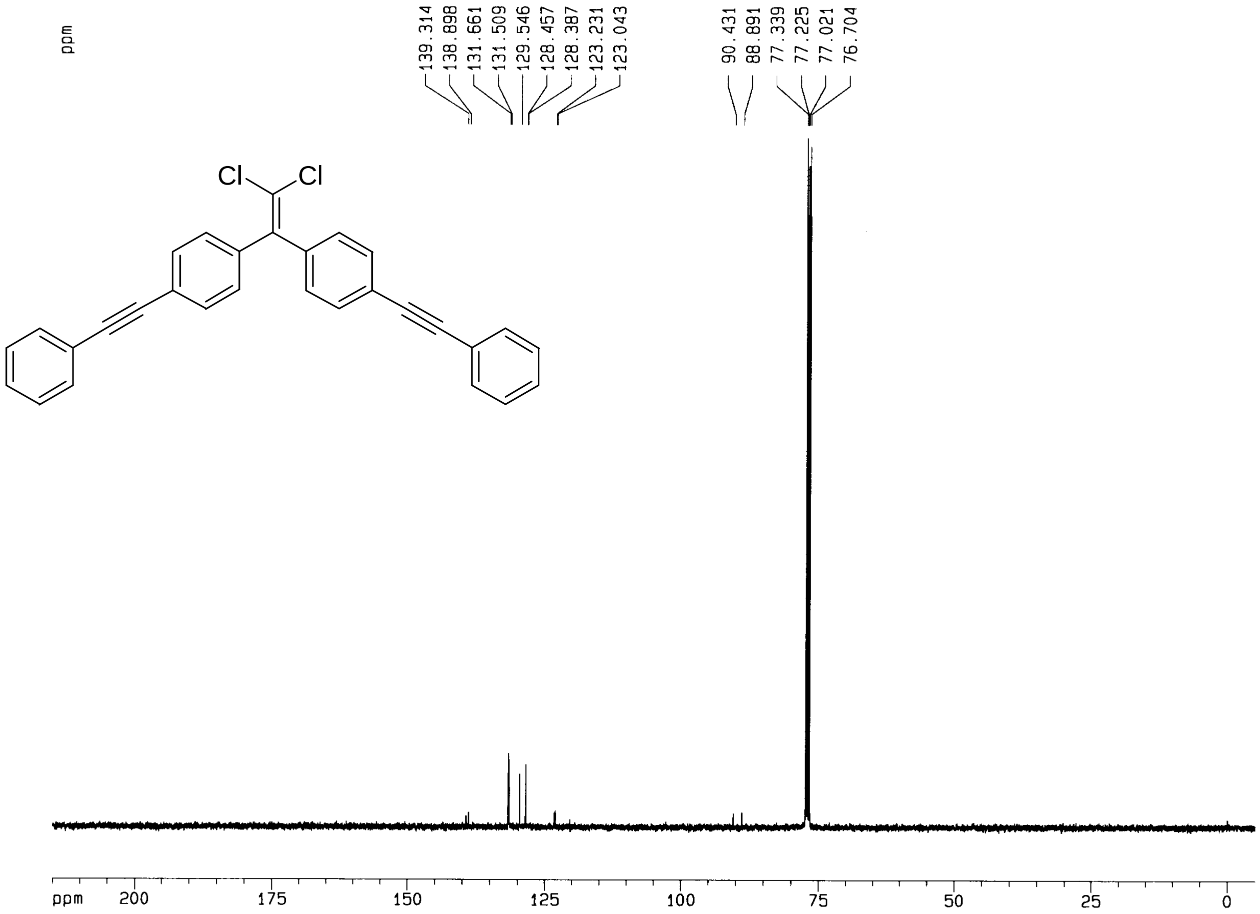


```
Current Data Parameters
NAME          JLJ-I-229
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20000718
Time              13.28
INSTRUM           spect
PROBHD   5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                  256
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300147 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -1.000 ppm
F2              -400.13 Hz
PPMCM           0.50000 ppm/cm
HZCM          200.06500 Hz/cm
```



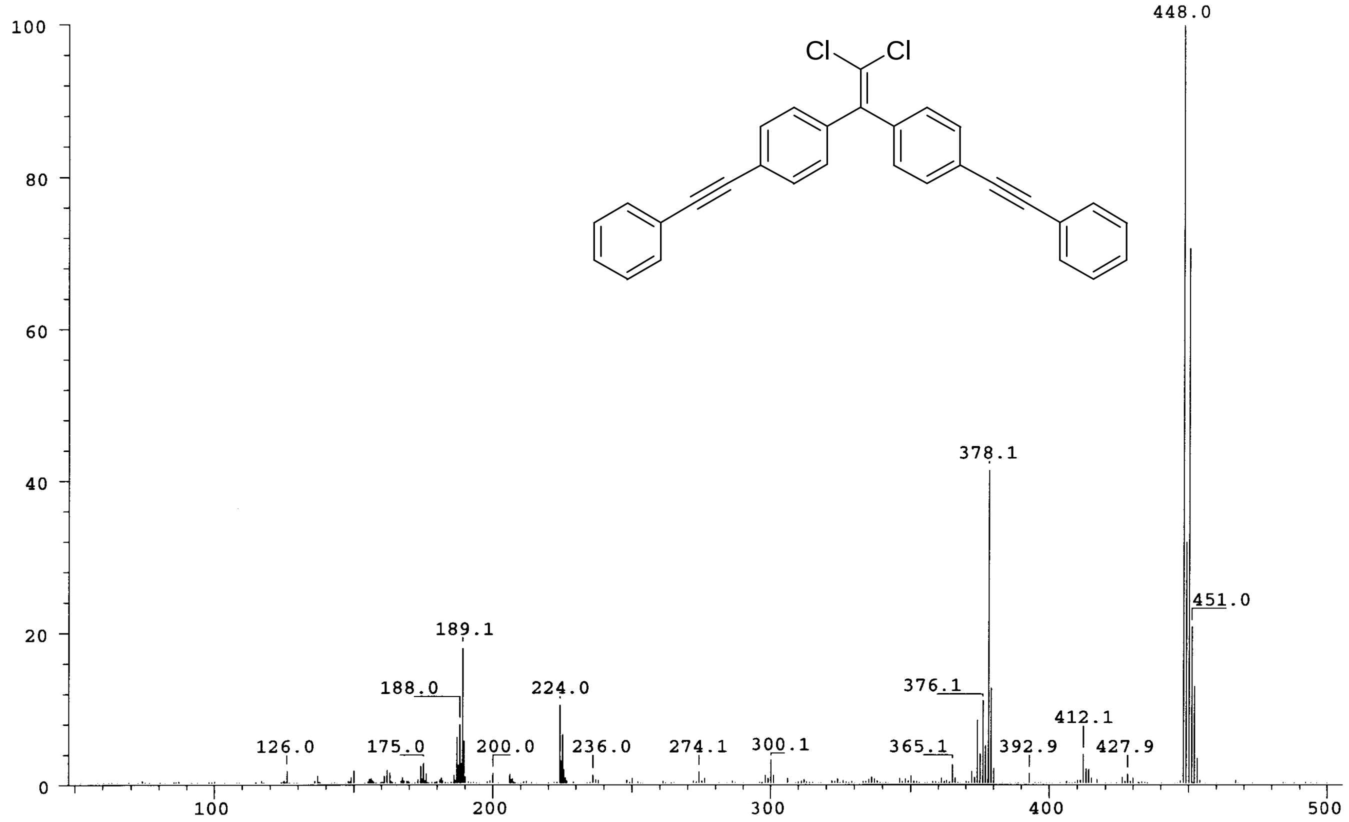
```
Current Data Parameters
NAME          JLJ-I-229
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20000718
Time              13.28
INSTRUM           spect
PROBHD    5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                  256
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300147 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               7.574 ppm
F1              3030.57 Hz
F2P               7.187 ppm
F2              2875.68 Hz
PPMCM           0.01936 ppm/cm
HZCM            7.74454 Hz/cm
```

JLJ-I-229
col.2; frac.2&3



```
Current Data Parameters
NAME             JLJ-I-229
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_             20000819
Time                 11.55
INSTRUM              spect
PROBHD     5 mm BBO BB-1
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       0
SWH              25125.629 Hz
FIDRES            0.383387 Hz
AQ               1.3042164 sec
RG                    4096
DW                  19.900 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
d12             0.00002000 sec

============ CHANNEL f1 ============
NUC1                   13C
P1                    8.30 usec
PL1                   0.00 dB
SFO1           100.6237959 MHz

============ CHANNEL f2 ============
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 18.00 dB
PL13                 18.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF             100.6127689 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                215.000 ppm
F1                21631.75 Hz
F2P                 -5.000 ppm
F2                 -503.06 Hz
PPMCM             11.00000 ppm/cm
HZCM            1106.74048 Hz/cm
```

```
SPEC:  jlji229 (01-Aug-00 18:58:09)                                          Scans:   1 > 109
Samp:  JLJ-I-229  C30 H18 Cl2  MW=448
Oper:  TDM                       Study:  EI + HR                             Client:  JLJ/JMT
Base:  448.03                    Masses:  50.00 > 550.00                     #Peaks:  345
Peak:  1000.0 mmu                Intensity:   2665531                        RIC:  12678547
REG #9 @ 12.83 min (EI +VE + -LMR  BSCAN (EXP) UP HR NRM) (+72-54)                 2.7E+06
```



Chapter 3

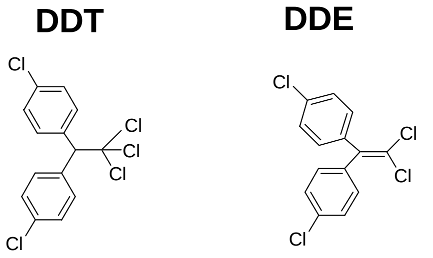
Novel Flame Retardant Polymers

DDT and DDE Flame Retardant Polymers

3.1 Introduction

In chapter 2 I discussed the synthesis and testing of monomeric DDT/DDE derivatives (Figure 1). The excellent results obtained from using these molecules and their analogs as flame retardant additives compelled us to develop novel flame retardant polymers utilizing these structures in the backbone of the polymer.

Figure 1



1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane

2,2-Bis(4-chlorophenyl)-1,1-dichloroethylene

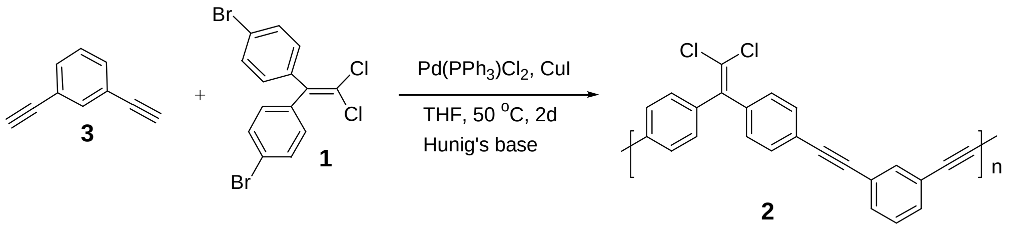
3.2 Results and Discussion for DDE based polymers

Flame propagation is a thermodynamically driven process. It is our objective to design a polymer in its lowest energy state in order to diminish the spreading of fires. One of the approaches to creating these flame resistant materials is by using functional groups on the polymer (i.e. halogens) or incorporating certain non-flammable elements (i.e. boron or phosphorous) into the backbone of the polymer chain, thus creating a polymer that is inherently flame retardant. Incorporation of these functional groups can act as radical traps in the vapor phase and or moieties that will cross-link during the burn process to create char in the condensed phase. These processes will increase the polymer's flame resistant capabilities.

As was discussed in Chapter 2, it is known that alkynes can crosslink during the combustion process to increase char formation in the condensed phase. With this in mind the incorporation of an alkyne into a polymer was pursued using the bromo-DDE analog

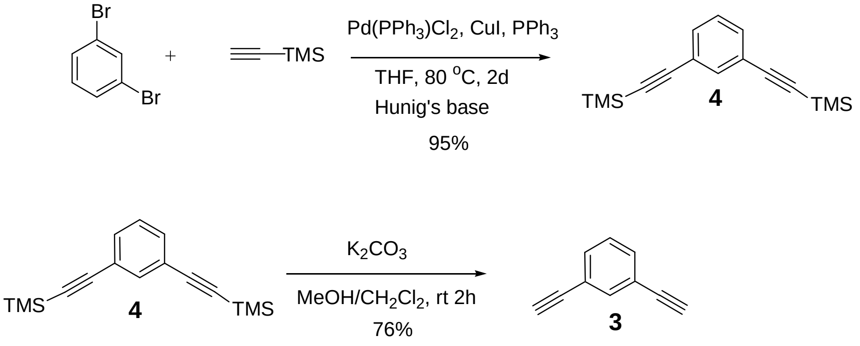
1 to make a poly[(2-phenylene-2’-phenylene-m-diethynylene)-1,1-dichloroethlyene] **2**. This polymer was made by a Sonogashira coupling of 1,3-diethynylbenzene (**3)** with 2,2-bis(4-bromophenyl)-1,1-dichloroethlyene (**1)** (Polymerization 1).[1]

Polymerization 1



1,3-Diethynylbenzene (**3)** was synthesized by a Sonogashira coupling of 1,3-dibromobenzene with trimethylsilylacetylene to give the trimethylsilyl protected 1,3-diethynylbenzene (**4)** followed by deprotection with potassium carbonate to yield 1,3-diethynylbenzene (**3)** (Reactions 1 & 2)

Reactions 1 & 2

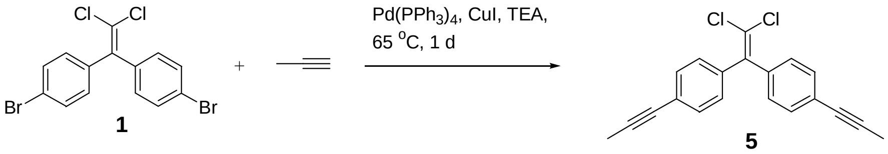


Polymer **2** suffered extended burn times negatively impacting its use in ABS, but the material may work well as a pristine polymer. We did not pursue the synthesis of a large amount of this polymer that would be necessary for such testing. The burn results are summarized in Table 1.

Another approach to making alkyne containing polymers is by utilizing the acyclic diyne metathesis polymerization (ADMET) made with a molybdenum catalyst.

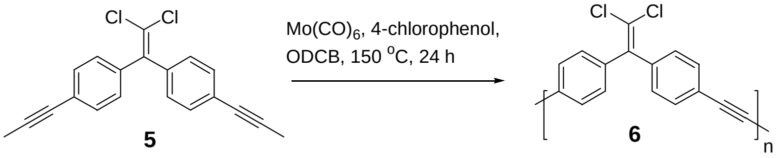
The monomer was synthesized from a DDE (**1**) analog. Starting with 2,2-bis(4-bromophenyl)-1,1-dichloroethylene (**1**) using Bunz's procedure for coupling with propyne, the diyne **5** was made.[2,3] (Reaction 3)

Reaction 3



The dipropyne monomer **5** was then polymerized using Bunz's ADMET process, which uses $Mo(CO)_6$ and 4-chlorophenol as a catalyst to produce polymer **6**.[2,3] (Polymerization 2)

Polymerization 2



PCFC date for the Alkyne Polymers.

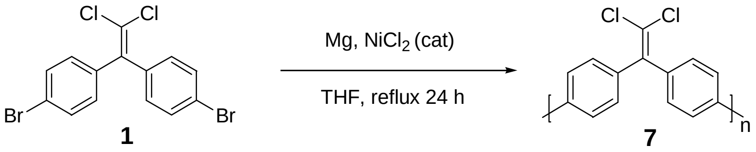
Polymer	HR capacity (J/g K)	Total Heat (kJ/g)	Char yields (%)
Polymer **2**	17	5.2	50.4
Polymer **6**	11	4.5	34.7

Both of these alkyne containing polymer have very low heat release capacities, and polymer **2** has a high char yield. Unfortunately due to processing difficulties these polymers will not make good thermoplastic polymers.

Thermal testing of this polymer was done as a blend with ABS and the UL-94 burn results are summarized in Table 1.

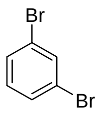
One of the problems with the incorporation of the alkyne functional group is that the crosslinking process is exothermic. This exothermic event adds energy to the burn process, therefore increasing burn times with the UL-94 test. In order to circumvent this process the DDE core was polymerized by direct aromatic polymerizations using aryl-aryl coupling procedures. Several reaction conditions were tried, but the procedure that yielded high molecular weight polymer is the polymerization of the biphenyl ethylene analog **1** in the presence of magnesium and catalytic nickel chloride (Polymerization 3).[4]

Polymerization 3

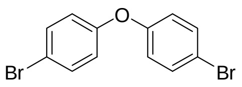


High molecular weight polymer **7** was synthesized, but its rigid structure yielded a polymer that does not melt. Several different linker groups were synthesized and co-polymerized with DDE analog **1** to help break up the stiffness in the polymer and lower the melting point (Table 2).

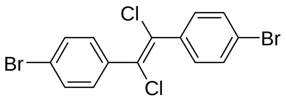
Table 2



8



9



10

Linker Groups

5 mol % **8**
M_w : 16,000
M_n : 2,300

5 mol % **9**
M_w : 8,500
M_n : 2,600

20 mol % **10**
M_w : 102,100
M_n : 68,000

10 mol % **8**
M_w : 65,300
M_n : 54,300

10 mol % **9**
M_w : 8,600
M_n : 2,500

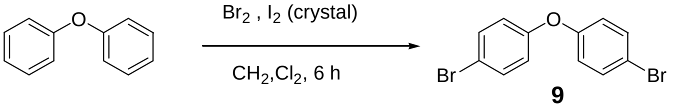
PCFC Results for Dichloroethylidene Polymer

Polymer	HR capacity (J/g K)	Total Heat (kJ/g)	Char yields (%)
Polymer **7**	12	4.9	56.6

The dichloroethylidene polymer **7** has a very low heat release capacity and very high char yields. Unfortunately due to its processing difficulties, it can not be used as a thermoplastic polymer. This data shows how good of a polymer this compound can be and gives a starting point to work with in similar materials.

The 1,3-dibromobenzene (**8)** was bought from Aldrich, the others were made in the laboratory. The synthesis of 4,4'-dibromodiphenylether (**9)** was achieved by brominating diphenylether in the presence of catalytic iodine (Reaction 4).

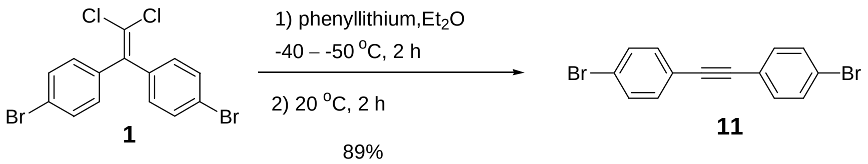
Reaction 4



9

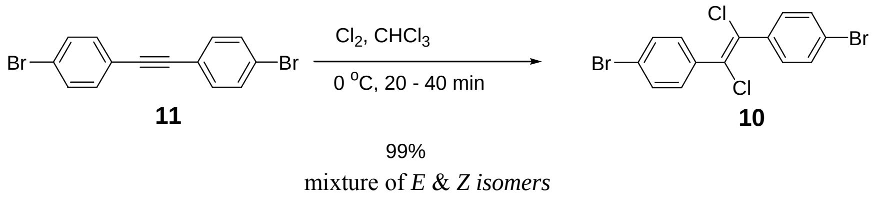
The synthesis of the E-1,2-bis(4-bromophenyl)-1,2-dichloroethylene required two steps. The starting product **1** was transformed to the 4,4'-dibromotolane **11** using phenyllithium at -40 to-50 °C for 2 hours followed by warming to room temperature and stirring for an additional 2 hours (Reaction 5).[6]

Reaction 5



The chlorination of the triple bond of **11** was achieved by bubbling chlorine gas through a solution of chloroform and the dibromotolane at 0 °C for 20 minutes to yield **10** Reaction 6).

Reaction 6



Even with the various linker groups the polymers synthesized with various mol % of **8, 9,** and **10** in the polymer backbone, these polymer were not melt blendable. In light of this fact, the polymer was pressed together using a Carver pellet press. A piece of it was held in and above the flame of a Bunsen burner. After removing the plastic from the ignition source, the flame went out.

In another attempt at making flame resistant polymers, the reaction of chloral hydrate directly into a polymer was investigated. It has been shown that chloral hydrate will condense with diphenylether in the presence of trifluoroacetic acid, trifluoroacetic anhydride, and boron trifluoride to yield polymer **15.** Polymer **15** gave the more stable dichlorovinylidene **16** after dehydrochlorination in refluxing pyridine (Polymerization 4).[5] This polymer has shown improved flame resistance by GE, so making large quantities of this polymer was never pursued.

Polymerization 4

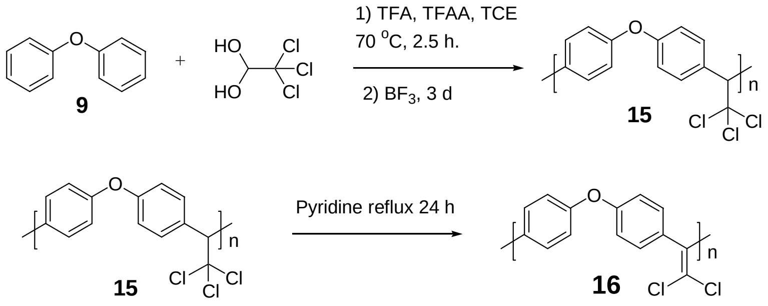


Table 1. HVUL-94 Burn Results.

Additive	First Ignition[a] (sec)	Observed Dripping[b]	Second Ignition[a] (sec)	Observed Dripping[b]	UL-94 Rating
2, 10wt%*; Sb2O3, 4wt%; PTFE, 1wt%; **ABS**	175, 192	No, No	0,0	No, No	?, ?
6, 8.5 wt%; Sb2O3, 4wt%; PTFE, 1wt%; **ABS**	198, 195	No, No	0, 0	No, No	?, ?
7, 10wt%; Sb_2O_3, 4wt%; PTFE, 1 wt%; **ABS**	40, 275	Yes[c], No	X, 7[d]	No, No	?, ?
7, 10wt%; Sb_2O_3, 4wt%; PTFE, 1 wt%;**HIPS**	30, 29	Yes[c], Yes[c]	19, X	Yes, No	?, ?
7, 10wt%*; Sb2O3, 4wt%; PTFE, 1 wt%; **ABS**	0, 33[d]	No, No	143[d], 45[d]	No, No	?, ?
7, 10wt%*; Sb2O3, 4wt%; PTFE, 1 wt%; **ABS**	51[d], 36[d]	No, No	42[d], 81[d]	No, No	?, ?
7, 10wt%*; Sb2O3, 4wt%; PTFE, 1 wt%; **HIPS**	134[d], 128[d]	No, No	158[d], 110[d]	No, No	?, ?

a Time to self-extinguishing in seconds after 1st, 2nd, 3rd 10 sec ignition. **b** Indicates that molten ABS did (Y) or did not (N) drip on to cotton patch underneath ignited bar during UL-94 test. **c** Indicates ignition of cotton patch underneath ignited bar of plastic. **d** Indicates time that only glowing, not flame occurred after re-application of flame. X indicates not enough bar remaining for 2nd ignition. * Wt % based on halogen content.

Table 1 summarizes the burn results from the following chapter and shows that while most of these polymers did not perform as flame retardant additives in commercial polymers. The extended burn times on the preceding polymers illustrate that these materials are forming large amounts of char. If not, they would have burned quickly and left no char. These extended burn time negatively impact their use as flame retardant additives, but as pristine polymers they could be good flame retardant materials. Unfortunately, without a glass transition temperature or a defined melting point these materials are not processible as thermoplastic polymers.

3.3 Experimental

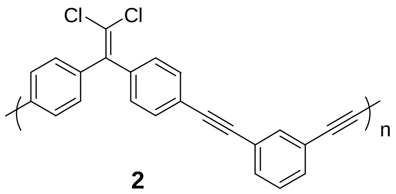
General Procedures: All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Silica TLC plates were 250 μm thick, 40 F254 grade from EM Science. Silica gel was grade 60 (230-400 mesh) from EM Science. ^{1}H NMR spectra were observed at 400 MHz and ^{13}C NMR spectra were observed at 100 MHz on a Brüker Avance 400 spectrometer. ^{1}H chemical shifts (δ) are reported in ppm downfield from tetramethysilane. IR spectra were obtained on a Nicolet Avatar 360 FTIR. Gas chromatography experiments were performed on a Hewlett-Packard GC model 5890A. Thermal gravimetric analysis (TGA) was performed with a Perkin Elmer TGA7 or TA Q 50 from 30 - 900 °C at 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) was performed with a Perkin Elmer DSC7 or TA Q 10 using a 30 - 450 °C scanning window at 10 °C/min. under nitrogen. Polymer blending/extrusion was done with a Custom Scientific Instruments CSI-183MMX Mini-Max Blender/Extruder or with a Brabender Prep-Center using a type 6/2 mixer head or Thermo Haake Mini lab Rheomex CTW5. An Atlas Electric HVUL-94 flame test station was used for the UL-94 flame tests. Melting points were obtained using a Büchi melting point apparatus. Reagent grade tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. Dry benzene, toluene, methylene chloride, and triethylamine were distilled over calcium hydride and under nitrogen. The molecular weights of the polymers have been analyzed on either a Waters GPC 150 C and/or a Polymer Laboratory GPC 220, using THF (40 ^{o}C, 1 mL/min) as the elutent. The GPC samples where analyzed by both refractive index and UV absorption. The synthesized polymers were compared with polystyrene standards with known molecular weights of 1000000, 900000, 435500, 96000, 30300, 22000, 5050, 1250, and 580. Unless otherwise stated, all other reagents were used as received. Mass spectrometry work was obtained from the Rice University Mass Spectrometry Laboratory.

General Procedure for Blending Flame Retardant Plastic and Additives in either the Brabender 30 ml Type 6/2 Mixing bowl – Prep Center or the Thermo Haake Mini lab Rheomex CTW5. The additives and plastics were weighed out in their respective amounts according to the wt % of additive. Heating temperatures for the blending bowl varied depending on the material involved. After the bowl had heated to the necessary processing temperature, the sample was poured quickly through the top opening of the Brabender while the blades were rotating at 50 RPM. The opening was then closed with the weighted handles and the sample was blended according to the type of flame retardant added. If a melt-blendable additive was used, the plastic and additives were blended for 10 min at 100 RPM. If a non-melt blendable additive was used, the plastic and additives were blended for 10-30 min at 150 RPM. If fibrillare PTFE (Dupont PTFE 30, 60 % PTFE in an aqueous suspension; density = 1.3 g/mL) was used as an anti-drip additive, the resin and the PTFE were blended first for 10 min at 150 RPM. The flame-retardant additives were added and the plastic was blended again for 10 min at 150 RPM. After the blending was complete and the blades were stopped, the bowl was opened and molten plastic with the additives were removed with a bronze spatula. The plastic was then blended in the CSI-183MMX blender and extruded to give bars for the UL-94 test.

General Procedure for Extruding Plastic in the UL-94 Test Bars. The plastic removed from the Brabender mixing center was then broken into smaller pieces and inserted into the heated cup of the CSI-183MMX blender until the cup was full. The plastic and additives were heated until molten and extruded into a heated 1/8” thick × ½” wide × 3” long rectangular bar mold. Heating temperatures for the blend cup and the extrusion mold varied depending on the material involved.

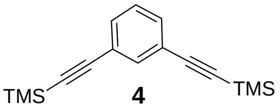
General Procedure for the HVUL-94 Burn Test. The flame resistance of the new polymers was tested using the horizontal and vertical Underwriters Laboratory test for flammability of plastic materials (HVUL-94). Two ⅛ inch thick × ½ inch wide × 3 inches long plastic (polymer + anti-drip additive) rectangular bars were used for this test. All flame tests were done in an Atlas Electric HVUL-94 flame test station. The methane tank pressure regulator was set to 20 psi. The pressure regulator on the HVUL-94 test station was set to 4.5 psi. The Bunsen burner flame height was 125 mm, and the height from the top of the Bunsen burner to the bottom of the test bar was 70 mm. The flame is blue with an intense blue inner cone with a flow rate 90 cc/min. All test bars underwent two trials; each trial consisting of ignition for 10 seconds, followed by flame removal and a recording of the time for the bar to be considered self-extinguished.

General Procedure for the Pyrolysis Combustion Flow Calorimetry (PCFC).[6,7] PCFC measurements were taken using 0.1-0.2 mg of the polymer sample with an interface temperature just below the onset of decomposition. The samples were pyrolyzed to a temperature of 930 °C at 4.3 °C/s in a nitrogen atmosphere. The polymer was then completely combusted at 900 °C. The sample results are an average of five measurements.[6,7] The PCFC is a new method used to characterize the potential flame retardancy of a polymeric material. It gives three important data points that are used to evaluate the materials performance: 1. Heat Release Capacity, a calculated variable derived from the polymeric structure, this is a true material property which is dependent upon thermodynamic state variables, independent of sample size and heating rate.[6,7] 2. Total Heat Release is a measured value that is derived from the controlled pyrolysis of the polymer in an inert gas (to avoid oxidizing the char). The fuel gas is then mixed with oxygen at elevated temperatures (900 °C) and the heat of combustion is measured.[6,7] 3. Char yields are important because char does not burn and it helps to add an insulating layer between the flame front and the polymeric fuel. It has been shown that the data obtained from PCFC measurements and correlates well with other pyrolysis methods such as, Cone Calorimetry, UL-94 test for flammability of plastic materials, and oxygen bomb calorimetry.[8]



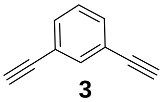
2

Poly[(2-phenylene-2'-phenylene-m-diethynylene)-1,1-dichloroethlyene] (2).[1] To a screw cap tube equipped with a stir bar was added **1,** (3.245 g, 8 mmol), 1,3-diethynylbenze (0.835 g, 8 mmol), Copper Iodide (0.076 g, 0.4mmol), bistriphenylphosphine palladium (II) dichloride (0.280 g, 0.4 mmol), and triphenylphosphine (0.210 g, 0.8 mmol). The flask was sealed with a septum, evacuated, and backfilled with nitrogen (3×). THF (30 mL), and Hunig's base (5.6 mL, 32 mmol) were added via syringe. The septum was replaced with a screw cap and placed in an oil bath at 50 °C for 2 d. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was removed from the filtrate via rotary evaporation and the resulting solid was dried in vacuo for 24 h. FTIR (KBr) 3417, 3034, 1588, 1503, 1400, 1014, 969, 855, 788, 733, 681. ^{1}H NMR (400 MHz, $CDCl_3$) δ Not Soluble. Mw: 4500; Mn: 1700.



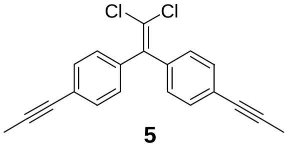
4

1,3-Bis[(trimethylsilyl)ethynyl]benzene (4).[1,9] To a screw cap tube equipped with a stir bar was added Copper Iodide (0.380 g, 2mmol), bistriphenylphosphine palladium(II) dichloride (0.702 g, 1 mmol), and triphenylphosphine (0.525 g, 2 mmol). The flask was sealed with a septum, evacuated, and backfilled with nitrogen (3×). THF (30 mL), Hunig's base (10.45 mL, 60 mmol), and phenyl acetylene (3.3 mL, 30 mmol) were added via syringe. To a 25 mL pear shaped flask was added 1,3-dibromobenze (2.42 mL, 20 mmol). The flask was frozen with liquid nitrogen, evacuated and backfilled with nitrogen (3×). The degassed 1,3-benzene was added to the screw cap tube via cannula and rinsed with dry THF (2 × 10 mL). TMS acetylene (8.5 mL, 60 mmol) was added to the screw cap tube via syringe. The septum was replaced with a screw cap and placed in an oil bath at 80 °C for 2 d. The reaction mixture was then diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was extracted with methylene chloride (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was removed from the filtrate via rotary evaporation and the resulting solid was dried in vacuo for 24 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (td, J =1.63, 0.52 Hz, 1 H), 7.37 (dd, J =7.75, 1.55 Hz, 2 H), 7.21 (td, J =7.74, 0.53 Hz, 1 H), 0.2184 (s, 1 H)



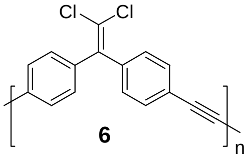
3

1,3-diethynylbenzene (3).[9] To a 250 mL round bottom flask, equipped with a stir bar, was added **4**, potassium carbonate (10 equivalents), and MeOH/CH_2Cl_2 (1:1). The reaction was sealed under nitrogen and allowed to stir at room temperature for 2 h. The reaction mixture was then diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was removed via rotary evaporation and the resulting solid was dried in vacuo for 1 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, J =1.50 Hz, 1 H), 7.44 (dd, J =7.77, 1.62 Hz, 2 H), 7.26 (td, J = 7.77, 0.55 Hz, 1 H), 208 (s, 1 H).



5

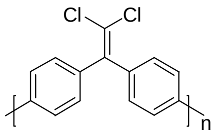
2,2-Bis(*p*-propynlphenyl)-1,1-dichloroethylene (5).[2,3] To a 250 mL round bottom flask, equipped with a stir bar and reflux condenser and purged with nitrogen, was added 2,2-bis(4-bromophenyl)-1,1-dichloroethylene **6** (4.06 g, 10 mmol) copper iodide (0.190 g, 1mmol), bistriphenylphosphine palladium(II) dichloride (0.351 g, 0.5 mmol). The flask was then sealed with a septum, evacuated, and backfilled with nitrogen (3×). Triethylamine (40 mmol) was added via syringe. Propyne was bubbled in with a balloon and the reaction was heated to 65 °C for 24 h. The reaction mixture was diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was removed from the filtrate via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. FTIR (KBr) 3420, 2916, 2253, 1588, 1504, 1400, 1021, 971, 855, 794, 686, 533. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.3 (dt, *J* = 8.4, 1.8 Hz, 4 H), 7.2 (dt, *J* = 8.5, 1.8 Hz, 4 H), 2.0 (s, 6 H).



6

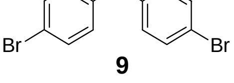
Poly[2,2-bis(p-ethynlphenyl)-1,1-dichloroethylene] (6).[2,3] To a 250 mL round bottom flask equipped with a stir bar and reflux condenser and purged with nitrogen, was added **5** (3.24 g, 10 mmol), molybdenum hexacarbonyl (.264 g, 1 mmol), 4-chlorophenol (1.28

g, 10 mmol), and o-dichlorobenzene (40 mL). The flask was then sealed with a septum and heated to 150 °C under a steady stream of nitrogen for 24 h. The mixture was then dissolved in methylene chloride and precipitated in methanol. The mixture was then dissolved in THF and precipitated in hexanes. Solvent was removed from the polymer in a vacuum desiccator for 24 h. FTIR (KBr). 3032, 1601, 1511, 1401, 1019, 970, 863, 832, 783, 728, 687, 571, 522. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.41 (m, 4 H), 7.28-7.21 (m, 4 H). Mn: 4,650; Mw: 28,600.



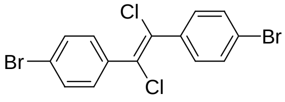
7

Poly[p-2,2-diphenyl-1,1-dichloroethylene] (7).[4] To a 250 mL three necked round bottom flask equipped with a stir bar and reflux condensor and purged with argon, was added **1**, magnesium turnings, and anhydrous nickel (II) chloride. The flask was then sealed under argon with a septa, evacuated and backfilled with argon (3×). THF (100 mL) was added via syringe. The reaction was heated to reflux for 24 h. The reaction mixture was then allowed to cool to room temperature, then poured into a vigorously stirred flask of MeOH (400 mL) to precipitate the polymer. This was followed by filtration of the polymer in a fritted funnel (medium porosity). The polymer was washed with copious amounts of MeOH and Et_2O. The polymer was dried in the vacuum oven 60 °C overnight. FTIR (KBr) 3417, 2359, 1902, 1629, 1582, 1485, 1391, 1070, 1008, 969, 855. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8-7 (m, 8 H). M_w: 110,000; M_n: 68,950.



9

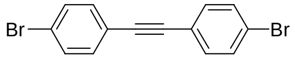
4,4’-Dibromodiphenylether (9).[10] To a 100 mL round bottom flask equipped with a stir bar and purged with nitrogen was added diphenyl ether and a crystal of iodine. Methylene chloride (10 mL) was added to the flask and the mixture was stirred until the solid dissolved. Bromine was added drop-wise via syringe and the reaction was allowed to stir for 6 h. The reaction was then diluted in methylene chloride and water. The organic layer was washed with sodium bisulfite (1 M) and extracted with methylene chloride (3×). The organic layers were combined and dried over magnesium sulfate and filtered through filter paper. Solvent was removed from the filtrate via rotary evaporation and the solid residue was dried in vacuo overnight. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4 (dt, J = 9, 2.8 Hz, 4H), 6.9 (dt, J = 9, 2.7 Hz, 4H).



10

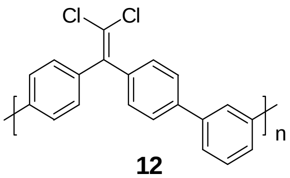
1,2-Bis(4-bromophenyl)-1,2-dichloroethylene (10). To a 100 mL three neck round bottom flask equipped with a stir bar, gas inlet and outlet, was added dibromotolane **11** and chloroform (50 mL). The reaction mixture was placed in an ice bath and chlorine was bubbled into the reaction (at a rate of approximately 1 bubble a second) for 40 min. The reaction was then diluted in methylene chloride and water. The organic layer was washed with sodium bisulfite (1 M) and extracted with methylene chloride (3×). The organic layers were combined and dried over magnesium sulfate and filtered through filter paper. Solvent was removed via rotary evaporation and the solid residue was dried in vacuo overnight. MP 124-126 °C. FTIR (KBr) 3431, 1902, 1578, 1477, 1388, 1188, 1067, 1008, 824, 776, 636, 512. ^{1}H NMR (400 MHz, $CDCl_3$) δ [cis] 7.6 (dt, J = 8.7, 2.2 Hz, 4 H), 7.5 (dt, J = 8.7, 2.2 Hz, 4 H); [tran] 7.3 (dt, J = 8.7, 2.2 Hz, 4 H), 7.1 (dt, J =

8.7, 3.3 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ [cis] 136.1, 131.6, 130.8, 130.0, 127.2, 123.4. ^{13}C NMR (100 MHz, $CDCl_3$) δ [trans] 135.9, 131.6, 131.2, 130.3, 123.2. HRMS Calc'd for $C_{14}H_8Br_2Cl_2$: 405.834782; Found: 405.834672; 0.27ppm error.



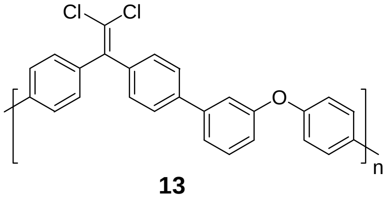
11

Dibromotolane (11).[11] To a 250 mL round bottom flask equipped with a stir bar was added **1**. The flask was sealed with a septa, then evacuated and backfilled with nitrogen (3×). Diethyl ether (100 mL) was added to the flask via syringe, and cooled to –40 to –50 °C. Phenyl lithium (1.8 M) was added to the reaction flask drop-wise via syringe. The reaction was stirred at –40 to –50 °C for 2 h, and then allowed to warm to room temperature overnight. The precipitate was filtered off and saved. The remaining ethereal filtrate was washed with water and extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate, and filtered through filter paper. Solvent was removed via rotary evaporation. The filter cake and the remaining solids after rotary evaporation were combined and dried in vacuo overnight. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5 (dt, J = 8.7, 2.1 Hz, 4 H), 7.4 (dt, J = 8.7, 2.0 Hz, 4 H).



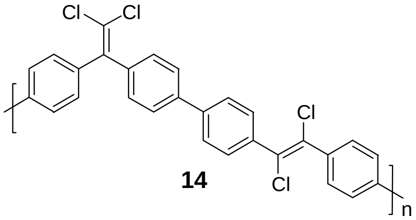
12

Poly[(2,2-diphenyl-m-phenyl)-1,1-dichloroethylene] (12).[4] To a 250 mL three necked round bottom flask, equipped with a stir bar and reflux condensor and purged with argon, was added **1**, 1,3-dibromobenezene(5 or 10 mol %), magnesium turnings, and anhydrous nickel(II)chloride. The flask was then sealed under argon with a septa, evacuated and backfilled with argon (3×). THF (100 mL) was added via syringe. The reaction was heated to reflux for 24 h. The reaction mixture was then allowed to cool to room temperature, then poured into a vigorously stirred flask of MeOH (400 mL) to precipitate the polymer. This was followed by filtration of the polymer in a fritted funnel (medium porosity). The polymer was washed with copious amounts of MeOH and Et_2O. The polymer was dried in the vacuum oven 60 °C overnight. FTIR (KBr) 3417, 3028, 2922, 2855, 2357, 1587, 1484, 1397, 1070, 1010, 968, 823, 696, 499. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8-7 (m, 12 H). (5 mol% of **8**) M_w: 16,000; M_n: 2300. (10 mol% of **8**) M_w: 65,300; M_n: 54,300.



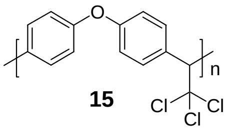
13

Poly[(2,2-diphenyl-p-diphenylether)-1,1-dichloroethylene] (13).[4] To a 250 mL three necked round bottom flask, equipped with a stir bar and reflux condensor and purged with argon, was added 2,2-bis(4-bromophenyl)-1,1-dichloroethylene, **1**, 4,4’-dibromophenyl ether (5 or 10 mol %), magnesium turnings, and anhydrous nickel(II) chloride. The flask was then sealed under argon with a septa, evacuated and backfilled with argon (3×). THF (100 mL) was added via syringe. The reaction was heated to reflux for 24 h. The reaction mixture was then allowed to cool to room temperature, then poured into a vigorously stirred flask of MeOH (400 mL) to precipitate the polymer. This was followed by filtration of the polymer in a fritted funnel (medium porosity). The polymer was washed with copious amounts of MeOH and Et_2O. The polymer was dried in the vacuum oven 60 °C overnight. FTIR (KBr) 3413, 2922, 1902, 1583, 1486, 1398, 1235, 1068, 1008, 822, 694, 501. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8-7 (m, 16 H). (5 mol% of **9**) M_w: 8500; M_n: 2600. (10 mol% of **9**)M_w: 8600.; M_n: 2500.



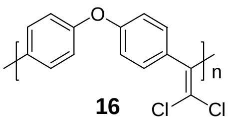
14

Poly[(2,2-diphenyl-p-1,2diphenyl-1,2-dichloroethylene)-1,1-dichloroethylene] (14).[4] To a 250 mL three necked round bottom flask, equipped with a stir bar and reflux condensor and purged with argon, was added 2,2-bis(4-bromophenyl)-1,1-dichloroethylene, **1**, 1,2-bis(4-bromophenyl)-1,2-dichloroethylene (20 or 100 mol %), magnesium turnings, and anhydrous nickel (II) chloride. The flask was then sealed under argon with a septa, evacuated and backfilled with argon (3×). THF (100 mL) was added via syringe. The reaction was heated at reflux for 24 hours. The reaction mixture was then allowed to cool to room temperature, then poured into a vigorously stirred flask of MeOH (400 mL) to precipitate the polymer. This was followed by filtration of the polymer in a fritted funnel (medium porosity). The polymer was washed with copious amounts of MeOH and Et_2O. The polymer was dried in the vacuum oven 60 °C overnight. FTIR (KBr) 3419, 3025, 2359, 1584, 1485, 1392, 1179, 1071, 1010, 972, 824, 754, 698, 492. ^{1}H NMR (400 MHz, $CDCl_3$) δ Not Soluble. (20 mol% of **10**) M_w: 102,100; M_n: 68,000. (100 mol% of **10**)M_w: 8700.; M_n: 2700.



15

Poly(diphenylether-chloral) (15).[5] To a 250 mL three neck round bottom flask, equipped with a stir bar, addition funnel, gas inlet, reflux condenser and purged with nitrogen, was added chloral hydrate **12** (1.65 g, 10 mmol). The flask was then sealed with septa, evacuated, and backfilled with nitrogen (3×). Trifluoroacetic acid (10 mL) was added *via* syringe, and trifluoroacetic anhydride (1.41 mL, 10 mmol) was added dropwise *via* an addition funnel over 1.5 h and stirred. To a separate 50 mL round bottom flask equipped with a stir bar was added diphenylether **9** (1.70 g, 10 mmol). The flask was then sealed with septa, evacuated, and backfilled with nitrogen (3×). Tetrachloroethane (10 mL) was added to the flask and allowed to stir. After the diphenylether dissolved, the solution was added drop-wise to the 250 mL flask *via* cannula. An additional 10 mL of tetrachloroethane was added to the 50 mL flask and was added drop-wise via cannula to the 250 mL flask. The mixture was heated to 70 °C for 2.5 h and allowed to stir. The reaction was allowed to cool to room temperature and BF_3 (gas) was bubbled into the mixture (approximately 1 bubble per second) for one hour and heated to 70 ^{o}C overnight. The addition of BF_3 (gas) was done for (approximately 1 bubble per second) an hour twice a day (morning and night) for 3 days. The reaction was then dissolved in chloroform and the solids precipitated with methanol. Solvent was removed from the polymer in a vacuum desiccators for 24 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.53 (m, 4 H), 6.98-6.94 (m, 4 H), 5.01 (s, 1 H). FTIR (KBr) 3054, 1596, 1500, 1242, 1172, 1015, 872, 792, 764, 715, 667, 567. Mn: 3500; Mw: 9400.



16

Polydichlorovinylidene (16).[5] To a 250 mL round bottom flask, equipped with a stir bar and reflux condenser and purged with nitrogen, was added poly(diphenylether-chloral) **13** (2.0 g). The flask was sealed with a septum, evacuated, and backfilled with nitrogen (3×). Pyridine (40 mL) was added to the flask via syringe and heated to reflux for 24 h. The cooled reaction was quenched in water and then the solids filtered, and washed with hot water (5×). The resulting polymer was dried in the vacuum oven 50 ^{o}C for 24 h. FTIR (KBr) 3035, 2359, 1593, 1498, 1240, 1167, 1015, 971, 874, 795, 750, 581. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.24 (m, 4 H), 6.97-6.90 (m, 4 H). Mn: 3500; Mw: 9400.

3.4 References

(1) Sonogashira, K.; Tohada, Y.; Hagihara, N. *Tetrahedron Lett*. **1975**, 50, 4467.

(2) Bunz, U.; Brizius, G.; Pschirer, N. G.; Steffen, W.; Stitzer, K.; zur Loye, H. C. J. *Am. Chem. Soc*. **2000**, 122.

(3) Bunz, U. H. F.; Kloppenburg, L.; Jones, D. *Marcromolecules* **1999**, 32, 4194-4203.

(4) Yamamoto, T.; Hayashi, Y.; Yamamoto, A. *Bull. Chem. Soc*. of Japan **1978**, 51, 2091-2097.

(5) Takakoshi, T.; U.S. Patent; 3824214. General Electric Company: United States, 1974.

(6) Lyon, R. E.; Walters, R. N. "A Microscale Combustion Calorimeter," Federal Aviation Administration, DOT/FAA/DAR-01/117, 2002.

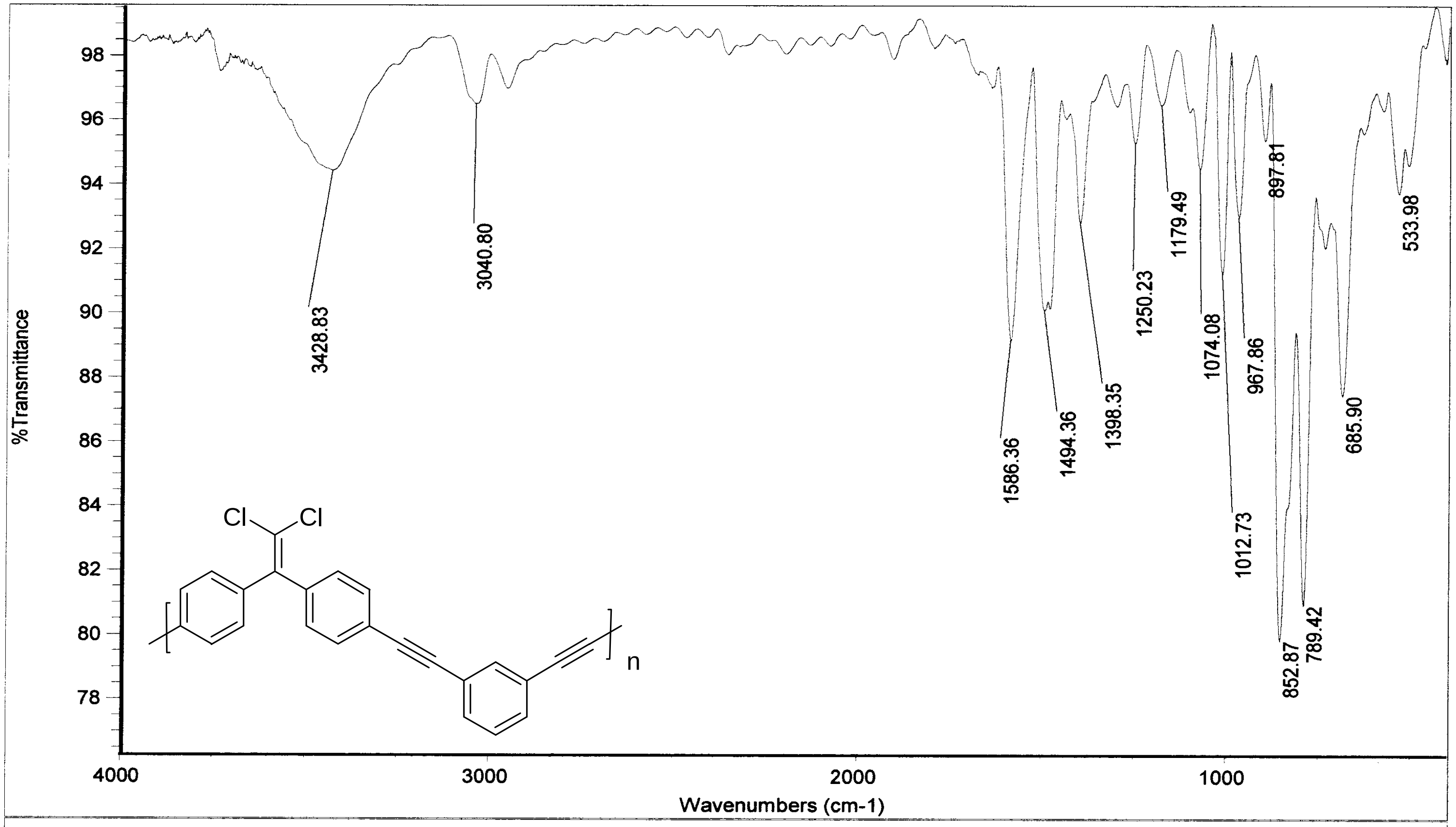
(7) Walters, R. N.; Lyon, R. E. In *International Aircraft Fire & Cabin Safety Research Conference*; FAA: Atlantic City New Jersey, 2001.

(8) Filipczak, R.; Lyon, R. E. "The Coorelation of Heat Release Calorimetry Measurements," Federal Aviation Administration, DOT/FAA/AR-TN02/104, 2002.

(9) Shortell, D. B.; Palmer, L. C.; Tour, J. M. *tetrahedron* **2001**, 57, 9055-9065.

(10) Rastko, M.; Bhattacharya, B.; *U.S. Patent* 4835322, Great Lakes Chemical Corp.: United States, 1989.

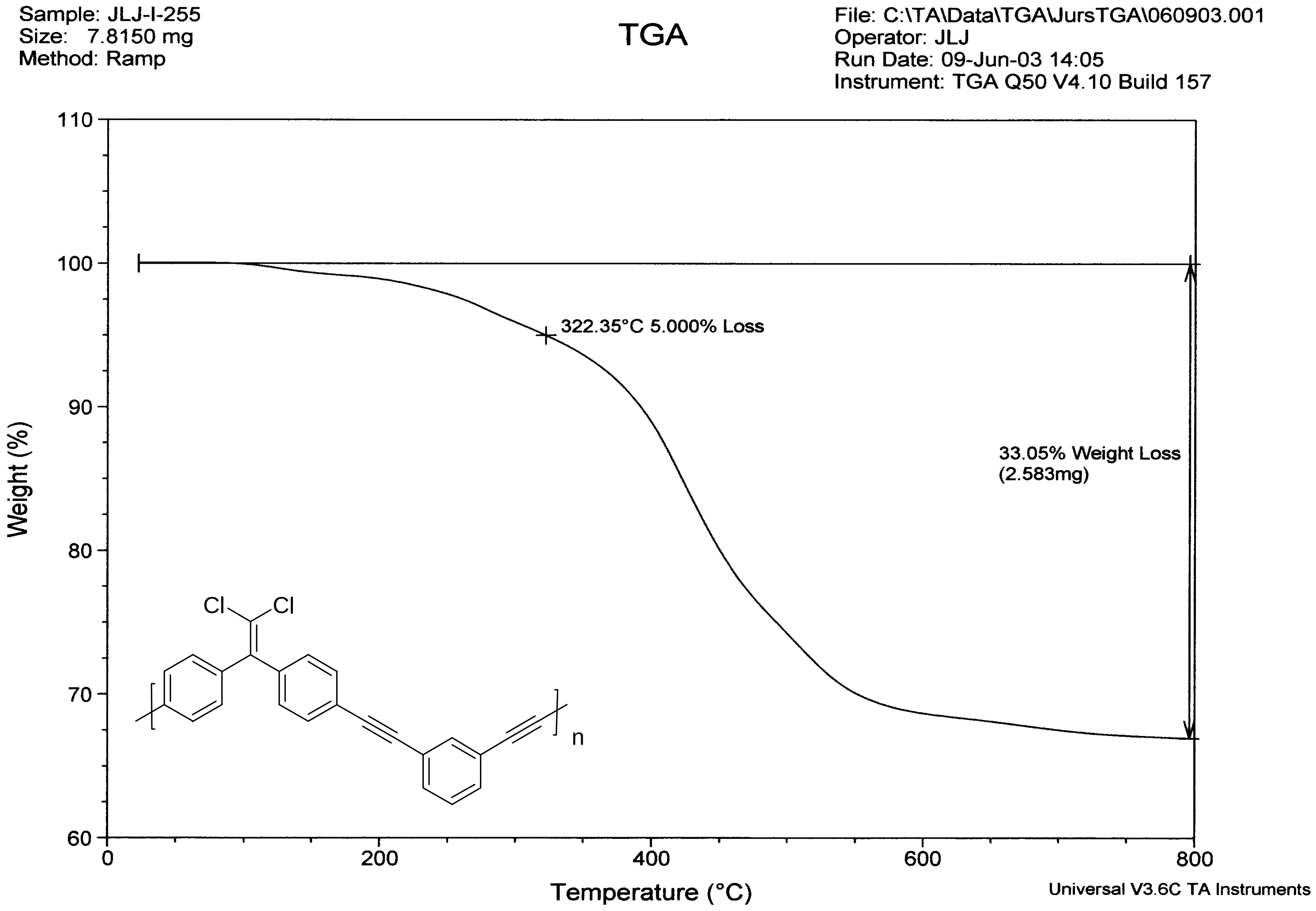
(11) Kovredov, A. I.; Shaugumbekova, Z. S.; Kazantsev, A. V.; Zakharkin, L. I. *Zhurnal Obshchei Khimmii* **1979**, 49, 1564-1566.



Date: Mon Jul 14 16:48:06 2003 **JLJ-I-255

Scans: 18

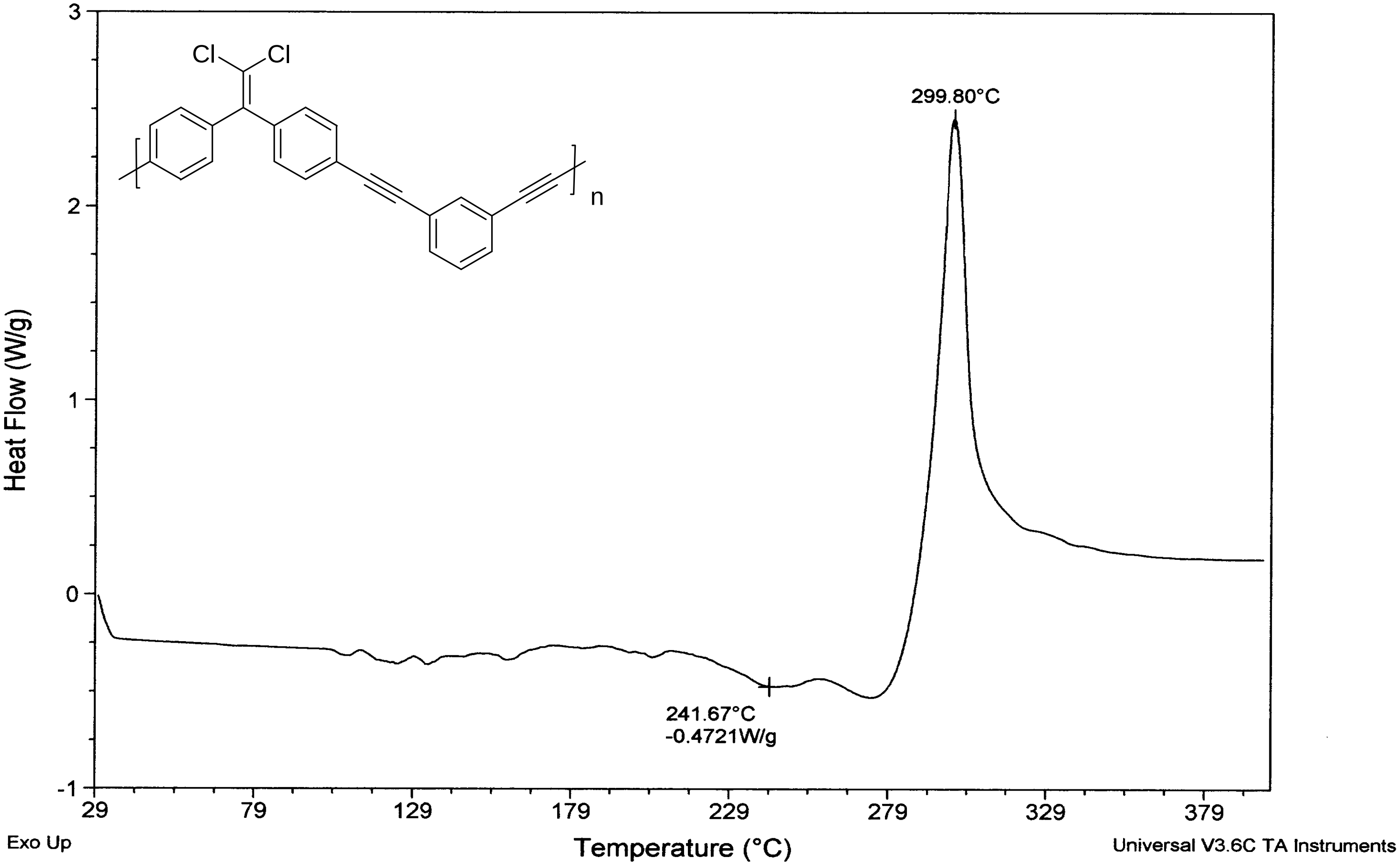
Resolution: 4.000


Sample: JLJ-I-255
Size: 7.8150 mg
Method: Ramp
TGA
File: C:\TA\Data\TGA\JursTGA\060903.001
Operator: JLJ
Run Date: 09-Jun-03 14:05
Instrument: TGA Q50 V4.10 Build 157
322.35°C 5.000% Loss
33.05% Weight Loss
(2.583mg)
Cl
Cl
n
Weight (%)
110
100
90
80
70
60
0
200
400
600
800
Temperature (°C)
Universal V3.6C TA Instruments

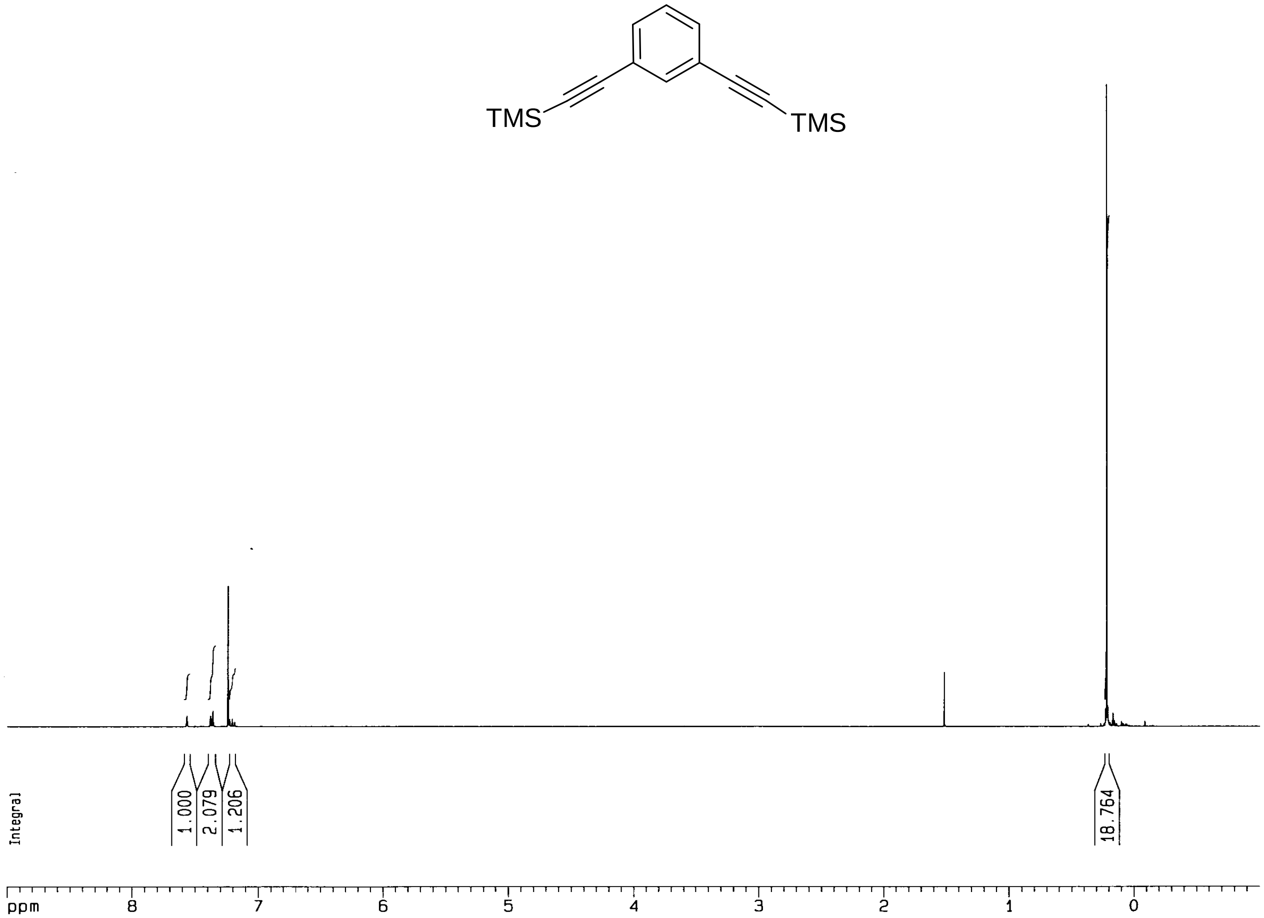
Sample: JLJ-III-183
Size: 7.2000 mg
Method: Ramp

DSC

File: C:\TA\Data\DSC\JursDSC\jj092002.001
Operator: JLJ
Run Date: 20-Sep-02 11:18
Instrument: DSC Q10 V6.16 Build 224

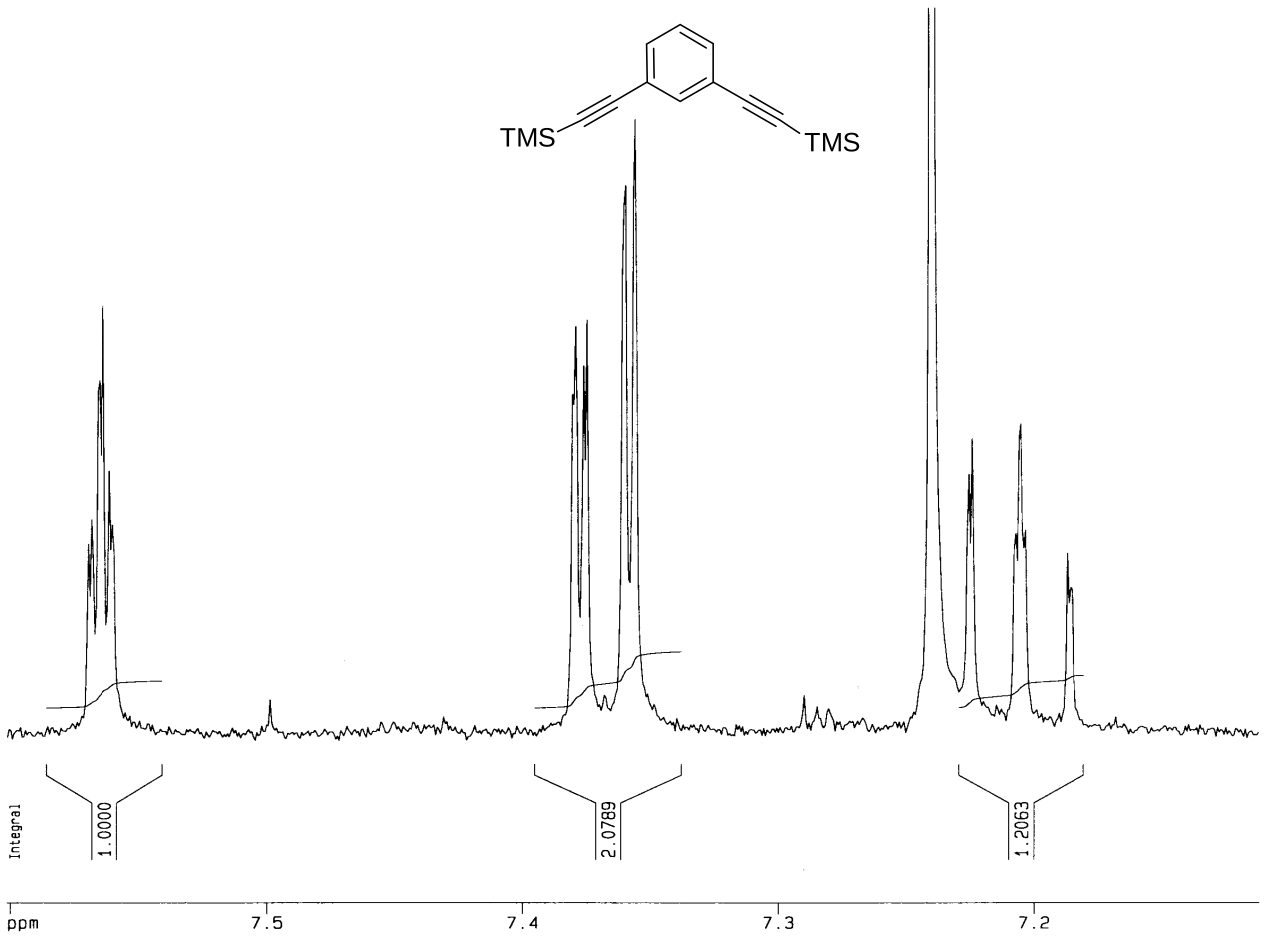


JLJ-I-215
Frac.1



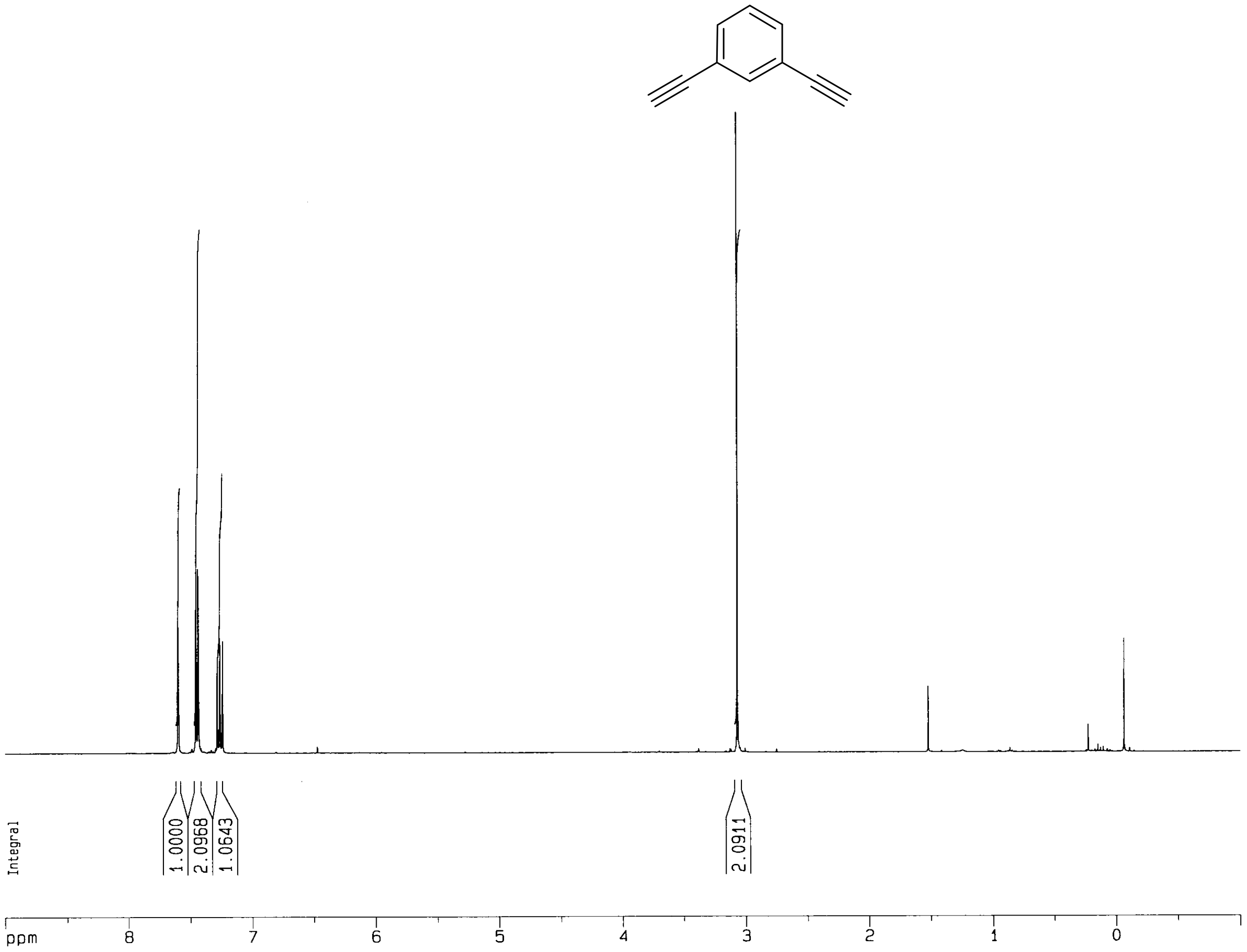
```
Current Data Parameters
NAME            JLJ-I-215
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20000622
Time                 9.46
INSTRUM             spect
PROBHD     5 mm BBO BB-1
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  574.7
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 ========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300174 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 9.000 ppm
F1                3601.17 Hz
F2P                -1.000 ppm
F2                -400.13 Hz
PPMCM             0.50000 ppm/cm
HZCM            200.06499 Hz/cm
```

JLJ-I-215
Frac.1



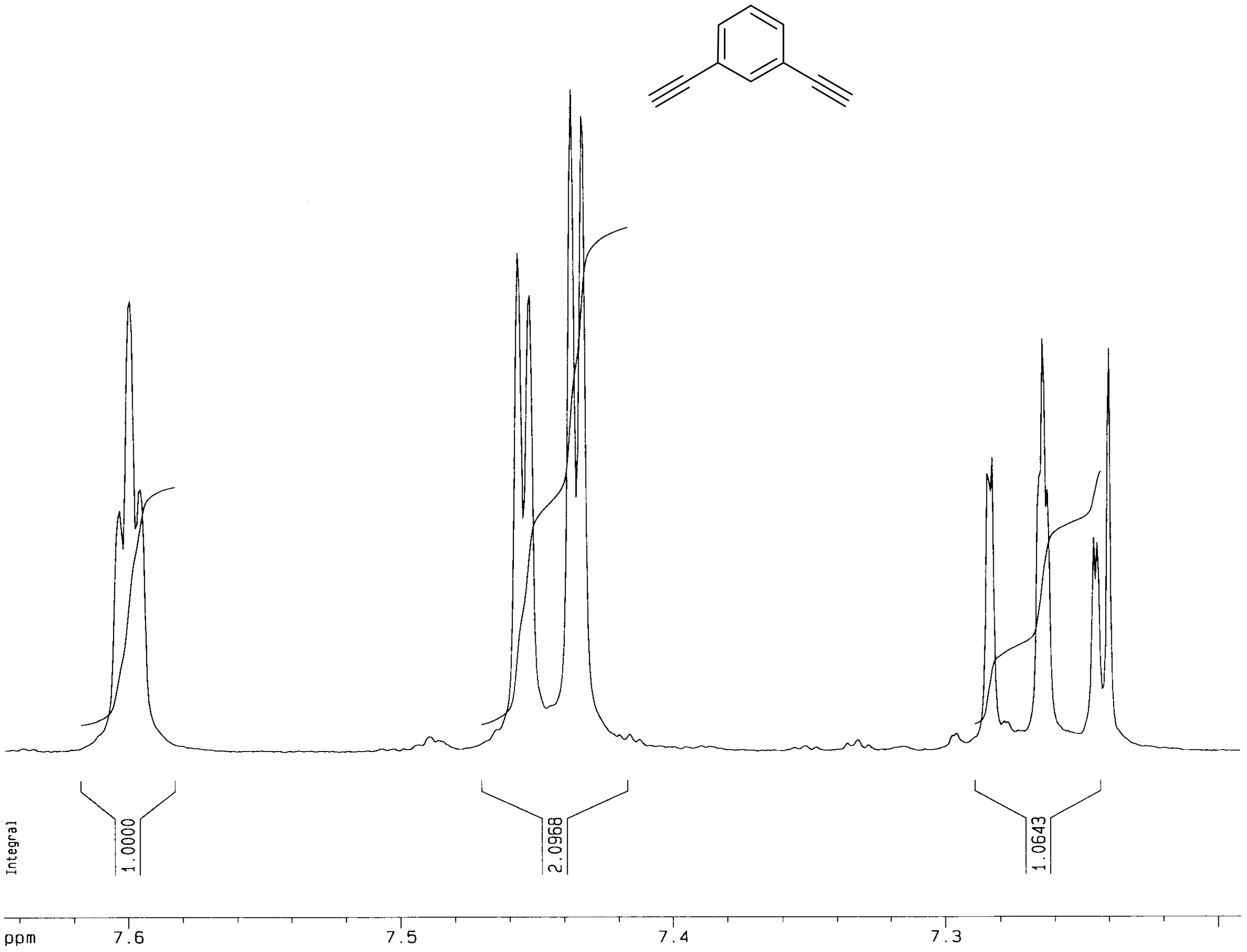
```
Current Data Parameters
NAME          JLJ-I-215
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20000622
Time               9.46
INSTRUM           spect
PROBHD   5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                574.7
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300174 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               7.601 ppm
F1              3041.51 Hz
F2P               7.112 ppm
F2              2845.72 Hz
PPMCM           0.02447 ppm/cm
HZCM            9.78939 Hz/cm
```

JLJ-I-239
col.1; frac.2

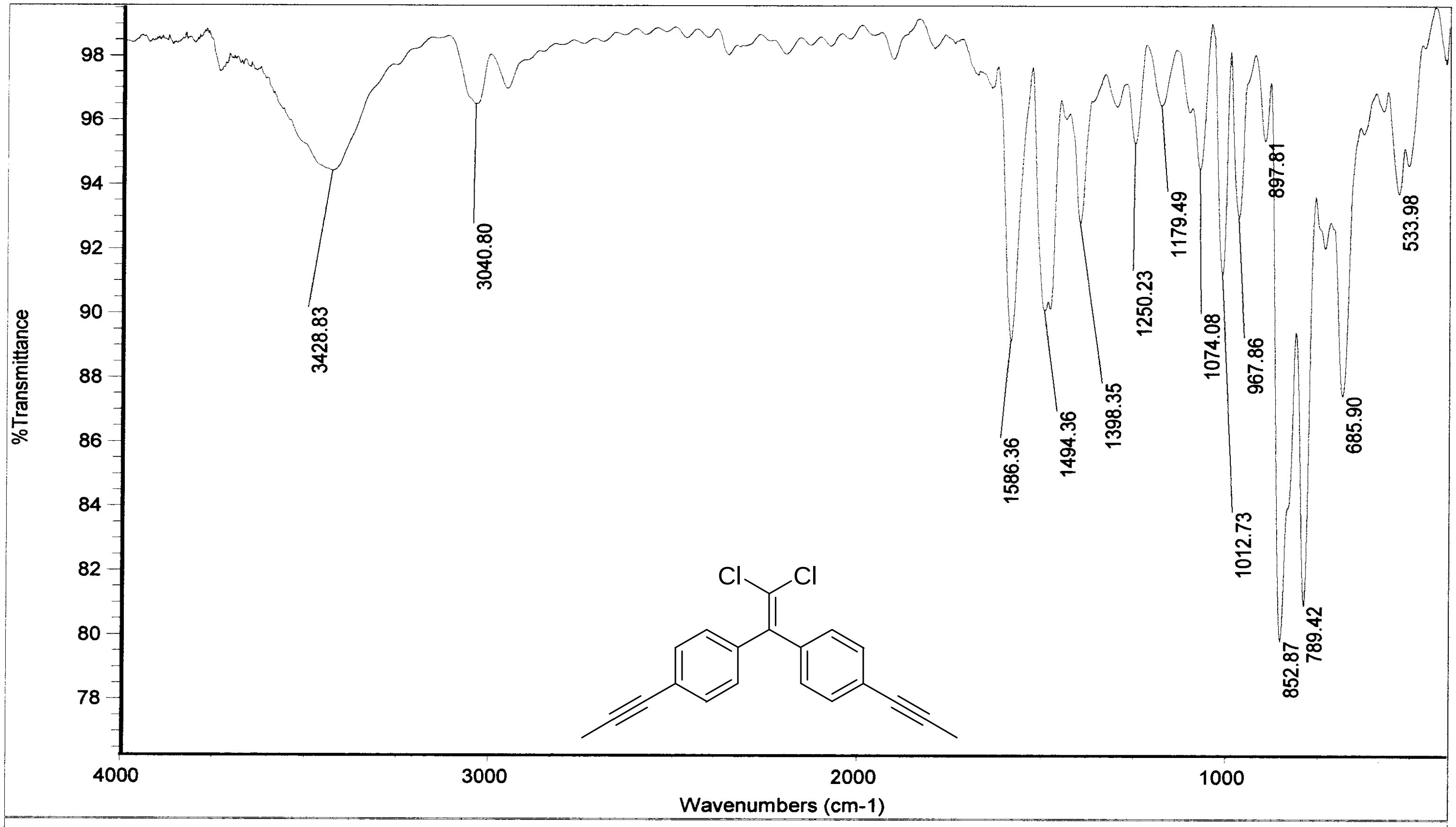


```
Current Data Parameters
NAME            JLJ-I-239
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20000724
Time                13.27
INSTRUM             spect
PROBHD   5 mm BBO BB-1
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                    362
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 =========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300174 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 9.000 ppm
F1                3601.17 Hz
F2P                -1.000 ppm
F2                -400.13 Hz
PPMCM             0.50000 ppm/cm
HZCM            200.06500 Hz/cm
```

JLJ-I-239
col.1; frac.2



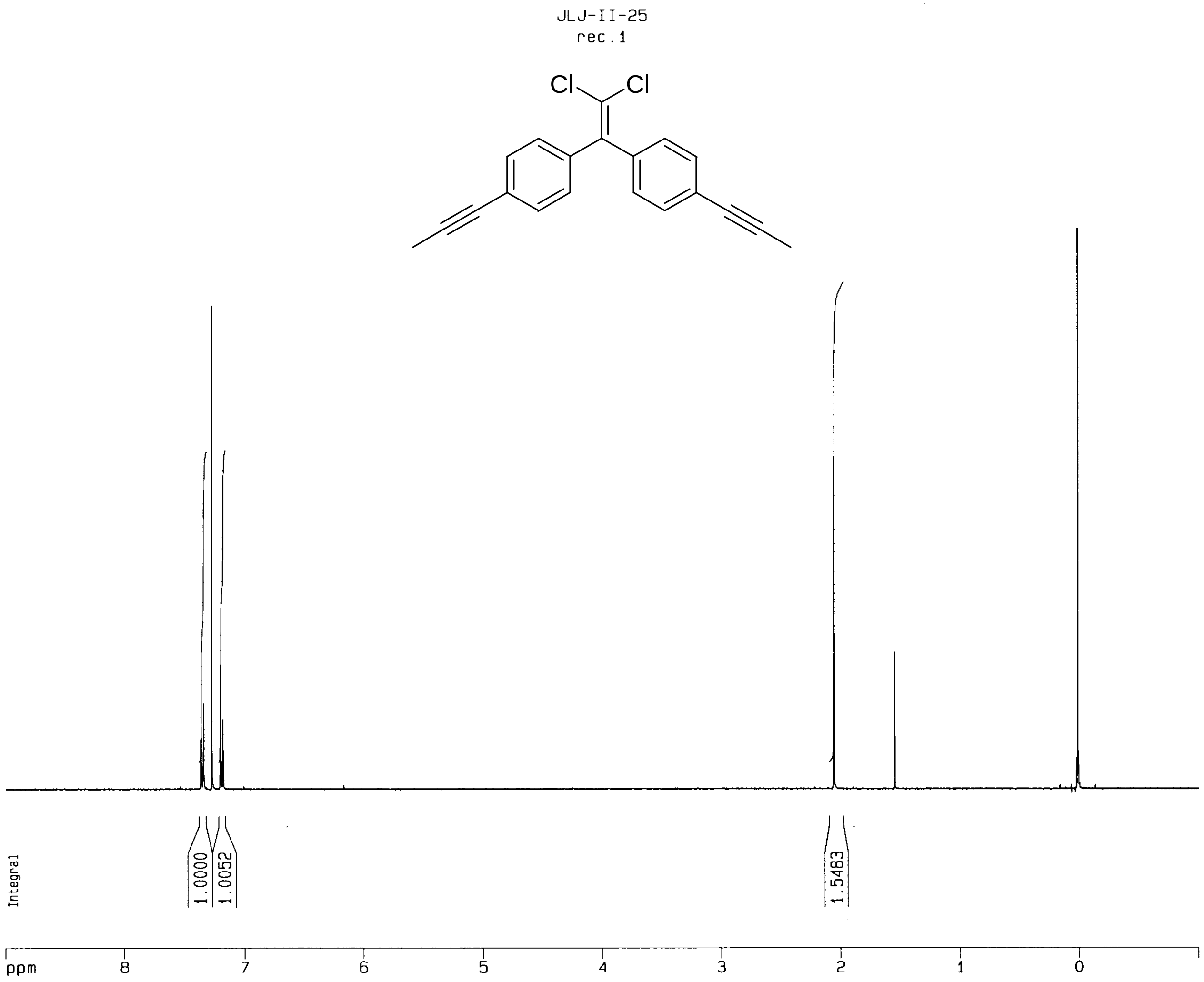
```
Current Data Parameters
NAME           JLJ-I-239
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20000724
Time               13.27
INSTRUM            spect
PROBHD     5 mm BBO BB-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                   362
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300174 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.646 ppm
F1               3059.31 Hz
F2P                7.192 ppm
F2               2877.57 Hz
PPMCM            0.02271 ppm/cm
HZCM             9.08668 Hz/cm
```



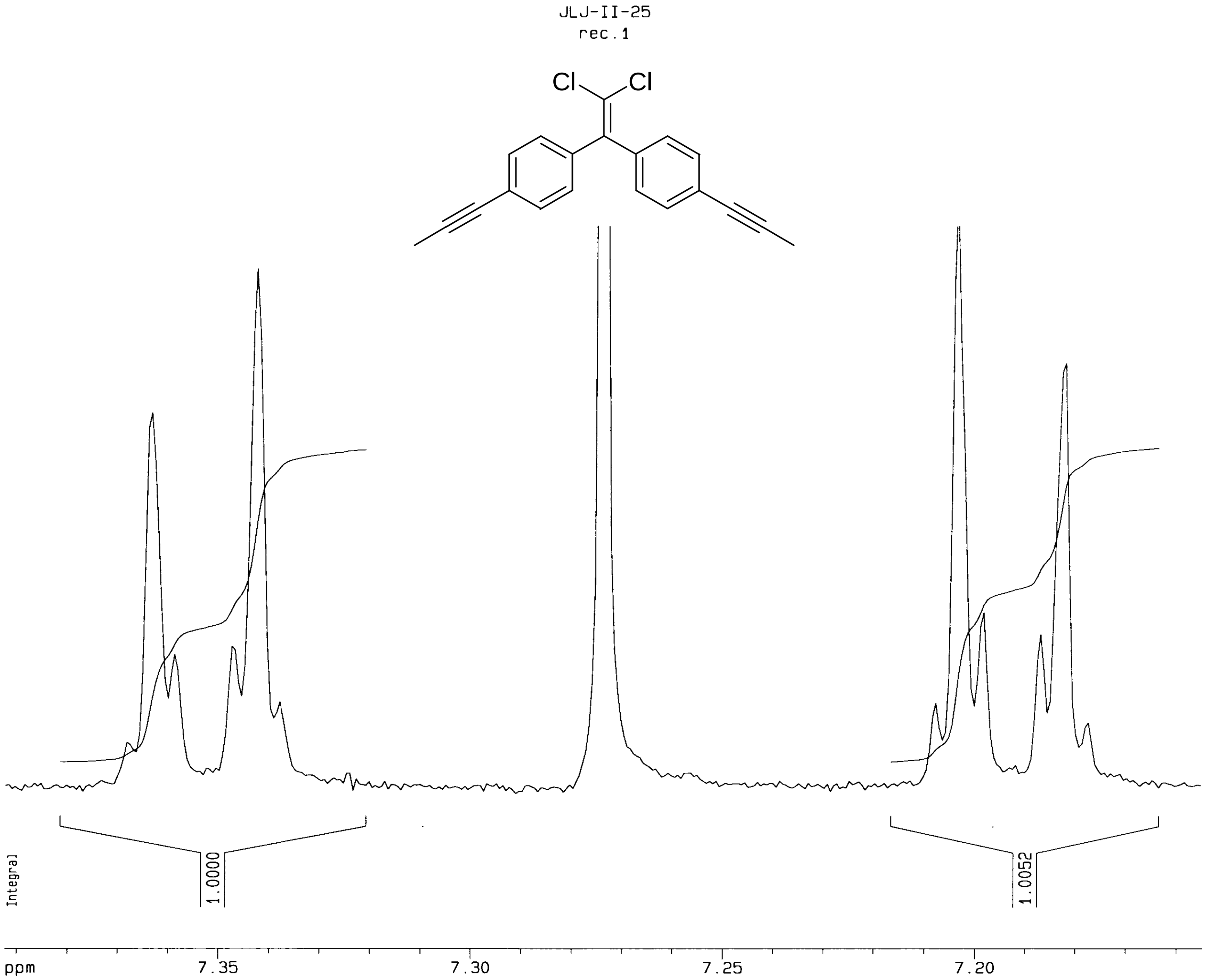
Date: Mon Jul 14 16:48:06 2003 **JLJ-I-255

Scans: 18

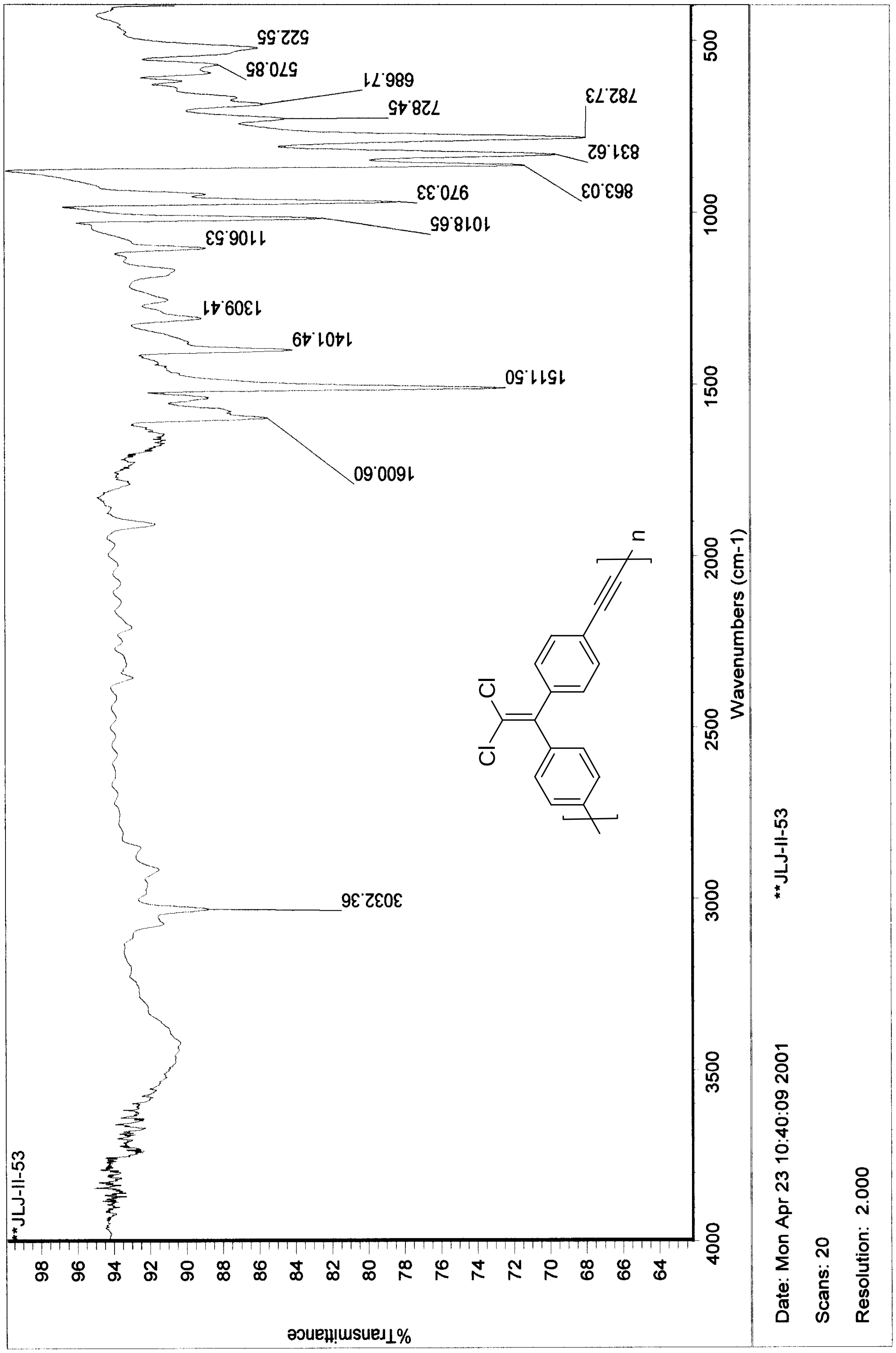
Resolution: 4.000



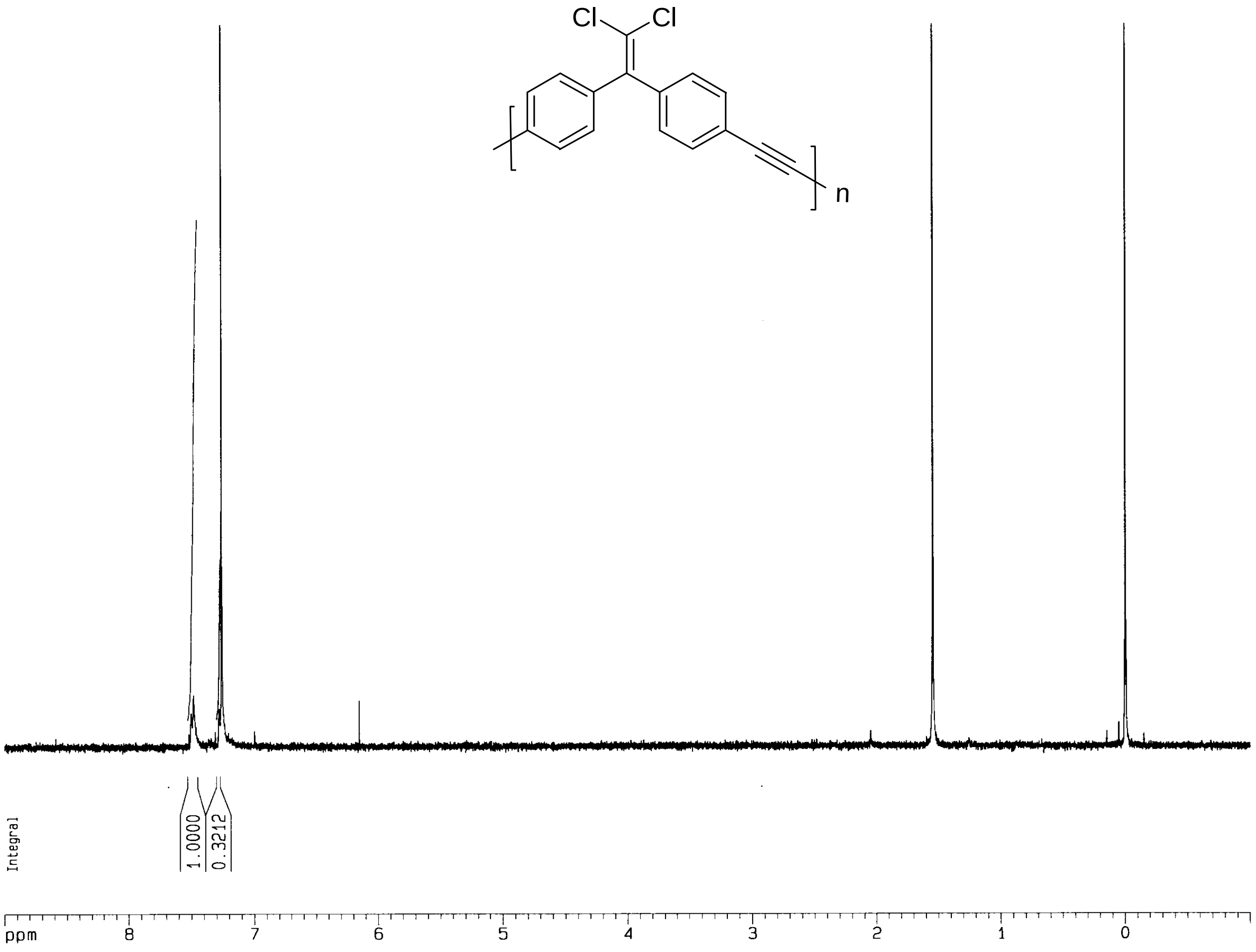
```
Current Data Parameters
NAME          JLJ-II-25
EXPNO                 6
PROCNO                1

F2 - Acquisition Parameters
Date_          20010124
Time              11.23
INSTRUM           spect
PROBHD    5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                812.7
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300040 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -1.000 ppm
F2              -400.13 Hz
PPMCM           0.50000 ppm/cm
HZCM          200.06500 Hz/cm
```



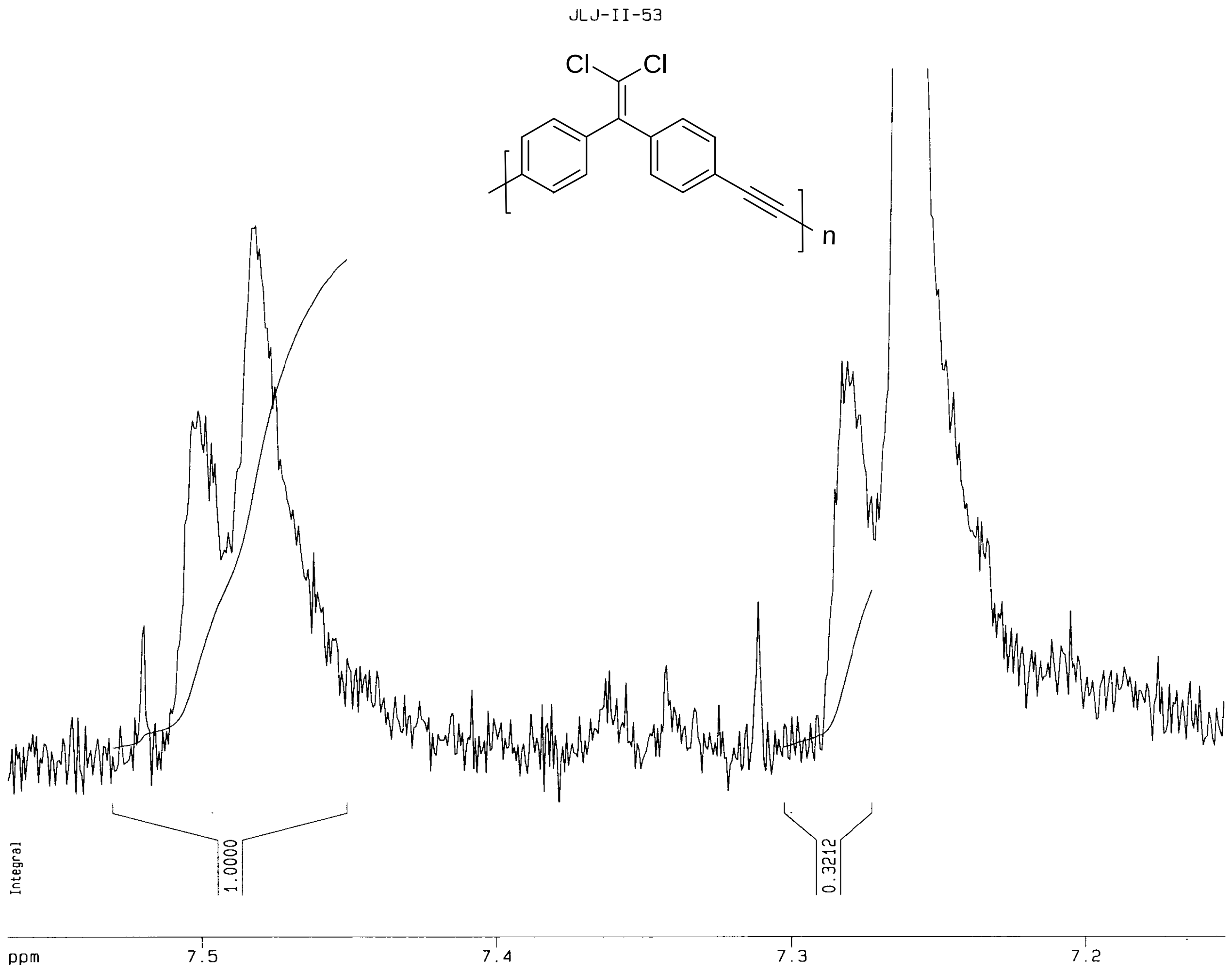
```
Current Data Parameters
NAME           JLJ-II-25
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20010124
Time               11.23
INSTRUM            spect
PROBHD    5 mm BBO BB-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 812.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300040 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.392 ppm
F1               2957.86 Hz
F2P                7.155 ppm
F2               2862.87 Hz
PPMCM            0.01187 ppm/cm
HZCM             4.74947 Hz/cm
```


**JLJ-II-53
%Transmittance
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
3032.36
1600.60
1511.50
1401.49
1309.41
1106.53
1018.65
970.33
863.03
831.62
782.73
728.45
686.71
570.85
522.55
Cl
Cl
n
Date: Mon Apr 23 10:40:09 2001
Scans: 20
Resolution: 2.000
**JLJ-II-53

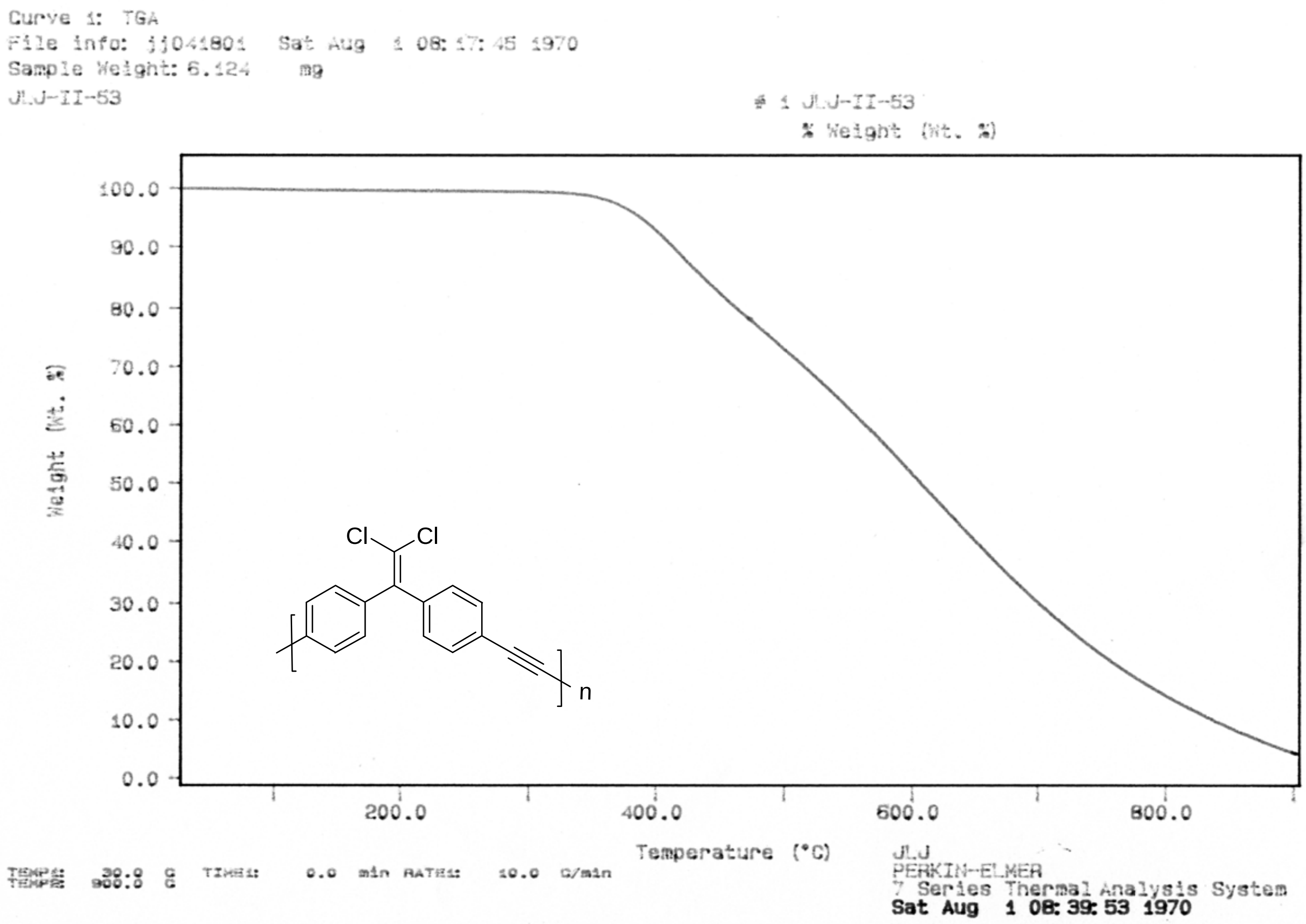
JLJ-II-53



```
Current Data Parameters
NAME              JLJ-II-53
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20010220
Time                  13.56
INSTRUM               spect
PROBHD    5 mm BBO BB-1
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                3.9584243 sec
RG                    812.7
DW                   60.400 usec
DE                     6.00 usec
TE                    300.0 K
D1               3.00000000 sec

============ CHANNEL f1 ========
NUC1                     1H
P1                    12.50 usec
PL1                    0.00 dB
SF01            400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF              400.1300093 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                    20.00 cm
F1P                   9.000 ppm
F1                  3601.17 Hz
F2P  .               -1.000 ppm
F2                  -400.13 Hz
PPMCM               0.50000 ppm/cm
HZCM              200.06500 Hz/cm
```



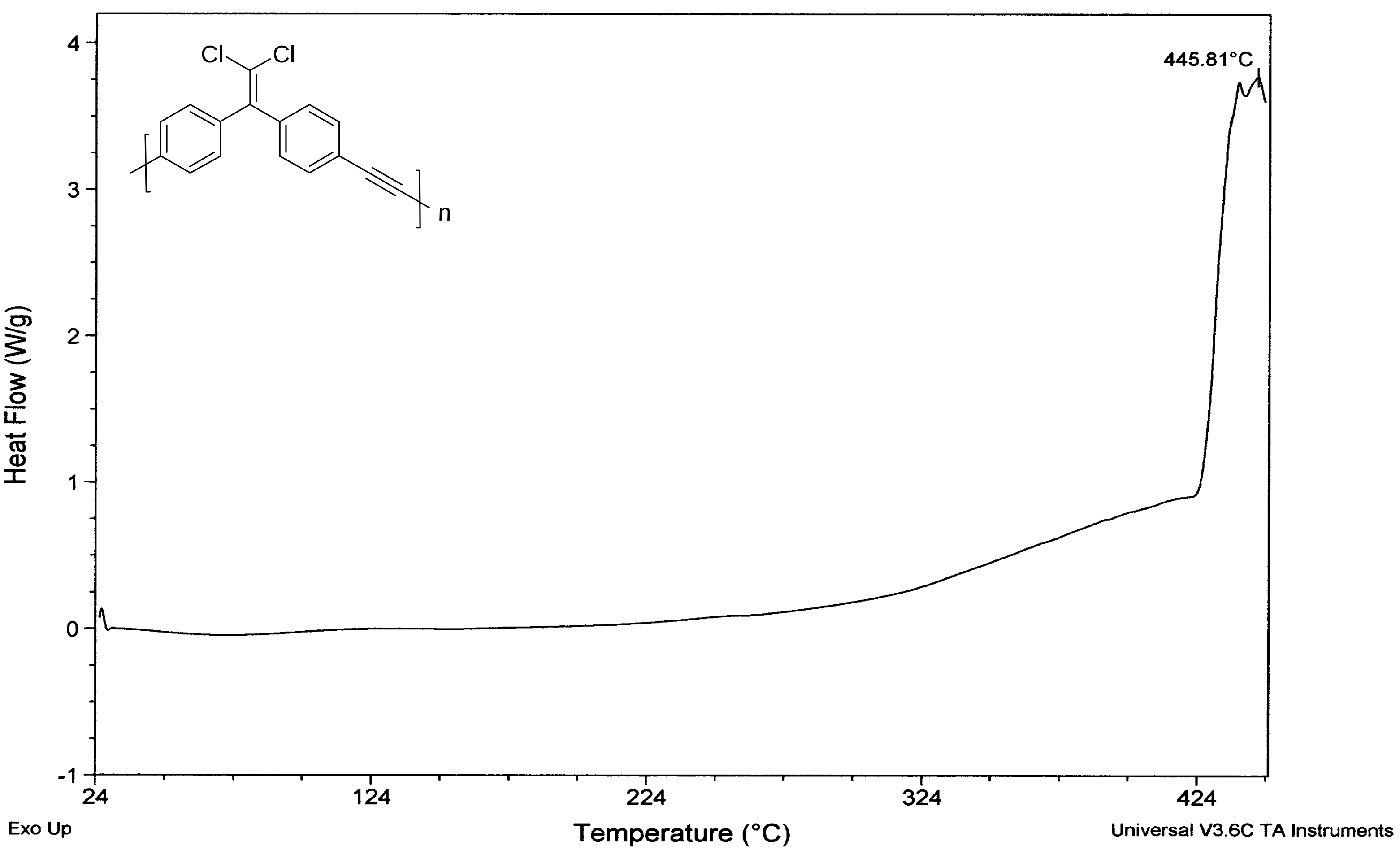
```
Current Data Parameters
NAME            JLJ-II-53
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20010220
Time                13.56
INSTRUM             spect
PROBHD    5 mm BBO BB-1
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  812.7
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 ========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300093 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 7.566 ppm
F1                3027.29 Hz
F2P                 7.153 ppm
F2                2862.11 Hz
PPMCM             0.02064 ppm/cm
HZCM              8.25866 Hz/cm
```

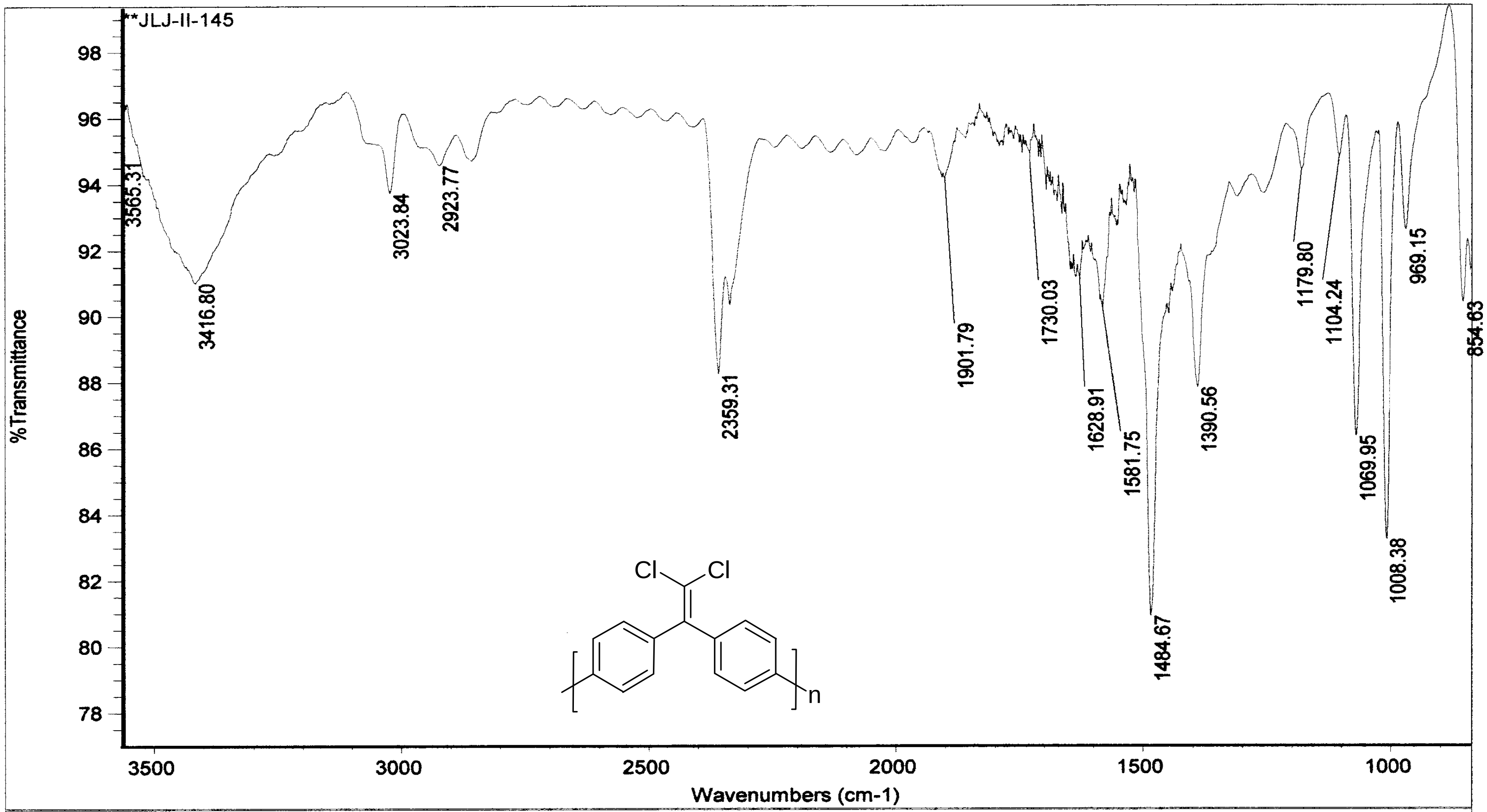

Curve 1: TGA
File info: jj041801 Sat Aug 1 08:17:45 1970
Sample Weight: 6.124 mg
JLJ-II-53
1 JLJ-II-53
% Weight (Wt. %)
Weight (Wt. %)
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
200.0
400.0
600.0
800.0
Temperature (°C)
Cl
Cl
n
TEMP1: 30.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 900.0 C
JLJ
PERKIN-ELMER
7 Series Thermal Analysis System
Sat Aug 1 08:39:53 1970

Sample: JLJ-II-53
Size: 6.2000 mg
Method: Ramp

DSC

File: C:\TA\Data\DSC\JursDSC\jj060603.001
Operator: JLJ
Run Date: 06-Jun-03 10:13
Instrument: DSC Q10 V6.21 Build 233

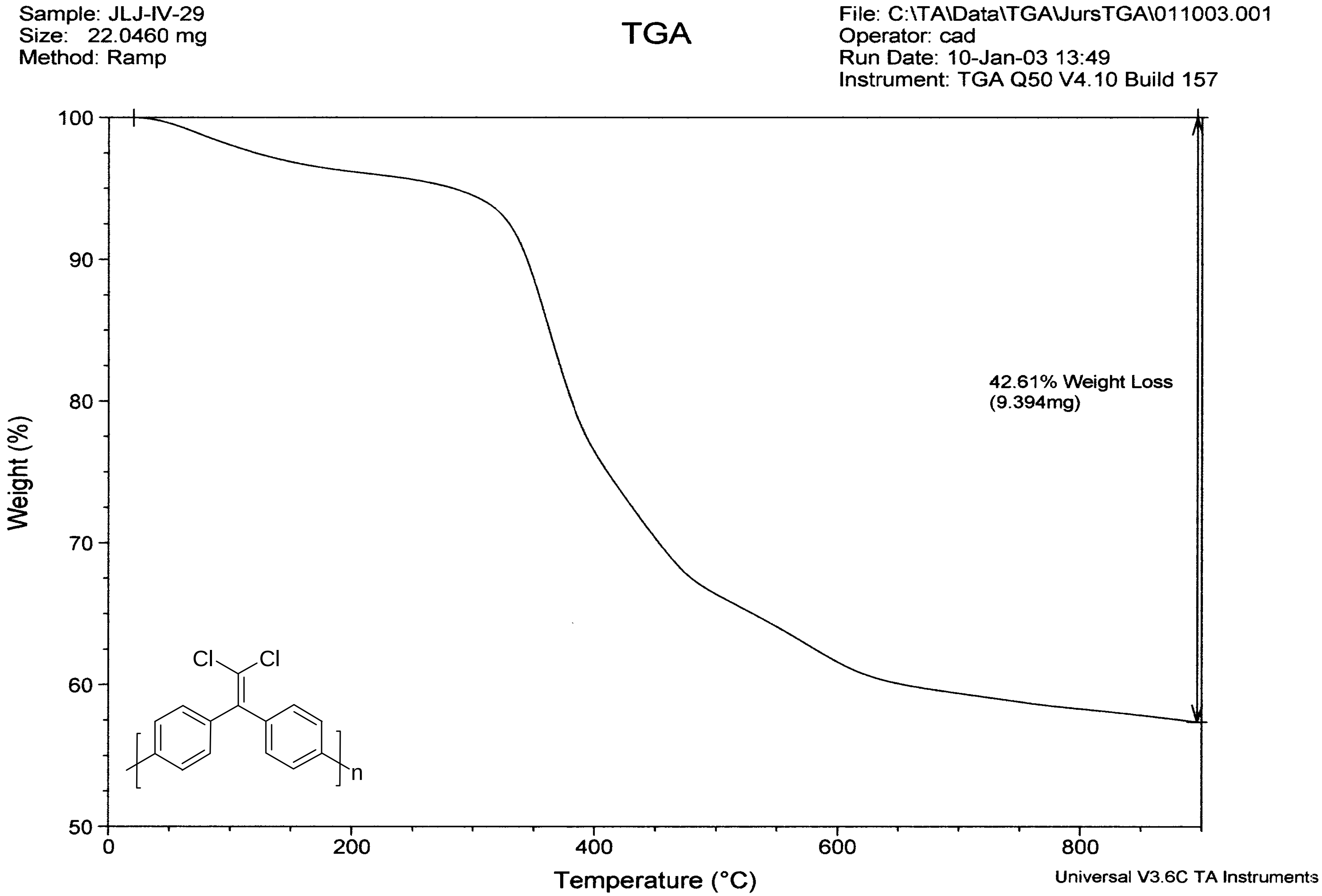


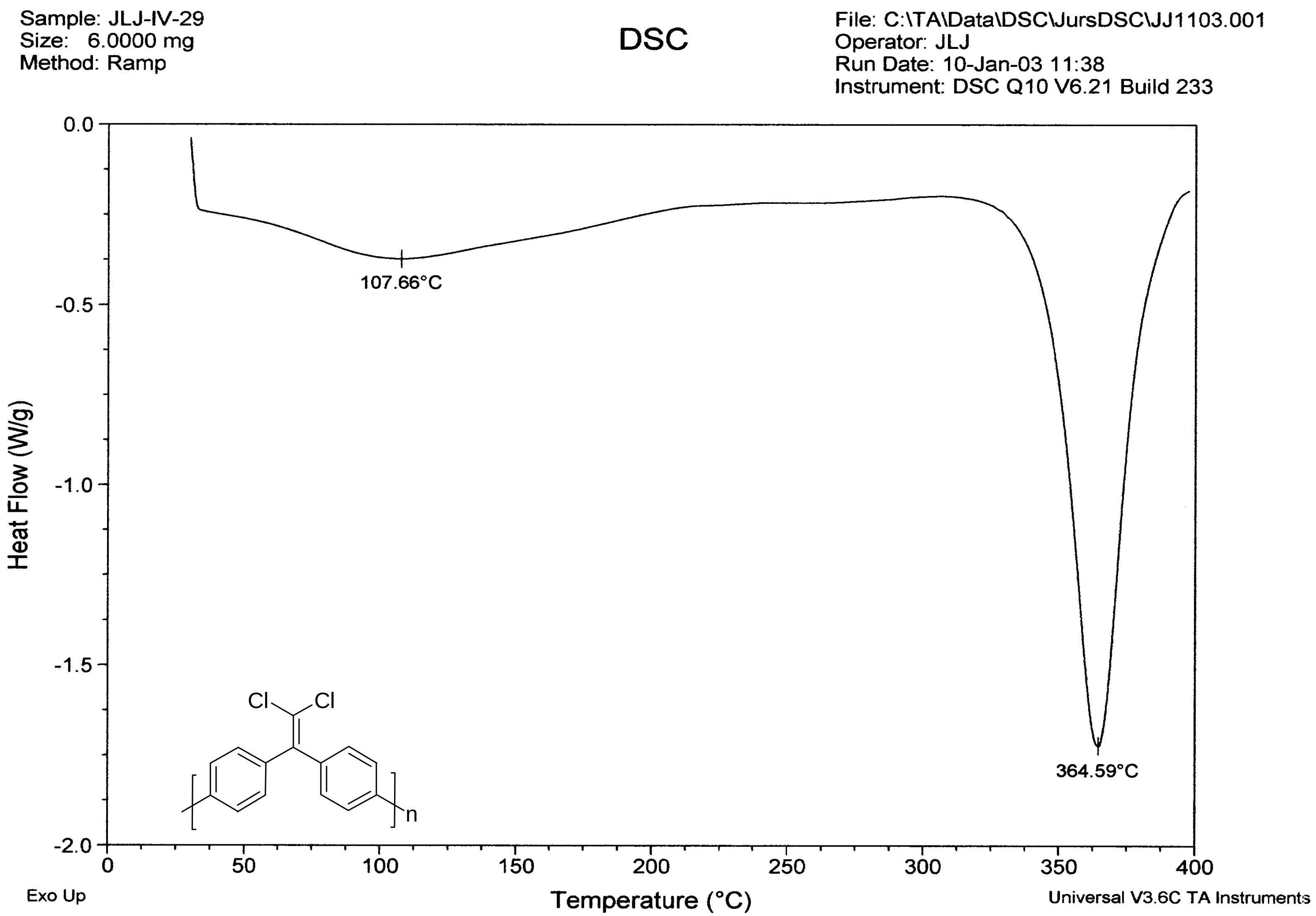


Date: Thu Jul 26 11:34:22 2001 **JLJ-II-145

Scans: 20

Resolution: 2.000

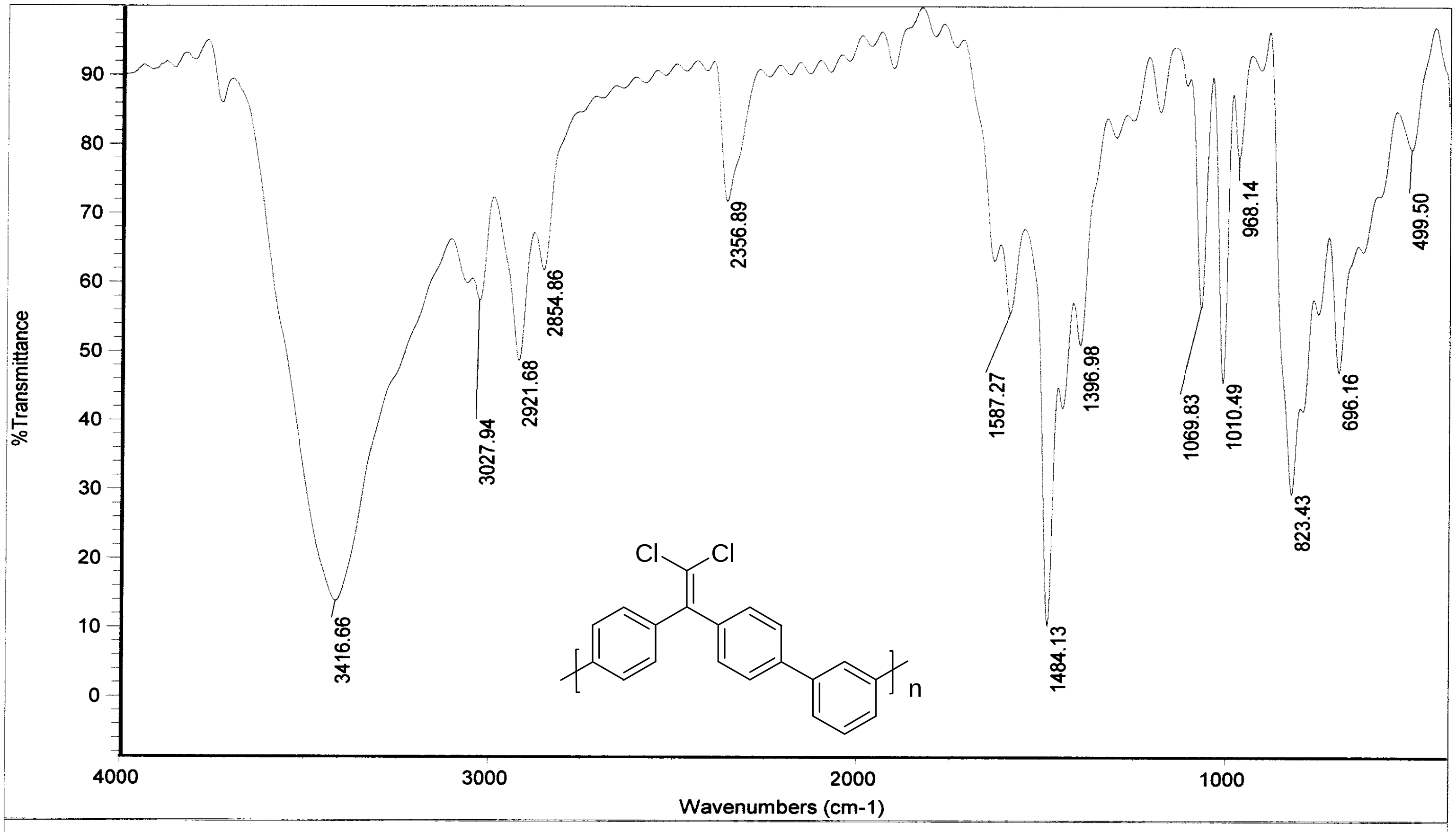

Sample: JLJ-IV-29
Size: 22.0460 mg
Method: Ramp
TGA
File: C:\TA\Data\TGA\JursTGA\011003.001
Operator: cad
Run Date: 10-Jan-03 13:49
Instrument: TGA Q50 V4.10 Build 157
Weight (%)
100
90
80
70
60
50
Temperature (°C)
0
200
400
600
800
42.61% Weight Loss
(9.394mg)
Cl
Cl
n
Universal V3.6C TA Instruments



Sample: JLJ-IV-29
Size: 6.0000 mg
Method: Ramp

DSC

File: C:\TA\Data\DSC\JursDSC\JJ1103.001
Operator: JLJ
Run Date: 10-Jan-03 11:38
Instrument: DSC Q10 V6.21 Build 233

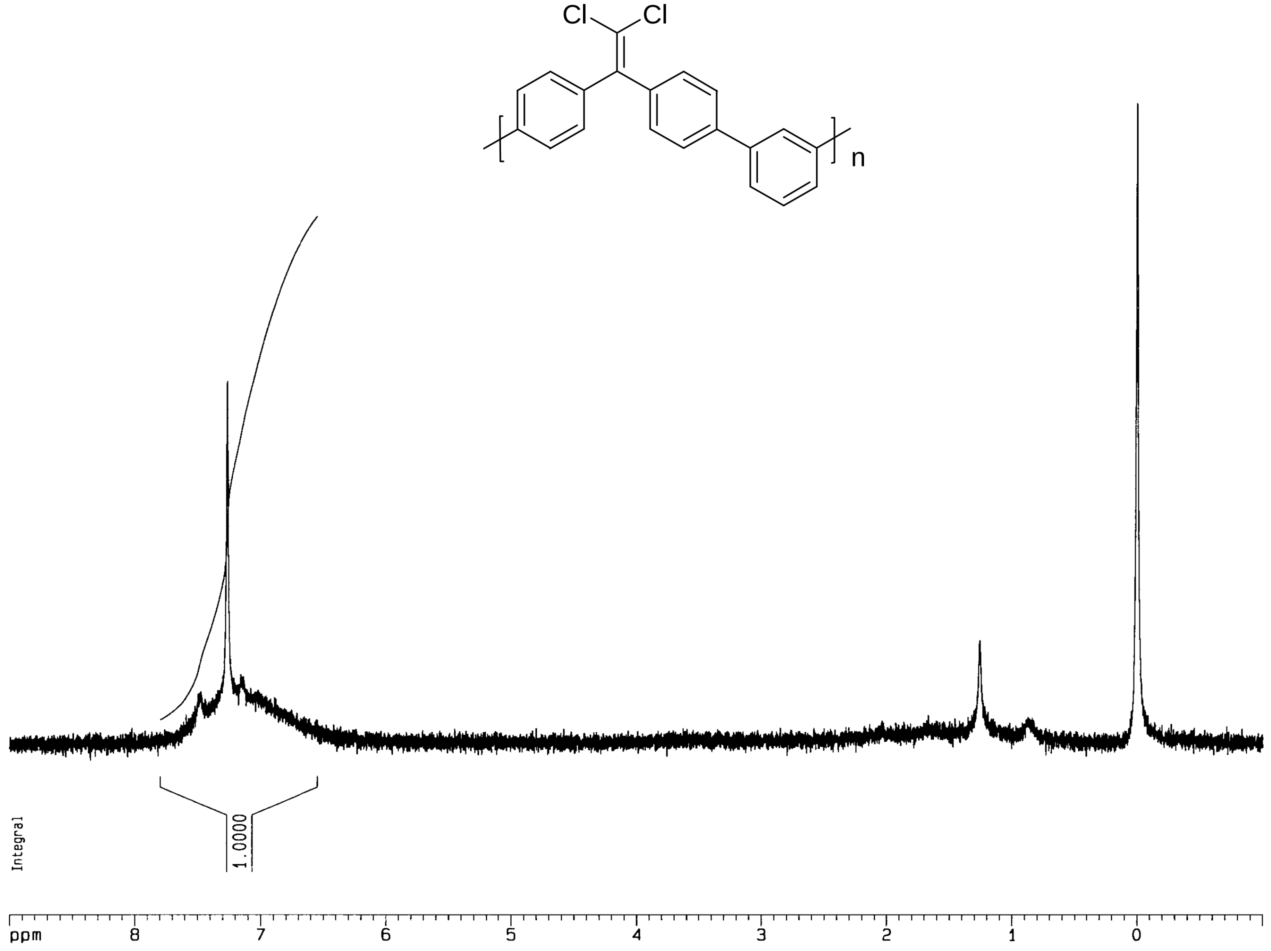


Date: Wed Jul 16 14:49:07 2003 ****JLJ-II-177

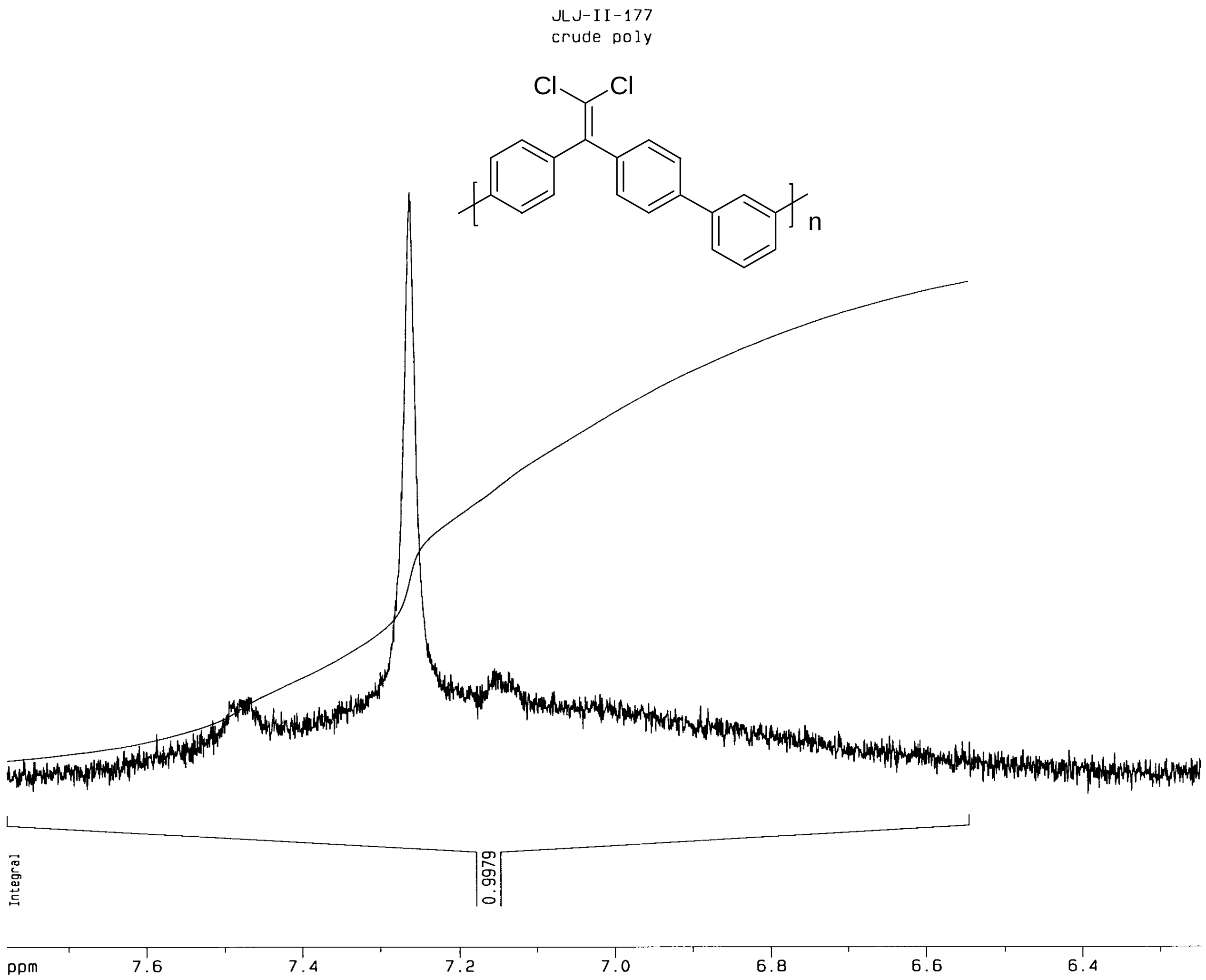
Scans: 18

Resolution: 4.000

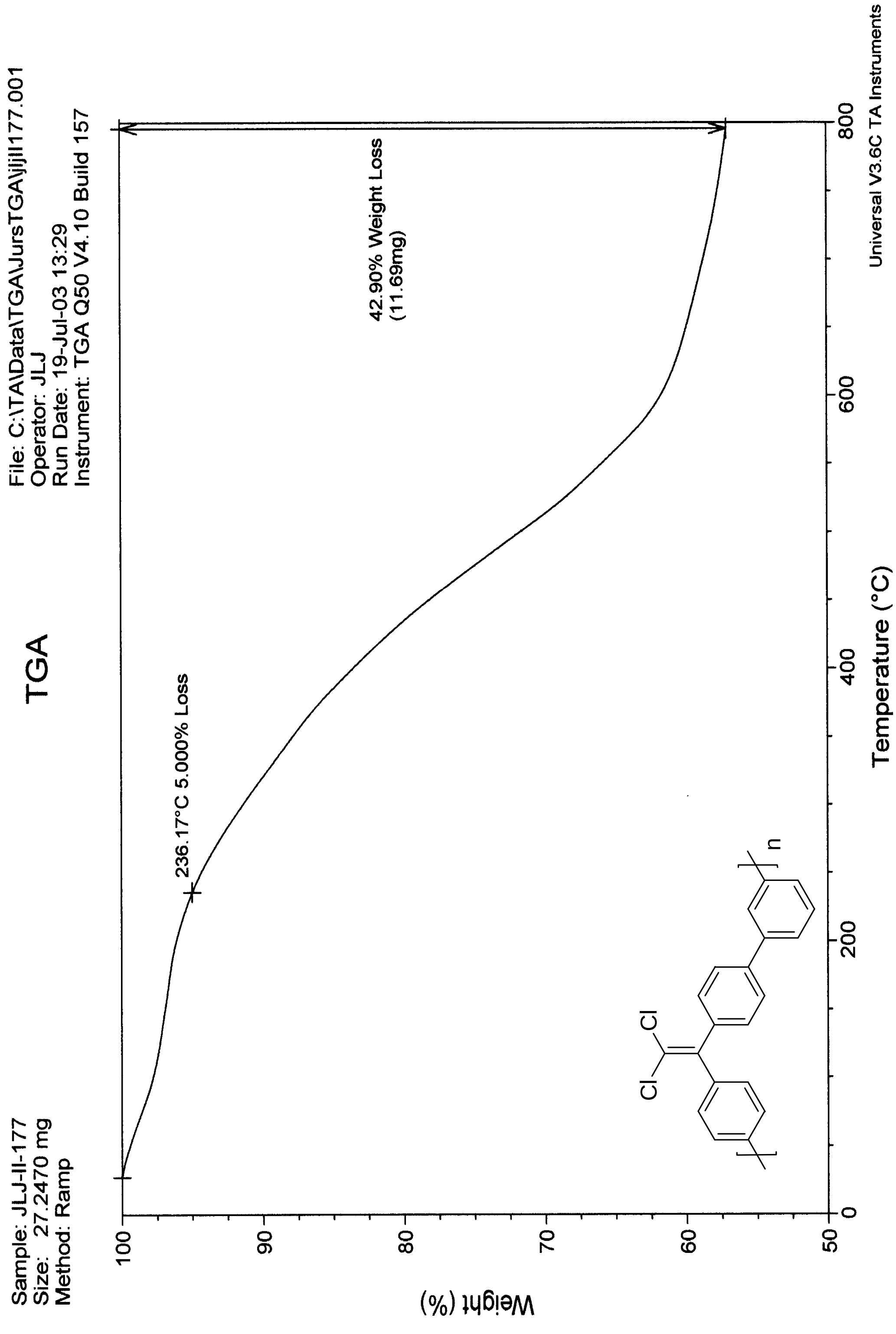
JLJ-II-177
crude poly

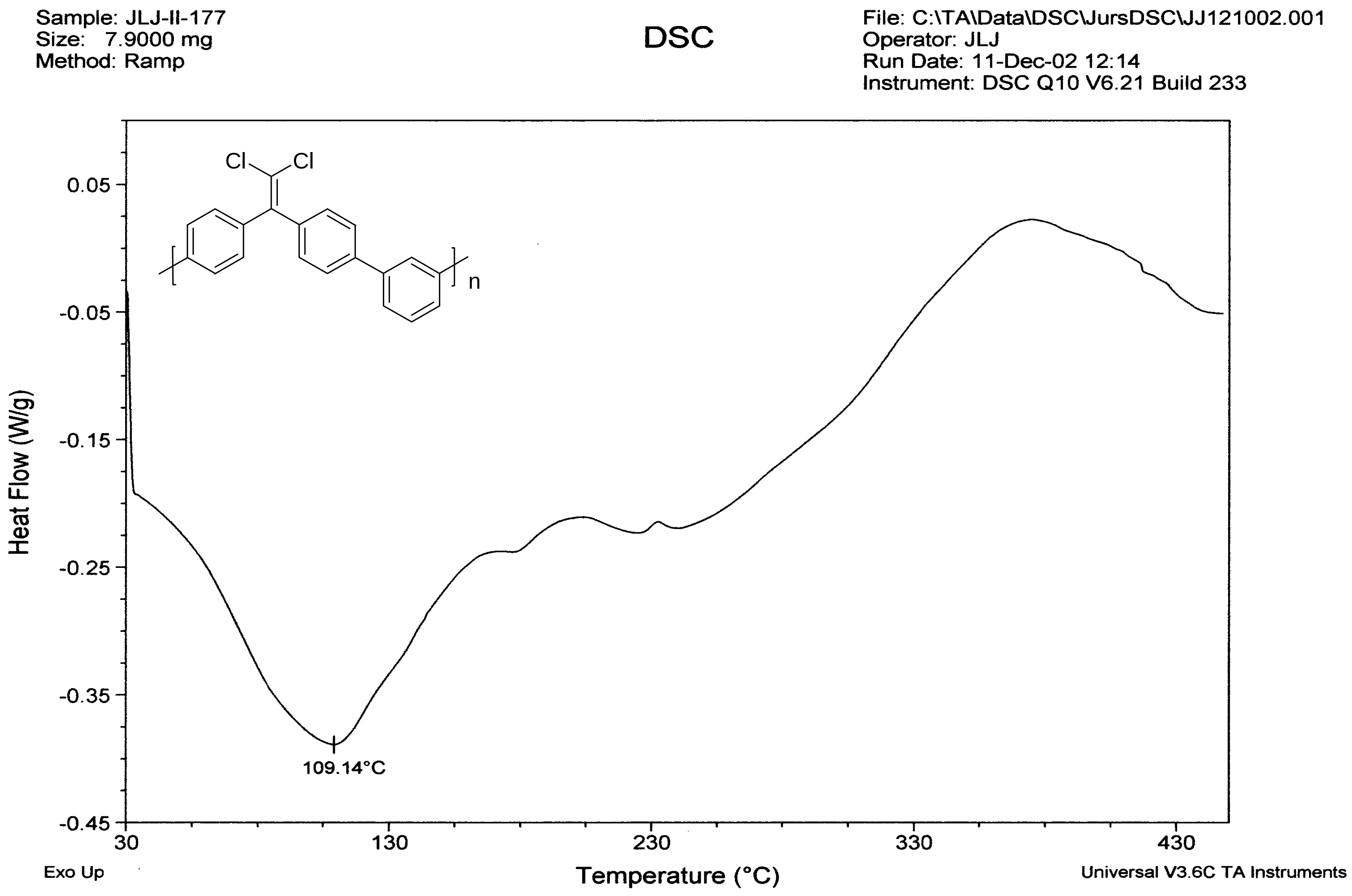


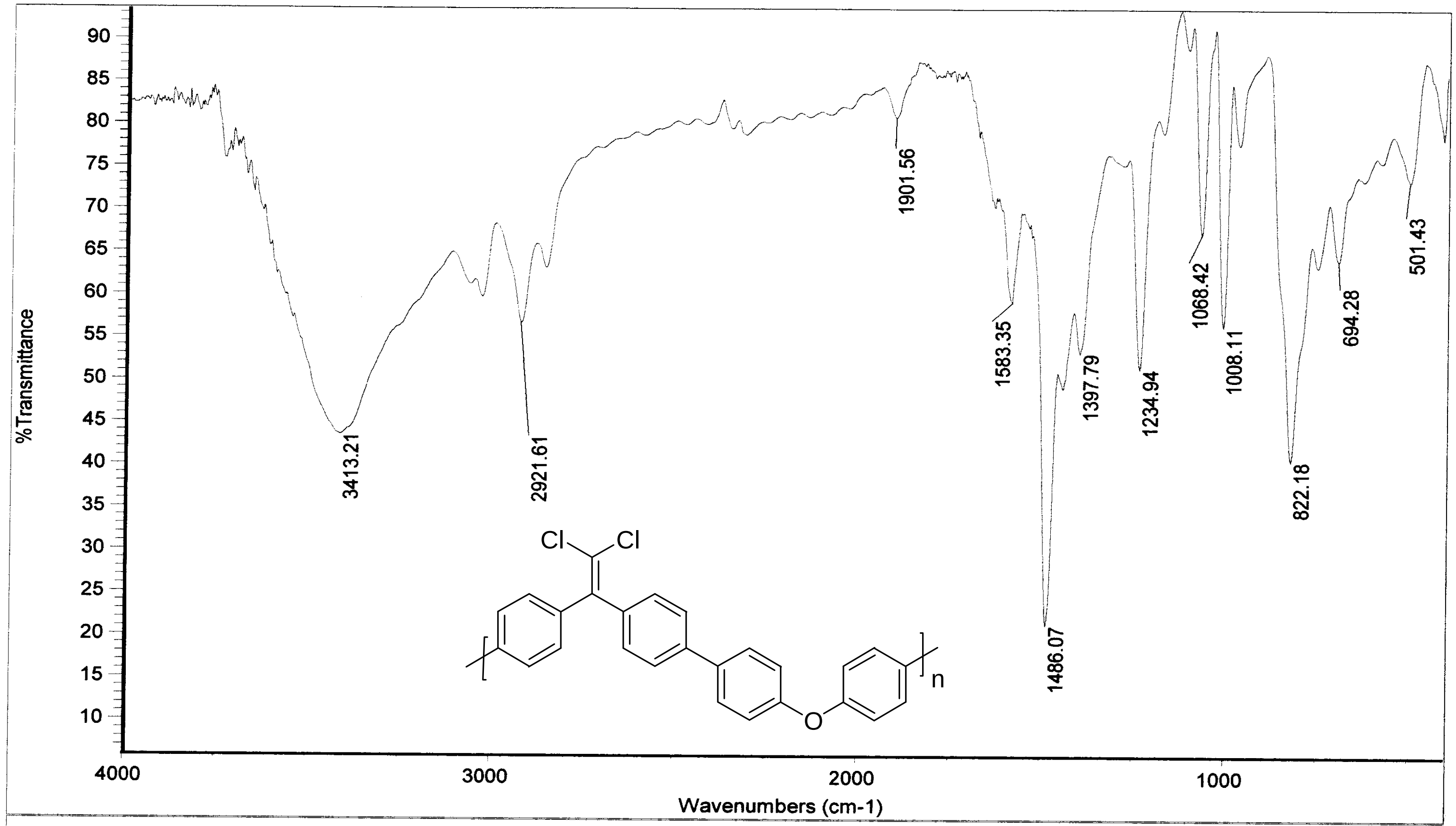
```
Current Data Parameters
NAME          JLJ-II-177
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20010823
Time               11.10
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 574.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300086 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06500 Hz/cm
```



```
Current Data Parameters
NAME          JLJ-II-177
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20010823
Time               11.10
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 574.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300086 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.779 ppm
F1               3112.79 Hz
F2P                6.248 ppm
F2               2500.17 Hz
PPMCM            0.07655 ppm/cm
HZCM            30.63094 Hz/cm
```


Sample: JLJ-II-177
Size: 27.2470 mg
Method: Ramp
TGA
File: C:\TA\Data\TGA\JursTGA\jjII177.001
Operator: JLJ
Run Date: 19-Jul-03 13:29
Instrument: TGA Q50 V4.10 Build 157
236.17°C 5.000% Loss
42.90% Weight Loss
(11.69mg)
Cl
Cl
n
Weight (%)
100
90
80
70
60
50
Temperature (°C)
0
200
400
600
800
Universal V3.6C TA Instruments


Sample: JLJ-II-177
Size: 7.9000 mg
Method: Ramp
DSC
File: C:\TA\Data\DSC\JursDSC\JJ121002.001
Operator: JLJ
Run Date: 11-Dec-02 12:14
Instrument: DSC Q10 V6.21 Build 233
Cl
Cl
n
109.14°C
Heat Flow (W/g)
0.05
-0.05
-0.15
-0.25
-0.35
-0.45
30
130
230
330
430
Temperature (°C)
Exo Up
Universal V3.6C TA Instruments

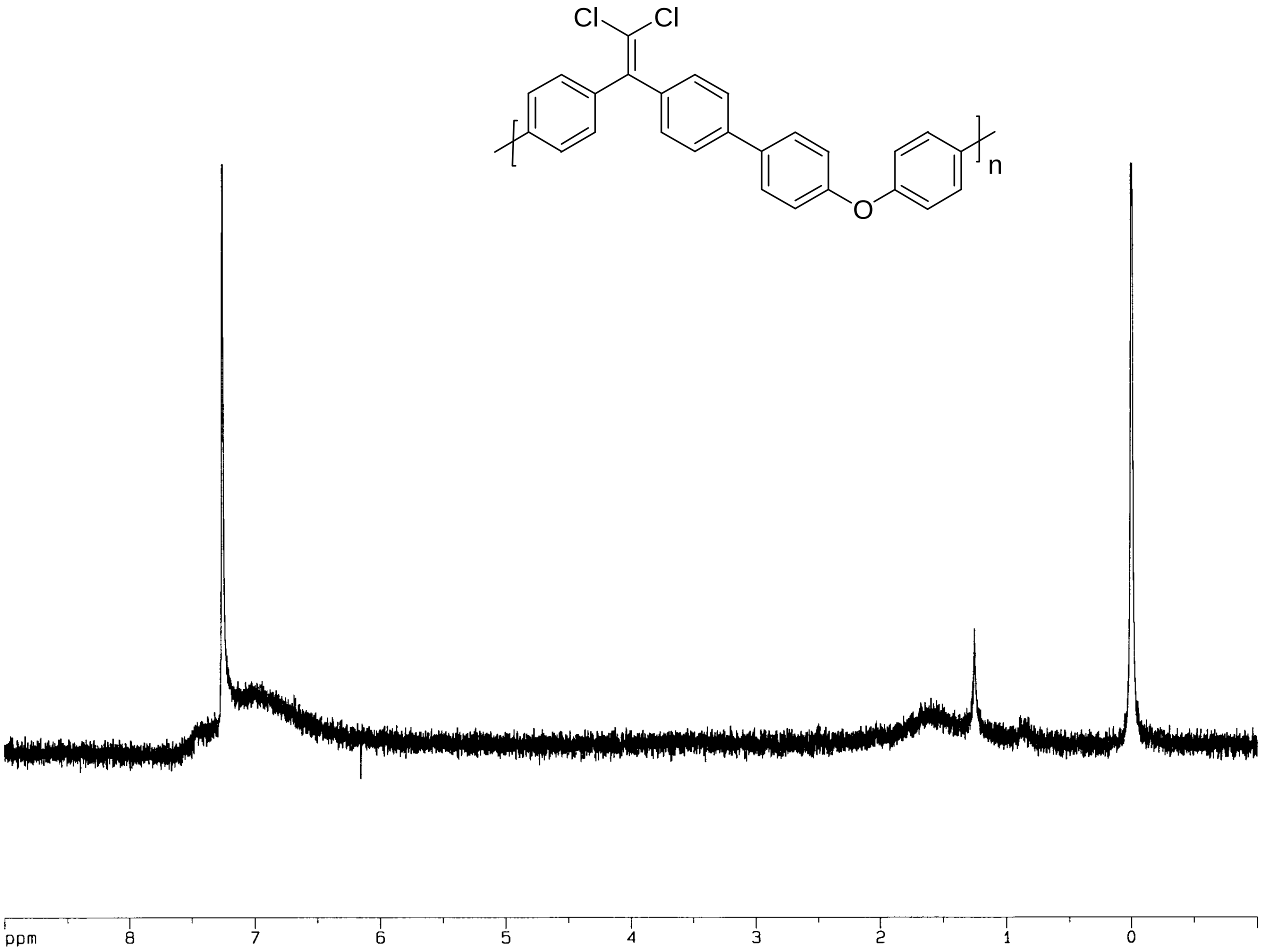


Date: Wed Jul 16 15:57:49 2003 ***JLJ-II-185

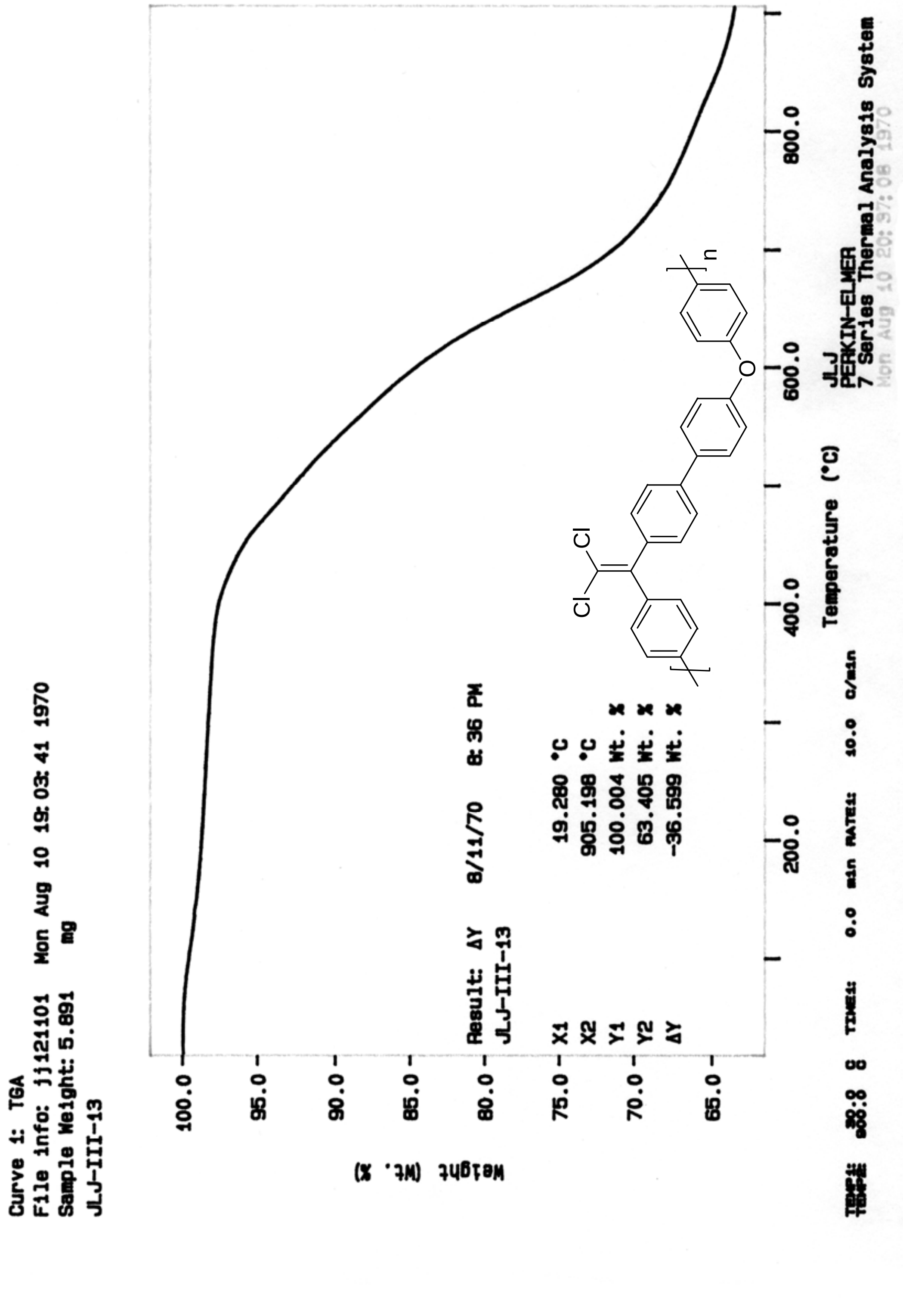
Scans: 18

Resolution: 4.000

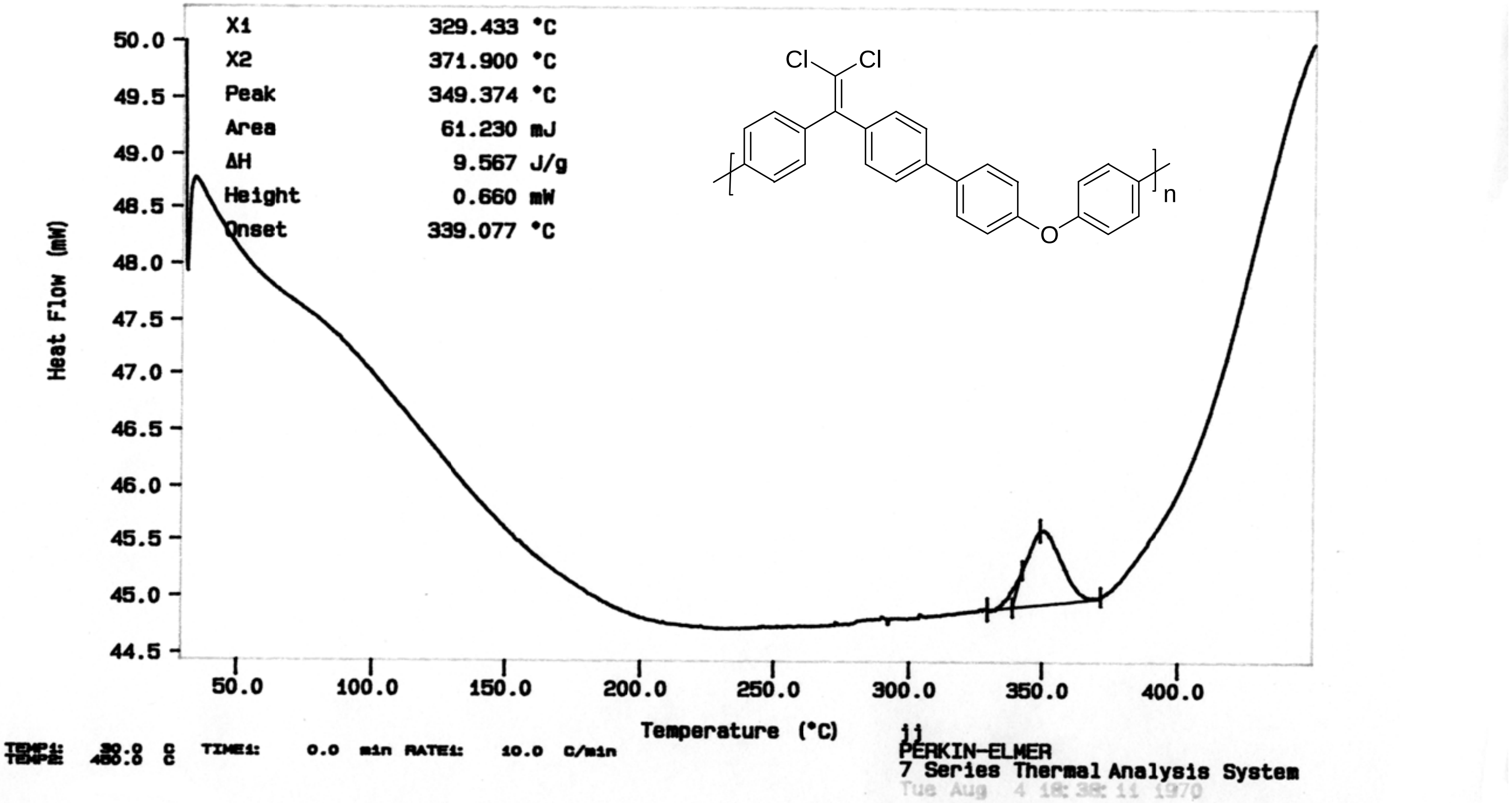
JLJ-II-185



```
Current Data Parameters
NAME          JLJ-II-185
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20010831
Time               16.49
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 812.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300091 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06500 Hz/cm
```


Curve 1: TGA
File info: jj121101 Mon Aug 10 19:03:41 1970
Sample Weight: 5.891 mg
JLJ-III-13
Weight (Wt. %)
100.0
95.0
90.0
85.0
80.0
75.0
70.0
65.0
Result: ΔY 8/11/70 8:36 PM
JLJ-III-13
X1 19.280 °C
X2 905.198 °C
Y1 100.004 Wt. %
Y2 63.405 Wt. %
ΔY -36.599 Wt. %
Cl
Cl
O
n
200.0
400.0
600.0
800.0
Temperature (°C)
TEMP1: 30.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 900.0 C
JLJ
PERKIN-ELMER
7 Series Thermal Analysis System
Mon Aug 10 20:37:08 1970

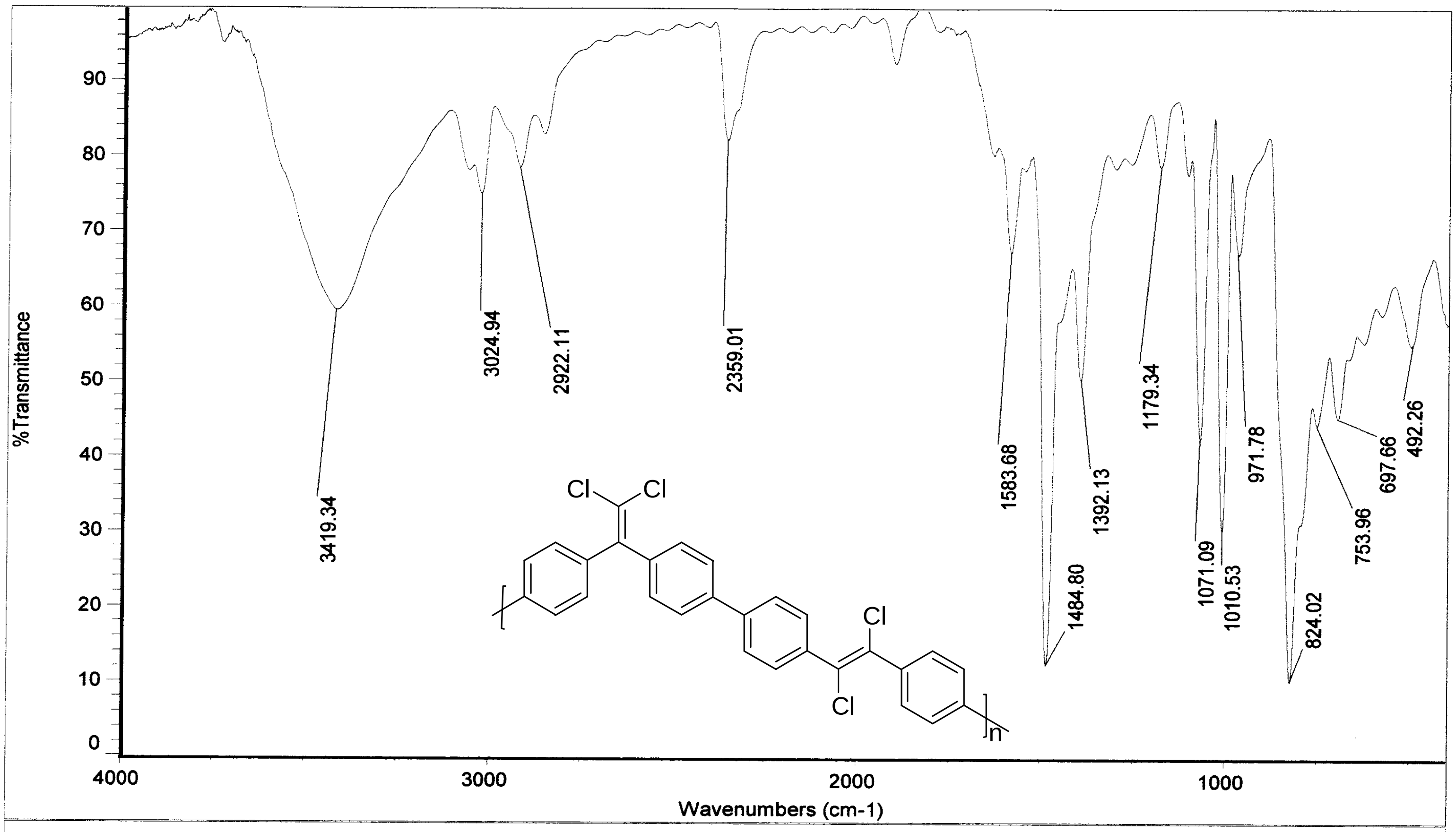
Curve 1: DSC
File info: jj112101   Tue Aug 4 17:05:36 1970
Sample Weight: 6.400   mg
JLJ-III-13



```
X1        329.433 °C
X2        371.900 °C
Peak      349.374 °C
Area       61.230 mJ
ΔH          9.567 J/g
Height      0.660 mW
Onset     339.077 °C
```

TEMP1: 30.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 450.0 C

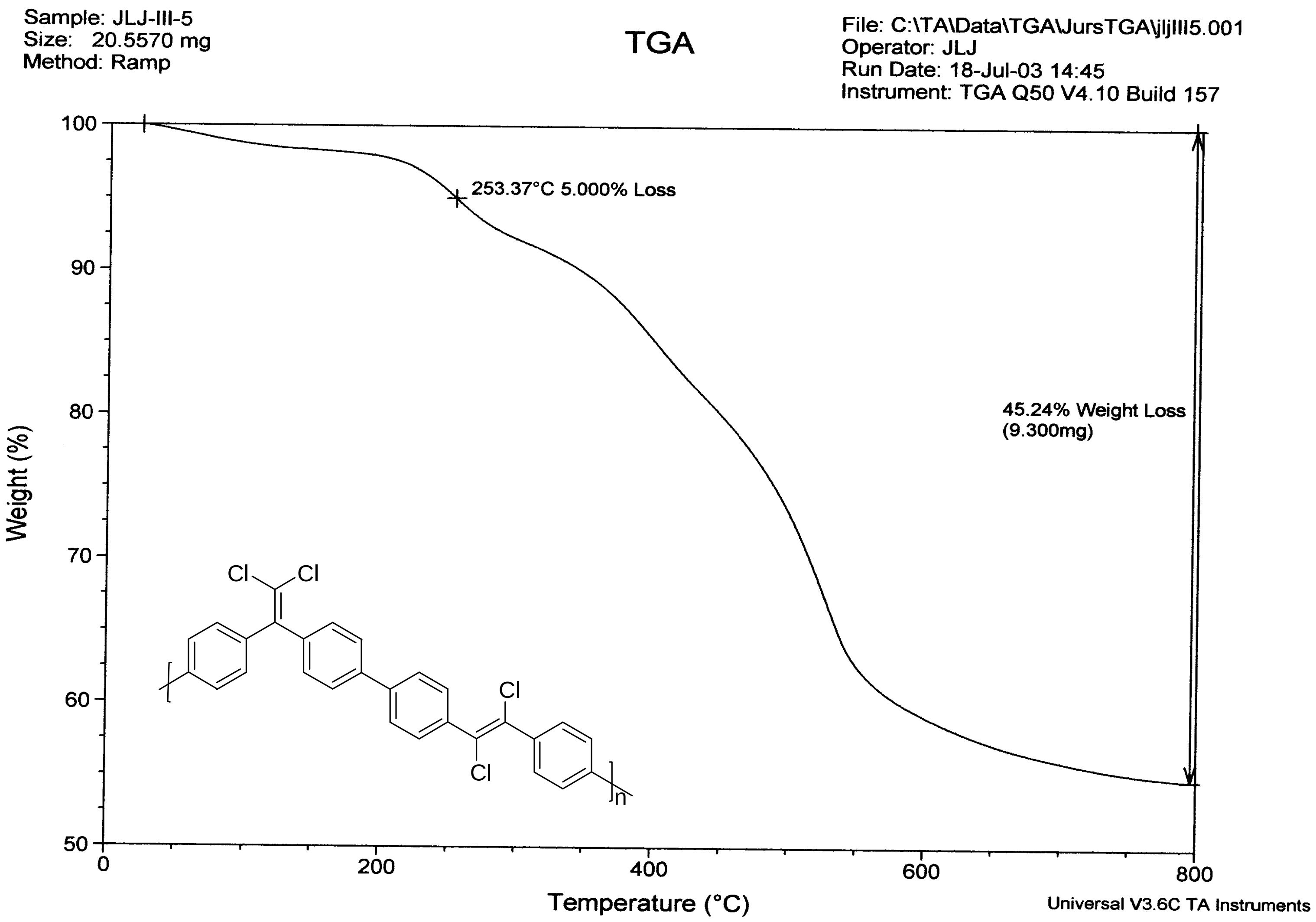
jj
PERKIN-ELMER
7 Series Thermal Analysis System
Tue Aug 4 18:38:11 1970

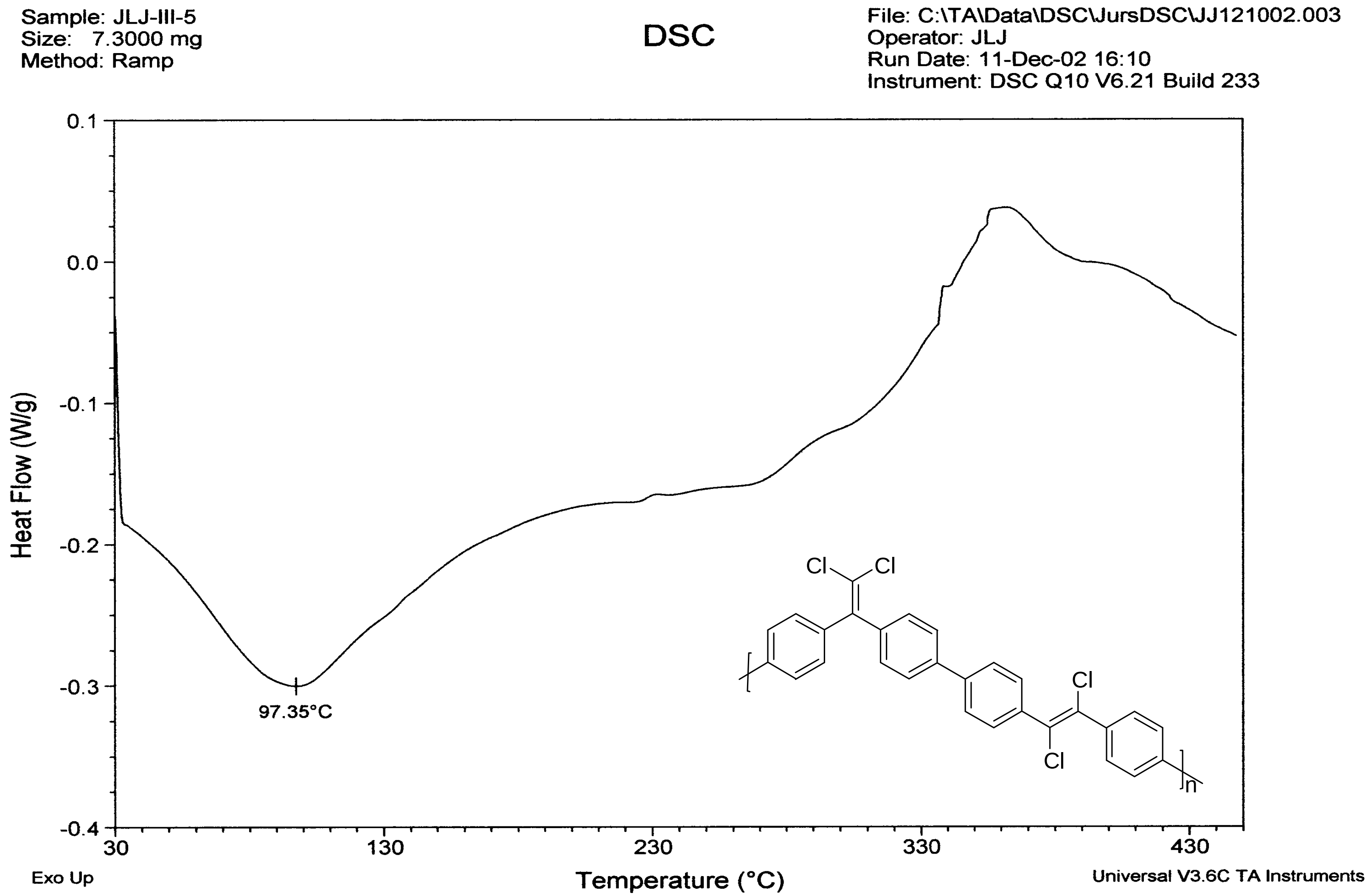


Date: Wed Jul 16 15:00:38 2003 ***JLJ-III-5

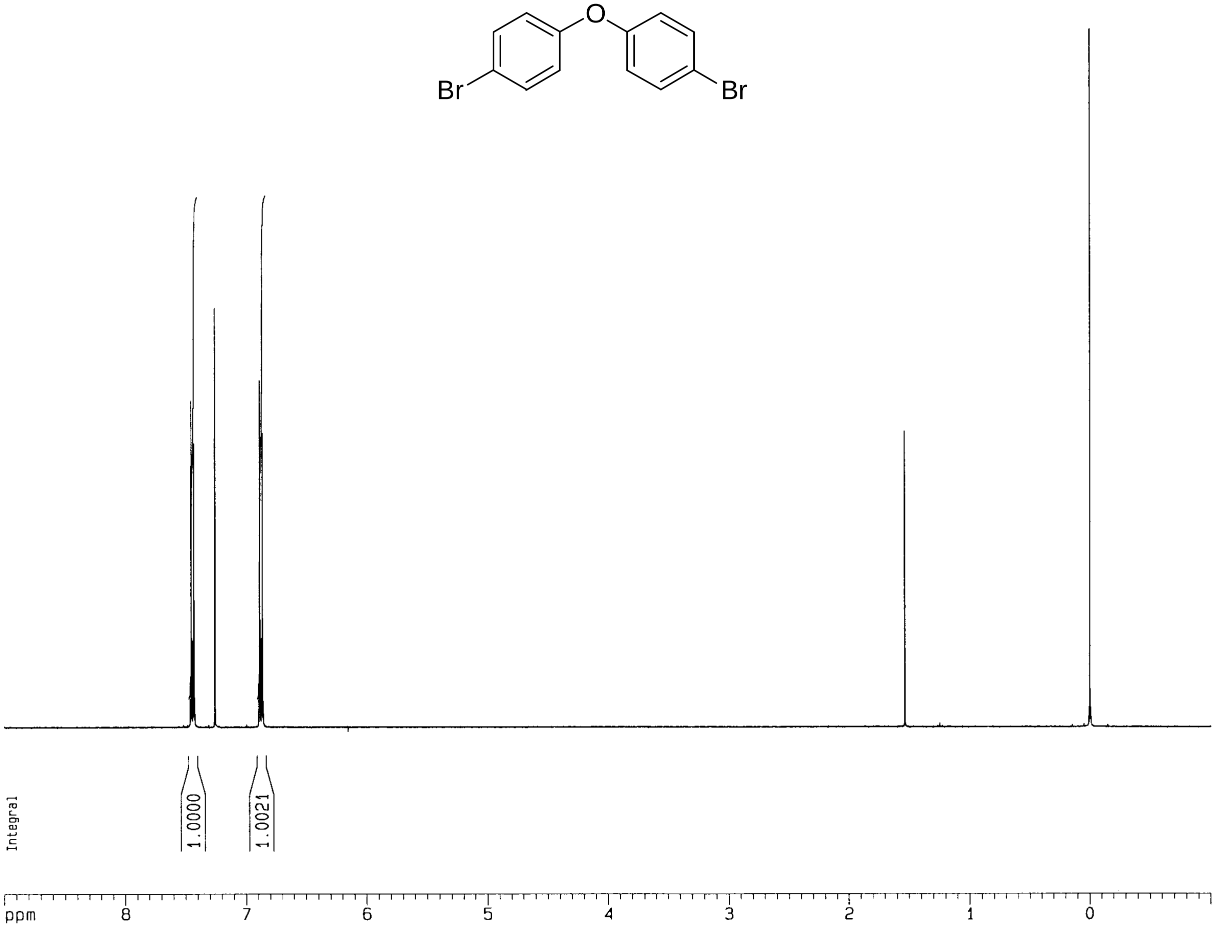
Scans: 18

Resolution: 4.000

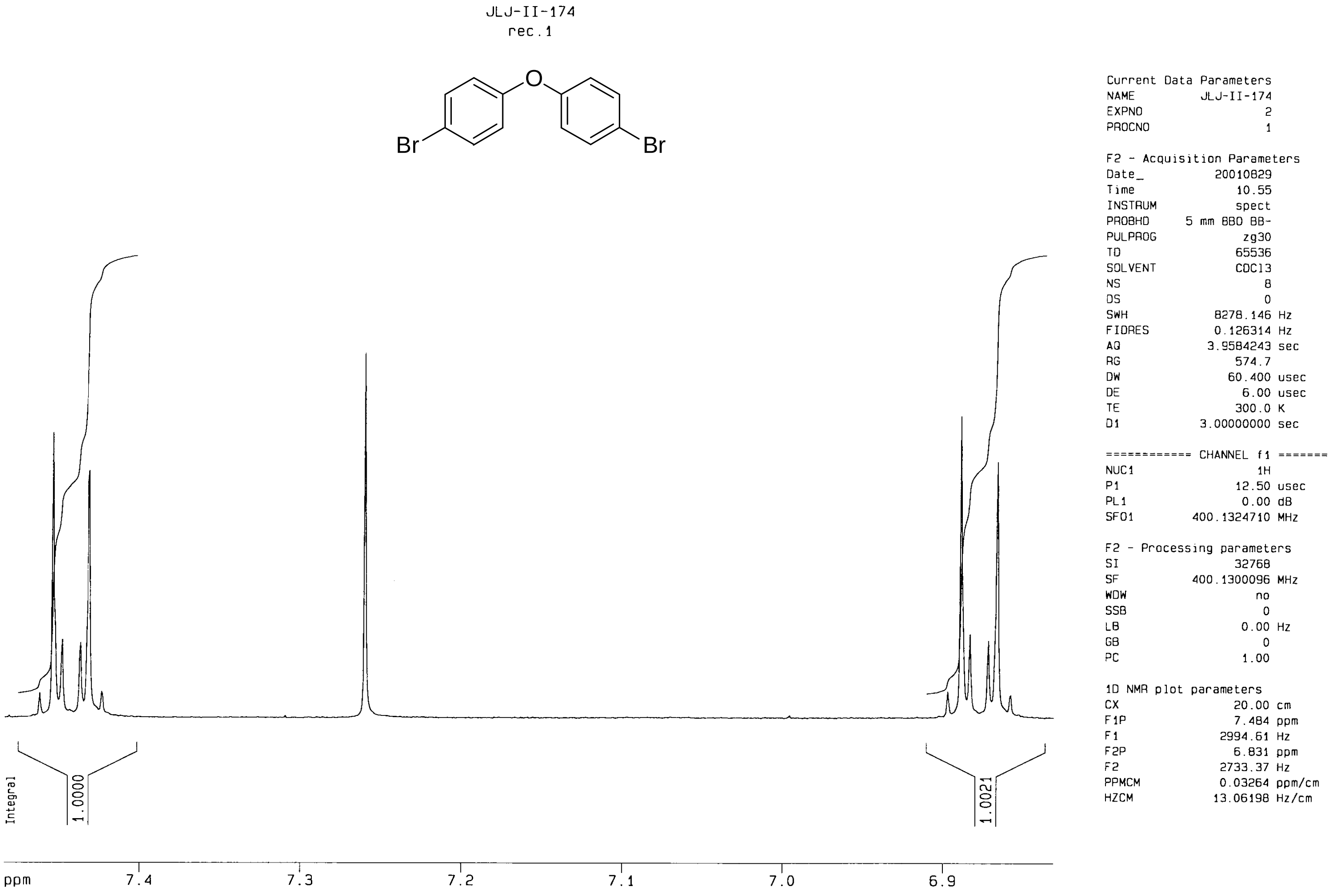
Sample: JLJ-III-5
Size: 20.5570 mg
Method: Ramp
TGA
File: C:\TA\Data\TGA\JursTGA\jljIII5.001
Operator: JLJ
Run Date: 18-Jul-03 14:45
Instrument: TGA Q50 V4.10 Build 157
253.37°C 5.000% Loss
45.24% Weight Loss
(9.300mg)
Weight (%)
100
90
80
70
60
50
0
200
400
600
800
Temperature (°C)
Universal V3.6C TA Instruments
Cl
Cl
Cl
Cl
n


Sample: JLJ-III-5
Size: 7.3000 mg
Method: Ramp
DSC
File: C:\TA\Data\DSC\JursDSC\JJ121002.003
Operator: JLJ
Run Date: 11-Dec-02 16:10
Instrument: DSC Q10 V6.21 Build 233
Heat Flow (W/g)
0.1
0.0
-0.1
-0.2
-0.3
-0.4
30
130
230
330
430
Temperature (°C)
Exo Up
Universal V3.6C TA Instruments
97.35°C
Cl
Cl
Cl
Cl
n

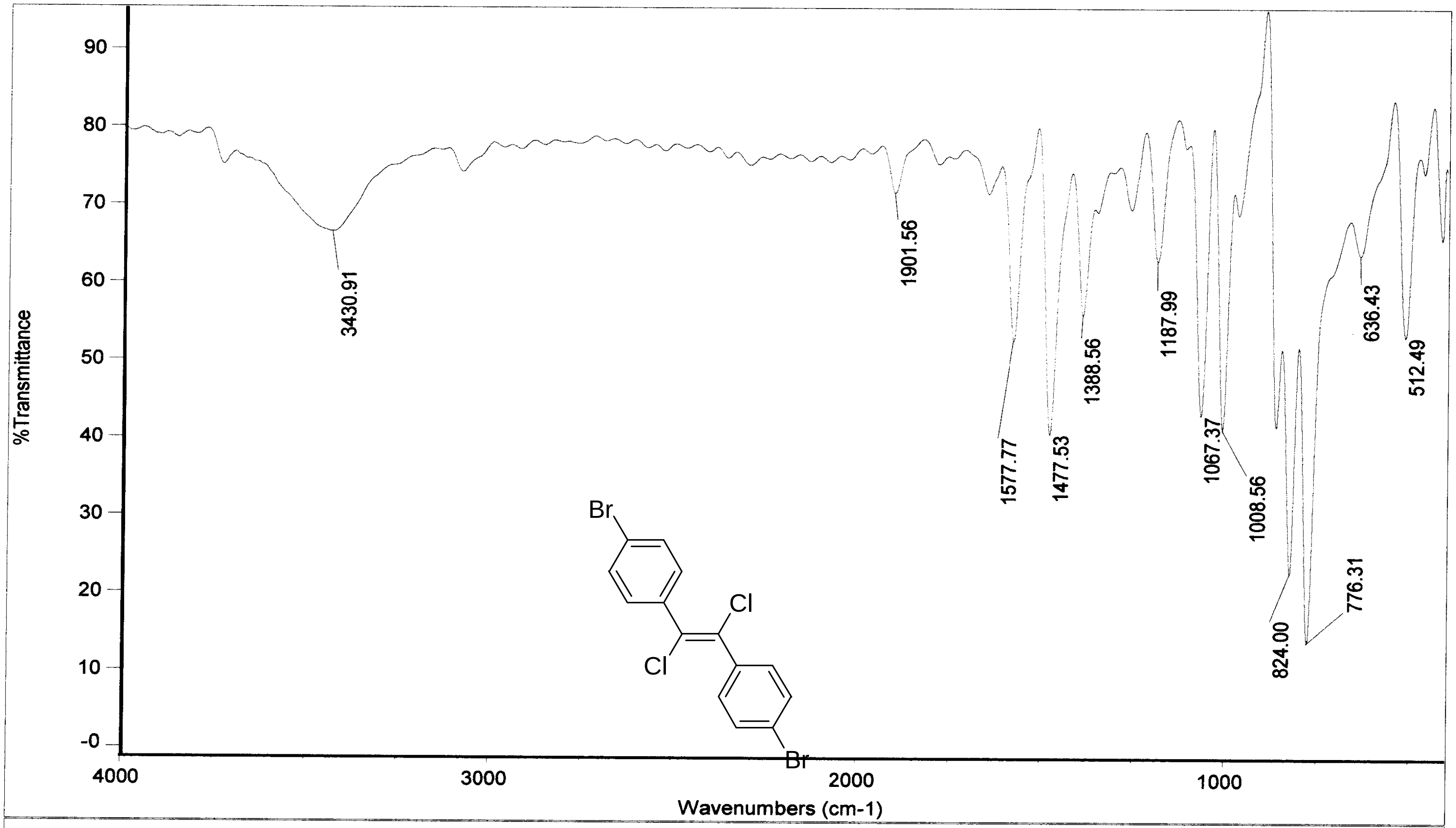
JLJ-II-174
rec.1



```
Current Data Parameters
NAME          JLJ-II-174
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20010829
Time               10.55
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDC13
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 574.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300096 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06500 Hz/cm
```



```
Current Data Parameters
NAME          JLJ-II-174
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20010829
Time               10.55
INSTRUM            spect
PROBHD      5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 574.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300096 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.484 ppm
F1               2994.61 Hz
F2P                6.831 ppm
F2               2733.37 Hz
PPMCM            0.03264 ppm/cm
HZCM            13.06198 Hz/cm
```

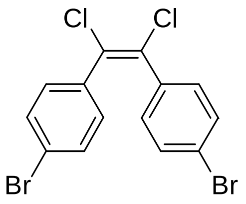


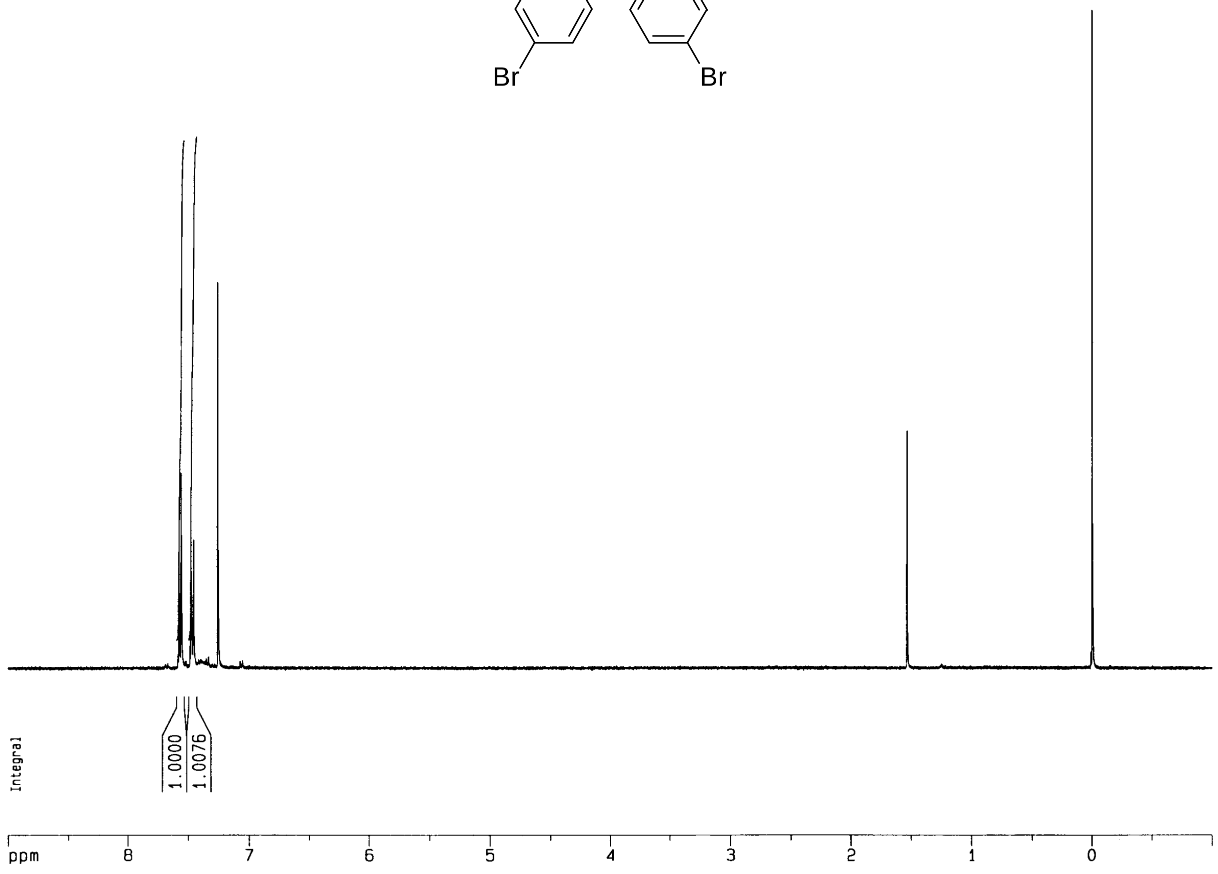
Date: Thu Jul 17 15:37:33 2003 ****JLJ-II-191

Scans: 18

Resolution: 4.000

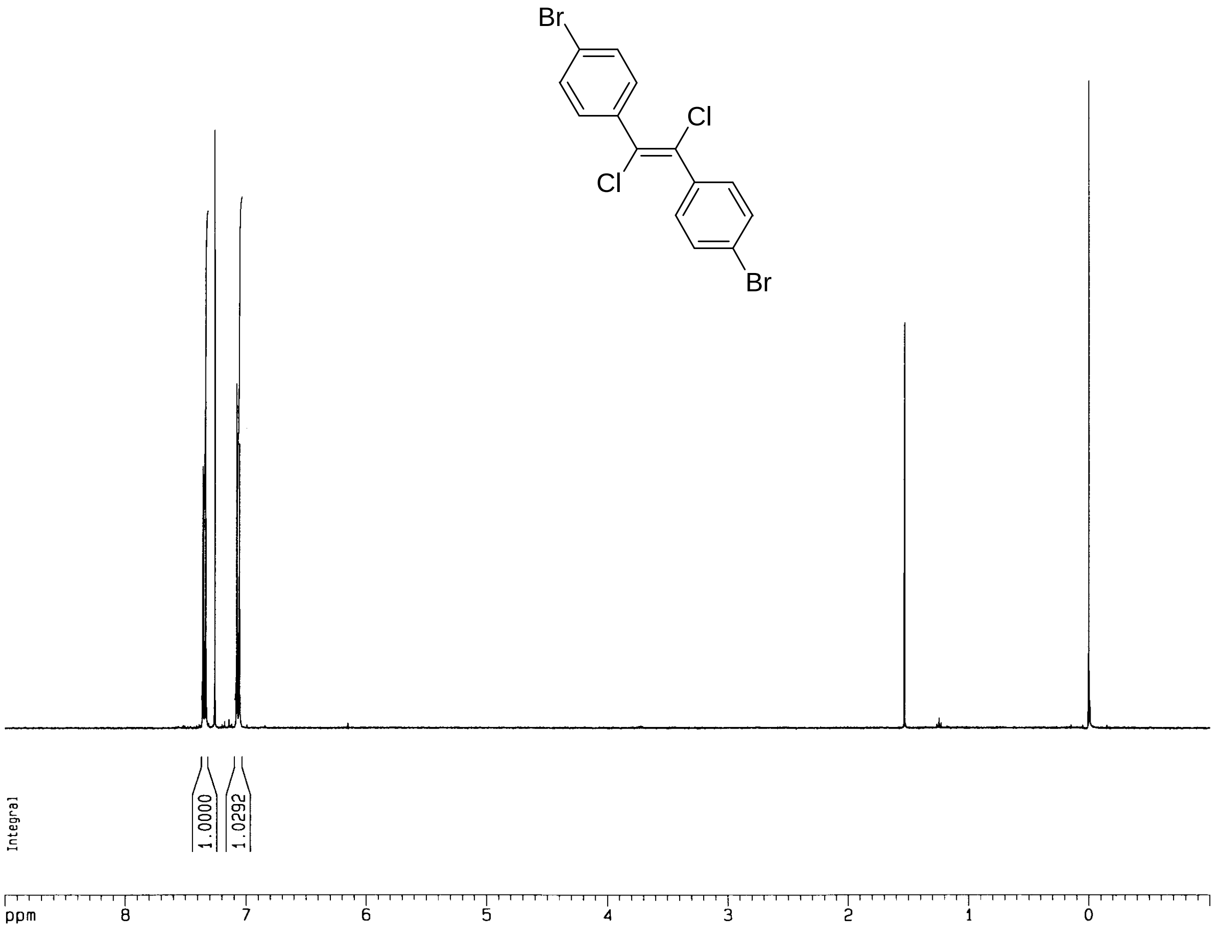
JLJ-II-191
rec.1 (cis)





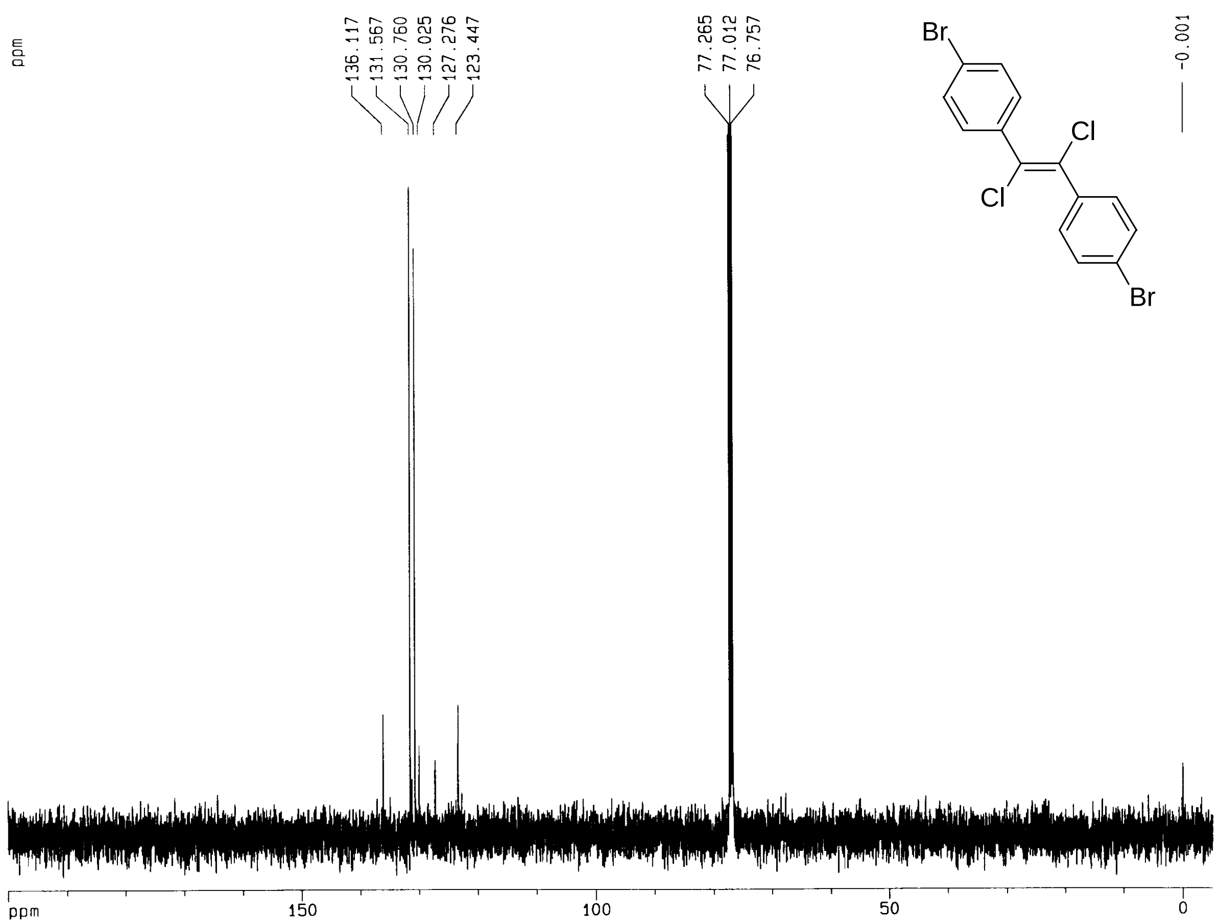
```
Current Data Parameters
NAME          JLJ-II-191
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20010921
Time               14.30
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             4006.410 Hz
FIDRES          0.061133 Hz
AQ             8.1789427 sec
RG                 812.7
DW               124.800 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1316126 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300096 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06500 Hz/cm
```

JLJ-II-191
rec.2(needles) (TRANS)

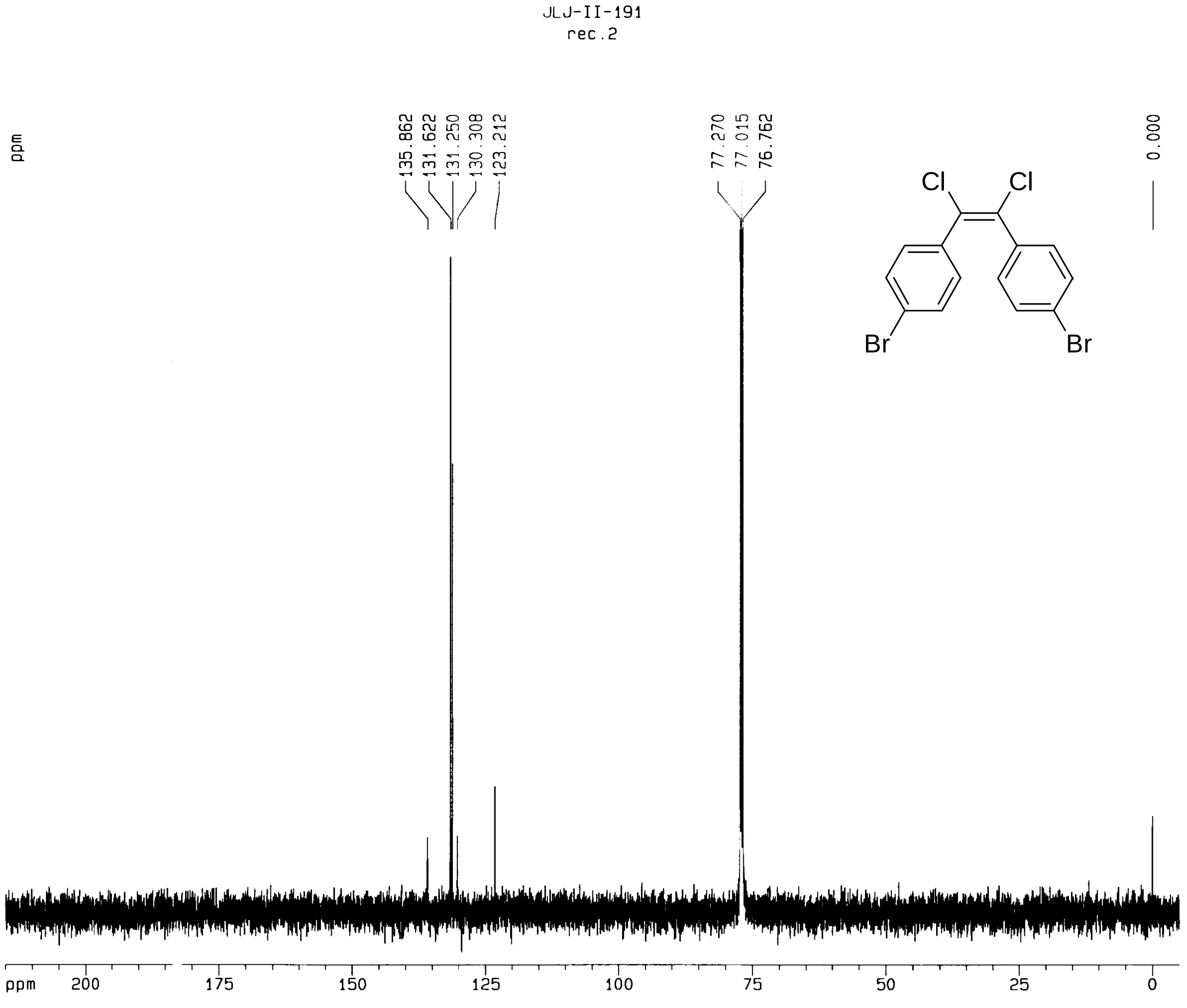


```
Current Data Parameters
NAME          JLJ-II-191
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20010924
Time               15.03
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 812.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300093 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06500 Hz/cm
```

JLJ-II-191
rec.1 (concentrated)

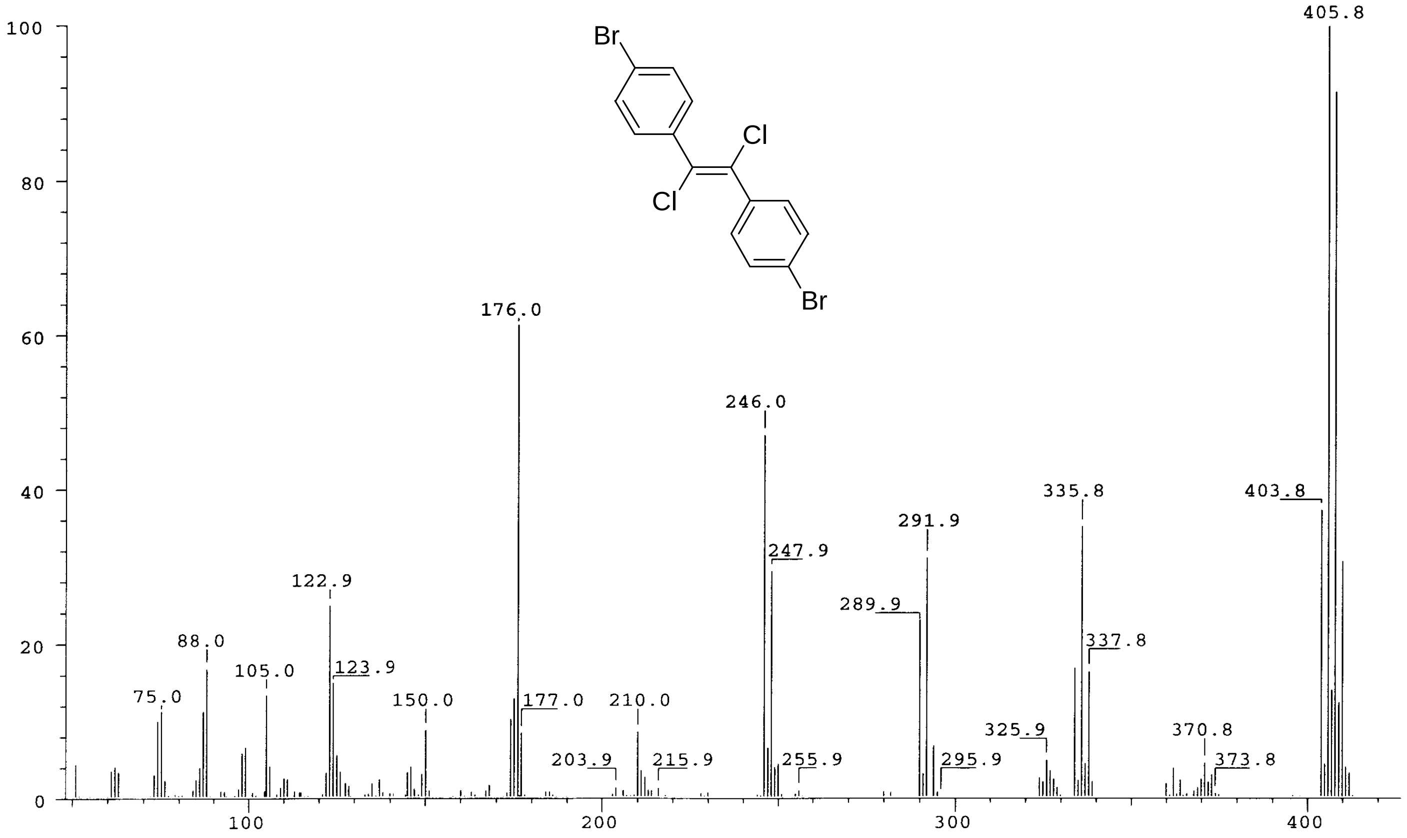


```
Current Data Parameters
NAME          JLJ-II-191
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20010925
Time               11.12
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   312
DS                     0
SWH            31446.541 Hz
FIDRES          0.479836 Hz
AQ             1.0420724 sec
RG               11585.2
DW                15.900 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                 13C
P1                  5.80 usec
PL1                 0.00 dB
SFO1         125.7715719 MHz

============ CHANNEL f2 ============
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -1.00 dB
PL12               22.60 dB
PL13               22.60 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577900 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              200.000 ppm
F1              25151.56 Hz
F2P               -5.000 ppm
F2               -628.79 Hz
PPMCM           10.25000 ppm/cm
HZCM          1289.01746 Hz/cm
```

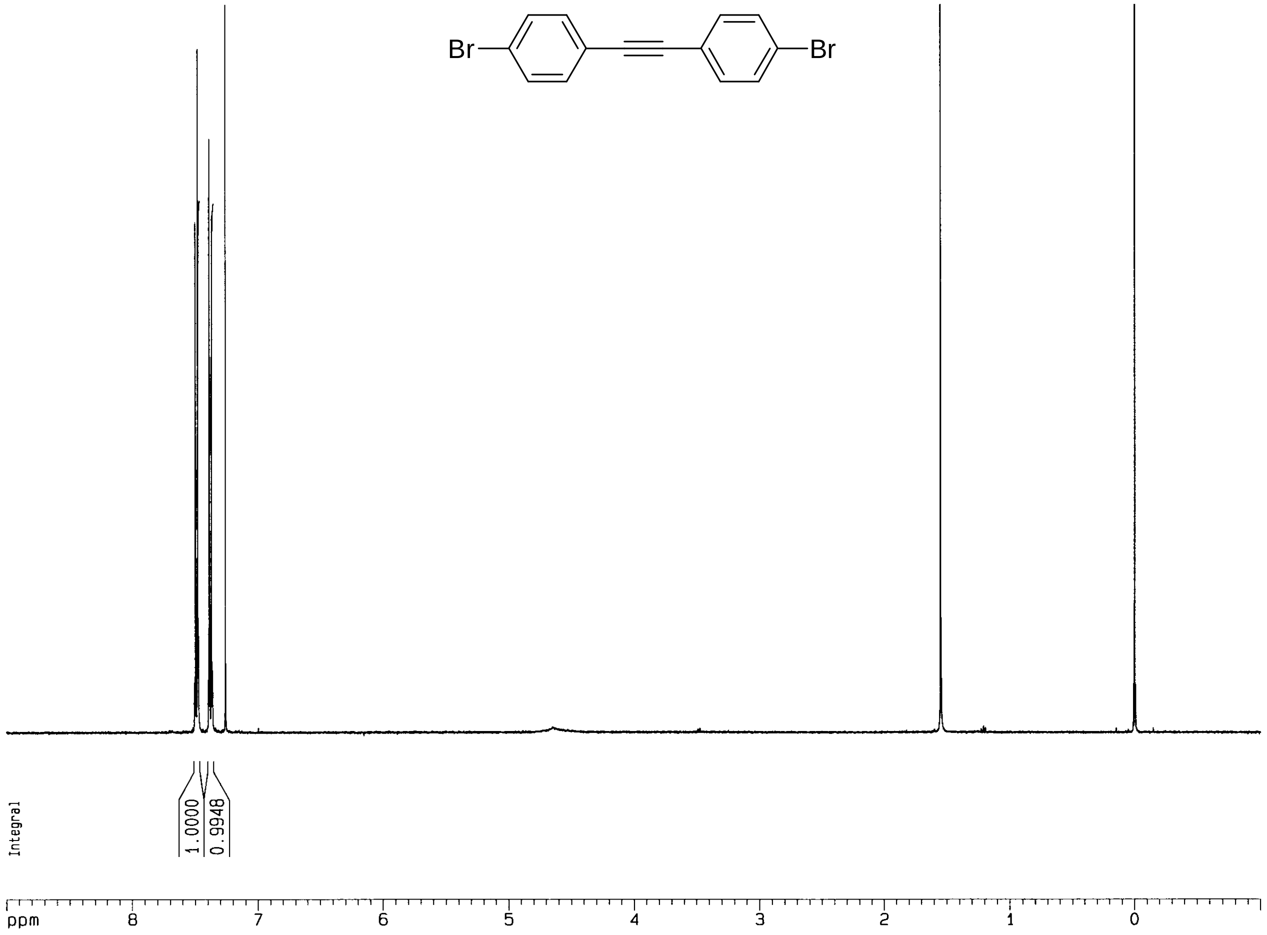


```
Current Data Parameters
NAME          JLJ-II-191
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20010925
Time               10.41
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1949
DS                     0
SWH            31446.541 Hz
FIDRES          0.479836 Hz
AQ             1.0420724 sec
RG                  1024
DW                15.900 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                 13C
P1                  5.80 usec
PL1                 0.00 dB
SFO1         125.7715719 MHz

============ CHANNEL f2 ============
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -1.00 dB
PL12               22.60 dB
PL13               22.60 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577891 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              215.000 ppm
F1              27037.93 Hz
F2P               -5.000 ppm
F2               -628.79 Hz
PPMCM           11.00000 ppm/cm
HZCM          1383.33569 Hz/cm
```

```
SPEC: jlji191b (19-Oct-01 14:54:00)                                   Scans:   1 > 123
Samp: JLJ-II-191  C14 H8 Br2 Cl2   405.834782
Oper: TDM                       Study:  EI + HR                       Client:  JLJ/JMT
Base: 405.78                    Masses:  50.00 > 450.00               #Peaks:  208
Peak: 1000.0 mmu                Intensity:   2502798                  RIC:  22699367
REG #9 @ 8.98 min (EI +VE +LMR  BSCAN (EXP) UP HR NRM) (+46-10)              2.5E+06
```

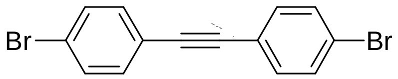


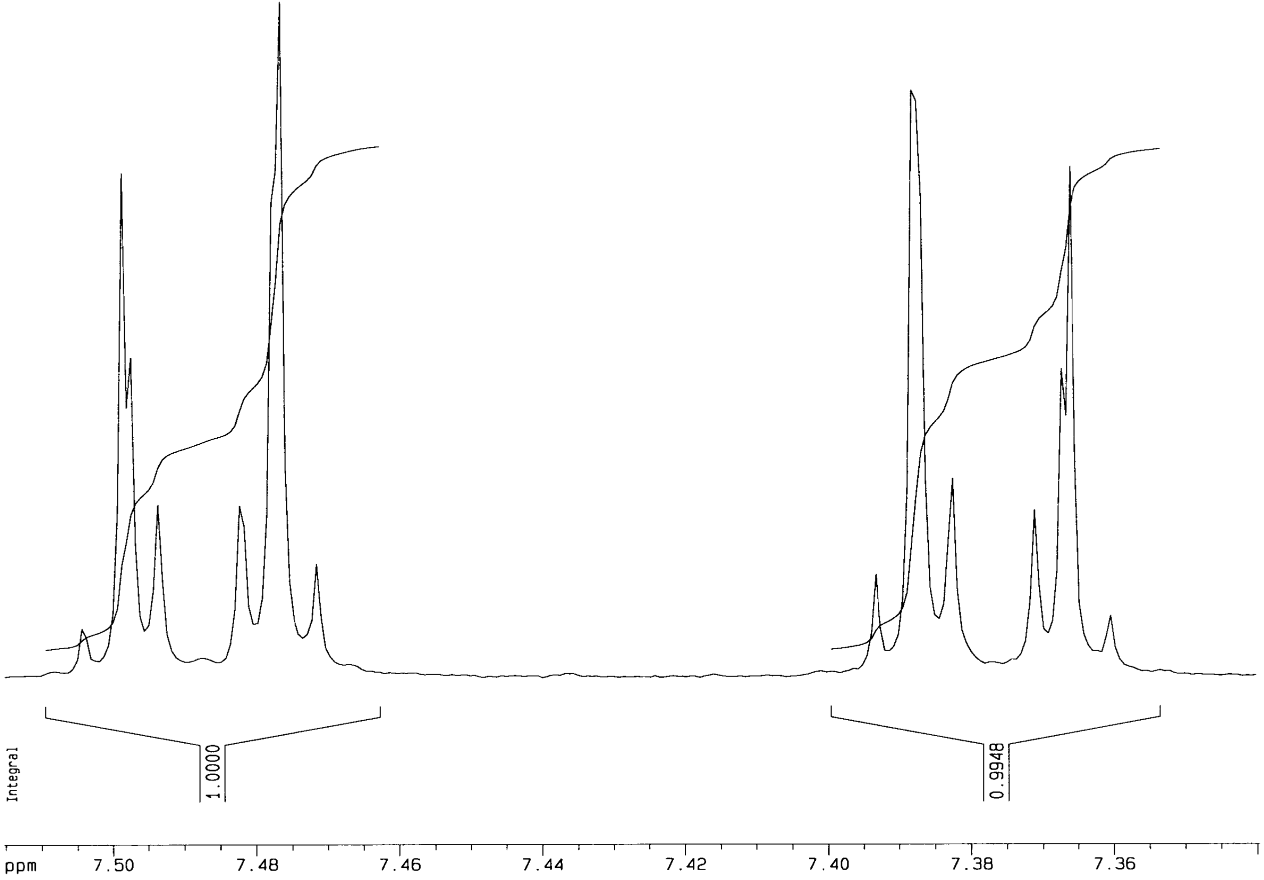
JLJ-II-171
filter cake



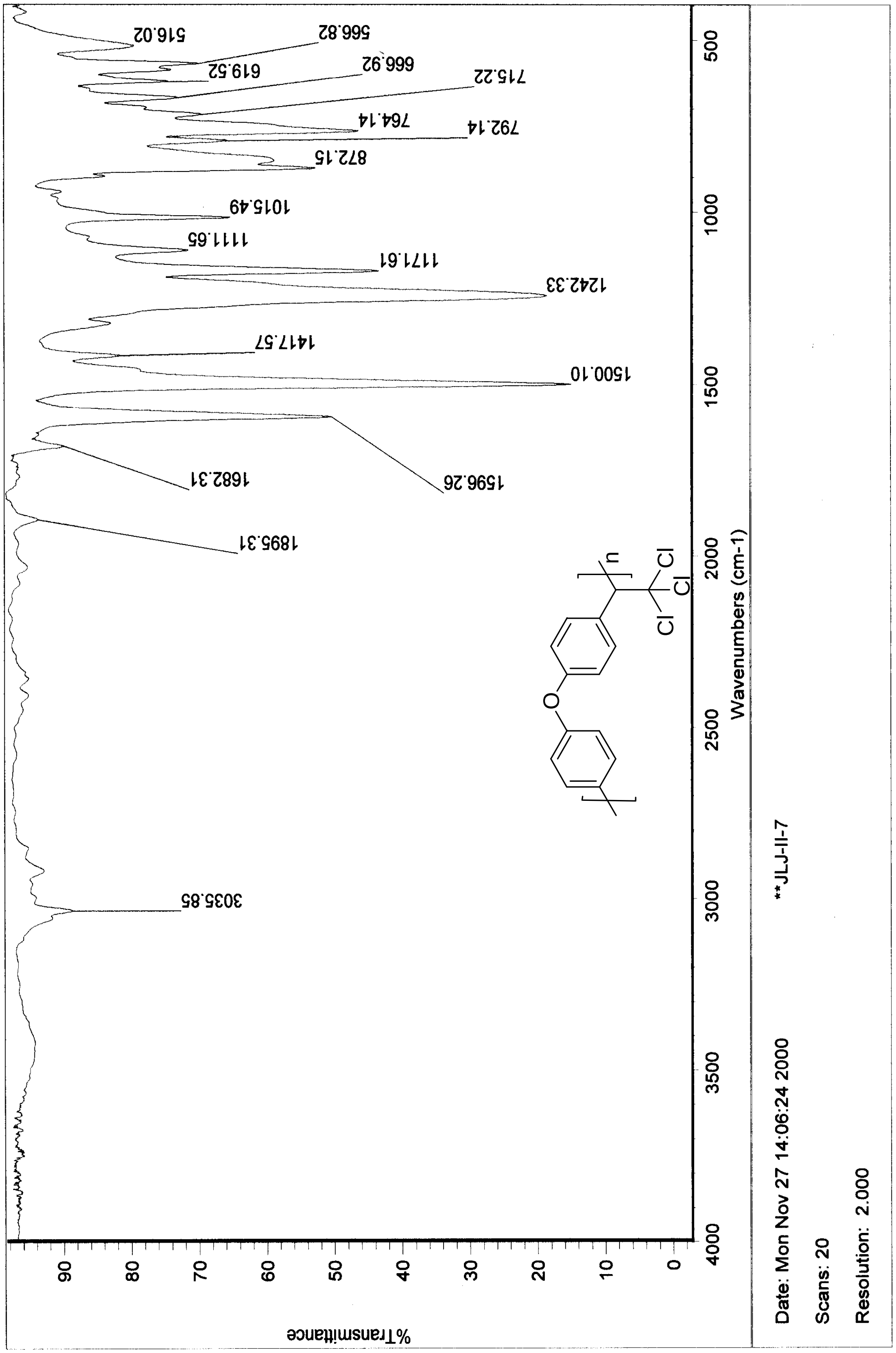
```
Current Data Parameters
NAME          JLJ-II-171
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20010817
Time               14.19
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 812.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300093 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06500 Hz/cm
```

JLJ-II-171
filter cake





```
Current Data Parameters
NAME          JLJ-II-171
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20010817
Time               14.19
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 812.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300093 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.515 ppm
F1               3007.07 Hz
F2P                7.340 ppm
F2               2936.87 Hz
PPMCM            0.00877 ppm/cm
HZCM             3.50976 Hz/cm
```



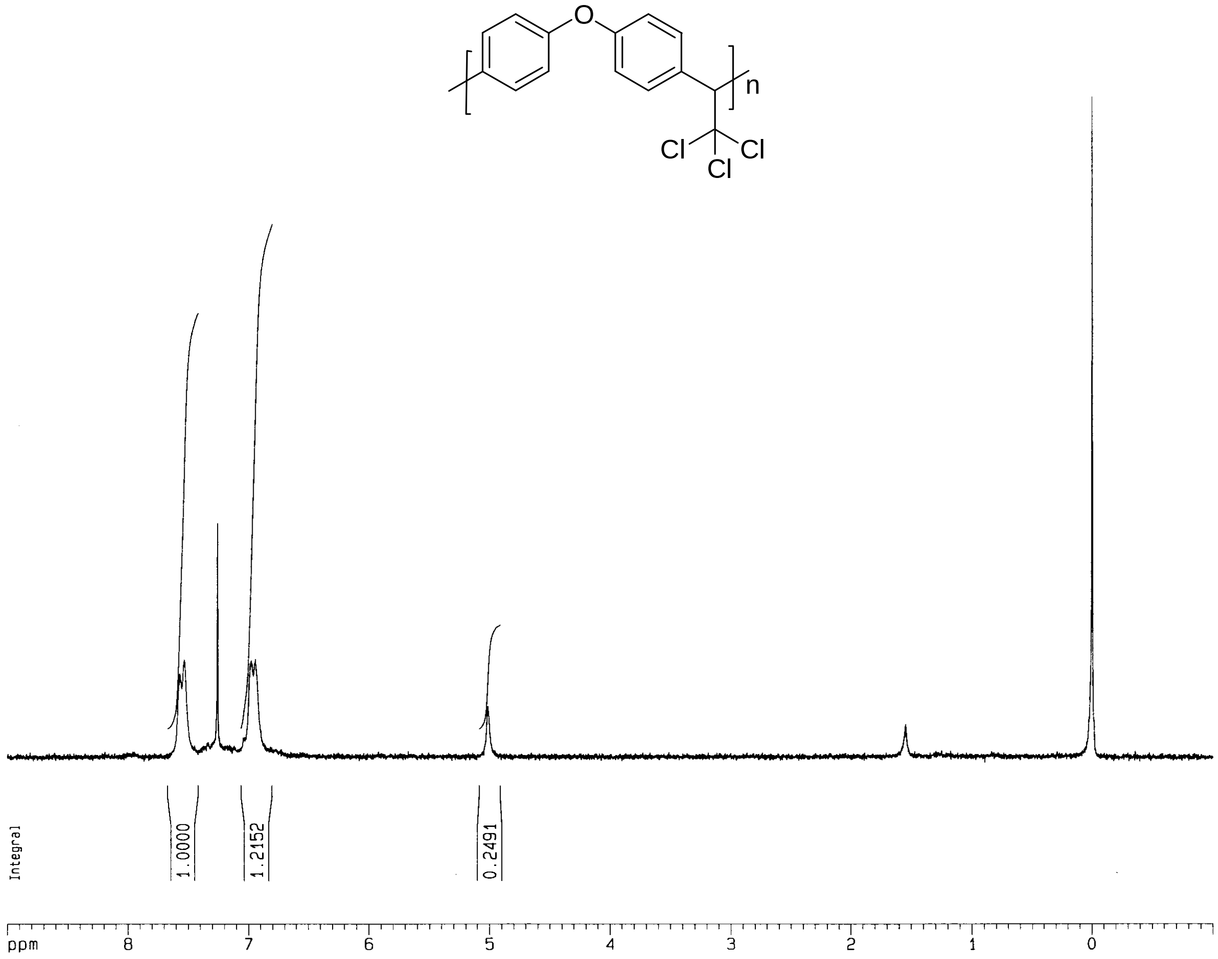
**JLJ-II-7

Date: Mon Nov 27 14:06:24 2000

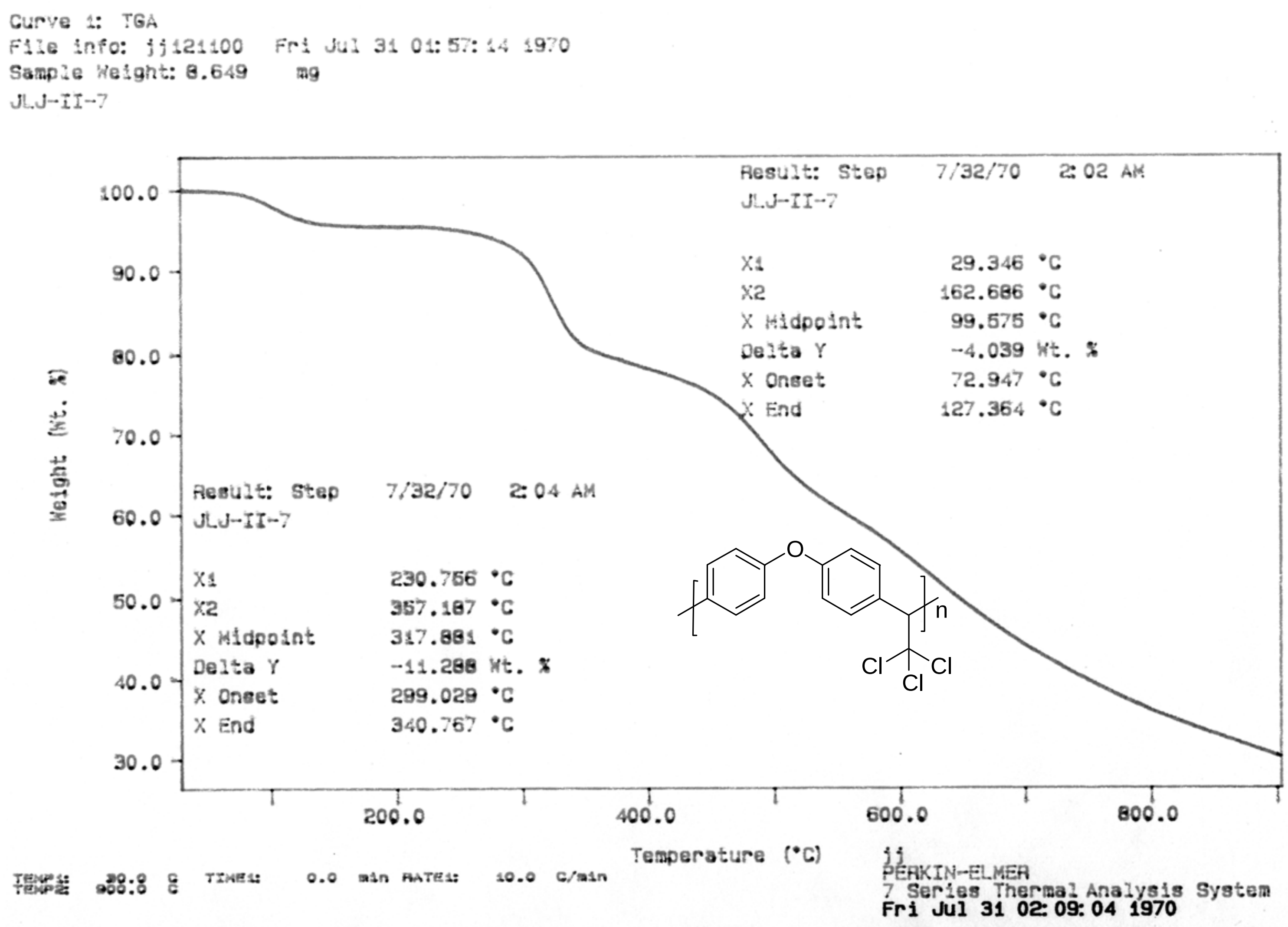
Scans: 20

Resolution: 2.000

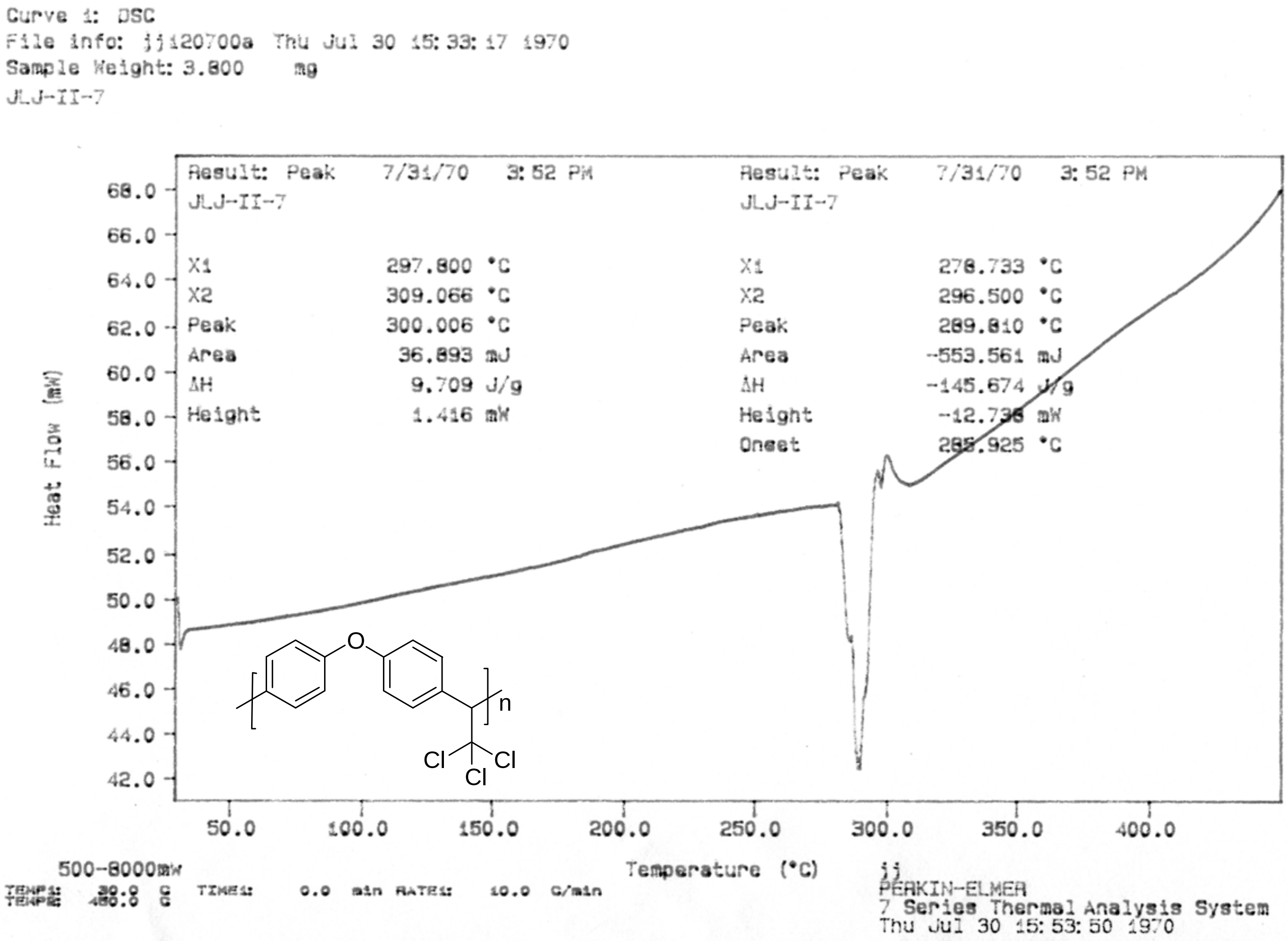
JLJ-II-7
crude



```
Current Data Parameters
NAME            JLJ-II-7
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20001110
Time               14.29
INSTRUM            spect
PROBHD      5 mm Dual 13
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             4125.413 Hz
FIDRES          0.125898 Hz
AQ             3.9715316 sec
RG                2896.3
DW               121.200 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec
P1                  8.00 usec
SFO1         200.1312359 MHz
NUC1                  1H
PL1                 0.00 dB

F2 - Processing parameters
SI                 16384
SF           200.1300086 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               1801.17 Hz
F2P               -1.000 ppm
F2               -200.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           100.06500 Hz/cm
```



```
Curve 1:  TGA
File info:  jj121100   Fri Jul 31 01:57:14 1970
Sample Weight: 8.649     mg
JLJ-II-7

Result:  Step     7/32/70     2:02 AM
JLJ-II-7

X1                    29.346  °C
X2                   162.686  °C
X Midpoint            99.575  °C
Delta Y               -4.039  Wt. %
X Onset               72.947  °C
X End                127.364  °C

Result:  Step     7/32/70     2:04 AM
JLJ-II-7

X1              230.756  °C
X2              357.187  °C
X Midpoint      317.881  °C
Delta Y         -11.288  Wt. %
X Onset         299.029  °C
X End           340.767  °C

TEMP1:    30.0  C   TIME1:     0.0  min RATE1:    10.0  C/min
TEMP2:   900.0  C

jj
PERKIN-ELMER
7 Series Thermal Analysis System
Fri Jul 31 02:09:04 1970
```



Curve 1: DSC
File info: jj120700a Thu Jul 30 15:33:17 1970
Sample Weight: 3.800 mg
JLJ-II-7

Result: Peak 7/31/70 3:52 PM
JLJ-II-7

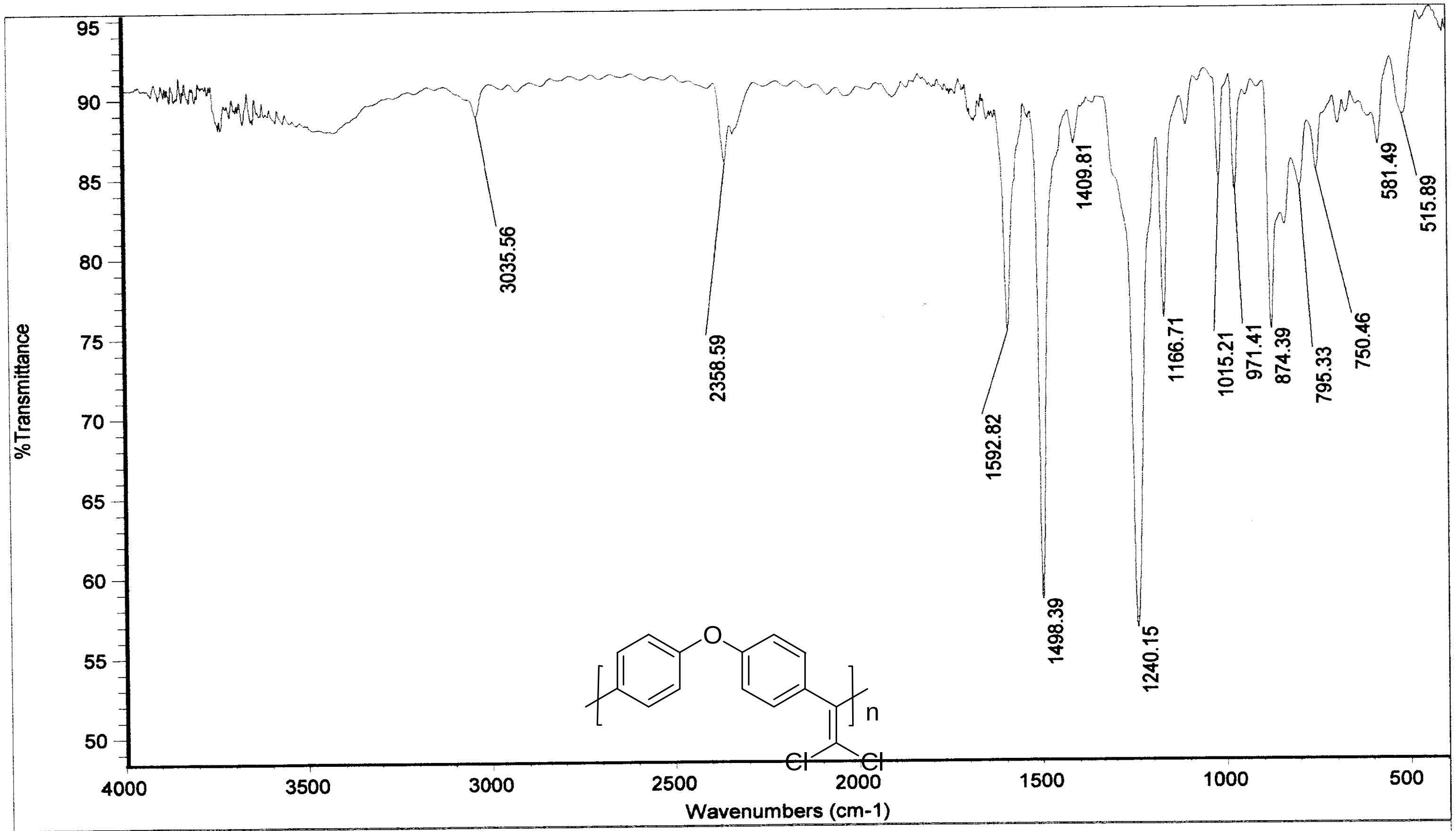
X1	297.800	°C
X2	309.066	°C
Peak	300.006	°C
Area	36.893	mJ
ΔH	9.709	J/g
Height	1.416	mW

Result: Peak 7/31/70 3:52 PM
JLJ-II-7

X1	278.733	°C
X2	296.500	°C
Peak	289.810	°C
Area	-553.561	mJ
ΔH	-145.674	J/g
Height	-12.736	mW
Onset	285.925	°C

500-8000mW
TEMP1: 30.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 450.0 C

jj
PERKIN-ELMER
7 Series Thermal Analysis System
Thu Jul 30 15:53:50 1970



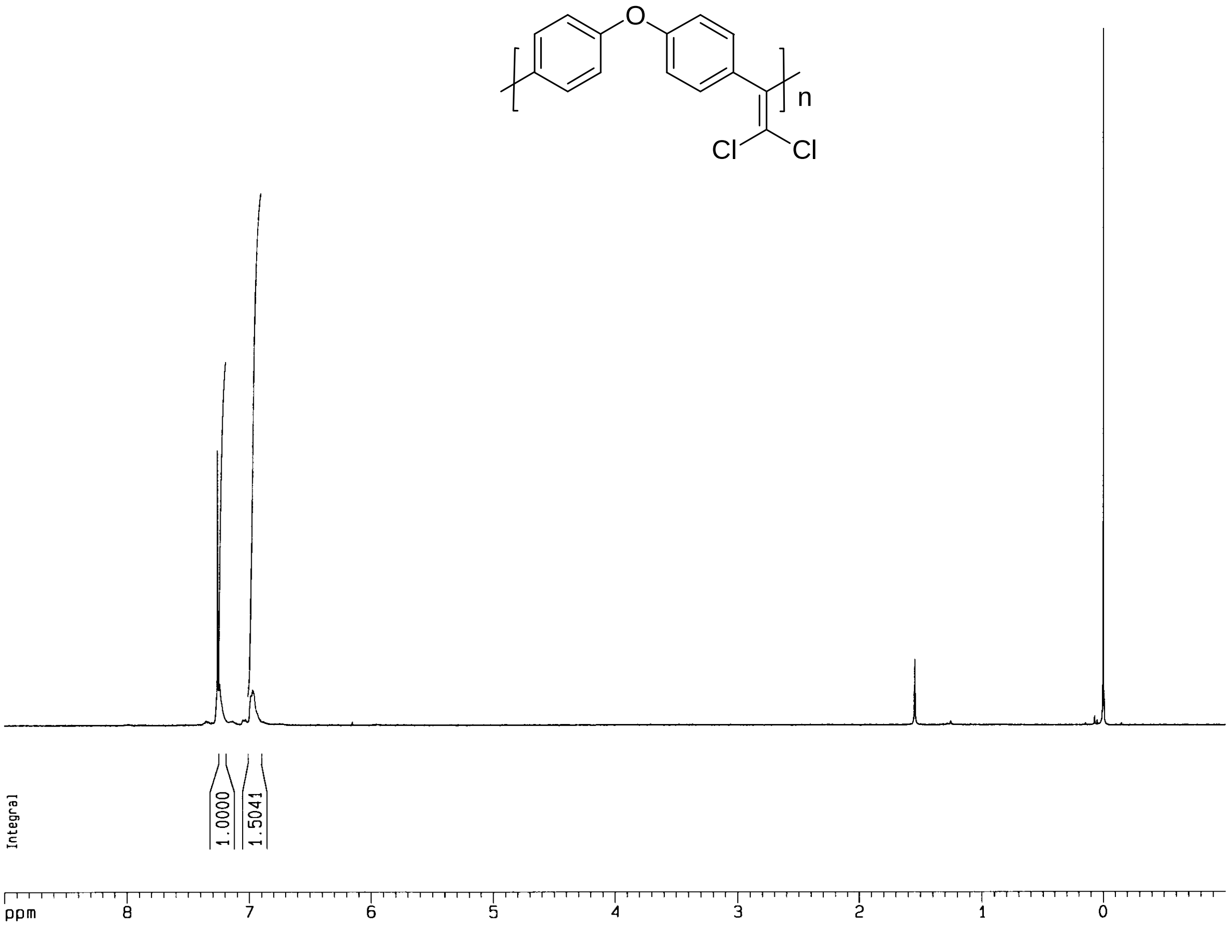
Date: Thu Dec 14 11:10:04 2000

***JLJ-II-15

Scans: 20

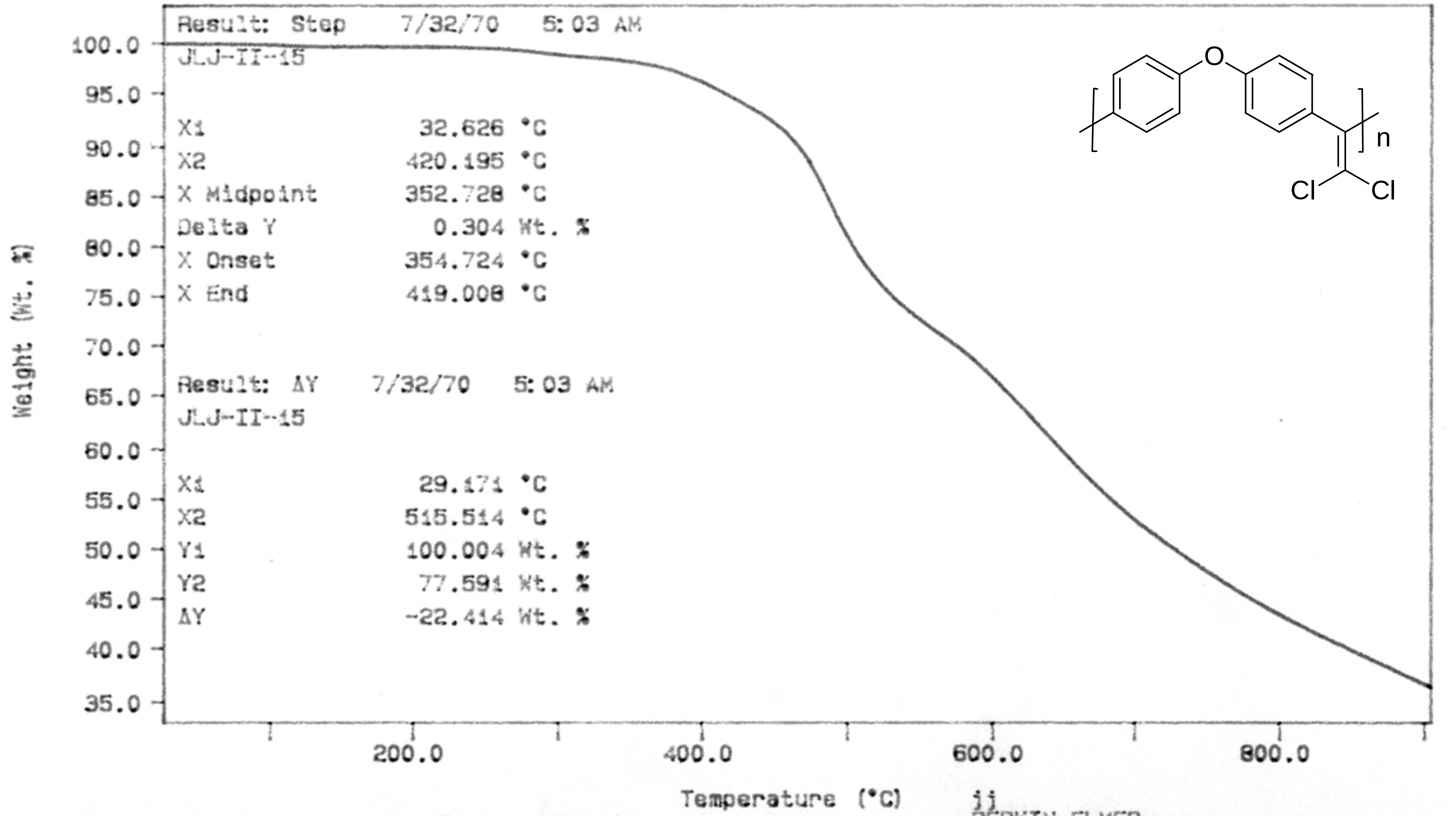
Resolution: 2.000

JLJ-II-15
crude



```
Current Data Parameters
NAME           JLJ-II-15
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20001129
Time               15.20
INSTRUM            spect
PROBHD    5 mm BBO BB-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 812.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300093 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06499 Hz/cm
```

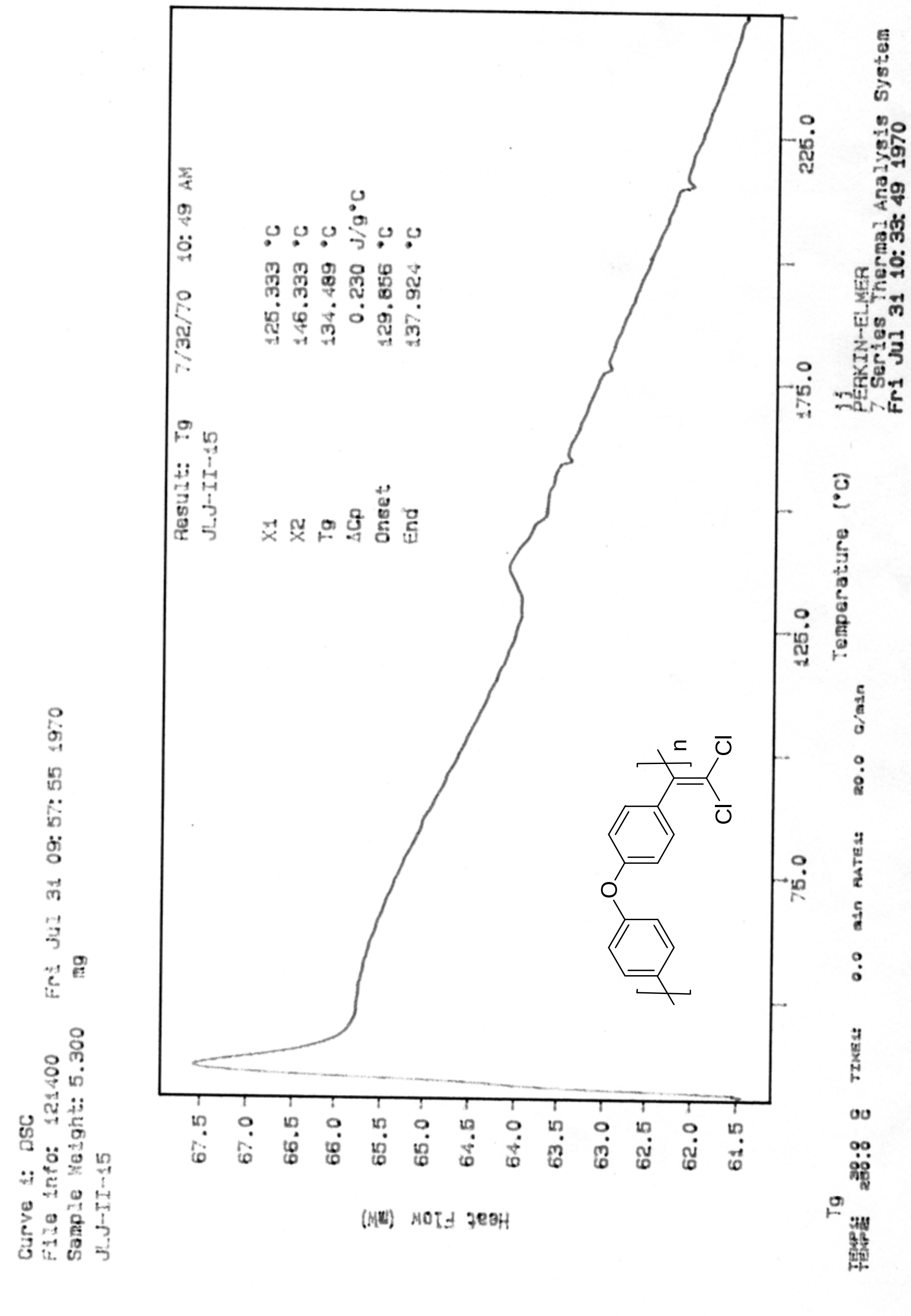
```
Curve 1: TGA
File info: 121200     Fri Jul 31 05:02:28 1970
Sample Weight: 5.133    mg
JLJ-II-15
```



```
Result: Step    7/32/70    5:03 AM
JLJ-II-15

X1               32.626 °C
X2              420.195 °C
X Midpoint      352.728 °C
Delta Y           0.304 Wt. %
X Onset         354.724 °C
X End           419.008 °C

Result: ΔY    7/32/70    5:03 AM
JLJ-II-15

X1               29.171 °C
X2              515.514 °C
Y1              100.004 Wt. %
Y2               77.591 Wt. %
ΔY              -22.414 Wt. %
```

```
TEMP1:   30.0  C   TIME1:    0.0  min  RATE1:    10.0  C/min
TEMP2:  900.0  C
```

```
jj
PERKIN-ELMER
7 Series Thermal Analysis System
Fri Jul 31 05:34:23 1970
```



Curve 4: DSC
File info: 121400 Fri Jul 31 09:57:55 1970
Sample Weight: 5.300 mg
JLJ-II-15

Result: Tg 7/32/70 10:49 AM
JLJ-II-15

X1 125.333 °C
X2 146.333 °C
Tg 134.489 °C
ΔCp 0.230 J/g°C
Onset 129.856 °C
End 137.924 °C

Tg
TEMP1: 30.0 C TIME1: 0.0 min RATE1: 20.0 C/min
TEMP2: 250.0 C

11
PERKIN-ELMER
7 Series Thermal Analysis System
Fri Jul 31 10:33:49 1970

Chapter 4

Novel Flame Retardant Polymers

Bisphenol C Flame Retardant Polymers

4.1 Introduction

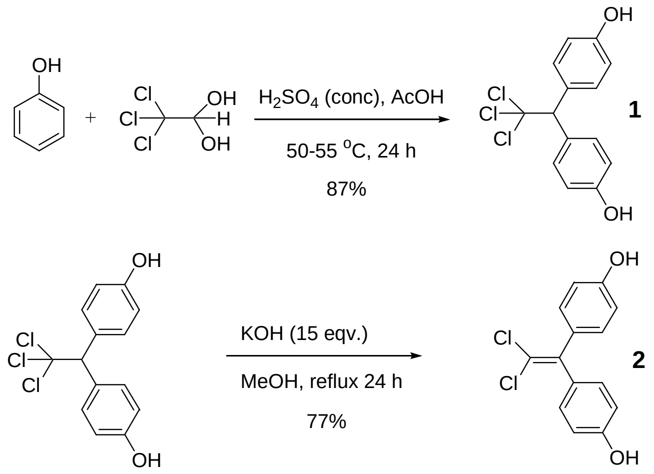
The monomer that we have used as a backbone for our work toward flame retardant polymers is commonly called bisphenol C (BPC) or 1,1-dichloro-2, 2-bis(4-hydroxyphenyl)ethylene. As has been shown by many research groups, BPC can be used as a blendable additive in a commercial plastic or as part of a polymer back bone to effectively impart flame resistance to certain polymeric materials.[1-9] When thermally decomposed, BPC exothermically produces volatile products such as HCl and CO_2.[8-10] It is these pyrolysis byproducts and the high char forming nature of BPC that cause flame resistance in these polymers and blends.

The thrust of our research has been to incorporate the BPC moiety into a polymer backbone that can impart flame retardancy without additives. The incorporation of this monomer into a thermoplastic has been approached several ways including the following: nucleophilic aromatic polymerizations[11], nucleophilic displacement under Phase Transfer Conditions (PTC),[12] diene metathesis (ADMET),[13-15] urethane chemistry,[16] and lastly a vinyl addition polymerization.

4.2 Results and Discussion- Bisphenol C and BPC polycarbonate

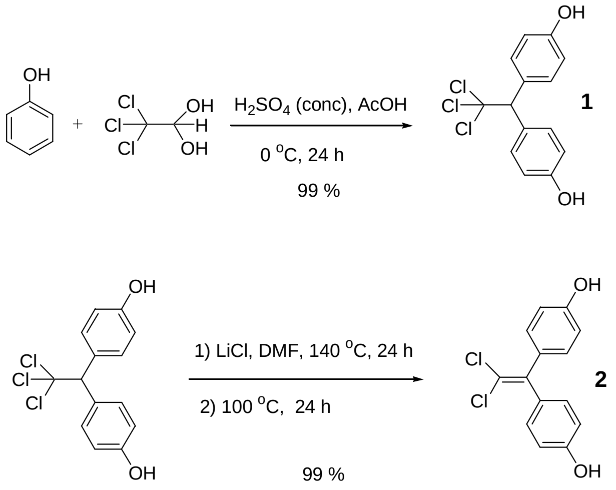
The original research into the BPC molecule was done by Ex-Lax Inc. in Brooklyn, New York.[17] It was believed from other sources that these bisphenolic compounds would have laxative properties, so the development of BPC was pursued.[18] The synthesis of BPC was carried out by condensing phenol with chloral to produce 1,1,1-trichloro-2,2-bis(p-hydroxyphenyl)ethane (**1**) followed by a dehydrohalogenation to give the corresponding dehydrohalogenated compound BPC (**2**) (Reactions 1 & 2).[17]

Reactions 1 & 2



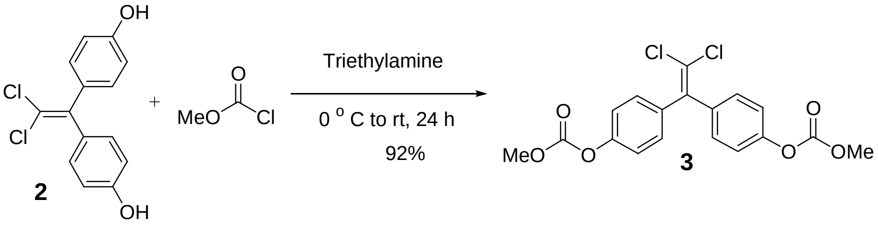
Stewart's process for the synthesizing BPC results in higher yields.[1] Using her reaction conditions, the BPC monomer can be made in quantitative yield (Reaction 2 & 3). Several decolorizing and recrystallization steps are then needed to obtain material that is suitable for condensation polymerizations, but overall this procedure requires less workup time and produces higher yields.

Reaction 2 & 3



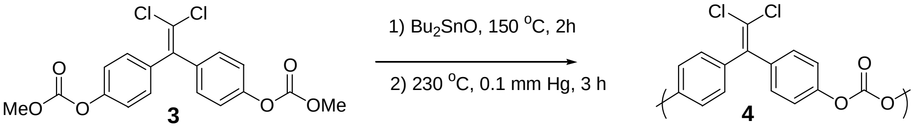
The use of BPC as a flame retardant additive or polymer was not developed until the late 70's by General Electric.[2,19] The flame-resistant properties of polycarbonate were improved by co-polymerizing BPC with bisphenol A (BPA).[2,19] Phosgene gas is used in GE's process but because of the high toxicity of phosgene, we opted to use non-phosgene polymerizations procedure.[20] In the route to making polycarbonate monomers, bisphenol C was transformed into the dicarbonate by condensation with methyl chloroformate to give bisphenol C bis(methylcarbonate) (**3)** (Reaction 5).[20]

Reaction 5



The polymer **4** was by polymerizing **3** using dibutyltin oxide as a catalyst, with high heat and vacuum to drive off CO_2 and MeOH (Polymerization 1).[20]

Polymerization 1



Unfortunately, during the course of this reaction, much of the monomer sublimed, resulting in low molecular weight polymer. The synthesized polymer was sent to FAA for further testing with pyrolysis combustion flow calorimetry (PCFC). The flame retardant properties of this polycarbonate was tested by GE, so no full scale flammability testing was pursued by us.[2]

PCFC Data for the Polycarbonates

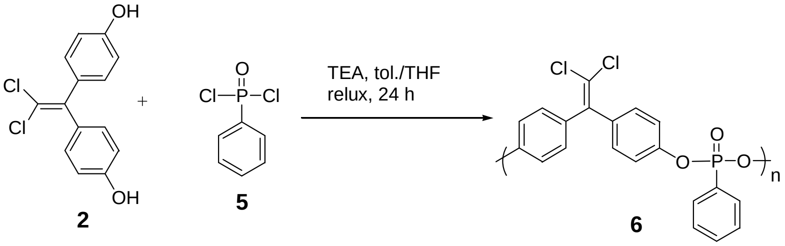
Polymer	HR capacity (J/g K)	Total Heat (kJ/g)	Char yields (%)
BPC Polycarbonate **1**	29	3	50.1
BPA Polycarbonate	359	16.3	21.7

The PCFC results obtained from the BPC polycarbonate show a much lower heat release capacity and also a much higher char yield, compared to traditional BPA polcarbonate. It is because of this data that the FAA is interested in pursuing polymer with the BPC structure.

4.3 Results and Discussion- Phosphorous and BPC polymers

The next class of polymer synthesized in the lab was designed to contain phosphorus since it has been theorized in the literature that phosphorus acts both in the solid and vapor phase to stop burning.[21] The first polymer that incorporated phosphorus and BPC in the backbone synthesized by a condensation of BPC with phenylphosphonic dichloride (**5)** to yield polymer **6** (Polymerization 2).

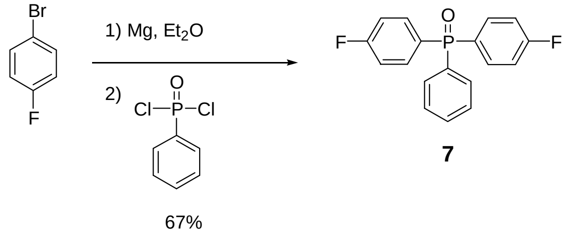
Polymerization 2



Several different reaction conditions were tried that resulted in a brittle low molecular weight material. A full bar could not be made and tested in the HVUL-94, but in the improvised pellet test. The improvised pellet test was developed here in the laboratory as a screening tool for small quantities of polymer. The polymer is pressed into a pellet (400 mg) using a Carver IR pellet press to make a small pellet, which is then subjected to the UL-94 flame test. Polymer **6** was pressed into a pellet and upon ignition of the polymer in the HVUL-94 did not ignite. The polymer did drip, but did not burn the cotton below.

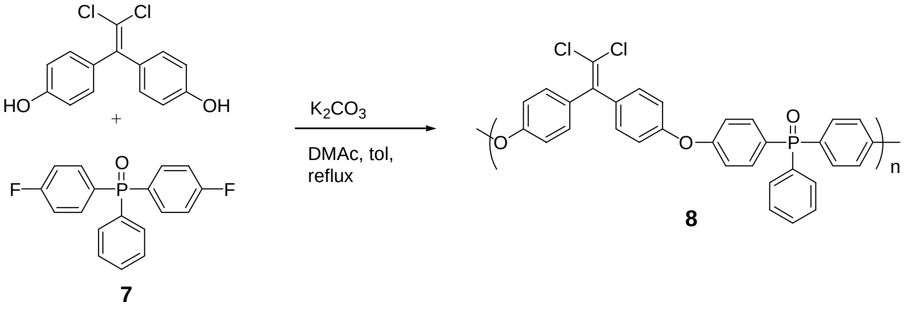
Another approach to incorporating phosphorous with the BPC moiety utilized a different condensation polymerization method, the nucleophilic aromatic substitution reaction. Bis(4-fluorophenyl)phenylphosphine oxide (**7)** was synthesized by coupling the Grignard reagent derived from 1-bromo-4-fluoro benzene with dichlorophenylphosphine oxide (Reaction 3).[22]

Reaction 3



This monomer was subsequently polymerized with BPC under basic reaction conditions to give polymer **8** (Polymerization 3).[11]

Polymerization 3



8 was obtained in low molecular weight (M_w: 4000; M_n: 3500) but with the pellet burn test the resulting polymer did not burn or drip upon ignition by the Bunsen Burner.

PCFC Data for the Phosphorous/BPC polymers

Polymer	HR capacity (J/g K)	Total Heat (kJ/g)	Char yields (%)
Polymer **6**	47	8.7	49.2

Polymer **8**	95	10.1	59.8

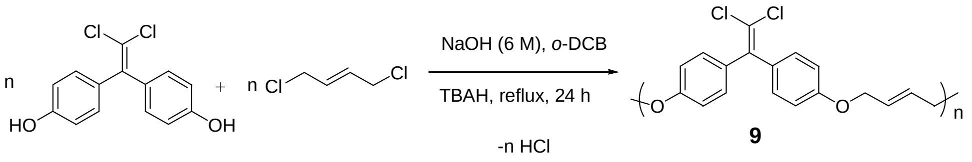
Both of these new BPC polymers show low heat release capacity and the incorporation of the highly aromatic moieties in polymer **8**, that gives it the highest char yields of any of the new polymers. Polymer **6** does have a glass tranition temperature but due to its low molecular weight, is not processible.

4.4 Results and Discussion- BPC Polyarylethers

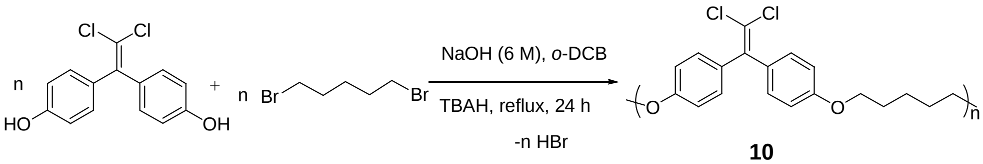
The inflexibility of most aromatic polymer is a problem because they do not melt, making processing them difficult. To make flexible polymers with distinct melting points and glass transition temperatures aliphatic and olefinic groups were added to the polymeric backbone. The quandary of using these types of functional groups is that theoretically they should increase the amount of fuel for the fire, and therefore the flammability of the polymer. On the other hand, it is known in flame retardant chemistry that olefins can cross-link during the burning process and increase char formation.[9] In addition, Wagner describes some of his unsaturated polyethers as having a high degree of thermal stability as measured by thermogravimetric analysis.[14]

The first polymer with a flexible backbone was synthesized by a process known in the literature for making bisphenol A polyaryl ether under phase (Polymerization 4 & 5). transfer catalysis conditions (PTC).[12] We used this procedure to couple BPC with 1,4-dichloro-2-butene (DCB) or 1,5-dibromobutane to yield polyether **9 & 10** (polymerization 4 & 5).

Polymerization 4 & 5



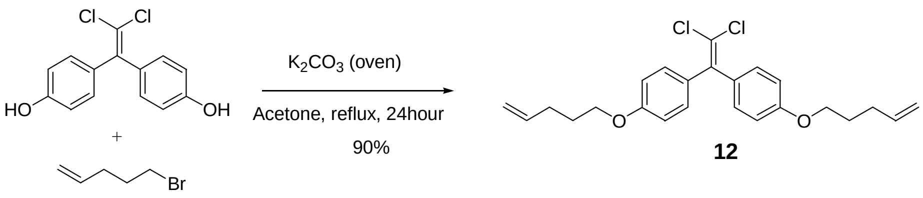
9



10

The next approach at obtaining high molecular weight polymers was to explore Acyclic Diene Metathesis polymerizations (ADMET).[13] The aim was to achieve high molecular weight flame resistant polymers. We modeled the reaction using aliphatic diene monomers such as, 1,5-hexadiene and 1,9-decadiene, under test conditions to optimize conditions before making BPC-derived products. At this point we decided to functionalize the BPC with an olefin. Wagener has done considerable work on the influence of the neighboring group effect, and how it affects the ADMET reaction. His studies have concluded that atoms such as, oxygen and sulfur act as Lewis Bases, complexing with the metal (Ru) and hindering the metathesis reaction.[23] In order to circumvent this problem we have incorporated three methylene spacers groups into the monomer. This was achieved by condensing BPC with 5-bromo-1-pentene under basic conditions to yield monomer **12** (Reaction 4).

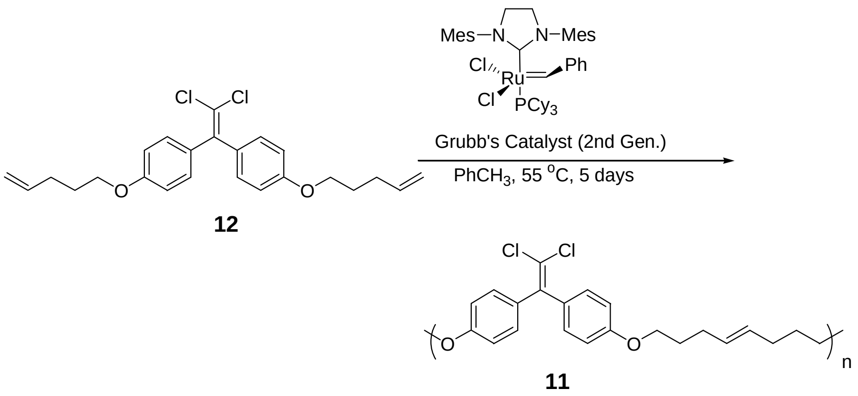
Reaction 4



12

After purification of this monomer with multiple recrystallization from methanol, we polymerized this molecule using Grubb's Catalyst (2nd Generation) in toluene, at 55 ^{o}C with a positive flow of argon for 5 days to yield polyether **11**. (Polymerization 6).

Polymerization 6



The incorporation of the aliphatic (pentane) and olefinic (butene, octene) functionalities in the present work has yielded polymers amorphous and processible polymers with a defined T$_g$. In addition these materials are flame retardant with little to no additives being required (1 wt % PTFE was used as an anti-drip additive).

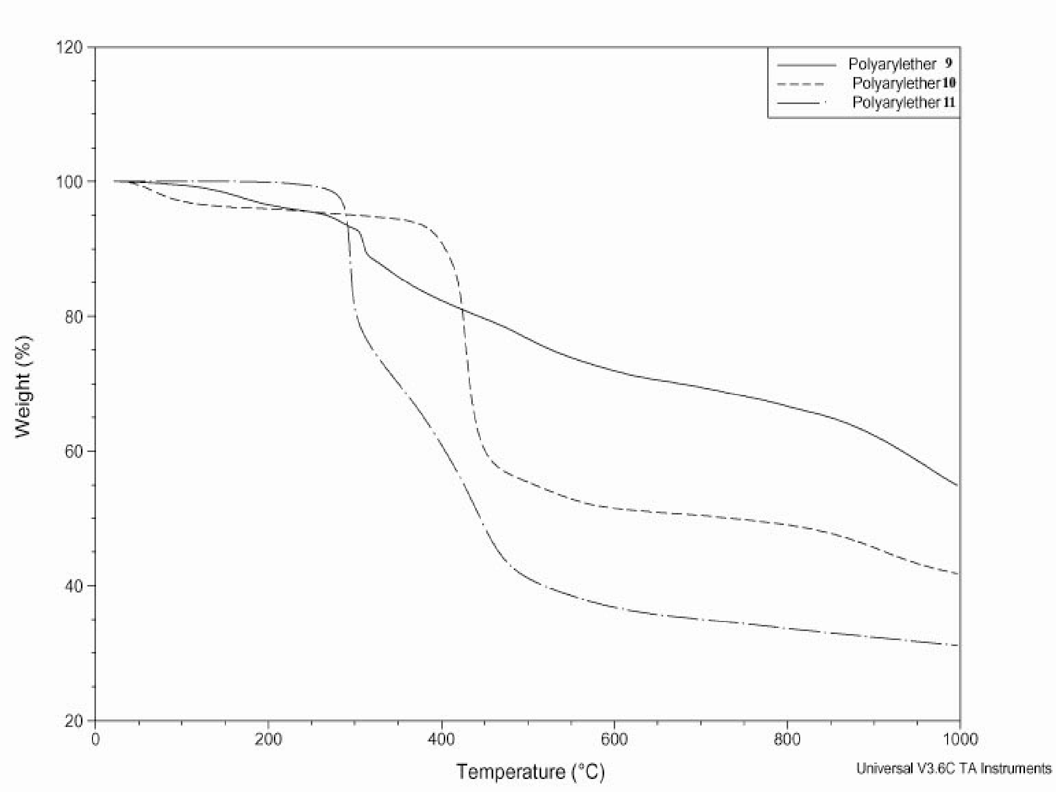
Polyarylether **9** was the first to be synthesized using PTC conditions. It is the most thermally stable of the three polymers. Comparisons of the TG analysis and PCFC data from the three polyarylethers shows that **9** gives the highest char yields (58 %) followed by **10**, and **11**. The thermal stability of the polymers is reduced with the incorporation of more aliphatic/olefinic groups, which results in a lower percentage of the char yields, which is apparent when you compare heat release capacity and char yields of polyarylether **9** and **11**.

PCFC Results for the Polyarylethers

Polymer	HR capacity (J/g K)	Total Heat (kJ/g)	Char yields (%)
Polyarylether **9**	37	8	58
Polyarylether **10**	205	13	37
Polyarylether **11**	146	18	20
Polyethylene	1676	42	0
Polystyrene	927	39	0

The PCFC total heat release data correlates well with the TGA char yields. Polyarylether **11** has a lower heat release capacity than polyarylether **10**, but also has a lower char yield. The thermal stability of these polymers can be attributed to the BPC structure, in addition the olefin functionality in polyarylether **9** and **11** might also give rise to its thermal resistance. Wagener has observed the same phenomena in some of the polymers his group has made, he states that some of the vinyl ether polymers which are a result of the ADMET polymerization have displayed a high thermal stability.[16] Our data analysis has also resulted in the same conclusion, while char yields are low for polyarylether **11** the heat release capacity is also low. The initial loss of mass in polymers **9** and **10**, which is not observed in polymer **11**, maybe a result of water or solvent, but the important result is the overall weight loss of the material (Figure 1).

Figure 1

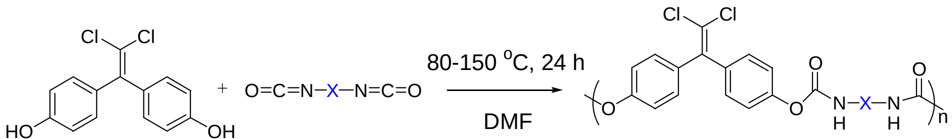


The flammability of the three polyarylethers **9, 10,** and **11** was measured using the standard UL-94 test for plastic flammability. All three samples obtained a V-0 rating when two sample bars were exposed to two, 10-second flame ignitions. All samples were mixed with 1 wt % PTFE as an anti-drip additive. It is important to note that the samples were tested without anti-drip additive, and did not burn but dripped excessively, making characterization impossible. An anti-drip additive was used to overcome this problem. The polymer samples all give good results without the need for a synergist such as antimony oxide to impart flame retardancy. It was observed that while these polymers where subjected to prolonged exposure to the Bunsen burner flame, the fire never consumed them. The UL-94 sample results can be seen Table 1.

4.5 Results and Discussion- BPC Polyurethanes

Our next approach to making flexible flame retardant thermoplastics has been to utilize urethane chemistry. Polyurethanes have found uses in application such as flexible foams and coatings. They are generally not considered good flame-retardants, but we thought that co-polymerizing them with BPC could yield a flexible flame-resistant polymer. Two different polymerization methods were tried. The first was a solution polymerization of various diisocyanate (HDI, MDI, TDI) and bisphenol C in dimethylformamide to make the BPC polyurethanes **13** (Polymerization 6).

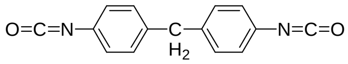
Polymerization 6

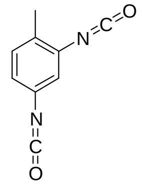


13

X = HDI (hexamethylenediisocyanate), MDI (methylenediisocyanate), TDI (toluenediisocyanate)

$O=C=N-(CH_2)_6-N=C=O$





These polymerizations resulted in medium to low molecular polymers. The next method for making the urethane polymer was a melt polymerization of each diisocyante and BPC. This method gave a hard and virtually insoluble polymer, making molecular weight measurements by GPC inaccurate. The flame resistant properties of the polymers from MDI and HDI were determined, and both showed good flame retardant characteristics, using the improvised pellet burn test. The polyurethane made with BPC and MDI showed the best results, since that it did not ignite after the flame was removed. These urethane polymer do not have a defined glass transition temperature so melt processing them into full bars was not pursued. The use of these polymers as heat resistance rigid foams is a possibility for future applications.

PCFC Results for the BPC polyurethanes.

Polymer	HR capacity (J/g K)	Total Heat (kJ/g)	Char yields (%)
Polyurethane (HDI)	498	19.3	8.4
Polyurethane (MDI)	135	10.6	22.4
Polyurethane (TDI)	188	17.6	12

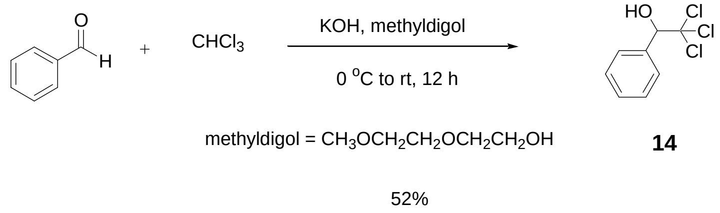
The HDI polyurethane has the highest heat release capacity while the MDI polyurethane has the lowest heat release capacity and the highest char yield. These are not the best results obtained for a flame retardant plastic, they provide a starting point in making new polyurethane foams more fire resistant.

4.6 Results and Discussion- Asymmetrical BPC Polymers

Vinyl addition polymer such as polyacrylate are not usually flame resistant, and therefore are not suitable options for flame retardant polymers. Using the excellent flame retardant characteristics of BPC molecule, we have made new asymmetric BPC (ABPC) monomers containing an easily polymerized acrylate functional group. Acrylate polymers are known for their resistance to heat, sunlight, and weathering properties which makes them excellent candidates for flame retardant polymers.[24] Our approach to increasing the flame retardancy of acrylate polymers was to incorporate BPC as a pendant group hanging off the acrylate skeleton. As I will show, this work has produced a flame retardant processible polymer that can be easily melted and molded. Such properties make the commercialization of the polymer more likely.

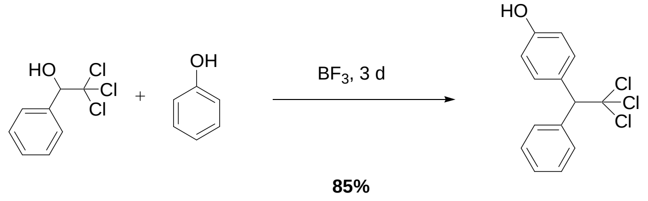
ABPC structures are made from inexpensive and readily available starting materials. The first step is to produce the trichloroethanol carbinol **14**. The carbinol is synthesized by slowly adding a solution of potassium hydroxide and methyldigol (diethylene glycol monomethylether) to a stirring solution of benzaldehyde and chloroform chilled at 0 °C (Reaction 5).[25]

Reaction 5



The resulting carbinol **14** was purified by vacuum distillation and subsequently coupled with phenol in the presence of BF_3 gas over several days to yield **15**.[25] This process requires several daily additions of BF_3 gas and mechanical stirring to mix the dark viscous product which is then purified by column chromatography (Reaction 6).

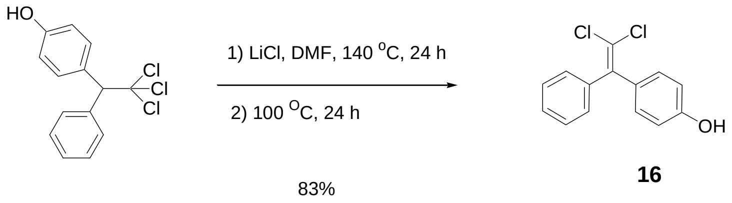
Reaction 6



15

The dehydrohalogenation of ABPC is done using the standard procedure of lithium chloride in DMF at 140 °C for 24 hours then slowly decreasing the heat to 100 °C, to yield the asymmetrical BPC analog **16** (Reaction 7).[1,26]

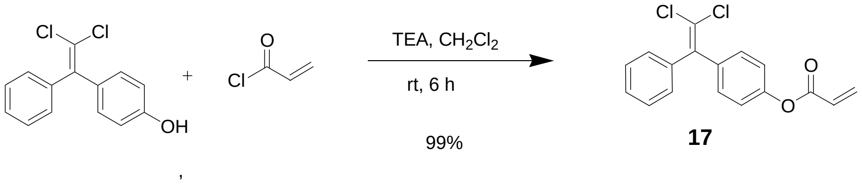
Reaction 7



16

The final step to afford the acrylate monomer is the addition of acryloyl chloride to a solution of ABPC and triethylamine in methylene chloride to produce the acrylate monomer **17** (Reaction 8).

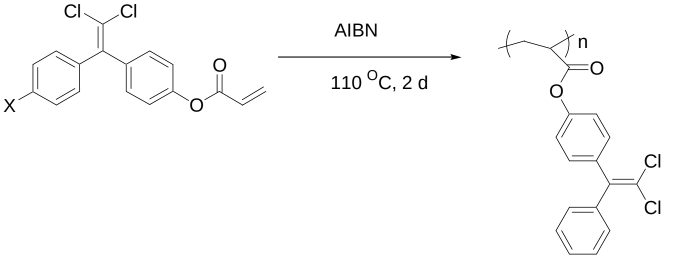
Reaction 8



17

The acrylate polymer **14** was made by a bulk polymerization catalyzed by 2,2'-azobisisobutyronitrile (AIBN) at 110 °C for 2 d (Polymerization 7)

Polymerization 7



18

The burn results for polymer **18** shows that it works well as a flame retardant material without the need for a synergist (Table 2). The polymer dripped but did not ignite the cotton when it was subjected to the UL-94 flame test and with the addition of 1 wt% PTFE did not drip at all. The PCFC results show that these polymers have a high heat release capacity, the polymer is considered to be a V-0 material according to the UL-94 test for flammability of plastic materials (Table 1).

PCFC result for the Polyacrylates.

Polymer	HR capacity (J/g K)	Total Heat (kJ/g)	Char yields (%)
Polyacrylate **18**; X = H	185	12	17.1
Polyacrylate; X = Cl	224	10	11

Table 1. HVUL-94 Burn Results

Additive	**First Ignition[a] (sec)**	**Observed Dripping[b]**	**Second Ignition[a] (sec)**	**Observed Dripping[b]**	**UL-94 Rating**
Polyarylether **9**, 1wt % PTFE	3, 0	No, No	0, 0	No, No	V-0
Polyarylether **10**, 1wt % PTFE	1, 6	No, No	3, 0	No, No	V-0
Polyarylether **11**, 1wt %PTFE	6, 0	No, No	0, 2	No, No	V-0
Polyarylether **9**, 10wt % ClPE	2, 5	No, No	6, 9	No, No	V-0
Polyacrylate **18**	0, 0	No, No	1, 1	No, Yes	V-0
Polyacrylate **18**, 1wt % PTFE	0, 0	No, No	0, 0	No, No	V-0

a Time to self-extinguishing in seconds after 1st, 2nd, 3rd 10 sec ignition. **b** Indicates that molten ABS did (Y) or did not (N) drip on to cotton patch underneath ignited bar during UL-94 test. **c** Indicates ignition of cotton patch underneath ignited bar of plastic. **d** Indicates time that only glowing, not flame occurred after re-application of flame. X indicates not enough bar remaining for 2nd ignition. * Wt % based on halogen content.

The flammability of the three polyarylethers (**9, 10** and **11)** and polyacrylate **18,** measured using the standard UL-94 test for plastic flammability, obtained a V-0 rating when two sample bars were exposed to two, 10-second flame ignitions. All sample were mixed with 1 wt % PTFE as an anti-drip additive. It is important to note that the samples were tested without anti-drip additive, and did not burn but dripped excessively, making characterization impossible; it is this reason that an anti-drip additive was used. The polymer samples all give good results without the need for a synergist, such as antimony oxide to impart flame retardancy. It was observed that while these polymers where subjected to prolonged exposure to the Bunsen burner flame, the fire never consumed them.

4.7 Experimental

General Procedures: All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Silica TLC plates were 250 μm thick, 40 F254 grade from EM Science. Silica gel was grade 60 (230-400 mesh) from EM Science. ^{1}H NMR spectra were observed at 400 MHz and ^{13}C NMR spectra were observed at 100 MHz on a Brüker Avance 400 spectrometer. ^{1}H chemical shifts (δ) are reported in ppm downfield from tetramethysilane. IR spectra were obtained on a Nicolet Avatar 360 FTIR. Gas chromatography experiments were performed on a Hewlett-Packard GC model 5890A. Thermal gravimetric analysis (TGA) was performed with a Perkin Elmer TGA7 or TA Q 50 from 30 - 900 °C at 10 °C/min under nitrogen. Differential scanning calorimetry

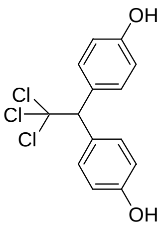
(DSC) was performed with a Perkin Elmer DSC7 or TA Q 10 using a 30 - 450 °C scanning window at 10 °C/min. under nitrogen. Polymer blending/extrusion was done with a Custom Scientific Instruments CSI-183MMX Mini-Max Blender/Extruder or with a Brabender Prep-Center using a type 6/2 mixer head or Thermo Haake Mini lab Rheomex CTW5 . An Atlas Electric HVUL-94 flame test station was used for the UL-94 flame tests. Melting points were obtained using a Büchi melting point apparatus. Reagent grade tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. Dry benzene, toluene, methylene chloride, and triethylamine were distilled over calcium hydride and under nitrogen. The molecular weights of the polymers have been analyzed on either a Waters GPC 150 C and/or a Polymer Laboratory GPC 220, using THF (40 ^{o}C, 1 mL/min) as the elutent. The GPC samples where analyzed by both refractive index and UV absorption. The synthesized polymers were compared with polystyrene standards with known molecular weights of 1000000, 900000, 435500, 96000, 30300, 22000, 5050, 1250, and 580. Unless otherwise stated, all other reagents were used as received. Mass spectrometry work was obtained from the Rice University Mass Spectrometry Laboratory.

General Procedure for Blending Flame Retardant Plastics & Additives in either the Brabender 30 ml Type 6/2 Mixing bowl or the Thermo Haake Mini lab Rheomex CTW5 – Prep Center.[27] The additives and plastics were weighed out in their respective amounts according to the wt % of additive. Heating temperatures for the blending bowl varied depending on the material involved. After the bowl had heated to the necessary processing temperature, the sample was poured quickly through the top opening of the Brabender while the blades were rotating at 50 RPM. The opening was then closed with the weighted handles and the sample was blended according to the type of flame retardant added. If a melt-blendable additive was used, the plastic and additives were blended for 10 min at 100 RPM. If a non-melt blendable additive was used the plastic and additives were blended for 10-30 min at 150 RPM. If fibrillare PTFE (Dupont PTFE 30, 60 % PTFE in an aqueous suspension; density = 1.3 g/mL) was used as an anti-drip additive, the resin and the PTFE were blended first for 10 min at 150 RPM. The flame-retardant additives were added and the plastic was blended again for 10 min at 150 RPM. After the blending was complete and the blades were stopped, the bowl was opened and molten plastic with the additives were removed with a bronze spatula. The plastic was then blended in the CSI-183MMX blender and extruded to give bars for the UL-94 test.

General Procedure for Extruding Plastic in the UL-94 Test Bars. The plastic removed from the Brabender mixing center was then broken into smaller pieces and inserted into the heated cup of the CSI-183MMX blender until the cup was full. The plastic and additives were heated until molten and extruded into a heated 1/8” thick × ½” wide × 3” long rectangular bar mold. Heating temperatures for the blend cup and the extrusion mold varied depending on the material involved.

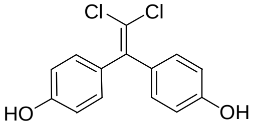
General Procedure for the HVUL-94 Burn Test. The flame resistance of the new polymers was tested using the horizontal and vertical Underwriters Laboratory test for flammability of plastic materials (HVUL-94). Two ⅛ inch thick × ½ inch wide × 3 inches long plastic (polymer + anti-drip additive) rectangular bars were used for this test. All flame tests were done in an Atlas Electric HVUL-94 flame test station. The methane tank pressure regulator was set to 20 psi. The pressure regulator on the HVUL-94 test station was set to 4.5 psi. The Bunsen burner flame height was 125 mm, and the height from the top of the Bunsen burner to the bottom of the test bar was 70 mm. The flame is blue with an intense blue inner cone with a flow rate 90 cc/min. All test bars underwent two trials; each trial consisting of ignition for 10 seconds followed by flame removal and a recording of the time for the bar to be considered self-extinguished.

General Procedure for the Pyrolysis Combustion Flow Calorimetry (PCFC).[28,29] PCFC measurements were taken using 0.1-0.2 mg of the polymer sample with an interface temperature just below the onset of decomposition. The samples were pyrolyzed to a temperature of 930 °C at 4.3 ^{o}C/s in a nitrogen atmosphere. The polymer was then completely combusted at 900 °C. The sample results are an average of five measurements.[28,29] The PCFC is a new method used to characterize the potential flame retardancy of a polymeric material. It gives three important data points that are used to evaluate the materials performance: 1. Heat Release Capacity, a calculated variable derived from the polymeric structure, this is a true material property which is dependent upon thermodynamic state variables, independent of sample size and heating rate.[28,29] 2. Total Heat Release, is measured value that is derived from the controlled pyrolysis of the polymer in an inert gas (to avoid oxidizing the char). The fuel gas is then mixed with oxygen at elevated temperatures (900 °C) and the heat of combustion is measured.[28,29] 3. Char yields are important because char does not burn and helps to add an insulating layer between the flame front and the polymeric fuel. It has been shown that the data obtained from PCFC measurements and correlates well with other pyrolysis methods such as, Cone Calorimetry, UL-94 test for flammability of plastic materials, and oxygen bomb calorimetry.[30]



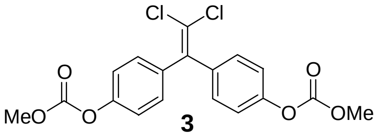
1

2,2-Bis(p-hydroxyphenyl)-1,1,1-Trichloroethane (1).[1] To a 1 L round bottom flask, equipped with a mechanical stirrer, thermometer, addition funnel, and purged with nitrogen, was added phenol (131 g, 1. 3 mol), chloral hydrate (104 g, 0.63 mol) and acetic acid (120 mL). The reaction was sealed under nitrogen with a septum and placed in a cooling bath at 0 °C. Concentrated sulfuric acid (60 mL) and acetic acid (60 mL) was added drop-wise via the addition funnel, over 90 min period. Then an additional 150 mL of sulfuric acid was added to the reaction mixture dropwise at a rate so that the internal temperature of the reaction never rose above 5 °C. The mixture was then allowed to warm to room temperature overnight (12 h). The reaction mixture was then quenched with ice and water and diluted to twice its volume. The precipitated powder was then filtered through a fritted filter and washed with copious amounts of water (3 L) to remove all excess acid. The resulting solid was then dried for 24 h in a vacuum oven at 95 °C. MP 204-206 °C. FTIR (KBr) 3215, 1894, 1606, 1510, 1449, 1369, 1246, 1179, 1113, 1020, 827, 751, 710, 576, 540. ^{1}H NMR (400 MHz, CD_3OD) δ 7.45 (dt, J = 8.62, 2.43 Hz, 4 H), 6.74 (dt, J =8.73, 2.54 Hz, 4 H), 4.28 (s, 1 H).



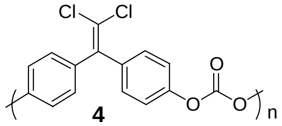
2

2,2-Bis(p-hydroxyphenyl)-1,1-dichloroethylene (2).[1] To a 2 L round bottom flask, equipped with a stir bar and reflux condensor and purged with nitrogen was added **1**, LiCl (0.5 equivalents), and DMF (1 L). The flask was then sealed under nitrogen with a septum and heated to 140 °C for 16 h. The reaction was then cooled to 100 °C for another 16 h. The heat was removed and the mixture was then allowed to cool to room temperature. The reaction mixture was diluted with a large amount of water (3× its volume) to precipitate the product. The resulting solid was filtered through a fritted funnel and washed with copious amounts of water (2 – 3 L) to remove the DMF. The product was dried in a vacuum oven for 24 at 60 ^{o}C. FTIR (KBr) 3129, 1594, 1507, 1437, 1229, 1169, 973, 863, 833, 772, 592, 556. ^{1}H NMR (400 MHz, CD_3OD) δ 7.07 (dt, J =8.77, 2.12 Hz, 4 H), 6.74 (dt, J =8.76, 2.11 Hz, 4H).



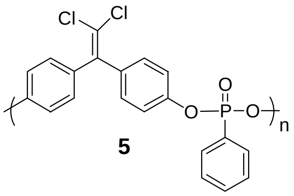
3

2,2-Bis(p-methylphenylcarbonate)-1,1-dichloroethylene (3).[20] To a 250 mL round bottom flask equipped with a stir bar and purged with nitrogen was added **2** (2.81 g, 10 mmol). The flask was then sealed under nitrogen with a septum and cooled to 0 °C. Triethylamine (3.09 mL, 40 mmol) and dry THF (100 mL) were added via syringe. Methyl chloroformate (3.09 mL, 40 mmol) was added slowly, drop-wise, via syringe to the reaction. The reaction was allowed to warm to room temperature and stirred for 24 h. The mixture was then poured through filter paper and the filtrate was condensed via rotary evaporation. The residue was introduced drop-wise into 500 mL of water and stirred for 1 h. The resulting precipitate was then collected by filtration. This solid was dried in vacuo for 24 h. FTIR (KBr) 2960, 1758, 1598, 1508, 1441, 1407, 1267, 1217, 1058, 1014, 933, 863, 778, 743, 697, 623, 539, 510. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dt, J = 8.78, 2.32 Hz, 4 H), 7.16 (dt, J =8.81, 2.36 Hz, 4 H), 3.91 (s, 6 H).



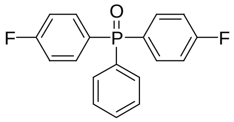
4

Poly[2,2-bis(*p*-phenylcarbonate)-1,1-dichloroethylene] (4).[20] To a 50 mL round bottom flask equipped with a stir bar and purged with nitrogen was added **3** (3.69 g, 9.28 mmol) and dibutyltinoxide (0.011 g, 0.046 mmol). The flask was sealed under nitrogen with a septum. The reaction was heated to 160 °C. After 2 h the mixture was then evacuated (0.5 mm Hg) and the temperature was to 230 °C for 2.5 h. The mixture was dissolved in a minimum amount of chloroform and precipitated with methanol. Methanol was removed from the polymer by placing the product in a vacuum desiccators for 24 h. FTIR (KBr) 1774, 1504, 1223, 1189, 1160, 1017, 862, 768, 515. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.31 (m, 4 H), 7.27-7.25 (m, 4 H). Mw: 14600; Mn: 4650.



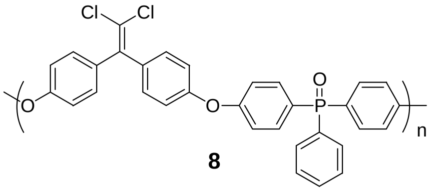
5

Poly[2,2-bis(*p*-phenylphosphate)-1,1-dichloroethylene] (5). To a 250 mL round bottom flask equipped with a stir bar and reflux condenser and purged with nitrogen was added **2** (7.04 g, 25 mmol). The flask was sealed with a septum, evacuated, and backfilled with nitrogen (3×). Triethylamine (6.21 mL, 52.5 mmol), toluene (70 mL), and THF (30 mL) were added via syringe and allowed to stir at room temp for an hour. To a separate 25 mL pear shaped flask that was sealed with a septum, evacuated, and backfilled with nitrogen (3×) was added phenylphosphonic dichloride and toluene (15 mL). This solution was then added to the 250 mL flask dropwise via cannula. An additional (15 mL) of toluene was added to the pear shaped flask. This rinse was added dropwise to the 250 mL flask via cannula. The reaction was heated to reflux for 24 h. The cooled mixture were dissolved in methylene chloride and precipitated as a resin in methanol. The methanol was decanted off and the resin was redissolved in methylene chloride and transferred to a clean flask. The solvent was removed via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. FTIR (KBr) 3059, 1599, 1502, 1273, 1196, 1164, 1129, 920, 742, 692, 591, 508. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.91 (m, 2 H), 7.60-7.51 (m, 4 H), 7.49-7.46 (m, 4 H), 7.24-7.11 (m, 4 H). Mw: 6800; Mn: 3000.



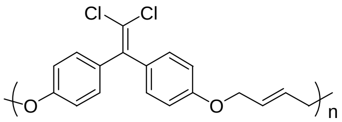
7

Bis(4-fluorophenyl)phenylphosphine oxide (7).[22] To a 100 mL 3 neck round bottom flask equipped with stir bar and reflux condensor with argon was sealed with septa, then flame dried, evacuated and backfilled with argon (3×). Magnesium (100 mmol, 2.4 g) was added to the flask and the septum was replaced and the reaction flask was evacuated and back filled to replace the atmosphere (3×). Diethyl ether (50 mL) was added to the flask via syringe and then 1-bromo-4-fluorobenzene (50 mmol, 8.75 g) was added to the reaction flask with constant stirring. The reaction mixture boiled vigorously. An ice bath was used to keep the reaction mixture from boiling over. After the boiling had decreased, the reaction mixture was heated to reflux for 30 minutes. The mixture was then allowed to cool to room temperature. To a separate 25 mL pear shaped flask that was evacuated and backfilled with argon (3×) was added dichlorophenylphosphonate (100 mmol, 14.2 mL) and diethyl ether (20 mL, 2×). This mixture was then added to the 100 mL reaction flask slowly drop-wise via cannula at in an ice bath at 0 °C. After the vigorous reaction slowed down the reaction was heated to reflux for an hour. The reaction was quenched with water and diluted with ether. The two layers where separated and the organic layer was washed with water and brine solution (3×). The organic layer was dried over magnesium sulfate and filtered through filter paper. Solvent was removed via rotary evaporation. The final product was isolated via column chromatography (10:1, chloroform: ethyl acetate). FTIR (KBr) 3450, 3058, 1909, 1666, 1587, 1491, 1432, 1393, 1194, 1113, 1006, 828, 710, 621, 478. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (m, 5 H), 7.55 (m, 1 H), 7.49 (m, 2 H), 7.21 (m, 4 H).



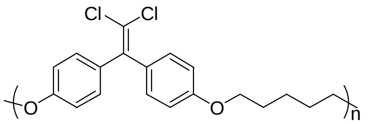
8

Polyphosphoroether (8).[11] To a 250 mL three neck round bottom flask equipped with a mechanical stirrer, Claisen adapter, dean stark trap, and condensor was added **2** (10 mmol, 2.81 g), Bis(4-fluorophenyl)phenylphosphine oxide (10 mmol, 3.14 g), and potassium carbonate (11.5 mmol, 1.59 g) in the dry box. The reaction flask was removed from the dry box and setup in the hood. N, N-dimethylacetamide (57 mmol, 54 mL) and toluene (50 mL) was added via syringe. The reaction was heated to reflux for 2 days to azeotrope the water from the reaction. The reaction was then cooled to room temperature and the product was precipitated in methanol. FTIR (KBr) 3401, 3047, 1588, 1496, 1238, 1168, 1112, 865, 830, 694, 541. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61(m), 7.38 (m), 7.22 (m), 7.0 (m). Mw: 4000; Mn: 3500.



9

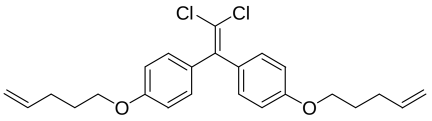
Polyether (9).[12] It is important to note that the order of addition of the reagents is critical for optimum reaction conditions. To a 500 mL three neck round bottom flask equipped with a mechanical stirrer and a reflux condensor was added **2** (10 mmol, 2.81 g), and sodium hydroxide solution (6 M, 33 mL), tertiarybutlyammonium hydrogen sulfate (TBAH) (2 mmol, 0.68 g), *o*-dichlorobenzene (33 mL), and finally 1,4-dichloro-2-butene (10 mmol, 1.057 mL). The reaction was heated to reflux for 2 days. The reaction was then cooled and separated into two layers and the organic layer was diluted with toluene. The organic layer was washed with slightly acidic aqueous solution (HCL 0.1 N) and with water (2×). The product was then precipitated by pouring the organic layer in MeOH. FTIR (KBr) 3427, 3036, 2862, 1603, 1506, 1296, 1237, 1171, 1084, 1010, 972, 828, 611. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.5 Hz, 4 H), 6.85 (d, *J* = 8.5 Hz, 4 H), 6.06 (s, 2 H), 4.55 (s, 4 H). Mw: 27,000; Mn: 5800. T_g: 80 °C.



10

Polyether (10).[12] It is important to note that order of addition of the reagents is critical for optimum reaction conditions. To a 500 mL three neck round bottom flask equipped with a mechanical stirrer and a reflux condensor was added **2** (10 mmol, 2.81 g) and sodium hydroxide solution (6 M, 33 mL), tertiarybutlyammonium hydrogen sulfate (TBAH) (2 mmol, 0.68 g), *o*-dichlorobenzene (33 mL), and finally 1,5-dibromopentane

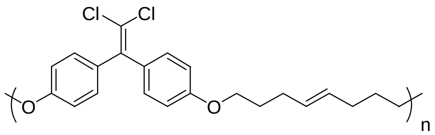
(10 mmol, 1.06 mL). The reaction was heated to reflux for 2 days. The reaction was then cooled and separated into two layers and diluted with toluene. The organic layer was washed with slightly acidic aqueous solution (HCL 0.1 N) and with water (2×). The product was then precipitated by pouring the organic layer in MeOH. FTIR (KBr) 3427, 2939, 1605, 1508, 1244, 1172, 1025, 831, 611, 461. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.1 (d, J = 8.8 Hz, 4 H), 6.8 (d, J = 8.7, 4 H), 3.9 (t, J = 6.4), 1.8 (m, 4 H), 1.6 (m, 2 H). Mw: 27,000; Mn: 6800. T_g: 69 °C.



13

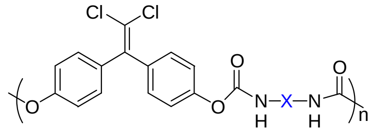
1,1-dichloro-2,2-bis(*p*-oxy-4-pentenephenyl)ethylene (13). To a 500 mL round bottom flask equipped with a stir bar and reflux condensor was added **2** (40 mmol, 11.25 g), potassium carbonate (200 mmol, 27.64 g). The reaction was sealed with a septa under nitrogen. The reaction mixture was then evacuated and backfilled with nitrogen (3×). Acetone (250 mL) and 5-bromo-1-pentene (100 mmol, 11.8 mL) was added via syringe. The reaction was heated to reflux for 24 hours. The reaction was then diluted with ethyl acetate and the organic layer was washed with water (3×). The organic layer was then dried over magnesium sulfate and filtered through filter paper. The solvent was then removed via rotary evaporation and dried *in vacuo* overnight. The product was purified in MeOH several times. Mp 62 °C. FTIR (KBr) 2938, 2868, 1603, 1509, 1464, 1397, 1243, 1169, 1117, 1022, 910, 850, 773, 627, 528. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (dt, J = 8.9, 2.5 Hz, 4 H), 6.8 (dt, J = 8.9, 2.5, 4 H), 5.85 (ddt, J = 17.0, 10.3, 6.7 Hz, 2 H), 5.06 (dtd, 17.1, 1.7, 1.7 Hz, 2 H), 4.9 (dtd, J = 10.2, 1.6, 1.6 Hz, 2 H), 3.9 (t, J = 6.4 Hz, 4

H), 2.2 (q, *J* = 7.3 Hz, 4 H), 1.8 (quin, *J* = 6.9 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 139.8, 137.8, 131.9, 130.8, 117.5, 115.2, 114.0, 67.1, 30.1, 28.4. HRMS Calc'd for $C_{24}H_{26}Cl_2O_2$: 416.130986. Found: 416.130986. 0.42 ppm error.

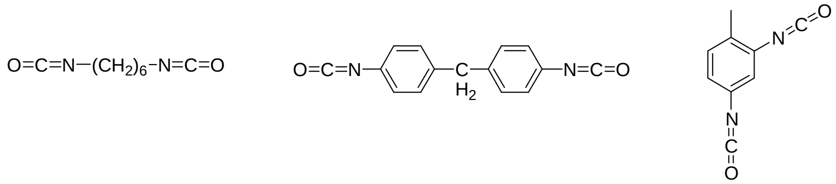


11

Polyether (11).[13-15,23] To a 100 mL shlenk flask equipped with a stir a bar and reflux condensor, was added **9** (20 mmol, 8.33 g) and Grubb's catalyst (2nd Generation; 0.2 mmol, 170 mg) in the dry box. The reaction hardware was sealed with a septa and removed from the dry box and setup in the hood then evacuated and backfilled with nitrogen (3×). Toluene (20 mL) was added via syringe and the reaction was heated to 55 °C for 5 days under a positive pressure of argon to remove ethylene. Opening the flask to air and diluting with toluene quenched the reaction. The product was then precipitated by pouring the organic layer in MeOH. FTIR (KBr) 3429, 3034, 2934, 2538, 2358, 1888, 1604, 1507, 1466, 1389, 1249, 1172, 969, 827, 725, 610, 525. ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (m), 6.82 (m), 5.84 (m), 5.50 (m), 5.03 (m), 3.95 (m), 2.50 (m), 2.22 (m), 1.83 (m). Mw: 19000; Mn: 8500. T_g: 42 °C.

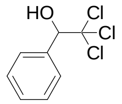


13



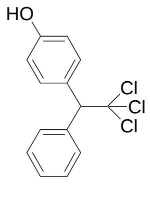
X = HDI (hexamethylenediisocyanate), MDI (methylenediisocyanate), TDI (toluenediisocyanate)

General Procedure for BPC Polyurethanes (13). To a 250 mL round bottom flask equipped with a stir bar was added **2** (10 mmol, 2.81 g). The flask was then sealed with a septa then evacuated and backfilled with nitrogen (3×). Dimethylformamide (50 mL) and the diisocyante HDI, MDI, or TDI; 10 mmol, 1.65 mL) were. The reaction mixture was heated to 80-155 °C for two days. The product was then precipitated by pouring the organic layer in MeOH. X = HDI, FTIR (KBr) 3415, 2324, 1741, 1660, 1504, 1386, 1199, 858. X = MDI, FTIR (KBr) 3413, 1741, 1601, 1497, 1406, 1309, 1191, 1003, 851, 808, 751, 505. X = TDI, FTIR (KBr) 3297, 2929, 2359, 1741, 1622, 1602, 1539, 1501, 1414, 1198, 1100, 1005, 856. ^{1}H NMR (400 MHz, $CDCl_3$) δ Not soluble. X = HDI, Mw: 39,000; Mn: 12,200. X = MDI, Mw: 27,800; Mn: 11,150. X = TDI, Mw: 6,400; Mn: 2,175.



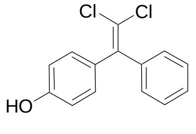
14

2,2,2-Trichloro-1-phenyl-ethanol (14).[25] To a 250 mL three necked round bottom flask equipped with a stir bar, addition funnel, and purged with nitrogen was added benzaldehyde and chloroform. Potassium hydroxide (1.2 equivalents) (KOH) dissolved in diethylene glycol monomethyl ether (methyldigol) was added dropwise via the addition funnel. The reaction mixture was cooled to 0 °C while the KOH and methyldigol was added slowly over 6 h. The reaction was then allowed to warm to room temperature with stirring for 12 h. The reaction was then poured into cold water and diluted with methylene chloride. The two layers were separated and the organic layer was washed with HCl (0.1 N), and H_2O (2x). The organic layer was dried over magnesium and filtered through filter paper. Solvent was removed via rotary evaporation. The final product was isolated via vacuum distillation 85 – 110 °C (1 atm). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6 (m, 2H), 7.4 (m, 3H), 5.2 (s, 1H), 3.2 (s, 1H).



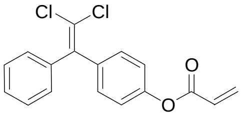
15

2-(*p*-hydroxyphenyl)-2'-(phenyl)-1,1,1-trichloroethane (15).[25] To a 100 mL three necked round bottom flask, equipped with a stir bar, mechanical stirrer and a gas inlet tube was added **10** and phenol (0.98 equivalents), the flask was sealed with a septa and boron trifluoride (BF_3) was bubbled into the solution for 20 m with constant stirring. The thick solution was stirred vigorously and BF_3 was bubbled into the reaction mixture every 12 h for 3 to 5 days. The reaction was then poured into cold water and diluted with ethyl acetate. The two layers were separated and the organic layer was washed with K_2CO_3 (1 M, 2x) and H_2O (2x). The organic layer was dried over magnesium and filtered through filter paper. Solvent was removed via rotary evaporation. The final product was isolated via column chromatography (9:1; hexane/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6 (dt, *J* = 6.9, 1.5 Hz, 2H), 7.4 (dt, *J* = 8.7, 2.5 Hz, 2H), 7.3 (m, 3H), 6.8 (dt *J* = 8.7, 2.6, 2H), 5.0 (s, 1H), 4.7 (s, 1H).



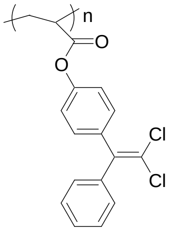
16

2-(*p*-hydroxyphenyl)-2’-(phenyl)-1,1-dichloroethane (16). To a 250 mL round bottom flask, equipped with a stir bar and reflux condensor and purged with nitrogen, was added 2-(*p*-hydroxyphenyl)-2’-(phenyl)-1,1,1-Trichloroethane, KOH (7 equivalents), and MeOH (150 mL). The flask was then sealed under nitrogen with a septum and heated to reflux for 24 h. The reaction mixture was then diluted with ethyl acetate. The organic layer was washed with H_2O (3×) and the aqueous layer was then extracted with ethyl acetate (3×). The organic layers were combined and dried over magnesium sulfate and filtered through filter paper. Solvent was then removed via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. MP 140-143 °C. FTIR (KBr) 3153, 2357, 1600, 1504, 1439, 1243, 1211, 1171, 970, 855, 740, 698, 629, 570. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 (m, 5H), 7.1 (dt, *J* = 8.8, 2.5 Hz, 2H), 6.8 (dt, *J* = 8.8, 2.5 Hz, 2H), 4.8 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 140.0, 131.0, 129.3, 128.2, 127.9, 115.0. HRMS Calc’d for $C_{14}H_{10}Cl_2O_1$: 264.0109. Found: 264.0105; 1.24 ppm error.



17

Acrylic acid [2-(*p*-hydroxyphenyl)-2’-(phenyl)-1,1-dichloroethane] ester (17). To a 100 mL round bottom flask equipped with a stir bar and purged with nitrogen was added **16.** The reaction flask was evacuated and backfilled with nitrogen (3×). Methylene chloride and triethylamine (1.5 equivalents) were added to the flask via syringe and cooled on an ice bath. Acryloyl chloride (1.1 equivalents) was slowly added dropwise via syringe. The ice bath was removed and the resulting solution was allowed to warm to room temperature and stirred for 12 h. The reaction was then quenched by opening the flask to air, and the reaction mixture was rotovaped to dryness. The final product was isolated via column chromatography (9:1; Hexane/Ethyl acetate). MP 81-84 °C. FTIR (KBr) 3456, 1737, 1587, 1496, 1405, 1160, 976, 850, 753, 688, 622, 523. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3(m, 7H), 7.1 (dt, *J* = 8.8, 2.4 Hz, 2H), 6.6 (dd, *J* = 17.4, 1.2 Hz, 1H), 6.3 (q, *J* = 9.2 Hz, 1 H), 6.0 (dd, *J* = 10.4, 1.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 150.5, 140.1, 139.7, 137.3, 133.2, 131.0, 129.7, 128.7, 128.5, 128.2, 121.8, 120.2. HRMS Calc'd for $C_{17}H_{12}Cl_2O_2$: 318.0214. Found: 318.0218; 1.30 ppm error.



18

Polyacrylate (18). To a 100 mL round bottom flask equipped with a stir bar was added the acrylate monomer **17** and 2,2'-azobisisobutyronitrile (AIBN: 1000/1; monomer/initiator) and sealed with a septa under nitrogen. The reaction flask was evacuated and backfilled with nitrogen (3×). The reaction mixture was then placed in an oil bath at 110 °C and stirred for 2 d. The reaction was then cooled to room temperature, dissolved in chloroform. The product was then precipitated by pouring the chloroform solution in MeOH. FTIR (KBr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (m, 4H), 6.9 (m, 5H), 2.8 (m, 1H), 2.3 (m, 1H), 1.9 (m, 1H). Mw: 607,300; Mn: 321,200. T_g: 70 °C. Elem. Anal. Calc'd for $C_{17}H_{12}Cl_2O_2$: C 64.1; H 3.4; Found: C 49.1; H 2.9.

4.8 References

(1) Stewart, J. R; Ph.D. Thesis, University of Massachusetts: Amherst, Massachusetts, **2000**.

(2) Factor, A.; Orlando, C. M. *J. Poly. Sci.: Poly. Chem. Ed.* **1980**, *18*, 579-592.

(3) Russanov, A. L.; Korshak, V. V. *Uspekhi Khimii* **1989**, *58*, 1006-1031.

(4) Russanov, A. L. *Prog. Polym. Sci.* **1994**, *19*, 589-662.

(5) Jurs, J. L.; Mickelson, E. T.; Abramowitz, D. B.; Tour, J. M. In *International SAMPE Symposium*: Long Beach, California, 2000.

(6) Jurs, J. L.; Tour, J. M. *International Aircraft Fire and Cabin Safety Research Conference*: Atlantic City, New Jersey, 2001.

(7) Jurs, J. L.; Tour, J. M. *Polymer* **2003**, *44*.

(8) Lyon, R. *International Aircraft Fire and Cabin Safety Research*: Atlantic City, New Jersey, 2001.

(9) Zang, H.; Westmoreland, P. R.; Farris, R. J.; Coughlin, E. B.; Plichata, A. *Polymer* **2002**, *43*, 5463-5472.

(10) Stoliariv, S. I.; Westmoreland, P. R. *International Aircraft Fire & Cabin Safety Research Conference*; Atlantic City, New Jersey, 2001.

(11) Riley, D. J.; Gungor, A.; Scrinivasan, S. A.; Sankarapandian, M.; Tchatchoua, C.; Muggli, M. W.; Ward, T. C.; McGrath, J. E. *Poly. Eng. and Sci.* **1997**, *37*, 1501-1511.

(12) Boileau, S. *New Methods for Polymer Synthesis*; Plenum Press: New York, 1992.

(13) Wagener, K. B.; Boncella, J. M.; Nel, J. G. *Marcromolecules* **1991**, *24*, 2649-2657.

(14) Wagener, K. B.; Brzezinska, K. *Marcromolecules* **1991**, *24*, 5273-5277.

(15) Wagener, K. B.; Lehman, S. E. *Marcromolecules* **2002**, *35*, 48-53.

(16) Lenz, R. W. *Organic Chemistry of Synthetic High Polymers*; Interscience Publishers: New York, 1967.

(17) Hubacher, M. H. *J. Org. Chem* **1959**, *24*, 1949-1951.

(18) Hubacher, M. H.; Doernberg, S.; Horner, A. *J. Am. Pharm. Assoc.* **1953**, *42*, 23.

(19) Mark, V.; Hedges, C. V. In *U.S. Patent* 4182838; General Electric Company: United States, 1980.

(20) Haba, O.; Ueda, M.; Kuze, S. *J. Poly. Sci.: Part A: Polymer Chem.* **1999**, *37*, 2087-2093.

(21) Troitzsch, J. *International Plastics Flammability Handbook*; 2nd Ed. ed.; Hanser Publishing: New York, 1990.

(22) Whitaker, C. M.; Kott, K. L.; McMahon, R. J. *J. Org. Chem* **1995**, *60*, 3499-3508.

(23) Wagener, K. B.; Brzezinska, K.; Anderson, J. D.; Younkin, T. R.; Steppe, K.; DeBoer, W. *Marcromolecules* **1997**, *30*, 7363-7369.

(24) Horn, M. B. *Acrylic Resins*; 2 nd ed.; Reinhold Publishing Corporation: New York, 1962.

(25) Goodford, P. J.; Hudson, A. T.; Sheppey, G. C.; Wootton, R. *J. Med. Chem.* **1976**, *19*, 1239-1247.

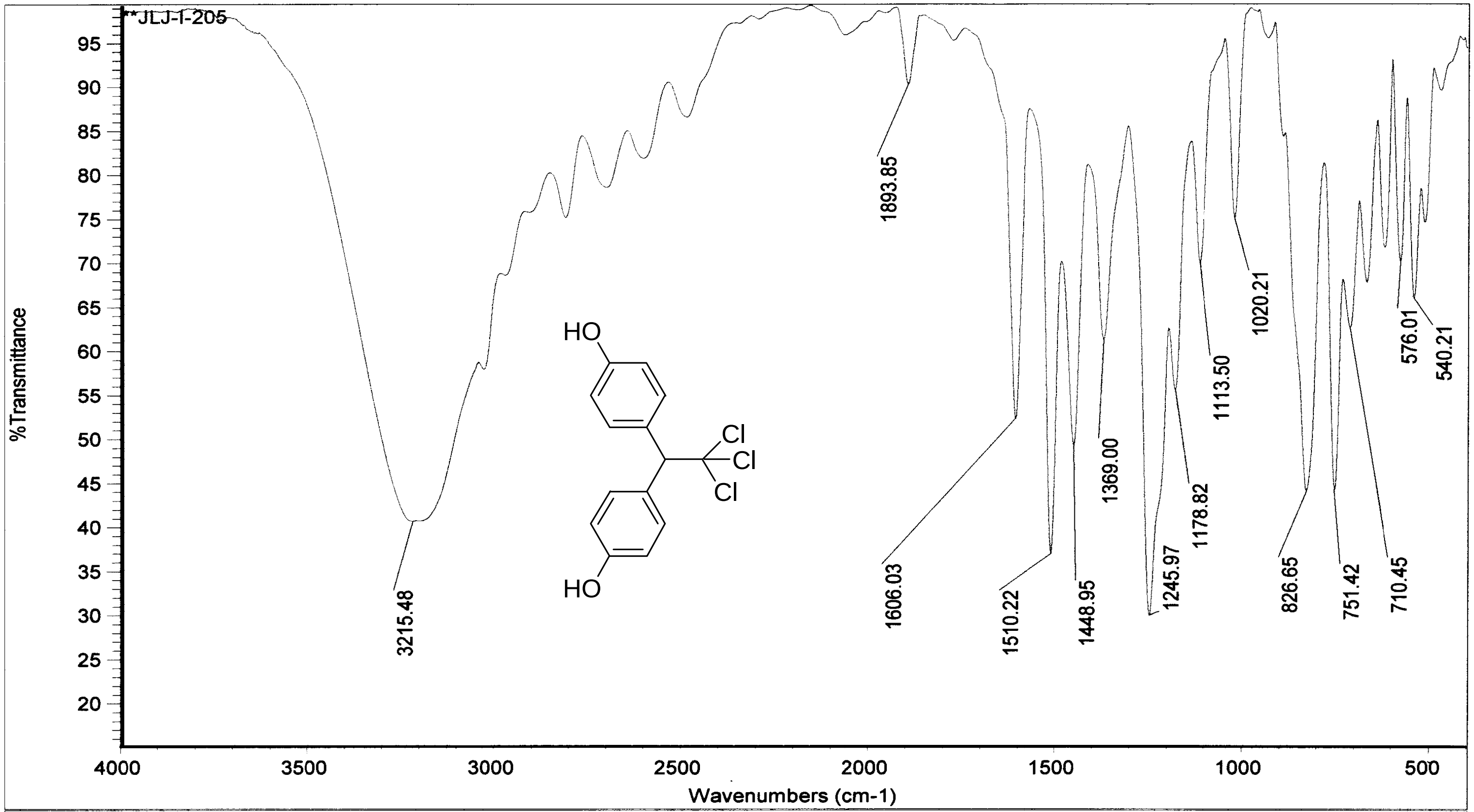
(26) Sundstrom, G. *J. Argic. Food Chem.* **1977**, *25*, 18-21.

(27) Morgan, A. B. In; Ph.D. Thesis, University of South Carolina: Columbia, **1998**.

(28) Lyon, R. E.; Walters, R. N. "A Microscale Combustion Calorimeter," Federal Aviation Administration, DOT/FAA/AR-01/117, 2002.

(29) Walters, R. N.; Lyon, R. E. In *International Aircraft Fire & Cabin Safety Research Conference*; FAA: Atlantic City New Jersey, 2001.

(30) Filipczak, R.; Lyon, R. E. "The Coorelation of Heat Release Calorimetry Measurements," Federal Aviation Administration, DOT/FAA/AR-TN02/104, 2002.

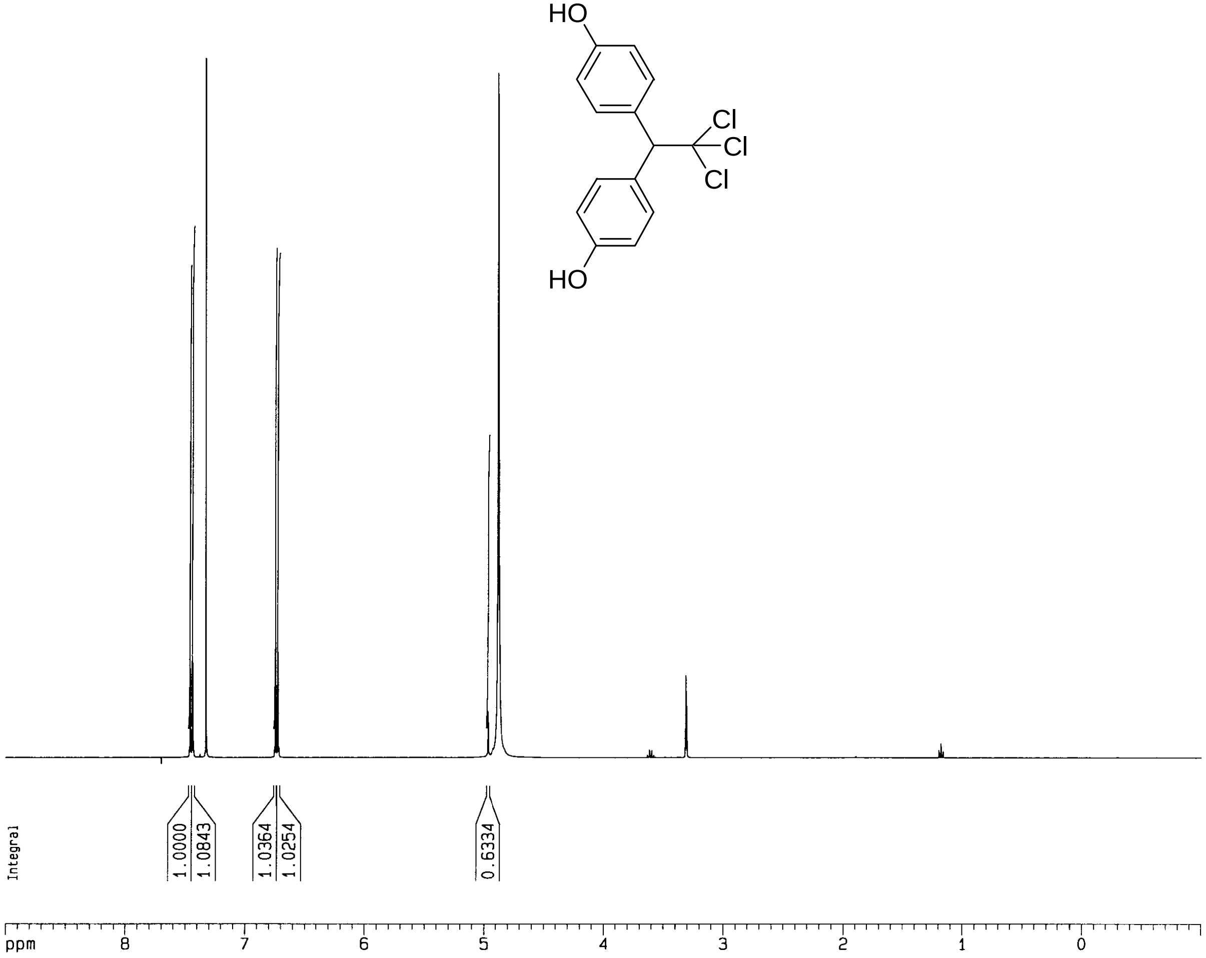


Date: Thu Jun 22 13:38:13 2000 **JLJ-I-205

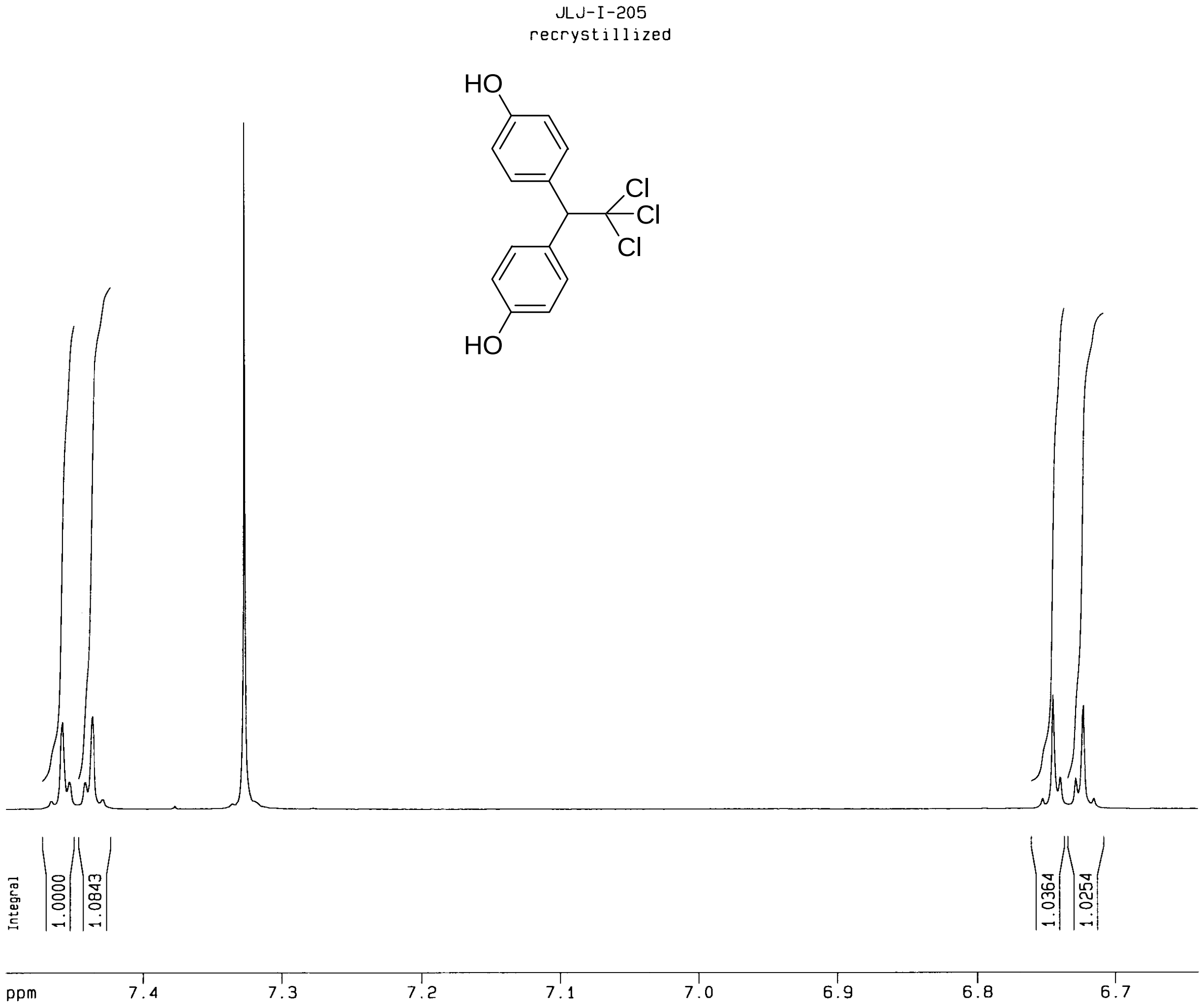
Scans: 20

Resolution: 4.000

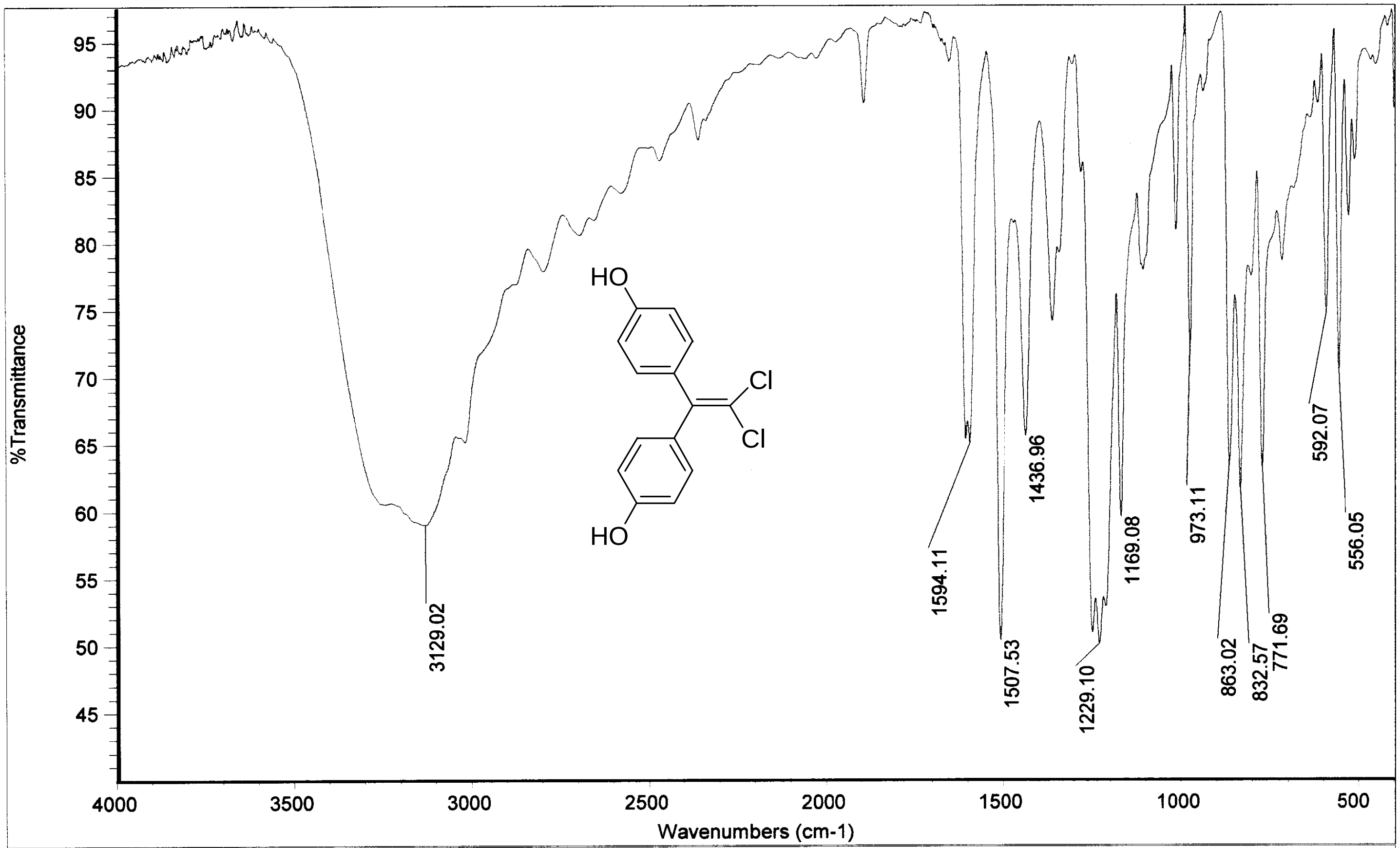
JLJ-I-205
recrystillized



```
Current Data Parameters
NAME          JLJ-I-205
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20000617
Time              13.19
INSTRUM           spect
PROBHD    5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT            MeOH
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                  256
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 =========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1293890 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               9.000 ppm
F1              3601.16 Hz
F2P              -1.000 ppm
F2              -400.13 Hz
PPMCM           0.50000 ppm/cm
HZCM          200.06470 Hz/cm
```



```
Current Data Parameters
NAME           JLJ-I-205
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20000617
Time               13.19
INSTRUM            spect
PROBHD   5 mm BBO BB-1
PULPROG             zg30
TD                 65536
SOLVENT             MeOH
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                   256
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1293890 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.499 ppm
F1               3000.45 Hz
F2P                6.641 ppm
F2               2657.15 Hz
PPMCM            0.04290 ppm/cm
HZCM            17.16537 Hz/cm
```

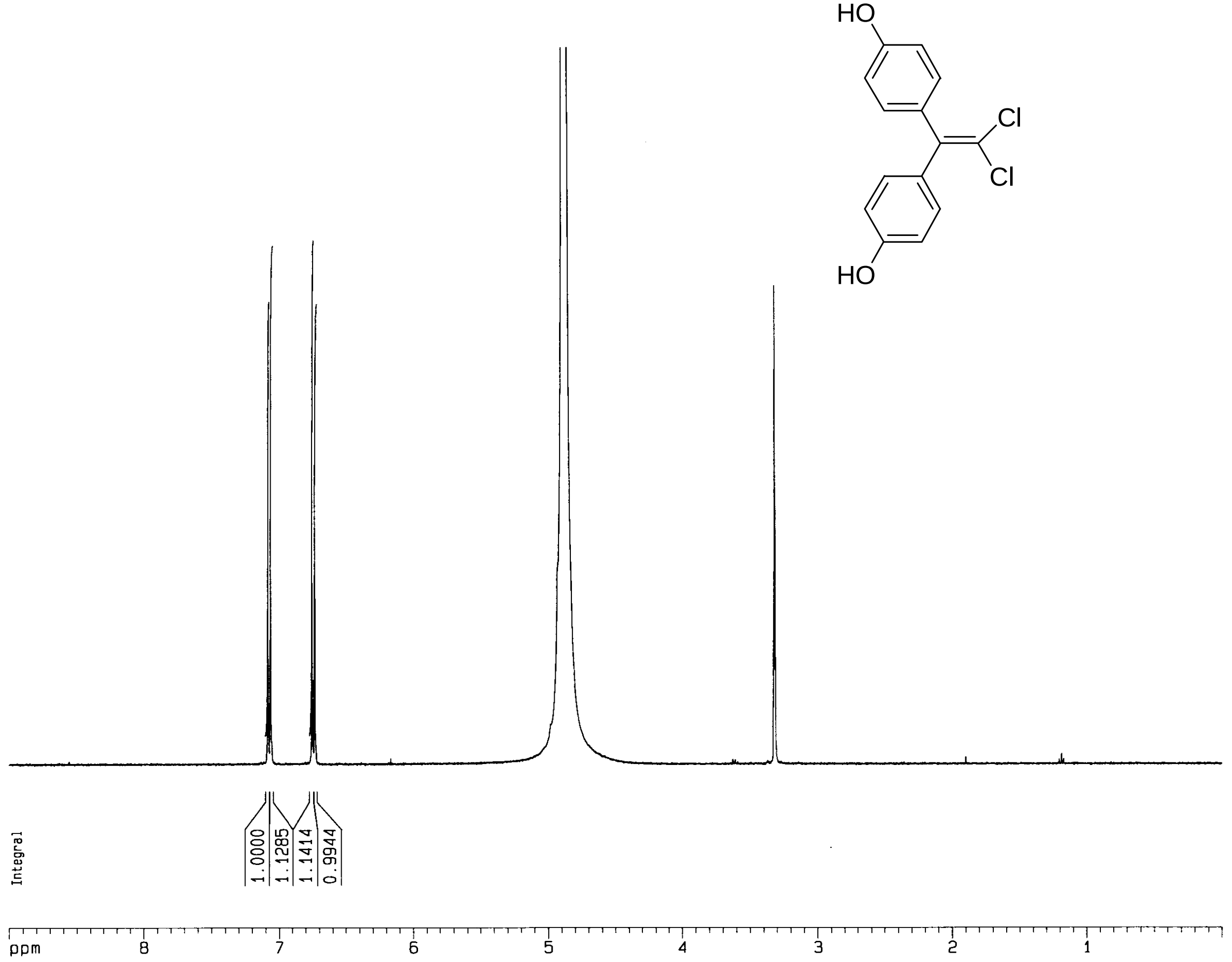


Date: Wed Sep 20 13:34:44 2000 ***JLJ-I-223

Scans: 20

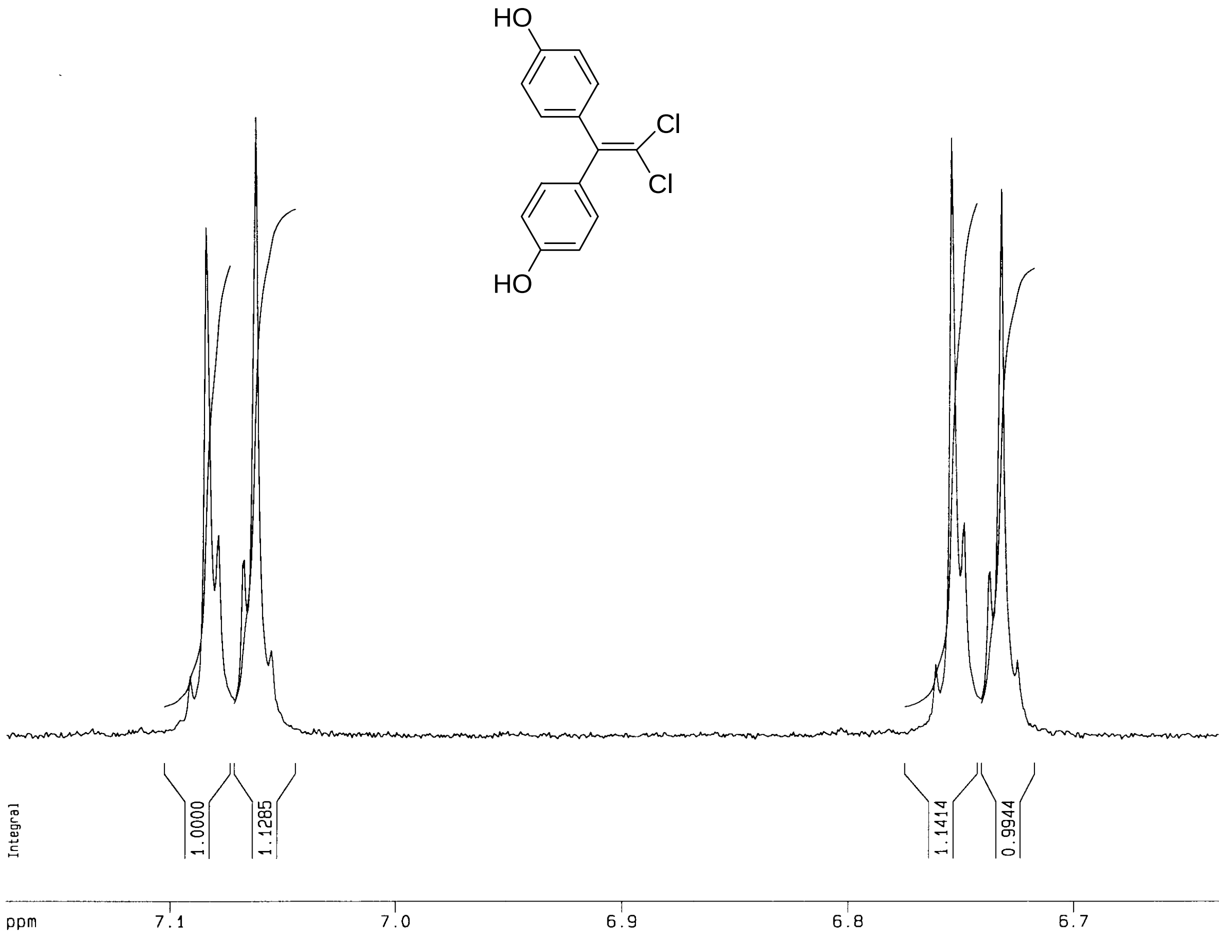
Resolution: 2.000

JLJ-I-223
recrystillized

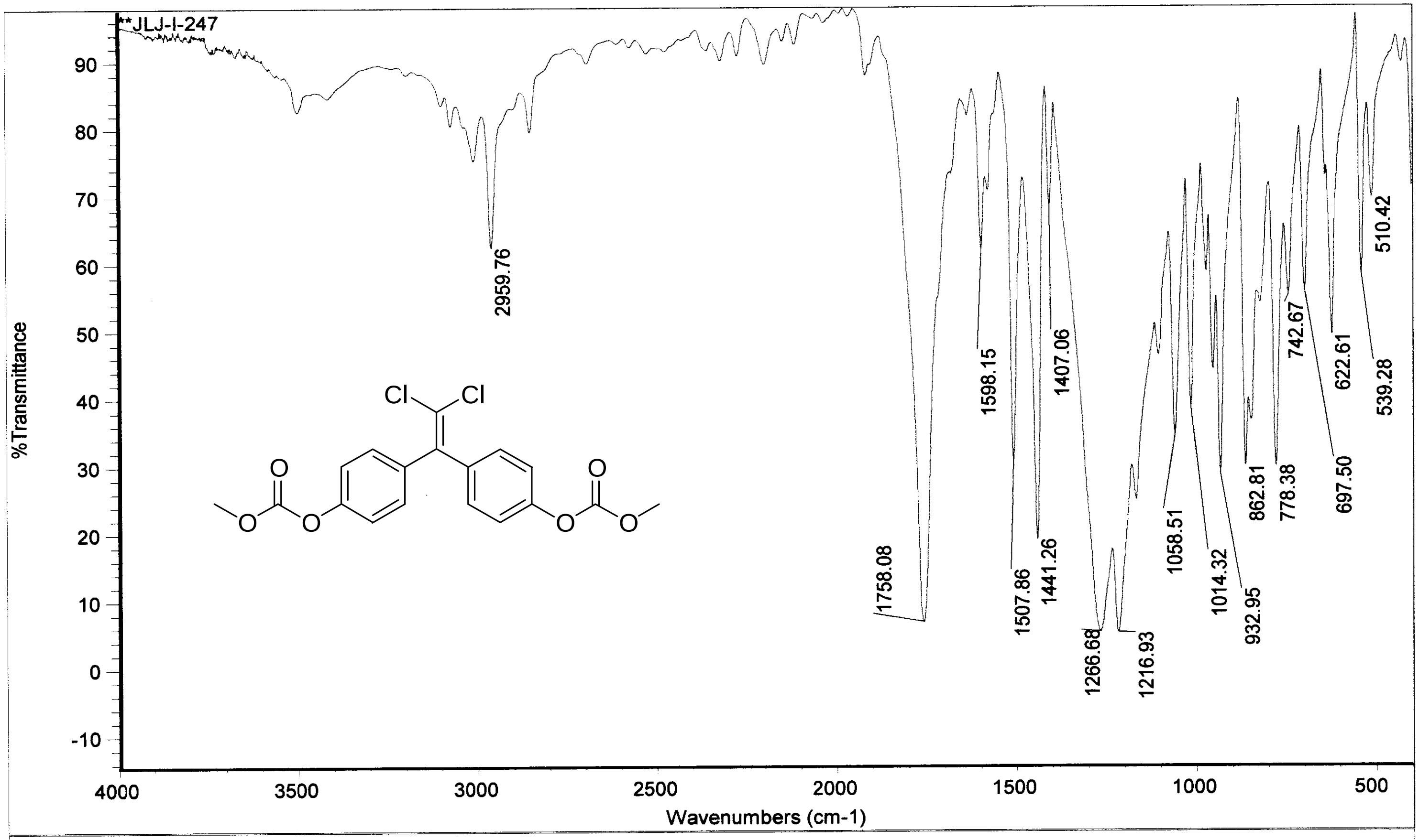


```
Current Data Parameters
NAME           JLJ-I-223
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20000628
Time               14.20
INSTRUM            spect
PROBHD    5 mm BBO BB-1
PULPROG             zg30
TD                 65536
SOLVENT             MeOH
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                   181
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300034 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            0.45000 ppm/cm
HZCM           180.05850 Hz/cm
```

JLJ-I-223
recrystillized



```
Current Data Parameters
NAME            JLJ-I-223
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20000628
Time                14.20
INSTRUM             spect
PROBHD    5 mm BBO BB-1
PULPROG              zg30
TD                  65536
SOLVENT              MeOH
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                    181
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 ========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300034 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 7.172 ppm
F1                2869.81 Hz
F2P                 6.636 ppm
F2                2655.17 Hz
PPMCM             0.02682 ppm/cm
HZCM             10.73196 Hz/cm
```

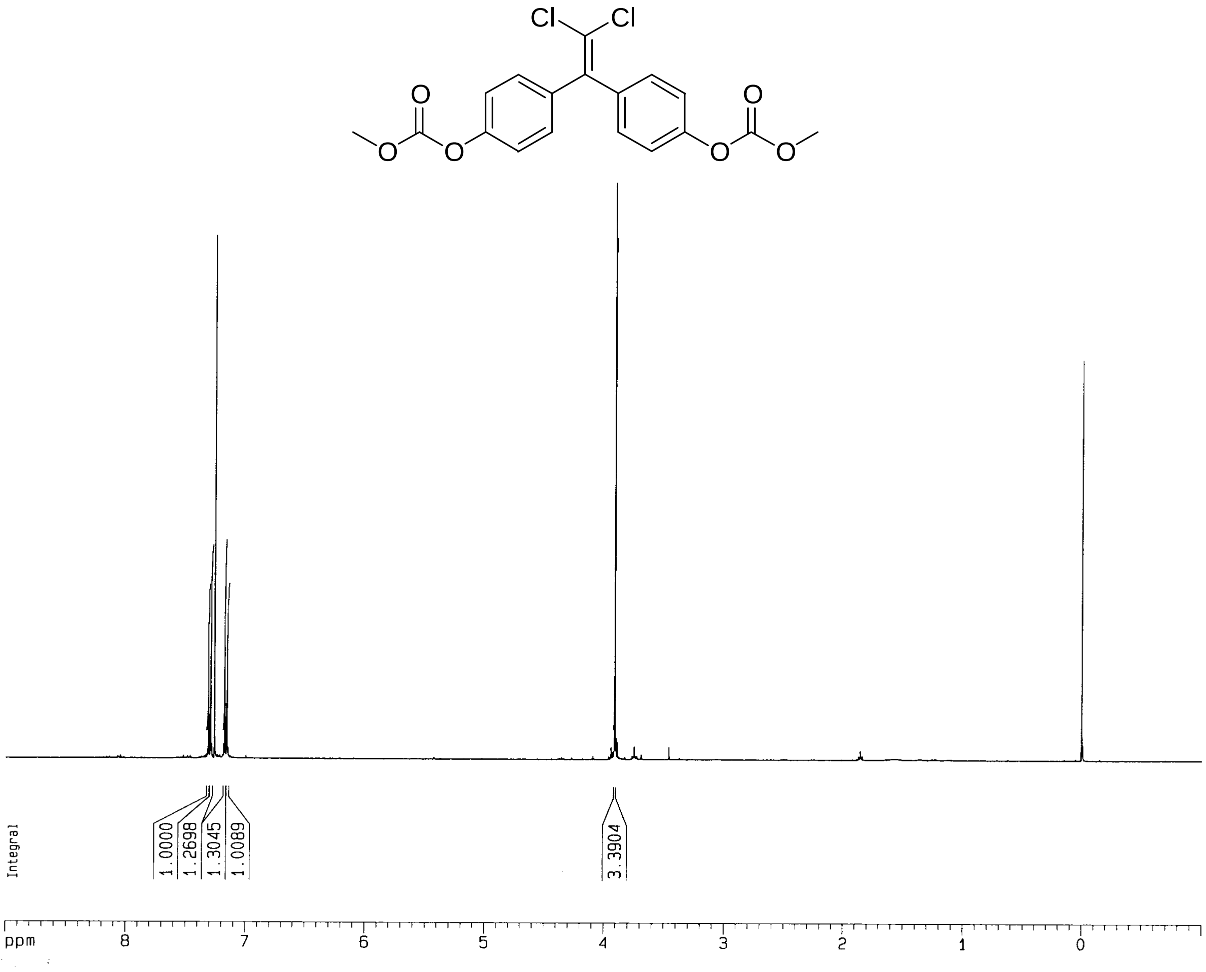


Date: Wed Sep 20 17:03:11 2000 **JLJ-I-247

Scans: 20

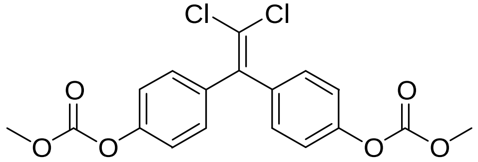
Resolution: 2.000

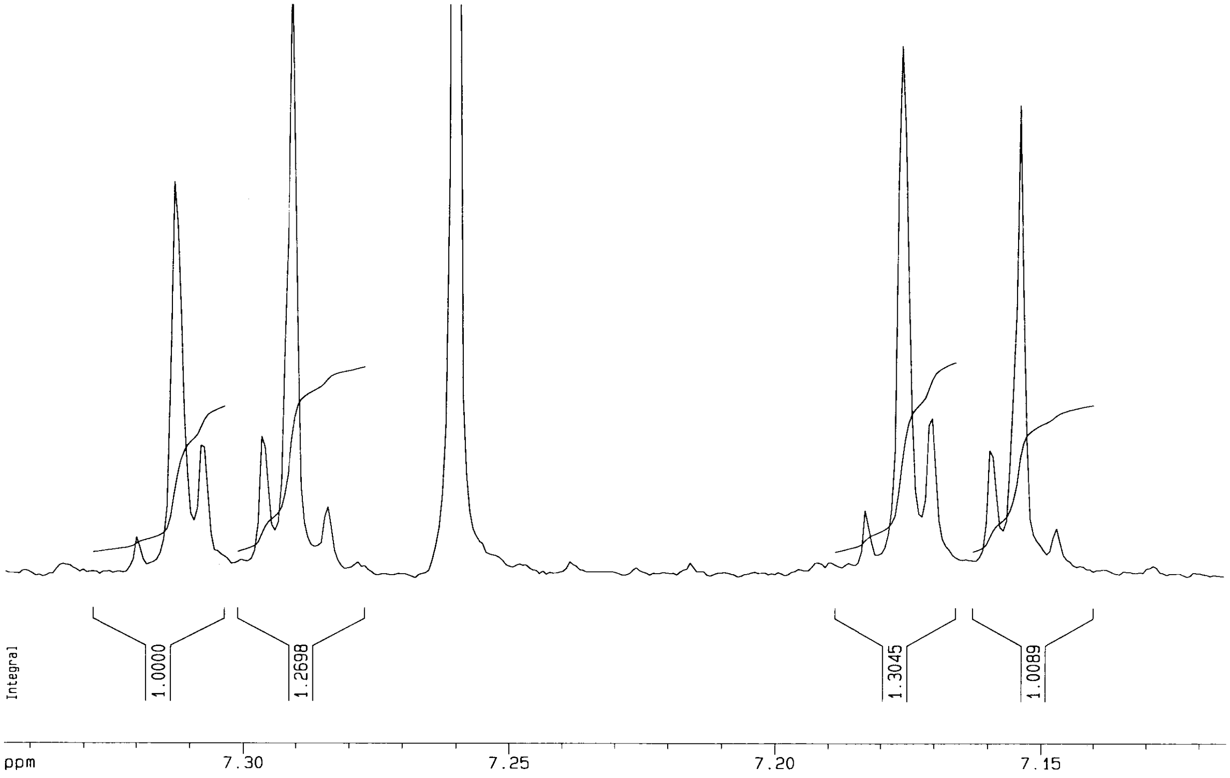
JLJ-I-247
crude



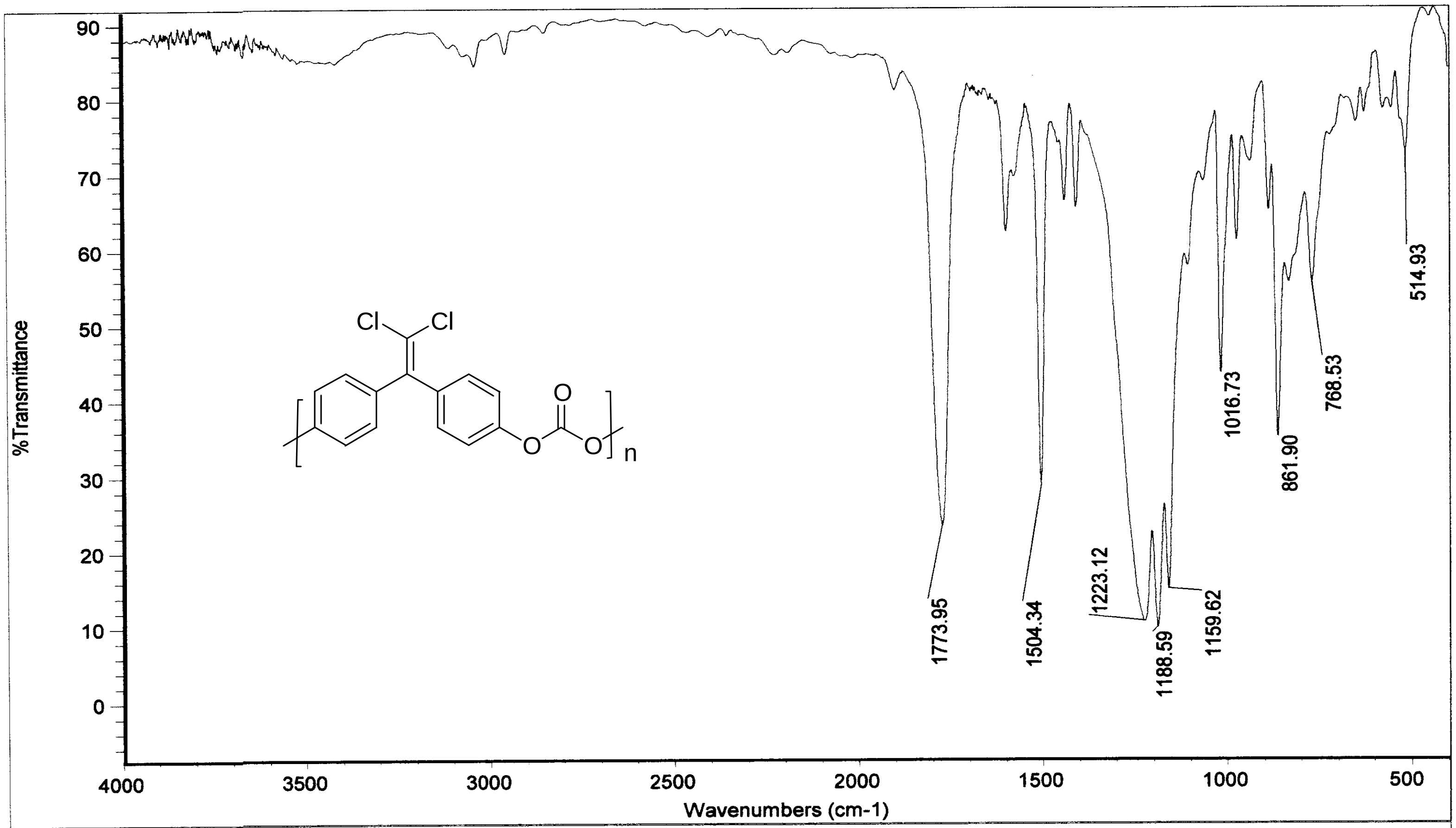
```
Current Data Parameters
NAME          JLJ-I-247
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20000803
Time              14.09
INSTRUM           spect
PROBHD   5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                645.1
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300093 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -1.000 ppm
F2              -400.13 Hz
PPMCM           0.50000 ppm/cm
HZCM          200.06500 Hz/cm
```

JLJ-I-247
crude





```
Current Data Parameters
NAME          JLJ-I-247
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20000803
Time              14.09
INSTRUM           spect
PROBHD   5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                645.1
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1         3.00000000 sec

============ CHANNEL f1 =========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300093 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               7.345 ppm
F1              2938.89 Hz
F2P               7.115 ppm
F2              2846.94 Hz
PPMCM           0.01149 ppm/cm
HZCM            4.59711 Hz/cm
```

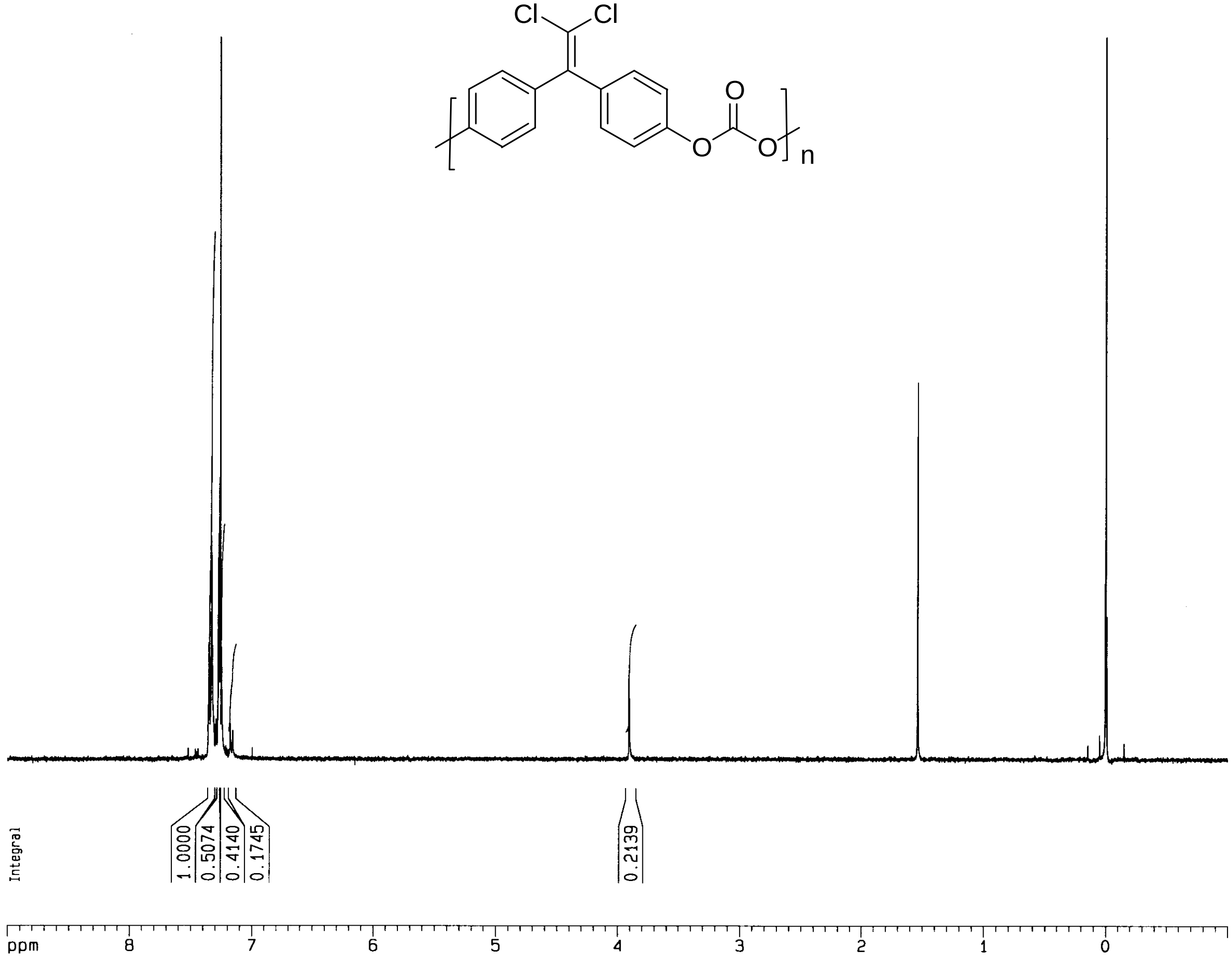


Date: Wed Oct 18 18:22:57 2000 **JLJ-II-5

Scans: 20

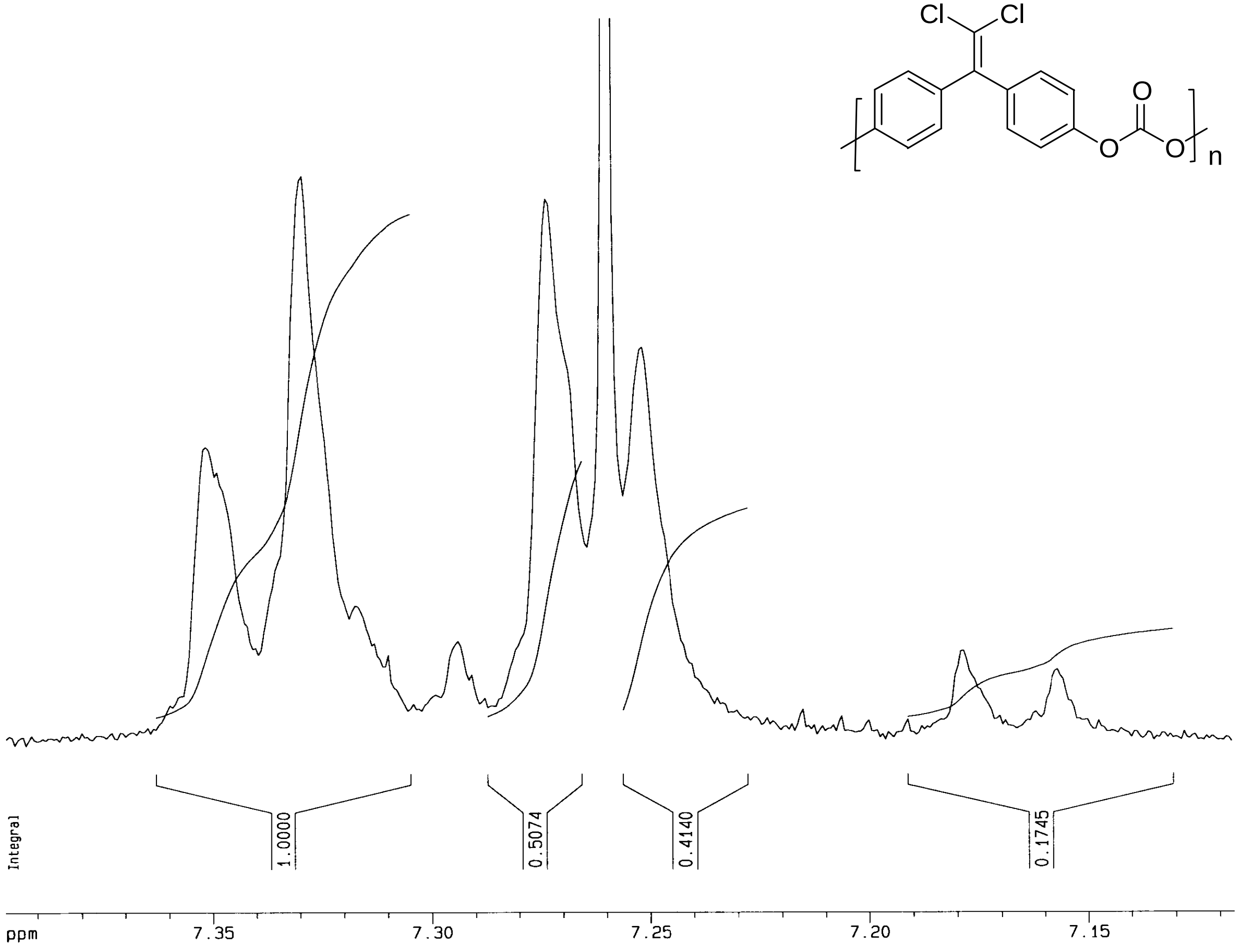
Resolution: 2.000

JLJ-II-1
polymerization

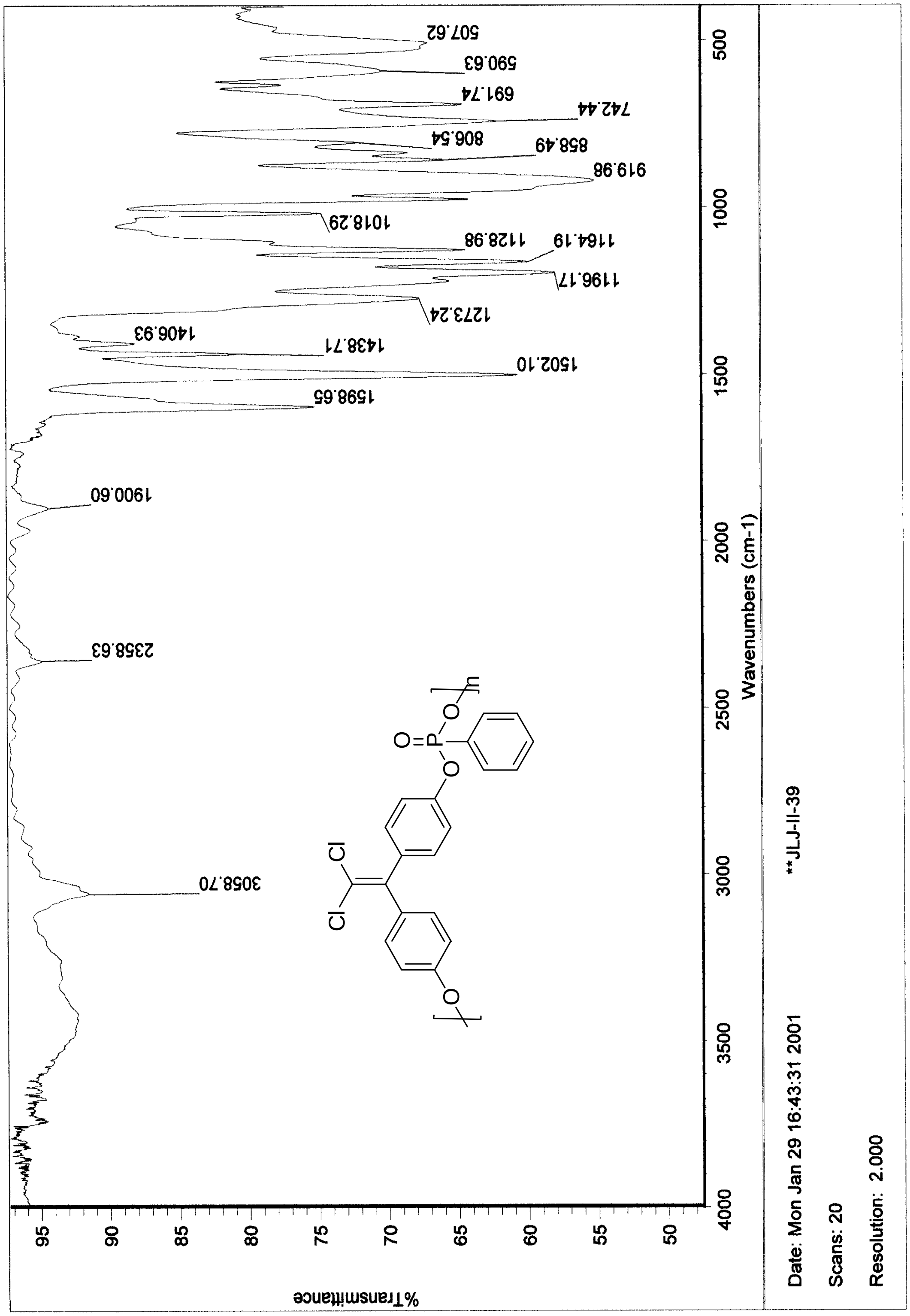


```
Current Data Parameters
NAME             JLJ-II-1
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20001016
Time                11.19
INSTRUM             spect
PROBHD     5 mm BBO BB-1
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  812.7
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 ========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300093 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 9.000 ppm
F1                3601.17 Hz
F2P                -1.000 ppm
F2                -400.13 Hz
PPMCM             0.50000 ppm/cm
HZCM            200.06500 Hz/cm
```

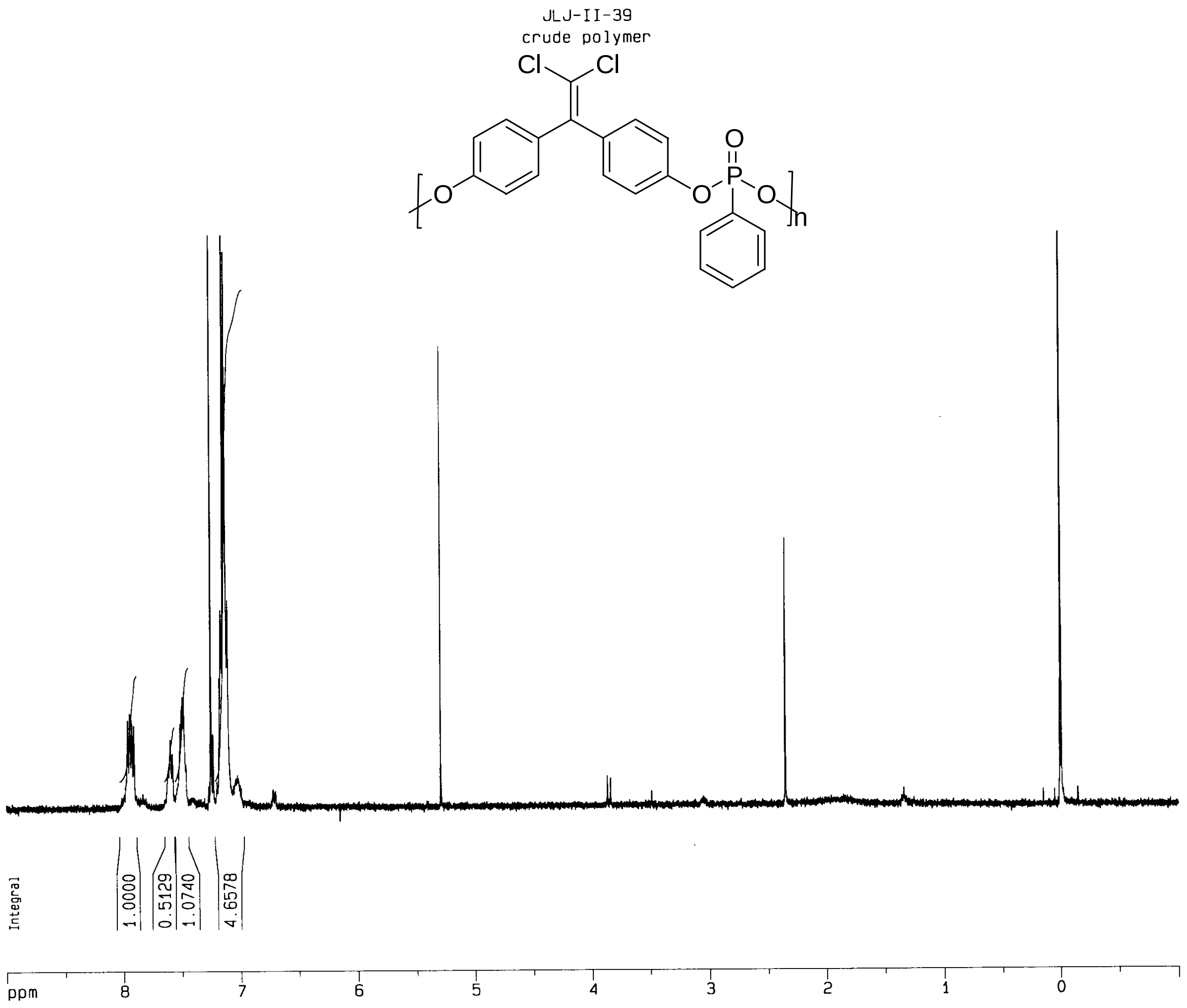
JLJ-II-1
polymerization



```
Current Data Parameters
NAME            JLJ-II-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20001016
Time               11.19
INSTRUM            spect
PROBHD    5 mm BBO BB-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 812.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300093 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.397 ppm
F1               2959.86 Hz
F2P                7.117 ppm
F2               2847.64 Hz
PPMCM            0.01402 ppm/cm
HZCM             5.61122 Hz/cm
```

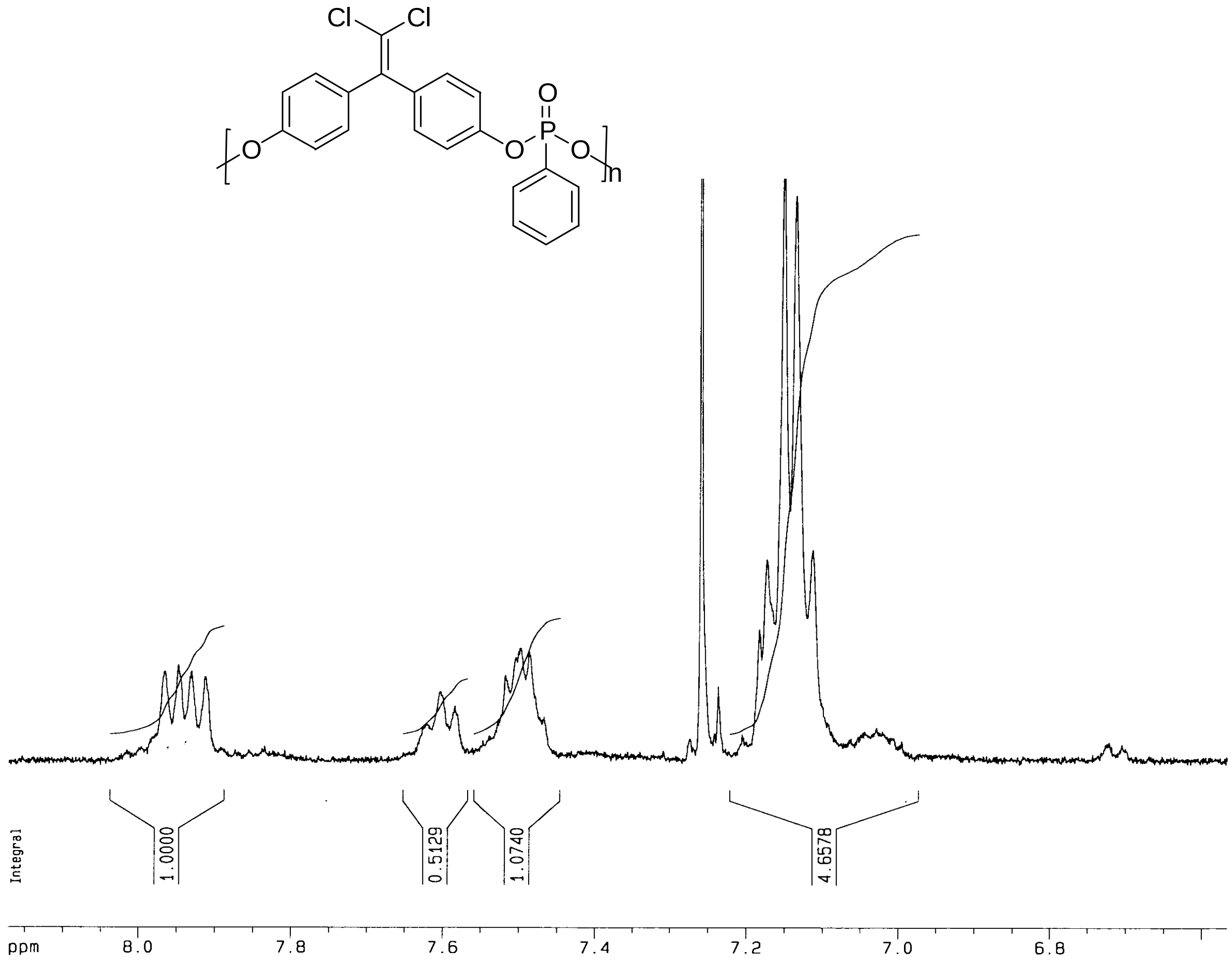


%Transmittance
95
90
85
80
75
70
65
60
55
50
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
3058.70
2358.63
1900.60
1598.65
1502.10
1438.71
1406.93
1273.24
1196.17
1164.19
1128.98
1018.29
919.98
858.49
806.54
742.44
691.74
590.63
507.62
Cl
Cl
O
O
O
P
O
n
Date: Mon Jan 29 16:43:31 2001
Scans: 20
Resolution: 2.000
**JLJ-II-39

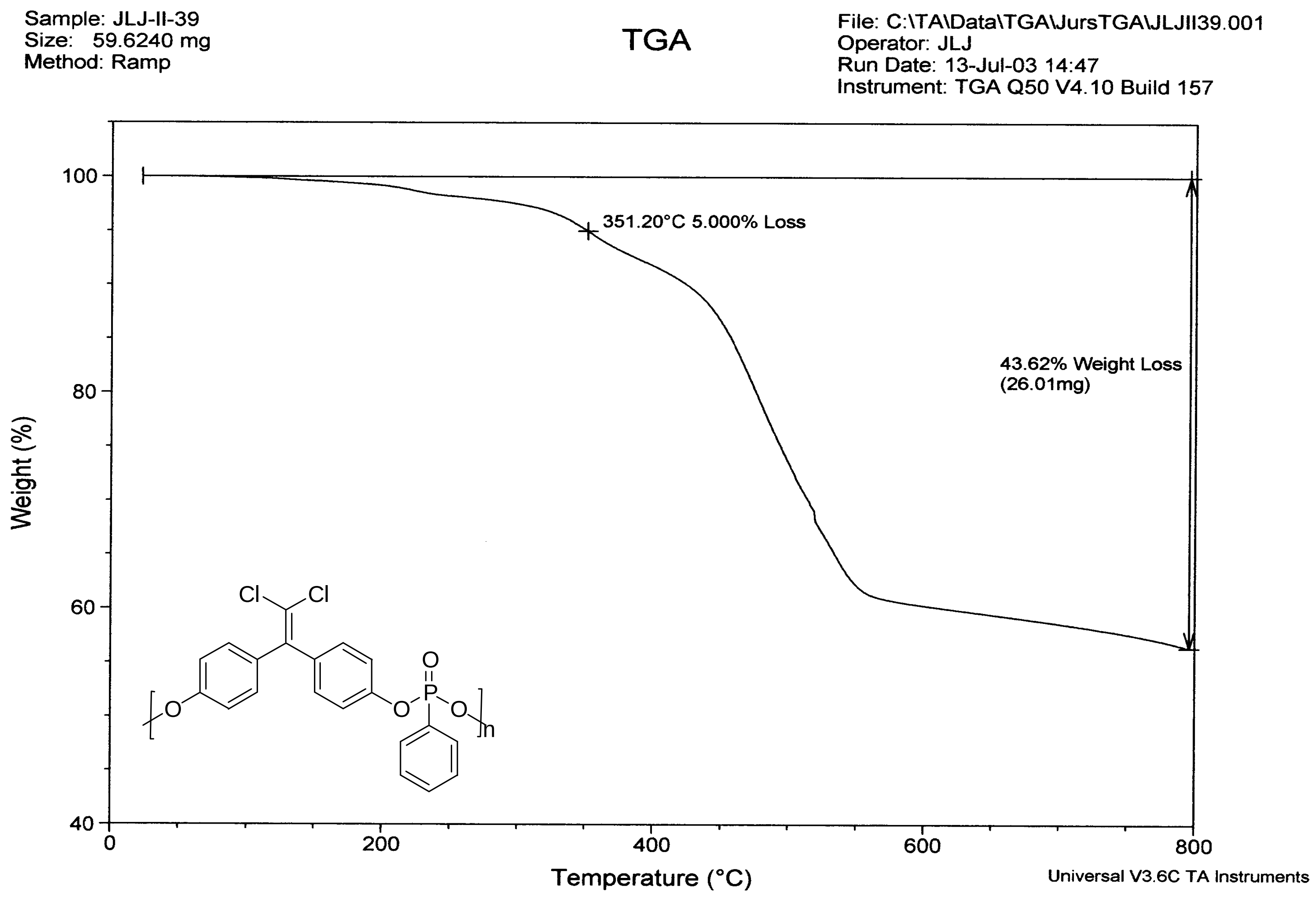

JLJ-II-39
crude polymer

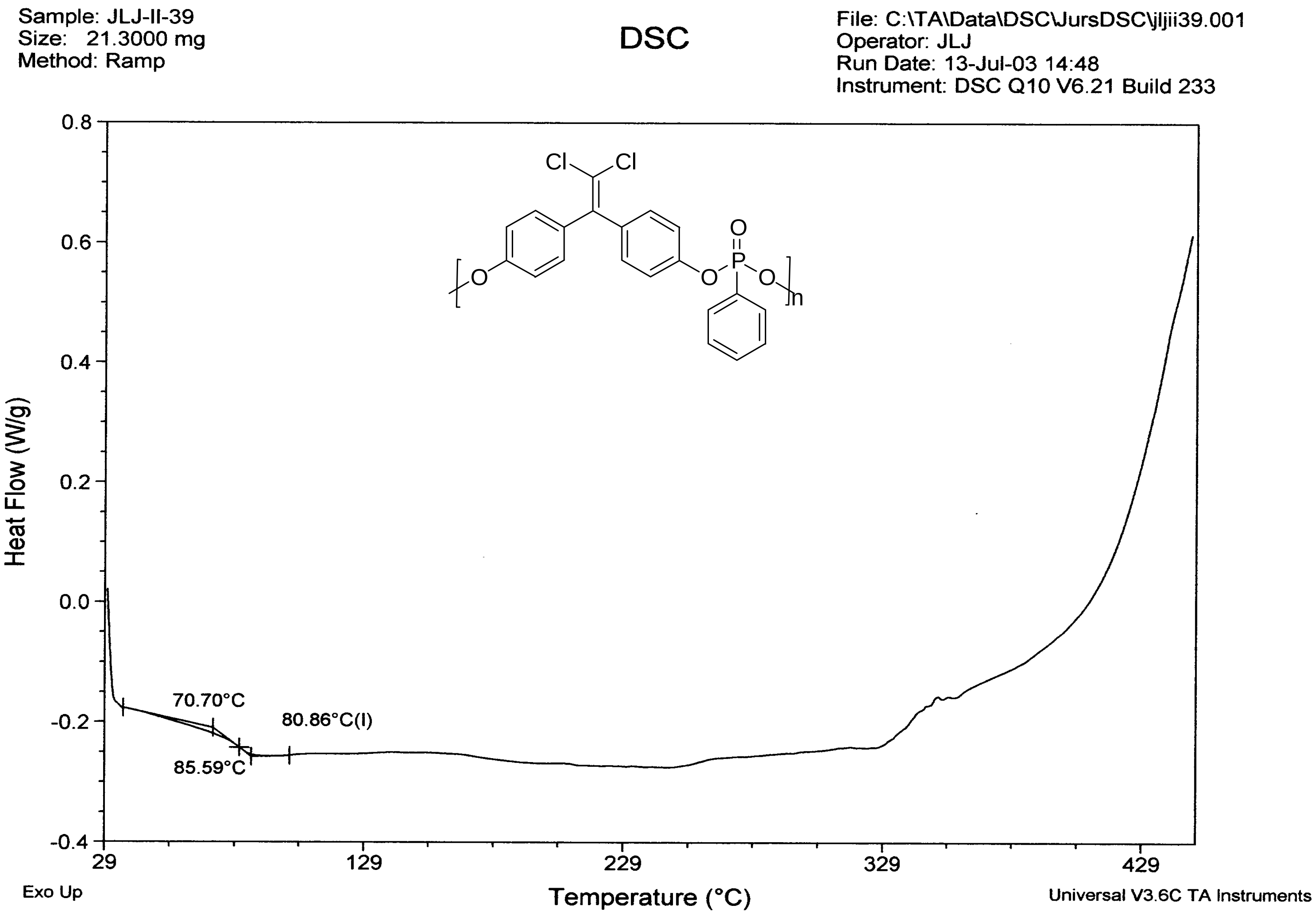
```
Current Data Parameters
NAME            JLJ-II-39
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20010124
Time                11.30
INSTRUM             spect
PROBHD    5 mm BBO BB-1
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  812.7
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 =========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300099 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 9.000 ppm
F1                3601.17 Hz
F2P                -1.000 ppm
F2                -400.13 Hz
PPMCM             0.50000 ppm/cm
HZCM            200.06500 Hz/cm
```

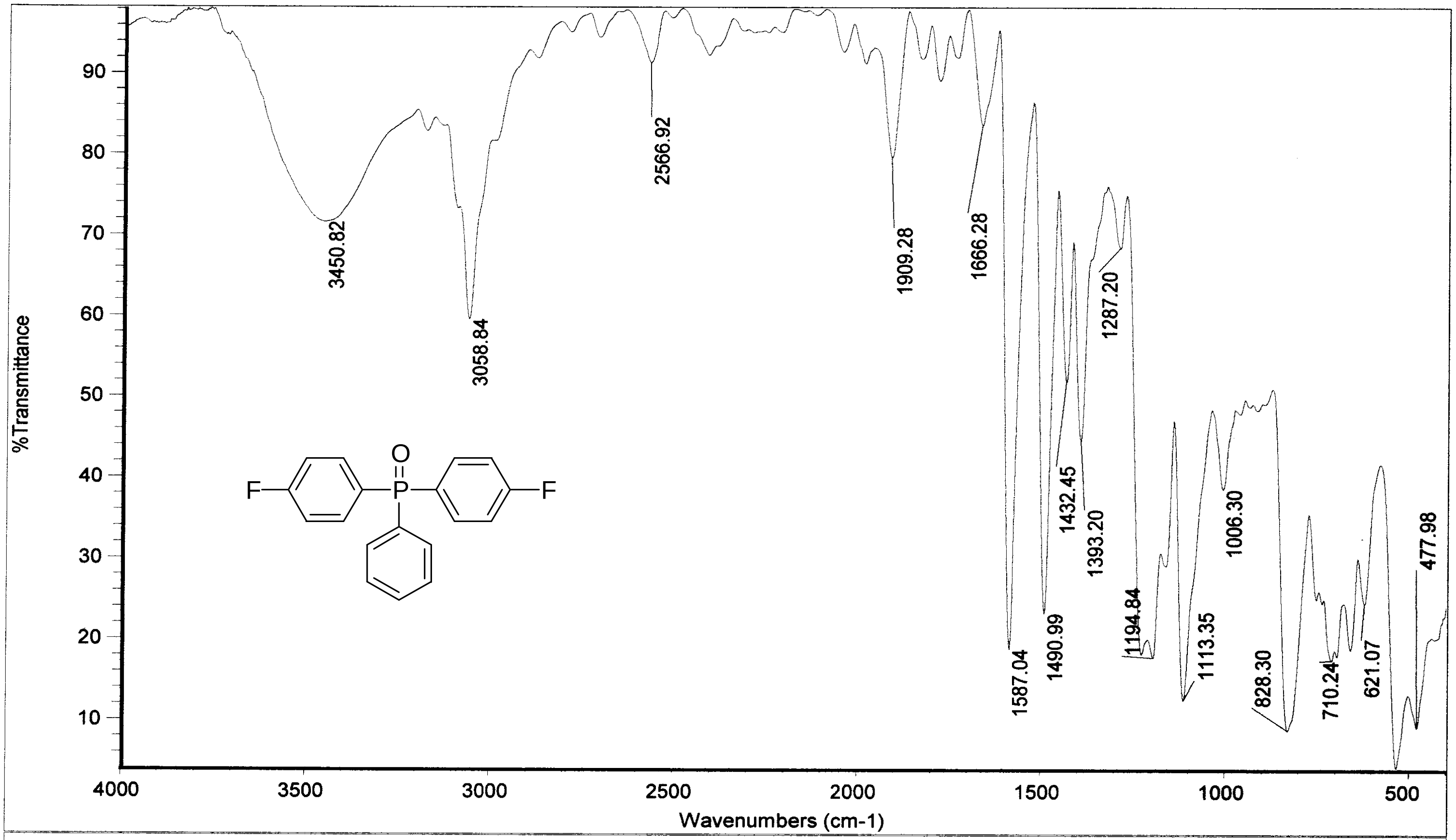
JLJ-II-39
crude polymer



```
Current Data Parameters
NAME          JLJ-II-39
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20010124
Time              11.30
INSTRUM           spect
PROBHD   5 mm BBO BB-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                812.7
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1          3.00000000 sec

============ CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300099 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               8.171 ppm
F1              3269.50 Hz
F2P               6.566 ppm
F2              2627.42 Hz
PPMCM           0.08023 ppm/cm
HZCM           32.10395 Hz/cm
```


Sample: JLJ-II-39
Size: 59.6240 mg
Method: Ramp
TGA
File: C:\TA\Data\TGA\JursTGA\JLJII39.001
Operator: JLJ
Run Date: 13-Jul-03 14:47
Instrument: TGA Q50 V4.10 Build 157
351.20°C 5.000% Loss
43.62% Weight Loss
(26.01mg)
Cl
Cl
O
O
P
O
O
n
Weight (%)
100
80
60
40
0
200
400
600
800
Temperature (°C)
Universal V3.6C TA Instruments


Sample: JLJ-II-39
Size: 21.3000 mg
Method: Ramp
DSC
File: C:\TA\Data\DSC\JursDSC\jljii39.001
Operator: JLJ
Run Date: 13-Jul-03 14:48
Instrument: DSC Q10 V6.21 Build 233
Cl
Cl
O
O
P
O
O
n
70.70°C
80.86°C(I)
85.59°C
Heat Flow (W/g)
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
29
129
229
329
429
Exo Up
Temperature (°C)
Universal V3.6C TA Instruments

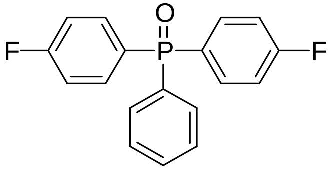


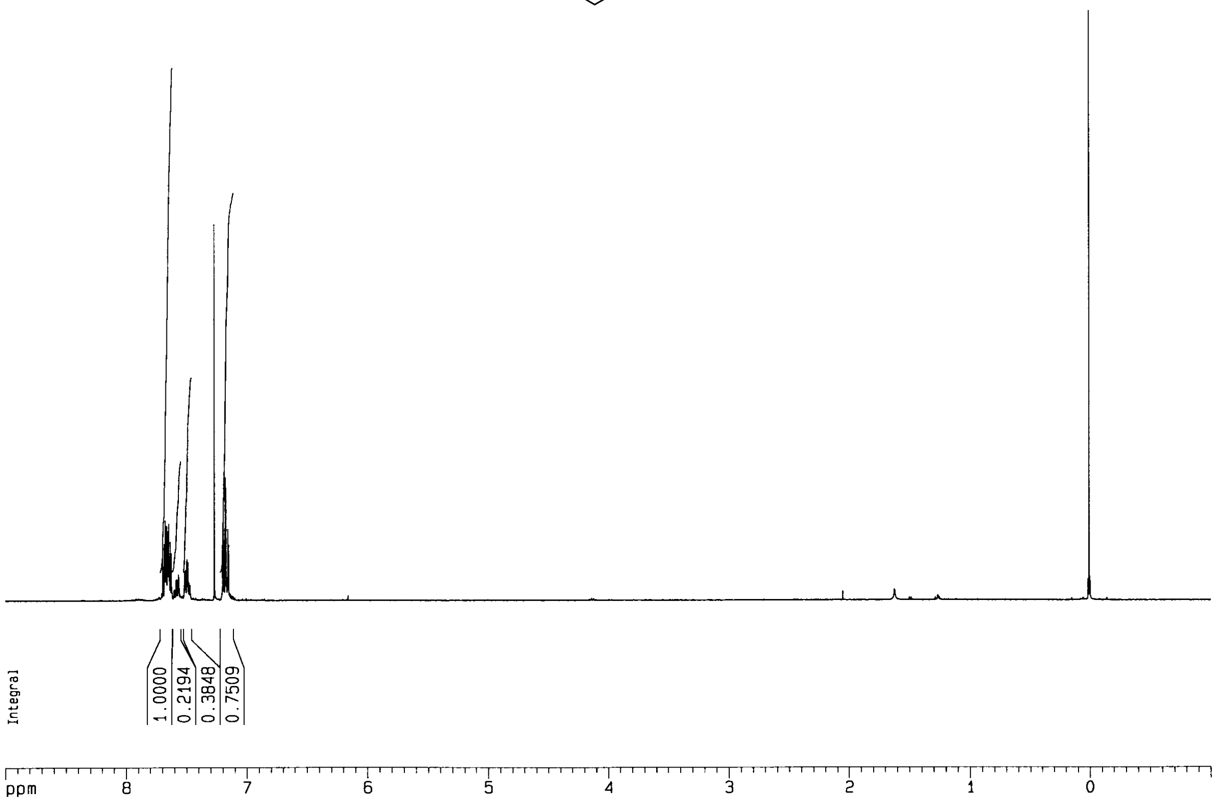
Date: Mon Sep 02 13:12:28 2002 **JLJ-III-41

Scans: 32

Resolution: 4.000

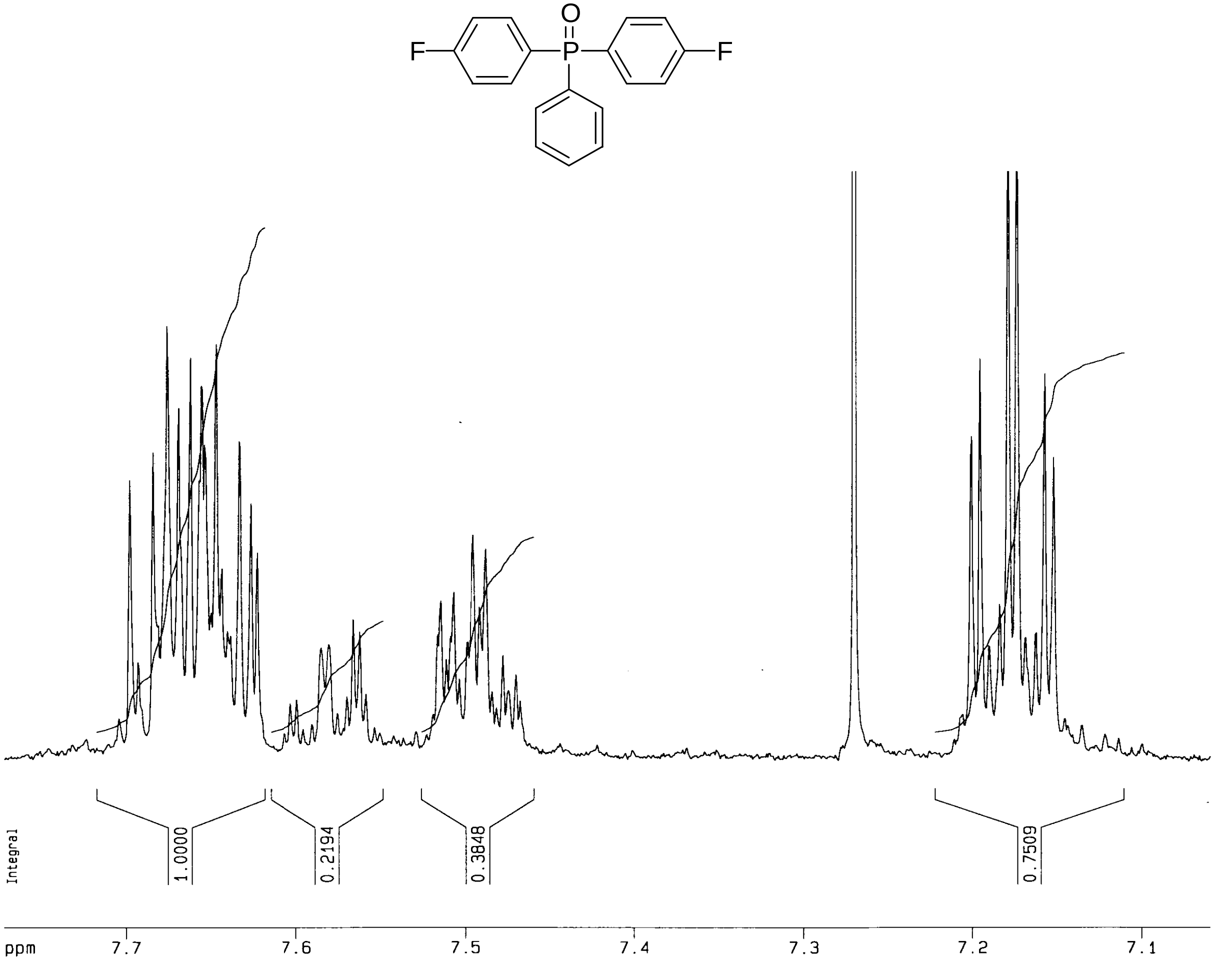
JLJ-III-41
crude



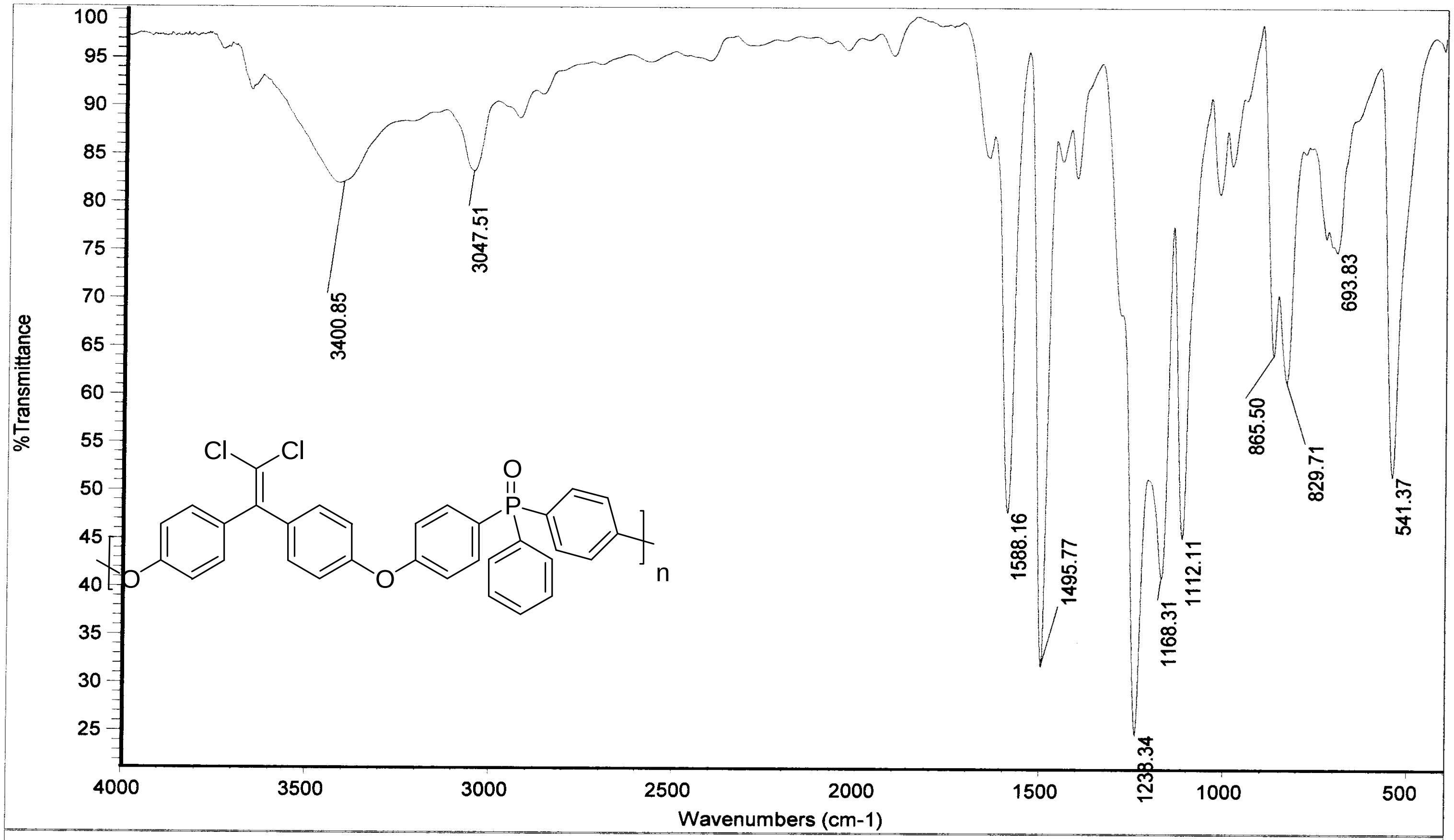


```
Current Data Parameters
NAME          JLJ-III-41
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20020204
Time               15.06
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 645.1
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300061 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06500 Hz/cm
```

JLJ-III-41
crude



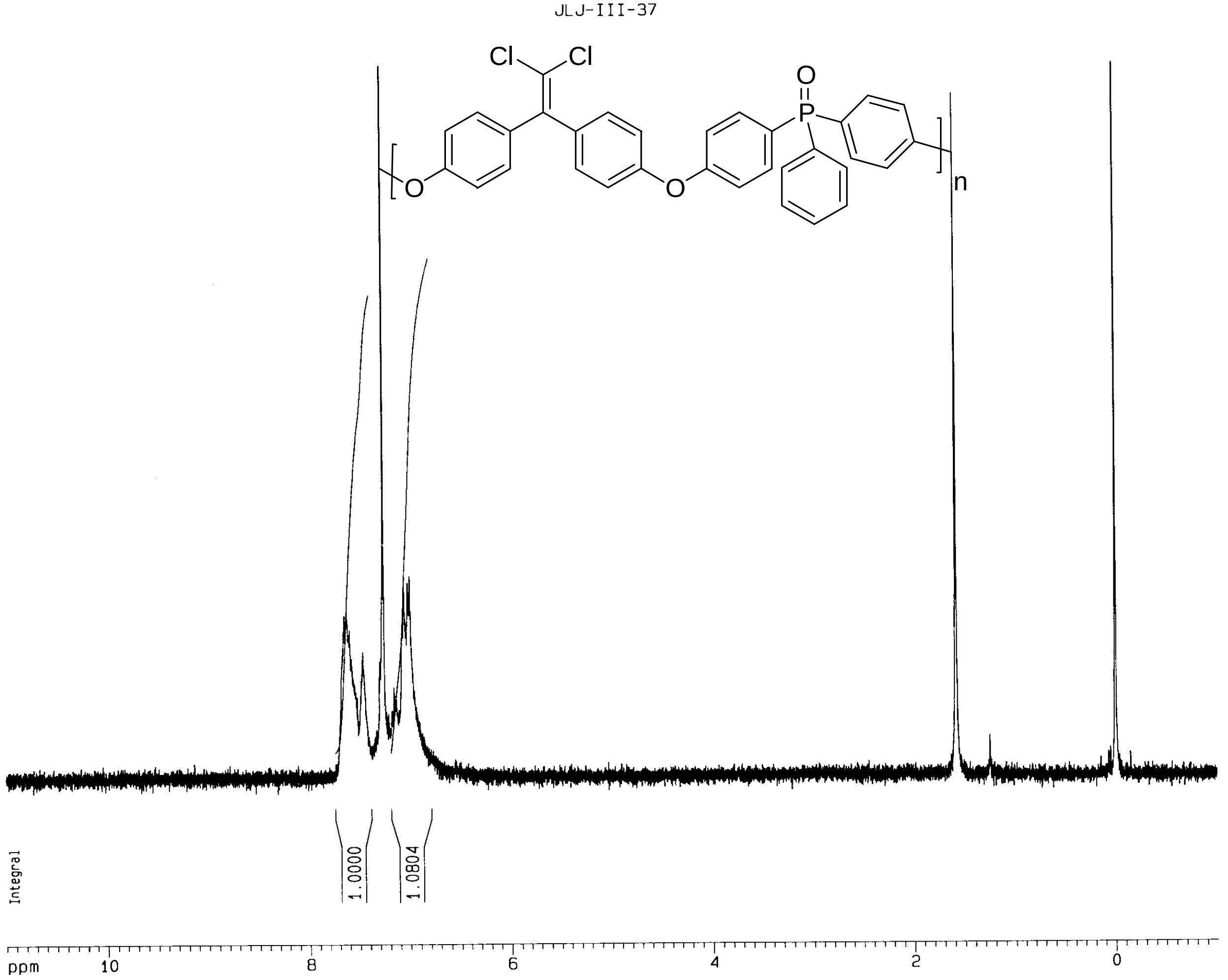
```
Current Data Parameters
NAME          JLJ-III-41
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20020204
Time               15.06
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 645.1
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300061 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.772 ppm
F1               3109.81 Hz
F2P                7.060 ppm
F2               2824.79 Hz
PPMCM            0.03562 ppm/cm
HZCM            14.25113 Hz/cm
```



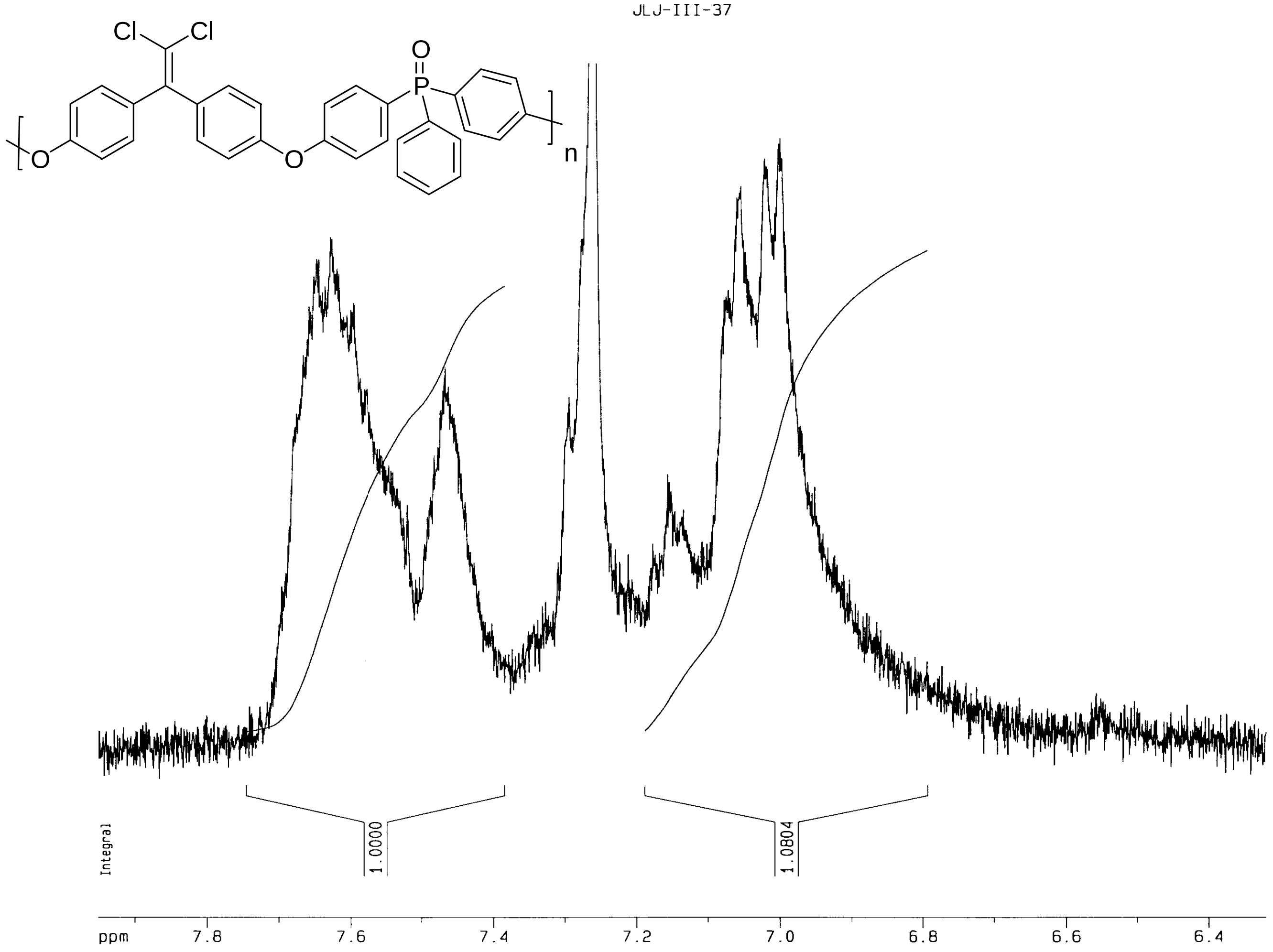
Date: Mon Sep 02 14:29:04 2002 **JLJ-III-37

Scans: 18

Resolution: 4.000



```
Current Data Parameters
NAME          jlj-iii-37
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20020902
Time               17.39
INSTRUM            spect
PROBHD      5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 574.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300091 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P               11.000 ppm
F1               4401.43 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.60000 ppm/cm
HZCM           240.07800 Hz/cm
```

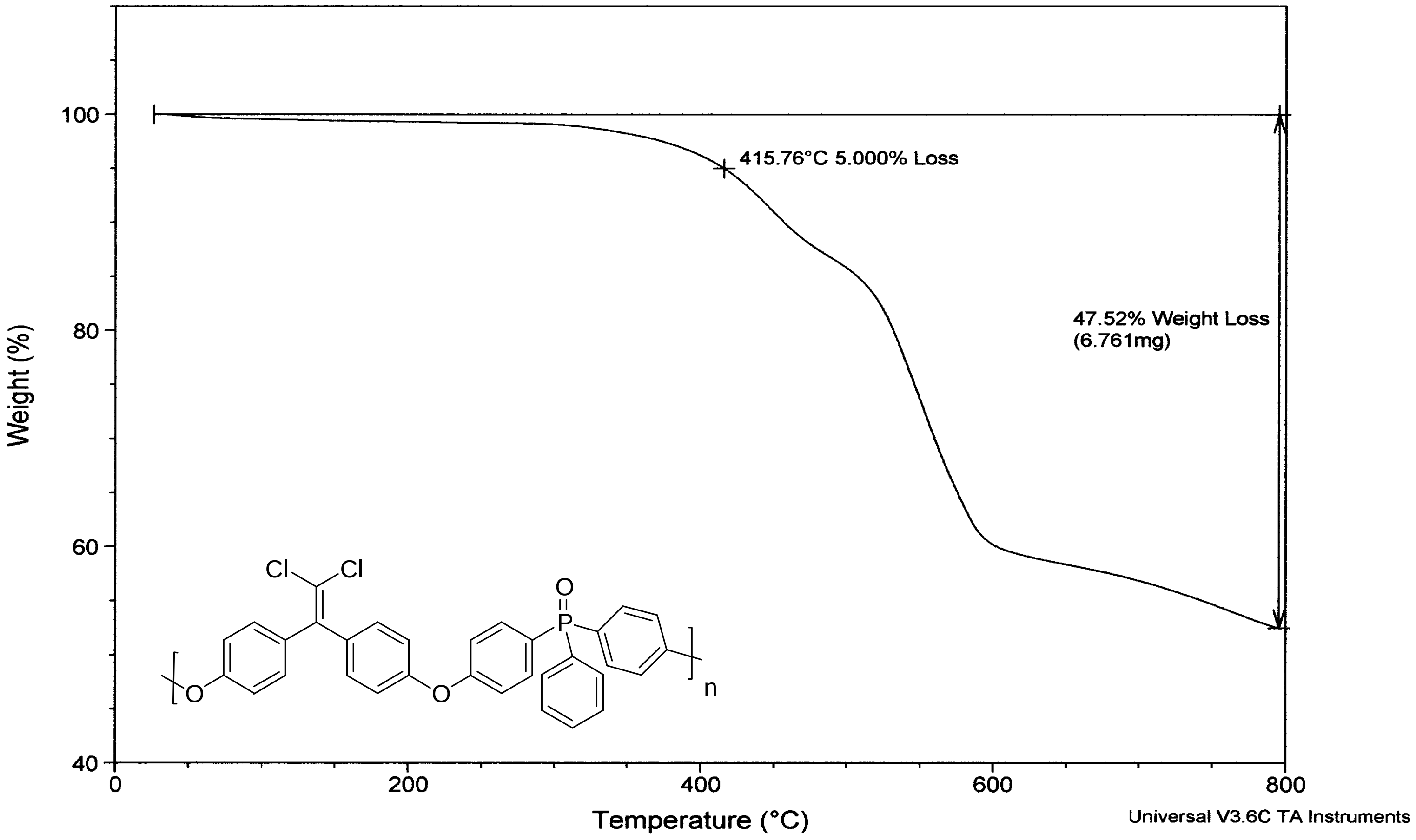


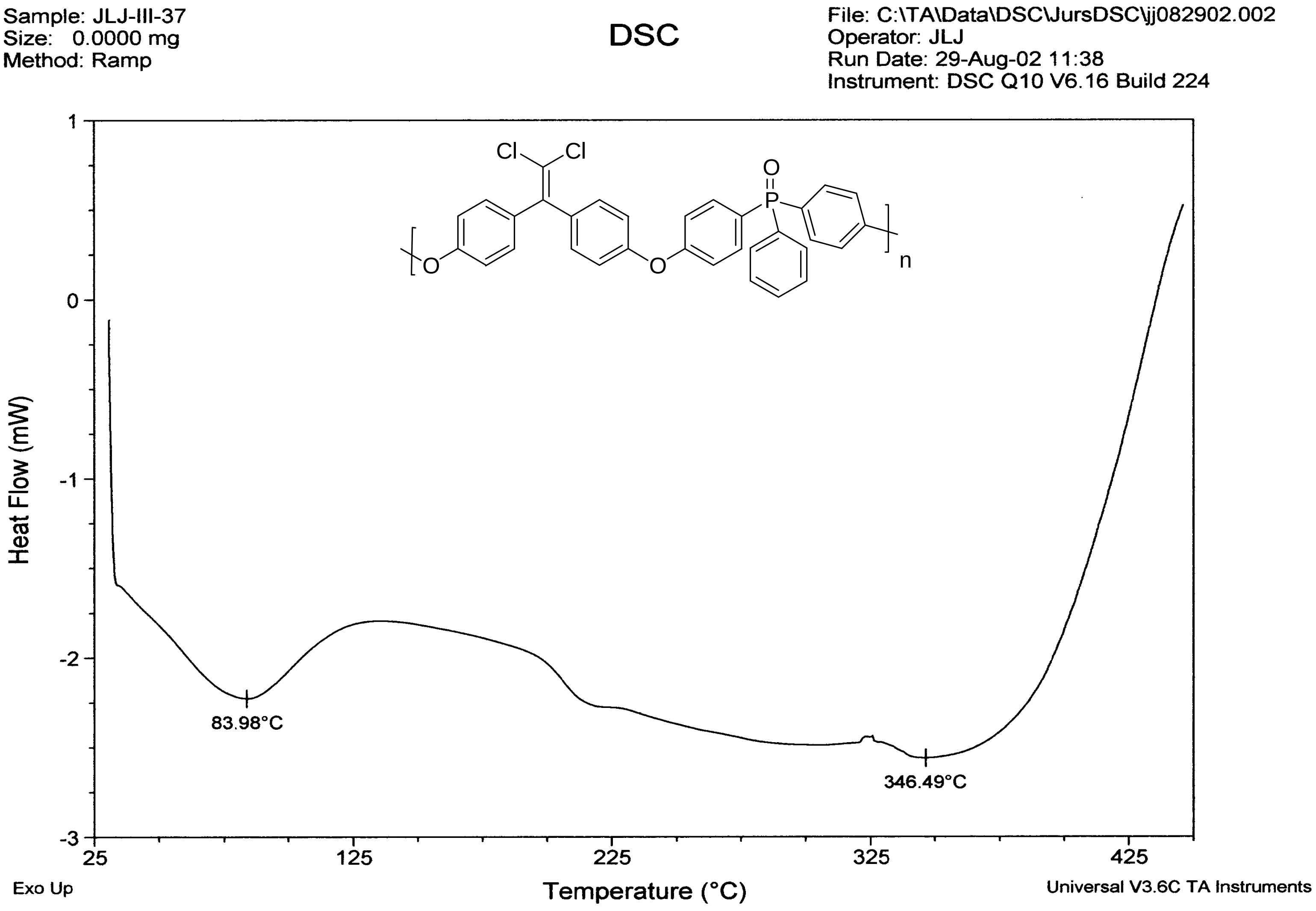
```
Current Data Parameters
NAME          jlj-iii-37
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20020902
Time               17.39
INSTRUM            spect
PROBHD      5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 574.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300091 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.951 ppm
F1               3181.32 Hz
F2P                6.321 ppm
F2               2529.19 Hz
PPMCM            0.08149 ppm/cm
HZCM            32.60643 Hz/cm
```

Sample: JLJ-III-37
Size: 14.2280 mg
Method: Ramp

TGA

File: C:\TA\Data\TGA\JursTGA\jljIII37.001
Operator: JLJ
Run Date: 19-Jul-03 16:04
Instrument: TGA Q50 V4.10 Build 157

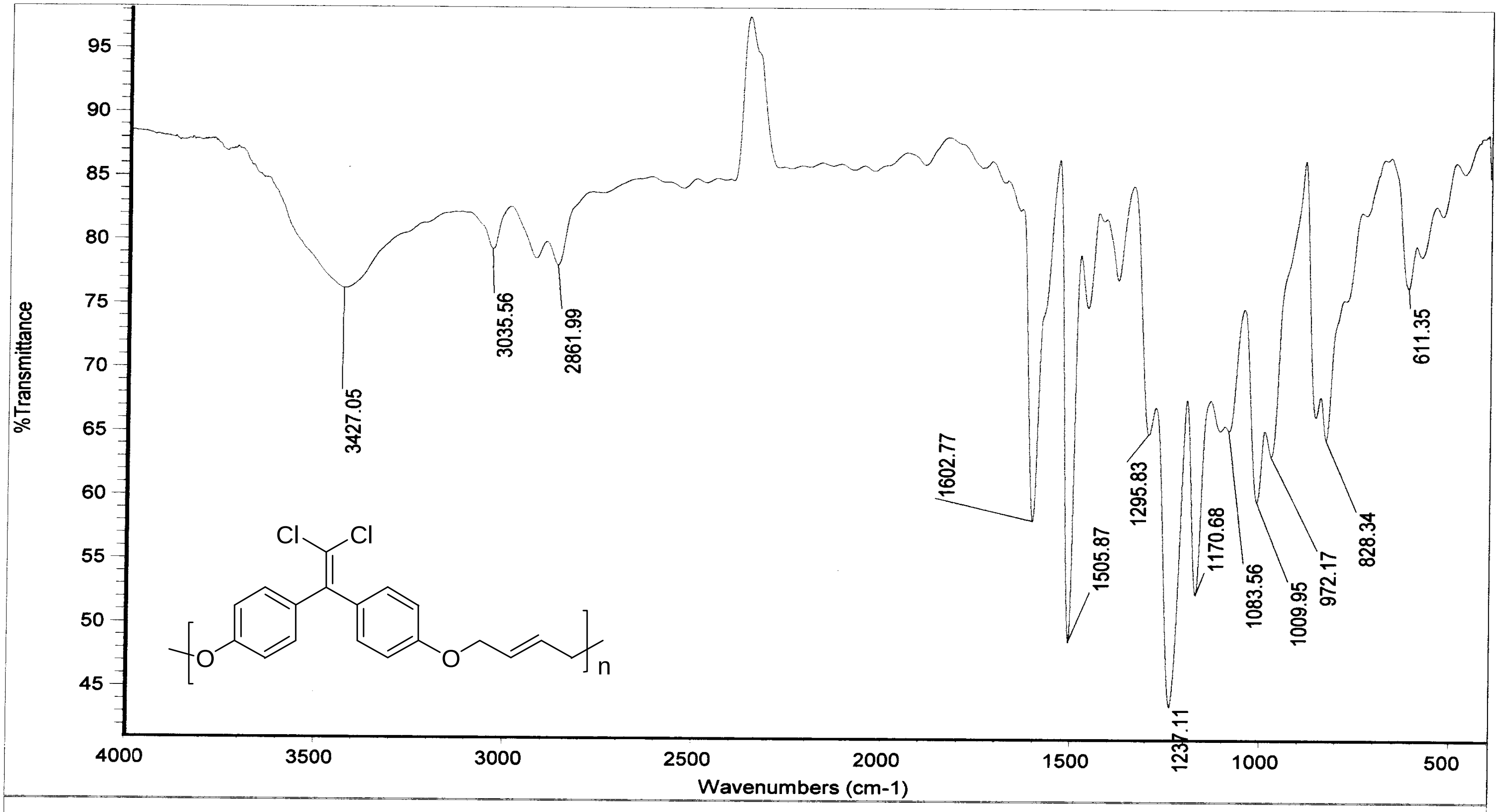




Sample: JLJ-III-37
Size: 0.0000 mg
Method: Ramp

DSC

File: C:\TA\Data\DSC\JursDSC\jj082902.002
Operator: JLJ
Run Date: 29-Aug-02 11:38
Instrument: DSC Q10 V6.16 Build 224

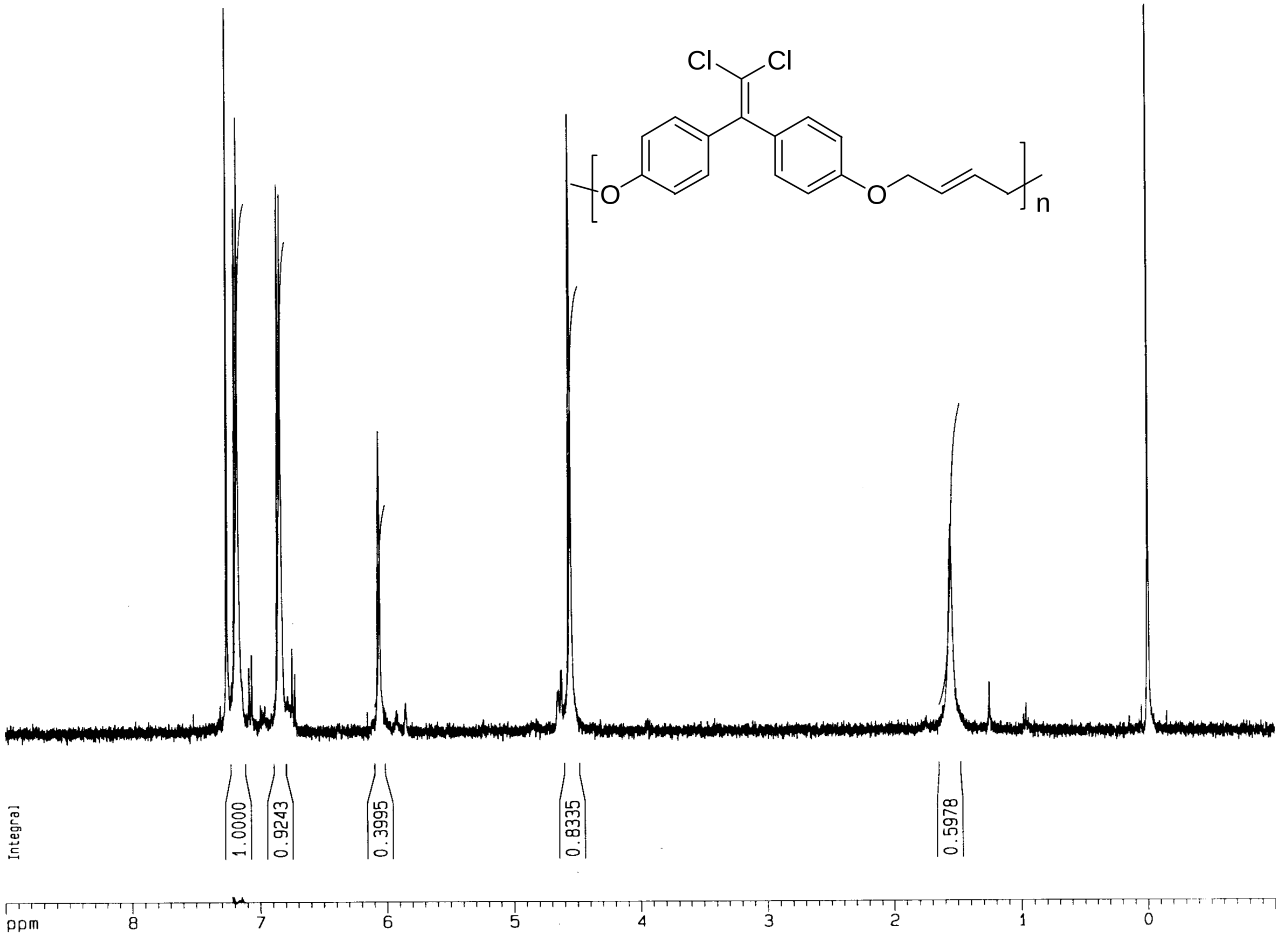


Date: Mon Sep 02 16:06:12 2002 **JLJ-III-71

Scans: 18

Resolution: 4.000

JLJ-III-71

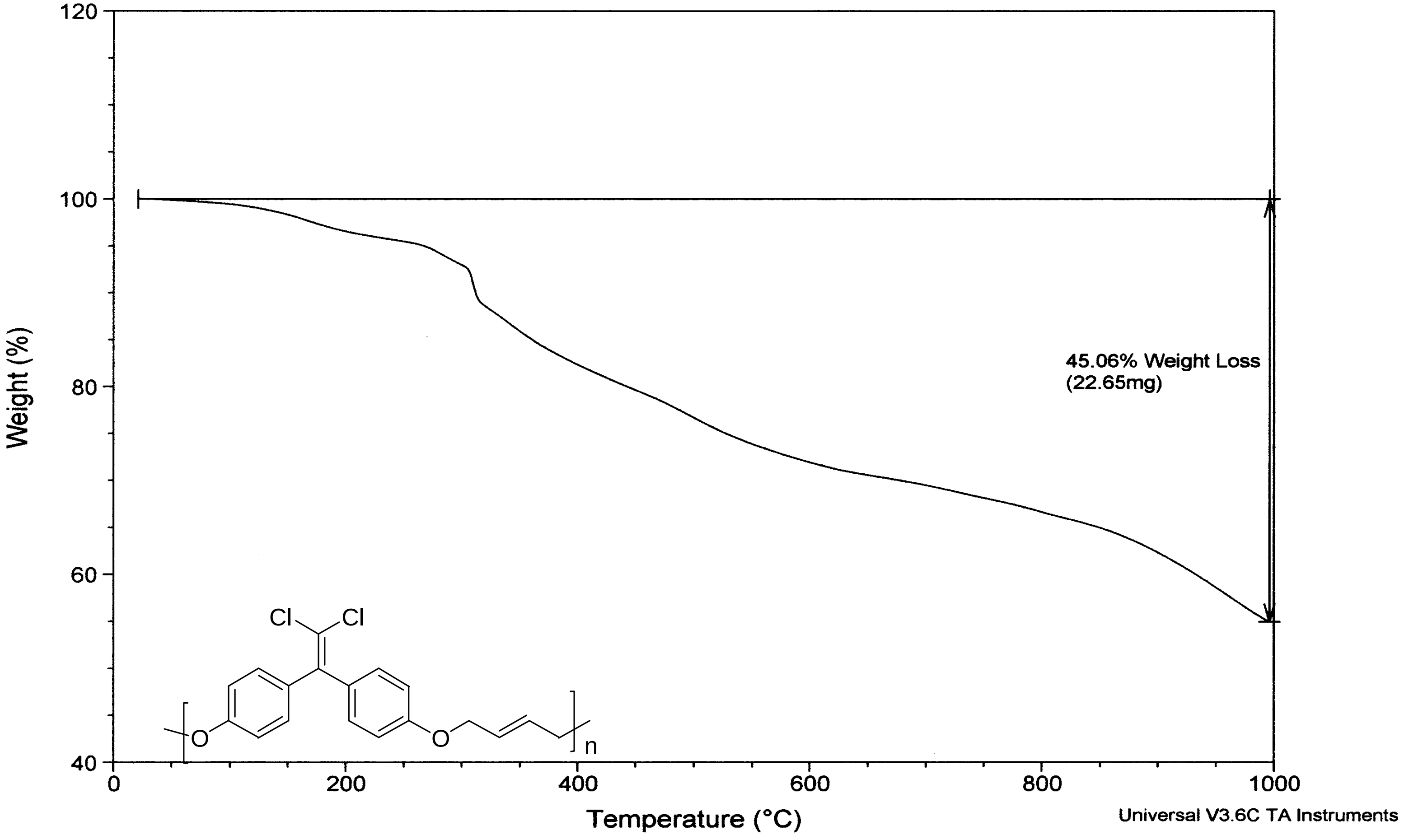


```
Current Data Parameters
NAME           jlj-iii-71
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20020902
Time                17.46
INSTRUM             spect
PROBHD      5 mm BBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  574.7
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 =========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300096 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 9.000 ppm
F1                3601.17 Hz
F2P                -1.000 ppm
F2                -400.13 Hz
PPMCM             0.50000 ppm/cm
HZCM            200.06500 Hz/cm
```

Sample: JLJ-III-155
Size: 50.2670 mg
Method: Ramp

TGA

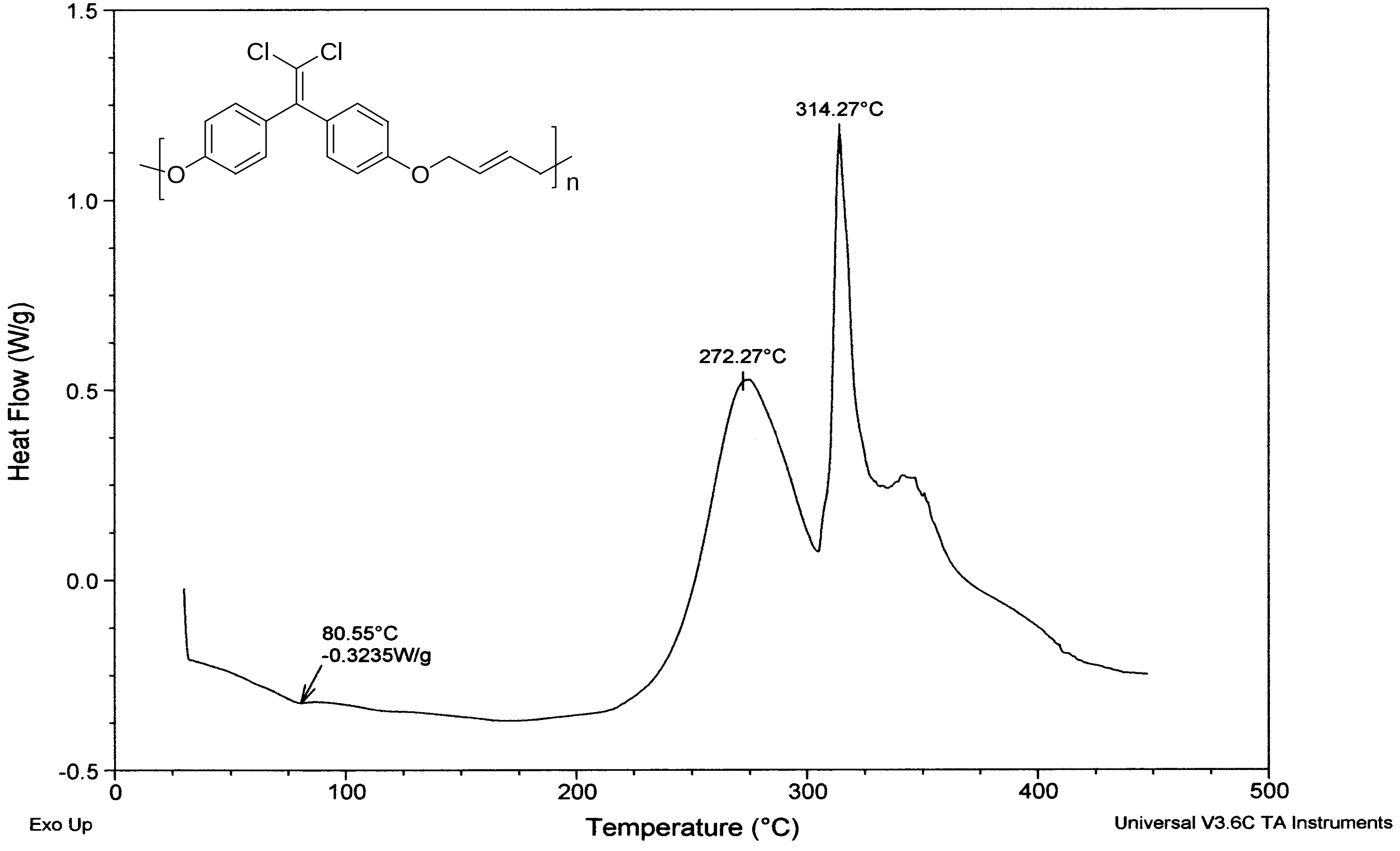
File: C:\TA\Data\TGA\JursTGA\110402.001
Operator: JLJ
Run Date: 04-Nov-02 10:35
Instrument: TGA Q50 V4.10 Build 157

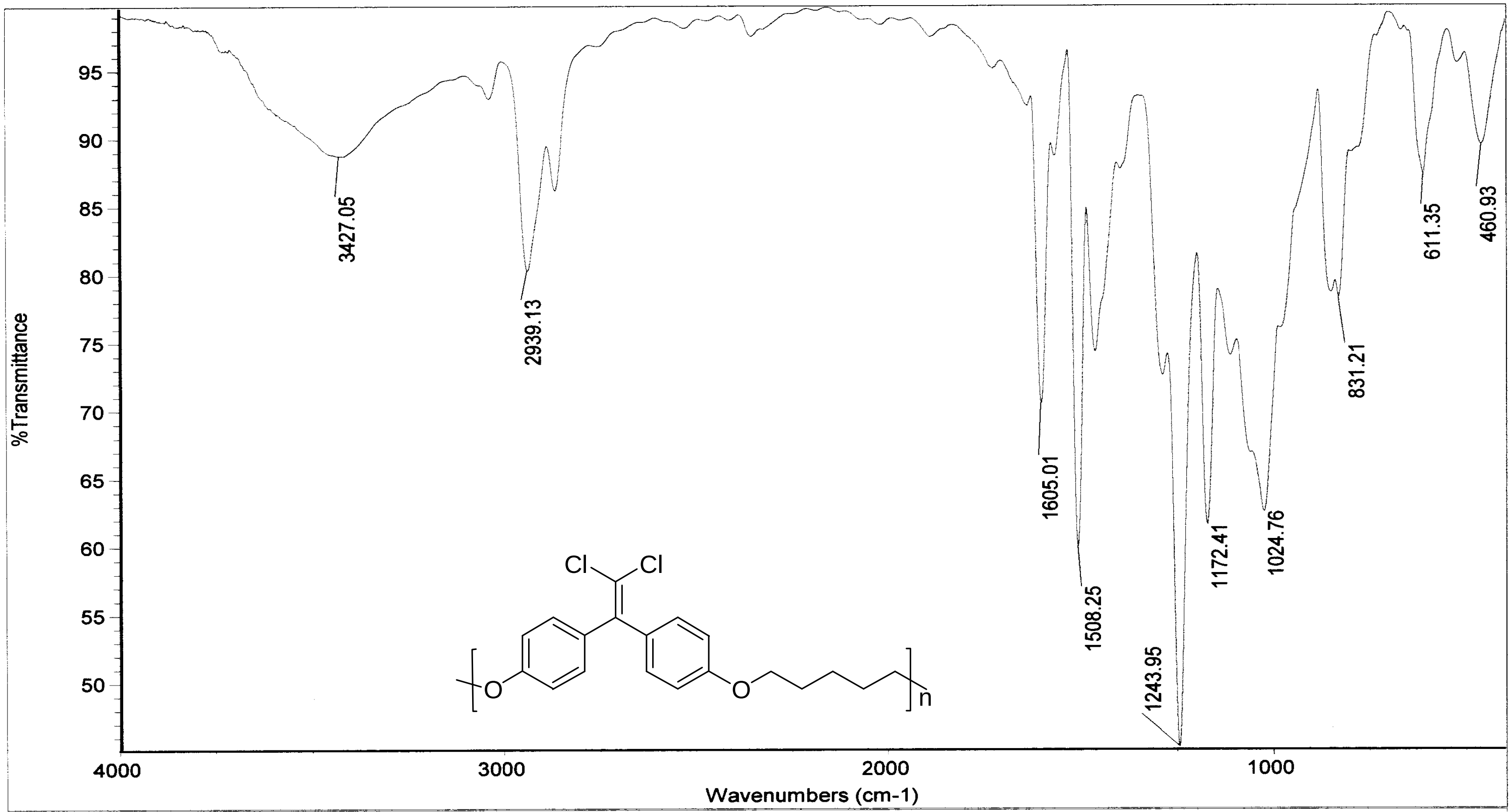


Sample: JLJ-III-155
Size: 10.4000 mg
Method: Ramp

DSC

File: C:\TA\Data\DSC\JursDSC\JJ110402.001
Operator: JLJ
Run Date: 04-Nov-02 10:30
Instrument: DSC Q10 V6.21 Build 233



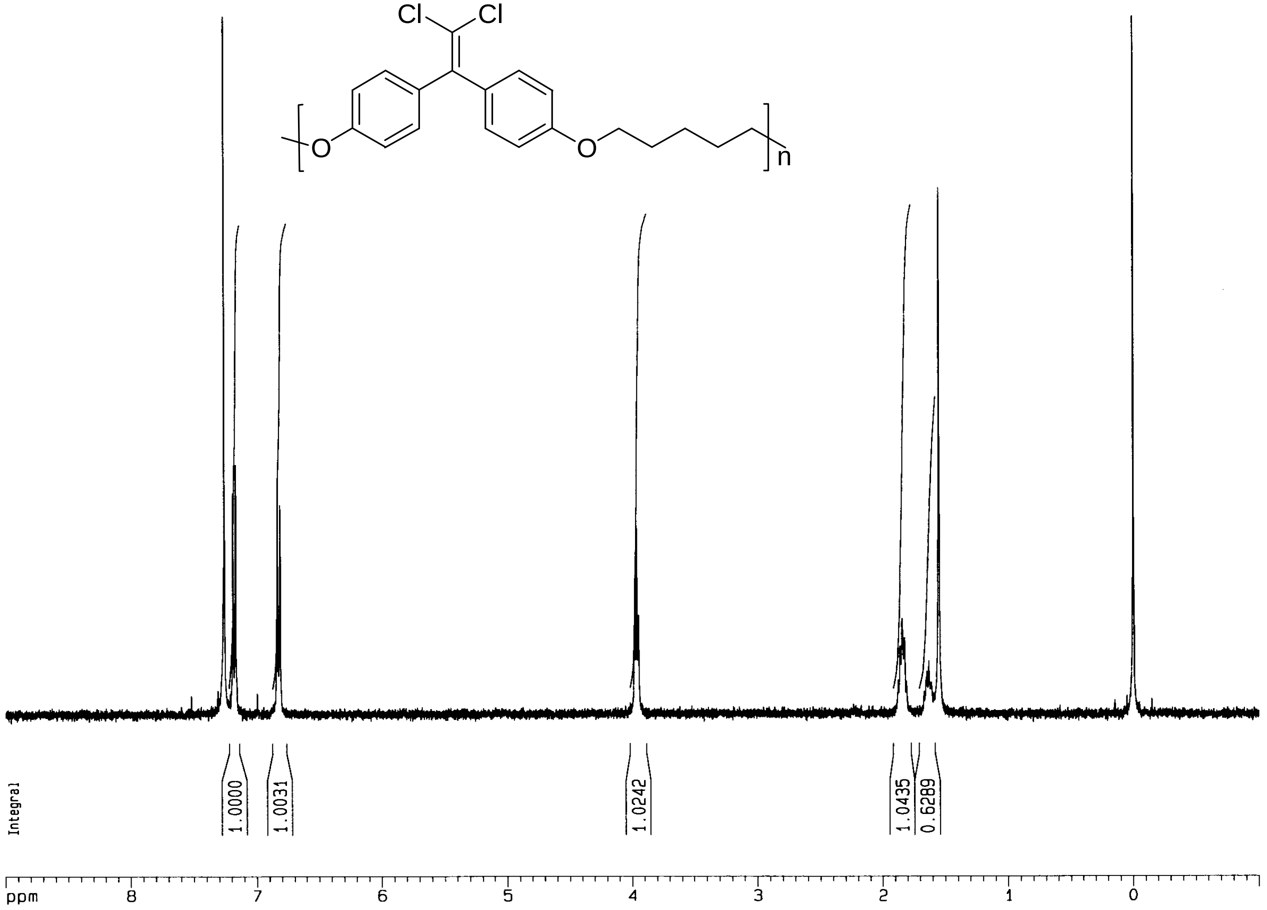


Date: Sat Jul 12 17:11:43 2003 **JLJ-III-193

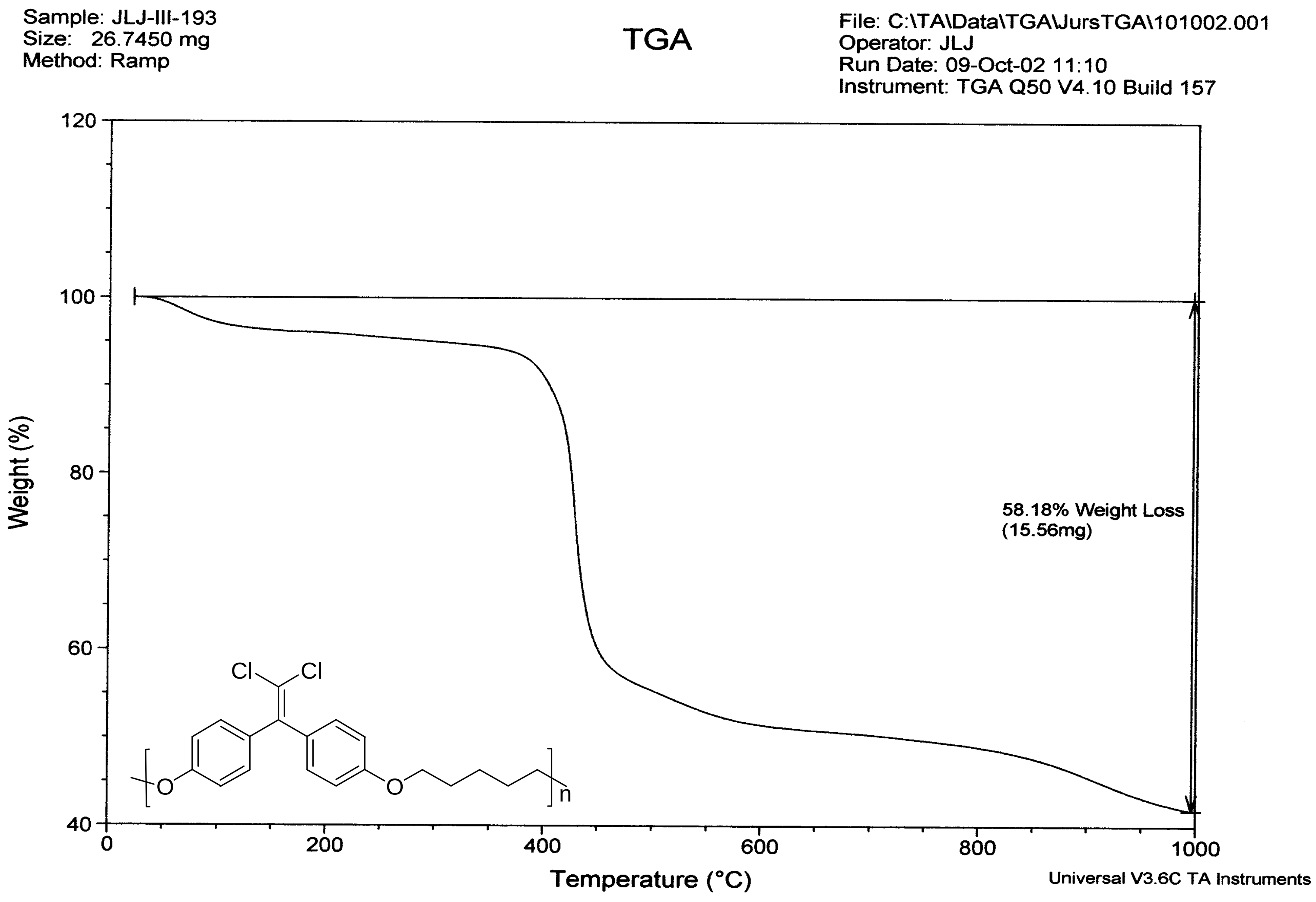
Scans: 18

Resolution: 4.000

JLJ-III-193



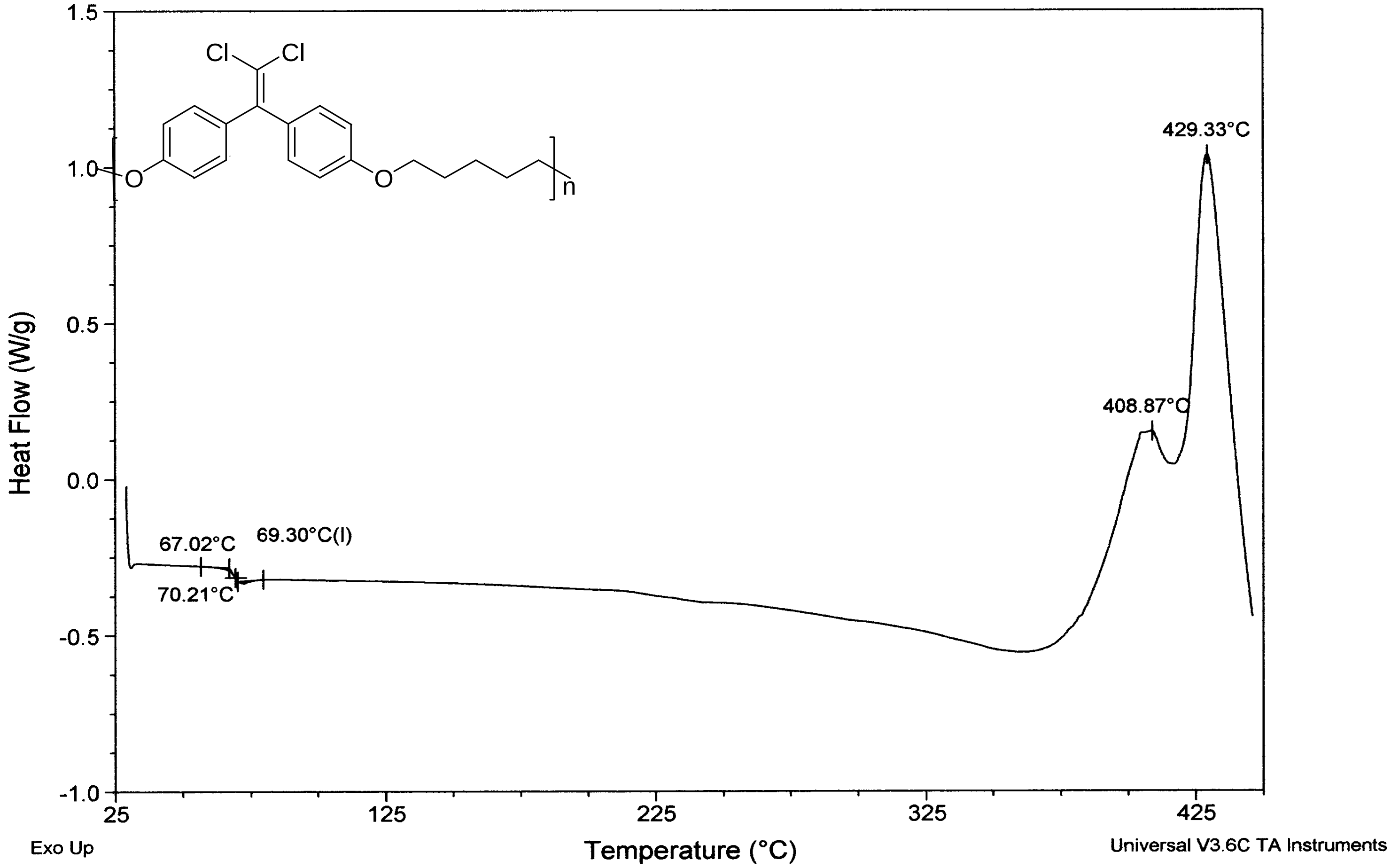
```
Current Data Parameters
NAME           jljiii193
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030220
Time               16.28
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 724.1
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300093 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06500 Hz/cm
```

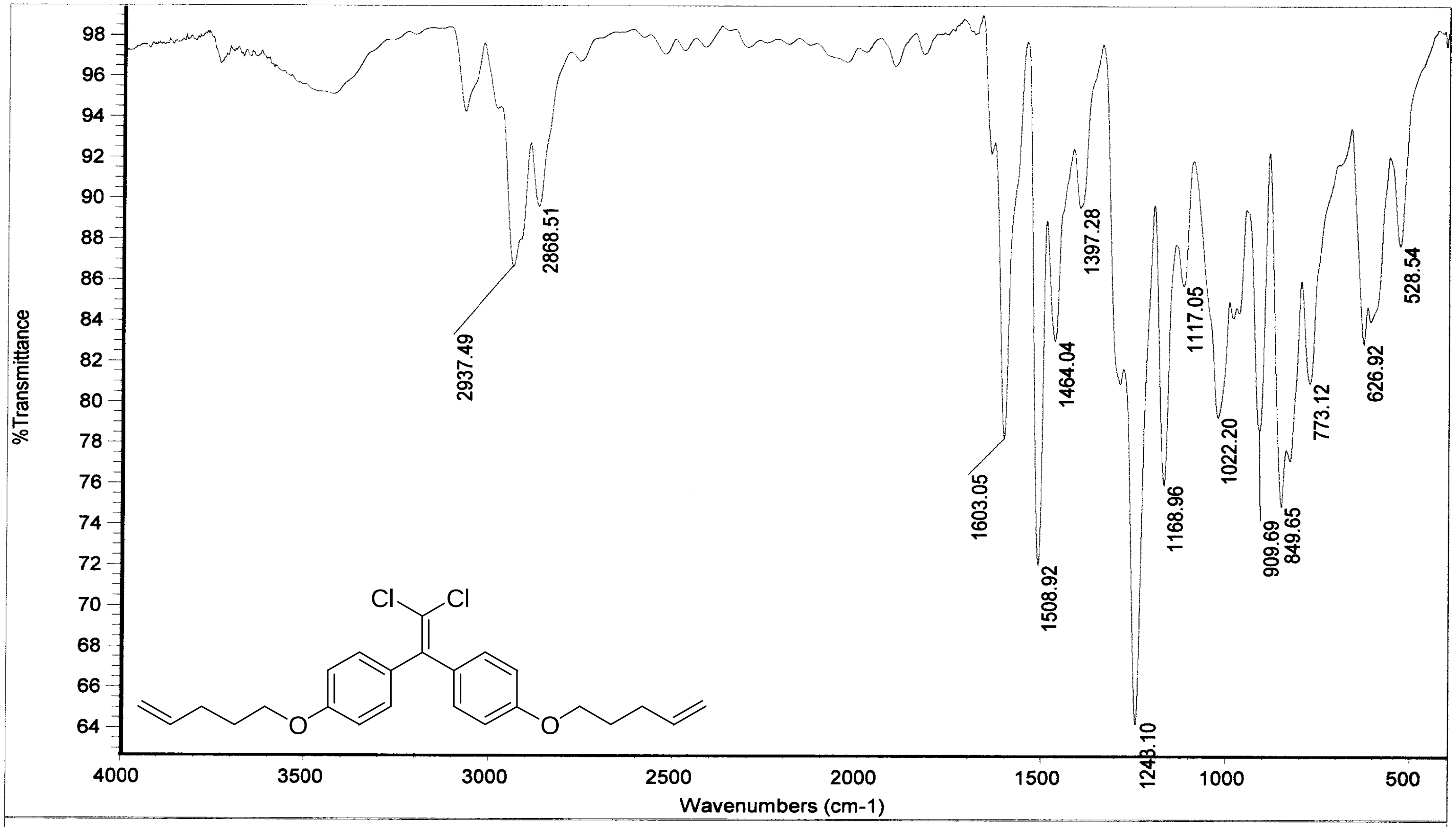

Sample: JLJ-III-193
Size: 26.7450 mg
Method: Ramp
TGA
File: C:\TA\Data\TGA\JursTGA\101002.001
Operator: JLJ
Run Date: 09-Oct-02 11:10
Instrument: TGA Q50 V4.10 Build 157
Weight (%)
120
100
80
60
40
0
200
400
600
800
1000
Temperature (°C)
58.18% Weight Loss
(15.56mg)
Cl
Cl
O
O
n
Universal V3.6C TA Instruments

Sample: JLJ-III-193
Size: 4.4000 mg
Method: Ramp

DSC

File: C:\TA\Data\DSC\JursDSC\JJ112602.003
Operator: JLJ
Run Date: 26-Nov-02 13:40
Instrument: DSC Q10 V6.21 Build 233



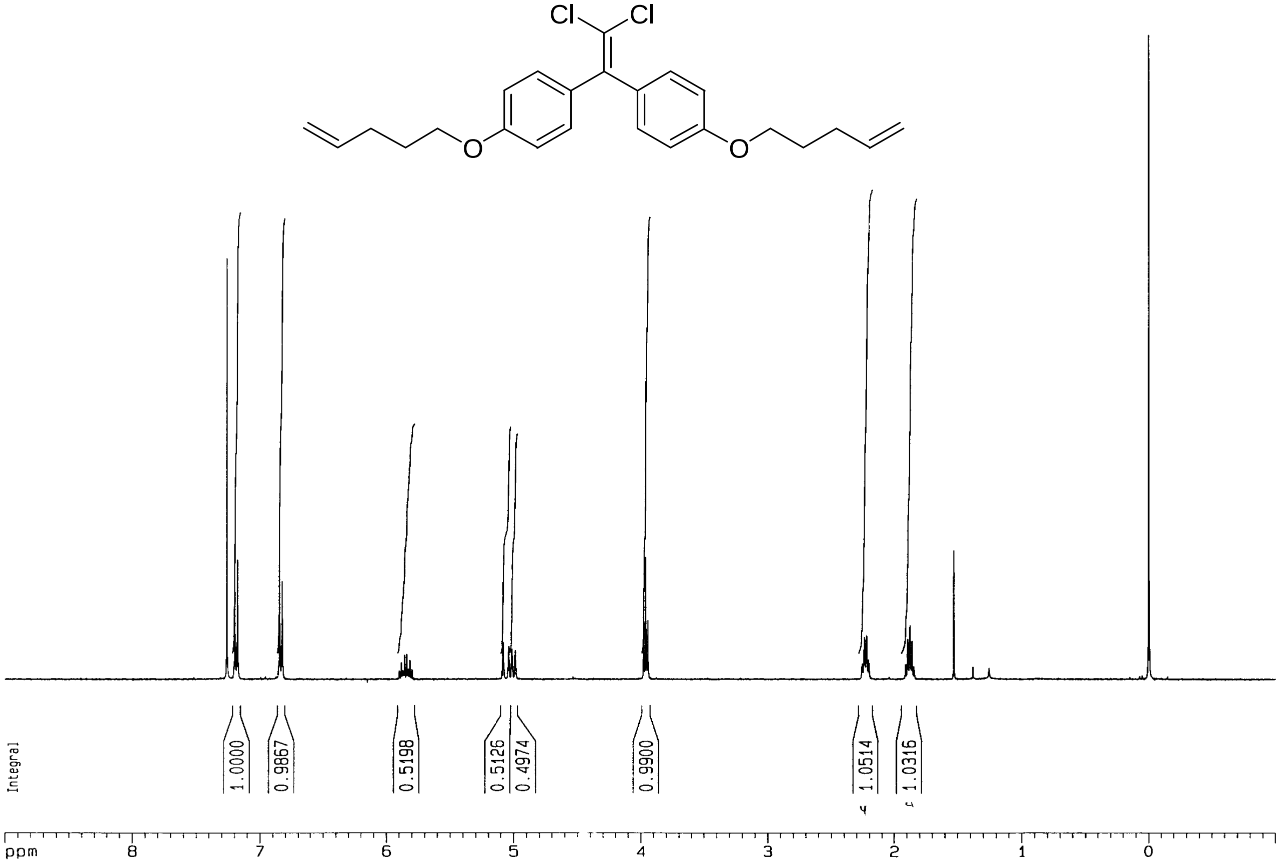


Date: Mon Sep 02 13:46:45 2002 **DDE-pentene

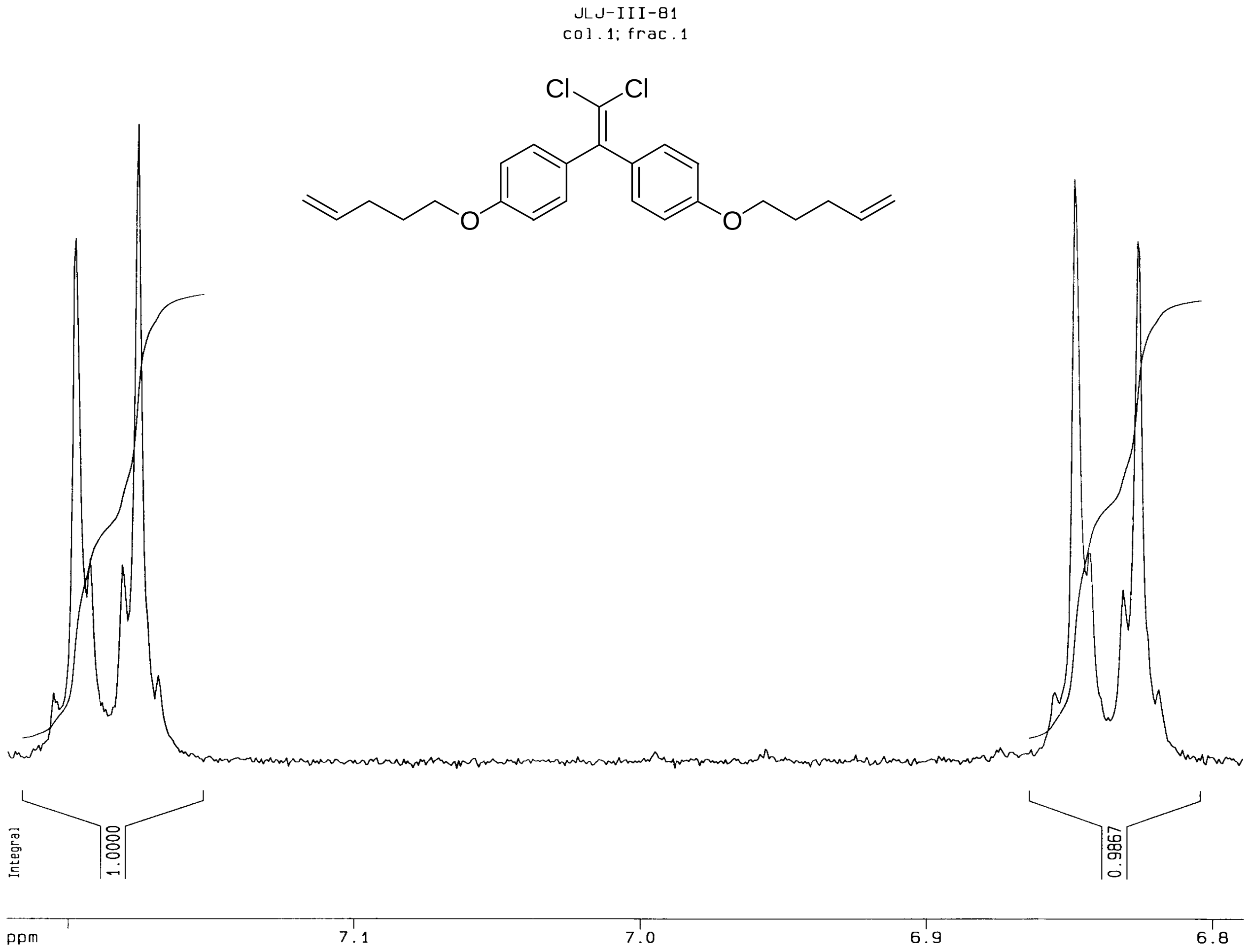
Scans: 32

Resolution: 4.000

JLJ-III-81
col.1; frac.1

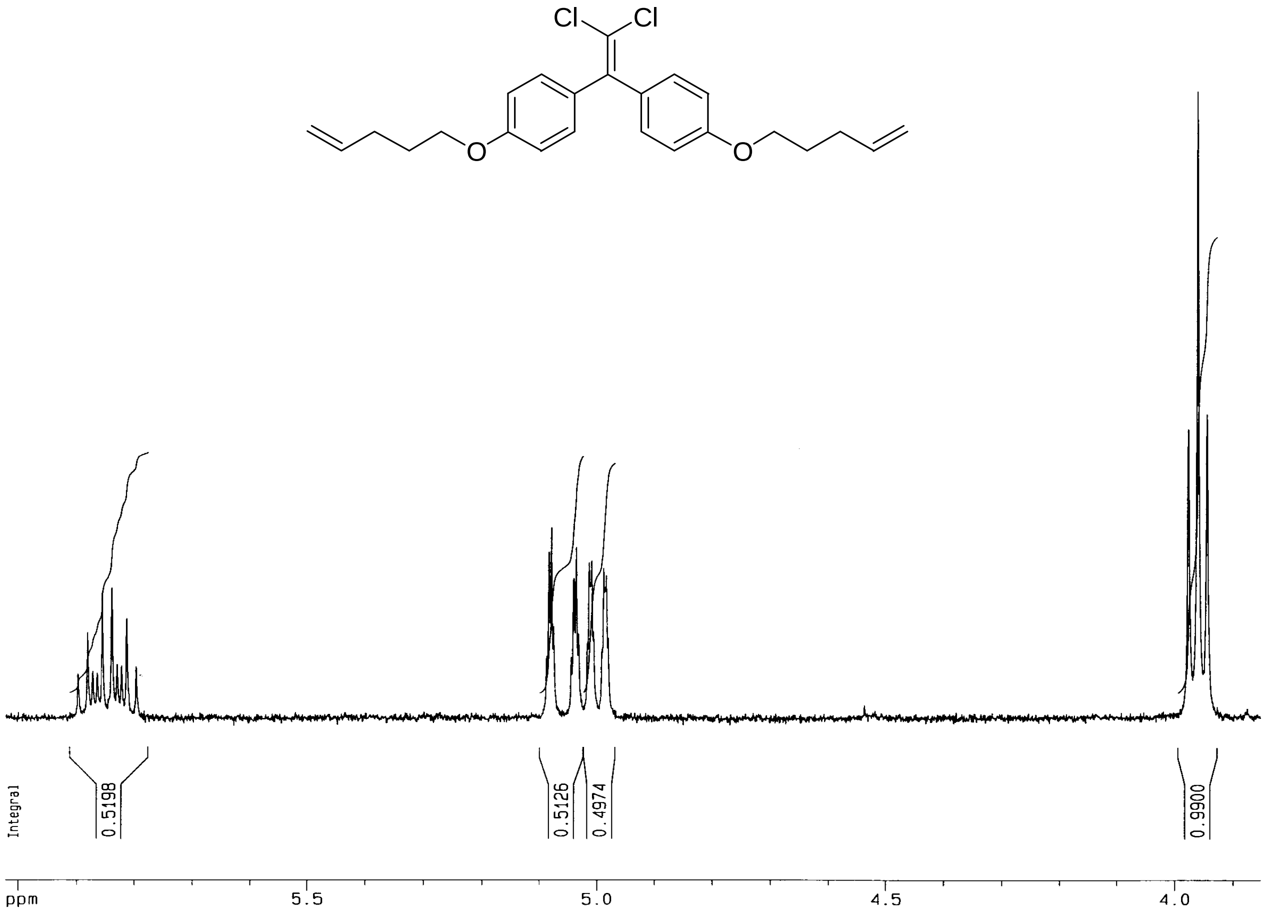


```
Current Data Parameters
NAME             jljiii81
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20020513
Time                15.06
INSTRUM             spect
PROBHD     5 mm BBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  645.1
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 ========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300096 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 9.000 ppm
F1                3601.17 Hz
F2P                -1.000 ppm
F2                -400.13 Hz
PPMCM             0.50000 ppm/cm
HZCM            200.06500 Hz/cm
```



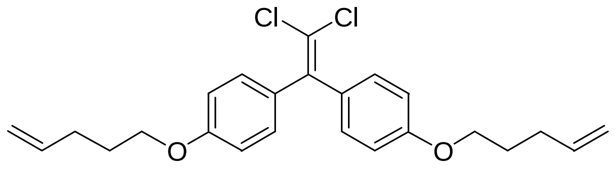
```
Current Data Parameters
NAME            jljiii81
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20020513
Time               15.06
INSTRUM            spect
PROBHD    5 mm 880 BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 645.1
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300096 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.221 ppm
F1               2889.48 Hz
F2P                6.789 ppm
F2               2716.58 Hz
PPMCM            0.02160 ppm/cm
HZCM             8.64479 Hz/cm
```

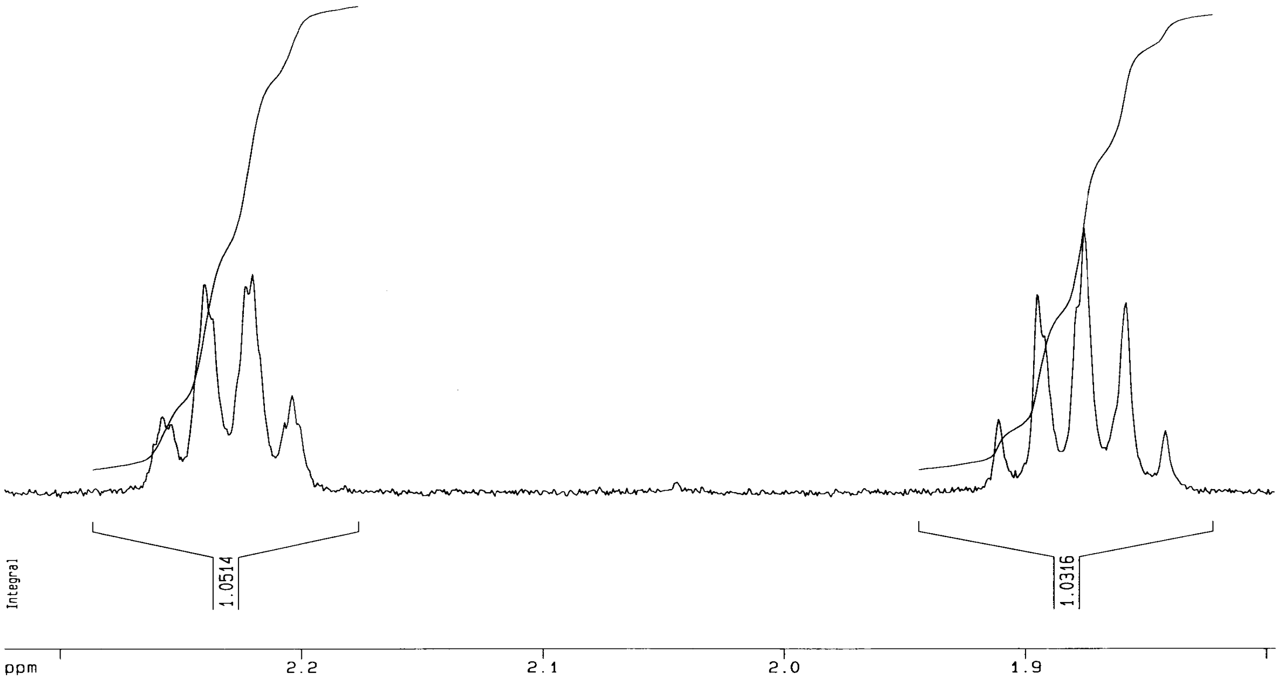
JLJ-III-81
col.1; frac.1



```
Current Data Parameters
NAME            jljiii81
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20020513
Time               15.06
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 645.1
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300096 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                6.021 ppm
F1               2409.21 Hz
F2P                3.853 ppm
F2               1541.53 Hz
PPMCM            0.10842 ppm/cm
HZCM            43.38402 Hz/cm
```

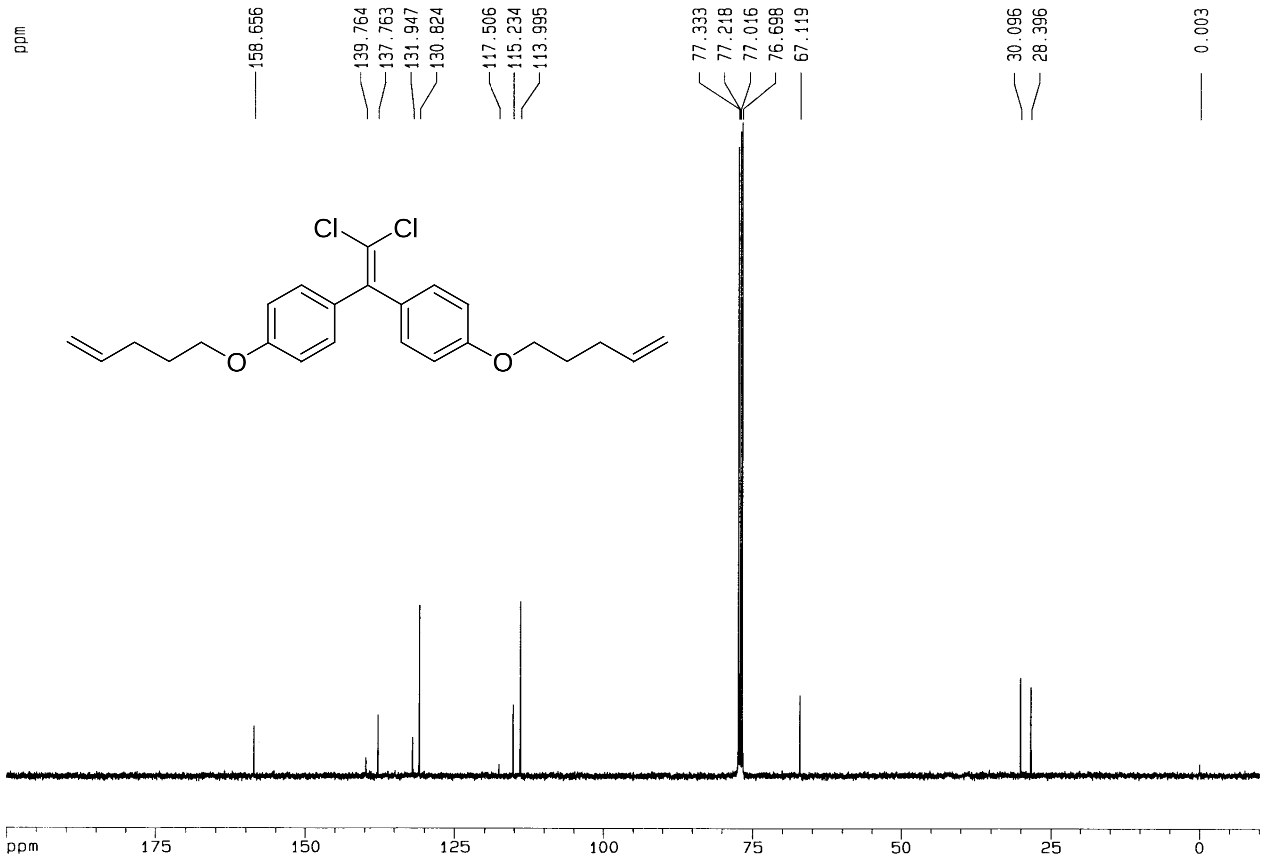
JLJ-III-81
col.1; frac.1





```
Current Data Parameters
NAME            jljiii81
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20020513
Time               15.06
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 645.1
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300096 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                2.323 ppm
F1                929.45 Hz
F2P                1.796 ppm
F2                718.76 Hz
PPMCM            0.02633 ppm/cm
HZCM            10.53415 Hz/cm
```

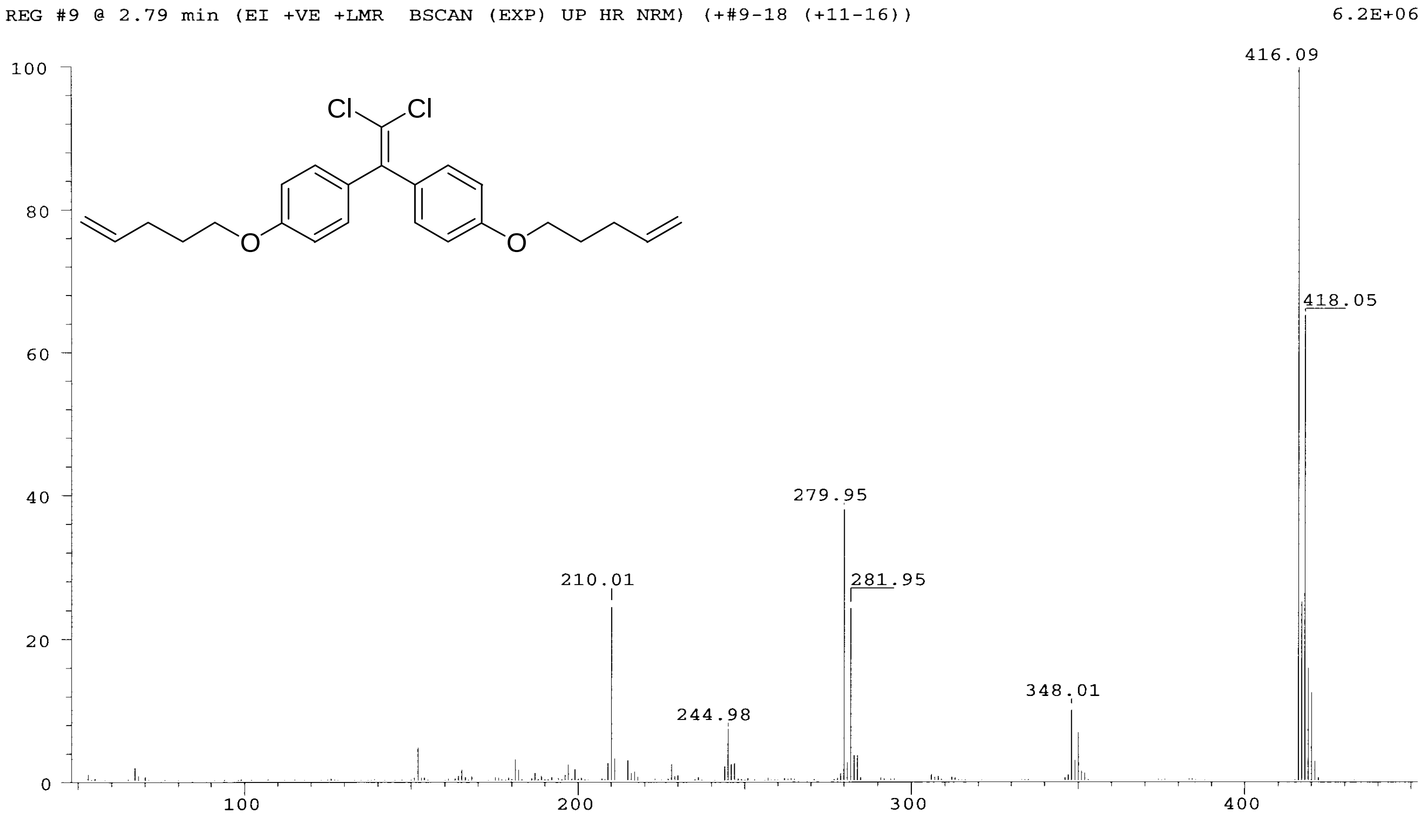
DDE-Pentene

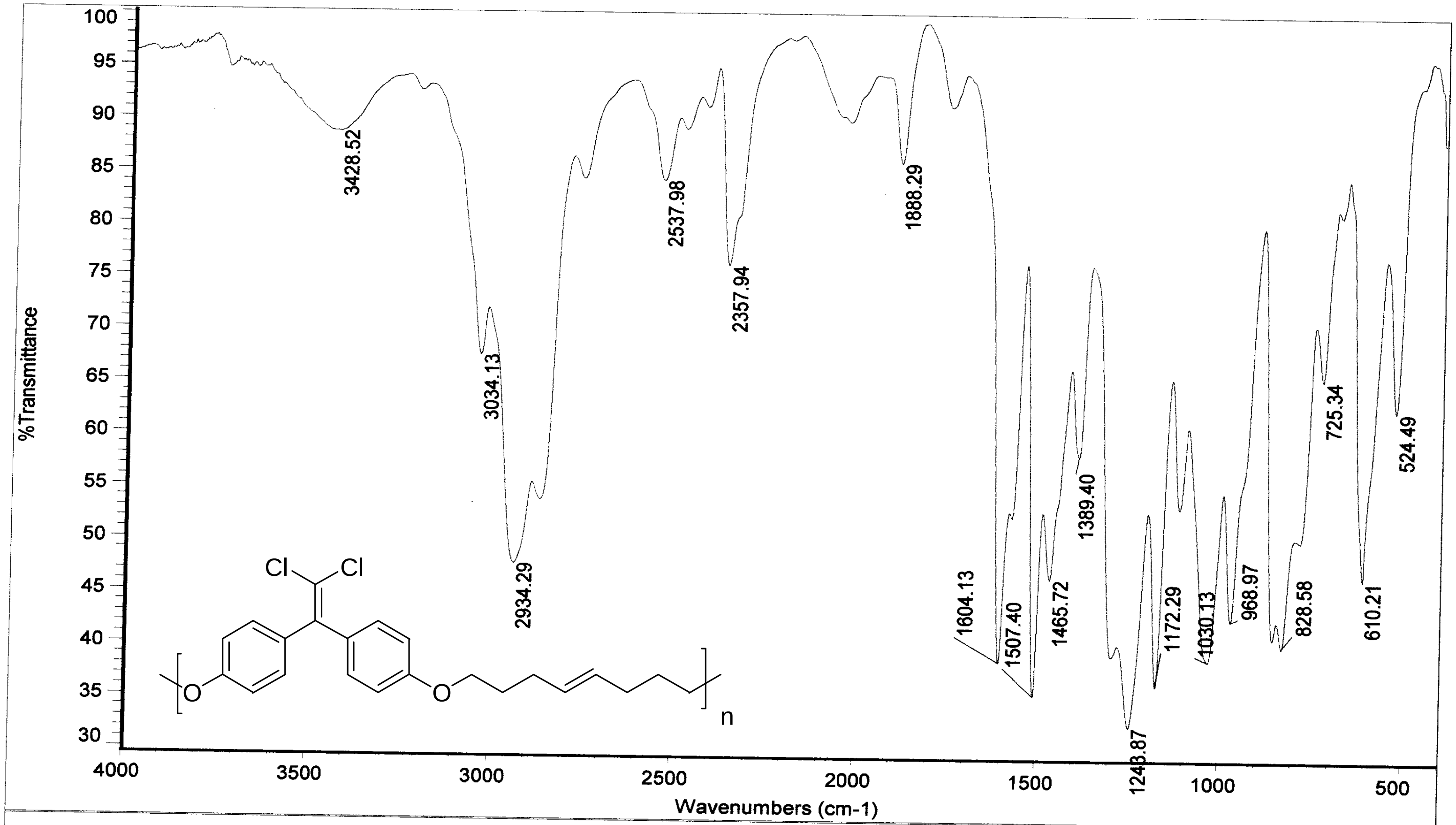


```
Current Data Parameters
NAME      jlj-ddepentene
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20020902
Time               19.00
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   921
DS                     0
SWH            25125.629 Hz
FIDRES          0.383387 Hz
AQ             1.3042164 sec
RG                3549.1
DW                19.900 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 ===========
NUC1                 13C
P1                  8.30 usec
PL1                 0.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 ===========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127697 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              200.000 ppm
F1              20122.55 Hz
F2P              -10.000 ppm
F2              -1006.13 Hz
PPMCM           10.50000 ppm/cm
HZCM          1056.43408 Hz/cm
```

SPEC: jlj-iii-139 (17-Feb-03 17:57:34)
Samp: JLJ-III-139 C24 H26 O2 Cl2 416.130986
Oper: TDM Study: EI + HR
Base: 416.09 Masses: 50.00 > 450.00
Peak: 1000.0 mmu Intensity: 6169300
REG #9 @ 2.79 min (EI +VE +LMR BSCAN (EXP) UP HR NRM) (+#9-18 (+11-16))

Scans: 1 > 20
Client: DK/JMT
#Peaks: 238
RIC: 25765258

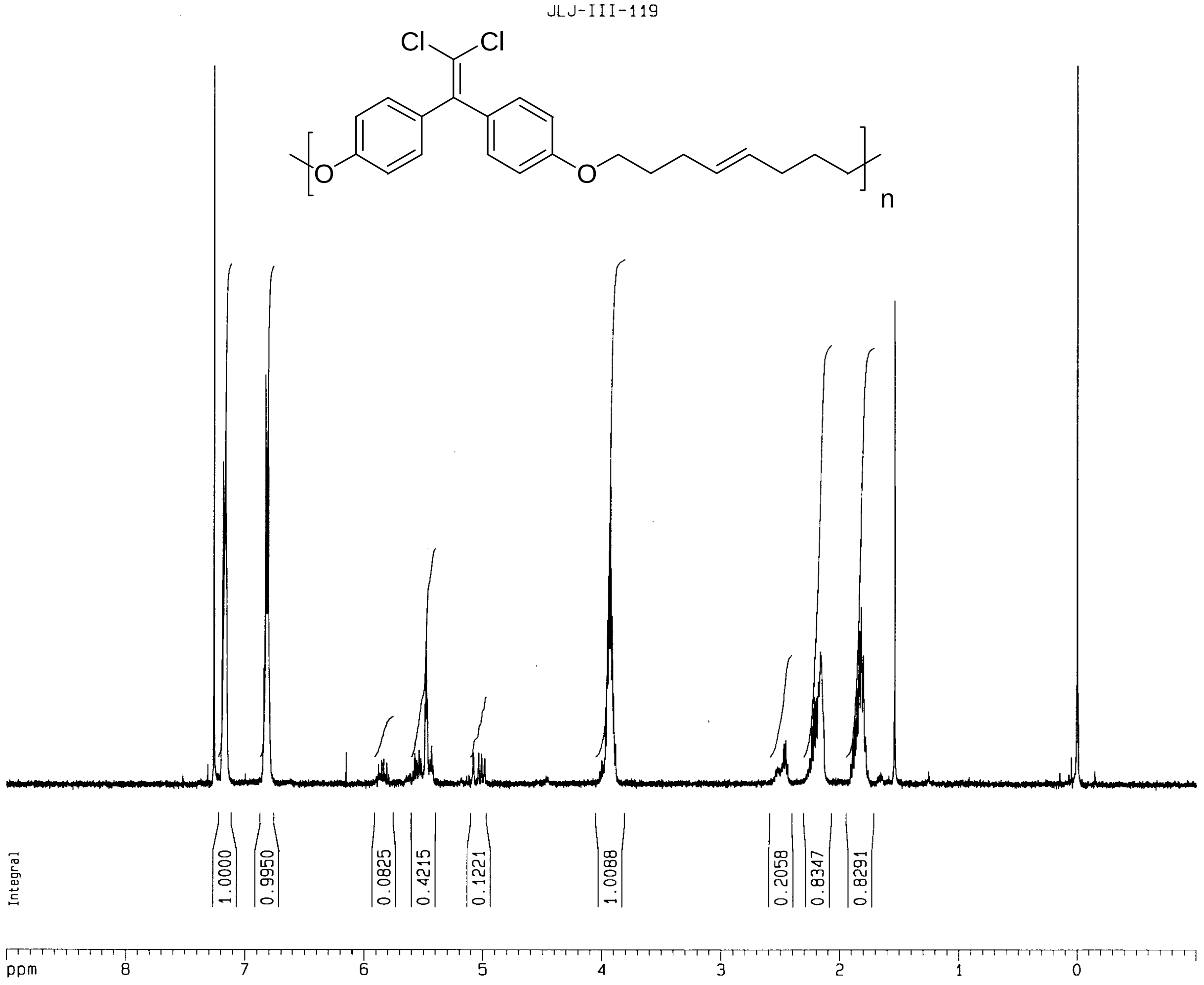




Date: Mon Sep 02 14:55:37 2002 **JLJ-III-109

Scans: 18

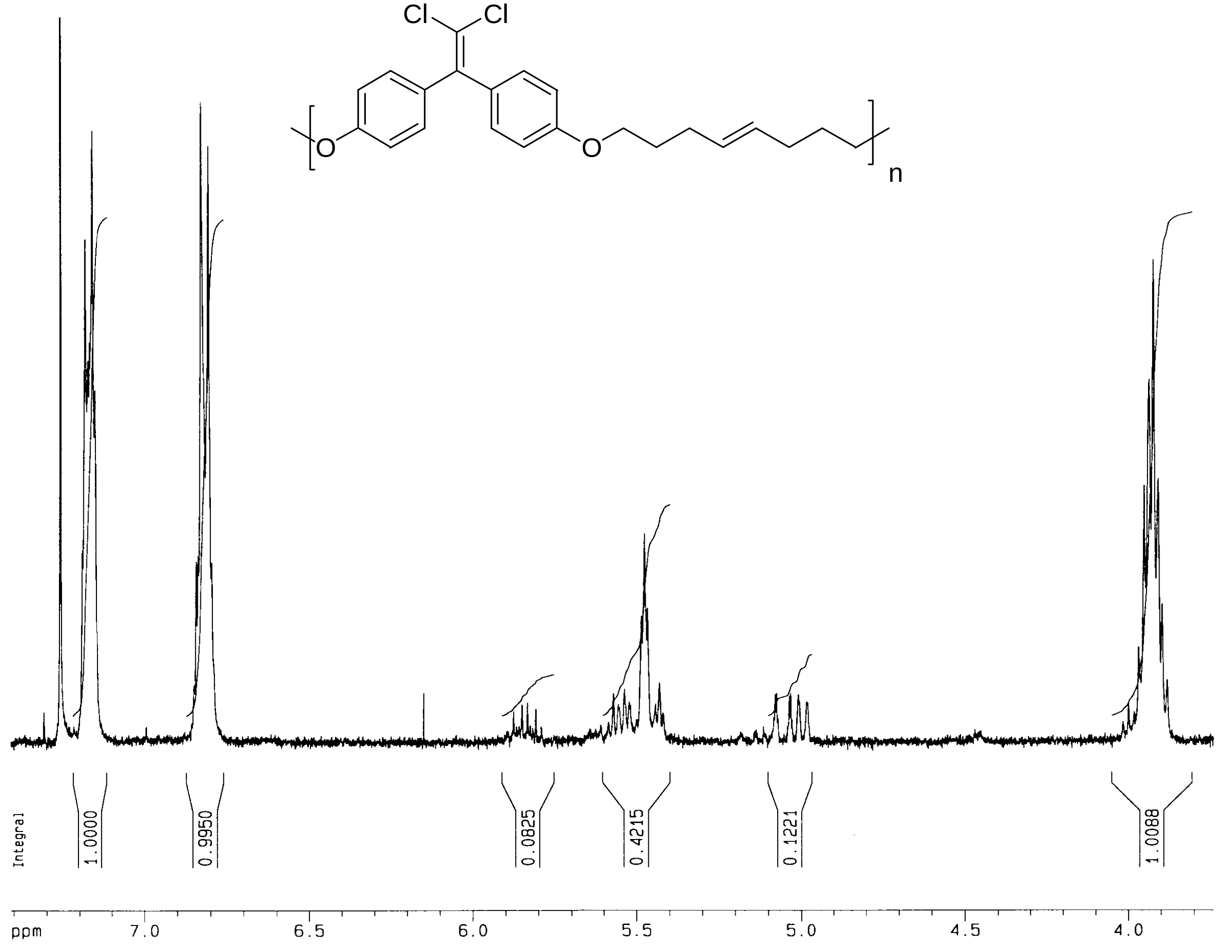
Resolution: 4.000



JLJ-III-119

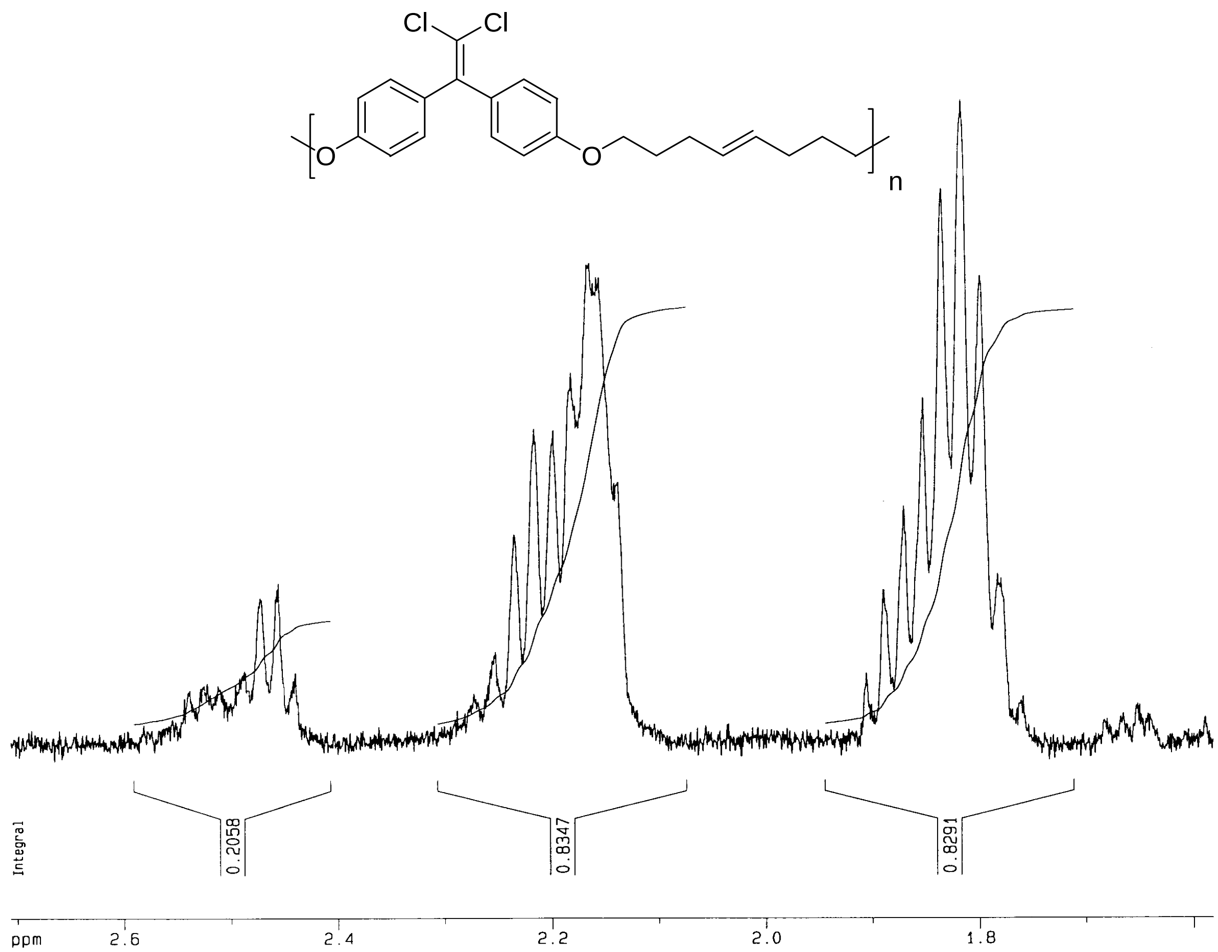
```
Current Data Parameters
NAME          jlj-iii-119
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20020902
Time                18.02
INSTRUM             spect
PROBHD     5 mm BBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  574.7
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             3.00000000 sec

============ CHANNEL f1 ========
NUC1                   1H
P1                  12.50 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300099 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 9.000 ppm
F1                3601.17 Hz
F2P                -1.000 ppm
F2                -400.13 Hz
PPMCM             0.50000 ppm/cm
HZCM            200.06500 Hz/cm
```

JLJ-III-119



```
Current Data Parameters
NAME         jlj-iii-119
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20020902
Time               18.02
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 574.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1          3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300099 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.409 ppm
F1               2964.65 Hz
F2P                3.741 ppm
F2               1496.94 Hz
PPMCM            0.18340 ppm/cm
HZCM            73.38549 Hz/cm
```

JLJ-III-119

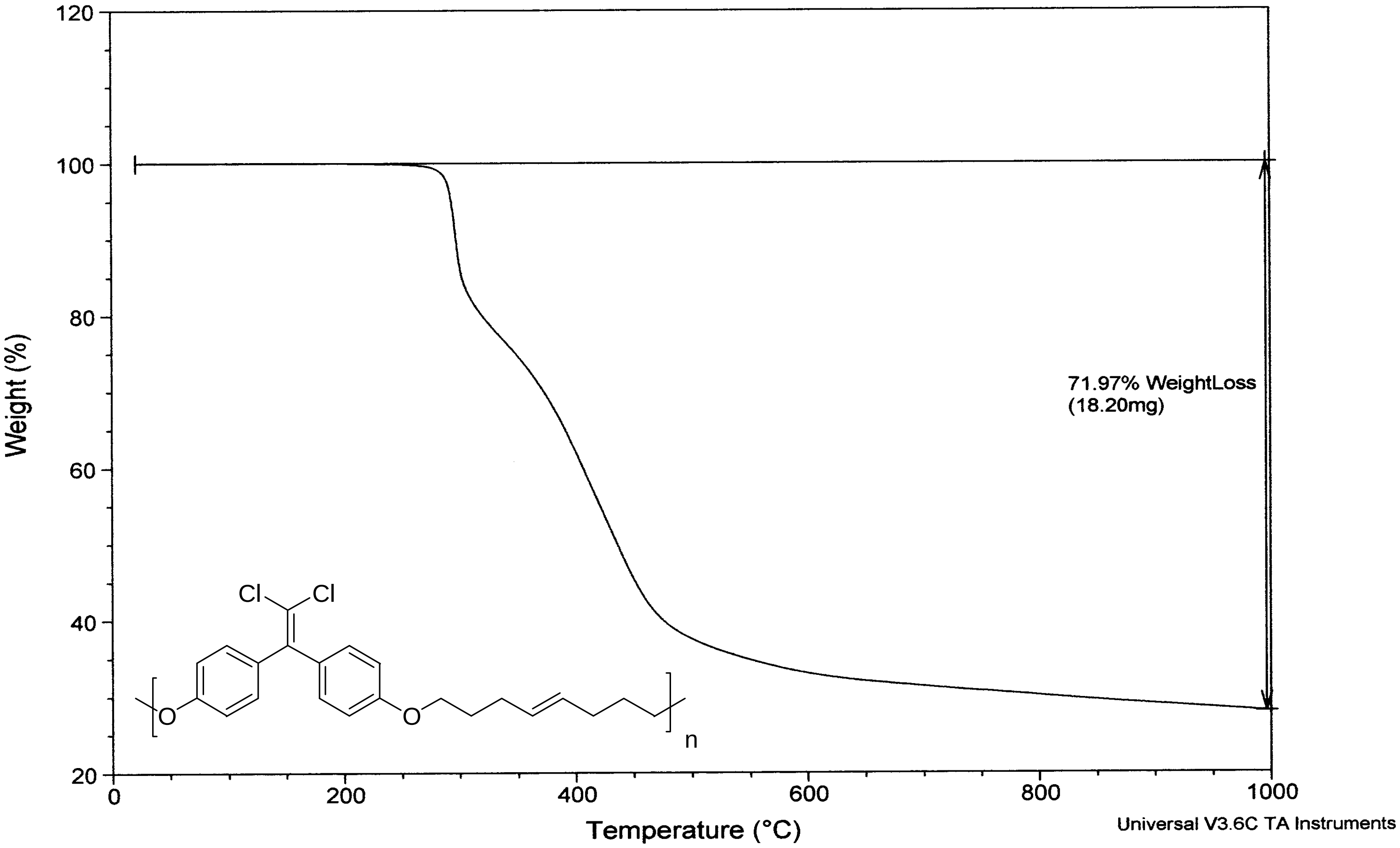


```
Current Data Parameters
NAME        jlj-iii-119
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20020902
Time              18.02
INSTRUM           spect
PROBHD     5 mm BBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                574.7
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 =========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300099 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               2.707 ppm
F1              1082.99 Hz
F2P               1.582 ppm
F2               632.87 Hz
PPMCM           0.05625 ppm/cm
HZCM           22.50596 Hz/cm
```

Sample: JLJ-III-191
Size: 25.2880 mg
Method: Ramp

TGA

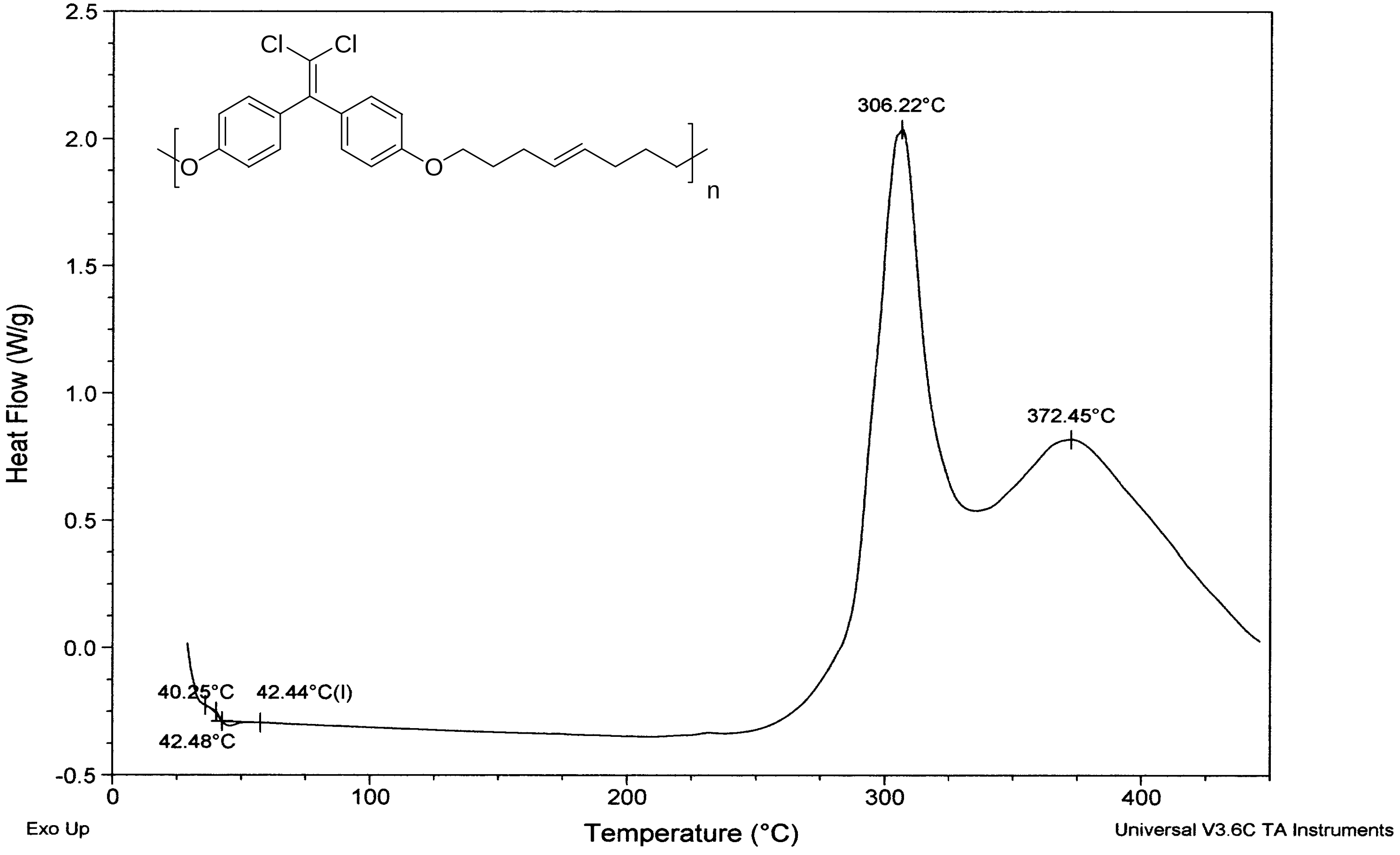
File: C:\TA\Data\TGA\chris dyke\cd-1-87.002
Operator: JLJ
Run Date: 29-Oct-02 11:06
Instrument: TGA Q50 V4.10 Build 157

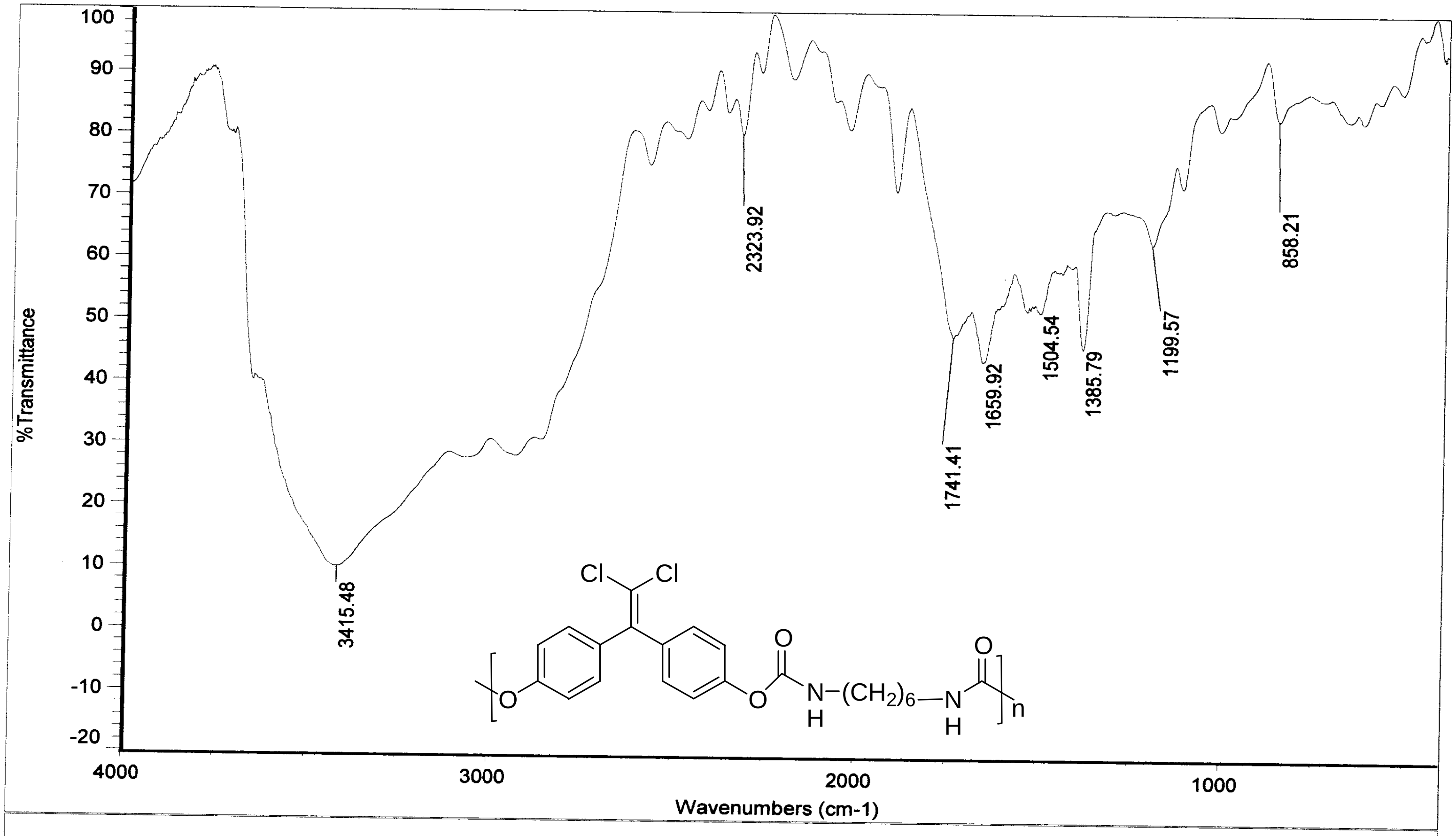


Sample: JLJ-III-191
Size: 13.3000 mg
Method: Ramp

DSC

File: C:\TA\Data\DSC\JursDSC\JJ120202.006
Operator: JLJ
Run Date: 02-Dec-02 16:21
Instrument: DSC Q10 V6.21 Build 233

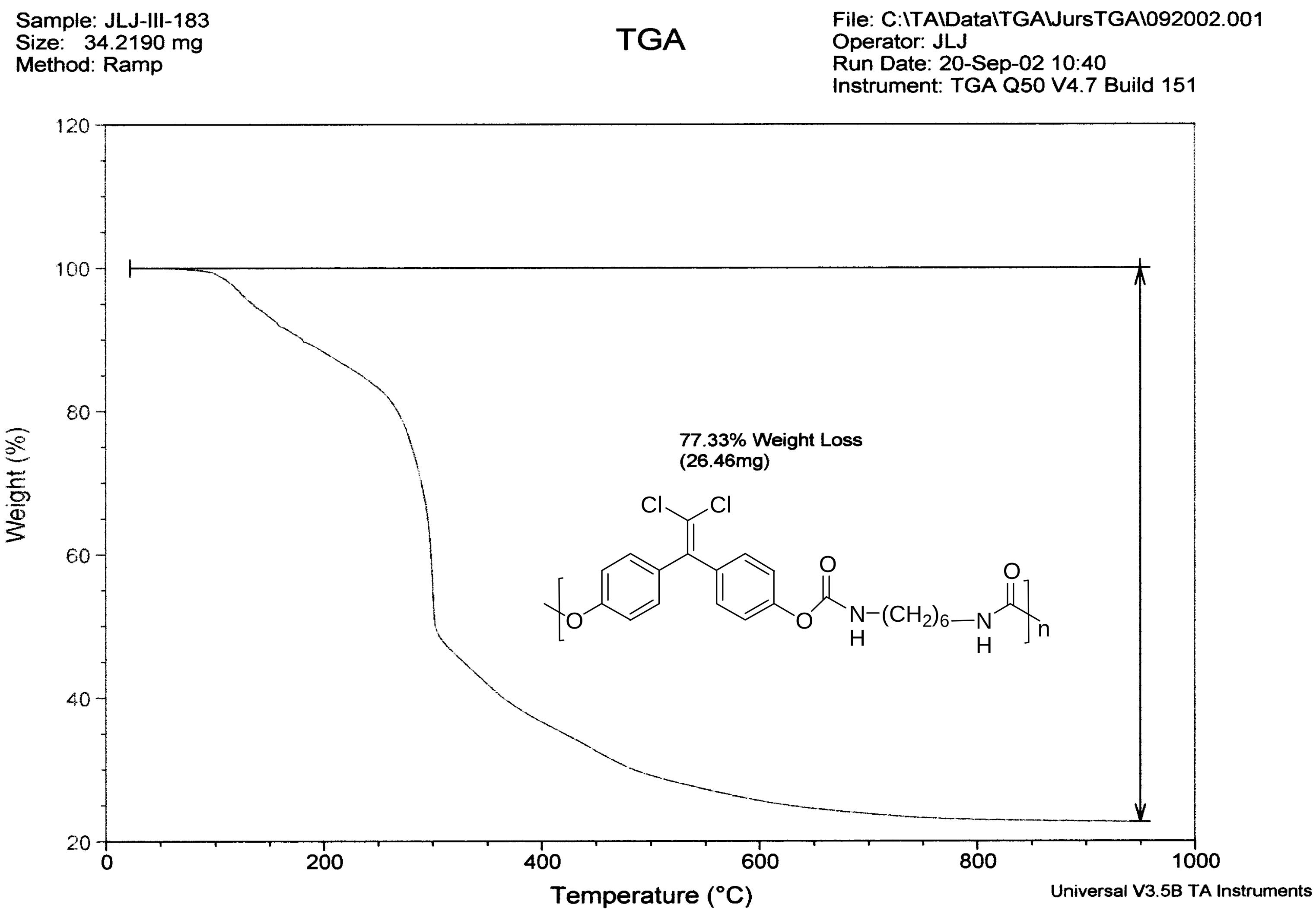


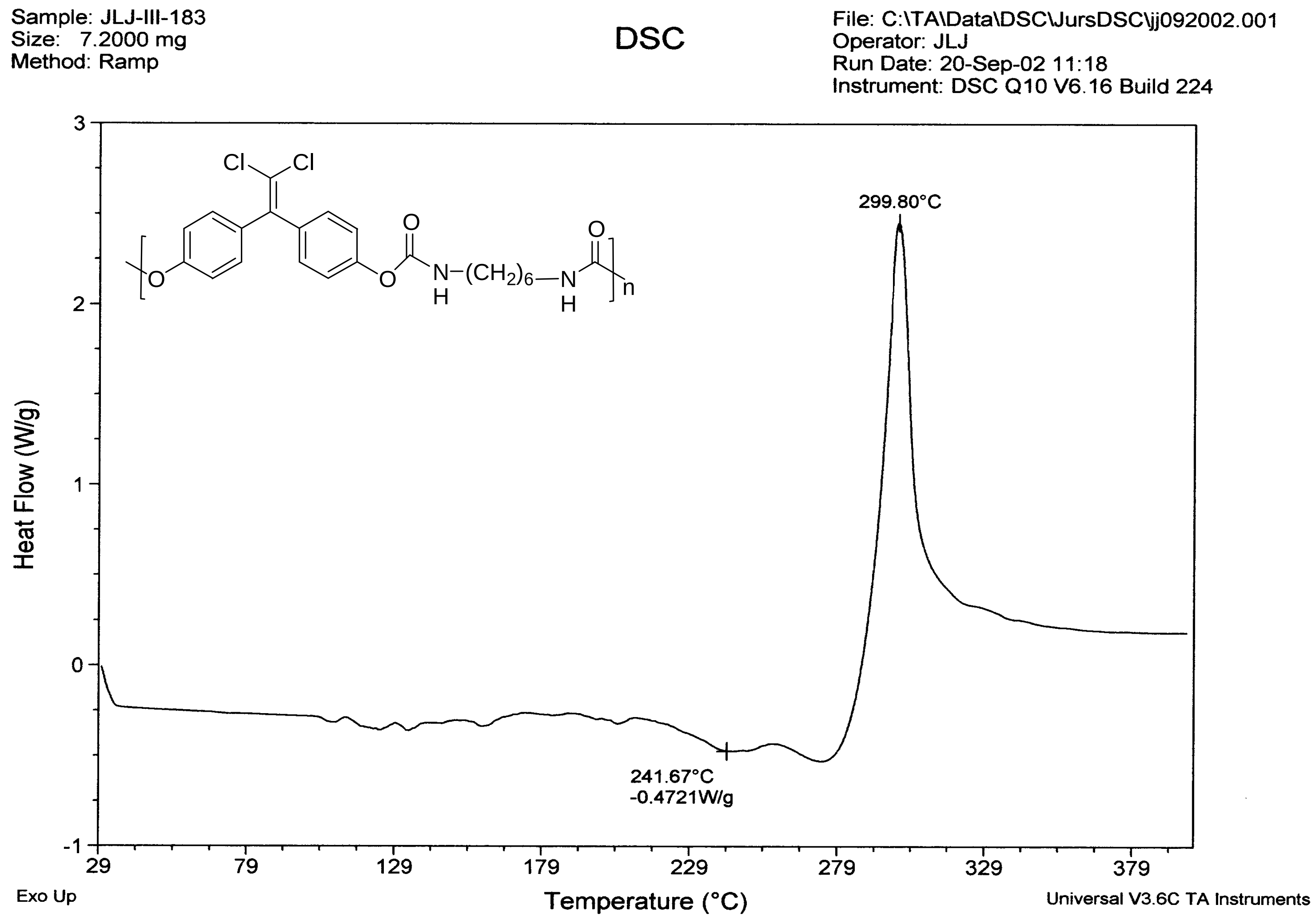


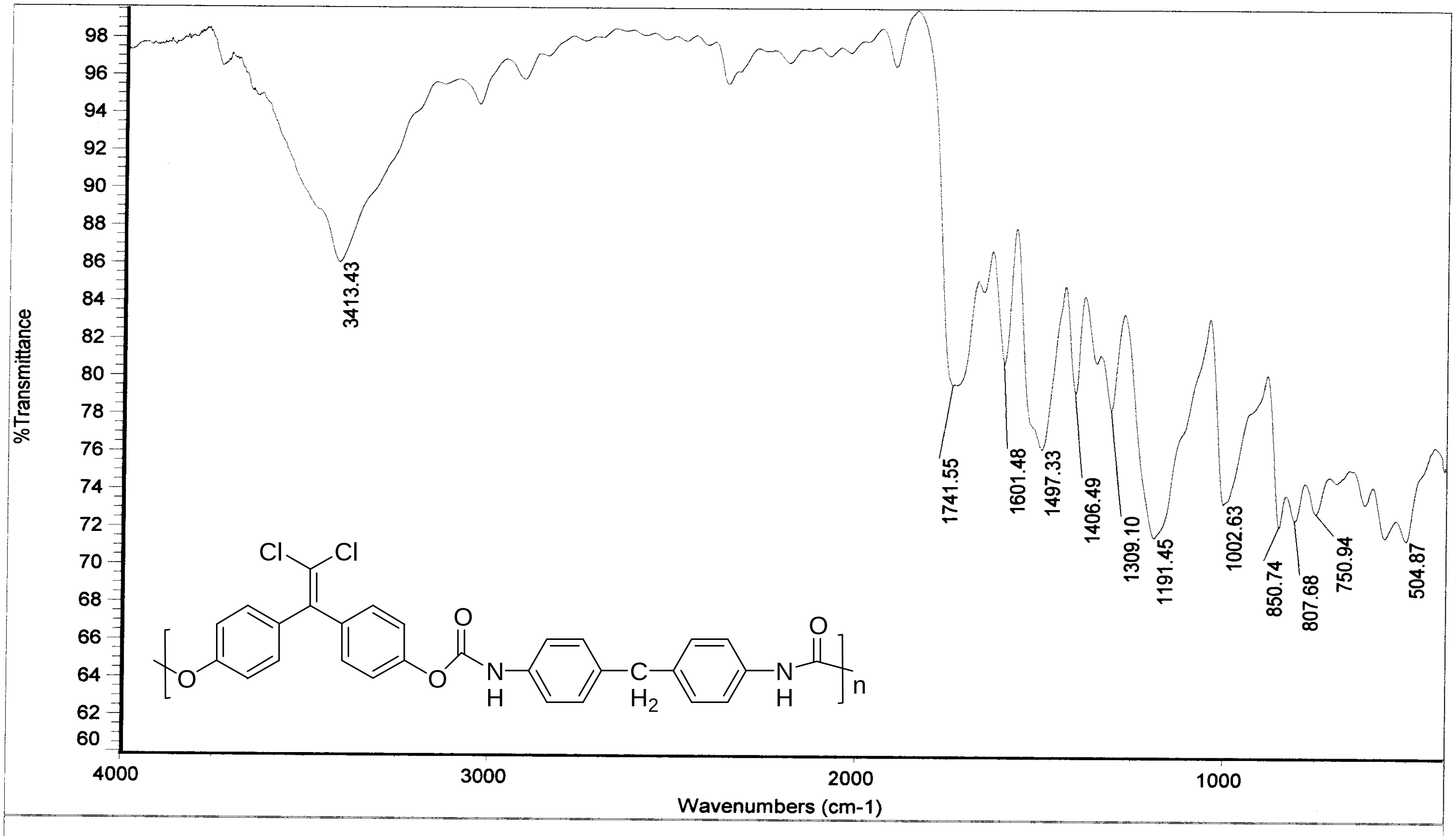
Date: Mon Jul 14 11:19:18 2003 ****JLJ-III-183

Scans: 18

Resolution: 4.000


Sample: JLJ-III-183
Size: 34.2190 mg
Method: Ramp
TGA
File: C:\TA\Data\TGA\JursTGA\092002.001
Operator: JLJ
Run Date: 20-Sep-02 10:40
Instrument: TGA Q50 V4.7 Build 151
120
100
80
60
40
20
Weight (%)
0
200
400
600
800
1000
Temperature (°C)
77.33% Weight Loss
(26.46mg)
Cl
Cl
O
O
O
O
N−(CH2)6—N
H
H
n
Universal V3.5B TA Instruments

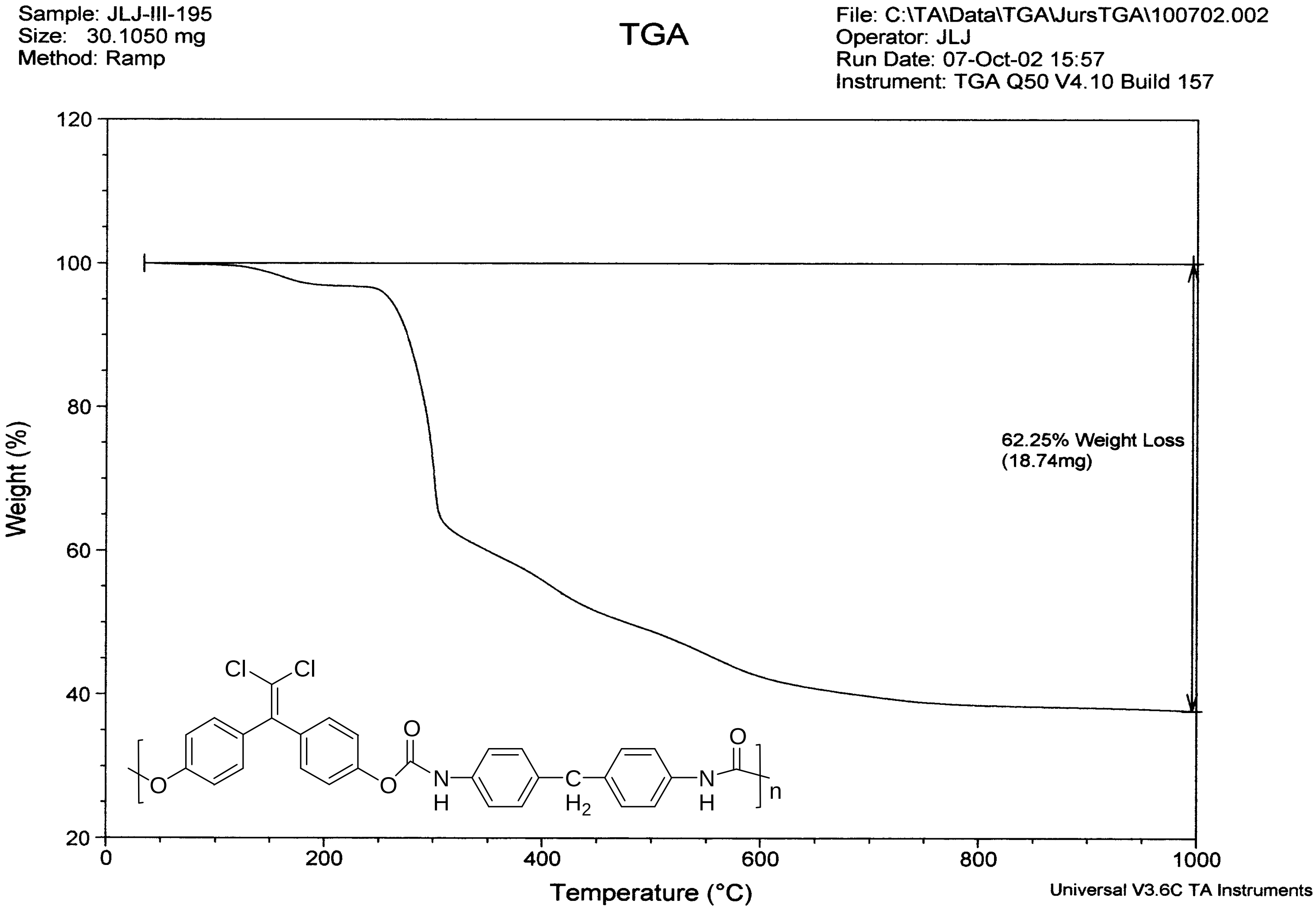

Sample: JLJ-III-183
Size: 7.2000 mg
Method: Ramp
DSC
File: C:\TA\Data\DSC\JursDSC\jj092002.001
Operator: JLJ
Run Date: 20-Sep-02 11:18
Instrument: DSC Q10 V6.16 Build 224
Cl
Cl
O
O
O
O
N–(CH2)6—N
H
H
n
299.80°C
241.67°C
-0.4721W/g
Heat Flow (W/g)
3
2
1
0
-1
29
79
129
179
229
279
329
379
Temperature (°C)
Exo Up
Universal V3.6C TA Instruments



Date: Mon Jul 14 14:12:18 2003 **JLJ-III-195

Scans: 18

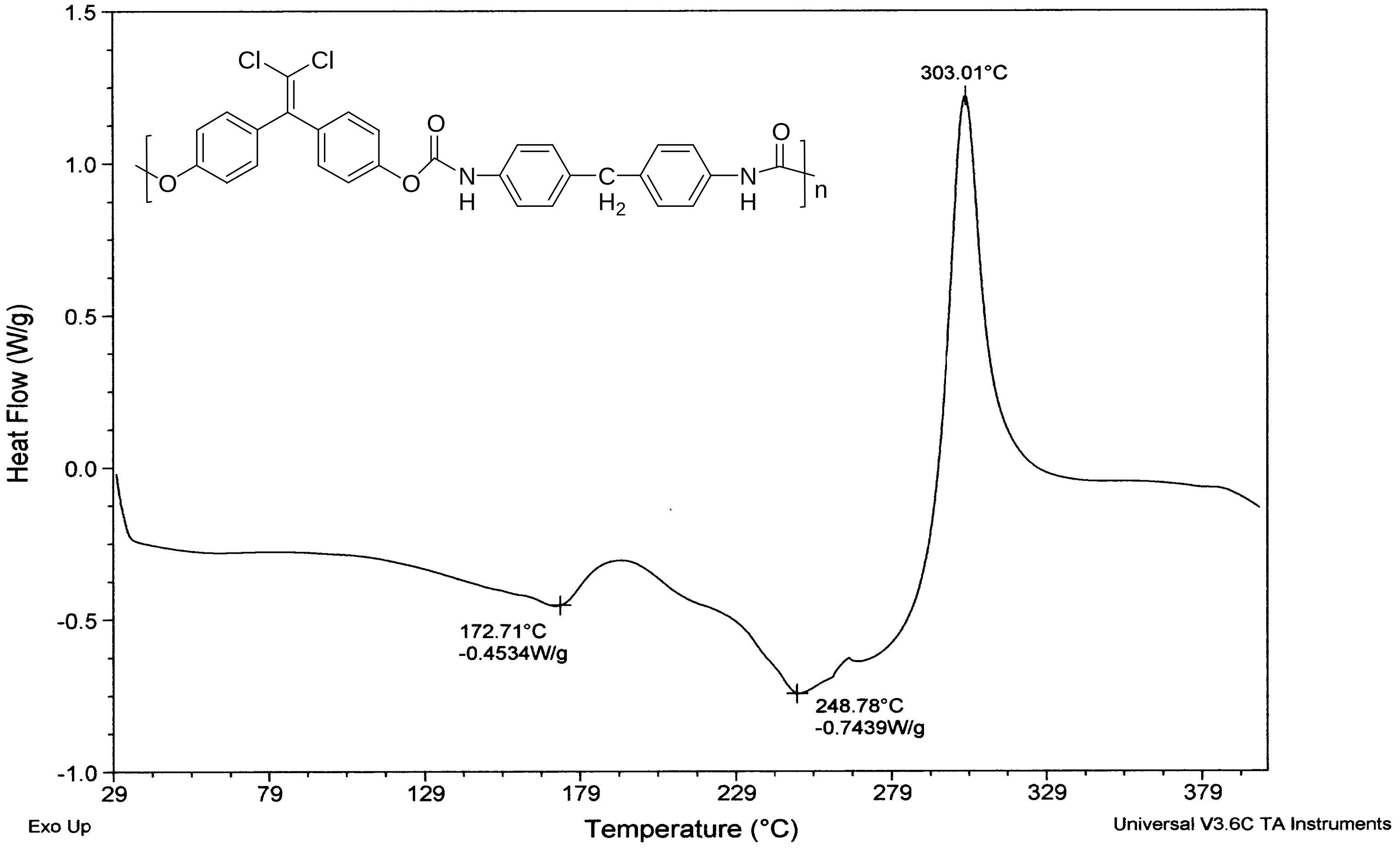
Resolution: 4.000

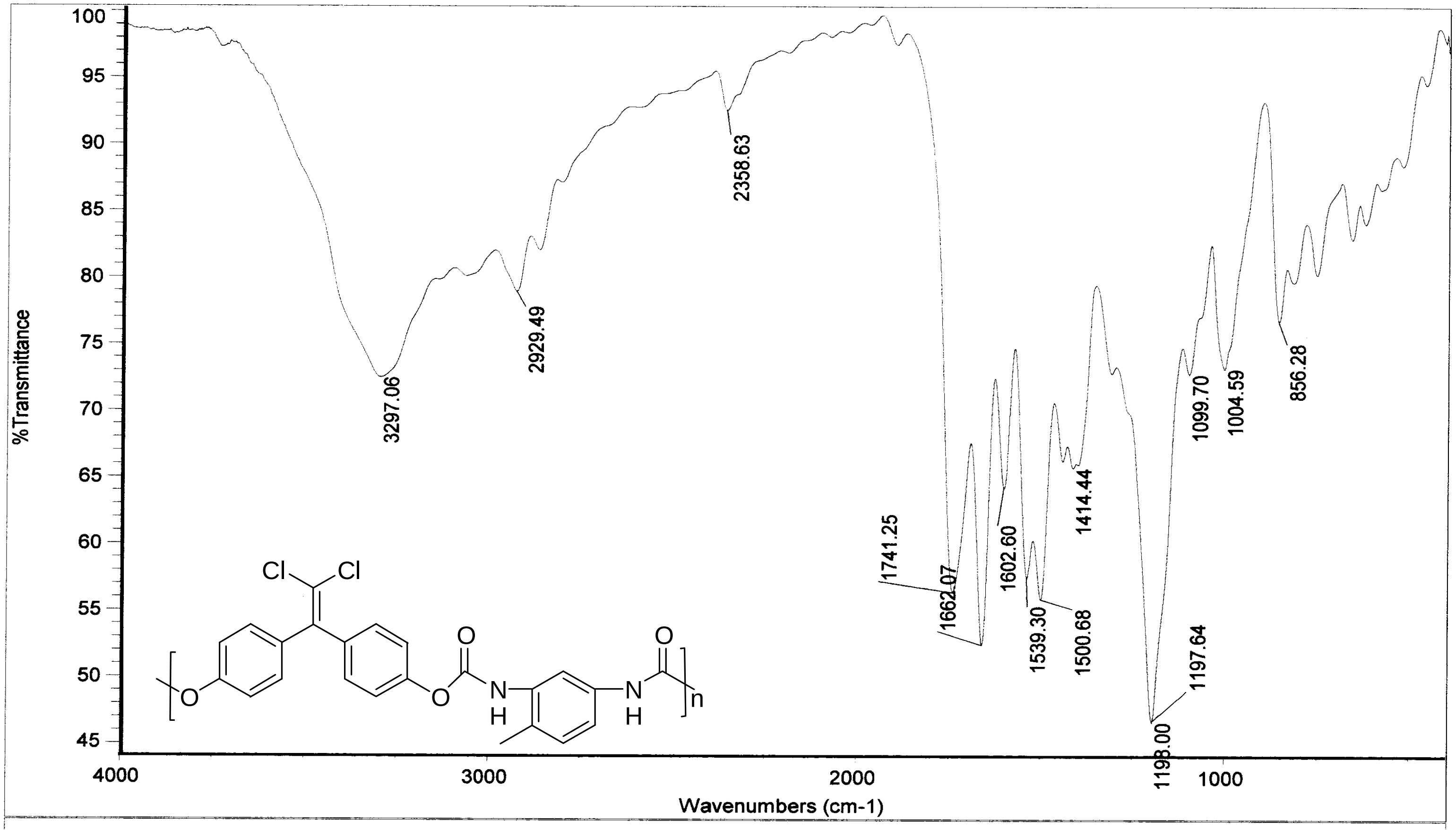

Sample: JLJ-III-195
Size: 30.1050 mg
Method: Ramp
TGA
File: C:\TA\Data\TGA\JursTGA\100702.002
Operator: JLJ
Run Date: 07-Oct-02 15:57
Instrument: TGA Q50 V4.10 Build 157
120
100
80
60
40
20
Weight (%)
0
200
400
600
800
1000
Temperature (°C)
62.25% Weight Loss
(18.74mg)
Cl
Cl
O
O
O
N
H
C
H2
N
H
O
n
Universal V3.6C TA Instruments

Sample: JLJ-III-195
Size: 9.2000 mg
Method: Ramp

DSC

File: C:\TA\Data\DSC\JursDSC\jj092002.002
Operator: JLJ
Run Date: 27-Sep-02 11:27
Instrument: DSC Q10 V6.16 Build 224

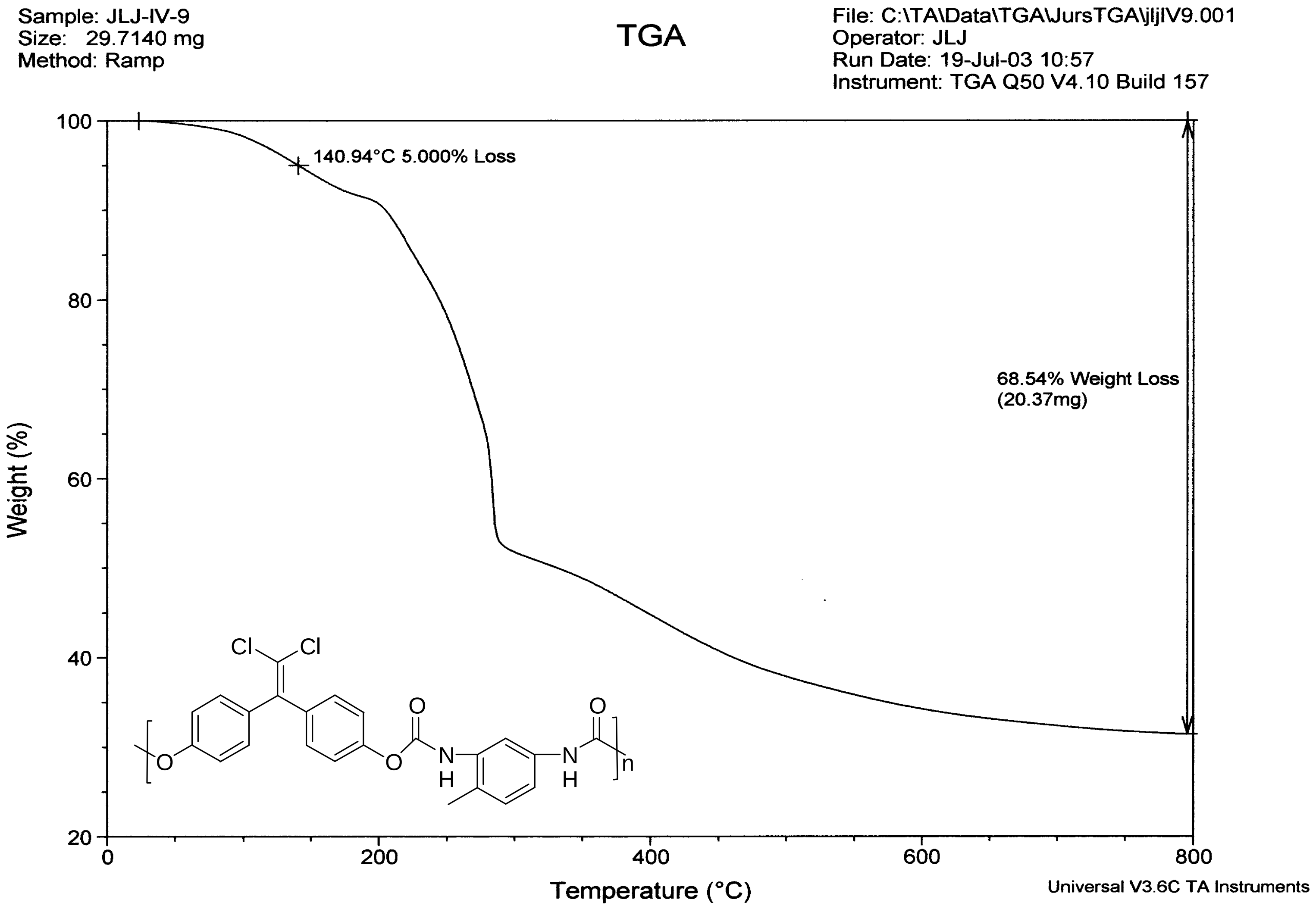




Date: Mon Jul 14 11:10:39 2003 **JLJ-IV-9

Scans: 18

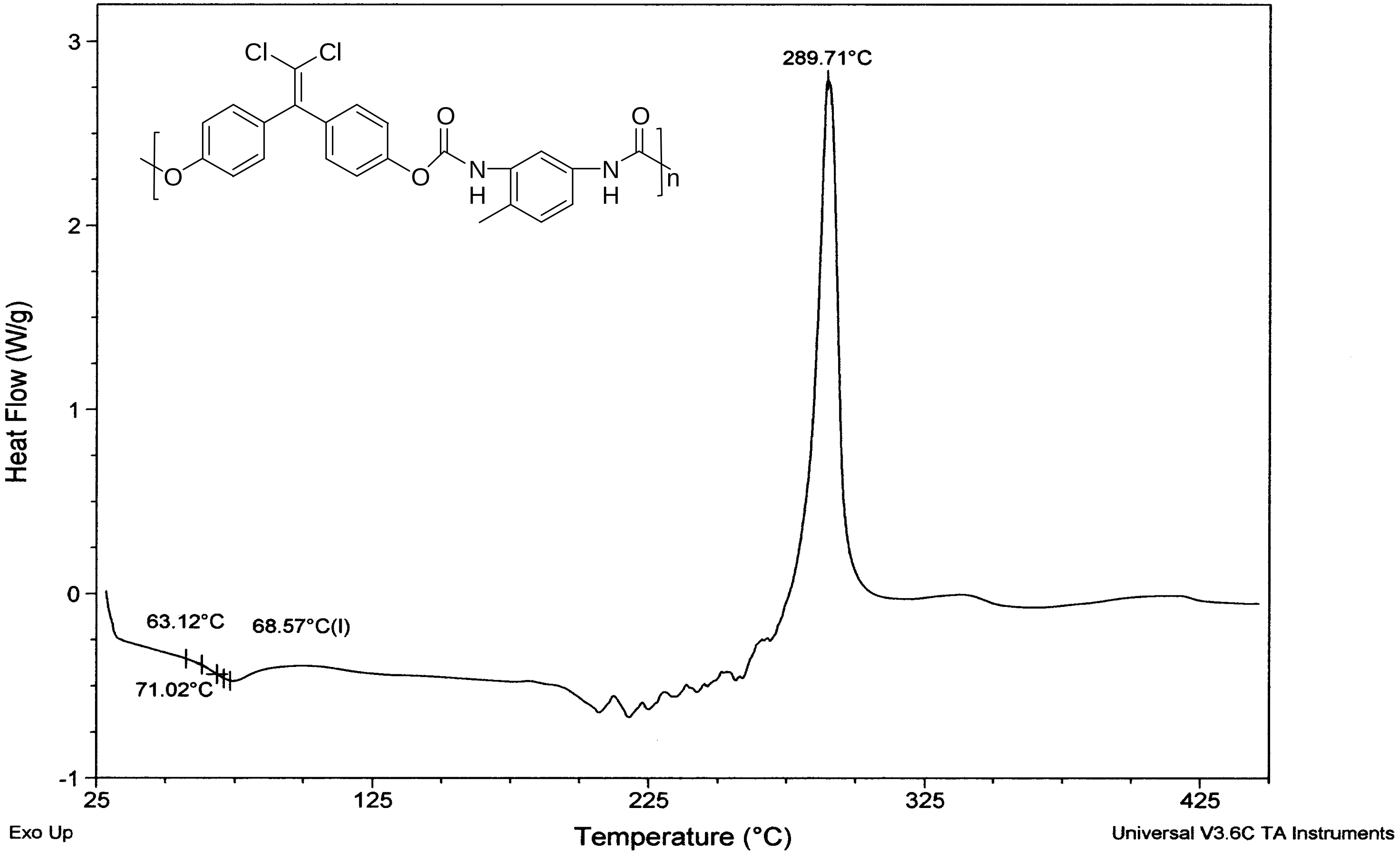
Resolution: 4.000


Sample: JLJ-IV-9
Size: 29.7140 mg
Method: Ramp
TGA
File: C:\TA\Data\TGA\JursTGA\jljIV9.001
Operator: JLJ
Run Date: 19-Jul-03 10:57
Instrument: TGA Q50 V4.10 Build 157
140.94°C 5.000% Loss
68.54% Weight Loss
(20.37mg)
Weight (%)
100
80
60
40
20
0
200
400
600
800
Temperature (°C)
Universal V3.6C TA Instruments
Cl
Cl
O
O
O
N
H
N
H
O
n

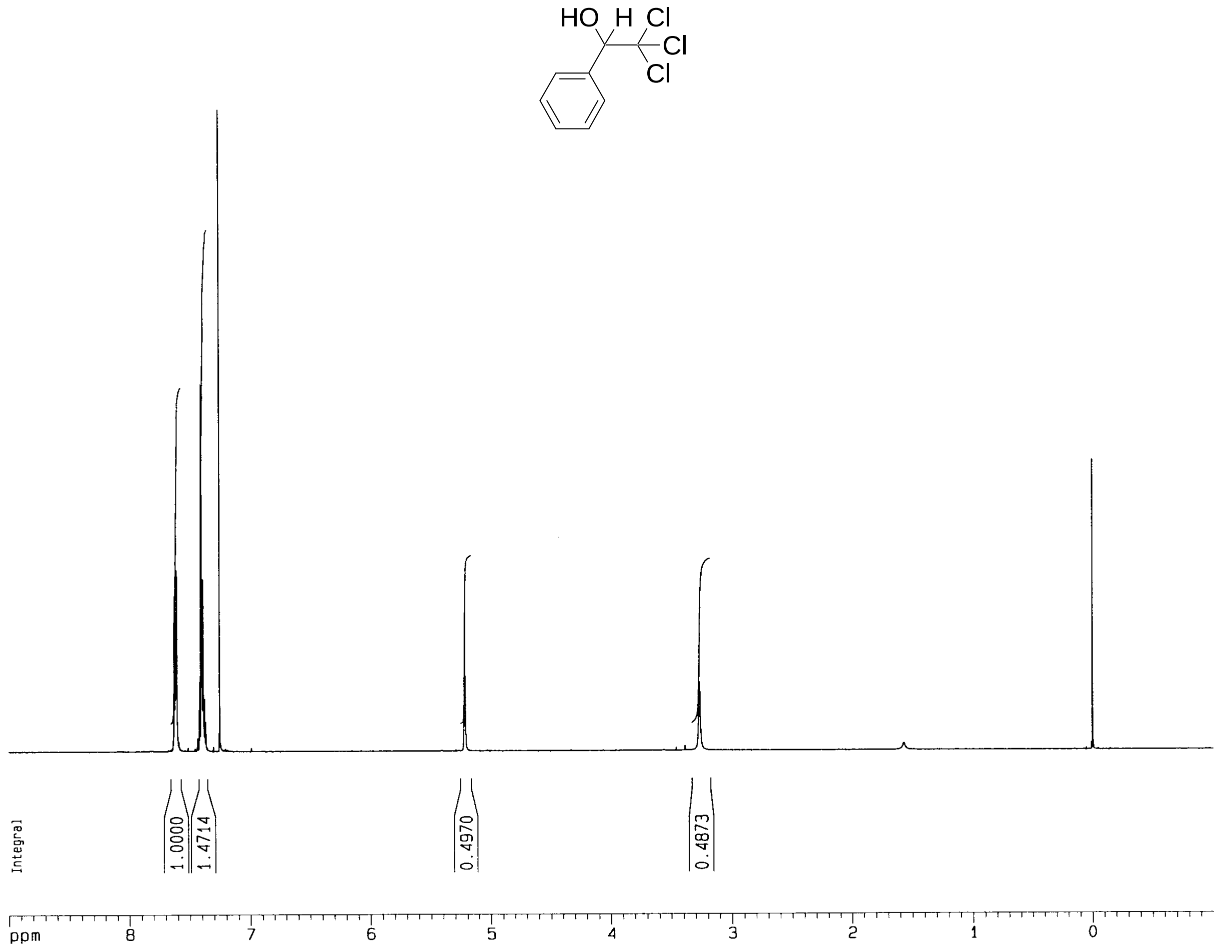
Sample: JLJ-IV-9
Size: 17.0000 mg
Method: Ramp

DSC

File: C:\TA\Data\DSC\JursDSC\JLJIV9.001
Operator: JLJ
Run Date: 21-Jul-03 09:47
Instrument: DSC Q10 V6.21 Build 233

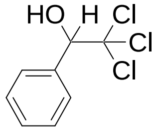


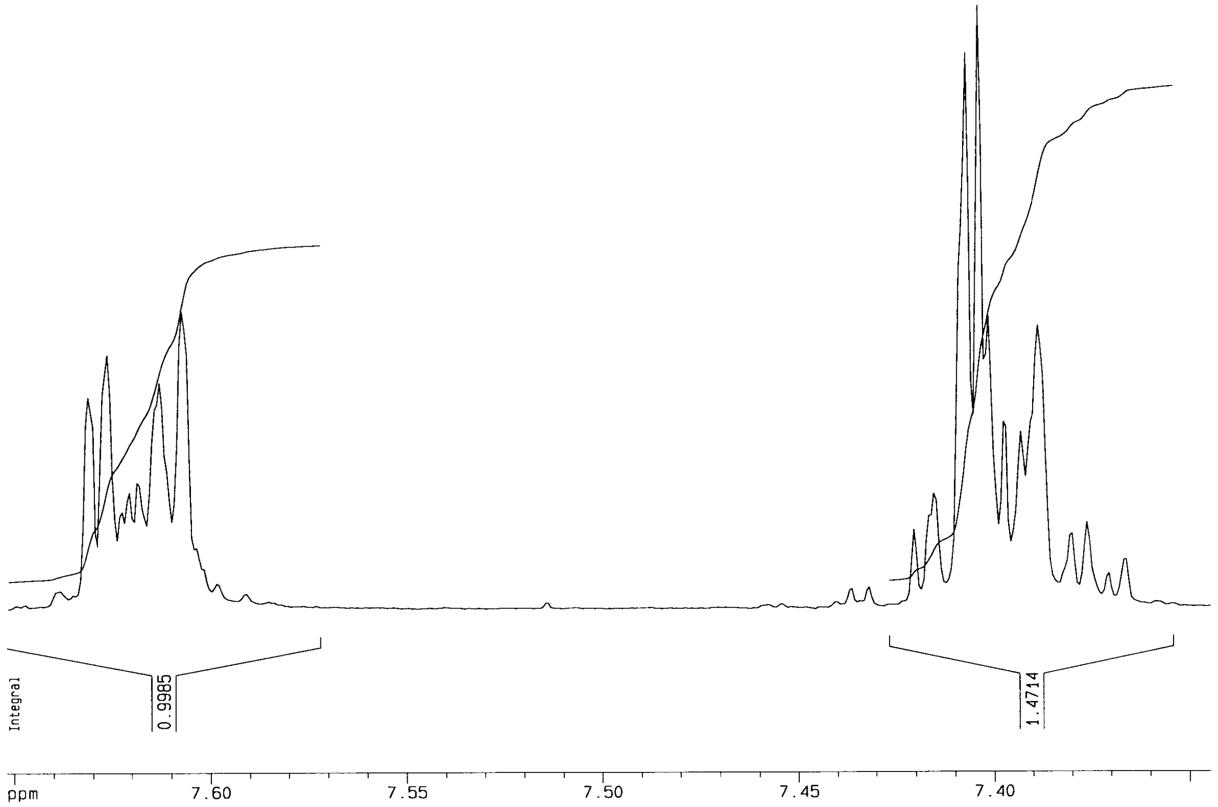
JLJ-IV-103
post-dist. and Vac.



```
Current Data Parameters
NAME            jljiv103
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030403
Time               11.02
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 406.4
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300116 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06496 Hz/cm
```

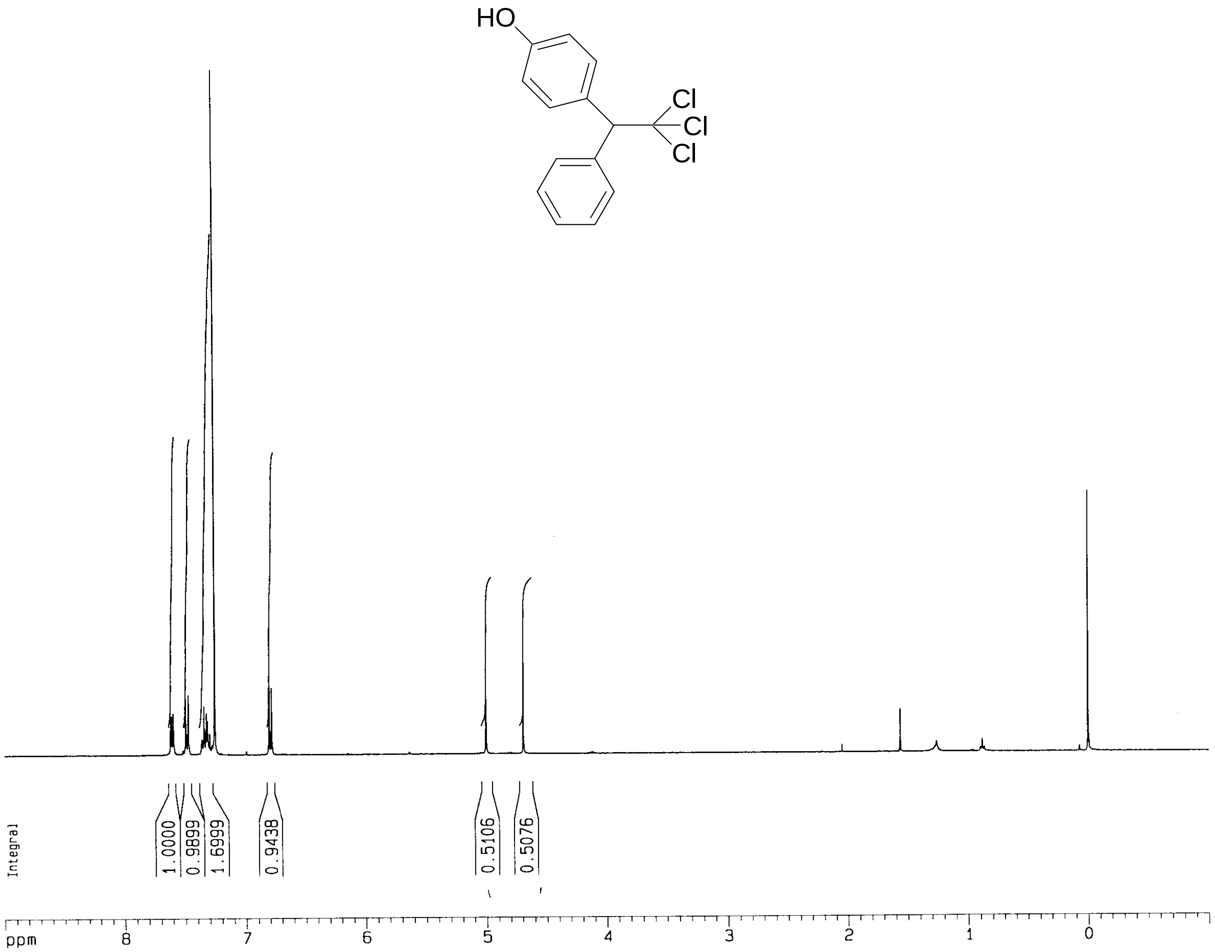
JLJ-IV-103
post-dist. and Vac.



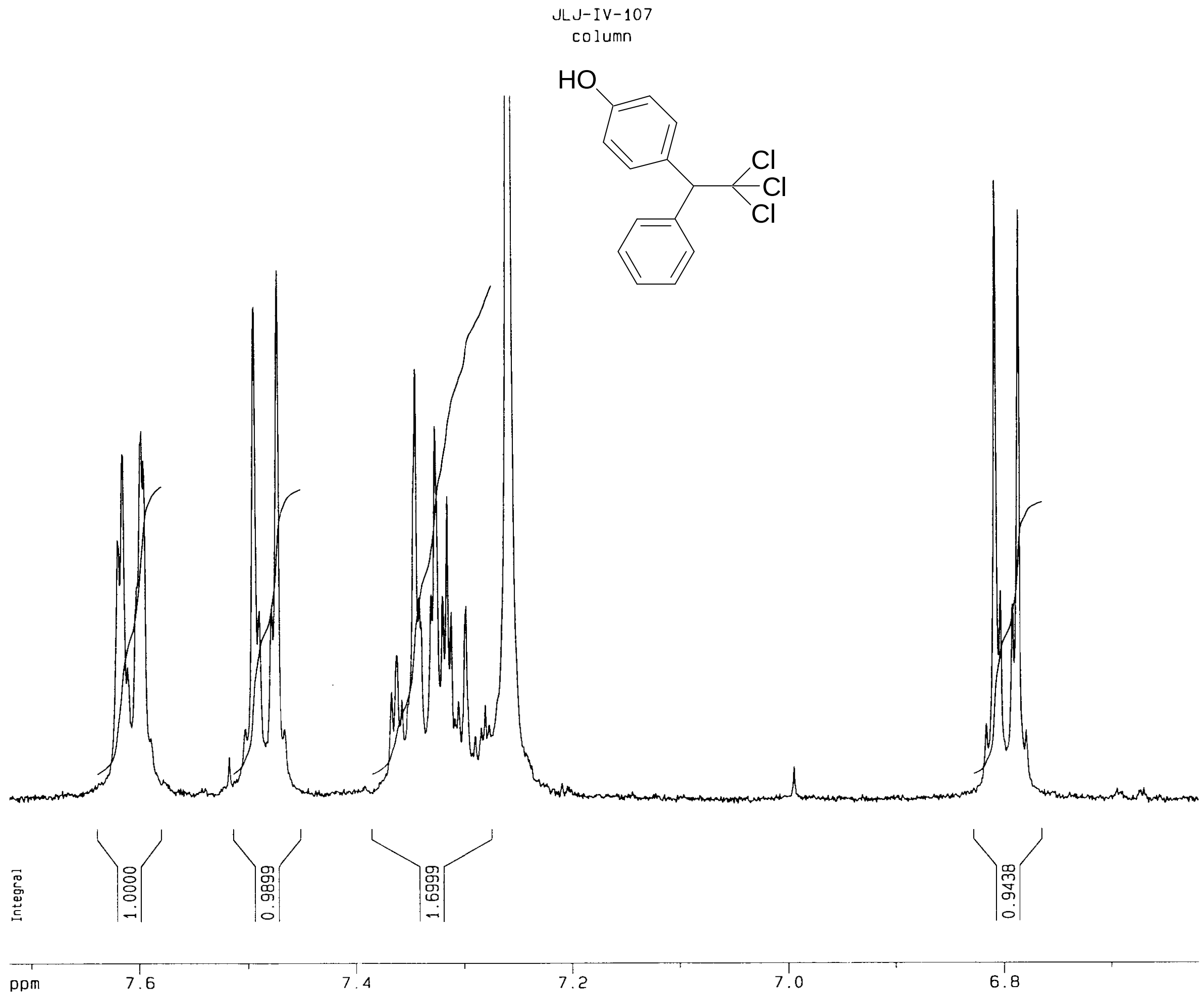


```
Current Data Parameters
NAME            jljiv103
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030403
Time               11.02
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 406.4
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300116 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.652 ppm
F1               3061.76 Hz
F2P                7.345 ppm
F2               2938.78 Hz
PPMCM            0.01537 ppm/cm
HZCM             6.14891 Hz/cm
```

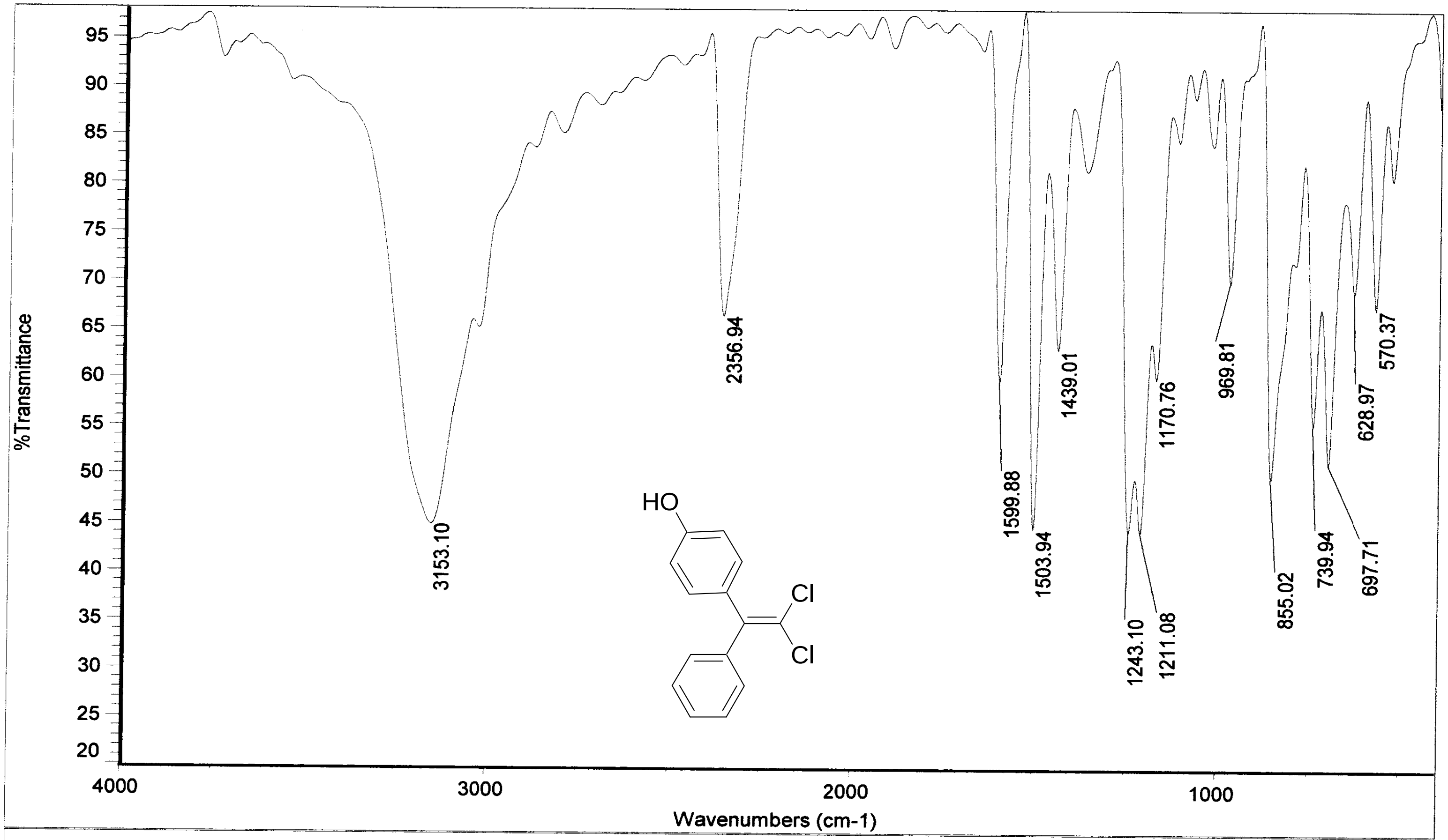
JLJ-IV-107
column



```
Current Data Parameters
NAME            jljiv107
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030410
Time               16.28
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 645.1
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300099 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06500 Hz/cm
```



```
Current Data Parameters
NAME            jljiv107
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030410
Time               16.28
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 645.1
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300099 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.721 ppm
F1               3089.32 Hz
F2P                6.620 ppm
F2               2648.69 Hz
PPMCM            0.05506 ppm/cm
HZCM            22.03163 Hz/cm
```

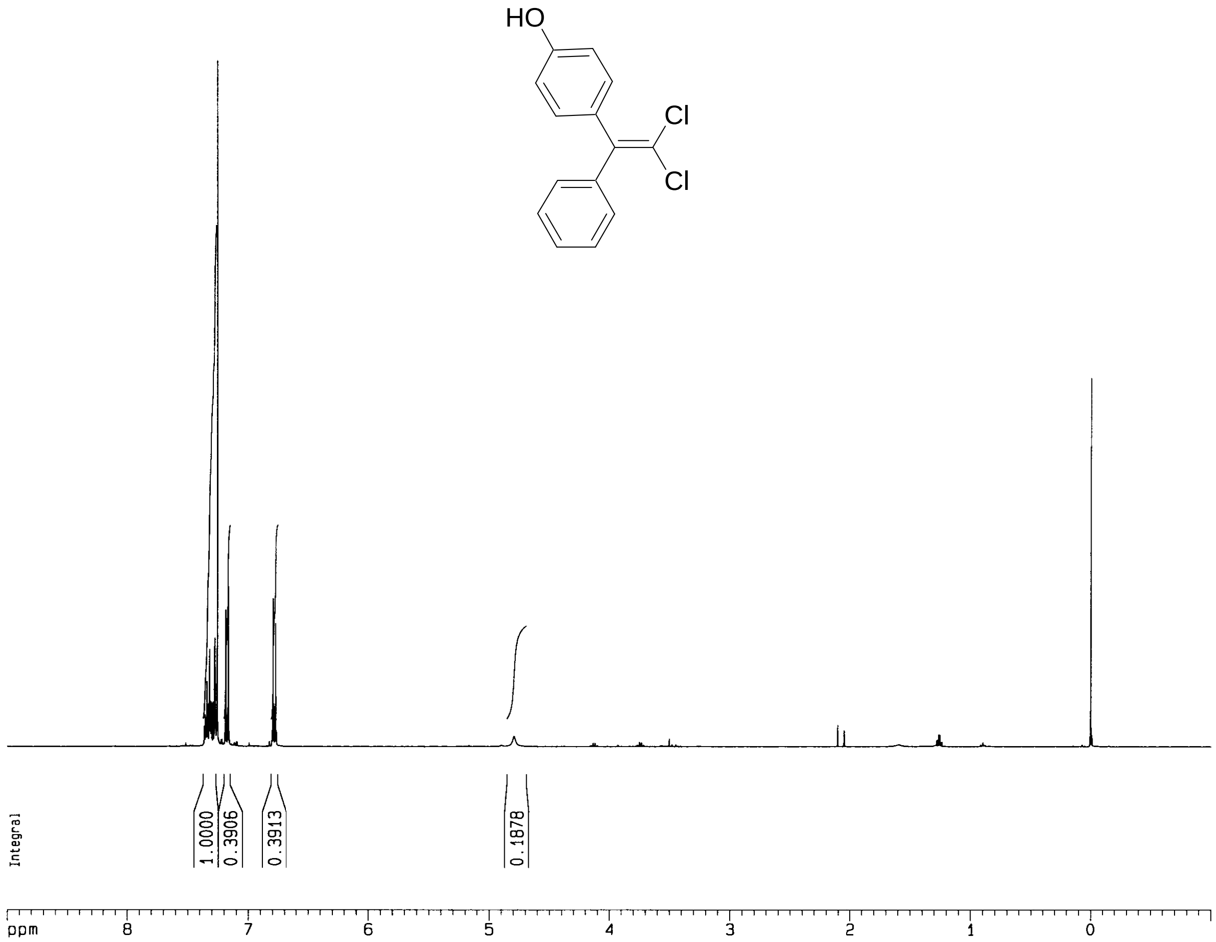


Date: Wed Jul 16 15:10:44 2003

Scans: 18

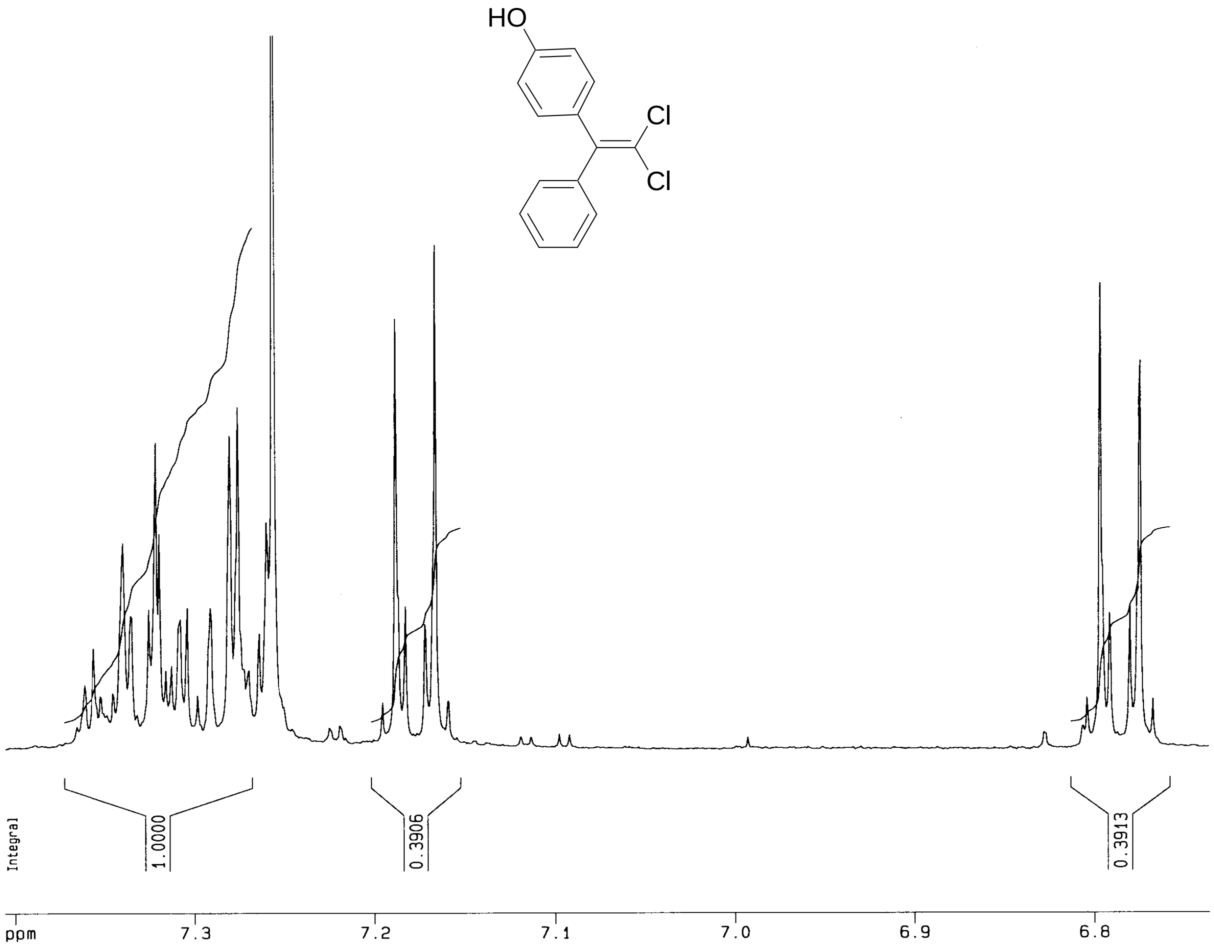
Resolution: 4.000

JLJ-IV-136
crude

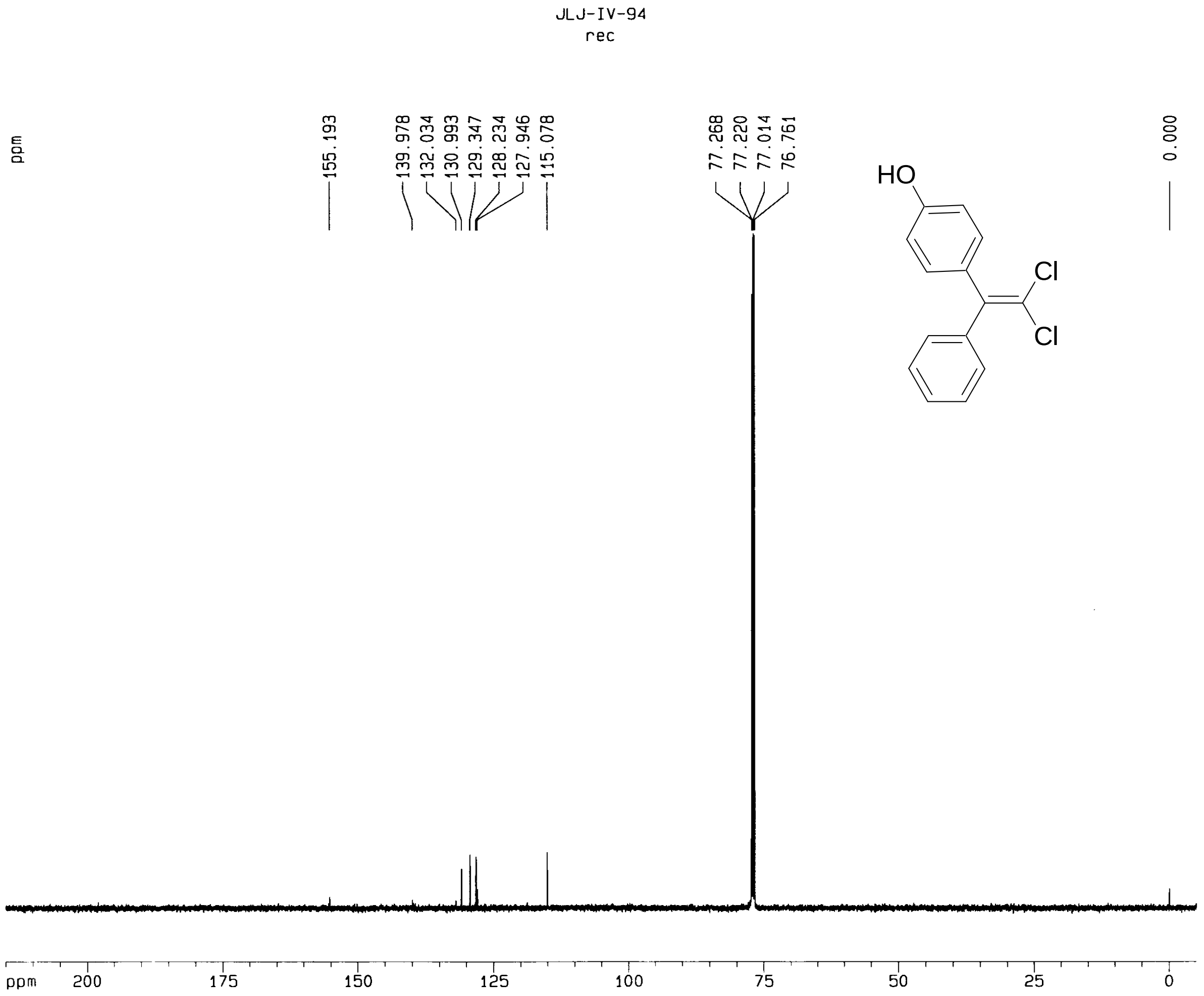


```
Current Data Parameters
NAME            jljiv136
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030524
Time               11.47
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 645.1
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300109 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06500 Hz/cm
```

JLJ-IV-136
crude

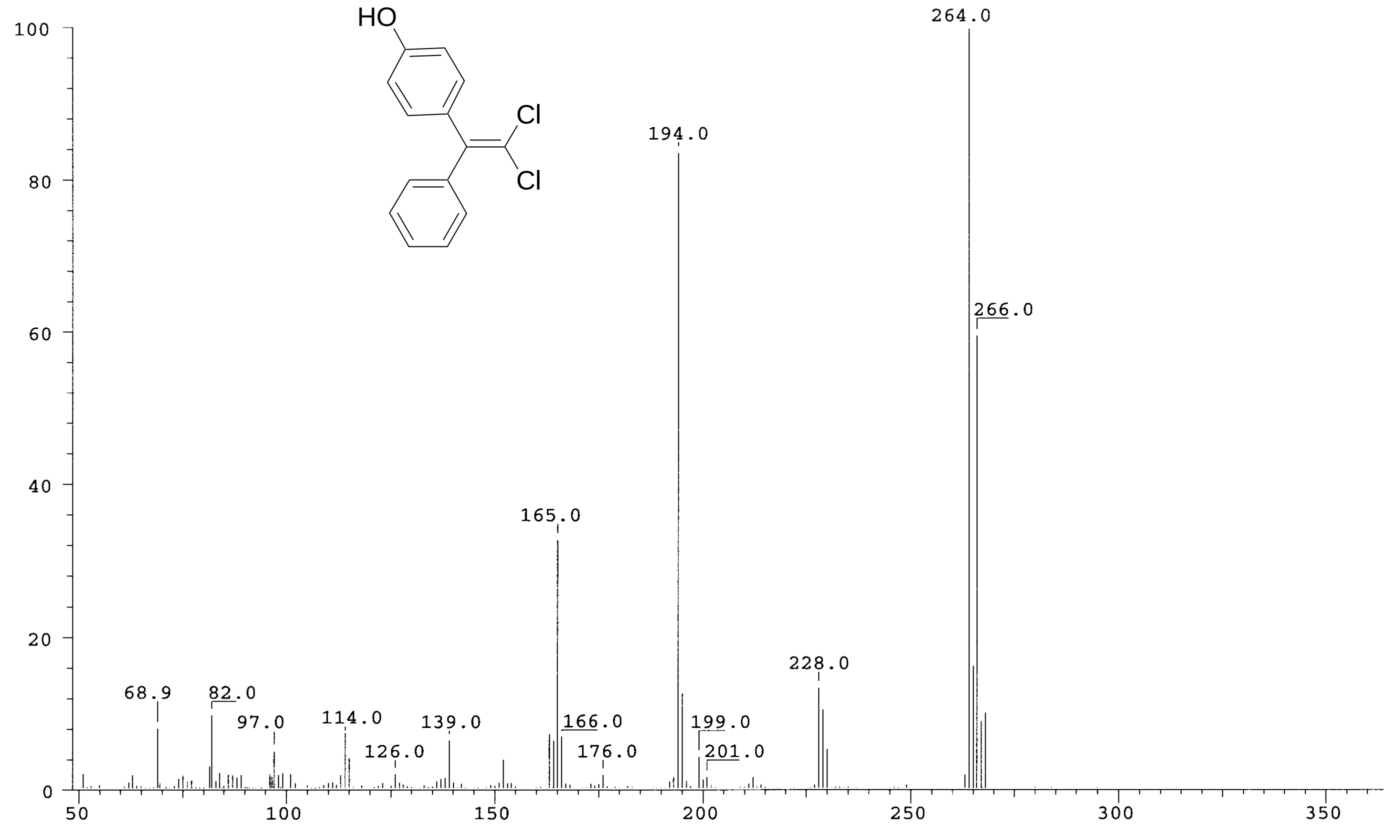


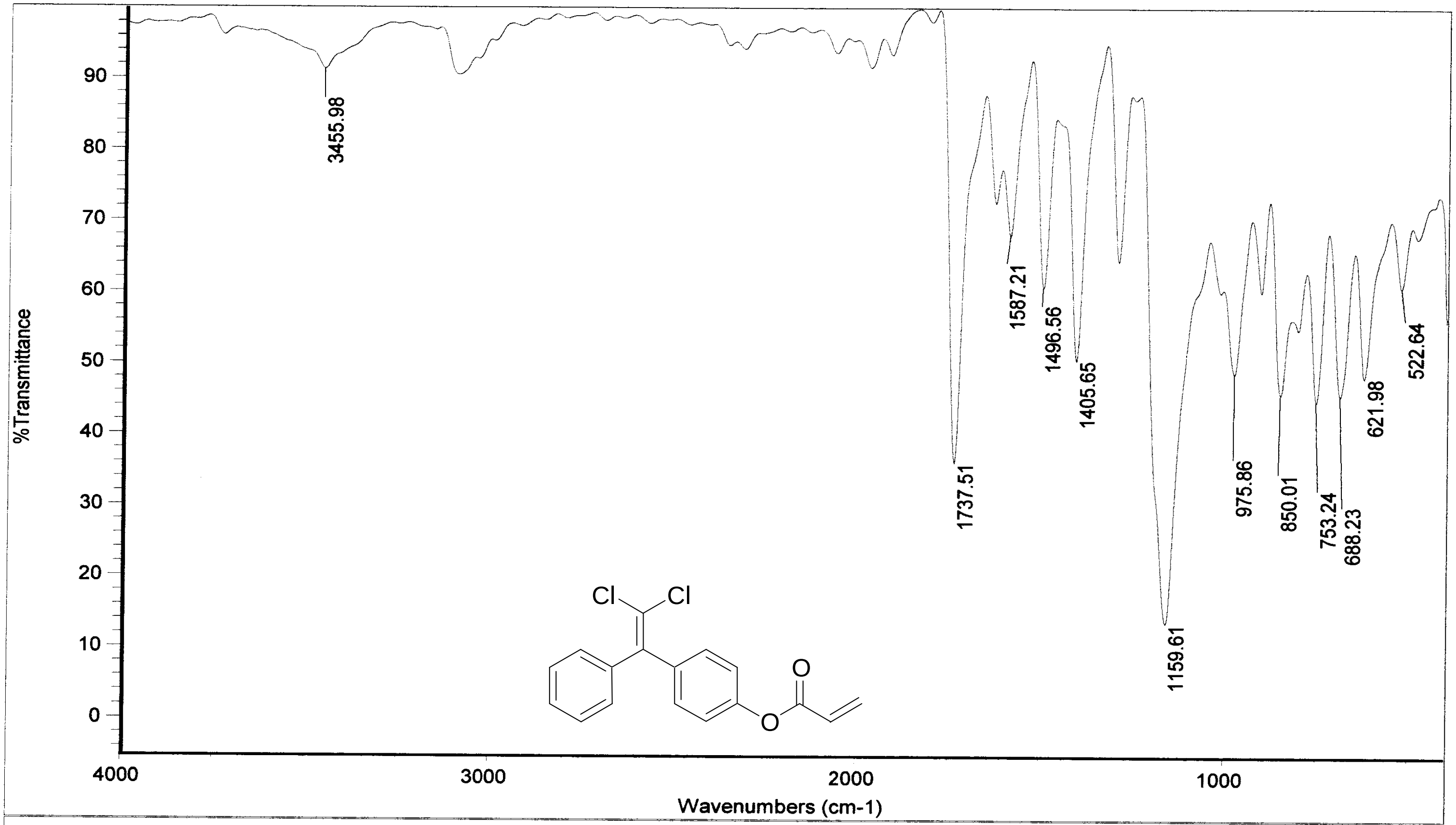
```
Current Data Parameters
NAME            jljiv136
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030524
Time               11.47
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 645.1
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SF01         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300109 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.406 ppm
F1               2963.27 Hz
F2P                6.736 ppm
F2               2695.38 Hz
PPMCM            0.03348 ppm/cm
HZCM            13.39491 Hz/cm
```



```
Current Data Parameters
NAME             jljiv94
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030717
Time               14.59
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT            CDCl3
NS                   796
DS                     0
SWH            31446.541 Hz
FIDRES          0.479836 Hz
AQ             1.0420724 sec
RG                  4096
DW                15.900 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                 13C
P1                  5.80 usec
PL1                 0.00 dB
SFO1         125.7715719 MHz

============ CHANNEL f2 ============
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -1.00 dB
PL12               22.60 dB
PL13               22.60 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577891 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              215.000 ppm
F1              27037.93 Hz
F2P               -5.000 ppm
F2               -628.79 Hz
PPMCM           11.00000 ppm/cm
HZCM          1383.33569 Hz/cm
```

```
SPEC: jlj-iv-94a (03-Aug-03 16:05:33)                                    Scans:   1 > 93
Samp: C14H10Cl2O1 mw=265.13
Oper: Xiao                    Study:  EI +                               Client:  Jurs/Tour
Base: 263.96                  Masses:  50.00 > 500.00                    #Peaks:  251
Peak: 1000.0 mmu              Intensity:   10785897                      RIC: 53972450
REG #9 @ 13.44 min (EI +VE +LMR  BSCAN (EXP) UP HR NRM) (+77-7)                  1.1E+07
```



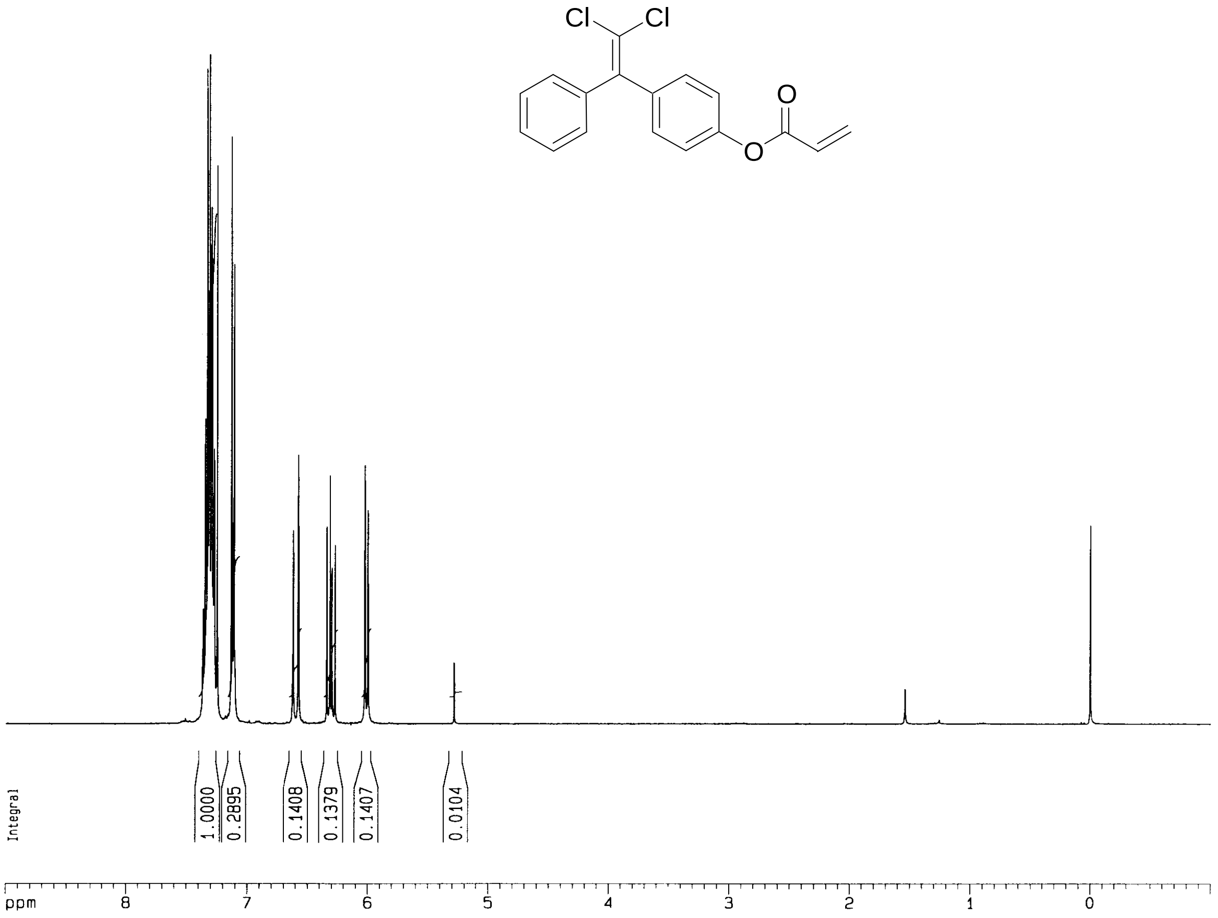


Date: Sat Jul 19 17:49:24 2003 ****JLJ-IV-137

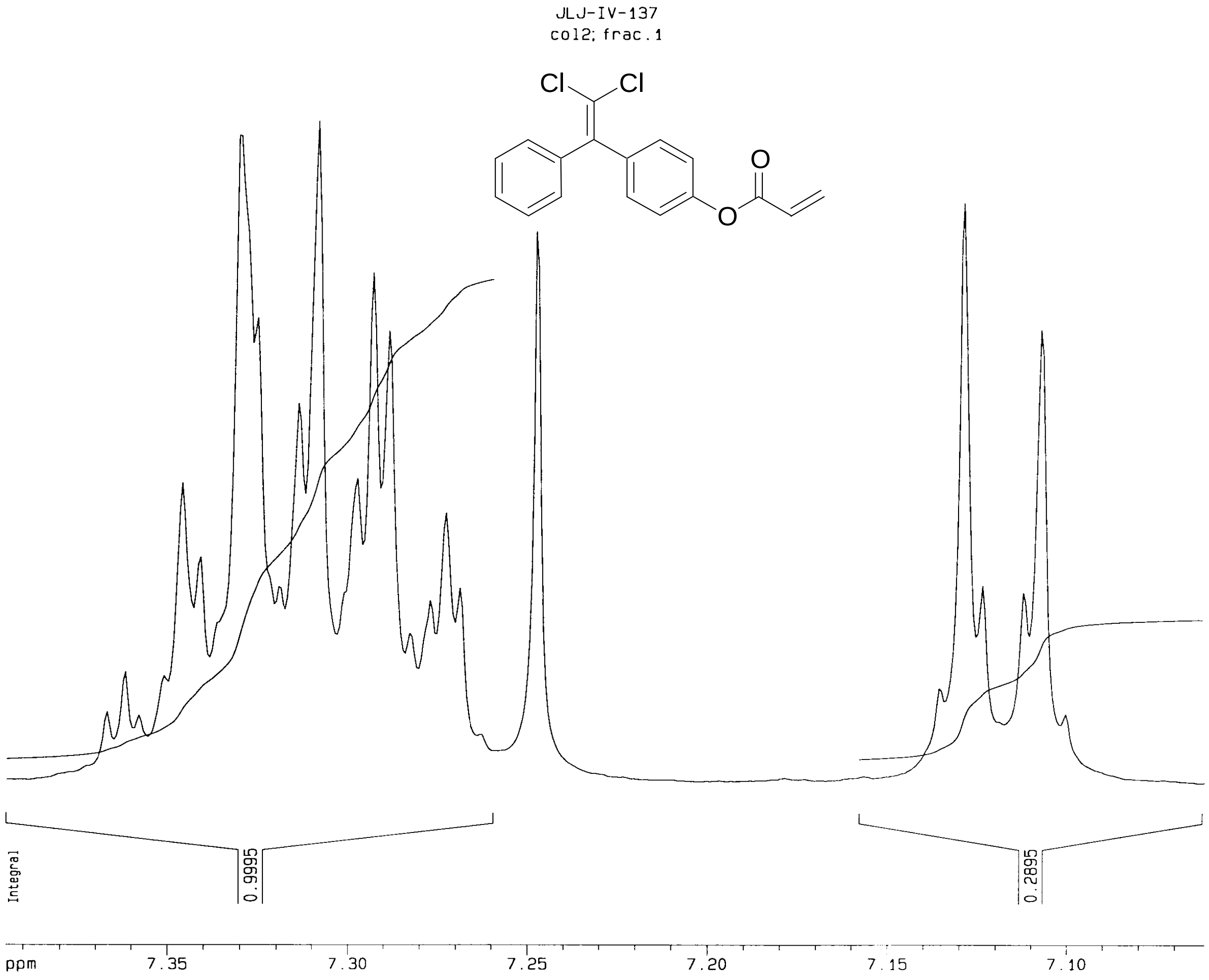
Scans: 18

Resolution: 4.000

JLJ-IV-137
col2; frac.1

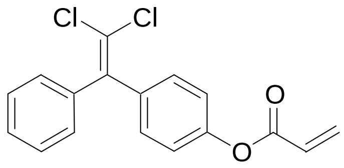


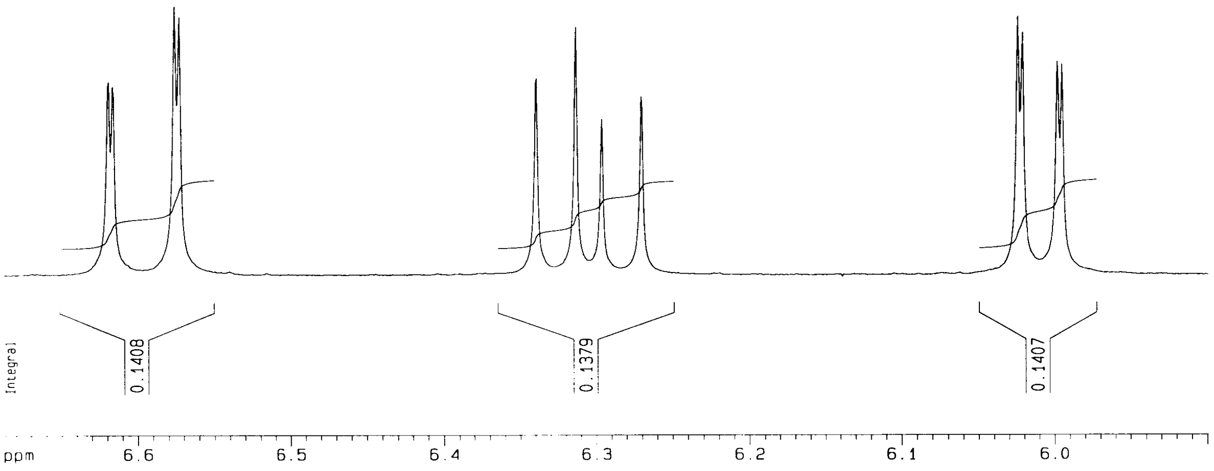
```
Current Data Parameters
NAME            jljiv137
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030719
Time               17.20
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                   256
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300147 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06500 Hz/cm
```



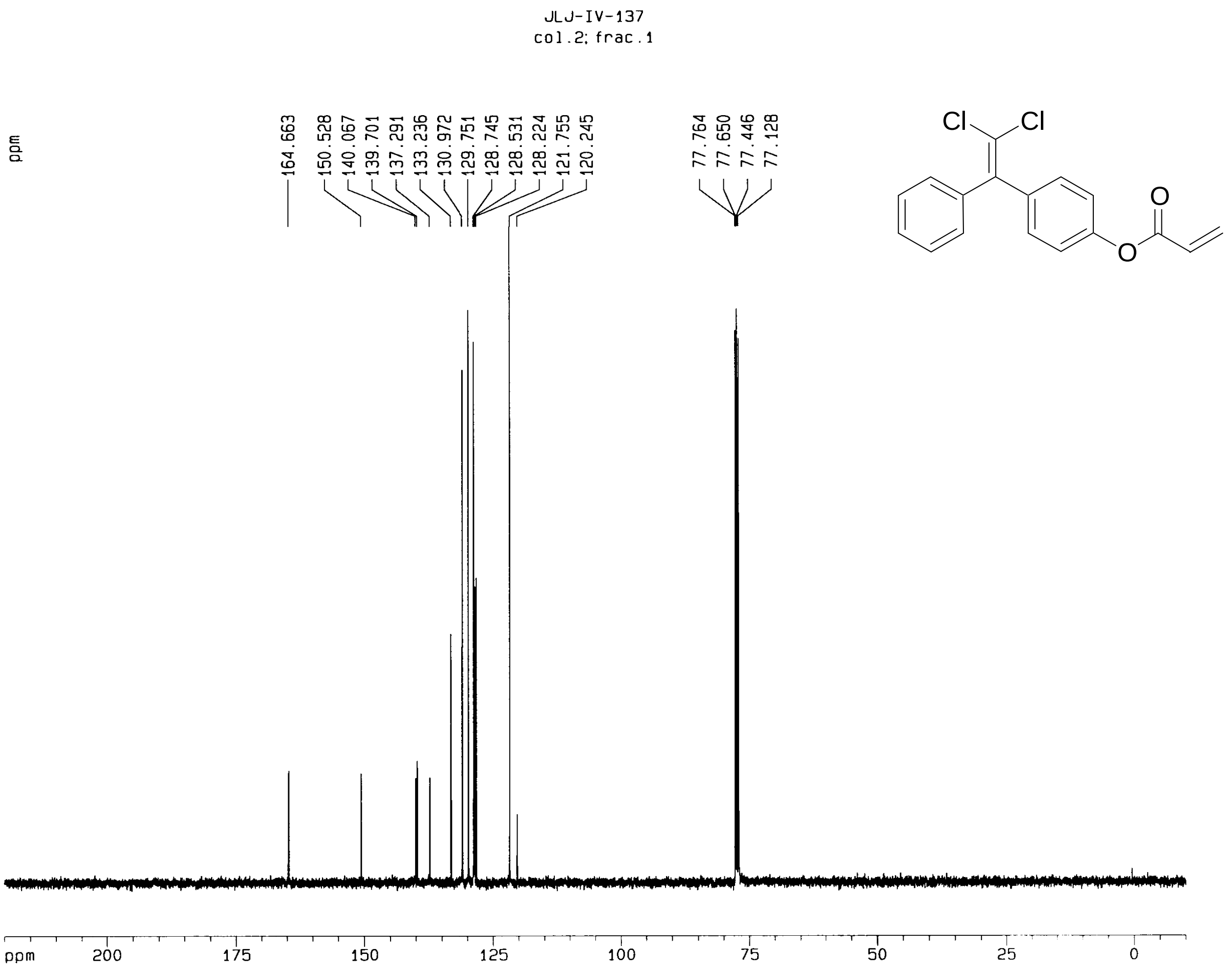
```
Current Data Parameters
NAME            jljiv137
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030719
Time               17.20
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                   256
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            3.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300147 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                7.395 ppm
F1               2958.86 Hz
F2P                7.062 ppm
F2               2825.63 Hz
PPMCM            0.01665 ppm/cm
HZCM             6.66167 Hz/cm
```

JLJ-IV-137
col2; frac.1



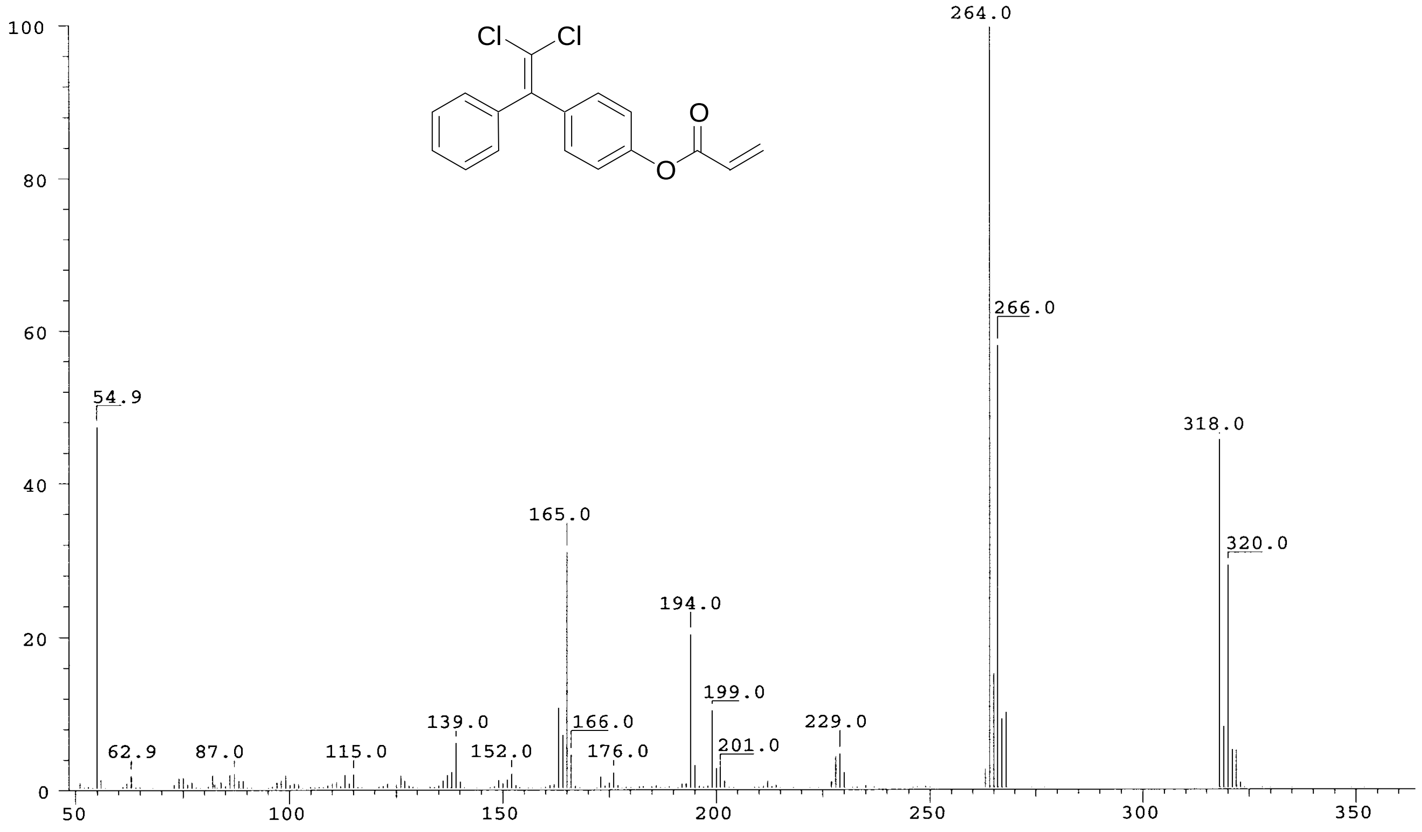


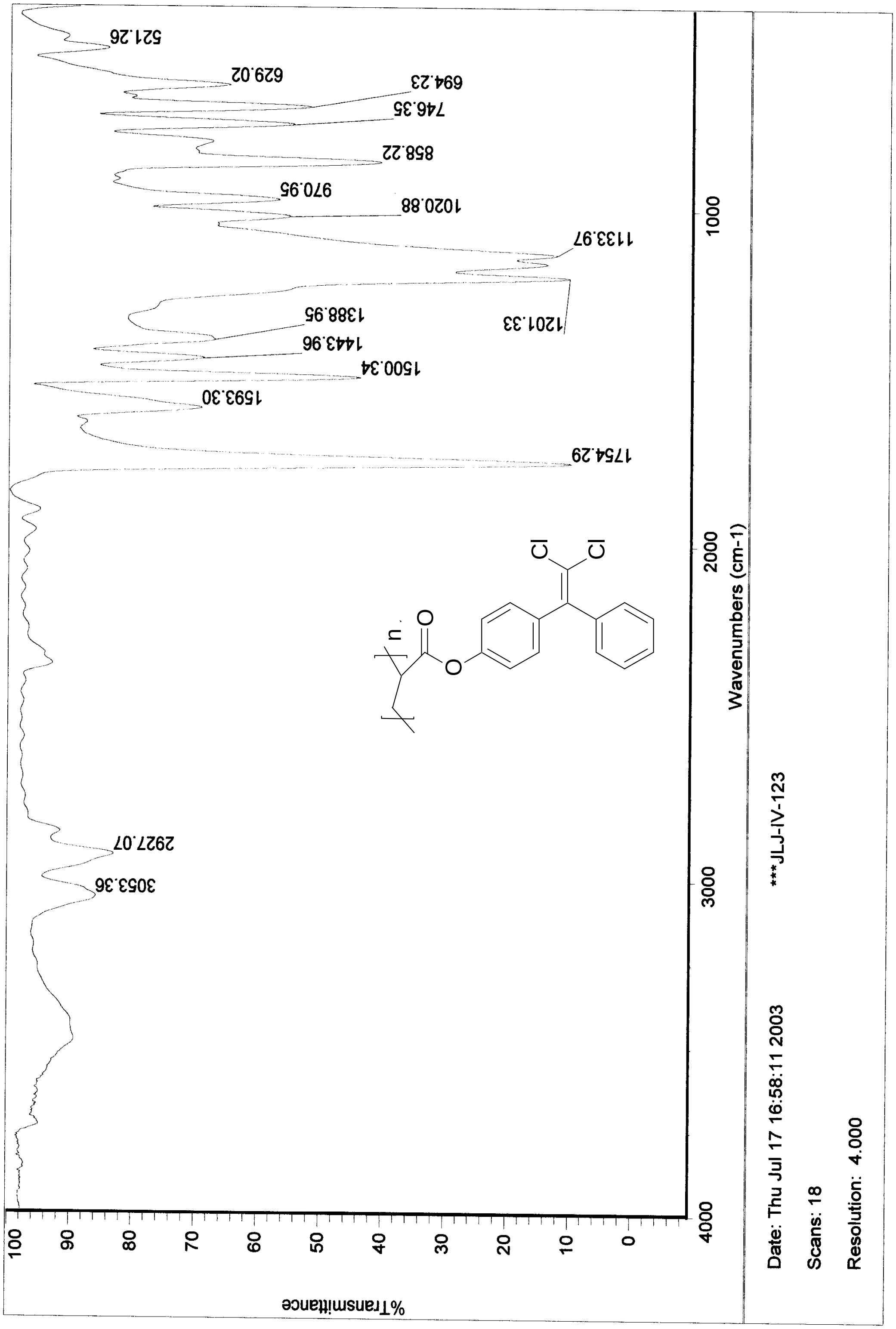
```
Current Data Parameters
NAME            jljiv137
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20030719
Time              17.20
INSTRUM           spect
PROBHD     5 mm BBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                  256
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec

============ CHANNEL f1 ========
NUC1                 1H
P1                12.50 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300147 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               6.688 ppm
F1              2676.26 Hz
F2P               5.899 ppm
F2              2360.54 Hz
PPMCM           0.03945 ppm/cm
HZCM           15.78609 Hz/cm
```



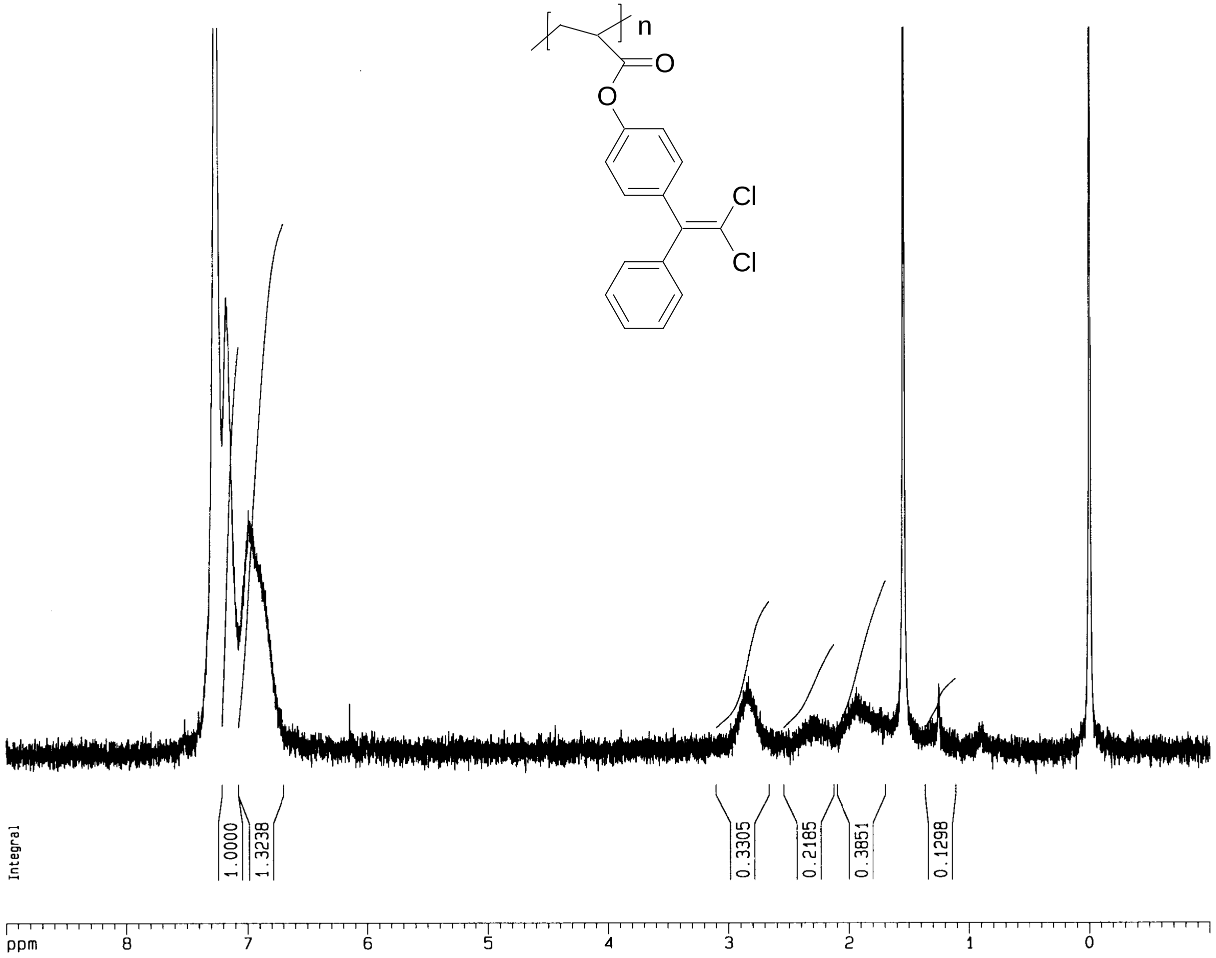
```
Current Data Parameters
NAME            jljiv137
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030719
Time               17.58
INSTRUM            spect
PROBHD    5 mm BBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   470
DS                     0
SWH            25125.629 Hz
FIDRES          0.383387 Hz
AQ             1.3042164 sec
RG                  4096
DW                19.900 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                 13C
P1                  8.30 usec
PL1                -3.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 ============
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127290 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              220.000 ppm
F1              22134.80 Hz
F2P              -10.000 ppm
F2              -1006.13 Hz
PPMCM           11.50000 ppm/cm
HZCM          1157.04639 Hz/cm
```

```
SPEC:  jlj-iv-137 (03-Aug-03 15:38:06)                                                  Scans:   1 > 66
Samp:  C17H12Cl2O2 mw=319.181
Oper:  Xiao                       Study:  EI +                                           Client:  Jurs/Tour
Base:  263.96                     Masses:  50.00 > 500.00                                #Peaks:  298
Peak:  1000.0 mmu                 Intensity:   21412800                                  RIC:  110131933
REG #9 @ 9.39 min (EI +VE +LMR  BSCAN (EXP) UP HR NRM) (+53-6)                                       2.1E+07
```




%Transmittance
100
90
80
70
60
50
40
30
20
10
0
4000
3000
2000
1000
Wavenumbers (cm-1)
3053.36
2927.07
1754.29
1593.30
1500.34
1443.96
1388.95
1201.33
1133.97
1020.88
970.95
858.22
746.35
694.23
629.02
521.26
O
O
n
Cl
Cl
Date: Thu Jul 17 16:58:11 2003
***JLJ-IV-123
Scans: 18
Resolution: 4.000

JLJ-IV-147
Polymer

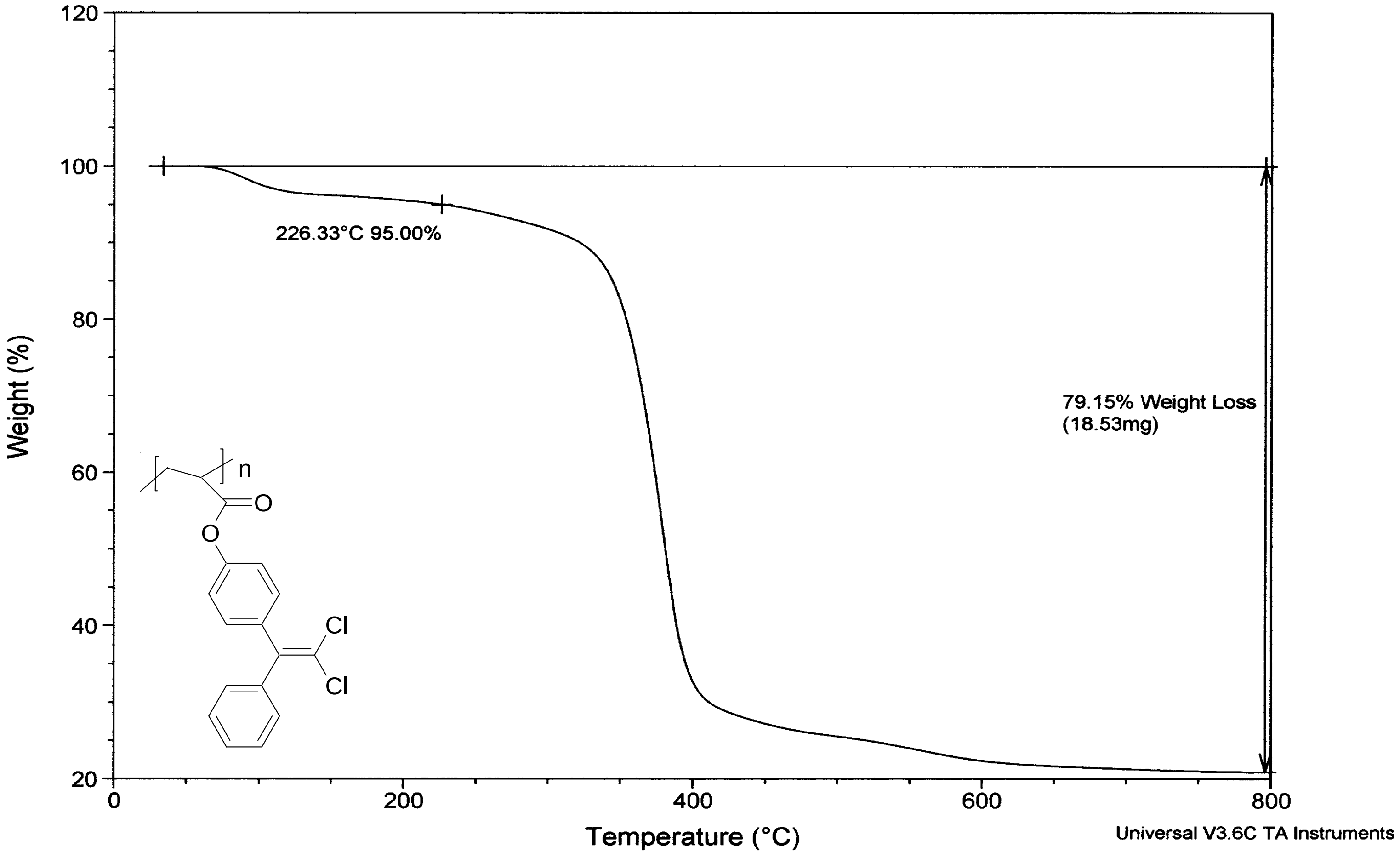


```
Current Data Parameters
NAME            jljiv147
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030605
Time               11.33
INSTRUM            spect
PROBHD     5 mm BBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 574.7
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1          3.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 12.50 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300099 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.50000 ppm/cm
HZCM           200.06500 Hz/cm
```

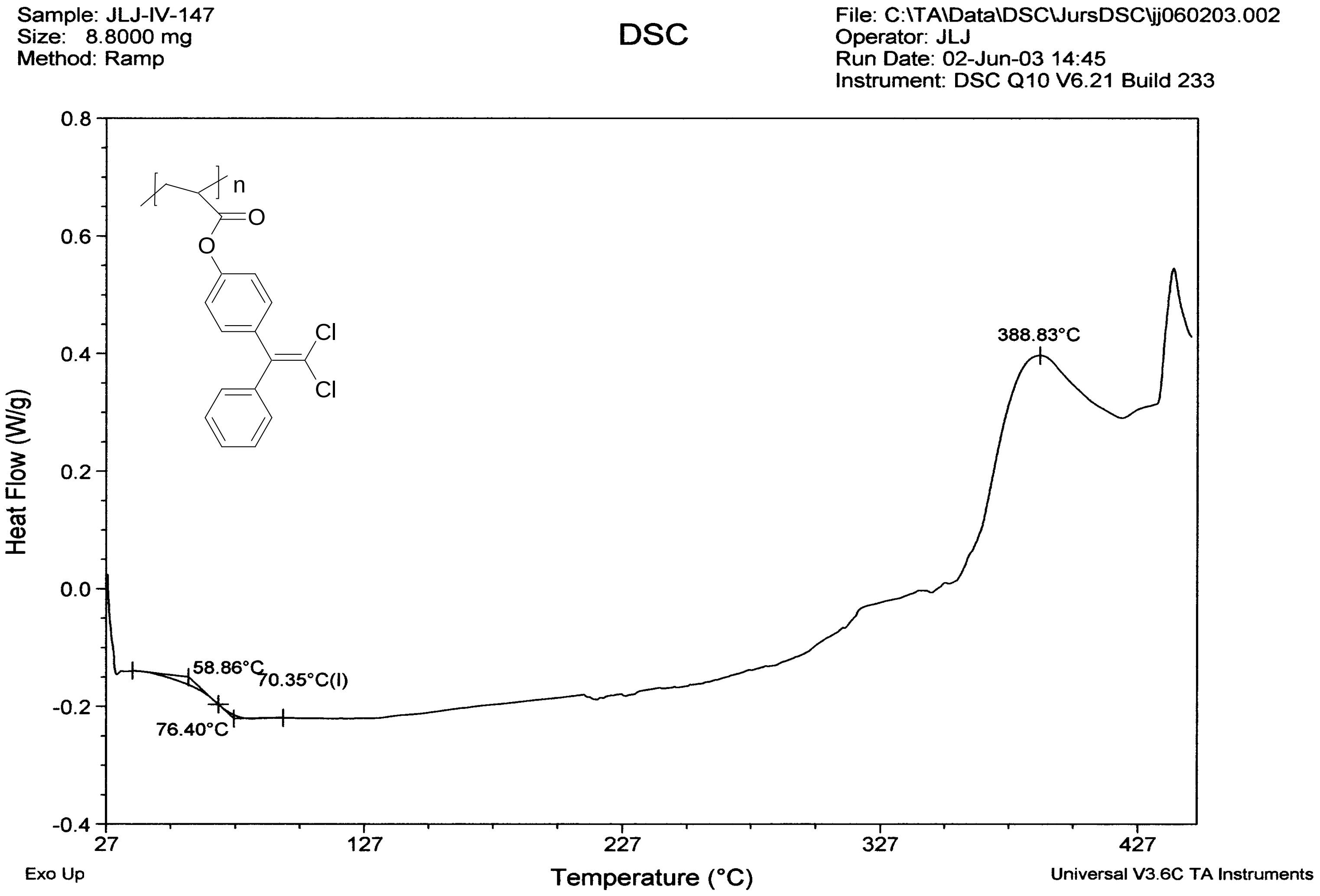
Sample: JLJ-IV-147
Size: 23.4130 mg
Method: Ramp

TGA

File: C:\TA\Data\TGA\JursTGA\060203.001
Operator: JLJ
Run Date: 02-Jun-03 14:14
Instrument: TGA Q50 V4.10 Build 157



Universal V3.6C TA Instruments



Sample: JLJ-IV-147
Size: 8.8000 mg
Method: Ramp

File: C:\TA\Data\DSC\JursDSC\jj060203.002
Operator: JLJ
Run Date: 02-Jun-03 14:45
Instrument: DSC Q10 V6.21 Build 233